ABSTRACT

STASIW, DANIEL EARL. Exploring Molecular Electronic Structure Through Donor-Bridge-Acceptor Biradicals. (Under the direction of Dr. David A. Shultz.)

Structure-property relationships are developed through Donor-Bridge-Acceptor (D-B-A) biradical complexes as models of charge transfer excited states. By using a semiquinone (SQ) donor radical and a nitronylnitroxide (NN) acceptor radical, the magnetic exchange ($J_{DA}$) is related to electronic coupling ($H_{DA}$) via a valence bond configuration interaction (VBCI) model. Through auxochromic substituents, the torsional dependence of electronic coupling is investigated for para-phenylene bridged D-B-As. Then, by varying the number of bridge units from 0 to 2, the exponential decay in electronic coupling versus radical distance as well as the electronic coupling of one bridge unit to another is determined for oligo(para-phenylene), oligo(2,5-thiophene), and oligo(2,5-selenophene). This is followed by an analysis of cross-conjugated D-B-As where the electronic coupling of a meta-phenylene cross-conjugated bridge is found to involve a spin polarized $\pi$-system to stabilize a singlet ground state. Applying concepts of the meta-phenyl system to cross-conjugated thiophene systems shows similar results with more ferromagnetic coupling. Finally, adding substituents ortho-to the SQ and para- to the NN in a meta-phenylene bridged cross-conjugated biradical complex provides single molecule models of quantum interference effect transistors.
Daniel is originally from Bethlehem, PA and received his B.S. in Chemistry with a minor in Physics from Millersville University of Pennsylvania. While at Millersville, he worked on iridium based N-heterocyclic carbene catalysts with Prof. Edward Rajaseelan. As a member of the local ACS chapter, he traveled to the ACS National Meeting in San Francisco where he presented a poster on his undergraduate research. Following graduation from MU with honors, he joined the David Shultz research group in 2010 to work on cobalt valence tautomers and donor-bridge-acceptor biradicals. He has presented his research at multiple meetings including the South-Eastern Regional Meeting of the American Chemical Society (SERMACS), the Electron Donor-Acceptor Interactions Gordon Research Conference, as well as several local meetings. During his time in the group, he has received the award for outstanding graduate research in the area of inorganic chemistry and a certificate of achievement in teaching. He also received the Graduate Assistance in Areas of National Need - Nanoscale Electronic and Energy Materials (GAANN-NEEM) fellowship two years in a row.
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# TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................ vi
LIST OF FIGURES ....................................................................................................... viii
LIST OF SCHEMES ................................................................................................... xvi
LIST OF ABBREVIATIONS ......................................................................................... xviii

I. General Introduction to Donor-Bridge-Acceptor Biradicals ............................. 1
   A. Introduction ........................................................................................................ 1
   B. The Utility of Hund's Rule in Predicting Ground Spin-States in S > 1/2 Molecules ... 4
   C. Measuring Exchange Coupling in Biradical Complexes ...................................... 8
   D. Electron Paramagnetic Resonance of Biradicals .................................................. 14
   E. Donor-Bridge-Acceptor Valence Bond Configuration Interaction Model ............ 16
      1. Photoinduced Electron Transfer and Electronic Coupling .............................. 19
      2. Metal-Molecule-Metal Conductance and Electronic Coupling .......................... 21
      3. Connecting PET, Conductance, and Biradicals Through Electronic Coupling .... 24
   G. Development of Versatile Synthetic Routes to Donor-Bridge-Acceptor Biradical Complexes ................................................................. 26
   H. Experimental ...................................................................................................... 33

II. Experimentally Illustrating McConnell's Electronic Coupling Model Through Independent Donor-Bridge and Bridge-Acceptor Torsions in Donor-Bridge-Acceptor Biradicals .................................................................................. 37
   A. Introduction to Electronic Coupling Torsional Dependence in Donor-Bridge-Acceptor Biradical Complexes .................................................................... 37
   B. Discussion of Results for Steric Inhibition of Resonance Complexes ................. 41
      1. Synthesis of Steric Inhibition of Resonance Complexes .................................. 41
      2. Structural and Magnetic Features of Twisted Donor-Bridge-Acceptor Biradical Complexes ............................................................... 44
      3. Spectroscopy of sterically hindered donor-bridge-acceptor biradical complexes. 51
   C. Experimental ...................................................................................................... 59

III. Superexchange Contributions to Distance Dependence of Electron Transfer/Transport in Donor-Bridge-Acceptor Biradicals .............................................................. 73
   A. Introduction to Distance Dependence of Donor-Bridge-Acceptor Complexes .......... 73
   B. Discussion of Results for SQ-Bridge-NN Distance Dependence Complexes ........ 76
      1. Synthesis of Distance Dependence SQ-Bridge-NN Biradical Complexes .......... 76
2. Structural and Magnetic Properties of SQ-Bridge-NN Distance Dependence Complexes ................................................................. 81
3. D-B-A Electronic Coupling Parameters and Spectroscopy ...................... 89
C. Exploring Another Electron Rich Bridge for Distance Dependence: Selenophene ....................................................... 97
   1. Introduction to Other Chalcogen Bridged Biradicals .......................... 97
   2. Synthesis of Selenophene Bridged Biradicals .................................... 98
   3. Discussion of Results for Selenophene Bridged Biradicals .................. 101
D. Experimental ............................................................................. 106

IV. Electronic and Exchange Coupling in Cross-Conjugated D–B–A Biradicals: Mechanistic Implications for Quantum Interference Effects ................................................. 127
A. Introduction to Cross-Conjugated Donor-Bridge-Acceptor Systems ........... 127
   1. Disjoint and Nondisjoint Biradicals ................................................... 129
   2. Molecular Orbital Analysis of meta-Phenylene vs. para-Phenylene Bridges in D-B-A Molecules .................................................. 130
B. Cross-Conjugated Biradicals: Systems Where Hund’s Rule Does Not Apply .............................. 134
   1. Synthesis of the Cross-Conjugated meta-Phenylene Biradical ................. 134
   2. Discussion of Results for Quantum Interference Effects in a meta-Phenylene Bridged Biradical .............................................. 135
   3. Direct Comparison of Electronic Coupling Between Conjugated and Cross-Conjugated D-B-As and the Relationship to Quantum Interference Effects ...... 160
C. Electron Rich Cross-Conjugated Thiophene Biradicals ......................... 163
   1. Synthesis of Cross-Conjugated Thiophenes ........................................ 165
   2. Discussion of Results for Cross-Conjugated Thiophenes ...................... 167
D. Gating Quantum Interference: Substituent Effects on Electronic and Exchange Coupling in Cross-Conjugated Donor-Bridge-Acceptor Biradical Complexes ........ 177
   1. Introduction to substituent effects on cross-conjugated donor-bridge-acceptor biradical complexes .................................................. 177
   2. Discussion of Results for Substituted meta-Phenylenes ....................... 180
E. Experimental ............................................................................. 195

REFERENCES ......................................................................................... 226

APPENDICES ....................................................................................... 241

Appendix A: Valence Tautomers for Device Applications, Crystal Solvation Studies, and Solution Phase Valence Tautomerism ......................................................... 242
   1. Cobalt Valence Tautomers and Molecular Spintronics .......................... 242
   2. Solution Phase Valence Tautomerism ............................................... 247
   3. Experimental ............................................................................. 255
Appendix B: Crystallographic Data .......................................................... 256
LIST OF TABLES

Table I. Synthetic route comparisons based on yield, purification, protections, number of steps, and approximate time to final product formation. ................................................................. 32

Table II-1. Structural deviation parameters for 1-pPh, 1-MePh, 1-PhMe, 1-pXylyl, 1-PhMe₄, and 1-BCO. ................................................................................................................................. 46

Table II-2. Measured exchange coupling (J_DA) and calculated electronic coupling (H_DA) values for 1-pPh, 1-MePh, 1-PhMe, 1-pXylyl, 1-PhMe₄, and 1-BCO. ........................................... 47

Table III-1. Structural Deviation Parameters and NN oxygen-oxygen intermolecular distances for Complexes 1, 1-pPh, 1-Ph₂, 2-(2,5)T, and 2-T₂. ....................................................... 83

Table III-2. Select Torsion Angles for Complexes 1, 1-pPh, 1-Ph₂, 2-(2,5)T, and 2-T₂. .... 84

Table III-3. Hyperfine Coupling Constants for KSQ-T and KSQ-T-d from EPR Spectroscopy. ............................................................................................................................... 89

Table III-4. Exchange Coupling, Electronic Coupling, and D→B-A Electron Transfer Energies for 1, 1-pPh, 1-Ph₂, 2-(2,5)T, and 2-T₂. n represents the number of bridge units. 91

Table III-5. Proton hyperfine coupling constants for KSQ-T and KSQ-Se determined by EPR. ................................................................................................................................. 104

Table IV-1. Electronic Absorption Spectral Band Assignments for 1-mPh. .................... 146

Table IV-2. Select torsion angles for 1-mPh, 2-(2,5)T, 2-(3,5)T, and 2-(2,4)T. .......... 169

Table IV-3. Structural Deviation Parameters and NN oxygen-oxygen intermolecular distances for 2-(2,5)T, 2-(3,5)T, and 2-(2,4)T. ................................................................. 170

Table IV-4. Select torsion angles for 1-mPh, 1-NO₂, 1-OMe, 1-CN, and 1-Me. ............ 185
Table IV-5. Cyclic voltammetry redox potentials for 1-mPh, 1-NO₂, 1-CN, 1-OMe, 1-Me, Tp^{Cum,Me}Zn(SQ), and Ph-NN in DCM with a scan rate of 40 mV/s. ............................................ 194
LIST OF FIGURES

Figure I-1. Diagram of solar energy conversion utilizing a photoinduced electron transfer within a D-B-A molecule.................................................................................................................. 1

Figure I-2. Diagram of a circuit containing a diode (right) and the molecular equivalent (left) using Donor (D) and Acceptor (A) electrodes with an organic semiconducting Bridge (B). .. 2

Figure I-3. Visual Representation of Hund's Rule (left) and the Pauli Exclusion Principle (right). ......................................................................................................................................... 6

Figure I-4. Energy level diagrams of a two electron triplet ground state (left) and singlet ground state (right) with corresponding signs of $2J_{DA}$ ........................................................................................................ 9

Figure I-5. Theoretical plot of $\chi_{\text{Para}}$ versus T for $-100 \leq J_{DA} \leq +100$ cm$^{-1}$ (left) and $\chi_{\text{Para}}$ T versus T for $-500$ cm$^{-1} \leq J_{DA} \leq +500$ cm$^{-1}$ (right). ................................................................. 12

Figure I-6. Spitting of a degenerate triplet state (left) into $m_S = -1$, $m_S = 0$, and $m_S = +1$ states.................................................................................................................................................. 13

Figure I-7. Simulations of imino nitroxide (orange, $a_N = 9$ gauss, 4.5 gauss), nitronyl nitroxide (blue, $a_N = 7.5$ gauss), and SQ-para-phenylene-NN (green, apparent $a_N = 3.6$ gauss). ............................................................................................................................................. 16

Figure I-8. Electronic couplings with representations of respective fragment orbitals (left) and VBCI state interactions (right). ............................................................................................................................................. 17

Figure I-9. An example of a compound used for PET studies................................................................. 20

Figure I-10. An example Jablonski diagram of a PET system with one bridge unit. ............ 21

Figure I-11. An example of a break junction conductance device. ...................................................... 22
Figure I-12. Electron/hole transfer mechanisms for D-B-A systems. .................................................. 24
Figure I-13 Relationship between PET rate constants ($k_{D\rightarrow A}$), MMM conductance devices ($g$), and electronic coupling ($H_{DA}^2$). ........................................................................................................ 25
Figure II-1. (Left) The interaction of two p-orbitals at angle $\phi$. (Right) The overlap density between the two p-orbitals as a function of angle $\phi$. ................................................................. 38
Figure II-2. Re-plotted electronic coupling ($V_{DA} = H_{DA}$) versus $|\cos(\phi)|$ instead of $\phi$ from Harriman. ................................................................................................................................. 40
Figure II-3. Line bond drawings of sterically hindered D-B-A biradicals studied for torsional dependence of $J_{DA}$ and $H_{DA}$........................................................................................................................................ 41
Figure II-4. Bond-line drawings and thermal ellipsoid plots (hydrogen atoms and cumenyl groups omitted for clarity) of sterically hindered D-B-A biradical complexes. ................. 45
Figure II-5. (A) Magnetic susceptibility of 1-pPh (black), 1-MePh (red), 1-PhMe (blue), 1-pXylyl (green), and 1-PhMe4 (purple) with fit parameters. (B) Magnetic susceptibility of 1-BCO with fit parameters collected by Jinyuan Zhang. .................................................. 47
Figure II-6. Experimental (red) and calculated (blue) powder X-ray diffraction of 1-MePh, 1-PhMe, and 1-pXylyl........................................................................................................................................... 48
Figure II-7. 3-dimensional plots of $J_{DA}$ versus $\cos^2(\phi_{SQ})$ and $\cos^2(\phi_{NN})$. ................................. 49
Figure II-8. 3-dimensional plots of $H_{DA}$ versus $\cos(\phi_{SQ})$ and $\cos(\phi_{NN})$. ........................................... 50
Figure II-9. Stack plot of extinction coefficients for 1-pPh (red), 7 1-MePh (blue), 1-PhMe (green), 1-pXylyl (purple), and 1-PhMe4 (black). .......................................................................................... 52
Figure II-10. Electronic absorption spectra of 1-MePh in toluene (red) and DMSO (blue). Inset is an expansion of the 12,000 cm$^{-1}$ to 18,000 cm$^{-1}$ region. ..................................................... 53
Figure II-11. (Left) Variable-temperature electronic absorption of 1-MePh from 5 K to 300 K. (Right) Normalized intensities of 424 nm (blue) and 356 nm (red) absorptions as a function of temperature and fit to a Boltzmann population for $S = 0$ (red) and $S = 1$ (blue).

Figure II-12. (Left) Variable-temperature electronic absorption of 1-PhMe from 5 K to 300 K. (Middle) Variable-temperature electronic absorption of 1-pXylyl from 5 K to 300 K. (Right) Variable-temperature electronic absorption of 1-PhMe$_4$ from 5 K to 250 K.

Figure II-13. Calculated pure singlet and triplet spectra of 1-MePh via VT-EAS results.

Figure II-14. Resonance Raman stack plot of 1 (black), 1-pPh (red), 1-MePh (blue), and 1-pXylyl (green) using a 407 nm excitation.

Figure II-15. Arrow pushing line bond drawing showing structure of SQ (SOMO) $\rightarrow$ NN (LUMO) CT excited state. The 1603 cm$^{-1}$ stretch in the resonance Raman thus comes from the quinoidal character of the complex.

Figure II-16. Resonance Raman absorption profile for 1-MePh overlaid on the absorption spectrum of 1-MePh. Resonance Raman enhancement data points (red circles) were collected at 407, 458, 488, 514, 568, and 647 nm.

Figure II-17. CASSCF(4,4) $S=1$ state spin density.

Figure III-1 Line bond drawings of D-B-A biradical analogs of oligo(para-phenylene) and oligo(2,5-thiophene) used for distance dependence studies.

Figure III-2 Thermal ellipsoid plots of 1 (top), 1-pPh (middle left), 1-Ph$_2$ (bottom left), 2-(2,5)T (middle right), and 2-T$_2$ (bottom right).
Figure III-3 Plots of the paramagnetic susceptibility-temperature product ($\chi_{\text{para}}$•T) vs. temperature for 1-Ph$_2$ (red), 2-T$_2$ (blue) and 2-T (black) with best fit lines for 1-Ph$_2$ and 2-T$_2$ in red and blue respectively. ................................................................. 84

Figure III-4. (Left) EPR spectrum of KSQ-T as 0.2 mM solution in THF (red), simulation (blue), and the residual (green). ........................................................................................................ 86

Figure III-5. NMR Spectra of S3 and S3-d in DMSO-$d_6$. ........................................................................................................ 87

Figure III-6. (Left) EPR of KSQ-T-$d$ as a 0.2 mM solution in THF (red), simulation (blue), and the residual (green) ........................................................................................................ 88

Figure III-7. Extinction coefficients of 1 (red), 1-pPh (blue), 1-Ph$_2$ (green), 2-(2,5)T (purple), and 2-T$_2$ (black). ........................................................................................................ 90

Figure III-8. Exponential dependence of $J_{DA}$ and $H_{DA}$ on distance for oligo(para-phenylene)-bridged biradical series, 1, 1-pPh, and 1-Ph$_2$ (A) and for oligo(2,5-thiophene)-bridged series, 1, 2-(2,5)T, and 2-T$_2$ (B) ........................................................................................................ 92

Figure III-9. Bond line drawings of electron rich thiophene and selenophene bridged D-B-A biradicals. ........................................................................................................ 98

Figure III-10. Normalized electronic absorption of 2-(2,5)T (green), 2-T$_2$ (red), 3-Se (blue), 3-Se$_2$ (black) in DCM. ........................................................................................................ 102

Figure III-11. (Left) EPR of KSQ-Se as a 0.2 mM solution in THF (red), simulation (blue), and residual (green) ........................................................................................................ 103

Figure III-12. Electronic absorption spectra in DCM before (solid lines) and after (dashed lines) air and light free crystallization attempts for 3-Se and 3-Se$_2$. ........................................................................ 106

Figure IV-1. Line bond drawings of 1-pPh and 1-mPh used for cross-conjugation studies. 128
Figure IV-2. Line drawing of tetramethyleneethane (TME) (left) and corresponding SOMOs (right). .............................................................. 129

Figure IV-3. Line drawing of trimethylenemethane (TMM) (left) and meta-xyylene (right). ........................................................................................................................................ 130

Figure IV-4. Hückel MOs and orbital coefficients for NN LUMO (left top), SQ SOMO (left bottom), and the SQ-based SOMO for Tp\textsuperscript{Cum,Me}Zn(SQ-pPh-NN) (right). ........................................ 132

Figure IV-5. Hückel molecular orbital cartoon for SQ-para-phenylene-NN where red is positive and blue is negative. ........................................................................................................ 133

Figure IV-6. Hückel molecular orbital cartoon for SQ-meta-phenylene-NN where red is positive and blue is negative. ........................................................................................................ 133

Figure IV-7. Experimental vs. simulation of the meta-phenylene-bridged biradical EPR spectrum .............................................................................................................................. 135

Figure IV-8. Line drawing (left), ORTEP crystal structure (middle), and space-filling model (right) of Tp\textsuperscript{Cum,Me}Zn(SQ-mPh-NN) (1-mPh) .................................................................................. 136

Figure IV-9. Stack plot of difference variable temperature spectra obtained by subtracting a spectrum at 298K from the higher temperature spectra ........................................................................................................ 138

Figure IV-10. Magnetometry data for the meta-phenylene biradical indicating antiferromagnetic coupling of the SQ donor and the NN acceptor. .................................................. 139

Figure IV-11. ORTEP of two Tp\textsuperscript{Cum,Me}Zn(SQ-mPh-NN) molecules connected by a close crystallographic contact. ........................................................................................................ 140

Figure IV-12. ORTEP of two Tp\textsuperscript{Cum,Me}Zn(SQ-pPh-NN) molecules connected by a close crystallographic contact. ........................................................................................................ 140
Figure IV-13. (Left) EPR of Δm_s = 2 transition at 80 K for 1-mPh occurring due to thermal population of the ground state triplet. Double integration of this spectrum versus temperature creates the integrated spectral area data points in the Curie plot (Right). ......................... 142

Figure IV-14. Electronic absorption spectra of Tp_{Cum,Me}Zn(SQ-mPh-NN) (1-mPh) (red), Tp_{Cum,Me}Zn(SQ-pPh-NN) (1-pPh) (blue), and Tp_{Cum,Me}Zn(SQ-NN) (1) (green). ......................... 144

Figure IV-15. Important HMO fragments for 1-mPh (left) and 1-pPh (right). ......................... 149

Figure IV-16. Variable temperature electronic absorption of 1-mPh as a thin polystyrene film from 298K (red) to 5K (purple). ................................................................. 151

Figure IV-17. (Left) Calculated Boltzmann distributions using 2J_{DA} = -64 cm^{-1} (solid lines) and normalized peak intensities (♦) for transitions at 27,000cm^{-1} and 31,300 cm^{-1}. (Right) Calculated Boltzmann distributions using 2J_{DA} = -64 cm^{-1} (solid lines) and normalized peak intensities (♦) for transitions at 27,000cm^{-1} and 24,900 cm^{-1}. ........................................... 152

Figure IV-18. Deconvoluted pure singlet (blue) and pure triplet (red) electronic absorption spectra for 1-mPh by variable temperature electronic absorption spectroscopy. .................. 153

Figure IV-19. Possible electronic configurations contributing for 1-mPh. ......................... 155

Figure IV-20. Spin polarization in 1-mPh. ................................................................. 159

Figure IV-21. Cartoon descriptions of the dominant CI mechanisms for antiferromagnetic exchange coupling of SQ and NN spins in cross-conjugated 1-mPh (left) and ferromagnetic exchange coupling in conjugated 1-pPh (right). ......................................................... 161

Figure IV-22. Resonance effect of various donor and acceptor positions on a thiophene ring. ........................................................................................................................................................................ 164

Figure IV-23. Line bond drawing of 2-(2,5)T, 2-(3,5)T, and 2-(2,4)T.................................. 165
Figure IV-24. Thermal ellipsoid plots of 2-(2,5)T,\textsuperscript{94} 2-(3,5)T, and 2-(2,4)T. ...................... 168
Figure IV-25. Oxygen-oxygen close contact in 2-(2,4)T preliminary crystal structure. ...... 171
Figure IV-26. Magnetometry of 2-(3,5)T (blue) and 2-(2,4)T (red)................................. 172
Figure IV-27. (Left) EPR of 2-(3,5)T $\Delta m_s = 2$ transition at 24 K in 2-MeTHF. Double integration of the $\Delta m_s = 2$ transition versus temperature yields data points (blue) for the Curie plot of 2-(3,5)T (right). ............................................................... 173
Figure IV-28. Electronic absorption spectra of 2-(2,5)T (green), 2-(3,5)T (blue), and 2-(2,4)T (red) with expansion of 10,000 cm$^{-1}$ to 20,000 cm$^{-1}$ region (inset). ......................... 175
Figure IV-29. (Top) Important fragment HMOs for 2-(3,5)T (left) and 2-(2,4)T (right) where red is positive and blue is negative. (Bottom) Spin polarization of the $\pi$-system for 2-(3,5)T (left) and 2-(2,4)T (right) where blue is (+) spin and green is (-) spin. ..................... 176
Figure IV-30. (Left) Frontier orbitals for a \textit{para}- and \textit{meta}-coupled phenylene ring. (Right) A cartoon of a quantum interference effect transistor (QuiET)....................................................... 178
Figure IV-31. Line bond drawings of 1-mPh, 1-NO$_2$, 1-OMe, 1-CN, and 1-Me. ............ 178
Figure IV-32. Thermal ellipsoid plots with relevant torsion angles for substituted \textit{meta}-phenylenes.......................................................... 185
Figure IV-33. Magnetometry stack plot for 1-mPh (red),\textsuperscript{145} 1-NO$_2$ (blue), 1-OMe (green), 1-CN (purple), and 1-Me (black). .............................................................. 187
Figure IV-34. (A) $J_{DA}$ vs. cos$^2(\phi_{NN})$, (B) $J_{DA}$ vs. cos$^2(\phi_{SQ})$, and (C) contour plot of cos$^2(\phi_{SQ})$ vs. cos$^2(\phi_{NN})$ for 1-mPh, 1-NO$_2$, 1-OMe, 1-CN, and 1-Me. Red lines in A and B connect the data point for 1-mPh to 1-Me and do not represent a fit of the data. The colored surface in C
reflects the $J_{DA}$ values across the data by simply connecting the data points with a surface and does not represent a fit to the data. ................................................................. 188

Figure IV-35. Variable-temperature electron paramagnetic resonance stack plot of 1-mPh, \textsuperscript{145} 1-NO$_2$, 1-OMe, 1-CN, and 1-Me. Intensities normalized and shifted vertically for comparison purposes. .................................................................................................................. 190

Figure IV-36. Electronic absorption stack plot for 1-mPh (red), \textsuperscript{145} 1-NO$_2$ (blue), 1-OMe (green), 1-CN (purple), and 1-Me (black). ............................................................... 192

Figure IV-37. Oxidation half of cyclic voltammetry for 1-mPh, 1-NO$_2$, 1-OMe, and Tp$^{Cum,Me}$Zn(SQ) referenced to Fc/Fc$^+$ couple. ................................................................. 195
LIST OF SCHEMES

Scheme I-1. Synthesis of Tp$^{Cum,Me}$Zn(SQ-NN) via bromoguaiacol starting material. .......... 26
Scheme I-2. Traditional synthetic route to synthesize Tp$^{Cum,Me}$Zn(SQ-Ph-NN) as previously reported. .................................................................................................................. 28
Scheme I-3. Improved synthesis of 9 via IBX oxidation, sodium meta-bisulfite reduction... 29
Scheme I-4. Aldehyde adduct formation from decomposition of sodium meta-bisulfite...... 30
Scheme I-5. Improved synthetic scheme to Tp$^{Cum,Me}$Zn(SQ-pPh-NN) (1-pPh) which obviates the need for protecting groups. ............................................................................................................. 31

Scheme II-1. Synthesis of 1-MePh. ................................................................................................. 42
Scheme II-2. Synthesis of 1-PhMe, 1-pXylyl, and 1-PhMe$_4$................................................. 43

Scheme III-1. Synthesis of 1-Ph$_2$. ......................................................................................... 77
Scheme III-2. Synthesis of 2-(2,5)T. ......................................................................................... 78
Scheme III-3. Synthesis of 5-T$_2$.............................................................................................. 79
Scheme III-4. Synthesis of KSQ-T and its Deuterium-labeled analog KSQ-T-d. ................. 80
Scheme III-5. Synthesis of 3-Se.................................................................................................. 99
Scheme III-6. Synthesis of 3-Se$_2$. .......................................................................................... 100
Scheme III-7. Synthesis of KSQ-Se following the same general procedure as KSQ-T...... 101

Scheme IV-1. Synthesis of 1-mPh............................................................................................ 134
Scheme IV-2. Synthesis of 2-(3,5)T. ....................................................................................... 166
Scheme IV-3. Synthesis of 2-(2,4)T. ....................................................................................... 167
Scheme IV-4. Synthesis of 1-NO$_2$. ....................................................................................... 181
Scheme IV-5. Synthesis of 1-OMe................................................................. 182
Scheme IV-6. Synthesis of 1-CN............................................................... 183
Scheme IV-7. Synthesis of 1-Me............................................................... 184
LIST OF ABBREVIATIONS

D-B-A : donor-bridge-acceptor
SQ : semiquinone
NN : nitronylnitroxide

$H_{DA}$ : Donor-Acceptor electronic coupling constant
$H_{DB}$ : Donor-Bridge electronic coupling constant
$H_{BA}$ : Bridge-Acceptor electronic coupling constant
$H_{BB}$ : Bridge-Bridge electronic coupling constant

PET : photoinduced electron transfer
MMM: metal-molecule-metal
STM-BJ: scanning-tunneling microscopy break junction

VBCI : valence bond configuration interaction
QuIET : Quantum Interference Effect Transistor

MO : molecular orbital
AO : atomic orbital

HMO : Hückel molecular orbital
HDVV : Heisenberg-Dirac-Van Vleck

HOMO : highest occupied molecular orbital
LUMO : lowest unoccupied molecular orbital
SOMO : singly occupied molecular orbital

CT : charge transfer
GS: ground state
ES: excited state
GC: ground configuration
EC: excited configuration
CTC: charge transfer configuration
DEC: double excited configuration
CAS: complete active space
TDDFT: time-dependent density functional theory
SQUID: superconducting quantum interference device
EPR: electron paramagnetic resonance
VT-EPR: variable-temperature electronic paramagnetic resonance
EAS: electronic absorption spectroscopy
VT-EAS: variable-temperature electronic absorption spectroscopy
XRD: X-ray diffractometry
PXRD: powder X-ray diffractometry
FM: ferromagnetic
AFM: antiferromagnetic
IBX: o-iodoxybenzoic acid
DCM: dichloromethane
MeOH: methanol
THF: tetrahydrofuran
2-MeTHF: 2-methyltetrahydrofuran
Et₂O : diethyl ether

EtOAc : ethyl acetate

DMF : N,N-dimethylformamide

DMSO : dimethyl sulfoxide

Pd(PPh₃)₄ : tetrakis(triphenylphosphine) palladium(0)

NBS : N-bromosuccinimide

BPO : benzoyl peroxide

TLC : thin layer chromatography

ls : low spin

hs : high spin

VT : valence tautomer

ITO : indium tin oxide
I. General Introduction to Donor-Bridge-Acceptor Biradicals

A. Introduction

Throughout this work, exploration of molecular electronic structure will provide detailed insight into how Donor-Bridge-Acceptor (D-B-A) biradicals can provide us electronic coupling information across organic bridge fragments with various conformations and substituents. There have been promising approaches for integration of D-B-A molecules into solar energy conversion electrochemical cells\textsuperscript{1,2} (Figure I-1), application for nano-scale molecular electronics\textsuperscript{3,4} (Figure I-2), as well as understanding the fundamentals of Donor-Acceptor interactions from the perspective of superexchange.\textsuperscript{5-7}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Diagram of solar energy conversion utilizing a photoinduced electron transfer within a D-B-A molecule. The Donor (D) is photo excited. Then an electron is transferred through the Bridge (B) to the Acceptor (A). Once in the charge separated state, the D-B-A can participate in other oxidation-reduction reactions and return to its original state.}
\end{figure}
Figure I-2. Diagram of a circuit containing a diode (right) and the molecular equivalent (left) using Donor (D) and Acceptor (A) electrodes with an organic semiconducting Bridge (B). The molecular D-B-A triad acts as a molecular rectifier, similar to a diode, by only allowing transfer from the Donor to the Acceptor.

The rest of Chapter I will first focus on prediction of ground spin state of biradicals and the concepts involved in measuring the electron-electron exchange coupling through electron spin resonance (EPR) as well as magnetometry. Following this, an explanation of the Valence Bond Configuration Interaction (VBCI) theory used to describe the biradical electronic structure discussed in this work will be covered. Once a foundation for the electronic structure of D-B-A biradicals is laid, we will take a look at how donor-acceptor biradical electronic structure relates to photoinduced electron transfer (PET) D-B-A systems, metal-molecule-metal (MMM) conductance devices, and what allows us to make direct comparisons between the three systems. Finally, Chapter I concludes with a discussion of the evolution of the synthesis of D-B-A molecules utilizing a semiquinone (SQ) donor, a nitronylnitroxide (NN) acceptor and an organic bridge fragment.

In Chapter II, we use the VBCI model to investigate the torsional dependence of the electronic coupling within SQ-B-NN biradicals over 72% of the possible torsional range. Using the McConnell model for electronic coupling in D-B-A systems, we compare our system with similar effects in PET systems and MMM single molecule devices. Due to
the asymmetric nature of D-B-A systems, we show how there is a nonlinear relationship between $J_{DA}$, and thus $H_{DA}$, and the torsion angles in a D-B-A.

Chapter III takes a look at two common bridge backbones, oligo$(para$-phenylene) and oligo$(2,5$-thiophene), which are used in electron transport systems and how the electronic coupling decreases as a function of distance. Studies of exponential distance dependence between donor and acceptor have been studied through PET$^{10,15–17}$ and MMM conductance,$^{18–21}$ but our system allows for comparison of the bridge-bridge electronic coupling constant, $H_{BB}$, using the McConnell model for electronic coupling. By utilizing the information learned about electron rich thiophenes, we can compare the effect of the heteroatom on electronic coupling distance dependence by exploring the effects of other chalcogenophene bridges commonly used for electron transport devices.

Chapter IV switches the focus from conjugated D-B-A systems to the electronic coupling in cross-conjugated D-B-A biradical complexes. The first section begins by comparing the electronic coupling through $para$- and $meta$-phenylene bridges. Bardeen$^{22}$ has shown that $meta$–coupled systems extend the lifetime of charge–separated states, while Wasielewski$^{23}$ has shown through photoinduced electron transfer (PET) in weakly coupled D-B-As that cross conjugation can also provide increased charge–separated lifetimes. Between Wasielewski and Bardeen, no comparison of electronic coupling $meta$- and $para$-through a benzene ring has been described. In addition, we show how cross-conjugation in a $meta$-phenylene ring does not cut off communication through the $\pi$-system, but rather uses a $\pi$-system based spin polarization mechanism to provide coupling instead.
In the second section of chapter IV, we continue with cross-conjugated bridges but move back to the electron rich thiophene moiety. Cross-conjugated thiophene systems have been studied using two homoradicals\textsuperscript{24,25} and through single molecule device conductance\textsuperscript{26} but remain unexplored in PET D-B-A systems. Due to our precise synthetic control and the asymmetric nature of our SQ-B-NN system, we investigate how the sign and magnitude of the exchange coupling through a cross-conjugated thiophene depends on the location of the donor and acceptor on the ring/bridge.

The final section of chapter IV extends our studies of cross-conjugated systems and applies it to the concept of a Quantum Interference Effect Transistor (QuIET).\textsuperscript{27,28} While there has been theoretical studies on both QuIET-like devices,\textsuperscript{27–34} there have been no experimental studies of model systems. By placing electron-donating and electron-withdrawing substituents ortho- to SQ and para- to NN, the previously studied SQ-meta-Phenylene-NN system can be used as a model for QuIET systems where the substituents affect the magnitude of electronic coupling between donor and acceptor via the π-system in contrast to earlier studies implicating the importance of the σ-system.

B. The Utility of Hund's Rule in Predicting Ground Spin-States in S > 1/2 Molecules

The most straightforward method to predict the sign of exchange coupling ($J > 0 \equiv$ ferromagnetic, $J < 0 \equiv$ antiferromagnetic) between the Donor π-radical and Acceptor π-radical in SQ-Bridge-NN system is to make use of the simple Hückel MO (HMO) theory treatment. This is remarkable since simple HMO theory does not treat spin explicitly! Nevertheless, HMO theory can be used to predict the ground spin state. The simplest way to
accomplish this is to apply Hund's rule.\textsuperscript{35} Hund's rule generally states that spin is maximized for the lowest energy degenerate electronic configuration.\textsuperscript{36} Both Hund's Rule and the Pauli Exclusion Principle are derived from electron indistinguishability.

Let us consider a system with two Atomic Orbitals (AOs), A and B, containing two electrons, 1 and 2, where indistinguishability allows for the symmetric spatial wavefunction is (Eq. I.1) and the anti-symmetric spatial wavefunction (Eq. I.2).

\[ \Psi_{\text{Sym}} = \frac{1}{\sqrt{2}} (\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)) \]  

\[ \Psi_{\text{Anti}} = \frac{1}{\sqrt{2}} (\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)) \]  

Using Eq. (I.3) we can determine the energy of the spatial wavefunctions as shown in Eq. (I.4) and (I.5) respectively.

\[ E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]  

\[ E_{\text{Sym}} = \frac{1/2 \langle (\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)) | H | (\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)) \rangle}{1/2 \langle \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) | \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) \rangle} \]  

\[ E_{\text{Anti}} = \frac{1/2 \langle (\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)) | H | (\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)) \rangle}{1/2 \langle (\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)) | (\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)) \rangle} \]  

For these energies, a coulomb integral, \( j \) is represented by Eq. (I.6)

\[ j = \langle \phi_A^2(1) | H | \phi_B^2(2) \rangle \text{ and } j = \langle \phi_B^2(1) | H | \phi_A^2(2) \rangle \]  

and an exchange integral, \( k \) represented by Eq. (I.7).

\[ k = 2 \langle \phi_A(1)\phi_B(1) | H | \phi_A(2)\phi_B(2) \rangle \]
By considering Eq. (I.6) and (I.7) in Eq. (I.4) and (I.5), we get the energy for the singlet (symmetric) and triplet (antisymmetric) states shown in Eq. (I.8 a) and (I.8 b) respectively.

\[
\text{(a) } E_{\text{Singlet}} = \left[ \frac{j + k}{1+0} \right] = j + k \quad \text{(b) } E_{\text{Triplet}} = \left[ \frac{j - k}{1+0} \right] = j - k
\]

**Figure I-3.** Visual Representation of Hund’s Rule (left) and the Pauli Exclusion Principle (right). \( \phi_A \) (green) and \( \phi_B \) (grey) are two orthogonal p-orbitals where the brown section is the overlap between them.

The result from these energies is represented visually in Figure I-3 where the coulomb integral results from electron-electron repulsion between (1) and (2) when they are localized only within the green and grey regions. The exchange integral results from the electron-electron repulsion between the two electrons when they are within the brown region. If we examine the triplet energy again, we see the exchange integral is subtracted from the electron-electron repulsion energy which is a mathematical representation of the Pauli
Exclusion Principle. We can use Eqs. (I.8 a) and (I.8 b) to determine the energy difference between the singlet and triplet states, as shown in Eq. (I.9), to be \(2k\).

\[
E_{\text{Singlet}} - E_{\text{Triplet}} = (j + k) - (j - k) = 2k
\]  

Equation I.9

The consequence of this relationship is that if there is a large overlap density (not the overlap integral) between two orbitals, the electrons prefer to stay aligned parallel to avoid the electron-electron repulsion inside the overlap region. This is important as this effect can be seen in interactions between electrons in MOs as well as AOs.\(^{37}\)

As stated above, this simple AO representation of Hund's rule can be extended to MOs.\(^{38}\) For a biradical, each electron is contained in separate singly-occupied molecular orbitals (SOMOs) that can share overlap density just like two atomic orbitals considered previously. Overlap between two SOMOs are determined by comparison of Hückel AO coefficients on fragment orbitals.\(^{37}\) To make these comparisons, the molecular version of Hund's rule uses fragment orbitals just as the atomic version uses AOs. For a more complete analysis using the molecular orbital Hund's rule, configuration interaction must also be taken into consideration.. Based on previous work,\(^{4,39}\) it has been shown that the overall exchange coupling due to a molecular version of Hund's rule can be expressed as shown in Eq. (I.10)

\[
J = J_{FM} + J_{AFM} = 2k_{ab} - \frac{4H_{ab}}{U}
\]  

Equation I.10

where \(J_{FM}\) is ferromagnetic exchange coupling, \(J_{AFM}\) is antiferromagnetic exchange coupling, \(2k_{ab}\) is a two site electron repulsion exchange integral, \(U\) is the charge transfer energy, and \(H_{DA}\) is the electronic coupling matrix element that describes the interaction between electrons in orbitals a and b. If orbitals a and b are orthogonal, then \(J_{AFM} = 0\) and the
coupling will be ferromagnetic. A more useful model, one that correlates exchange coupling with spectroscopic parameters will be presented below, will show that there are pathways for which the \( \mathbf{H}_{\text{Da}/U} \) term provides ferromagnetic coupling. Nevertheless, through MO theory and Eq. (I.10), it is possible to have a simple understanding of electronic coupling in biradical systems.

**C. Measuring Exchange Coupling in Biradical Complexes**

Directly measuring the exchange coupling parameter \( J \) for systems containing unpaired electrons is possible through magnetometry\(^{40}\) and Electron Paramagnetic Resonance (EPR) spectroscopy. The most straightforward method is via a superconducting quantum interference device (SQUID) magnetometer. Using the Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian in Eq. (I.11), we can model a paramagnetic system with two unpaired electrons.

\[
\hat{H}_0 = -2J_0 \hat{S}_i \hat{S}_j \tag{I.11}
\]

To work with the HDVV Hamiltonian, the total spin of the system must be described as in Eq. (I.12) where the eigenvalue of \( S_{\text{Tot}}^2 \) is shown in Eq. (I.13).

\[
\hat{S}_{\text{Tot}}^2 = (\hat{S}_i + \hat{S}_j)^2 = \hat{S}_i^2 + \hat{S}_j^2 + 2\hat{S}_i \hat{S}_j \tag{I.12}
\]

\[
\hat{S}_{\text{Tot}} \Psi = S(S+1) \Psi \tag{I.13}
\]

Using Eq. (I.13), we can determine the total energy of the system in Eq. (I.14).

\[
E_{\text{Tot}} = -J_0 \left[ S_{\text{Tot}} (S_{\text{Tot}} + 1) - S_i (S_i + 1) - S_j (S_j + 1) \right] \tag{I.14}
\]
For a triplet state, \( S_{\text{Tot}} = 1 \) and \( S_i = S_j = 1/2 \). With this fact, Eq. (I.14) can be rewritten into Eq. (I.15) for the energy of the triplet.

\[
E_{\text{Triplet}} = -J \left[ 1(1+1) - 1/2(1/2+1) - 1/2(1/2+1) \right] = -J_{DA}/2
\]

For a singlet state, \( S_{\text{Tot}} = 0 \), and \( S_i = S_j = 1/2 \). Again, Eq. (I.14) can be rewritten into Eq. (I.16) for the energy of the singlet.

\[
E_{\text{Singlet}} = -J \left[ 0 - 1/2(1/2+1) - 1/2(1/2+1) \right] = 3J_{DA}/2
\]

By subtracting the energy of the triplet from the energy of the singlet, we obtain Eq. (I.17) which describes the energy difference between the singlet and the triplet to be \( 2J_{DA} \).

\[
\Delta E_{ST} = E_s - E_T = \frac{3J_{DA}}{2} - \left( -\frac{J_{DA}}{2} \right) = 2J_{DA}
\]

By looking at the mixing between two radical centers, we can see two possibilities as shown in Figure I-4.

Figure I-4. Energy level diagrams of a two electron triplet ground state (left) and singlet ground state (right) with corresponding signs of \( 2J_{DA} \).

If the triplet state is lower in energy than the singlet, based on Eq. (I.17), \( J_{DA} \) will be positive. Similarly, if the singlet state is lower in energy than the triplet, Eq. (I.17) shows \( J_{DA} \) to be
negative. The electronic coupling constant of a system can be directly related to magnetic susceptibility through Van Vleck’s equation\textsuperscript{40,41} shown below in Eq. (I.18)

$$\chi_{\text{Para}} = \frac{N \sum_n E_n^{(1)} e^{-E_n^{(0)}/k_BT}}{k_B T \sum_n e^{-E_n^{(0)}/k_BT}}$$ \textsuperscript{I.18}

where $N$ is Avogadro’s Number, $k_B$ is the Boltzmann constant, $T$ is temperature, and $E_n$ is the energy of a given state. Using the HDVV Hamiltonian shown in Eq. (I.11) and some unit conversions, we can rewrite Eq. (I.18) into Eq. (I.19)

$$\chi_{\text{Para}} = \frac{N g^2 \beta^2}{2 k_B T} \sum_S S(S+1)(2S+1) e^{-E_S/\beta T} \sum_S (2S+1) e^{-E_S/\beta T}$$ \textsuperscript{I.19}

where $\beta$ is Bohr magneton, $S$ is the total spin of a given state, $E_S$ is the energy of a given state, and $g$ is the electron g-factor which is $\sim 2$ for organic radicals. For two electron system with $S = 1$ and $S = 0$,

$$\chi_{\text{Para}} = \frac{g^2 0.125 \text{emuK/mol}}{T} \left( 0(0+1)(2*0+1)e^{-E_{11}/\beta T} + 1(1+1)(2*1+1)e^{-E_{12}/\beta T} \right)$$ \textsuperscript{I.20}

$$\chi_{\text{Para}} = \frac{g^2 0.125 \text{emuK/mol}}{T} \left( \frac{-E_{11}}{6 e^{-E_{11}/\beta T}} - \frac{-E_{12}}{1 e^{-E_{12}/\beta T} + 3 e^{-E_{12}/\beta T}} \right)$$ \textsuperscript{I.21}

multiplying Eq. (I.21) by $\exp(E_S/k_BT)$ we obtain Eq. (I.23).
\[
\chi_{\text{para}} = g^2 0.125 \text{emuK/mol} \frac{(E_s - E_t)}{T} \frac{6e^{-E_s/k_BT}}{1 + 3e^{-E_s/k_BT}}
\]

Looking back at Eq. (1.17), we see that Eq. (1.22) can be modified to Eq. (1.23).

\[
\chi_{\text{para}} = g^2 0.125 \text{emuK/mol} \frac{2J_{DA}}{T} \frac{6e^{-E_s/k_BT}}{1 + 3e^{-E_s/k_BT}}
\]

Alternatively, if we assume the triplet state is the ground state, we can arbitrarily assign the energy of \( E_T \) to be zero converting Eq. (1.17) into Eq. (1.24) and Eq. (1.21) into (1.25).

\[
\Delta E_{ST} = E_s - "0" = 2J_{DA}
\]

\[
\chi_{\text{para}} = g^2 0.125 \text{emuK/mol} \frac{6e^0}{1e^{-E_s/k_BT} + 3e^0}
\]

Simplification of Eq. (1.25) by substitution of Eq. (1.24) results in Eq. (1.26) which is equivalent to Eq. (1.23).

\[
\chi_{\text{para}} = g^2 0.125 \text{emuK/mol} \frac{6}{e^{-2J_{DA}/k_BT} + 3}
\]

Theoretical plots of various values of \( J_{DA} \) used in Eq. (1.26) are shown on the left side of Figure I-5 and clearly show the utility of plotting \( \chi_{\text{para}} \) versus temperature for \( J < 0 \).

However, when \( J > 0 \) the difference between data for \( J = 100 \text{ cm}^{-1} \) and for \( J = 5 \text{ cm}^{-1} \) is small which makes accurate fitting difficult. Commonly for compounds with \( J > 0 \), magnetometry data is instead plotted at \( \chi_{\text{para}}T \) versus temperature as shown on the right side of Figure I-5.

With a more obvious difference in data for compounds with \( J > 0 \), accurate fitting becomes
easier to visualize. The purple line in the $\chi_{\text{para}}T$ versus temperature plot represents the value of two uncoupled monoradicals (2•0.375 emu K / mol) to which all values of $J$ approach at high enough temperature using this model (see Eq. I.27).

**Figure I-5.** Theoretical plot of $\chi_{\text{para}}$ versus $T$ for $-100 \leq J_{DA} \leq +100$ cm$^{-1}$ (left) and $\chi_{\text{para}}T$ versus $T$ for $-500$ cm$^{-1} \leq J_{DA} \leq +500$ cm$^{-1}$ (right). Purple line at 0.75 emu K mol$^{-1}$ in $\chi_{\text{para}}T$ plot represents the value all theoretical lines are trending to at high temperatures for two $S=1/2$ radicals (see Eq. I.27).

$$\lim_{T \to \infty} \chi_{\text{para}} = \lim_{T \to \infty} \frac{g^2 0.125 \text{emu K/mol}}{T} \left( \frac{6}{e^{\frac{-2J_{DA}}{kT}} + 3} \right) = (2)^2 0.125 \left( \frac{6}{1 + 3} \right) = 0.75 \text{emu K/mol}$$

Practical magnetometry measurements are commonly influenced by structural elements of the sample and thus may require additional fit parameters to accurately describe the data collected. Additional common fit parameters include a Weiss correction ($\theta$) which describes weak intermolecular interactions and monoradical crystalline defects (0.375/T). We can include these additional corrections in Eq. (I.26) to form Eq. (I.28) and Eq. (I.29) where $X$ is the mol fraction of pure biradical.
\[ \chi_{\text{para}} = X \left( \frac{g^2 \cdot 0.125 \text{emuK/mol}}{T - \Theta} \left( \frac{6}{e^{\frac{-2J_{\text{tot}}}{k_B T}} + 3} \right) \right) + (1 - X) \left( \frac{0.375}{T} \right) \]

\[ \chi_{\text{para}} T = T \left( X \left( \frac{g^2 \cdot 0.125 \text{emuK/mol}}{T - \Theta} \left( \frac{6}{e^{\frac{-2J_{\text{tot}}}{k_B T}} + 3} \right) \right) + (1 - X) \left( \frac{0.375}{T} \right) \right) \]

Alternatively to magnetometry, EPR can be used based on the same principles. We have established for a two electron system there is a singlet state \((S_{\text{Tot}} = 0)\) and a triplet state \((S_{\text{Tot}} = 1)\). For a triplet state in EPR spectroscopy, the magnetic field splits the degeneracy as shown in Figure I-6.

![Figure I-6](image)

**Figure I-6.** Spitting of a degenerate triplet state (left) into \(m_S = -1, m_S = 0, \) and \(m_S = +1\) states. Allowed \(\Delta m_s = 1\) transitions (green) and forbidden \(\Delta m_s = 2\) transitions (red) also shown.

EPR will only measure paramagnetic signals so we can use a Boltzmann distribution to determine the relative concentration of triplet states given in Eq. (I.30).
\[ n_{\text{eq}} = \frac{n_T}{n_S + n_T} \]  

I.30

EPR intensity is directly proportional to paramagnetic susceptibility by the Curie law\(^\text{40}\) as shown in Eq. (I.31)

\[ I_{\text{EPR}} \propto \chi_{\text{Para}} = \frac{C}{T} \]  

I.31

where \( T \) is absolute temperature and \( C \) is the Curie constant. The Curie constant is a physical constant specific for the type of material. The result of combining Eq. (I.30) and Eq. (I.31) is shown in Eq. (I.32).

\[ I_{\text{EPR}} \propto \chi_{\text{Para}} = \frac{C}{T} \frac{n_T e^{-E_T/k_B T}}{n_S e^{-E_S/k_B T} + n_T e^{-E_T/k_B T}} \]  

I.32

By multiplying by \( \exp(-E_S/k_B T) \) and substituting the result of Eq. (I.17), we obtain Eq. (I.33).

\[ I_{\text{EPR}} \propto \chi_{\text{Para}} = \frac{C}{T} \frac{3e^{(E_S - E_T)/k_B T}}{1 + 3e^{(E_S - E_T)/k_B T}} = \frac{C}{T} \frac{3e^{2J_{DA}/k_B T}}{1 + 3e^{2J_{DA}/k_B T}} \]  

I.33

With Eq. (I.33) we have a correlation between EPR intensity and the electronic coupling constant, \( J_{DA} \). This allows us to measure small values of \( J_{DA} \) using variable temperature EPR spectroscopy.

**D. Electron Paramagnetic Resonance of Biradicals**

For nitronylnitroxides, EPR plays an important qualitative role as they have a distinct 5-line hyperfine EPR pattern that can be contrasted with a by-product imino nitroxide's 7-line...
hyperfine pattern. Biradicals nitronyl nitroxides are also unique as they show a 5-line pattern with a reduced hyperfine (Figure 1-7).\textsuperscript{42,43} Using the spin Hamiltonian in Eq. (I.34) from

$$\hat{H} = g \mu_B B_0 (S_{z1} + S_{z2}) + a (S_{z1} I_{z1} + S_{z2} I_{z2}) + J' \hat{S}_1 \cdot \hat{S}_2$$ \hfill (I.34)

Atherton,\textsuperscript{43} we can determine the effect an $S = 1$ biradical has on the apparent hyperfine coupling observed in the EPR spectrum. By choosing the basis functions $|S, M_S, M_I, M_2\rangle$ where $S$ is the total spin, $M_S$ is the spin quantum number, $M_I$ is the nuclear spin on atom 1, and $M_2$ is the nuclear spin on atom 2, we can generate a matrix that represents Eq. (I.34) as shown in Eq. (I.35).

$$
\begin{tabular}{|c|c|c|c|}
\hline
& $|1, 1, M_S, M_2\rangle$ & $|1, 0, M_S, M_2\rangle$ & $|0, 0, M_S, M_2\rangle$ & $|1, -1, M_S, M_2\rangle$ \\
\hline
$<1, 1, M_S, M_2|$ & $\frac{1}{2} a (M_S + M_2)$ & $g B_0 \mu_B + \frac{J'}{4}$ & 0 & 0 \\
$<1, 0, M_S, M_2|$ & 0 & $\frac{J'}{4}$ & $\frac{1}{2} a (M_S - M_2)$ & 0 \\
$<0, 0, M_S, M_2|$ & 0 & $\frac{1}{2} a (M_S - M_2)$ & $-\frac{3J'}{4}$ & 0 \\
$<1, -1, M_S, M_2|$ & 0 & 0 & 0 & $\frac{1}{2} a (M_S + M_2) - g B_0 \mu_B + \frac{J'}{4}$ \\
\hline
\end{tabular}
$$ \hfill (I.35)

For a biradical with $a \ll J$, the off diagonal elements of equation (I.35) can be ignored and the energy of the $\Delta M_S = 1, \Delta M_I = 0$ transitions are as shown in Eq. (I.36).

$$\Delta E = \left(g \mu_B B_0 + \frac{1}{2} a (M_1 + M_2) + \frac{J'}{4} \right) - \left(\frac{J'}{4} \right)$$ \hfill (I.36)

As a consequence of the quantum mechanics through the total spin of the system, triplet biradicals have a splitting of $a/2$ (half the hyperfine of a monoradical). At a quick glance, an ideal EPR spectrum becomes a useful tool to determine the presence of different possible radical moieties.
Figure I-7. Simulations of imino nitroxide (orange, $a_N = 9$ gauss, 4.5 gauss), nitronyl nitroxide (blue, $a_N = 7.5$ gauss), and SQ-para-phenylene-NN (green, apparent $a_N = 3.6$ gauss).

E. Donor-Bridge-Acceptor Valence Bond Configuration Interaction Model

As discussed previously, HMO theory is useful for predicting the sign of the exchange coupling; however, spectroscopic transitions are observed between states, not just MOs. We can therefore more accurately describe the D-B-A system using a Valence Bond Configuration Interaction (VBCI) model.$^{4,6,7,44}$
Figure I-8. Electronic couplings with representations of respective fragment orbitals (left) and VBCI state interactions (right). $H_{DA}$ is the electronic coupling matrix element describing the mixing of ground (GC) and excited configurations (CTC). $U$ is the average ground to excited state transition energy, $K_0$ is the single site exchange integral responsible for the excited state singlet-triplet gap, and $2J$ is the difference in energy between the ground state singlet and ground state triplet.

The VBCI model uses configuration interaction, the mixing of states of the same symmetry, to determine the exchange coupling, $J_{DA}$, between the SQ Donor and the NN Acceptor and importantly relate it to the electronic coupling matrix element, $H_{DA}$. In Figure I-8, we see an energy level diagram for both electronic coupling matrix elements as well as the configurations derived from the VBCI model. In this model, NN SOMO and SQ SOMO are orthogonal ($H_{11} = 0$) but NN LUMO and SQ SOMO are not ($H_{12} \neq 0$). Using these three fragment orbitals, Eq. (I.37) was derived:

$$2J_{DA} = \frac{2H_{DA}^2 K_0}{U^2 - K_0^2}$$

I.37
which is similar to the four orbital model developed by Girerd.\textsuperscript{45} In Eq. (I.37), $J_{DA}$ is the exchange coupling constant, $K_0$ is a single site excited state exchange integral, and $U$ is the mean charge transfer energy. The consequence here is that without any excited state interactions, the ground state singlet and triplet are degenerate. However, using configuration interaction the VBCI model mixes excited CTCs (from lowest energy SQ→NN CT) into GCs which split the previously degenerate ground state singlet and triplet by $2J_{DA}$. The most important fact that stems from this VBCI model is that $U$ and $K_0$ are obtainable through electronic absorption spectroscopy and $2J_{DA}$ is obtainable through magnetometry.\textsuperscript{6,7,40,46}

Through the VBCI model and Eq. (I.37), it is possible to calculate the electronic coupling matrix element $H_{DA}$, the value that directly relates the strength of coupling between two radicals, through direct experimental measurement. It was then shown that since the magnetic exchange and electronic coupling are directly related to one another, it is possible to use the ratio in Eq. (I.38) to compute the electronic coupling of $\text{Tp}^{\text{Cum,Me}}\text{Zn(SQ-Ph-NN)}$, and thus any synthetically viable bridge, to within 10% of the electronic coupling determined by also measuring $U$ and $K_0$ to calculate $H_{DA}$.\textsuperscript{7}

\begin{equation}
\frac{J_{SQ-B-NN}}{J_{SQ-NN}} = \frac{H^2_{SQ-B-NN}}{H_{SQ-NN}^2}
\end{equation}


As electronic devices become smaller, components contained within these devices must become smaller as well. One candidate for miniaturization is molecular electronics, since molecules are naturally nano-scopic. Donor-Bridge-Acceptor (D-B-A) systems have a
direct correlation with electronic devices involving electron transport across a single molecule bridge where the donor and acceptor can be thought of as electrodes. There are three equally effective ways to study D-B-A systems including PET in D-B-A molecules, metal-molecule-metal (MMM) conductance, and stable biradical D-B-A complexes. All three provide insight into the electronic coupling matrix element, $H_{DA}$, which measures the interaction of Donor and Acceptor.

Our approach to studying D-B-A interactions – and one that focuses on the stronger, adiabatic coupling regime – employs metal complexes of D-B-A biradical ligands comprised of semiquinone (SQ) Donor and nitronyl nitrooxide (NN) Acceptor studied. These SQ-Bridge-NN biradical D-B-A systems are nominally ground-state analogues of photoinduced charge-separated states in analogous PET D-B-As which allow for a direct probe of the electronic coupling between the donor and the acceptor as well as any bridge-mediated effects on this coupling. As discussed previously, we have developed a straight forward valence-bond configuration interaction (VBCI) model which correlates the ground-state exchange coupling measured by magnetometry to the electronic coupling matrix element for the SQ donor to NN acceptor interaction. To effectively compare our method of studying D-B-As with others, we must understand how PET systems and break junction conductance systems relate their experimental methods to the donor-acceptor electronic coupling, $H_{DA}$.

1. Photoinduced Electron Transfer and Electronic Coupling

Using extended π-systems like those in Figure I-9, PET has been used to explore the effect of torsion angle on electronic coupling, substituent effects on electronic
coupling, and cross-conjugation in D-B-A molecules. PET in D-B-As, accomplishes this by charge-separated excited states.

Figure I-9. An example of a compound used for PET studies.

For example, Wasielewski has shown several structure–property relationships involving $H_{DA}$ which can be determined by fast kinetics in the presence of a static magnetic field via the exchange parameter, $J_{DA}$. The process of PET can be seen in a simple form in Figure I-10. Photo-excitation generally proceeds through the Donor ($\rightarrow$D*-B-A) which undergoes electron transfer to yield the charge-separated state, D+B-A· (a biradical). The electronic coupling is determined kinetically by making use of the energy gap between the singlet and triplet states of the transient charge-separated biradical. These D+B-A· photoinduced states are challenging to study as the D+B-A· charge-separated state is transient.
Figure I-10. An example Jablonski diagram of a PET system with one bridge unit. $k_{cs}$ is the charge separation rate constant, $k_{st}$ is the rate constant for the intersystem crossing from singlet to triplet, and $k_{cr}$ is the charge recombination rate constant.

The rate constant measured by PET is then related to electronic coupling by Eq. (I.39) developed by Marcus\textsuperscript{57} and widely used for studying electron transfer rate constants.

$$k_{ET} = \frac{|H_{DA}|^2}{\hbar \pi^2 \sqrt{\lambda k_B T}} \exp \left( \frac{- (\lambda + \Delta G^0)^2}{4 \lambda k_B T} \right)$$

Here, $k_{ET}$ is the electron transfer rate constant, $\hbar$ is the reduced Planck’s constant, $k_B$ is the Boltzmann constant, $\lambda$ is reorganization energy, $T$ is temperature in K, and $\Delta G^0$ is the Gibb's free energy change for the electron transfer. A quick glance at this equation shows us that $k_{ET}$ is directly proportional to the electronic coupling squared, $H_{DA}^2$.

2. **Metal-Molecule-Metal Conductance and Electronic Coupling**

Conductance ($g$) measurements across a MMM junction has been used by a wide variety of groups to study molecular wire behavior,\textsuperscript{58–60} torsional effects of the bridge,\textsuperscript{61} and molecular electronics.\textsuperscript{62–69} The MMM system is also commonly used as a theoretical basis to...
study electronic coupling of different bridge fragments. Conductance experiments are usually performed by a combination of layering a thiol or amine functionalized organic bridge fragment on a gold substrate and using a gold plated probe in scanning-tunneling or atomic force microscopy as shown by the example in Figure I-11.

![Figure I-11](image)

**Figure I-11.** An example of a break junction conductance device. The yellow circles on the right represent gold atoms on a surface with one end of a thiol terminated bridge covalently bound to it. The yellow circles on the left represents a gold covered STM tip interacting with one of the thiol terminated bridges.

By bringing the probe close to the substrate, the functionalized bridges which are already covalently attached to the substrate can covalently attach the other end of the bridge to the probe. If an electric bias is applied, the conductance (1/resistance) can be measured for the system. To ensure the conductance measured is through the functionalized bridge and not just from substrate to probe, the probe is moved away from the substrate, stretching the bridge between the metal contacts, until the connection between the probe and the bridge breaks causing a sharp decrease in the measured conductance. By performing this measurement
thousands of times, the average conductance for a functionalized bridge can be determined. Relating the conductance measured in this fashion to electronic coupling through the bridge can be accomplished through Eq. (I.40).81–84

\[
g = \frac{e^2}{\pi \hbar} |G_{DA}|^2 \Gamma_D \Gamma_A
\]

Here, \(g\) is the measured MMM conductance determined through break junction techniques. \(e^2/\pi \hbar\) is the conductance quantum, \(\Gamma_D\) and \(\Gamma_A\) are the widths of the donor and acceptor energy levels as modified by their coupling to metal electrodes. \(G_{DA}\) is Green’s function for the donor-acceptor interaction which contains electronic couplings (Eq. I.41):82

\[
G_{DA} = \frac{H_{DB1} H_{BA}}{(E - E_D - \Sigma^{(L)}_D)(E - E_A - \Sigma^{(R)}_A)} G_{1n}
\]

where \(H_{DB1}\) is the electronic coupling between the donor and the first bridge unit, \(H_{BA}\) is the electronic coupling between the last bridge unit and the acceptor, \(E\) is the Fermi energy, \(E_D\) and \(E_A\) are the energy of the donor and acceptor respectively, \(\Sigma^{(L)}_D\) and \(\Sigma^{(R)}_A\) are the self-energies of the donor and acceptor, and \(G_{1n}\) is Green’s function of bridge units to each other. These nearest neighbor electronic couplings have been related by McConnell for any D-B-A system through a second-order perturbation theory as shown in Eq. (I.42).9

\[
H_{DA} = \frac{H_{DB} H_{BA}}{\Delta} \left(\frac{H_{BB}}{\Delta}\right)^{n-1}
\]

The electronic coupling between donor and acceptor (\(H_{DA}\)) is directly proportional to the electronic coupling between each nearest neighbor (\(H_{DB}, H_{BA}, \text{ and } H_{BB}\)) where the number of bridge units in the system is \(n\). \(\Delta\) is the energy required to either transfer an electron from the donor to the bridge LUMO (electron transfer) or transfer a hole from the acceptor LUMO to
the bridge HOMO (hole transfer). The difference between electron transfer and hole transfer is described graphically in Figure I-12.

![Figure I-12. Electron/hole transfer mechanisms for D-B-A systems.](image)

Through Eq. (I.41) and (I.42), we can see how Eq. (I.40) relates the measured conductance, \( g \), to the donor-acceptor electronic coupling, \( H_{DA} \).

3. Connecting PET, Conductance, and Biradicals Through Electronic Coupling

As shown above, PET rate constants, MMM conductance, and the magnetic exchange in SQ-NN biradicals all provide a means to calculate \( H_{DA} \). In fact, Ratner\textsuperscript{81} and Nitzan\textsuperscript{83,85} have even shown that conductance (\( g \)) is proportional to the electron transfer rate constant (\( k_{ET} \)) which are both proportional to the donor-acceptor electronic coupling (\( H_{DA} \)). It then
stands to reason that if conductance and PET can be directly related through electronic coupling and our VBCI model (Eq. I.37) relates magnetometry of coupled biradicals to $H_{DA}$, then biradicals can be directly related to both conductance and PET rate constants through $H_{DA}$. Thus PET, break junction conductance, and biradical magnetic exchange are directly relatable, as seen in Figure I-13, with each having its own strengths and weaknesses in determining the electronic coupling across various bridge fragments.

**Figure I-13** Relationship between PET rate constants ($k_{D→A}$), MMM conductance devices ($g$), and electronic coupling ($H_{DA}^2$).
G. Development of Versatile Synthetic Routes to Donor-Bridge-Acceptor Biradical Complexes

As with most chemical syntheses, there are multiple ways of attaining the desired compound. Our first method\textsuperscript{86} used to synthesize Tp\textsuperscript{Cum,Me}Zn(SQ-NN) involved a wasteful, but successful procedure as shown in Scheme I-1.

\textbf{Scheme I-1.} Synthesis of Tp\textsuperscript{Cum,Me}Zn(SQ-NN) via bromoguaiacol starting material.
The tert-butylation of the benzene ring was low yielding and produced a lot of waste. To produce just ~10 mg of product required, at minimum, ~1 gram of starting material. Our second method\textsuperscript{7,47,87,88} has used a the synthetic route shown in Scheme I-2 using the previously synthesized para-phenylene bridge as an example. This synthesis requires protection of the reactive catecholate moiety for SQ-Bridge-NN biradical syntheses due to the tert-buty lithium being used. There are two issues with this second route. First, throughout this "traditional synthesis" there are several instances where chromatography is required to purify the resulting product.
Although this is common, it is wasteful due to the amount of solvent required. Second, the use of tert-butyl lithium restricts the scale at which this synthesis can be performed safely due to its pyrophoric nature. There are also two protection/deprotection steps using methoxymethyl chloride (MOMCI), an expensive-to-produce/purchase and carcinogenic protecting group, which are required due to the use of potentially coordinating metals during specific synthetic steps. While this is necessary for the traditional synthetic scheme, it adds time and materials required to the process. Even though the traditional route is proven and
trusted, it can be improved through a new methodology we developed with the use of a safer, cheaper, and easier to synthesize oxidant: o-iodoxybenzoic acid (IBX).

![Scheme I-3. Improved synthesis of 9 via IBX oxidation, sodium meta-bisulfite reduction.](image)

IBX had been used by Magdziak et al. for its utility in converting phenols into o-quinones then reducing those quinones to o-catechols. This appeals to us since we can use 2-tert-butylphenol to produce the catechol molecules we desire on large scales with minimal danger and waste. Initially, IBX was used to improve the efficiency of synthesizing 8 and 9 as shown in Scheme I-3. As implementation of this new scheme developed, some modifications to the synthesis had to be made. The new scheme encountered some unforeseen complications from an old purification technique used to purify aldehydes.

When compound 12 was subjected to a saturated solution of sodium meta-bisulfite, the
exposed aldehyde produced an adduct with the sodium bisulfite formed from decomposition of sodium meta-bisulfite as seen in Scheme I-4. To avoid the aldehyde adduct, an alternative reducing agent was found in L-ascorbic acid.\textsuperscript{91}

\begin{center}
\begin{align*}
2 \text{Na}^+ \left[ \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O}
\end{array} \right] & \overset{\text{H}_2\text{O}}{\longrightarrow} \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O}
\end{array} & + & \text{Na}^+ + \text{Na}^+ \left[ \begin{array}{c}
\text{H} \\
\text{O} \\
\text{S} \\
\text{O}
\end{array} \right]^- & \overset{\text{R-CHO}}{\longrightarrow} \begin{array}{c}
\text{HO} \\
\text{SO}_3\text{Na}
\end{array}
\end{align*}
\end{center}

\textbf{Scheme I-4.} Aldehyde adduct formation from decomposition of sodium meta-bisulfite.

A final difference between the new route and the traditional one is the iodine oxidation step. The new route eliminates the need for a phase transfer catalyst by changing the solvent from dichloromethane to diethyl ether based on a suggestion by former postdoctoral associate Dr. Kira Vostrikova. Originally, the phase transfer catalyst was used to ensure I\textsuperscript{-} would interact with the aqueous phase to carry out the oxidation and avoid making I\textsuperscript{3-}. However, diethyl ether can dissolve the reactants just as easily as dichloromethane and thus eliminates the need for a phase transfer catalyst since diethyl ether has partial solubility in water. Again using a phenylene bridged D-B-A as an example, an improved scheme for Tp\textsuperscript{Cum,Me}Zn(SQ-para-Phenylene-NN) with yields is shown in Scheme I-5.
Scheme I-5. Improved synthetic scheme to $T_{p}^{\text{Cum,Me}}Zn(SQ\text{-pPh-NN})$ (1-pPh) which obviates the need for protecting groups.

The new synthetic route has been used successfully to synthesize SQ-Bridge-NN biradicals containing with a wide variety of bridges which will be discussed throughout this work with consistent results. Several important comparisons between the new route and the old route can be found in Table I-1. Not only is the overall yield is higher, but also other
experimental factors such as fewer steps, less expensive materials, and less solvent required for purification prove the new scheme to be far superior to the traditional method.

Through the discovery of a simple oxidant in the literature, we have been able to improve the synthesis of most, if not all, current and future SQ-Bridge-NN based donor-bridge-acceptor biradicals as well as effectively halved the time required to complete each synthesis. By using parts of Scheme I-3 and Scheme I-5 interchangably in the synthesis of new SQ-Bridge-NN biradicals, we have also allowed for adaptability of the synthesis to unstable conditions such as reactive quinones or instances where IBX cannot work because the complex is too electron withdrawing.

Table I-1. Synthetic route comparisons based on yield, purification, protections, number of steps, and approximate time to final product formation.

<table>
<thead>
<tr>
<th></th>
<th>Bromoguaiacol</th>
<th>Traditional</th>
<th>IBX Scheme (I-5)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Overall Yield to Cat-mPh-NN</strong></td>
<td>1%</td>
<td>25%</td>
<td>30%</td>
</tr>
<tr>
<td><strong>Chromatography Purifications</strong></td>
<td>2</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td><strong>Protections / Deprotections</strong></td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td><strong>Number of Steps</strong></td>
<td>10</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td><strong>Approximate Time to Product (Days)</strong></td>
<td>10</td>
<td>12</td>
<td>6</td>
</tr>
</tbody>
</table>
H. Experimental

General Considerations. Reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer at room temperature. $^1$H and $^{13}$C chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. Infrared spectra were recorded on a Brüker Vertex 80v spectrometer with Brüker Platinum ATR attachment. Elemental analyses were performed by Atlantic Microlabs, Inc. High-resolution mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility. Compounds $^5$, $^8$, $^9$, $^{14}$, $^{15}$, $^{1-}$pPh, $^{7}$, $^{8}$ o-iodoxybenzoic acid (IBX), $^{89}$ 2,3-dimethyl-2,3-bis(hydroxyamino)butane (BHA), $^{95}$ and Zn(OH)Tp$^{Cum,Me}$ $^{96}$ were prepared according to published procedures.

Synthesis of 5-bromo-3-(tert-butyl)cyclohexa-3,5-diene-1,2-dione (6). To a 100 mL pear shaped flask, 3.00 g (13.1 mmol) $^5$ was added with about 20 mL DCM and 3.68 g (13.1 mmol) IBX. The flask was sealed with a rubber septum, attached to a nitrogen line, and allow to stir overnight. The reaction was checked for completion via $^1$H NMR in CDCl$_3$ and TLC by taking an aliquot from the reaction mixture and filtering it through glass wool/Celite in a glass pipette. Once the reaction was complete, the reaction was filtered into a separatory funnel where it was diluted with ethyl acetate, washed three times with saturated NaHCO$_3$ solution followed by saturated NaCl, and the organic layer dried over Na$_2$SO$_4$. The solvent from the collected filtrate was removed under reduced pressure to yield 2.93 g compound 6 (92% yield). The white solid collected by filtration into the separatory funnel was determined
to be 2-iodosobenzoic acid by $^1$H-NMR and was collected for reuse in future oxidations. $^1$H NMR (CDCl$_3$, $\delta$): 6.87 (d, 2.2 Hz, 1H), 6.79 (d, 2.2 Hz, 1H), 1.27 (s, 9H). IR (cm$^{-1}$): 1660 (s, C=O).

**Synthesis of 5-bromo-3-(tert-butyl)benzene-1,2-diol (7).** In a 250 mL separatory funnel, 6 was dissolved in diethyl ether and washed twice with 100 mL saturated Na$_2$S$_2$O$_5$ followed by 100 mL half-saturated NaHCO$_3$ solution then 100 mL saturated NaCl solution. The organic layer was collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure to yield 1.90 g of compound 7 (65% yield). Characterization of 7 matches reported values.$^{88}$

**Synthesis of 3’-(tert-butyl)-4’-hydroxy-[1,1’-biphenyl]-4-carbaldehyde (11).** To a 50 mL Schlenk flask, 1.00 g (4.36 mmol) 10 was added with 782 mg (5.23 mmol) 5 and a stir bar. The reaction flask was transferred into the glove box where 273 mg (0.24 mmol) tetrakis(triphenylphosphine) palladium(0) and ~15 mL THF were added. The reaction flask sealed with a glass stopper and removed from the glove box. To a 25 mL round bottom flask a 2M solution of potassium carbonate was bubbled with nitrogen for 1 hour then added via syringe to the reaction vessel. The reaction was refluxed 16 hours and checked by TLC (75% Et$_2$O in hexanes). The reaction was stopped by addition of ~10 mL deionized water with stirring in air for 30 minutes. The reaction was transferred to a separatory funnel and washed with saturated sodium bicarbonate then extracted with DCM. The DCM extractions were dried over sodium sulfate and the solvent was removed under reduced pressure. The resulting brown oil was partially dissolved in diethyl ether and filtered through medium porosity sintered glass. Approximately an equal volume of petroleum ether was added to the filtrate
and again filtered through medium porosity sintered glass. The solvent was removed under reduced pressure yielding a yellow solid which was recrystallized from warm toluene to yield 834 mg of compound 11 (75% yield). \(^1\)H NMR (CDCl\(_3\), \(\delta\)): 10.03 (s, 1H), 7.92 (d, \(^3\)J 8.2 Hz, 2H), 7.71 (d, \(^3\)J 8.2 Hz, 2H), 7.55 (d, \(^4\)J 2.3 Hz, 1H), 7.16 (dd, \(^3\)J 8.3 Hz, \(^4\)J 2.3 Hz, 1H), 6.77 (d, \(^3\)J 8.3 Hz, 1H), 5.04 (s, 1H), 1.38 (s, 9H).

**Synthesis of 5'-{}-(tert-butyl)-3',4'-dioxo-3',4'-dihydro-[1,1'-biphenyl]-4-carboxaldehyde (12).** To a 50 mL pear shaped flask, 593 mg (2.33 mmol) 11 and 1.33 g (4.75 mmol) IBX were added with 5 mL DMF and stirred shielded from light. After about 30 minutes the solution changed color from light yellow to green. The reaction was refluxed overnight and checked by TLC for the absence of starting material. Once all of the starting material had been consumed, the reaction was poured into 200 mL water, transferred to a separatory funnel, and extracted with ethyl acetate. The organic phase was washed three times with saturated sodium bicarbonate solution then three times with half saturated sodium chloride solution. The organic phase was then collected, dried over sodium sulfate, and the solvent removed under reduced pressure to yield compound 12 which was used directly in the next step.

**Synthesis of 3'-{}-(tert-butyl)-4',5'-dihydroxy-[1,1'-biphenyl]-4-carboxaldehyde (13).** Ensuring no IBX or starting material remained, quinone 12 was dissolved in 10 mL THF and 328 mg (1.86 mmol) ascorbic acid was dissolved in 10 mL deionized water. The two solutions were mixed in a separatory funnel causing the green color from the quinone to fade instantly to light yellow. Saturated sodium chloride solution was added and the product was extracted by ethyl acetate. The organic phase was dried over sodium sulfate and the
solvent removed under reduced pressure. The product is purified by flash chromatography (20% ethyl acetate in hexanes) to yield 401 mg of compound 13 (86% yield). $^1$H NMR data collected for compound 13 matched the reported synthesis.\textsuperscript{47}
II. Experimentally Illustrating McConnell's Electronic Coupling Model Through Independent Donor-Bridge and Bridge-Acceptor Torsions in Donor-Bridge-Acceptor Biradicals

A. Introduction to Electronic Coupling Torsional Dependence in Donor-Bridge-Acceptor Biradical Complexes

\( \pi \)-Orbital overlap in conjugated organic donor-bridge-acceptor (D-B-A) triads plays a vital role in determining the magnitude of electronic coupling, \( H_{DA} \), which is central to understanding intramolecular electron transfer and electron transport in single-molecule electronic devices. From molecular orbital (MO) theory, we understand that conjugation between \( \pi \)-systems provides a delocalization pathway across molecules comprised of multiple \( \pi \)-systems. Streitwieser\textsuperscript{97} shows that the overlap of two p-orbitals interacting at an angle \( \phi \) is dependent as the cosine of that angle as illustrated in Figure II-1. Since the overlap density is directly proportional to the electronic coupling in a molecule,\textsuperscript{98} the electronic coupling in a twisted system must also be proportional to the cosine of the dihedral angle between connecting units.
Wasielewski\textsuperscript{10} has shown using oligo(phenylene-ethylene)-bridged D-B-A molecules that PET derived $H_{DA}$ values follow a cosine dependence for each nearest neighbor interaction within the D-B-A system (Eq. II.1).

$$H_{ij} = H_{ij} \cos(\phi_{ij})$$  \hspace{1cm} \text{II.1}$$

If we input Eq. (II.1) into Eq. (I.42) from chapter I, we obtain Eq. (II.2) which describes electronic coupling between $H_{DB}$, $H_{BA}$, and $H_{BB}$ as a function of the torsion angles within the molecule.

$$H_{DA} = \frac{H_{DB} \cos(\phi_{DB}) H_{BA} \cos(\phi_{BA}) (H_{BB} \cos(\phi_{BB}))}{\Delta}$$ \bigg\}^{n-1}  \hspace{1cm} \text{II.2}$$

Similarly to Wasielewski’s work, Harriman\textsuperscript{11,99} and Wenger\textsuperscript{13} have shown torsional dependence of $H_{DA}$ values derived from PET rates, while Newton\textsuperscript{100} described a modified McConnell\textsuperscript{9} superexchange model accounting for both $\pi$- and $\sigma$ contributions. Due to the inherent connection between intramolecular electron transfer rates and electron transport in single-molecule devices,\textsuperscript{81,85} Mayor\textsuperscript{14,61} has shown a torsion dependence of conductance for
single-molecule electronic devices. These reports of bond torsion attenuation of electronic coupling, and by relation, exchange coupling, electron transfer rate constants and conductance in single molecule electronic devices, have been plotted as $H_{DA}$ vs. $\cos \phi$ or $\cos^2 \phi$. However, when the donor-acceptor dyad is asymmetric, the McConnell model dictates that $H_{DB}$ must be different than $H_{BA}$ as per Eq. (II.2). For example, by re-plotting reported data from Harriman in Figure II-2, we can see the discrepancy between published data and McConnell's model. Harriman's D-B-A system is designed so that they can assume the torsion angles between the donor and the bridge as well as the bridge and the acceptor are always fully conjugated ($\phi = 0^\circ$) through the ethyne linkers. By this logic, the only torsion angle that should effect the electronic coupling is the one between the phenyl rings on the bridge. By controlling the degree of torsion synthetically with a bridge linker, they were able to develop a plot of electronic coupling versus torsion angle.\textsuperscript{11} If we look back at Eq. (II.2), assume $\cos(\phi_{DB}) = \cos(\phi_{BA}) = 1$, and assume the only $H_{BB}$ coupling with torsional dependence is the one between the two phenyl rings, we get Eq. (II.3) which shows a linear relationship between the electronic coupling and the calculated torsion angle.

$$H_{DA} = \frac{H_{DB}H_{BA}H_{BB} \cos(\phi_{BB})}{\Delta}$$

We can then take the electronic coupling versus torsion angle data reported by Harriman and re-plot it as electronic coupling versus $\cos(\phi)$ in Figure II-2. According to Eq. (II.3), $H_{DA}$ varies linearly with $\cos(\phi)$. Looking at the re-plotted data in Figure II-2, there is clearly curvature to the data which indicates that there must be additional torsional effects not
accounted for. The additional torsional effects must then be coming from the donor-bridge and bridge-acceptor connections that were assumed to not have a torsional dependence.

**Figure II-2.** Re-plotted electronic coupling ($V_{DA} = H_{DA}$) versus $|\cos(\phi)|$ instead of $\phi$ from Harriman.\textsuperscript{11} The x-axis is plotted as an absolute value because the data from Harriman spans a range from 0° to 180° and we are currently only interested in the magnitude of $H_{DA}$. Solid black line is a visual aid connecting the weakest electronic coupling and strongest electronic coupling data points emphasizing the non-linear trend in the data.

It should also be mentioned that all reports on the effect of bond torsion on electronic coupling to date have been designed to only consider torsion within the bridge itself while assuming no torsional contribution from the donor-bridge and bridge-acceptor connections.

Through the established SQ-B-NN D-B-A model, we show nearest neighbor cosine dependence of electronic coupling over a wide range of dihedral angles through steric inhibition of resonance in which we compare a torsionally unhindered D-B-A to auxochromic substituted, torsionally hindered D-B-As in which the donor, bridge, and acceptor are separately rotated out of plane as depicted in Figure II-3. Herein, we present the first experimentally-determined 3-dimensional plot of electronic coupling vs. both donor-and
acceptor torsions. Our analysis allows for experimentally illustrating the McConnell model using measured exchange coupling.

![Figure II-3](image-url) Line bond drawings of sterically hindered D-B-A biradicals studied for torsional dependence of $J_{DA}$ and $H_{DA}$.

**B. Discussion of Results for Steric Inhibition of Resonance Complexes**

1. **Synthesis of Steric Inhibition of Resonance Complexes**

   The synthesis of 1-pPh has been reported previously. The synthesis of 1-PhMe and 1-pXylyl were initially completed by Dr. Guangbin Wang and the synthesis of 1-BCO was completed by Shultz group member Jinyuan Zhang. For the synthesis of 1-MePh, as shown
in Scheme II-1, 16 and 17 were reacted under Suzuki conditions to yield phenol 18 which was then oxidized to quinone 19 via IBX. Catechol 20 was then formed by reduction of 19 with ascorbic acid. In a concentrated methanol solution, BHA and 20 were reacted to form 21 which was then oxidized with elemental iodine to nitronylnitroxide 22. Formation of 1-MePh was affected by reacting 22 and Zn(OH)Tp^Cum,Me under standard conditions.  

Scheme II-1. Synthesis of 1-MePh.
Scheme II-2 shows the general synthesis for 1-PhMe, 1-pXylyl, and 1-PhMe₄. Compounds 9 and 23 were reacted under Suzuki conditions to yield 24. Using an acidic, refluxing methanol solution, 24 was deprotected to form catechol 25. Using BHA, catechol 25 was converted to 26 then oxidized to nitronylnitroxide 27. Under standard conditions, 27 and Zn(OH)TpCum,Me were reacted to form the respective biradical.

Scheme II-2. Synthesis of 1-PhMe, 1-pXylyl, and 1-PhMe₄.
2. Structural and Magnetic Features of Twisted Donor-Bridge-Acceptor Biradical Complexes

The key to this study is the specific structural information crystallography gives us about the complexes in Figure II-3. Thermal ellipsoid plots of these complexes with their corresponding line bond drawings are shown in Figure II-4. The variation in bond torsions connecting SQ with bridge and bridge with NN are also given in Figure II-4 along with SQ *ipso* carbon to NN *ipso* carbon distances for 1-*pPh*, 1-*MePh*, 1-*PhMe*, 1-*pXylyl*, 1-*PhMe4* and 1-*BCO* (see Appendix B for crystallographic details). Torsion angles for the (substituted) phenyl complexes were determined using the mean planes of the SQ rings and bridge rings (φ<sub>SQ-B</sub>), and the O-N-C-N-O atoms of NN and bridge rings (φ<sub>B-NN</sub>). By adding methyl groups to the ring, the torsion angles between the donor and the bridge (1-*MePh*, 1-*pXylyl* and 1-*PhMe4*) or the bridge and the acceptor (1-*PhMe*, 1-*pXylyl*, 1-*PhMe4*) are significantly more twisted compared to 1-*pPh*. SQ to NN distances given in Figure II-4 are consistent across the series at ~5.7Å meaning that any possible SQ-NN intramolecular through space interactions measured will be the same for all complexes.
Figure II-4. Bond-line drawings and thermal ellipsoid plots (hydrogen atoms and cumenyl groups omitted for clarity) of sterically hindered D-B-A biradical complexes. Donor-bridge and bridge-acceptor torsion angles (blue) as well as SQ-ipso to NN-ipso carbon distanced (red) are displayed. Magnetic exchange coupling parameters \( J_{DA} \) given were determined as shown in Figure II-5. The structure of 1-pPh was reported previously.\(^7\)

Bond lengths of \( o \)-SQ and nitronylnitroxide (NN) in all five complexes are within typically reported values based on \( \text{Tp}^{\text{Cum,Me}}(3,5\text{-di-}\text{tert\text{-}butylseminiquinone})^{96} \) and catechol-nitronylnitroxide\(^{102} \) structures and the structural deviation parameters for each complex are given in Table II-1. Complexes 1-Ph and 1-PhMe show slightly larger deviations in the \( o \)-SQ ring which may correspond to greater \( \pi \)-delocalization of the semiquinone ring into the bridge than for 1-MePh, 1-pXylyl, and 1-PhMe\(_4\). However, the same trend is not observed in
the structural deviation of the NNs. All of this information allows us to directly correlate torsion angles of crystalline material to measured magnetic moment while ensuring no unusual distortions in the donor and acceptor moieties.

A stack plot of magnetometry data for 1-pPh, 1-MePh, 1-PhMe, 1-pXylyl, 1-PhMe₄, and 1-BCO is shown in Figure II-5A and 1-BCO in Figure II-5B. These data were fit using the HDVV expression in Eq. (I.29) where \( J_{DA} \) and \( \theta \) are fit parameters to give the exchange coupling values. The values of \( J_{DA} \) given in Table II-2 are an average of a heating and cooling experiment and the error reflects the range of measured \( J_{DA} \). Using Eq. (I.38) and the reported values for \( J_{DA} \) and \( H_{DA} \) for 1, the values of \( H_{DA} \) can be calculated and are given in Table II-2.

| Complex   | \( \sigma \)-SQ \( \sum |\Delta l| \) (Å) | NN \( \sum |\Delta l| \) (Å) |
|-----------|------------------------------------------|------------------------------|
| 1-pPh     | 0.014                                    | 0.025                        |
| 1-MePh    | 0.008                                    | 0.010                        |
| 1-PhMe    | 0.010                                    | 0.013                        |
| 1-pXylyl  | 0.007                                    | 0.026                        |
| 1-PhMe₄   | 0.005                                    | 0.015                        |
Figure II-5. (A) Magnetic susceptibility of 1-pPh (black), 1-MePh (red), 1-PhMe (blue), 1-pXylyl (green), and 1-PhMe₄ (purple) with fit parameters. (B) Magnetic susceptibility of 1-BCO with fit parameters collected by Jinyuan Zhang.

Table II-2. Measured exchange coupling ($J_{DA}$) and calculated electronic coupling ($H_{DA}$) values for 1-pPh, 1-MePh, 1-PhMe, 1-pXylyl, 1-PhMe₄, and 1-BCO.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_{DA}$ (cm⁻¹)</th>
<th>$H_{DA}$ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-pPh</td>
<td>98 ± 2</td>
<td>4529</td>
</tr>
<tr>
<td>1-MePh</td>
<td>81 ± 7</td>
<td>4076</td>
</tr>
<tr>
<td>1-PhMe</td>
<td>71 ± 5</td>
<td>3816</td>
</tr>
<tr>
<td>1-pXylyl</td>
<td>36 ± 1</td>
<td>2717</td>
</tr>
<tr>
<td>1-PhMe₄</td>
<td>2 ± 0.03</td>
<td>640</td>
</tr>
<tr>
<td>1-BCO</td>
<td>1 ± 0.03</td>
<td>320</td>
</tr>
</tbody>
</table>

It is important to note that magnetometry is a bulk measurement of a sample whereas X-ray crystallography is a measurement of a single crystal which is a representative sample of the bulk material. In order to attempt to confirm that the bulk measured material was the same structure and morphology as the single crystal structure, powder X-ray diffraction (PXRD) measurements were performed on the magnetometry samples. A PXRD experiment takes crystalline material and gently crushes it to fit within a quartz capillary tube. The
capillary tube is then centered in an X-ray beam and rotated to collect diffracted radiation. If the sample is totally crystalline, the refraction pattern shows a specific series of sharp absorptions that correlates directly to parameters for the single crystal measurements. If a sample is non-crystalline, the PXRD spectrum lacks these sharp absorptions and instead shows many broad features. Given a solved crystal structure, a PXRD spectrum can be calculated and compared to the experimental PXRD spectrum. The experimental and calculated PXRD spectra for 1-MePh, 1-PhMe, and 1-pXylyl are shown in Figure II-6.

![Figure II-6. Experimental (red) and calculated (blue) powder X-ray diffraction of 1-MePh, 1-PhMe, and 1-pXylyl.](image)

By visual inspection of the PXRD plots in Figure II-6, it is clear that even though the magnetometry samples are indeed crystalline, something about either the sample preparation or the sample itself does not lend itself to using PXRD to confirm crystallinity of a bulk sample of organic biradical. If through the grinding process enough heat is generated to allow the torsion angles to shift slightly or for some solvent to be released from the crystal, it will significantly change the PXRD spectrum compared to the one calculated from the crystal.
structure. Another issue could be the significant disorder that is common in the cumenyl groups and methyl groups on the NN ring. While this disorder does not greatly affect the torsion angles of the SQ-B-NN core, it can affect the quality of the PXRD spectrum making it difficult, if not impossible, to directly correlate single crystal data to bulk PXRD data.

Knowing the exact torsion angles from crystallography and the exchange coupling constants from magnetometry allows us to create an experimental model of McConnell's equation. If we relate Eq. (II.2) where \( n = 1 \) with Eq. (I.37) to form Eq. (II.4), we can then plot \( J_{DA} \) versus \( \cos^2(\phi_{SQ}) \) versus \( \cos^2(\phi_{NN}) \) to give the 3-dimensional plots in Figure II-7.

\[
J_{DA} = H_{DA}^2 = \frac{H_{DB}^2 \cos^2(\phi_{DB}) H_{BA}^2 \cos^2(\phi_{BA})}{\Delta^2}
\]  

**Figure II-7.** 3-dimensional plots of \( J_{DA} \) versus \( \cos^2(\phi_{SQ}) \) and \( \cos^2(\phi_{NN}) \). Filled, colored circles are experimental data and colored mesh surface is created from the \( J_{DA} \) from CAS SCF calculations across all torsion angles. The color bar on the right side of each plot correlates the value of \( J_{DA} \) to colors on the plots.

The mesh surface in Figure II-7 was created by complete active space self-consistent field (CASSCF) calculations from the Kirk group and reinforces the fact that the relationship between \( J_{DA} \) and torsion angles within a D-B-A is non-planar. As \( \cos(\phi_{SQ}) \) or \( \cos(\phi_{NN}) \)
become more twisted and closer to 0 (ϕ = 90°), the exchange coupling between donor and acceptor becomes attenuated as predicted by the modified McConnell equation (Eq. II.4). 1-pPh and 1-pXylyl experimental data points lie away from the calculated surface, as seen in the right side of Figure II-7, which is likely a consequence of multiple biradicals per unit cell combined with disorder in the NN ring. Since $H_{DA}$ is more directly related to rate constants determined by PET and conductance determined by MMM break junctions, we can convert the $J_{DA}$ versus $\cos^2(\phi)$ plots Figure II-7 to the $H_{DA}$ versus $\cos(\phi)$ plots in Figure II-8 using Eq. (I.38) and relate Figure II-8 to Eq. (II.2) directly. Here we can plainly see, as was the case in Figure II-7, just how non-planar the surface is. We can also see that the surface seems to be more complicated than just two planes interacting which could be due to a combination of neglecting σ-superexchange in Eq. (II.2) as well as neglecting the fact that $A$ should also have a torsional dependence.

**Figure II-8.** 3-dimensional plots of $H_{DA}$ versus $\cos(\phi_{SQ})$ and $\cos(\phi_{NN})$. Filled, colored circles are $H_{DA}$ values from experimental data and the colored mesh surface is created from converting the $J_{DA}$ values from CAS calculations to $H_{DA}$ values with Eq. (I.38). The color bar on the right side of each plot correlates the value of $H_{DA}$ to colors on the plots.
Since 1-PhMe₄ does not display perfectly perpendicular donor-bridge and bridge-acceptor fragments, Jinyuan Zhang prepared 1-BCO (BCO = bicyclo[2.2.2]octane) which possesses a σ-only bridge comprised entirely of sp³-hybridized carbons, as seen in Figure II-3. The exchange coupling parameter for 1-BCO, $J_{DA} = +1 \text{ cm}^{-1}$ (Figure II-5B), is equivalent, within the limitations of our measurements, to the σ-supерexchange through a para-phenylene ring perpendicular to both SQ and NN. Moreover, since all the carbon atoms of the phenylene ring are sp² and those of the 1-BCO bridge are sp³, there is no measureable hybridization-dependent difference in the magnitude of σ-supерexchange, nor is there a measureable difference due to the fact that 1-BCO is comprised of three –CH₂CH₂-σ-pathways while para-phenylene has just two.


A significant torsion in a conjugated π-system causes the orbital overlap between individual fragments to decrease which can sometimes have an observable effect on the electronic structure. For this series of D-B-As, the effect on the electronic structure is manifest in the electronic absorption spectrum by changing the band shape and intensity of transitions that correspond to the charge transfer from the donor to the acceptor as seen in the electronic absorption stack plot of 1-pPh, 1-MePh, 1-PhMe, 1-pXylyl, and 1-PhMe₄ in Figure II-9.
Figure II-9. Stack plot of extinction coefficients for 1-pPh (red), 1-MePh (blue), 1-PhMe (green), 1-pXylyl (purple), and 1-PhMe4 (black). Inset is an expansion of the 10,000 cm$^{-1}$ to 20,000 cm$^{-1}$ region.

The transition at $\sim$23,000 cm$^{-1}$ in 1-pPh and 1-MePh corresponds to the SQ (SOMO) $\rightarrow$ NN (LUMO) charge transfer of strong intensity, which is notably diminished in 1-PhMe, 1-pXylyl, and 1-PhMe4. There is also an increase in intensity of a transition at $\sim$26,000 cm$^{-1}$ in 1-PhMe and 1-pXylyl which may correspond to the remnants of the charge transfer band shifting to higher energy. In the spectrum for 1-MePh, there is a noticeable decrease in intensity of the CT band at $\sim$23,000 cm$^{-1}$ compared to 1-pPh, which reflects the increased dihedral angle between the SQ and bridge. Synthesis of 1-MePh provides us with the opportunity to test the solvatochromic nature of the SQ (SOMO) $\rightarrow$ NN (LUMO) CT band. If the band is in fact a charge transfer from SQ to NN, then the energy maximum of this band should shift with change in the polarity of the solvent.$^{105,106}$ In Figure II-10, the electronic absorption spectra of 1-MePh in toluene and DMSO are shown to have slight differences in
peak intensities for the CT band, but the difference between the energy maximum the lower energy peak is only ~200 cm⁻¹. This small shift may either be due to the fact that the ground state biradical is relatively non-polar and inherently does not show strong solvatochromism,¹⁰⁷ or this band is more closely related to a π → π* band than a charge transfer band. No matter which is the case, since this band is unique to the SQ-B-NN biradical spectrum, specifically to the interaction between SQ and NN, we will continue to call this transition a "charge transfer" in order to distinguish it from other transitions in the SQ-B-NN spectra.

Figure II-10. Electronic absorption spectra of 1-MePh in toluene (red) and DMSO (blue). Inset is an expansion of the 12,000 cm⁻¹ to 18,000 cm⁻¹ region.

When comparing the electronic absorption spectra of 1-pPh and 1-MePh versus 1-PhMe, 1-pXylyl, and 1-PhMe₄, it seems clear that the conjugation between the bridge and acceptor has a greater effect on the transitions observed which follows the prediction in
earlier work.\textsuperscript{48} In \textbf{1-PhMe} and \textbf{1-pXylyl}, it appears that the CT band formerly at \approx 23,000 cm\(^{-1}\) has shifted/greatly decreased in intensity and is extremely attenuated in \textbf{1-PhMe}\(_4\). In fact, the spectrum of \textbf{1-PhMe}\(_4\) is remarkable in the fact that, aside from the SQ and NN specific bands in the 10,000 cm\(^{-1}\) to 20,000 cm\(^{-1}\) region, it shares no visible relationship to any of the other complexes.

![Figure II-11](image_url)

Figure II-11. (Left) Variable-temperature electronic absorption of \textbf{1-MePh} from 5 K to 300 K. (Right) Normalized intensities of 424 nm (blue) and 356 nm (red) absorptions as a function of temperature and fit to a Boltzmann population for \(S = 0\) (red) and \(S = 1\) (blue).
In order to try to determine the exchange coupling between donor and acceptor in solution, variable temperature studies were conducted on 1-MePh, 1-PhMe, 1-pXylyl, and 1-PhMe₄. However, only 1-MePh showed any noticeable change in relative absorption between 5K and 300K (Figure II-11). By looking back at the stack plot of Figure II-9, we see the major distinguishing feature of 1-MePh versus the other complexes is the clearly visible SQ (SOMO) → NN (LUMO) CT band at ~24,000 cm⁻¹. Figure II-11 (left) shows a stack plot for variable temperature electronic absorption spectra for 1-MePh of temperatures ranging from 5K to 300K. In 1-MePh, the absorbance of the charge transfer band around ~28 000 cm⁻¹ increases in intensity as the temperature is lowered indicating an increase in the triplet ground state population. Spectra that lack this band, such as those for 1-PhMe, 1-pXylyl, and 1-PhMe₄, show little to no change between 5 K and 300 K in VT-EAS as seen Figure II-12. The lack of change may be due to the SQ (SOMO) → NN (LUMO) band getting shifted underneath the π → π* band at ~26,000 cm⁻¹ or having the intensity of this band decreased to the point at which it barely contributes to the overall electronic absorption spectrum. The
decrease in absorbance with decreasing temperature around 28 000 cm$^{-1}$ can be used to fit the population of the ground state singlet population. The relative absorbance versus temperature at these energies can be fit to a triplet and singlet Boltzmann population as shown in Eq. (II.5) where $N_T$ and $N_S$ are the triplet and singlet population, $k_B$ is Boltzmann's constant, and $J_{DA}$ is the magnetic exchange.

$$N_T = \frac{3 e^{\frac{2 J_{DA}}{k_B T}}}{3 e^{\frac{2 J_{DA}}{k_B T}} + 1} \quad ; \quad N_S = \frac{e^{\frac{-2 J_{DA}}{k_B T}}}{3 + e^{\frac{-2 J_{DA}}{k_B T}}} \quad \text{II.5}$$

Based on the Boltzmann populations in Figure II-11, pure singlet and triplet spectra for 1-MePh are computed and are displayed in Figure II-13. The singlet and triplet spectra appear to be very similar in shape, which indicates minimal structural difference between the singlet and triplet states. In the other complexes studied, the lack of a clear charge transfer band, whether it is shifted to higher energy or greatly reduced in intensity, makes discerning the difference between singlet and triplet states nearly impossible. Interestingly, the shape of the triplet spectrum in Figure II-13 looks similar to the non-polar toluene spectrum in Figure II-10 while the singlet spectrum in Figure II-13 looks similar to the polar DMSO spectrum in Figure II-10. However, this may just be coincidence since the difference in the lower energy maxima of the singlet and triplet CT bands is only ~50 cm$^{-1}$. 


In order to determine the role of the bridge in the SQ (SOMO) → NN (LUMO) CT, we can use resonance Raman to probe the enhancement caused by the CT band. Resonance Raman spectra of 1, 1-\(p\)Ph, 1-MePh, and 1-\(p\)Xylyl are shown in Figure II-14. In the resonance Raman spectra, the peak at 1603 cm\(^{-1}\) Raman shift is clearly absent in the spectrum of 1 meaning it must belong to a bridge mode in complexes 1-\(p\)Ph, 1-MePh, 1-PhMe, and 1-\(p\)Xylyl. By comparing the peak intensity at 1603 cm\(^{-1}\) to the peak intensity of nearby peaks around ~1380 cm\(^{-1}\), we can see the sterically hindered bridges have similar stretching patterns but 1-MePh has a more intense stretch at 1603 cm\(^{-1}\) than 1-\(p\)Xylyl. The varying intensity of this peak may be related to the coupling between Bridge and NN based on the spectra of 1-Ph, 1-MePh, 1-PhMe, and 1-\(p\)Xylyl.
Figure II-14. Resonance Raman stack plot of 1 (black), 1-pPh (red), 1-MePh (blue), and 1-pXylyl (green) using a 407 nm excitation. Spectra are referenced to the solvent or solid matrix they were collected in. The * in the 1-MePh spectrum is the Na$_2$SO$_4$ internal standard used to calibrate the spectrum.

Figure II-15. Arrow pushing line bond drawing showing structure of SQ (SOMO) → NN (LUMO) CT excited state. The 1603 cm$^{-1}$ stretch in the resonance Raman thus comes from the quinoidal character of the complex.

To prove that the stretch at 1603 cm$^{-1}$ comes from the SQ (SOMO) → NN (LUMO) CT, a resonance Raman absorption profile was performed by the Kirk group on 1-MePh and is shown in Figure II-16. The Raman enhancement of the stretch at 1603 cm$^{-1}$ as a function of excitation wavelength is given as red circles and tracks well with the charge transfer band in the electronic absorption spectrum of 1-MePh. This data combined with the results of Figure
II-14 show that enhancement of bridge stretching modes is only dependent on the torsion between bridge and acceptor, confirming the importance of phenylene-NN conjugation over SQ-phenylene conjugation.

![Figure II-16](image)

**Figure II-16.** Resonance Raman absorption profile for 1-MePh overlaid on the absorption spectrum of 1-MePh. Resonance Raman enhancement data points (red circles) were collected at 407, 458, 488, 514, 568, and 647 nm.

C. Experimental

**General Considerations.** Reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer at room temperature. $^1$H and $^{13}$C chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. EPR spectra were recorded on an IBM ER200D-SRC EPR spectrometer in CH$_2$Cl$_2$. Infrared spectra were recorded on a Bruker Vertex 80v spectrometer with Bruker Platinum ATR
attachment. Elemental analyses were performed by Atlantic Microlabs, Inc. Mass spectra were obtained at the NCSU Mass Spectrometry Facility located in the Department of Chemistry. Single crystal XRD structures were determined by Lukasz Wojtas at FSU and Roger Sommer at NCSU. Compounds $9,10^{8}$, $16,10^{9}$, $17,11^{10}$, $23a,11^{11}$, $23b,11^{12}$, $23c,11^{13}$, 2,3-dimethyl-2,3-bis(hydroxyamino)butane (BHA),$^{95}$ o-iodoxybenzoic acid (IBX),$^{89}$ and Zn(OH)Tp$^{Cum,Me},9^{6}$ were prepared as previously reported.

**Electronic Structure Calculations.** All calculations were performed with the ORCA 3.0.2 program suite.$^{11^{14}}$ A density functional theory (DFT) geometry optimization was done with the def2-SVP basis$^{11^{15}}$ and the PBE GGA functional.$^{11^{16}}$ Quasi-restricted orbitals (QROs) were generated from the DFT calculations, and from these the NN HOMO, SOMO, and LUMO and the SQ SOMO were selected and used for the subsequent CASSCF(4,4)/NEVPT2 calculations. An initial CASSCF calculation was performed on the planar geometry ($\phi_{NN}=\phi_{SQ}=0^\circ$) to ensure that the correct SQ-NN biradical ferromagnetic state was obtained (see Figure II-17). The orbitals generated from this calculation were then subsequently used for the rigid PES scans.

![Figure II-17. CASSCF(4,4) S=1 state spin density.](image)
3′-(tert-Butyl)-4′-hydroxy-2-methyl-[1,1′-biphenyl]-4-carboxaldehyde (18). To a 100 mL oven dried Schlenk flask 874 mg (3.16 mmol) 16, 571 mg (2.87 mmol) 17, and 165 mg Pd(PPh₃)₄ were added with 10 mL tetrahydrofuran in a nitrogen environment. In a 25 mL round bottom flask, a 2 M solution of K₂CO₃ was prepared and bubbled with nitrogen for 30 min. Using a nitrogen purged syringe, 4.6 mL of the 2M K₂CO₃ solution was added to the reaction vessel. The flask was then fit with a condenser and refluxed in the dark for 18 h. Upon reaction completion, 30 mL deionized water was added and the mixture stirred in air for 30 min. The mixture was transferred to a separatory funnel, diluted with ethyl acetate, and washed with saturated NaCl solution three times. The organic layer was collected, dried over Na₂SO₄, and the solvent removed under reduced pressure. Purification via column chromatography (SiO₂, 15% ethyl acetate in hexanes) produced 371 mg (48%) compound 18.

1H NMR (300 MHz, DMSO-d₆, δ): 9.99 (s, 1H), 9.61 (s, 1H), 7.80 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.13 (d, J = 2.1 Hz, 1H), 7.08 (dd, J = 8.1 Hz, J = 2.1 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 2.34 (s, 3H), 1.37 (s, 9H). 13C NMR (100 MHz, DMSO-d₆, δ): 193.34, 156.33, 136.47, 135.76, 135.24, 132.23, 131.04, 127.94, 127.76, 127.70, 116.77, 35.02, 30.03, 21.02. IR (solid) νₓ-max (cm⁻¹): 3201 (br, OH), 1686 (s, C=O). Elemental Analysis Calculated: (C: 80.56, H: 7.51). Found: (C: 80.56, H: 7.68).

5′-(tert-Butyl)-2-methyl-3′,4′-dioxo-3′,4′-dihydro-[1,1′-biphenyl]-4-carboxaldehyde (19). To a 25 mL round bottom flask 326 mg (1.21 mmol) 17 and 485 mg (1.73 mmol) IBX were added with 5 mL dimethylformamide and stirred in the dark for 3 days. The completed reaction was poured into 150 mL deionized water, stirred for 30 min,
then transferred to a separatory funnel with ~100 mL ethyl acetate. The mixture was then washed three times with a saturated NaHCO$_3$ solution followed by three washes of saturated NaCl. The organic layer was collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure to yield 332 mg (97%) of compound 19. $^1$H NMR (300 MHz, CDCl$_3$, δ): 10.04 (s, 1H), 7.81 (s, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.43 (d, $J = 7.8$ Hz, 1H), 7.80 (d, $J = 2.3$ Hz, 1H), 6.31 (d, $J = 2.3$ Hz, 1H), 2.46 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$, δ): 191.47, 180.26, 179.60, 153.05, 151.50, 144.03, 137.31, 136.18, 135.64, 132.22, 128.54, 127.94, 127.32, 35.88, 29.41, 20.43. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 1693 (s, C=O), 1682 (s, C=O), 1662 (s, C=O). Mass spectrometry (m/z): calculated for C$_{18}$H$_{19}$O$_3$ (M+H)$^+$: 283.1334, found: 283.1324 (M+H)$^+$.

3'-($\text{tert}$-\text{Butyl})-4',5'-dihydroxy-2-methyl-$[1,1'$-biphenyl]-4-carboxaldehyde (20). Quinone 19 (254 mg, 0.90 mmol) was dissolved in 10 mL tetrahydrofuran and added to a separatory funnel containing 350 mg (1.99 mmol) ascorbic acid dissolved in 10 mL water. The mixture was shaken for about 5 minutes then 10 mL saturated NaCl solution was added and the layers allowed to separate. The organic layer was diluted with 50 mL ethyl acetate and washed three times with a saturated NaCl solution. The organic layer was collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure to yield 213 mg (75%) of compound 20. $^1$H NMR (300 MHz, DMSO-$d_6$, δ): 9.92 (s, 1H), 9.52 (s, 1H), 8.22 (s, 1H), 7.73 (s, 1H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 7.8$ Hz, 1H), 6.65 (d, $J = 2.0$ Hz, 1H), 6.56 (d, $J = 2.0$ Hz, 1H), 2.28 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$, δ): 193.30, 148.90, 145.45, 144.40, 136.35, 136.13, 135.21, 132.17, 130.90, 130.38, 127.63, 118.41, 114.14, 35.02, 30.10, 20.97. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3475 (m, OH), 3259 (br, OH), 1662 (s,
C=O). Mass spectrometry (m/z): calculated for C_{18}H_{21}O_{3} (M+H)^+: 285.1491, found: 285.1483 (M+H)^+.

2-(3'-((tert-Butyl)-4',5'-dihydroxy-2-methyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (21). To a 6 mL round bottom flask 125 mg (0.44 mmol) 20 and 160 mg (1.08 mmol) BHA were added and pump/purged with nitrogen 5 times. Using a nitrogen purged syringe, 2 mL methanol was added and the reaction was stirred under nitrogen in the dark for 3 days. The product of this reaction was checked by NMR for absence of aldehyde and the crude product was used directly in the synthesis of compound 21. ^1H NMR (300 MHz, DMSO-d6, δ): 7.73 (s, 1H), 7.32 (m, 2H), 7.10 (d, J = 7.1 Hz, 1H), 6.64 (s, 1H), 6.55 (s, 1H), 4.48 (s, 1H), 2.23 (s, 3H), 1.35 (s, 9H), 1.08 (s, 12H). IR (solid) ν_{max} (cm\(^{-1}\)): 3285 (br, -OH).

2-(3'-((tert-Butyl)-4',5'-dihydroxy-2-methyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (22). To a 100 mL round bottom flask, 536 mg (1.29 mmol) 21 was dissolved in 30 mL diethyl ether, 10 mL pH 7 buffer and was chilled to 0°C. In a separatory funnel, 493 mg (1.94 mmol) I\(_2\) was dissolved in 30 mL diethyl ether and added dropwise to the stirring reaction flask. The reaction mixture was then diluted with 90 mL pH 7 buffer and transferred to a separatory funnel where 100 mL Na\(_2\)S\(_2\)O\(_3\) was added and the mixture shaken. The aqueous layer was removed and the organic layer then washed with a saturated NaCl solution three times. The organic layer was dried over Na\(_2\)SO\(_4\) and the solvent removed under reduced pressure to yield 316 mg of blue colored compound 22 (59% yeild). EPR (~0.2 mM in CH\(_2\)Cl\(_2\)): a\(_N\) = 7.62 G. IR (solid) ν_{max} (cm\(^{-1}\)): 3198 (br, -
OH). Mass spectrometry (m/z): calculated for C_{24}H_{31}N_{2}O_{4}Na (M+Na)^+: 434.218153, found: 434.2175 (M+Na)^+.

Tp^{Cum,Me}Zn(SQ-Me-Ph-NN) (1-MePh). To a 25 mL oven dried Schlenk flask, 30 mg (0.07 mmol) 22 and 62 mg (0.09 mmol) Zn(OH)Tp^{Cum,Me} were added and pump / purged with nitrogen 5 times. Using a nitrogen purged syringe, ~2 mL methanol was added and the reaction stirred for 2 hours. The reaction was then opened to air and allowed to stir overnight in the dark. The solvent was removed under reduced pressure and the product purified by column chromatography (basic alumina, 50:50 ethyl acetate:hexanes) to yield 70 mg (88%) of complex 1-MePh. Crystals of 1-MePh were grown from slow evaporation of methanol containing a few drops of CH_{2}Cl_{2}. IR (solid) v_{max} (cm^{-1}): 2543 (w, -BH). EPR (~0.2 mM in CH_{2}Cl_{2}): apparent a_{N} = 3.65 G. Mass spectrometry (m/z): calculated for C_{63}H_{76}BN_{8}O_{4}Zn (M+H)^+: 1083.5374, found: 1083.5389 (M+H)^+. Elemental analysis
Calculated: (C: 69.77, H: 6.97, N: 10.33), Found: (C: 69.64, H: 6.98, N: 10.31).

3’-(tert-Butyl)-4’,5’-bis(methoxymethoxy)-3-methyl-[1,1’-biphenyl]-4-carboxaldehyde (24a). To a solution of 23a (205 mg, 1.10 mmol), 9 (350 mg, 1.07 mmol), Pd(PPh_{3})_{4} (124 mg, 0.107 mmol), Cs_{2}CO_{3} (0.413 g, 2.14 mmol), ethanol (5 mL) and toluene (15 mL) was stirred under nitrogen. The reaction mixture was heated to 70°C and held at this temperature for an additional 48 h. After this time, the reaction mixture was cooled to room temperature and quenched by 20 mL of water. The layers were separated and the aqueous layer was extracted with CH_{2}Cl_{2}. The combined organic layers were dried over Na_{2}SO_{4}, filtered, and concentrated in vacuo, and purified by column chromatography (4:1 hexanes: Diethyl ether) to give 24a as a yellow oil (250 mg, 63 %). ^{1}H NMR (300 MHz, CDCl_{3}) \delta
(ppm): 10.28 (s, 1H), 7.84 (d, 1H, $J = 7.8$ Hz), 7.53 (d, 1H, $J = 8.1$ Hz), 7.42 (s, 1H), 7.29 (d, 2H, $J = 2.1$ Hz), 5.26 (s, 2H), 5.25 (s, 2H), 3.67 (s, 3H), 3.54 (s, 3H), 2.73 (s, 3H), 1.48 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 192.3, 150.6, 146.5, 144.0, 141.2, 134.7, 132.7, 130.4, 125.1, 119.8, 113.9, 99.2, 95.7, 57.7, 56.5, 35.4, 27.7, 19.9. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 1693 (s, -C=O).

3'-(tert-Butyl)-4',5'-dihydroxy-3-methyl-[1,1'-biphenyl]-4-carboxaldehyde (25a). A solution of 24a (0.360 g, 0.968 mmol) in methanol (3 mL) was added 3 drops of 12 M HCl and 1 drop of water. The reaction mixture was stirred at reflux for overnight. After cooling to room temperature, the solvent was removed. The crude solid was extracted with CH$_2$Cl$_2$. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, concentrated in vacuo, and purified with recrystallization from MeOH/ether solvents to give 25a as a light-orange solid. Yield: 250 mg (91 %). $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 10.05 (s, 1H), 9.49 (s, 1H), 8.26 (s, 1H), 7.67 (s, 1H, $J = 8.1$ Hz), 7.37 (s, 1H, $J = 8.1$ Hz), 7.30 (s, 1H), 6.85 (s, 2H, $J = 8.1$ Hz), 5.59 (s, 1H), 2.33 (s, 3H), 1.23 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 192.6, 146.1, 145.5, 145.0, 140.6, 136.1, 132.0, 128.9, 123.8, 116.1, 111.6, 34.4, 29.4, 19.1. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3350 (br, -OH), 1669 (s, -C=O). Mass spectrometry ($m/z$): calculated for C$_{18}$H$_{19}$O$_3$ (M-H)$^-$: 283.1334, found: 283.1343 (M-H)$^-$. 

2-(3'-(tert-Butyl)-4',5'-dihydroxy-3-methyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (26a). A solution of 25a (40.0 mg, 0.151 mmol) in 4 mL of methanol was added 2,3-dimethyl-2,3-bis(hydroxyamino)butane (44.8 mg, 0.302 mmol) under nitrogen. The reaction mixture was allowed to stir at room temperature for overnight. The solvent was removed under vacuum to give 26a as a yellow solid (40 mg, 64%), which
was unstable and was used directly in the next step without further purification. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 9.47 (s, 1H), 8.12 (s, 1H), 7.68 (s, 1H), 7.65 (s, 2H), 7.27 (d, 1H, $J = 8.4$ Hz), 6.90 (s, 1H), 6.86 (s, 1H), 4.89 (s, 1H), 2.42 (s, 3H), 1.38 (s, 9H), 1.09 (s, 6H), 1.07 (s, 6H). IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 3250 (br, -OH).

$2$-(3'-($\text{tert}$-\text{Butyl})-4',5'$-\text{dihydroxy}-3$-\text{methyl}-[1,1'$-\text{biphenyl}$]-4$-yl$)-4,4,5,5$,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (27a). To a solution of 26a (41.8 mg, 0.101 mmol) in CH$_2$Cl$_2$ was added 10 mL of buffer (pH = 7) in water and cetyl trimethylammonium bromide (10.0 mg). The mixture was stirred at 0°C. Iodine (39.8 mg, 0.157 mmol) in CH$_2$Cl$_2$ was added dropwise. The reaction mixture was held at 0 °C for an additional 30 min. The reaction mixture was diluted with 10 mL of buffer (pH = 7) in water and 10 mL of dichloromethane. The organic layer was separated and washed with a saturated solution of sodium thiosulfate and brine, dried and the solvent was removed to give 27a as a purple solid (39.0 mg, 93%). IR (CH$_2$Cl$_2$ film) $v$ (cm$^{-1}$): 3242 (br, -OH). EPR (~0.2 mM in CH$_2$Cl$_2$): $a_N = 7.19$ G.

Tp$^{\text{Cum,Me}}$Zn(SQ-Ph-Me-NN) (1-PhMe). To a solution of Zn(OH)Tp$^{\text{Cum,Me}}$ (122 mg, 0.176 mmol) in CH$_2$Cl$_2$/methanol was added 27a (72.0 mg, 0.176 mmol) under nitrogen. The reaction mixture was allowed to stir at room temperature over 1 h, and then opened to air for overnight. A brown reaction mixture was purified by flash column chromatography (4:1 Hexanes/EtOAc) to give 1-PhMe as a brown solid (148 mg, 77%). Crystals of 1-PhMe were grown by slow evaporation of methanol containing a few drops of CH$_2$Cl$_2$. IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 2538 (w, -BH). EPR (ca. 0.2 mM in CH$_2$Cl$_2$): apparent $a_N = 3.99$ G. Mass spectrometry ($m/z$): calculated for C$_{63}$H$_{75}$BN$_8$O$_4$Zn (M)$^+$: 1083.5290, found: 1083.5269

3'-{(tert-Butyl)-4',5'-bis(methoxymethoxy)-2,5-dimethyl-[1,1'-biphenyl]-4-carbaldehyde (24b).} A 50 mL Schlenk flask containing 9 (325 mg, 1.53 mmol), 23b (550 mg, 1.68 mmol), Pd(PPh₃)₄ (142 mg, 0.123 mmol), Cs₂CO₃ (1.00 g, 3.07 mmol) and ethanol (5 mL) in dried toluene (10 mL) was placed under N₂ and refluxed for 48 h. The reaction mixture was added water (30 mL), stirred for 30 minutes and filtered through Celite. The solvents were removed under reduced pressure. The residue was then extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo and purified by column chromatography (4:1 hexanes:EtOAc) to give 24b as a yellow oil (240 mg, 51%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 10.26 (s, 1H), 7.68 (s, 1H), 7.14 (s, 1H), 7.01 (d, 1H, J = 1.8 Hz ), 6.95 (d, 1H, J = 2.1 Hz), 5.27 (s, 2H), 5.20 (s, 2H), 3.68 (s, 3H), 3.52 (s, 3H), 2.66 (s, 3H), 2.32 (s, 3H), 1.45 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 192.6, 149.9, 147.4, 145.5, 143.3, 137.9, 135.4, 134.2, 133.6, 133.3, 132.9, 121.3, 115.4, 99.2, 95.6, 57.7, 56.4, 35.4, 30.7, 20.1, 19.1. IR (solid) vₘₐₓ (cm⁻¹): 1691 (s, -C=O). Mass spectrometry (m/z): calculated for C₂₃H₃₀O₅ (M+H)⁺: 387.2172, found: 387.2156 (M+H)⁺.

3'-(tert-Butyl)-4',5'-dihydroxy-2,5-dimethyl-[1,1'-biphenyl]-4-carboxaldehyde (25b). To a 50 mL round bottom flask containing 24b (200 mg, 0.518 mmol) in 3 mL of methanol was added 3 drops of 12 M HCl and 1 drop of water and the solution was stirred at reflux for overnight. The solvent was removed in vacuum. Afterward, the crude mixture was extracted using CH₂Cl₂. The organic solution was washed with water, and then dried over
Na₂SO₄ and evaporated. The crude product was followed by purifying with recrystallization from MeOH/ether solvents to provide 25b as a light-orange solid. Yield: 140 mg (91 %). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 10.20 (s, 1H), 9.54 (s, 1H), 8.26 (s, 1H), 7.69 (s, 1H), 7.14 (s, 1H), 6.83 (d, 1H, J = 2.1 Hz), 6.70 (d, 2H, J = 1.8 Hz), 5.76 (s, 1H), 2.59 (s, 3H), 2.28 (s, 3H), 1.36 (s, 9H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 193.3, 148.1, 143.2, 142.8, 138.2, 136.4, 134.2, 133.8, 133.5, 132.5, 131.5, 120.1, 113.6, 34.9, 29.7, 20.2, 19.1. IR (solid) ν max (cm⁻¹): 3366 (br, -OH), 1669 (s, -C=O). Mass spectrometry (m/z): calculated for C₁₉H₂₅O₃ (M+H)⁺: 299.1647, found: 299.1624 (M+H)⁺.

2-(3'-(tert-Butyl)-4',5'-dihydroxy-2,5-dimethyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (26b). A 10 mL Schlenk flask containing 25b (120 mg, 0.402 mmol) in 4 mL of methanol was added 2,3-dimethyl-2,3-bis(hydroxyamino)butane (125 mg, 0.845 mmol). The mixture was stirred at room temperature for 48 h. The solvent was evaporated, and the product was dried in vacuum to give 26b as a yellow solid (140 mg, 84 %). The product was immediately used for the next step without further purification, due to its instability. ¹H NMR (300 MHz, DMSO) δ (ppm): 9.38 (s, 1H), 8.03 (s, 1H), 7.62 (s, 1H), 7.49 (s, 1H), 6.87 (s, 1H), 6.54 (s, 1H), 4.87 (s, 1H), 2.34 (s, 3H), 2.19 (s, 3H), 1.35 (s, 9H), 1.09 (s, 6H), 1.08 (s, 6H). IR (solid) ν max (cm⁻¹): 3480 (br, -OH).

2-(3'-(tert-Butyl)-4',5'-dihydroxy-2,5-dimethyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (27b). A 250 mL round bottom flask containing 26b (88.8 mg, 0.215 mmol) in CH₂Cl₂ and pH 7 buffer in water was added cetyl trimethylammonium bromide (13.0 mg) as a phase transfer catalyst and was cooled to 0°C. Iodine (84.7 mg, 0.334 mmol) in CH₂Cl₂ was added dropwise. The solution was stirred at
0°C for an additional 30 minutes. The organic layer was then separated and washed with a saturated solution of sodium thiosulfate and brine. The organic layer was then separated, dried, and the solvent was removed to afford a purple solid 27b (80.0 mg, 91%). IR (CH$_2$Cl$_2$ film) ν (cm$^{-1}$): 3216 (br, -OH). EPR (~0.2 mM in CH$_2$Cl$_2$): $a_N = 7.50$ G.

$\text{Tp}^{\text{Cum,Me}}\text{Zn(SQ-pXylyl-NN)}$ (1-pXylyl). A 25 mL Schlenk flask containing 27b (72.0 mg, 0.176 mmol) and Zn(OH)$\text{Tp}^{\text{Cum,Me}}$ (122 mg, 0.176 mmol) with 10 mL of distilled MeOH and 10 mL of distilled CH$_2$Cl$_2$ and was stirred for 2 h under nitrogen and then opened to air for overnight. A brown solution was formed and the crude reaction mixture was purified by flash column chromatography (Hexanes/EtOAc 4/1) to afford 1-pXylyl as a brown solid (148 mg, 77%). Crystals of 1-pXylyl were grown from slow evaporation of methanol containing a few drops of CH$_2$Cl$_2$. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2536 (w, -BH). EPR (~0.2 mM in CH$_2$Cl$_2$): apparent $a_N = 3.89$ G. Mass spectrometry ($m/z$): calculated for C$_{64}$H$_{77}$BN$_8$O$_4$Zn (M)$^+$: 1096.5446, found: 1096.5439 (M)$^+$. Elemental analysis Calculated: (C: 69.67, H: 7.06, N: 10.20), Found: (C: 73.42, H: 7.62, N: 11.78).

4-Bromo-2,3,5,6-tetramethylbenzaldehyde (23c). To a 100 mL oven dried Schlenk flask, 4.01 g (13.72 mmol) of 1,4-dibromo-2,3,5,6-tetramethylbenzene was added and pump purged with nitrogen five times. To the reaction flask, 30 mL of dried and degassed tetrahydrofuran was added and the flask chilled to -78°C. Using a nitrogen purged syringe, 8.7 mL (13.92 mmol) of 1.6 M n-butyllithium in hexanes was added dropwise and stirred for 1 h. Using another nitrogen purged syringe, 6 mL (77.49 mmol) of dried and degassed N,N-dimethylformamide was added dropwise and was then allowed to warm to room temperature. Once warm, the reaction was opened to air and 30 mL diethyl ether was added. The reaction
mixture was transferred to a separatory funnel where it was washed three times with saturated NaCl solution. The organic layer was collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO$_2$, 100% Hexanes followed by 1:1 Hexanes:Et$_2$O) to yield 3.02 g (91%) of a white solid 23c. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 10.59 (s, 1H), 2.45 (s, 6H), 2.44 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 196.31, 135.66, 135.54, 134.64, 134.03, 20.94, 17.03. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 1687 (s, -C=O). Elemental Analysis Calculated: (C: 54.79, H: 5.43). Found: (C: 55.71, H: 5.56). These experimental values match previously reported results.$^{113}$

3'-(tert-Butyl)-4',5'-dihydroxy-2,3,5,6-tetramethyl-[1,1'-biphenyl]-4-carboxaldehyde (25c). To a 50 mL oven dried Schlenk flask, 1.22 g (3.18 mmol) of 9, 502 mg (2.08 mmol) of 23c, 1.35 g (6.36 mmol) of K$_3$PO$_4$, and 4Å molecular sieves were added and placed under a nitrogen environment where 200 mg (0.93 mmol) of ethyldiphenylphosphine and 123 mg (0.13 mmol) Pd$_2$(dba)$_3$ were added with 20 mL dried toluene. The reaction was fit with a condenser under nitrogen purge and heated to 130°C for 4 days. The reaction was then cooled, filtered into a separatory funnel, and diluted with ethyl acetate. The organic layer was washed once with saturated NaHCO$_3$ solution followed by two washes of saturated NaCl solution. The organic layer was then dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The crude reaction mixture was then redissolved in a 1:1 ethyl acetate : methanol mixture and 10 drops of concentrated HCl was added. The reaction was fit with a condenser and heated to reflux for 16 h. After the reaction was cooled to room temperature, the mixture was transferred to a separatory funnel, washed with saturated NaHCO$_3$ and saturated NaCl. The organic layer was dried over Na$_2$SO$_4$ and
the solvent removed under reduced pressure. The product was purified by column chromatography (SiO$_2$, 40% EtOAc in Hexanes) to yield 255 mg (38%) of 25c. $^1$H NMR (400 MHz, DMSO-$d_6$, δ): 10.67 (s, 1H), 6.52 (s, 1H), 6.43 (s, 1H), 5.70 (s, 1H), 5.62 (s, 1H), 2.40 (s, 6H), 1.94 (s, 6H), 1.39 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$, δ): 196.96, 146.93, 143.05, 142.21, 136.90, 135.05, 134.03, 132.83, 119.76, 113.31, 60.71, 34.89, 29.82, 21.21, 17.82, 16.08, 14.31. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3201 (br, -OH). Mass spectrometry ($m/z$): calculated for C$_{21}$H$_{27}$O$_3$ (M+H)$^+$: 327.1960, found: 327.1949 (M+H)$^+$.

2-(3'-((tert-Butyl)-4',5'-dihydroxy-2,3,5,6-tetramethyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (26c). To a 10 mL round bottom flask, 255 mg (0.78 mmol) of 25c was added with 345 mg (1.96 mmol) of BHA and pump purged with nitrogen five times. Using a nitrogen purged syringe, 2 mL of degassed and dried methanol was added to the reaction flask. The reaction was shielded from light and allowed to stir under nitrogen at room temperature for 5 days upon which the product had precipitated. The product was collected by vacuum filtration to yield 80 mg (22%) crude 26c which was used directly in the synthesis of 27c. $^1$H NMR (300 MHz, DMSO-$d_6$, δ): 9.47 (s, 1H), 8.03 (s, 1H), 7.31 (s, 1H), 6.95 (s, 1H), 6.37 (s, 1H), 6.27 (s, 1H), 5.31 (s, 1H), 2.05 (s, 6H), 1.57 (s, 6H), 1.33 (s, 9H), 1.12 (s, 6H), 0.99 (s, 6H). IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3266 (br, -OH).

2-(3'-((tert-Butyl)-4',5'-dihydroxy-2,3,5,6-tetramethyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (27c). To a 100 mL round bottom flask, 80 mg (0.17 mmol) of 26c was added with 20 mL diethyl ether, 10 mL buffer (pH = 7), and chilled to 0°C. To a 125 mL separatory funnel, 67 mg (0.26 mmol) I$_2$ was added with 20 mL diethyl ether and added dropwise to the stirring reaction mixture. After all of the I$_2$ was
added, the reaction was warmed to room temperature and transferred to a separatory funnel with 100 mL buffer (pH = 7). The organic layer was washed once with saturated Na$_2$S$_2$O$_3$ solution followed by saturated NaCl solution. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure to yield 65 mg (81%) of purple solid 27c. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3253 (br, -OH). EPR (X-Band, 298 K): $a_N = 7.45$ G (1:2:3:2:1). Mass spectrometry ($m/z$): calculated for C$_{27}$H$_{38}$N$_2$O$_4$ (M+H)$^+$: 454.2831, found: 452.2816 (M+H)$^+$.

Tp$^{\text{Cum,Me}}$Zn(SQ-PhMe$_4$-NN) (1-PhMe$_4$). To an oven dried 25 mL schlenk flask, 64 mg (0.14 mmol) of 27c was added with 150 mg (0.22 mmol) of Zn(OH)Tp$^{\text{Cum,Me}}$ and pump purged with nitrogen five times. Using a purged syringe, 10 mL of a 1:1 mixture of dry and degassed dichloromethane and methanol was added to the reaction mixture with stirring. The reaction was allowed to stir for 2 h under nitrogen then opened to air and stirred overnight. The solvent was removed under reduced pressure and the product purified by column chromatography (Basic Alumina, 1:1 EtOAc:Hexanes) to yield 150 mg (94%) of 1-PhMe$_4$. Crystals of 1-PhMe$_4$ were grown from slow evaporation of benzene in ethanol. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2532 (w, -BH). EPR (~0.2 mM in CH$_2$Cl$_2$): apparent $a_N = 3.74$ G. Mass spectrometry ($m/z$): calculated for C$_{66}$H$_{82}$BN$_8$O$_4$Zn (M+H)$^+$: 1125.5843, found: 1125.5833 (M+H)$^+$. Elemental Analysis Calculated: (C: 70.36, H: 7.25, N: 9.95). Found: (C: 69.92, H: 7.23, N: 9.58).
III. Superexchange Contributions to Distance Dependence of Electron Transfer/Transport in Donor-Bridge-Acceptor Biradicals

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**A. Introduction to Distance Dependence of Donor-Bridge-Acceptor Complexes**

When designing molecular electronic devices, a common goal is to use a conductive polymer in order to facilitate the flow of electrons from the source electrode (donor) to the drain electrode (acceptor) with a minimal loss of current. To this effect, oligo(*para*-phenylene)\(^4,17,47,48,87,117\) and especially oligo(*2,5*-thiophene)\(^21,58,59,118–128\) bridges have become important bridge-types in the construction of opto-electronic, spintronic, molecular electronic devices. Since oligo(*para*-phenylene) and oligo(*2,5*-thiophene) based materials are so widely studied, we show how our biradical complexes containing *para*-phenylene and *2,5*-thiophene bridges can be used to determine the distance dependence of the magnetic and electronic coupling mediated by these bridges in the strong coupling limit. Studies of the distance dependence of electronic coupling in D-B-As are all related by a stretched exponential as described by McConnell\(^9\) through Eq. (III.1) and thus also Eq. (III.2) based on the relationship between \(H_{DA}\) and \(J_{DA}\) described previously.

\[
\frac{H}{H_0} = \exp\left(\frac{\beta}{2}(r - r_0)\right) \quad \text{III.1}
\]

\[
\frac{J}{J_0} = \exp[\beta(r - r_0)] \quad \text{III.2}
\]
In both Eq. (III.1) and Eq. (III.2), the subscript 0 indicates the coupling and distance for a D-A lacking a bridge. The value of $\beta$ can be associated with the efficiency of electronic coupling through a D-B-A system where the smaller the value, the further apart the donor and acceptor can be and still have appreciable coupling. It is important to note that there are two modes of transport in D-B-A systems with drastically different ranges of $\beta$. One mode is through electron hopping from donor to bridge to acceptor. This mechanism, commonly explored in both PET$^{10,129}$ and conductance$^{21,58,69,130}$ D-B-A systems with long bridges between donor and acceptor, allows the electron to be localized on the bridge to facilitate fast transfer from donor to acceptor and commonly shows $\beta$ values in the 0.01 to 0.1 Å$^{-1}$ range. Another mechanism of electron transport is through tunneling, or superexchange, from donor to acceptor through the bridge. This mode is common in short connection PET$^{16,131,132}$ and conductance$^{21,60,133,134}$ systems with a $\beta$ range between 0.1 and 1.0 Å$^{-1}$ and is the sole mode possible for the SQ-B-NN biradicals studied here due to the nature of the coupling between donor and acceptor.

The novelty of our SQ-B-NN biradical approach is that through the use of a common donor and acceptor, we are able to directly compare the distance dependence through magnetic exchange ($J_{DA}$) and electronic exchange coupling ($H_{DA}$) of these two bridge types where there are no studies that directly compare the two utilizing the exact same donor and acceptor. Using a D-B-A biradical approach, we can determine the distance dependence of $H_{DA}$ for both of these important bridge structure types through direct measurement of the magnetic exchange coupling constant ($J_{DA}$) by variable-temperature magnetic susceptibility measurements of the D-B-A biradical complexes 1, 1-pPh, 1-Ph2, 2-(2,5)T and 2-T2
depicted in Figure III-1. There have been both experimental and computational reports of determining $H_{DA}$ for \textit{para}-phenylene\textsuperscript{135–137} and for 2,5-thiophene\textsuperscript{138,139} bridges using Donor-Acceptor\textsuperscript{140} and mixed valence\textsuperscript{15} approaches in the literature. However, few of these reports have the combined advantages of using an electron spin-spin exchange parameter to compute $H_{DA}$ along with molecular structure determination, while avoiding categorization of degree of delocalization in mixed-valence compounds.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Line bond drawings of D-B-A biradical analogs of oligo(\textit{para}-phenylene) and oligo(2,5-thiophene) used for distance dependence studies.}
\end{figure}
B. Discussion of Results for SQ-Bridge-NN Distance Dependence Complexes

1. Synthesis of Distance Dependence SQ-Bridge-NN Biradical Complexes

Synthesis and characterization of $1^{47}$ and $1$-$p$Ph$^7$ have been reported previously. The syntheses and characterizations of $1$-Ph$_2$ and $2$-$(2,5)$T were completed by former Shultz group members Dr. Guangbin Wang and Dr. Geoffrey Lewis respectively. The respective synthetic outlines are reproduced here in order to provide a consistent description of the complexes used in this study.

For the synthesis of $1$-Ph$_2$, as outlined in Error! Reference source not found., aldehyde $28^{141}$ was reacted with CH$_2$I$_2$/I$_2$ to yield 4´-iodophenylbenzaldehyde $29$. Protected catechol $31$ was formed by Suzuki coupling of $29$ and boronic acid $30$. De$^{142}$ Deprotection of $31$ in refluxing methanol under acidic conditions yielded catechol $32$ in excellent yield. Condensation of $32$ with BHA$^{95}$ followed by oxidation with I$_2$ yielded catechol-nitronylnitroxide $34$. Compound $34$ and Zn(OH)Tp$^{Cum,Me}$, under standard conditions,$^{7,47,96,142}$ yielded semiquinone biradical formation and complexation for $1$-Ph$_2$. 
Scheme III-1. Synthesis of 1-Ph₂.

For the synthesis of 2-(2,5)T, as outlined in Error! Reference source not found., commercially available thiophene 35 was first reacted with BHA\textsuperscript{95} followed by oxidation with PbO₂ to yield thiophene-nitronylnitroxide 37. Phenol 16, prepared by literature methods,\textsuperscript{143} and compound 37 were reacted under Suzuki conditions to yield phenol 38. Using IBX,\textsuperscript{89} phenol 38 was oxidized to quinone 39, followed by reduction with ascorbic acid and buffer (pH = 7) to catechol 40. Semiquinone biradical formation of 2-(2,5)T was completed with compound 40 and Zn(OH)Tp\textsuperscript{Cum,Me} under standard conditions.\textsuperscript{7,47,96,142}
Scheme III-2. Synthesis of 2-(2,5)T.

For the synthesis of 2-T_2, as outlined in Scheme III-3, commercially available bithiophene aldehyde 20 was brominated with N-bromosuccinimide at low temperature to yield bithiophene bromide 21. Compound 21 was reacted with compound 16 under Suzuki conditions to yield phenol 22. Compound 22 was oxidized with IBX giving quinone 23 followed by reduction with ascorbic acid to yield catechol-aldehyde 24. Catechol 24 was condensed with BHA then oxidized to yield catechol-nitronylnitroxide 26. Semiquinone
biradical formation/complexation was completed by reacting compound 26 and 
Zn(OH)Tp^{Cum,Me} giving 5-T_2 under standard conditions.\textsuperscript{7,47,96,142}

\textbf{Scheme III-3. Synthesis of 5-T_2.}
For the synthesis of **KSQ-T** and **KSQ-T-d**, as outlined in Scheme III-4, compound **S3** was formed under Suzuki conditions using compound **S1**, prepared as previously reported,\(^7\) and commercially available **S2**. Deuteration of **S3** was selectively performed by reacting n-butyllithium with **S3** at \(-78^\circ\text{C}\) followed by MeOD quench to give **S3-d**.

Deprotection of **S3/S3-d** was completed in warm acidic methanol to produce **S4/S4-d** in excellent yield. Using Ag\(_2\)CO\(_3\)/Celite, half of **S4/S4-d** was oxidized to **S5/S5-d** under inert atmosphere. Comproportionation of **S4/S4-d** and **S5/S5-d** to form semiquinone **KSQ-T/KSQ-T-d** was carried out, and stored, under inert atmosphere.

**Scheme III-4.** Synthesis of **KSQ-T** and its Deuterium-labeled analog **KSQ-T-d**.
2. Structural and Magnetic Properties of SQ-Bridge-NN Distance Dependence Complexes

Structural parameters of biradical crystals can provide physical evidence of the presence of the SQ and NN radicals through comparison of the bond lengths to previously published work, information about intramolecular geometries, as well as details of intermolecular interactions. Thermal ellipsoid plots of complexes 1, 1-pPh, 1-Ph₂, 2-(2,5)T, and 2-T₂ are shown in Figure III-2 in which both hydrogen atoms and cumenyl groups were omitted for clarity. The bond lengths for the o-SQ and NN components in each complex fall within typical values. The structural deviation parameters for these radicals are summarized in Table III-1. In each case, structural deviations of $\Sigma|\Delta_i| \approx 0.01\AA$ for the o-SQ component and $\Sigma|\Delta_i| \approx 0.02\AA$ for the NN component are small when compared to previously reported semiquinone-like ligands$^{142}$ and the ZnO₂N₃ coordination sphere is identical to other $\text{Tp}^{\text{Cum,Me}}\text{Zn}(\text{SQ-Bridge-NN})$ biradical complexes.$^{4,7,142,145}$
Another important factor discernible through crystallography is the distances between oxygen atoms on the paramagnetic nitronylnitroxide acceptors which possess appreciable spin density. These distances are determined to ensure the results of the magnetic susceptibility measurements reflect the *intramolecular* exchange coupling, $J_{DA}$, and not *intermolecular* exchange. The closest intermolecular contact for these oxygen atoms in each complex studied is given in Table III-1. All of these values are all outside the range for significant *intermolecular* contributions to the measured magnetic exchange couplings.¹⁴⁶,¹⁴⁷
Table III-1. Structural Deviation Parameters and NN oxygen-oxygen intermolecular distances for Complexes 1, 1-pPh, 1-Ph₂, 2-(2,5)T, and 2-T₂.

| Complex | o-SQ $\sum |\Delta l|$ (Å) | NN $\sum |\Delta l|$ (Å) | Intermolecular O-O Distance (Å) |
|---------|-----------------|-----------------|-----------------------------|
| 1       | 0.011           | 0.015           | 4.691                       |
| 1-pPh   | 0.014           | 0.025           | 4.861                       |
| 1-Ph₂   | 0.017           | 0.019           | 6.088                       |
| 2-(2,5)T| 0.008           | 0.026           | 4.604                       |
| 2-T₂    | 0.008           | 0.017           | 7.967                       |

As we saw in Chapter II, the torsion between D-B-A fragments has a strong effect on the SQ-NN exchange/electronic coupling and will modulate the donor-acceptor interaction. Due to the limited number of complexes in this series, we cannot create the same type of multi-dimensional plot shown in Chapter II and must accept that the torsional effects on the exchange coupling will manifest themselves as "uncertainty" in the measured exchange coupling, $J_{DA}$. However, we can comment on the relative planarity of each set of complexes in order to establish the lack of major torsional effects skewing the experimental data. Complex 1 has a nearly coplanar conformation of SQ and NN groups while complexes 1-pPh and 1-Ph₂ possess moderate bond torsions. In comparison, complexes 2-(2,5)T and 2-T₂ show more coplanarity than their phenyl-bridged counterparts.
Table III-2. Select Torsion Angles for Complexes 1, 1-pPh, 1-Ph₂, 2-(2,5)T, and 2-T₂.

<table>
<thead>
<tr>
<th>Complex</th>
<th>SQ-Bridge Torsion Angle (°)</th>
<th>Bridge-NN Torsion Angle (°)</th>
<th>Bridge-Bridge Torsion Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1-pPh</td>
<td>35.9</td>
<td>15.2</td>
<td>---</td>
</tr>
<tr>
<td>1-Ph₂</td>
<td>26.6</td>
<td>39.3</td>
<td>34.6</td>
</tr>
<tr>
<td>2-(2,5)T</td>
<td>11.4</td>
<td>1.9</td>
<td>---</td>
</tr>
<tr>
<td>2-T₂</td>
<td>14.8</td>
<td>30.6</td>
<td>3.7</td>
</tr>
</tbody>
</table>

The magnetometry for crystals of 1-Ph₂ and 2-T₂, displayed as paramagnetic susceptibility-temperature products (χₚₐ₉a•T) vs. temperature, are shown in Figure III-3. The χₚₐ₉a•T data were fit as using an HDVV Hamiltonian, as described in Eq. (I.29), giving a ferromagnetic Jₐₐ = +20 cm⁻¹ for 1-Ph₂, and Jₐₐ = +108 cm⁻¹ for 2-T₂.

Figure III-3 Plots of the paramagnetic susceptibility-temperature product (χₚₐ₉a•T) vs. temperature for 1-Ph₂ (red), 2-T₂ (blue) and 2-T (black) with best fit lines for 1-Ph₂ and 2-T₂ in red and blue respectively. Theoretical lines for 2-T correspond to J = +220 cm⁻¹ with θ = -0.1 K (pink) and for J = +172 cm⁻¹ with θ = -0.1 K (green).
The magnetic susceptibility data for 2-(2,5)T shows what appears to be a linear relationship suggesting Curie-Weiss behavior with $J_{DA} > \sim 250 \text{ cm}^{-1}$. Since we couldn't reliably measure the exchange coupling with the SQUID magnetometer, we required an alternate method for estimating $J_{DA}$. In cases where the singlet of the ferromagnetically coupled biradical is not appreciably thermally populated at 300K, the exchange coupling parameter can be estimated from the ratio of the spin density ($\rho$) on the bridge ring at the carbon attached to the NN radical to the corresponding SQ ring carbon spin density. Since the spin densities are directly proportional to the proton hyperfine coupling constants, we can use EPR to estimate the SQ-NN coupling for 2-(2,5)T. Since the proton hyperfine to the protons on the SQ have already been reported in the literature, we just need to determine the proton hyperfine to the proton on the thiophene ring where the NN is attached. In order to do that, we have to be able to assign a hyperfine couplings to the protons on the thiophene ring.

KSQ-T was synthesized as described in Scheme III-4 as a donor-bridge analog of 2-(2,5)T in order to determined the proton hyperfine coupling between the SQ radical and protons on the rings. The EPR of a dilute solution of KSQ-T was determined and simulated with five different hyperfine couplings, one for each proton on the molecule. The experimental and simulated EPR spectrum of KSQ-T, along with simulation parameters and a labeled line bond drawing, is shown in Figure III-4.
Figure III-4. (Left) EPR spectrum of **KSQ-T** as 0.2 mM solution in THF (red), simulation (blue), and the residual (green). The simulated spectrum was produced in WinSIM using proton hyperfine coupling simulation parameters given in Table III-3 as well as a line width of 0.100 gauss, 31.000% Lorantzian line shape, and a g-shift of -0.266 gauss. (Right) Line bond structure of **KSQ-T** with hydrogen atoms labeled.

Once a set of hyperfine couplings for **KSQ-T** had been determined, the easiest way to assign the coupling which belonged to the H5 position was to synthesize a compound which replaces H5 with an EPR silent deuterium, as described in Scheme III-4 for **KSQ-T-d**. The percent of deuteration of **KSQ-T-d** was calculated using the integration of residual signal for H5 in the 1H-NMR shown in Figure III-5.
Figure III-5. NMR Spectra of S3 and S3-d in DMSO-d6. With selective deuteration at H₅, the signal at 7.49 ppm is dramatically reduced in intensity. Based on integration, ~75% H₅ has been replaced with deuterium. Consequently, the signals corresponding to H₃ and H₄ collapse from doublet of doublets to doublets with a reduction in \( J_{3,4} \) coupling by 0.1 Hz and a reduction in \( J_{1,2} \) coupling by 0.2 Hz.

A dilute solution EPR spectrum of KSQ-T-d was then collected and simulated in the same way as KSQ-T, but with one fewer hyperfine parameter. The experimental and simulated EPR spectrum of KSQ-T-d, along with simulation parameters and a labeled line bond drawing, is shown in Figure III-6.
Figure III-6. (Left) EPR of KSQ-T-d as a 0.2 mM solution in THF (red), simulation (blue), and the residual (green). The simulated spectrum was produced in WinSIM using 28.28% KSQ-T with a line width of 0.100 gauss, a 39.31% Lorentzian line shape, and a g-shift of -0.195 gauss as well as 78.72% KSQ-T-d with a line width of 0.260 gauss, a 28.15% Lorentzian line shape, and a g-shift of -0.205 gauss. Proton hyperfine coupling simulation parameters for KSQ-T-d are given in Table III-3. (Right) Line bond structure of KSQ-T-d with hydrogen atoms labeled.

By using previously reported proton hyperfine couplings for 3,5-di-tert-butylsemiquinone\textsuperscript{149} and the simple HMO spin densities for the KSQ-T SOMO, the proton hyperfine couplings were assigned as summarized in Table III-3.
Table III-3. Hyperfine Coupling Constants for K\textsubscript{SQ}-T and K\textsubscript{SQ}-T\textsubscript{d} from EPR Spectroscopy. Hyperfine couplings were assigned based on simulation of K\textsubscript{SQ}-T\textsubscript{d} and the hyperfine coupling constants for 3,5-di-\textit{tert}-butylsemiquinone.\textsuperscript{149}

<table>
<thead>
<tr>
<th>Atom</th>
<th>K\textsubscript{SQ}-T Hyperfine Coupling Constant</th>
<th>K\textsubscript{SQ}-T\textsubscript{d} Hyperfine Coupling Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{1}</td>
<td>0.78</td>
<td>0.73</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>2.61</td>
<td>2.59</td>
</tr>
<tr>
<td>H\textsubscript{3}</td>
<td>1.31</td>
<td>1.32</td>
</tr>
<tr>
<td>H\textsubscript{4}</td>
<td>0.29</td>
<td>0.26</td>
</tr>
<tr>
<td>H\textsubscript{5}</td>
<td>1.04</td>
<td>----</td>
</tr>
</tbody>
</table>

By knowing these proton hyperfine couplings, $J_{DA}$ for 2-(2,5)T can be estimated from Eq. (III.3),\textsuperscript{47}

$$J_{SQ-T-NN} = J_{SQ-NN} \left( \frac{\rho_{SQ-T}}{\rho_{SQ}} \right) = J_{SQ-NN} \left( \frac{a_{SQ-T}}{a_{SQ}} \right) = 550 \text{ cm}^{-1} \left( \frac{1.04}{3.33} \right) = 172 \text{ cm}^{-1}$$

III.3
giving $J_{SQ-T-NN} = 172 \text{ cm}^{-1}$. This value of $J_{DA}$ for 2-(2,5)T clearly represents a lower limit as there is no indication of thermal population of the exchange coupled singled state via a downward infection in the warmer temperature region (50–300K) of the experimental $\chi_{para} \cdot T$ data. Clearly, the experimental $\chi_{para} \cdot T$ data (50–300K) lie above the theoretical curve for $\chi_{para} \cdot T(J = +172 \text{ cm}^{-1})$ as shown in Figure III-3. Instead, the theoretical curve for $J_{DA} = 220 \text{ cm}^{-1}$ was found to correlate better with the experimental data below ~220 K and therefore we will use $J_{DA} = +220 \text{ cm}^{-1}$ for 2-(2,5)T.


To begin to analyze this series of complexes, electronic absorption spectroscopy can be used to confirm the presence of the SQ and NN through characteristic low energy transitions as well as provide a comparison of the SQ SOMO to NN LUMO transition.
energy, $\Delta$, according to McConnell’s model of electronic coupling (Eq. I.42). Figure III-7 shows an overlay of electronic absorption spectra for 1, 1-pPh, 1-Ph$_2$, 2-(2,5)T, and 2-T$_2$ with labels for characteristic transitions for SQ-B-NN D-B-A biradicals. Values of $\Delta$ as determined by the spectra in Figure III-7 are tabulated in Table III-4.

Through use of the previously determined electronic coupling for 1, $H_{SQ\text{-}NN}$, and the ratio of magnetic exchange to electronic coupling previously described in Chapter I, $H_{DA}$ was calculated for each complex in this study. Values of $J_{DA}$ and $H_{DA}$ for these complexes are given in Table III-4 and these data are shown graphically in Figure III-8A and B as a ratio to
the values determined for 1 as per Eq. (III.2) and (III.1) respectively. Assuming the thiophene-bridged and bithiophene-bridged mixed valence compounds Wenger has studied are Class III delocalized, the values of $H_{DA}$ for 2-(2,5)T and 2-T2 are within 10% of previously reported values.\textsuperscript{150}

**Table III-4.** Exchange Coupling, Electronic Coupling, and D→B-A Electron Transfer Energies for 1,\textsuperscript{7} 1-pPh,\textsuperscript{7} 1-Ph2, 2-(2,5)T, and 2-T2. \textit{n} represents the number of bridge units.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_{DA}$ (cm\textsuperscript{-1})</th>
<th>$H_{DA}$ (cm\textsuperscript{-1})</th>
<th>$\Delta_{\text{(n)}}$ (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>550</td>
<td>10622</td>
<td>N.A.</td>
</tr>
<tr>
<td>1-pPh</td>
<td>100</td>
<td>4529</td>
<td>22,900</td>
</tr>
<tr>
<td>1-Ph2</td>
<td>20</td>
<td>2015</td>
<td>24,200</td>
</tr>
<tr>
<td>2-(2,5)T</td>
<td>~220</td>
<td>~6718</td>
<td>21,000</td>
</tr>
<tr>
<td>2-T2</td>
<td>108</td>
<td>4707</td>
<td>19,200</td>
</tr>
</tbody>
</table>

By using the plots in Figure III-8A and B, we were able to determine the decay constant $\beta$, describing the exponential distance dependence of both the magnetic exchange coupling\textsuperscript{151–153} and the electronic coupling matrix element.\textsuperscript{154}
In Figure III-8A, we have determined the value of $\beta = 0.39 \text{ Å}$ for oligo(\textit{para}-phenylene)-bridged SQ-B-NN biradicals from $J_{DA}$ values for SQ-(Ph)$_n$-NN biradicals is similar to that found for oligo(\textit{para}-phenylene) bridges in PET D-(\textit{para}-Ph)$_n$-A ($n = 1-5$) compounds determined from charge separation rate constants ($\beta = 0.46 \text{ Å}^{-1}$),\textsuperscript{17} oligo(\textit{para}-phenylene) bridges probed by electron transfer in a zinc(II) porphyrin system ($\beta = 0.4 \text{ Å}^{-1}$)\textsuperscript{155} and for $\alpha,\omega$-oligo(\textit{para}-phenylene)-dithiols using break junction conductive atomic force microscopy methods ($\beta = 0.41 \text{ Å}^{-1}$).\textsuperscript{20} Figure III-8B shows the intramolecular distance dependence of $H_{DA}$ and $J_{DA}$ for the oligo(2,5-thiophene) series where the solid lines represent fits to the data using $J_{DA} = +220 \text{ cm}^{-1}$ for 2-(2,5)$T$ while the dashed lines are fits to data using $J_{DA} = +172 \text{ cm}^{-1}$ from Eq. (III.3). The stretched exponential decay fits using $J_{DA} = +220 \text{ cm}^{-1}$ are decidedly better than those using $J_{DA} = +172 \text{ cm}^{-1}$ with an $R^2$ of 0.998 versus 0.991 for...
the fits for the values of $J_{DA}$ respectively. The $\beta$ values determined from fits to the electronic coupling ($H/H_0$) and exchange coupling ($J/J_0$) parameters can be considered as an internal check on the quality of the fit as they should provide the same value. We can see the internal check holds for the fits using $J_{DA} = +220$ cm$^{-1}$ but not for those using $J_{DA} = +172$ cm$^{-1}$ (Figure III-8B). Therefore, the $\beta$ value that we determined for the oligo(2,5-thiophene)-bridged SQ-B-NN species is 0.22 Å$^{-1}$. Interestingly, this value for $\beta$ is twice as large as that determined by PET measurements of porphyrin-oligo(2,5-thiophene)-fullerene triads bridged by 4, 8, and 12 thiophene repeat units ($\beta = 0.11$ Å$^{-1}$)$^{156}$ and break junction conductance measurements on a series of oligo(2,5-thiophene) molecular wires with 5, 8, 11, and 14 thiophene repeat units ($\beta = 0.1$ Å$^{-1}$)$^{66}$ In these solution phase studies, it was determined that the effective conjugation length was approximately 5 thiophene repeat units. To explain the remarkably small value for $\beta$ in the PET experiments, it was suggested to result from highly efficient molecular wire behavior with an extraordinarily large correlation length.$^{17}$ These previously reported values of $\beta$ represent a significant difference with the results for the thiophene bridged SQ-B-NN biradicals and can be explained by either significant differences in how the bridge interacts with the donor and acceptor or the previously reported values are relying on incoherent hopping as the main mechanism of electron transport$^{17}$ as opposed to coherent superexchange, such as which is found in donor acceptor biradicals, since the PET measurements show evidence for hole character on the thiophenes ($nT^+$).$^{157}$

Alternatively, the $\beta$ value can deviate from the previously discussed exponential distance dependence through conformational flexibility of the bridge.$^{158}$ However,
conformational flexibility is not an issue in these D-B-A molecules since the magnetic exchange, and thus the electronic coupling ($H_{DA}$), are determined by analysis of solid-state magnetic susceptibility data and not solution phase measurements. Interestingly, there has been some recent work that shows that the conductance can display a non-exponential distance dependence and even increase for bridges with more than three repeat units.\textsuperscript{121,159–161} This unique dependence is suggested to be a result from a decrease in $\Delta$ indicating a greater resonance between the donor and the bridge. Other sources of variation in $\beta$ can occur in PET or conductance experiments if the bridge is capable of being oxidized or reduced as observed by Wasielewski.\textsuperscript{17,51} This system provides incoherent charge hopping which affects the electron transfer rate constant. The increase in the charge recombination rate constant past three bridge units indicates the molecular wire behavior in D-B-A systems does not have to derive from an energetically favorable redox difference between donor and acceptor.

As described in Chapter I, PET rate constants, break junction conductance, and donor acceptor biradical exchange are all related to the electronic coupling matrix element ($H_{DA}$) through McConnell's expression (Eq. I.42).\textsuperscript{9} If we use the $H_{DA}$ values we have determined for oligo(paraphenyleno)- and oligo(2,5-thiophene)-bridged SQ-B-NN systems and the electron transfer energies ($\Delta_{(n)} \approx \Delta$) as reported in Table III-4, we can estimate the bridge-bridge electronic coupling, $H_{BB}$. For a D-B-A system with a single bridge ($n =1$) the term for $H_{BB}$ is reduced to 1 and the $H_{DB}H_{BA}$ product can be determined from Eq. (III.4), where the subscript ($n$) denotes the number of bridge repeat units.

$$H_{DB}H_{BA} = H_{DA(1)}\Delta_{(1)}$$

\textsuperscript{III.4}
By using this relationship, we can use the ratio of the two-bridge repeat unit to the D-B-A with one bridge to estimate the value of $H_{BB}$ Eq. (III.5).

$$H_{BB} = \frac{H_{DA(2)}A_{(2)}^2}{H_{DA(1)}A_{(1)}}$$

By plugging in the values from Table III-4, we have determined that $H_{BB} \sim 11,400$ cm$^{-1}$ for the phenyl-phenyl interaction and $H_{BB} \sim 12,300$ cm$^{-1}$ for the thiophene-thiophene interaction, which is approximately an 8% difference in magnitude. It is very important to note that the $A$ values from Table III-4 are estimates as there is no way to measure $A$ directly for the SQ-B-NN system. This also means that the magnitudes of calculated $H_{BB}$ values are also gross estimates since the error in knowing $A$ gets propagated through the calculation. However, it is reasonably safe to assume that we can still compare the relative ratio between the calculated $H_{BB}$ values for the phenyl-phenyl interaction and the thiophene-thiophene interaction in order to compare the two bridge types while using the same donor and acceptor for the system. Through this estimation, we can see that the difference in $H_{DA}$ values for oligo($para$-phenylene)- versus oligo(2,5-thiophene)-bridged D-B-A is not directly related to the difference in $H_{BB}$ values. In fact, the larger $H_{DA}$ values for oligo(2,5-thiophene)-compared to oligo($para$-phenylene)-bridged SQ-B-NN systems come from the combination of smaller $A$ values for the oligo(2,5-thiophene)s and their larger $H_{DB}$ and/or $H_{BA}$ values.

This specifically underscores the importance of the excited state interactions between the donor or acceptor and the bridge in order to enhance the coherent superexchange mechanism for electron transfer and transport. The importance of $A$ in determining $H_{DA}$ is then highlighted in explaining deviations in exponential decay laws for $\beta$ that do not derive from a
hopping mechanism.\textsuperscript{159} McConnell’s model enforces this importance by discussing $\beta$ in terms of $\Delta$, $H_{BB}$, and the length of the bridge repeat unit, $R_0$ according to Eq. (III.6).

$$\beta = \frac{2}{R_0} \ln \left| \frac{\Delta}{H_{BB}} \right|$$  \hspace{1cm} \text{III.6}

For our SQ-B-NN system, the dominant contributor to differences in oligo\textit{(para-phenylene)} and oligo\textit{(2,5-thiophene)} $\beta$ values appears to be $\Delta$ based on the experimentally estimated $\Delta$, $H_{BB}$, and $R_0$ values. The computational analysis of Eng and Albinsson,\textsuperscript{159} who noted that $\beta$ is not specifically related to the nature of the bridge but is rather a property of the entire D-B-A ensemble, shows a good agreement with this experimental conclusion. Furthermore, a simple relationship has been derived that relates $\beta$ to the effective barrier height ($\Delta E_{\text{eff}}$) for an electron tunneling through a square potential barrier as shown in Eq. (III.7),\textsuperscript{162,163}

$$\Delta E_{\text{eff}} = \left( \frac{\hbar^2}{8m_e} \right) \beta^2 = (0.952 \text{eV} \times \AA^2) \beta^2$$  \hspace{1cm} \text{III.7}

where $m_e$ is the mass of the tunneling electron. Using Eq. (3.8) and the experimentally determined $\beta$ values for our SQ-B-NN distance dependence series, we find $\Delta E_{\text{eff}} = 1168$ cm\textsuperscript{-1} for the phenyl-phenyl interaction and 372 cm\textsuperscript{-1} for the thiophene-thiophene interaction. Based on our experimentally determined values of $\beta$, the effective barrier height for oligo\textit{(para-phenylene)} is approximately three times greater than that for oligo\textit{(2,5-thiophene)}.

By using the same donor and acceptor for this distance dependence study, we have been able to see how an $\sim 8\%$ difference in $H_{BB}$ couplings alone between two bridge types cannot explain differences in the exponential distance dependence across a D-B-A. Instead, we see that $\beta$ for a bridge type depends on the entire system working together. This enforces
the idea that the contacts between the electrodes (i.e. the donor and acceptor) and the bridge are just as important as the molecular structure of the bridge itself.\textsuperscript{164}

C. Exploring Another Electron Rich Bridge for Distance Dependence: Selenophene

1. Introduction to Other Chalcogen Bridged Biradicals

The results shown in the previous section focus mainly on two very different bridge types. However, the structure of thiophene lends us a way to study the effects of the heteroatom on the electronic coupling by replacing the sulfur atom with other chalcogens. While less common than oligo(2,5-thiophene), other important bridge types utilized in long range electron transfer/transport are oligo(2,5-selenophene)\textsuperscript{165–170} and oligo(2,5-furan)-bridged\textsuperscript{119,167,171,172} D-B-A systems. By swapping the sulfur in thiophene with a less electron rich oxygen in furan, we would expect the overall electronic coupling ($H_{DA}$) to be weaker from either $\Delta$ being larger or any of the $H_{DB}$, $H_{BB}$, or $H_{BA}$ couplings being smaller.$^{167}$ Conversely, by swapping the sulfur atom with a more electron rich selenium atom, we would expect the overall electronic coupling ($H_{DA}$) to be stronger from either $\Delta$ being smaller or any of the $H_{DB}$, $H_{BB}$, or $H_{BA}$ couplings being larger.$^{167}$

Upon initial investigation, we found that furan derivatives were simply not stable enough to undergo the required chemical transformations for the synthesis of the SQ-furan-NN and SQ-bifuran-NN D-B-A complexes, so focus was turned to the more stable selenophene bridged biradicals instead. Through use of the established SQ-B-NN molecular architecture, we can attempt to compare the effects of the heteroatom in the bridge using 3-Se and 3-Se$_2$, shown in Figure III-9.
2. Synthesis of Selenophene Bridged Biradicals

For the synthesis of 3-Se, as shown in Scheme III-5, 48, prepared as previously reported,\textsuperscript{173} was reacted with 9 under standard Suzuki coupling conditions to yield 49. Protected catechol 49 was deprotected under acidic conditions to yield compound 50 in excellent yield. Catechol 50 was reacted with BHA to yield condensation product 51 followed by oxidation with I\textsubscript{2} to yield nitronylnitroxide 52. Compound 52 was finally reacted with Zn(OH)Tp\textsuperscript{Cum,Me} under standard conditions\textsuperscript{7,47,96} to yield 3-Se.
Scheme III-5. Synthesis of 3-Se.

For the synthesis of 3-Se2, as shown in Scheme III-6, 53, prepared as reported previously,174 was reacted with 9 under standard Suzuki coupling conditions to yield 54. Protected catechol 54 was deprotected under acidic conditions to yield compound 55. Catechol 55 was reacted with BHA to yield condensation product 56 followed by oxidation with I2 to yield nitronylnitroxide 57. Compound 57 was finally reacted with Zn(OH)TpCum,Me under standard conditions7,96,102 to yield 3-Se2.
Scheme III-6. Synthesis of 3-Se₂.

For the synthesis of KSQ-Se, as shown in Scheme III-7, S1 was reacted with S6 under Suzuki conditions to yield protected catechol S7 which was immediately deprotected under acidic conditions to S8. Half of catechol S8 was reacted with Fetizon's reagent to produce quinone S9 in excellent yield. An equal amount of S8 and S9 were reacted in a comproportionation to yield KSQ-Se for dilute solution EPR studies.
3. Discussion of Results for Selenophene Bridged Biradicals

In order to gauge the effect of the selenium atom on the electronic coupling between SQ and NN, we can use the previously discussed oligo(2,5-thiophene)-bridged D-B-As as a comparison due to their similarity in structure. Due to this similarity, it is likely that oligo(2,5-thiophene) and oligo(2,5-selenophene) will have similar features in their electronic absorption spectra. We see this is indeed the case in Figure III-10 as the overall band shape of 2-(2,5)T and 3-Se are similar as are 2-T2 and 3-Se2. The major difference between these spectra is the shift of the SQ SOMO → NN LUMO absorption band of ~500 cm⁻¹ to lower energy for 3-Se and 3-Se2 compared to 2-(2,5)T and 2-T2. If $H_{DB}$, $H_{BA}$, and $H_{BB}$ for oligo(2,5-selenophene) are similar to those for oligo(2,5-thiophene) and we remember that these SQ SOMO → NN LUMO transitions are an approximation of $\Delta$ in Eq. (1.42), we can
conclude that the lower energy electronic transitions for 3-Se and 3-Se$_2$ should correlate to larger electronic couplings than 2-(2,5)T and 2-T$_2$.

Figure III-10. Normalized electronic absorption of 2-(2,5)T (green), 2-T$_2$ (red), 3-Se (blue), 3-Se$_2$ (black) in DCM. Absorption spectra were normalized to the NN $n$→π* transition at ~11,800 cm$^{-1}$. SQ SOMO → NN LUMO transitions range from ~18,000 cm$^{-1}$ for 3-Se$_2$ to ~21,000 cm$^{-1}$ for 2-(2,5)T.

As we discovered, we were unable to measure the exchange of 2-(2,5)T through magnetometry and thus estimated $J_{DA}$ from EPR hyperfine coupling constants. We assumed that we would also be unable to measure the exchange of 3-Se due to predicted similar, or larger, exchange couplings for oligo(2,5-selenophene)-bridged D-B-As compared to oligo(2,5-thiophene)-bridged D-B-As. As before with KSQ-T, a selenophene analog was synthesized as shown in Scheme III-7. By performing the same dilute solution EPR experiment on KSQ-Se as KSQ-T, we can again compare the spin density, $\rho$, at the
connecting carbon atoms of SQ and selenophene using proton hyperfine coupling to the SQ radical.

Figure III-11. (Left) EPR of KSQ-Se as a 0.2 mM solution in THF (red), simulation (blue), and residual (green). The simulated spectrum was produced in WinSIM using a line width of 0.157 gauss, a 99.25% Lorentzian line shape, and a g-shift of 0.515 gauss. Proton hyperfine coupling simulation parameters for KSQ-Se are given in Table III-5. (Right) Line bond structure of KSQ-Se with hydrogen atoms labeled.

By simulating the dilute solution EPR of KSQ-Se, we obtain the proton hyperfine coupling constants, displayed in Error! Reference source not found.. We can then use the proton hyperfine coupling constants from KSQ-T to make tentative assignments of the proton coupling constants for KSQ-Se.
Table III-5. Proton hyperfine coupling constants for KSQ-T and KSQ-Se determined by EPR.

<table>
<thead>
<tr>
<th>Atom</th>
<th>KSQ-T Hyperfine Coupling Constant</th>
<th>KSQ-Se Hyperfine Coupling Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>0.78</td>
<td>0.76</td>
</tr>
<tr>
<td>H₂</td>
<td>2.61</td>
<td>2.55</td>
</tr>
<tr>
<td>H₃</td>
<td>1.31</td>
<td>1.46</td>
</tr>
<tr>
<td>H₄</td>
<td>0.29</td>
<td>0.34</td>
</tr>
<tr>
<td>H₅</td>
<td><strong>1.04</strong></td>
<td><strong>1.11</strong></td>
</tr>
</tbody>
</table>

By using Eq. (III.8), we can again calculate what we can assume is a lower limit to the 3-Se exchange coupling we would observe in magnetometry. However, as we saw with 2-(2,5)T this calculated value of $J_{DA}$ is only an estimate and cannot easily be used to directly compare one exchange coupling to another. We can at least conclude that compared to the $J_{DA}$ for 2-(2,5)T determined in the same fashion (172 cm⁻¹), 3-Se is at least the same magnitude as 2-(2,5)T and would have similar issues in attempts to measure $J_{DA}$ through magnetometry. To further emphasize the fact that this value is an estimate, if the coupling constant for 3-Se had just a 5% error, the calculated value of 3-Se could be anywhere between 175 cm⁻¹ and 191 cm⁻¹. Therefore, due to the uncertainty of the exact proton hyperfine coupling constants, it is difficult to conclude if 3-Se indeed has a larger electronic coupling than 2-(2,5)T and, if so, by how much. Based on data from calculations of energy gaps, incorporation of selenophene in polymeric backbones of organic field effect transistors, and selenophene used in organic solar cells, we can see that oligo(2,5-selenophene) shows affinity for slightly better electron transfer/transport than oligo(2,5-thiophene). This should then correlate to a slightly larger electronic coupling, and thus a slightly larger magnetic exchange for oligo(2,5-selenophene)- compared to oligo(2,5-thiophene)-bridged D-B-As.
Unfortunately, all attempts at crystallizing 3-Se and 3-Se$_2$ resulted in dramatic changes in the electronic absorption spectra, which can be seen in Figure III-12, indicating decomposition of the biradical. Post-crystallization spectra in Figure III-12 were taken from dried crystallization attempts that were setup in a nitrogen environment shielded from light. Significant changes for 3-Se can be seen at $\sim$22,000 cm$^{-1}$ where the band in the post-crystallization attempt shifts slightly to lower energy and becomes less intense while the band at $\sim$20,500 cm$^{-1}$ remains unchanged. Differences in 3-Se$_2$ are even more dramatic where a new transition appears at $\sim$23,000 cm$^{-1}$ in the post-crystallization spectrum and the band shape of the transition around $\sim$19,000 cm$^{-1}$ degrades from two clear peaks in the reaction mixture spectrum to three in the post-crystallization spectrum. Due to the paramagnetic nature of the complexes, avenues for determining the products of the decomposition were extremely limited. Mass spectrometry on the crystallization attempts showed multiple products at higher ($m/z$) ratios than the calculated biradical molecular weight suggesting decomposition through oxidation of the biradicals. While selenophenes can become oxidized to the 1-oxide and 1,1-dioxide form, this process usually requires a directed synthetic approach.$^{177}$ However, it may be possible that the interaction between the SQ radical and the selenophene bridge rings increases the reactivity and causes decomposition in solution over long periods of time making crystallization difficult, if not impossible.
Figure III-12. Electronic absorption spectra in DCM before (solid lines) and after (dashed lines) air and light free crystallization attempts for 3-Se and 3-Se₂. Spectra were normalized to 11,800 cm⁻¹ in order to attempt to visually compare the relative intensities of various transitions.

D. Experimental

General considerations. Reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on either a Varian Mercury 300 MHz or a Varian Mercury 400 MHz spectrometer at room temperature. ¹H and ¹³C chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. Infrared spectra were recorded on a Brüker Vertex 80v spectrometer with Brüker Platinum ATR attachment. Electronic absorption spectra were collected on a Shimadzu UV-1601 UV-Visible Spectrophotometer. EPR spectra were collected on an IBM Instruments ER-200D-SRC Spectrometer. Microcrystalline samples of ~2 mM concentration were prepared in tetrahydrofuran, freeze-pump-thawed several times and the spectra were simulated using
WinSIM. Elemental analyses were performed by Atlantic Microlabs, Inc. High-resolution mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility and the Duke University Department of Chemistry Mass Spectrometry Facility. Single crystal XRD structures were determined by Paul Boyle and Roger Sommer at NCSU. Compounds 1\textsuperscript{,142} 1-pPh\textsuperscript{102}, 16,\textsuperscript{109} 21,\textsuperscript{178} 28,\textsuperscript{179} 30,\textsuperscript{142} 35,\textsuperscript{173} 41,\textsuperscript{180} S6,\textsuperscript{181} o-iodoxybenzoic acid (IBX),\textsuperscript{89,182–184} 2,3-dimethyl-2,3-bis(hydroxyamino)butane (BHA)\textsuperscript{95} and Tp\textsuperscript{Cum.Me}Zn(OH)\textsuperscript{96} were synthesized as previously described. Compounds 1-Ph\textsubscript{2}, 2-(2,5)T, 2-T\textsubscript{2}, KSQ-T, KSQ-T-d, 3-Se, 3-Se\textsubscript{2}, and KSQ-Se were prepared as outlined below.

**Magnetometry.** Magnetic susceptibility and saturation plots were performed on a Quantum Design MPMS-XL SQUID magnetometer. Microcrystalline samples of \(~15\text{ mg}\) were loaded into gelcap/straw holders and mounted to the sample rod with Kapton tape for susceptibility experiments. Raw susceptibility data was collected with an applied field of 0.7 T and corrected for diamagnetic response of the sample using Pascal’s constants as a first approximation, with a separate diamagnetic correction for the sample holder.

**X-Ray Diffraction.** Information including the experimental details of the structural determination of the new metal complexes in this work can be found in Appendix A.

**4'-Iodo-[1,1'-biphenyl]-4-carboxaldehyde (29).** A 50 mL Schlenk flask containing 28 (500 mg, 1.79 mmol), iodine (453 mg, 1.79 mmol) and CH\textsubscript{2}I\textsubscript{2} (8 mL) was degassed by 4 freeze-pump-thaw cycles. The reaction mixture was heated at 100 °C for 4 hours. Diiodomethane was removed under reduced pressure. The residue was dissolved in CHCl\textsubscript{3}, washed with a saturated solution of Na\textsubscript{2}SO\textsubscript{3} and brine, dried with sodium sulfate, filtered, and evaporated to dryness. The solid residue was purified by recrystallization from
CH$_2$Cl$_2$/hexanes mixed solvent to afford 29 as a brown solid (550 mg, 97 %). $^1$H NMR (300 MHz, CDCl$_3$, δ): 10.06 (s, 1H), 7.96 (d, $J = 8.3$ Hz, 2H), 7.82 (d, $J = 8.3$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.3$ Hz, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$, δ (ppm)): 191.9, 146.0, 139.3, 138.3, 135.6, 130.6, 129.2, 127.5, 94.7. IR (solid) ν$_{max}$ (cm$^{-1}$): 3056, 2922, 2822, 2727, 1692, 1600, 1572, 1547, 1475, 1417, 1383, 1306, 1286, 1258, 1208, 1164, 1104, 1062, 908, 840, 806. Mass spectrometry (m/z): 308.9763 (M+H)$^+$. 

3''-(tert-Butyl)-4''-5''-bis(methoxymethoxy)-[1,1':4',1''-terphenyl]-4-carboxaldehyde (31). To a 50 mL Schlenk flask, 29 (440 mg, 1.38 mmol), 30 (500 mg, 1.50 mmol), Pd(PPh$_3$)$_4$ (79.0 mg, 0.0684 mmol), cesium carbonate (890 mg, 2.73 mmol) and ethanol (5 mL) in dried toluene (10 mL) were added, placed under a nitrogen atmosphere, and refluxed for 48 h. After the reaction mixture was cooled to room temperature, 20 mL water was added and stirred for 30 min. The resulting mixture was filtered through Celite and the solvent removed under reduced pressure. The residue was extracted using CH$_2$Cl$_2$, washed with a saturated sodium bicarbonate solution followed by brine, dried with sodium sulfate, filtered, and concentrated in vacuo. The solid residue was purified by column chromatography (4:1 hexanes : ethyl acetate) to provide 31 as brown oil (440 mg, 66 %). $^1$H NMR (300 MHz, CDCl$_3$, δ): 10.07 (s, 1H), 7.97 (d, $J = 8.3$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.71 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.31 (s, 1H), 7.28 (s, 1H), 5.27 (s, 2H), 5.26 (s, 2H), 3.68 (s, 3H), 3.53 (s, 3H), 1.49 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$, δ): 192.0, 150.6, 146.8, 146.0, 143.9, 141.6, 138.3, 135.4, 135.3, 130.5, 127.8, 127.6, 119.5, 113.5, 99.2, 95.6, 57.8, 56.5, 35.5, 30.7. IR (thin film) ν$_{max}$ (cm$^{-1}$): 2955, 2900, 2822, 2727, 1700,
109

1602, 1571, 1551, 1524, 1471, 1435, 1391, 1360, 1324, 1264, 1233, 1213, 1162, 1077, 1030, 1007, 958, 880, 840, 818. Mass spectrometry (m/z): 457.1975 (M+Na)+.

3”-(tert-Butyl)-4”,5”-dihydroxy-[1,1’:4’,1”-terphenyl]-4-carboxaldehyde (32). To a 50 mL round bottom flask containing 31 (350 mg, 0.806 mmol) in methanol (3 mL) was added 3 drops of 12 M HCl and 1 drop of water and the solution was refluxed overnight. The solvent was removed under reduced pressure and the crude reaction mixture was extracted using CH₂Cl₂, washed with brine. The organic phase was then dried with sodium sulfate, filtered and concentrated in vacuo. The solid was recrystallized from a mixture of methanol and diethyl ether to provide 32 as a light-orange solid (250 mg, 90 %). ¹H NMR (300 MHz, DMSO-d₆, δ): 10.06 (s, 1H), 9.61 (s, 1H), 8.29 (s, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.02 (s, 1H), 6.98 (s, 1H), 1.40 (s, 9H). ¹³C NMR (75 MHz, CDCl₃, δ): 192.7, 145.5, 144.3, 141.4, 136.4, 136.0, 135.0, 130.2, 129.2, 127.6, 127.0, 126.7, 115.6, 111.2, 34.5, 29.4. IR (solid) νmax (cm⁻¹): 3489, 3417, 2956, 1664, 1600, 1571, 1488, 1435, 1400, 1373, 1358, 1300, 1286, 1218, 1190, 1169, 1151, 1108, 1068, 1003, 947, 875, 842, 813, 766, 753. Mass spectrometry (m/z): 369.1458 (M+Na)+.

2-(3”-(tert-Butyl)-4”,5”-dihydroxy-[1,1’:4’,1”-terphenyl]-4-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (33). A 10 mL Schlenk flask containing 32 (100 mg, 0.290 mmol) and BHA (90.0 mg, 0.600 mmol) with a minimal amount of methanol was pump/purged with nitrogen then stirred at room temperature for 48 h. The reaction was filtered and washed with cold methanol to yield 33 as a white solid (100 mg, 75 %). ¹H NMR (300 MHz, DMSO-d₆, δ): 9.57 (s, 1H), 8.22 (s, 1H), 7.79 (s, 2H), 7.68 (d, J = 8.1 Hz, 2H),
7.63 (d, J = 8.1 Hz, 2H), 7.57 (s, 2H), 6.98 (s, 1H), 6.94 (s, 1H), 4.55 (s, 1H), 1.40 (s, 9H), 1.09 (s, 6H) 1.07 (s, 6H). ^13^C NMR (75 MHz, CDCl$_3$, δ): 145.5, 144.0, 141.2, 140.1, 138.9, 138.1, 136.0, 129.7, 129.1, 127.0, 126.5, 125.7, 115.5, 111.2, 90.1, 66.1, 54.9, 34.5, 29.4, 24.4, 17.2. IR (solid) ν$_{\text{max}}$ (cm$^{-1}$): 3524, 3222, 2950, 2901, 1604, 1484, 1435, 1392, 1367, 1319, 1250, 1200, 1150, 1191, 1092, 1069, 947, 915, 875, 822, 769, 753, 722. Mass spectrometry (m/z): 477.2741 (M+H$^+$).

2-(3''-(tert-Butyl)-4'',5''-dihydroxy-[1,1':4',1''-terphenyl]-4-yl)-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (34). A 100 mL round bottom flask containing 33 (50.0 mg, 0.108 mmol) in CH$_2$Cl$_2$, pH 7 buffer and cetyltrimethyl ammonium bromide (10.0 mg, 0.0274 mmol) was cooled to 0°C. Iodine (43.2 mg, 0.170 mmol) in CH$_2$Cl$_2$ was added dropwise at 0°C. The mixture was stirred at 0°C for an additional 30 min. The organic layer was separated and washed with a saturated solution of sodium thiosulfate and brine. The organic phase was then dried with sodium sulfate, filtered and concentrated in vacuo. The solid residue was purified by recrystallization from CH$_2$Cl$_2$/hexanes mixed solvent to provide 34 as a blue-green solid (45.5 mg, 91%). IR (solid) ν$_{\text{max}}$ (cm$^{-1}$): 3505, 3195, 2925, 2850, 1653, 1603, 1536, 1483, 1422, 1387, 1361, 1322, 1311, 1254, 1215, 1165, 1133, 1106, 1070, 955, 872, 822, 800, 736, 699, 618, 540. EPR (CH$_2$Cl$_2$, 298 K) a$_N$ = 7.64 G. Mass spectrometry (m/z): 472.2353 (M-H$^-$).

Tp$^{\text{Cum,Me}}$Zn(SQ-Ph-Ph-NN) (1-Ph$_2$). A 25 mL Schlenk flask containing 34 (50.0 mg, 0.108 mmol), Tp$^{\text{Cum,Me}}$Zn(OH) (75.0 mg, 0.108 mmol) and 10 mL of 1:1 methanol/CH$_2$Cl$_2$ was pump/purged with nitrogen then stirred under N$_2$ at room temperature for 1 h and opened to air overnight. The brown precipitate was collected and dried
under vacuum. The solid was recrystallized from a CH$_2$Cl$_2$/methanol solution to yield 1-Ph$_2$ as a brown solid (100 mg, 81 %). IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2954, 2921, 2850, 2540, 1605, 1575, 1550, 1519, 1463, 1439, 1386, 1361, 1258, 1172, 1094, 1061, 821, 788, 746, 644. EPR (CH$_2$Cl$_2$, 298 K) $a_N = 3.92$ G. Elemental Analysis: Calculated(C: 71.23, H: 6.77, N: 9.77), Found: (C: 70.79, H: 6.94, N: 9.41).

2-(5'-Bromothiophen-2-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (36). In a 20 mL vial 35 (1.33 g, 6.96 mmol) was added with BHA (1.01 g, 6.82 mmol) and the solids were dissolved in 10 mL distilled methanol. The reaction was purged with N$_2$ and stirred for 24 h. The precipitate formed was collected yielding pure white 36 (1.57 g, 72%). $^1$H NMR (300 MHz, DMSO-$d_6$, $\delta$): 8.02 (s, 2H), 7.05 (d, $J = 3.91$ Hz, 1H), 6.90 (d, $J = 3.9$ Hz, 1H), 4.28 (s, 1H), 1.03 (s, 6H), 1.015 (s, 6H).

2-(5-Bromothiophen-2-yl)-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (37). To a 100 mL round bottom flask containing 36 (1.15 g, 3.58 mmol) and 40 mL distilled methanol, an excess of lead(IV) oxide was added and left to stir. After 30 min TLC (100% ethyl acetate) showed 37 ($\Delta R_f = 0.45$, deep blue) and 36 ($\Delta R_f = 0.11$, colorless, UV active). After 1 hour total reaction time no starting material was present. The reaction was filtered and solvent removed under reduced pressure. The product was purified by radial chromatography (gradient, 100% hexanes $\rightarrow$ 20% ethyl acetate in hexanes) yielding a pure blue solid, 37 (0.830 g, 73%) EPR (X-band, 298K): pentet, $a_N = 7.71$ G. IR (thin film) $\nu_{\text{max}}$ (cm$^{-1}$): 2998, 1431, 1401, 1368, 1199, 1141, 793.

2-(5-(3-(tert-Butyl)-4-hydroxyphenyl)thiophen-2-yl)-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (38). A 100 mL schlenk flask was charged with 37 (0.288
g, 1.04 mmol), 16 (0.366, 1.15 mmol) and Pd(PPh₃)₄ (65 mg, 0.0562 mmol). The Schlenk flask was sealed and pump-purged 3 times. 30 mL of dry, degased THF was then added along with 1.8 mL 2 M K₂CO₃. A reflux condenser was fit, the reaction freeze-pump-thawed 3 times, and the reaction was refluxed for 48 hours. The reaction mixture was allowed to cool to room temperature, washed with H₂O and filtered through a silica plug. The solvent was removed and the product was purified by column chromatography (98% CH₂Cl₂,2% methanol yielding 0.268 g (0.692 mmol, 66%) of 38 as a green solid. EPR (X-band, 298K): \( \alpha_N = 7.50 \) G. IR (solid) \( \nu_{max} \) (cm⁻¹): 2969, 2913, 2856, 2538, 1525, 1431, 1356, 1169, 1056, 831, 794, 644, 540. UV (CH₂Cl₂) \( \lambda_{max}, \) nm (ε): 351 (44391), 624 (487), 686 (697), 759.

3-(tert-Butyl)-5-(5-(1,3-dihydroxy-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl)thiophen-2-yl)cyclohexa-3,5-diene-1,2-dione (39). Phenol 37 (0.200 g, 0.516 mmol) was dissolved in 10 mL of CH₂Cl₂ and 10 mL methanol. IBX (0.87 g, 3.11 mmol) was added, the reaction turned dark red within 30 min, and reacted for 16 hours. The solvent was removed and the product was purified by column chromatography (50:50 hexanes/ethyl acetate) yielding 0.165 g (0.411 mmol, 80%) of 39 as a dark red solid. EPR (X-band, 298K): \( \alpha_N = 7.81 \) G. IR (solid) \( \nu_{max} \) (cm⁻¹): 2931, 2858, 1637, 1618, 1543, 1375, 1243, 1131, 812, 737. UV (CH₂Cl₂) \( \lambda_{max}, \) nm (ε): 312 (10281), 486 (4705)

2-(5-(3-(tert-Butyl)-4,5-dihydroxyphenyl)thiophen-2-yl)-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (40). A 100 mL Schlenk flask was charged with (212 mg, 0.528 mmol) 39 and 30 mL CH₂Cl₂ and the solution was freeze-pump-thawed three times. A degassed solution of ascorbic acid (93 mg, 52.8 mmol) in 30 mL of 0.1 M pH 7 buffer
solution was added to the reaction mixture. The reaction stirred for 3 h and monitored by TLC. The organic layer was removed via syringe and placed into an evacuated 50 mL round bottom flask where all but 5 mL of solvent was removed. 30 mL of petroleum ether was added and the product was placed in a -15°C freezer to precipitate. After 24 hours a green precipitate was collected by vacuum filtration yielding 127 mg (0.314 mmol, 60%) of 40. EPR (X-band, 298K): pentet, $a_N = 7.54$ G. IR (thin film) $v_{\text{max}}$ (cm$^{-1}$): 3175, 2955, 1600, 1431, 1356, 1289, 1207, 1131, 1066, 948, 793, 531. UV (CH$_2$Cl$_2$) $\lambda_{\text{max}}$, nm ($\varepsilon$): 355 (16374), 678 (295).

$\text{Tp}^{\text{Cum,Me}}\text{Zn(5-SQ-thiophen-2-yl-NN)}$ (2-(2,5)T). A dry 50 mL Schlenk flask was filled with 40 (97 mg, 0.240 mmol) and Zn(OH)$\text{Tp}^{\text{Cum,Me}}$ (165 mg, 0.238 mmol) and pump/purged with nitrogen several times. A mixture of 25 mL CH$_2$Cl$_2$ and 15 mL methanol were degassed and then transferred into the Schlenk flask. The reaction mixture immediately turned dark brown upon addition of the solvent and stirred under nitrogen for 12 hours. The reaction mixture was then exposed to air and the monitored by EPR. After 24 h, the solvent was removed under reduced pressure and the product was purified by column chromatography (100% CH$_2$Cl$_2$, basic alumina) yielding 186 mg (0.172 mmol, 72%) of 2-(2,5)T as a brown solid. The product was crystallized by slow evaporation of methanol. EPR (X-band, 298K): pentet, apparent $a_N = 3.96$ G. IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 2969, 2913, 2856, 2538, 1525, 1431, 1356, 1169, 1056, 831, 794, 644, 540. UV (CH$_2$Cl$_2$) $\lambda_{\text{max}}$, nm ($\varepsilon$): 386 (4863), 445 (10659), 475 (12325), 860 (467).

5'-Bromo-[2,2'-bithiophene]-5-carbaldehyde (42). To a 15 mL round bottom flask, 557 mg (2.87 mmol) 41 was added with 515 mg (2.89 mmol) NBS in 1.5 mL DMF and
stirred at -10°C in the dark for 18 hours. The reaction mixture was poured into 100 mL deionized water and stirred for 5 minutes after which a white solid precipitates and was collected via vacuum filtration to yield 738 mg (94%) of compound \( \text{42} \). \( \text{\textsuperscript{1}} \text{H-NMR} \) (300 MHz, CDCl\(_3\)) \( \delta \): 9.87 (s, 1H), 7.66 (d, \( J = 3.9 \) Hz, 1H), 7.18 (d, \( J = 3.9 \) Hz, 1H), 7.11 (d, \( J = 3.9 \) Hz, 1H), 7.04 (d, \( J = 3.9 \) Hz, 1H).

\( \text{5'}-(3-\text{tert-Butyl)-4-hydroxyphenyl})-2,2'-\text{bithiophene)-5-carboxaldehyde} \) \( \text{43} \). To a 100 mL oven dried Schlenk flask, 641 mg (2.32 mmol) \( \text{16} \), 624 mg (2.29 mmol) \( \text{42} \), and 150 mg (0.13 mmol) Pd(PPh\(_3\))\(_4\) were added with \( \sim 15 \) mL tetrahydrofuran under a nitrogen atmosphere. A 2 M K\(_2\)CO\(_3\) solution was degassed with nitrogen and 4 mL (8 mmol) was added to the reaction vessel by purged syringe. The reaction flask was fit with a condenser, refluxed for 2 days, and checked by thin layer chromatography (TLC) (75% ethyl acetate in hexanes) to ensure product formation. After the reaction was cooled to room temperature, \( \sim 30 \) mL deionized water was added and the mixture stirred in air for 30 min. The mixture was then transferred to a separatory funnel, diluted with 100 mL ethyl acetate, and washed twice with a saturated sodium chloride solution. The organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. The resulting brown oil was purified by column chromatography (20% ethyl acetate in hexanes) to yield 484 mg (62%) of compound \( \text{43} \). \( \text{\textsuperscript{1}} \text{H NMR} \) (400 MHz, DMSO-\( d_6 \), \( \delta \)): 9.87 (s, 1H), 9.82 (s, 1H), 7.98 (d, \( J = 3.9 \) Hz, 1H), 7.56 (d, \( J = 3.9 \) Hz, 1H), 7.52 (d, \( J = 3.9 \) Hz, 1H), 7.39 (m, 3H), 6.85 (d, \( J = 8.19 \) Hz, 1H), 1.38 (s, 9H). \( \text{\textsuperscript{13}} \text{C NMR} \) (100 MHz, DMSO-\( d_6 \)) \( \delta \) (ppm): 184.25, 157.36, 147.37, 146.58, 141.47, 139.81, 136.84, 133.16, 128.82, 125.25, 125.14, 124.72, 123.90, 117.60,
35.05, 29.90. IR (solid) ν\textsubscript{max} (cm\textsuperscript{-1}): 3330 (br, O-H), 1640 (s, C=O). Elemental Analysis: Calculated(C: 66.63, H: 5.30), Found: (C: 66.75, H: 5.38).

5'-5-(tert-Butyl)-3,4-dioxocyclohexa-1,5-dien-1-yl)-[2,2'-bithiophene]-5-carboxaldehyde (44). To a 50 mL round bottom flask, 230 mg (0.67 mmol) 43 and 376 mg (1.34 mmol) IBX was added with 2 mL N,N-dimethylformamide. The reaction was covered with aluminum foil and stirred in air for 20 h. After ensuring all of the starting material was consumed, the reaction was poured into 50 mL deionized water and diluted with ethyl acetate. The mixture was transferred to a separatory funnel and washed twice with saturated sodium bicarbonate followed by two washes of saturated sodium chloride. The organic layer was collected and dried over sodium sulfate and the solvent removed under reduced pressure to yield 228 mg (96%) of dark red compound 44. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, δ): 9.92 (s, 1H), 7.74 (d, J = 4.0 Hz, 1H), 7.59 (d, J = 4.0 Hz, 1H), 7.44 (d, J = 4.0 Hz, 1H), 7.41 (d, J = 4.0 Hz, 1H), 7.22 (d, J = 2.2 Hz, 1H), 6.64 (d, J = 2.2 Hz, 1H), 1.35 (s, 9H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ (ppm): 182.28, 179.77, 179.58, 151.84, 144.79, 143.61, 141.71, 141.27, 136.78, 132.06, 130.23, 127.49, 126.02, 120.03, 35.85, 29.20. IR (solid) ν\textsubscript{max} (cm\textsuperscript{-1}): 1658 (s, C=O), 1645 (s, C=O), 1637 (s, C=O). Mass spectrometry (m/z): 357.0610 (M+H)+.

5'-5-(3-(tert-Butyl)-4,5-dihydroxyphenyl)-[2,2'-bithiophene]-5-carboxaldehyde (45). The dark red quinone, 44 (228 mg, 0.64 mmol), was dissolved in 10 mL tetrahydrofuran and transferred to a separatory funnel. In a 125 mL Erlenmeyer flask, 125 mg (0.70 mmol) ascorbic acid was dissolved in 10 mL deionized water and added to the separatory funnel containing 44. Upon shaking the mixture, the dark red color faded to a light yellow. To separate the layers, 100 mL saturated sodium chloride solution was added and the organic
layer was diluted with 50 mL ethyl acetate. The organic layer was then washed twice with saturated sodium chloride solution, dried over MgSO$_4$, and the solvent removed under reduced pressure to yield 181 mg (79%) of compound 45. $^1$H NMR (400 MHz, DMSO-$d_6$, δ): 9.87 (s, 1H), 9.75 (s, 1H), 8.52 (s, 1H), 7.99 (d, $J = 4.0$ Hz, 1H), 7.55 (d, $J = 4.0$ Hz, 1H), 7.52 (d, $J = 4.0$ Hz, 1H), 7.28 (d, $J = 4.0$ Hz, 1H), 6.99 (d, $J = 2.0$ Hz, 1H), 6.96 (d, $J = 2.0$ Hz, 1H), 1.37 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 183.44, 146.80, 145.74, 145.43, 144.95, 140.64, 139.03, 136.27, 132.29, 127.98, 124.45, 122.92, 122.85, 114.81, 110.22, 34.29, 29.18. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3090 (br, OH), 1625 (s, C=O). Mass spectrometry (m/z): 359.0768 (M+H)$^+$.

2-(5'-(3-(tert-Butyl)-4,5-dihydroxyphenyl)-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (46). To a 5 mL round bottom flask, 101 mg (0.28 mmol) 45 was added with 84 mg (0.57 mmol) BHA and a magnetic stir bar. The flask is sealed with a rubber septum, attached to a Schlenk line, and pump/purged with nitrogen 5 times. Using a purged syringe, 2 mL of distilled and degassed methanol was added and heated gently to dissolve the contents of the flask. The reaction was stirred in the dark, under nitrogen, for 2 days and checked for completion by $^1$H-NMR. With an absence of a signal for the aldehyde proton of 45, the reaction is stopped by removing the solvent under reduced pressure and the crude product 46 (133.8 mg, 97%) is used directly in the synthesis of compound 47. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3250 (br, OH and NH).

2-(5'-(3-(tert-Butyl)-4,5-dihydroxyphenyl)-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (47). To a 100 mL round bottom flask, 142 mg (0.29 mmol) 46 was dissolved in 30 mL diethyl ether and 10 mL freshly prepared
buffer (pH 7). In a 125 mL separatory funnel, 119 mg (0.47 mmol) sublimed iodine was dissolved in 30 mL diethyl ether. The reaction flask was chilled to 0°C and the solution of iodine was added dropwise with stirring. Once all of the iodine was added, the reaction was warmed to room temperature and 100 mL buffer (pH 7) was added. The reaction was transferred to a separatory funnel and washed with a saturated sodium thiosulfate solution followed by two washes of saturated sodium chloride. The organic layer was collected, dried over MgSO₄, and the solvent removed under reduced pressure to yield 73 mg (51%) of compound 47. IR (solid) νₘₚₐₓ (cm⁻¹): 3070 (br, OH). EPR (X-Band, 298 K): pentet (1:2:3:2:1), aₙ = 7.8 G.

Tp²Cum,MeZn(5'-SQ-[2,2'-bithiophen]-5-y1-NN) (2-T₂). To an oven dried 25 mL Schlenk flask, 70 mg (0.14 mmol) 47 was added with 146 mg (0.21 mmol) Tp²Cum,MeZn(OH) and sealed with a rubber septum. The reaction flask was attached to a Schlenk line, pump/purged 5 times, and finally left under nitrogen. Using a purged syringe, 2 mL distilled and degassed methanol was added and the reaction stirred for 2 h under nitrogen. The reaction was then opened to air and stirred for 20 h upon which crude product precipitated from the reaction mixture. The product was collected by vacuum filtration and purified by column chromatography (basic alumina, 50% ethyl acetate in hexanes) to yield 91 mg (54%) of the biradical 2-T₂. The product was crystallized from slow evaporation of a solution composed of a few drops of acetonitrile in n-pentane. IR (solid) νₘₚₐₓ (cm⁻¹): 2550 (w, BH). EPR (X-Band, 298 K): pentet (1:2:3:2:1), apparent aₙ = 3.8 G. Mass spectrometry (m/z): 1157.4630 (M+H)^+.
Synthesis of 2-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)thiophene (S3). To a 100 mL oven dried Schlenk flask, 298 mg (0.78 mmol) S1 was added with 159 mg (0.98 mmol) S2, 2 mL 2M K$_2$CO$_3$, 216 mg (0.18 mmol) Pd(PPh$_3$)$_4$, ~20 mL tetrahydrofuran, and the reaction stirred under reflux for 18 hours. The reaction was cooled, opened to air, 30 mL deionized-water was added, and the mixture was transferred to a separatory funnel. The reaction solution was diluted with ethyl acetate and washed 3 times with saturated NaCl solution. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The resulting product mixture was purified by column chromatography (dichloromethane + 5 drops triethylamine on SiO$_2$) to yield 241 mg (91%) of S3. $^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$): 7.49 (dd, $J = 5.1$ Hz, $J = 1.1$ Hz, 1H), 7.38 (dd, $J = 3.6$ Hz, $J = 1.1$ Hz, 1H), 7.27 (d, $J = 2.2$ Hz, 1H), 7.16 (d, $J = 2.2$ Hz, 1H), 7.11 (dd, $J = 5.1$ Hz, 3.6 Hz, 1H), 5.26 (s, 2H), 5.18 (s, 2H), 3.56 (s, 3H), 3.45 (s, 3H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm): 150.62, 145.87, 144.16, 143.65, 129.37, 128.96, 125.77, 123.97, 117.97, 112.55, 99.28, 95.63, 57.69, 56.70, 35.43, 30.84. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2958, 2927, 2872, 2825, 1737, 1601, 1575, 1531, 1473, 1428, 1399, 1359, 1297, 1258, 1242, 1205, 1154, 1077, 1044, 1000, 960, 942, 865, 793, 694. HRMS-ESI ($m/z$): [M+H]$^+$ calcd for C$_{18}$H$_{24}$O$_4$S: 359.1288; found: 359.1283.

Synthesis of 3-(tert-butyl)-5-(thiophen-2-yl)benzene-1,2-diol (S4). To a 50 mL round bottom flask, 241 mg (0.71 mmol) S3 was added with 5 mL methanol, 3 drops of concentrated HCl and refluxed overnight. The reaction was checked by TLC and once no starting material remained, the reaction was cooled to room temperature and transferred to a separatory funnel. The organic layer was washed with saturated NaCl solution, dried over
Na$_2$SO$_4$, and the solvent removed under reduced pressure to yield 155 mg (83%) of S4. $^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$): 9.57 (s, 1H), 8.26 (s, 1H), 7.34 (dd, $J = 5.1$ Hz, $J = 1.1$ Hz, 1H), 7.14 (dd, $J = 3.5$ Hz, $J = 1.1$ Hz, 1H), 7.01 (dd, $J = 5.1$ Hz, $J = 3.5$ Hz, 1H), 6.89 (d, $J = 1.8$ Hz, 1H), 6.87 (d, $J = 1.8$ Hz, 1H), 1.32 (s, 9H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm): 146.01, 145.53, 144.71, 136.74, 128.79, 124.59, 124.30, 122.11, 115.34, 111.06, 34.98, 29.96. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3488, 3305, 3114, 3088, 3070, 2993, 2961, 2924, 2872, 1593, 1480, 1423, 1381, 1367, 1342, 1299, 1241, 1187, 1147, 1084, 1066, 1044, 941, 856, 837, 797, 751, 695, 641, 608, 487. HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{14}$H$_{16}$O$_2$S: 249.0944; found: 249.0943.

**Synthesis of 3-(tert-butyl)-5-(thiophen-2-yl)cyclohexa-3,5-diene-1,2-dione (S5).**

To a 50 mL oven dried round bottom flask, 30 mg (0.12 mmol) S4 was added with ~5 mL dichloromethane and purged with nitrogen for 10 minutes. To the purged solution, 133 mg Fetizon's reagent was added and refluxed for 2 hours. The reaction was filtered and the solvent removed under reduced pressure to yield 28 mg (94%) of S3. $^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$): 8.04 (d, $J = 3.9$ Hz, 1H), 7.98 (d, $J = 5.0$ Hz, 1H), 7.32 (dd, $J = 5.0$ Hz, $J = 3.9$ Hz, 1H), 7.29 (d, $J = 2.1$ Hz, 1H), 6.65 (d, $J = 2.1$ Hz, 1H), 1.28 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 180.13, 179.94, 151.63, 144.21, 141.19, 133.206, 131.41, 129.42, 129.33, 119.90, 35.92, 29.36. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 1641 (C=O). HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{14}$H$_{16}$O$_2$S: 249.0787; found: 249.0787.

**Synthesis of K$^+$SQ-T (S6).** To a 10 mL round bottom flask, 29 mg (0.08 mmol) S4 and 28 mg (0.08 mmol) S5 were added and transferred into a nitrogen glove box where ~2 mL tetrahydrofuran was added with an excess of tetrahydrofuran-washed potassium hydride.
The reaction was allowed to stir for 0.5 hours then filtered. A 0.2 mM solution was prepared in an EPR tube and freeze-pump-thawed 5 times for EPR studies.

5-(3-(tert-butyl)-4,5-dihydroxyphenyl)selenophene-2-carboxaldehyde (50). To a 100 mL Schlenk flask, 1.50 g (6.25 mmol) of 48, 2.44 g (6.42 mmol) of 9, and 400 mg (0.35 mmol) of Pd(PPh$_3$)$_4$ were added with 50 mL tetrahydrofuran under a nitrogen atmosphere. Using a purged syringe, 11 mL of nitrogen bubbled K$_2$CO$_3$ was added. A condenser was fit to the reaction vessel under nitrogen purge and the reaction heated to reflux while shielded from light overnight. The reaction was then cooled to room temperature, opened to air, and 30 mL water added. The reaction was transferred to a separatory funnel, diluted with ethyl acetate, and washed with saturated NaCl solution. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The product was purified by column chromatography (triethylamine treated SiO$_2$, 20% EtOAc in Hexanes) to yield 579 mg (23%) of a mixture of 49 and 50. The mixture was dissolved in 20 mL methanol and placed in a 50 mL round bottom flask where 5 drops of HCl was added and a condenser attached. The mixture was heated to reflux for 19 h then cooled to room temperature and transferred to a separatory funnel. The reaction was diluted with ethyl acetate and washed twice with saturated NaCl solution. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure to yield 423 mg (94%) of pure 50, a yellow solid. $^1$H NMR (400 MHz, DMSO-$d_6$, δ): 9.84 (s, 1H), 9.72 (d, $J = 1.7$ Hz, 1H), 8.73 (s, 1H), 8.16 (dd, $J = 4.1$ Hz, $J = 1.7$ Hz, 1H), 7.60 (dd, $J = 4.1$ Hz, $J = 1.7$ Hz, 1H), 7.01 (s, 2H), 1.37 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 184.7, 161.6, 146.3, 145.6, 136.4, 124.9, 124.8, 111.2, 34.4,
29.2. IR (solid) ν\textsubscript{max} (cm\textsuperscript{-1}): 3471 (br, -OH), 1629 (s, -C=O). Mass spectrometry (m/z): 323.01747 (M+H)+.

2-(5-(3-(tert-butyl)-4,5-dihydroxyphenyl)selenophen-2-yl)-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (52). To a 10 mL round bottom flask, 163 mg (0.50 mmol) of 50 and 184 mg (1.03 mmol) of BHA was added and pump purged with nitrogen five times. Using a purged syringe, 6 mL of dry and nitrogen bubbled methanol was added with light heat to dissolve the reactants. The reaction was allowed to stir under nitrogen and shielded from light for 19 h. Once the reaction was complete by \textsuperscript{1}H NMR, the solvent was removed under reduced pressure. The crude reaction mixture was then dissolved in 30 mL diethyl ether, 10 mL buffer (pH = 7) solution, and transferred to a 100 mL round bottom flask which was cooled to 0°C. To a 125 mL separatory funnel, 200 mg (0.79 mmol) of I\textsubscript{2} was added with 30 mL diethyl ether and added dropwise to the cold reaction mixture. After all of the I\textsubscript{2} solution was added, the reaction was allowed to stir for 10 minutes then diluted with 30 mL buffer (pH = 7) solution and transferred to a separatory funnel. The organic layer was washed with saturated Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution followed by saturated NaCl solution. The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent removed under reduced pressure to yield 165 mg (68%) of 52, a light brown solid. IR (solid) ν\textsubscript{max} (cm\textsuperscript{-1}): 3119 (br, -OH). EPR (X-Band, 298 K): pentet (1:2:3:2:1), a\textsubscript{N} = 7.36 G. Mass spectrometry (m/z): 450.10542 (M+H)+.

Tp\textsuperscript{Cum,Me}Zn(SQ-Se-NN) (3-Se). To an oven dried 25 mL Schlenk flask, 88 mg (0.18 mmol) of 52 and 127 mg (0.18 mmol) of Zn(OH)Tp\textsuperscript{Cum,Me} was added and pump purged with nitrogen five times. Using a purged syringe, 5 mL of dry and nitrogen bubbled
dichloromethane was added under a nitrogen atmosphere. The reaction was allowed to stir for 2 h under nitrogen then was opened to air to stir overnight. The solvent was then removed under reduced pressure and the product purified by chromatography (Basic alumina, 50% EtOAc in Hexanes) to yield 159 mg (75%) of 3-Se. Attempts at crystallizing 3-Se were carried out in DCM/MeOH, Bezene/MeOH, Benzene, Toluene, DCM/n-Hexane, and Benzene/n-Hexane at room temperature inside the glovebox and in sealed vials at -20°C and 5°C. In all cases no crystallization was observed. After 3-4 weeks of being in solution the majority of 3-Se had decomposed which further reduced the chance of crystal growth.

5'(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)-[2,2'-biselenophene]-5-carboxaldehyde (54). To a 100 mL Schlenk flask, 270 mg (0.71 mmol) of 9, 221 mg (0.60 mmol) of 53, and 135 mg (0.12 mmol) of Pd(PPh\textsubscript{3})\textsubscript{4} was added with 20 mL tetrahydrofuran under a nitrogen atmosphere. Using a purged syringe, 1 mL of nitrogen bubbled 2M K\textsubscript{2}CO\textsubscript{3} solution was added. A condenser was fit to the reaction vessel under nitrogen purge and the reaction heated to reflux for 2 days. The reaction was cooled to room temperature, opened to air, and 30 mL water added. The mixture was then transferred to a separatory funnel, diluted with ethyl acetate, and washed with saturated NaCl solution. The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent removed under reduced pressure. The product was purified by chromatography (triethylamine treated SiO\textsubscript{2}, 15% EtOAc in Hexanes) to yield 312 mg (96%) of crude 54. The crude product after chromatography showed evidence of a mixture of fully-, partially-, and un-protected hydroxyl groups and was thus used directly in the next step. IR (solid) ν\textsubscript{max} (cm\textsuperscript{-1}): 3476 (br, -OH). Mass spectrometry (m/z): 543.01781 (M+H)+.
5'-((3-((tert-butyl)-4,5-dihydroxyphenyl)-[2,2'-biselenophene]-5-carboxaldehyde (55). To a 100 mL round bottom flask, 584 mg (1.08 mmol) of 54 was added with 15 mL ethyl acetate, 5 mL methanol, and 10 drops of conc. HCl. Upon addition of HCl the solution changed color from orange to red. A condenser was attached and the reaction was heated to reflux for 18 h. The reaction was cooled to room temperature and transferred to a separatory funnel where the organic layer was washed with saturated NaCl solution. The organic layer was dried over Na₂SO₄ and the solvent removed under reduced pressure to yield 404 mg (83%) of 55, a dark yellow solid. ¹H NMR (400 MHz, DMSO-d₆, δ): 9.76 (s, 1H), 9.75 (s, 1H), 8.55 (s, 1H), 8.17 (d, J = 4.2 Hz, 1H), 7.63 (d, J = 4.2 Hz, 1H), 7.55 (d, J = 4.2 Hz, 1H), 7.37 (d, J = 4.2 Hz, 1H), 6.94 (d, J = 2.1 Hz, 1H), 6.91 (d, J = 2.1 Hz, 1H), 1.37 (s, 9H). ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 183.7, 160.6, 158.2, 146.5, 145.7, 145.3, 144.3, 138.8, 136.4, 127.2, 124.9, 124.8, 111.2, 34.4, 29.2. IR (solid) νmax (cm⁻¹): 3499 (br, -OH). Mass spectrometry (m/z): 452.94969 (M+H)⁺.

2-(5'-((3-((tert-butyl)-4,5-dihydroxyphenyl)-[2,2'-biselenophen]-5-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (56). To a 10 mL round bottom flask, 162 mg (0.36 mmol) of 55 was added with 127 mg (0.72 mmol) of BHA and pump purged with nitrogen five times. Using a purged syringe, 6 mL of dry and nitrogen bubbled methanol was added with light heat to dissolve the reactants. The reaction was allowed to stir under nitrogen and shielded from light for 3 days. Once the reaction was complete by ¹H NMR and IR, the orange precipitate was collected by vacuum filtration to yield 63 mg (30%) of crude 56. ¹H NMR (400 MHz, DMSO-d₆, δ): 8.59 (s, 1H), 7.82 (d, J = 4.2 Hz, 1H), 7.46 (d, J = 4.2 Hz,
1H), 7.40 (d, J = 4.2 Hz, 1H), 7.29 (d, J = 4.2 Hz, 1H), 6.90 (s, 1H), 6.88 (s, 1H), 6.09 (s, 1H), 1.37 (s, 9H), 0.99 (s, 12 H).

IR (solid) νmax (cm⁻¹): 3486 (br, -OH)

To a 100 mL round bottom flask, 63 mg (0.11 mmol) of 56 was added with 20 mL diethyl ether, 5 mL buffer (pH = 7) solution, and chilled to 0°C. To a 125 mL separatory funnel, 41 mg (0.16 mmol) of I₂ was added with 20 mL diethyl ether and added dropwise to the stirring reaction mixture while shielded from light. After all of the I₂ solution was added, the reaction was allowed to stir for 10 minutes before diluted with 50 mL buffer (pH = 7) solution and transferred to a separatory funnel. The organic layer was washed with saturated Na₂S₂O₃ solution followed by saturated NaCl solution then dried over Na₂SO₄. The solvent was removed under reduced pressure to yield 51 mg (82%) of 57, a dark brown solid. IR (solid) νmax (cm⁻¹): 3503 (broad, -OH). EPR (X-Band, 298 K): pentet (1:2:3:2:1), aN = 7.71 G. Mass spectrometry (m/z): 581.04421 (M+H)⁺.

TpCum,MeZn(SQ-Se-Se-NN) (3-Se₂). To a 25 mL oven dried Schlenk flask, 62 mg (0.11 mmol) of 57 was added with 158 mg (0.23 mmol) Zn(OH)TpCum,Me and pump purged with nitrogen five times. Using a purged syringe, 10 mL of a 1:1 mix of dry and nitrogen bubbled dichloromethane/methanol solution was added under a nitrogen atmosphere. The reaction was allowed to stir for 2 h under nitrogen then opened to air and allowed to stir overnight. The solvent was removed under reduced pressure and the product was purified by chromatography (Basic alumina, 50% EtOAc in Hexanes) to yield 125 mg (93%) of 3-Se₂. Attempts at crystallizing 3-Se₂ were carried out in DCM/MeOH, Bezene/MeOH, Benzene, Toluene, DCM/n-Hexane, and Benzene/n-Hexane at room temperature inside the glovebox.
and in sealed vials at -20°C and 5°C. In all cases no crystallization was observed. After 3-4 weeks of being in solution the majority of 3-Se₂ had decomposed which further reduced the chance of crystal growth.

**Synthesis of 2-(3-(tert-butyl)-4,5-bis(methoxymethoxy)phenyl)selenophene (S7).**
To an over dried 50 mL Schlenk flask, 700 mg (2.72 mmol) S₆, 1.14 g (3.00 mmol) S₁, and 48 mg (0.21 mmol) palladium(II) acetate were added with 5 mL dimethoxyethane and freeze pump thawed three times. Using a purged syringe, 3.4 mL of a degassed 2M solution of K₂CO₃ was added and a condenser attached under nitrogen purge. The reaction was heated to reflux for 18h and monitored by TLC. When complete, the reaction was diluted with DCM and transferred to a separatory funnel. The organic layer was washed with saturated NaCl solution twice, dried over Na₂SO₄, and the solvent removed under reduced pressure. The ^1^H-NMR of S₇ showed fully, partially, and unprotected catechol signals and the crude product was carried onto the next step.

**Synthesis of 3-(tert-butyl)-5-(selenophen-2-yl)benzene-1,2-diol (S₈).** To a 50 mL round bottom flask, 484 mg (1.26 mmol) S₇ was added with 10 mL methanol, 5 drops of concentrated HCl, and 3 drops of water. A condenser was attached and the reaction heated to reflux overnight. When the reaction was complete by TLC, the reaction was cooled and transferred to a separatory funnel. The organic layer was washed with saturated NaCl solution three times, dried over Na₂SO₄, and the solvent removed to yield 349 mg (94%) of S₈. ^1^H NMR (400 MHz, DMSO-d₆, δ): 8.08 (dd, J = 5.9 Hz, J = 1.1 Hz, 1H), 8.52 (dd, J = 3.8 Hz, J = 1.1 Hz, 1H), 7.31 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 2.2 Hz, 1H), 6.96 (dd, J = 5.9 Hz, J = 3.8 Hz, 1H). IR (solid) νmax (cm⁻¹): 3511 (br, -OH).
Synthesis of 3-(tert-butyl)-5-(selenophen-2-yl)cyclohexa-3,5-diene-1,2-dione (S9).

To a 50 mL oven dried round bottom flask, 175 mg (0.59 mmol) S8 was added with 450 mg Ag₂CO₃ on celite (Fetizone's reagent) and 20 mL DCM under inert atmosphere. A condenser was attached and the reaction refluxed for 30 minutes. Once no starting material remained by TLC, the reaction was flushed down a 3 cm thick celite plug with a 0.5 cm thick layer of SiO₂ on top using DCM. The solvent was removed under reduced pressure to yield 170 mg (98%) of S9. ¹H NMR (400 MHz, DMSO-d₆, δ): 8.08 (dd, J = 5.9 Hz, J = 1.1 Hz, 1H), 8.52 (dd, J = 3.8 Hz, J = 1.1 Hz, 1H), 6.96 (dd, J = 5.9 Hz, J = 3.8 Hz, 1H), 6.59 (d, J = 2.1 Hz, 1H), 6.34 (d, J = 2.1 Hz, 1H). IR (solid) ν_max (cm⁻¹): 1650 (s, -C=O)

Synthesis of KSQ-Se. To an oven dried 10 mL round bottom flask, 174 mg (0.58 mmol) S8 and 170 mg (0.58 mmol) S9 were added and transferred to a glovebox and dissolved in ~2 mL THF. Inside the glovebox in a 25 mL oven dried round bottom flask, 316 mg (7.8 mmol) potassium hydride in mineral oil (30% w/w) was added and washed with THF to remove the protective mineral oil. Using THF, the potassium hydride was added to the stirring reaction mixture and allowed to stir in the dark for 30 minutes. With a glass pipette filled with cotton and celite, the reaction mixture was filtered into a 25 mL volumetric flask. The reaction mixture was then serially diluted to 0.2 mM in THF for EPR studies. Due to the unstable nature of this compound, no further characterization was performed.
IV. Electronic and Exchange Coupling in Cross-Conjugated D–B–A Biradicals: Mechanistic Implications for Quantum Interference Effects

Part of the work in this chapter has been published in the Journal of the American Chemical Society 2013, 135, 14713

A. Introduction to Cross-Conjugated Donor-Bridge-Acceptor Systems

So far we have only focused on conjugated bridges between donor and acceptor due to their utility in studying distance and torsional effects with as strong as possible interaction between donor and acceptor. However, cross-conjugated bridges have an important role to play in understanding the electronic coupling in a D-B-A system. Wasielewski\textsuperscript{10,23,49,50,54–56} and Bardeen\textsuperscript{22,185,186} have reported \textit{meta}-coupled and cross-conjugated D-B-A molecules which have charge-separated states that have an order of magnitude longer lifetime then their \textit{para}-coupled and linearly-conjugated counterparts. This, combined with ultrafast spectroscopy, has allowed for detailed structure-property relationships to be established for electronic coupling in D-B-A molecules in the weak coupling (nonadiabatic) regime.\textsuperscript{50} MMM conductance devices also take advantage of cross-conjugates systems since it results in an effective barrier to efficient electron transmission in related electron transport systems where single molecules bridge nanoelectrode assemblies.\textsuperscript{68,71,187–189} Reduced transmission in these devices comes from destructive anti-resonances (quantum interference effects)\textsuperscript{68,71,188–191} which tend to cancel competing pathway contributions to electron transfer/transport.\textsuperscript{192–194}

It has even been suggested that by utilizing these quantum interference effects a system can have fast and reproducible switching\textsuperscript{187} such as in a molecular transistor. These studies show
that there is a direct relation between study of cross-conjugated systems and molecular electronics. In fact, calculations suggest that the electron density distribution directly affects transmission properties in simple cross-conjugated bridges like meta-phenylene in a predictable way by moving the destructive interference feature responsible for insulator behavior to positive and negative potentials relative to the Fermi energy which then turns on conduction through the bridge.

By using our SQ-B-NN system, we can probe the electronic coupling of cross-conjugated bridges in the strongly coupled (adiabatic) regime by comparing the electronic coupling of a conjugated para-phenylene D-B-A versus a cross-conjugated meta-phenylene bridged D-B-A as shown in Figure IV-1. However, in order to understand how cross-conjugated molecules effect the interaction of two radicals, we can examine the difference between disjoint and nondisjoint biradicals and how they relate to our SQ-B-NN system and use a simple MO model to predict the sign of the magnetic exchange between SQ and NN.

Figure IV-1. Line bond drawings of 1-pPh and 1-mPh used for cross-conjugation studies.
1. **Disjoint and Nondisjoint Biradicals**

   Biradicals in general can be separated into two types: disjoint and nondisjoint. By understanding a molecular version of Hund's rule, we can understand the preference for a biradical to have its unpaired electrons aligned parallel (ferromagnetically) or antiparallel (antiferromagnetically) based on overlap densities of molecular orbital fragments.

   A disjoint biradical is one in which the SOMOs can be isolated on two different fragments of the same molecule. There are many examples of this, but the simplest and most studied, is the tetramethylenethane (TME) biradical shown in Figure IV-2.

   ![Figure IV-2. Line drawing of tetramethylenethane (TME) (left) and corresponding SOMOs (right).](image)

   Because of the lack of any overlap between the two SOMOs in disjoint biradicals, the energy of the singlet state and the triplet state are predicted to be degenerate. By examining a simple derivative, Iwamura was able experimentally show weak antiferromagnetic coupling in a TME type biradical.

   A nondisjoint biradical is one in which the SOMOs are nearly the same energy and cannot be localized on completely different atoms. Two simple examples of this are trimethylenemethane (TMM) and *meta*-xylylene shown in Figure IV-3. Using photoelectron spectroscopy, Squires was able to experimentally determine the singlet–triplet energy gap.
for TMM. Past Shultz group projects have been focused on traditional TMM-type and meta-xylylene-type biradicals\textsuperscript{197–199} while recent work has focused on nondisjoint D-B-A biradicals.\textsuperscript{4,6,7,47,48} In nondisjoint biradicals, the two spin containing SOMOs have a non-zero exchange integral ($k$). The electrons therefore prefer to be aligned parallel to minimize the electron-electron repulsion in the overlap region.

![Figure IV-3](image)

**Figure IV-3.** Line drawing of trimethylenemethane (TMM) (left) and meta-xylylene (right).

2. **Molecular Orbital Analysis of meta-Phenylene vs. para-Phenylene Bridges in D-B-A Molecules**

HMO theory presents a quick and easy method to predict the sign of the exchange coupling. As described previously, we can use the evaluation of the overlap density on two different MO fragments to provide insight into whether the interaction will result in ferromagnetic exchange coupling or antiferromagnetic exchange coupling. Meta–coupled D-B-A systems are of interest because the localization of the Donor and the Acceptor cause recombination times in photoinduced charge–separated states to be longer than in delocalized systems.\textsuperscript{23} Bardeen\textsuperscript{22,185,186} was able to show through ultrafast kinetics that meta–coupled phenylacetylene dendrimers extend the excited charge–separated state lifetime of a D-B-A by 10-fold compared to para–coupled phenylacetylene dendrimers.
Using a \textit{meta}-phenylene-bridged biradical system, we can determine the exchange coupling, $J$, and thus the electronic coupling, $H_{DA}$, between the Donor and Acceptor to show with clarity the disruption of communication when compared to a previously characterized\textsuperscript{6,47} \textit{para}-phenylene-bridged biradical.

As a first approximation, we can use Hückel MO theory to predict how the Donor and Acceptor will interact with each other based on overlap density. Density functional theory (DFT) calculations on the SQ-NN system\textsuperscript{4,47} and the SQ-\textit{para}-phenylene-NN\textsuperscript{6,47} system have shown that the frontier SQ-NN orbitals are products of NN lowest unoccupied MO (LUMO) and SQ-SOMO mixing. Using Hückel MO theory we can show this mixing for the \textit{para}-phenylene-bridged D-B-A in Figure IV-4.
Figure IV-4. Hückel MOs and orbital coefficients for NN LUMO (left top), SQ SOMO (left bottom), and the SQ-based SOMO for Tp$^{Cum,Me}$Zn(SQ-pPh-NN) (right). Red and blue represent positive and negative respectively. Orbital coefficients are related to electron density.

We can look at the Donor SQ-based SOMO and the Acceptor NN-based LUMO to understand why the para-phenylene-bridged D-B-A shows ferromagnetic coupling and compare it to what we expect to see for the meta-phenylene-bridged D-B-A. For the para-phenylene SQ-Bridge-NN, we can see in Figure IV-5 that there is NN-LUMO character mixed into the SQ-SOMO as shown previously. Therefore, SQ-para-phenylene-NN is a nondisjoint biradical and the overlap density of the NN SOMO and the SQ SOMO is non-zero. The non-zero overlap density results in a sizable exchange integral and thus ferromagnetic coupling is both predicted and observed.$^{6,47}$
Figure IV-5. Hückel molecular orbital cartoon for SQ-para-phenylene-NN where red is positive and blue is negative. Depicted are the SQ-based SOMO and the NN LUMO.

If we now look at the meta-phenylene-bridged D-B-A molecule in Figure IV-6, we see that there is no mixing of the SQ SOMO and NN LUMO because of the node at the connecting carbon on the benzene ring. Therefore, SQ-meta-phenylene-NN is a disjoint biradical where the overlap density between NN SOMO and SQ SOMO is zero and singlet–triplet degeneracy or antiferromagnetic coupling is predicted. Furthermore, the coupling between donor and acceptor is expected to be weak, just as in Iwamura's\textsuperscript{46} disjoint biradical system.

Figure IV-6. Hückel molecular orbital cartoon for SQ-meta-phenylene-NN where red is positive and blue is negative. Depicted are the SQ-based SOMO and the NN SOMO.
B. Cross-Conjugated Biradicals: Systems Where Hund’s Rule Does Not Apply

1. Synthesis of the Cross-Conjugated meta-Phenylene Biradical

For the synthesis of 1-mPh, 5 was reacted with commercially available 58 under standard Suzuki conditions to yield phenol 59 in good yield. Compound 59 was then reacted with IBX to yield quinone 60 which was then reduced with ascorbic acid to catechol 61. Using BHA, 61 was transformed in methanol to 62 and then oxidized with iodine to nitronylnitroxide 65 in excellent yield. Catechol-nitronylnitroxide 63 was reacted with Zn(OH)TPcum,Me under standard conditions to yield biradical 1-mPh.

Scheme IV-1. Synthesis of 1-mPh.
2. Discussion of Results for Quantum Interference Effects in a \textit{meta}-Phenylene Bridged Biradical

To begin to understand the effect a \textit{meta}-phenylene coupling has between a SQ donor and a NN acceptor, several techniques can be used. These techniques include EPR spectroscopy to measure nitrogen hyperfine of the D-B-A biradical complex as it relates to the monoradical precursor, electronic absorption spectroscopy to measure electronic transitions between ground and excited states, and magnetometry to calculate the exchange coupling between the singlet and triplet ground states.

Starting off with EPR spectroscopy of the \textit{meta}-phenylene-bridged D-B-A, we see stack plot of the experimental and simulated EPR spectra shown in Figure IV-7. Simulation of the experimental spectrum shows a mixture of 5\% monoradical with $a_N = 7.54$ gauss and 95\% biradical with nominal $a_N = 3.70$ gauss.

\textbf{Figure IV-7.} Experimental vs. simulation of the \textit{meta}-phenylene-bridged biradical EPR spectrum. Simulation performed using WinSim LMB1 optimization. "Monoradical" $a_N = 7.54$ gauss, linewidth = 0.87 gauss, $x = 5\%$. Biradical nominal $a_N = 3.70$ gauss, linewidth = 3.47 gauss, $x = 95\%$. 
We can see there is an apparent monoradical impurity in Figure IV-7. Multiple recrystallization attempts produce a relatively similar concentration of monoradical impurity suggesting three possibilities: the complex is slowly decomposing into monoradical and the Zn(tris(pyrazolylborate)) during recrystallization, minor impurities of monoradical reactant are getting stuck inside the crystal lattice, or the signal is not an impurity but the result of hindered rotation within the molecule. To determine if the complex was decomposing causing the monoradical impurity, ~10 mg of the crystallized material was dissolved in THF and left in solution. After one week, the EPR spectrum of the biradical in solution was exactly the same as it was before suggesting this biradical complex is relatively stable in solution over extended periods of time. The best explanation of the shape of the biradical spectrum is hindered rotation caused by the close intramolecular contact of the nitronyl nitrooxide oxygen atom to one of the tris(pyrazolylborate) arms as seen in Figure IV-8.

![Figure IV-8](image)

*Figure IV-8.* Line drawing (left), ORTEP crystal structure (middle), and space-filling model (right) of $\text{Tp}^{\text{Cum,Me}}\text{Zn(SQ-mPh-NN)}\ (1\text{-mPh})$.  

136
This contact could cause hindered rotation of the bridge and the nitrooxide. Without rotation of the bridge and nitrooxide, dipolar interactions are not averaged in solution and the overall spectrum of the biradical is broadened. A simple test to see if hindered rotation is causing the breadth of the spectrum is to run variable temperature EPR at temperatures greater than 298 K to determine whether the biradical spectral features sharpen. In this case, a set of difference spectra become more useful to determine any changes occurring as the solution heats up. Figure IV-9 shows a stack plot of difference spectra for heating the meta-phenylene-bridged biradical complex. As temperature is increased, the bridge-NN fragment gains enough energy to pass over the rotational barrier caused by the steric interactions and a 5-line hyperfine pattern grows in with nominal $a_N = 3.70$ Gauss. Each spectrum was obtained by subtracting the higher temperature spectrum from a 298 K "background" and g-shifted so the apparent center peak at 3346 gauss was alligned for all temperatures. Finally, a second spectrum at room temperature was taken and compared to the original 298 K spectrum to ensure no decomposition had occurred during the experiments.
If the temperature was raised above ~390 K, the solution would start to decompose forming an iminonitroxide. Compared to the hyperfine of the simulated spectrum, the variable temperature value is higher, but likely more correct considering the simulation program only considers isotropic EPR signals.

A direct measurement of the electronic coupling between the donor and the acceptor in the meta-phenylene-bridged biradical complex can be determined through magnetometry. Plotting the data as \( \chi \) vs. \( T \) shows a maximum that is indicative of antiferromagnetic coupling between the \( S = 1/2 \) donor and the \( S = 1/2 \) acceptor. To fit the data, a derivation of the HDVV equation is used as shown in Eq. (1.2). The magnetic data and fit are shown in Figure IV-10 and show a coupling constant of \(-32 \text{ cm}^{-1}\) and 9\% monoradical impurity. Since magnetometry is a bulk measurement and subject to intermolecular interactions, it is imperative to check close contacts within the crystal cell to ensure that the antiferromagnetic...
coupling constant calculated by magnetometry is an *intramolecular* interaction and not influenced by *intermolecular* contacts.

**Figure IV-10.** Magnetometry data for the meta-phenylene biradical indicating antiferromagnetic coupling of the SQ donor and the NN acceptor. Magnetic susceptibility data was collected on a Quantum Design MPMS SQUID magnetometer at a constant field of 7000 Oe from 2 K to 10 K in steps of 0.2 K then from 10 to 300 K in steps of 5 K.

Upon closer inspection, we see the closest *intermolecular* contact between paramagnetic moieties is the distance between two NN oxygen atoms, as seen in Figure IV-11. Since there is a close contact between two paramagnetic moieties, there is a possibility for added antiferromagnetic coupling between the two nitroxides. However, we can compare the distance in Figure IV-11 to the same *intermolecular* contact in the *para*-phenylene-bridged D-B-A shown in Figure IV-12. Since the intermolecular distances between paramagnetic moieties in *meta-* and *para*-phenylene-bridged D-B-A biradical complexes are relatively the same, we can assume the same amount of antiferromagnetic coupling between molecules exists. To confirm the *intramolecular* coupling for *meta*-phenylene, an independent measurement of \( J_{DA} \) is required. This can be achieved using frozen solution variable
temperature EPR (VT-EPR) spectroscopy to make a Curie plot. Since we know that EPR signal intensity is proportional to magnetic susceptibility, it becomes a matter of choosing a signal that only represents the amount of ferromagnetically coupled triplet within the sample.

Figure IV-11. ORTEP of two $\text{Tp}^{\text{Cum,Me}}\text{Zn(SQ-mPh-NN)}$ molecules connected by a close crystallographic contact. Cumenyl groups on the Tp and hydrogen atoms have been omitted.

Figure IV-12. ORTEP of two $\text{Tp}^{\text{Cum,Me}}\text{Zn(SQ-pPh-NN)}$ molecules connected by a close crystallographic contact. Cumenyl groups on the Tp and hydrogen atoms have been omitted.
By doubly integrating the $\Delta m_s = 2$ signal, we obtain the area under the absorption which is a direct representation of the amount of signal produced for a given temperature. A combination of the Curie Law and a Boltzmann distribution, shown previously in Eq. (I.32), is modified slightly to account for any instrument error in Eq. (IV.1) and is used to fit the data collected with assistance from former group member Dr. Robert Schmidt in Figure IV-13.

$$I_{EPR} \propto \chi_{Para} = \frac{C}{T} \left( \frac{n_T e^{\frac{2J_{DA}}{k_B T}}}{n_S e^{\frac{2J_{DA}}{k_B T}} + n_T e^{\frac{2J_{DA}}{k_B T}}} \right) + k \quad \text{IV.1}$$

The fit parameters are the Curie constant $C$, the coupling constant $J_{DA}$, and a constant $k$ which accounts for instrument noise. The exchange coupling determined by VT-EPR is smaller in magnitude than as determined by magnetometry due to the possibility of various rotational confirmers in solution and thus the VT-EPR value is a solution-phase averaged exchange coupling.
Figure IV-13. (Left) EPR of $\Delta m_s = 2$ transition at 80 K for 1-mPh occurring due to thermal population of the ground state triplet. Double integration of this spectrum versus temperature creates the integrated spectral area data points in the Curie plot (Right). Data collected at 2 K intervals from 4.2 K to 60 K then in 5 K intervals from 60 K to 120 K.

Considering the similarity of the coupling constant obtained by both SQUID magnetometry and variable temperature EPR spectroscopy, we conclude that the coupling between donor and acceptor for the meta-phenylene spaced SQ-Bridge-NN is antiferromagnetic with $J \approx -32$ cm$^{-1}$. The reasoning behind the weak antiferromagnetic coupling is derived from $J = J_{FM} + J_{AFM}$ (Eq. I.10). In the Tp$^{Cum,Me}$Zn(SQ-mPh-NN) biradical, the ferromagnetic coupling pathway present is so weak that other antiferromagnetic pathways that exist in all SQ-Bridge-NN biradicals overwhelms the overall coupling constant between the donor and the acceptor.

To further confirm the magnetometry and VT-EPR measured exchange coupling, variable temperature electronic absorption spectroscopy can provide a third measurement through analysis of band growth/decay with temperature. However, in order to analyze variable temperature electronic absorption, we must first understand the room temperature fluid solution electronic absorption shown in Figure IV-14. Shultz has previously reported a
detailed electronic structure study of TpCum.Me\textsubscript{Zn}(SQ-NN) (1) and assigned the structured band at \( \sim 25,000 \text{ cm}^{-1} \) as a donor-acceptor intraligand SQ(SOMO) \( \rightarrow \) NN(LUMO) charge transfer (ILCT) transition.\textsuperscript{7} A following study of 1-\textit{pPh} showed a structured band at \( \sim 23,500 \text{ cm}^{-1} \) that was assigned as the donor-acceptor intraligand SQ(SOMO) \( \rightarrow \) NN(LUMO) charge transfer (ILCT) transition but with considerable Ph-NN character present in the acceptor orbital.\textsuperscript{4} Observation of ILCT bands in this energy region are characteristic of SQ-B-NN compounds. Through the VBCI model discussed in chapter I, we were able to show that the donor-acceptor ILCT band in both 1 and 1-\textit{pPh} is responsible for the large \textit{ferromagnetic} biradical exchange coupling (1; \( J \approx +550 \text{ cm}^{-1} \), 1-\textit{pPh}; \( J = +100 \text{ cm}^{-1} \)).\textsuperscript{4,7,102} Based on the difference in electronic absorption spectra, there exist fundamental differences in the electronic structures of 1-\textit{mPh} and 1-\textit{pPh} as they relate to the cross-conjugated nature of the bridge fragment in 1-\textit{mPh}. Most notably, the \( \sim 23,500 \text{ cm}^{-1} \) SQ(SOMO)\( \rightarrow \)Ph-NN(e1, LUMO) ILCT band characteristic of both 1 and 1-\textit{pPh} appears to be either absent or greatly reduced in intensity in 1-\textit{mPh}. As seen in previous chapters, a characteristic transition in the electronic absorption spectrum for these phenylene-bridged SQ-B-NN biradicals is the charge transfer band around \( \sim 27,000 \text{ cm}^{-1} \).\textsuperscript{7} This characteristic band can be seen in Figure IV-14 for the \textit{para}-phenylene-bridged biradical but not the \textit{meta}-phenylene-bridged biradical.\textsuperscript{7} However, it is common for this charge transfer band to shift based on molecular structure as we see for 1 where the charge transfer band is at \( \sim 24,500 \text{ cm}^{-1} \), as we saw in chapter II for 1-PhMe and 1-pXylyl (Figure II-9), and as reported previously by Shultz.\textsuperscript{47} Since the extinction coefficient of the nominal \( \pi \rightarrow \pi^* \) band for the \textit{meta}-phenylene spaced biradical (\( \varepsilon \approx 38,000 \text{ M}^{-1} \text{ cm}^{-1} \)) is more than twice that of the \textit{para}-phenylene complex (\( \varepsilon \approx \))
18,000 M\(^{-1}\) cm\(^{-1}\), it stands to reason that there are more transitions occurring at \(~27,000\) cm\(^{-1}\) than in previously characterized SQ-Bridge-NN biradicals.

![Figure IV-14](image-url)

**Figure IV-14.** Electronic absorption spectra of Tp\(^{\text{Cum,Me}}\)Zn(SQ-mPh-NN) (1-mPh) (red), Tp\(^{\text{Cum,Me}}\)Zn(SQ-pPh-NN) (1-pPh) (blue), and Tp\(^{\text{Cum,Me}}\)Zn(SQ-NN) (1) (green). Inset is an expansion of the n→\(\pi^*\) region.

The reduction in intensity for the SQ(SOMO)→Ph-NN(LUMO) ILCT band is a direct result of the dramatic reduction in orbital overlap between the SQ(SOMO) donor- and the Ph-NN(LUMO) acceptor orbitals in 1-mPh compared to 1-pPh, indicative of SQ-NN decoupling in 1-mPh due to the cross-conjugated nature of the meta-phenylene bridge. This is a very important distinction since strong configurational mixing of the SQ(SOMO)→bridge-NN(LUMO) ILCT excited configuration (\(^3\)EC(1)) into the ground state configuration (GC) is the primary mechanism for ferromagnetic exchange in D-B-A biradicals that possess conjugated bridges.\(^4,6,48\) The lack of a strong SQ(SOMO)→bridge-
NN(LUMO) ILCT band in 1-mPh is thus clearly related to the dramatic reduction in D→A coupling that results in a radical shift in both the magnitude and the sign of the exchange where \( J_{DA} = +100 \text{ cm}^{-1} \) in 1-pPh and \( J_{DA} = -35 \text{ cm}^{-1} \) in 1-mPh.

The following spectral assignments, calculations, and excited state analysis were made by our collaborator Prof. Martin Kirk and his group at the University of New Mexico. Electronic absorption spectral band assignments for 1-mPh have been made using a combination of bonding and time-dependent density functional theory (TDDFT) calculations on 1-mPh and Ph-NN, comparisons with our prior spectroscopic studies on Tp\textsuperscript{Cum,Me}Zn(SQ), Ph-NN, 1-pPh, and Tp\textsuperscript{Cum,Me}Zn(SQ-NN) (2), and complete active-space (CAS) multiconfiguration (MC) self-consistent field (SCF) calculations. The MC-SCF calculations combine an SCF and a full configuration interaction calculation using a complete active-space. The features of the spectrum labeled a-c (Figure IV-14) are discussed below, and the one-electron orbital contributions to the transitions are listed in Table IV-1.

Starting with band a, we see two low energy transitions. These weak bands are assignable as SQ- and NN-based transitions are also observed in the 10,000 - 20,000 cm\(^{-1}\) region for 1-mPh, 1-pPh and Tp\textsuperscript{Cum,Me}Zn(SQ-NN) (2). The broad, low energy transition in the 10,000 - 17,000 cm\(^{-1}\) region (\( \varepsilon \sim 625 \text{ M}^{-1} \text{ cm}^{-1} \)) corresponds to the electronic absorption spectrum for Tp\textsuperscript{Cum,Me}Zn(SQ) and the vibronically structured band observed at higher energy (12,000 – 20,000 cm\(^{-1}\)) corresponds to a Ph-NN transition. These data combined with the computationally derived transition energies and oscillator strengths allow us to assign the lower energy component of the broad (10,000 - 20,000 cm\(^{-1}\)) structured band (in \( n \)-hexane) in 1-mPh as arising from an SQ(HOMO) \( \rightarrow \) SQ(SOMO) transition and the

145
higher energy component as a [NN(SOMO)→ Ph-NN(LUMO) - Ph-NN(HOMO)→ NN(SOMO)] transition. The SQ(HOMO) → SQ(SOMO) transition is y-polarized and this polarization direction is orthogonal to the long z-axis (C2 axis) of the semiquinone unit and is predicted to possess a low oscillator strength. The [NN(SOMO)→ Ph-NN(LUMO) - Ph-NN(HOMO)→ NN(SOMO)] transition is also predicted to be weak due to the opposing nature (-) of the transition dipoles for the two one-electron promotions that contribute to the transition. The overall structure and intensity for band a in 1-mPh is virtually identical to the lowest energy band in 1-pPh, indicating that transitions 1 and 2 are essentially independent of the bridge connectivity and do not possess appreciable charge transfer character.

**Table IV-1.** Electronic Absorption Spectral Band Assignments for 1-mPh. One-electron promotion contributions given in brackets represent minor contributions to the transition, but are important for spin polarization contributions to the magnetic exchange interaction.

<table>
<thead>
<tr>
<th>Band</th>
<th>Experimental Energy (cm⁻¹)</th>
<th>Transition</th>
<th>Calculated Energy (cm⁻¹)</th>
<th>Calculated Oscillator Strength</th>
<th>Dominant MO Contributions to Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>15,700</td>
<td>1</td>
<td>13,380</td>
<td>0.0102</td>
<td>SQ (HOMO) → SQ (SOMO)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>18,256</td>
<td>0.0035</td>
<td>NN(SOMO) → Ph-NN(LUMO) - Ph-NN(HOMO)→ NN(SOMO)</td>
</tr>
<tr>
<td>b</td>
<td>23,000</td>
<td>3</td>
<td>22,801</td>
<td>0.0397</td>
<td>Ph-NN(HOMO)→SQ(SOMO) + Ph (HOMO)→SQ(SOMO); [Ph-NN(HOMO)→Ph-NN(LUMO)]</td>
</tr>
<tr>
<td>c</td>
<td>24,000-29,000</td>
<td>4</td>
<td>25,628</td>
<td>0.0815</td>
<td>SQ(SOMO)→Ph-NN(e1,LUMO); Ph-NN(HOMO)→Ph-NN(LUMO)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>28,874</td>
<td>0.0384</td>
<td>NN(SOMO) → Ph-NN(LUMO) + Ph-NN(HOMO)→NN(SOMO); SQ(HOMO)→NN(SOMO)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>28,691</td>
<td>0.2193</td>
<td>SQ(SOMO)→SQ-Ph(c2,LUMO)</td>
</tr>
</tbody>
</table>
For band b, computations indicate that a moderately intense Ph-NN(HOMO) → SQ(SOMO) + Ph (HOMO) → SQ(SOMO) transition possessing Ph-NN (π) → SQ (π) charge transfer character should be expected in this energy region. As mentioned above, an intense SQ(SOMO) → Ph-NN(e1, LUMO) transition is observed in this energy region for 1-pPh that has been assigned as the dominant contributor to the observed ground state ferromagnetic exchange coupling in this molecule. The direction of the Ph-NN (π) → SQ (π) charge transfer character (acceptor → donor) in transition 3 is the opposite of the SQ (π) → Ph-NN (π) charge transfer character (donor → acceptor) found in this energy region for 1-pPh. The reduced intensity of this band, coupled with no computed SQ(SOMO) → Ph-NN(e1, LUMO) CT contribution, explains the dramatic reduction in ferromagnetic contributions to the ground state magnetic exchange parameter, allowing weaker antiferromagnetic exchange interactions to dominate.

Band c is the most intense band in the spectrum of 1-mPh and there are a number of transitions computed to contribute to the intensity of this band. A slight shoulder is observed on the low-energy side of band c in the room temperature absorption spectrum at ~25,000 cm⁻¹ that is clearly revealed at 24,000 cm⁻¹ in the triplet absorption spectrum (red line, Figure IV-18) and at 26,000 cm⁻¹ in the singlet absorption spectrum (blue line, Figure IV-18). We assign these bands in 1-mPh as arising from exchange split singlet and triplet components of transition 4, which is comprised of SQ(SOMO) → Ph-NN(e1,LUMO) and Ph-NN(HOMO) → Ph-NN(LUMO) one-electron promotions. The SQ (π) → Ph-NN (π) charge transfer character present in transition 4 is identical to that observed for 1-pPh. However, there are
numerous one electron promotion contributions to transition 4 that contribute to a large reduction in the overall SQ ($\pi$)$\rightarrow$Ph-NN ($\pi$) charge transfer character of this transition, resulting in reduced charge transfer contributions to ferromagnetic exchange in 1-mPh. The Ph-NN(HOMO) $\rightarrow$ Ph-NN(LUMO) one-electron promotion contribution to transition 4 lacks charge transfer character and is computed at lower energy than the Ph-NN(SOMO) $\rightarrow$ Ph-NN(LUMO) + Ph-NN(HOMO) $\rightarrow$ Ph-NN(SOMO) transition. This likely reflects the large reduction in electron-electron repulsion that derives from an excited configuration having all of the NN frontier orbitals being singly-occupied. TDDFT calculations on Ph-NN show the Ph-NN(HOMO) $\rightarrow$ Ph-NN(LUMO) transition occurring at 25,959 cm$^{-1}$, and this provides additional support for these one-electron promotions contributing to transition 4. The state that arises from a Ph-NN(HOMO) $\rightarrow$ Ph-NN(LUMO) (Figure IV-15, left) one-electron promotion is of interest, since this state is known to strongly mix through CI into the ground-state wavefunction to produce negative spin density on the NN bridgehead carbon.\cite{48, 202} This CI mixing is important since the NN(SOMO) wavefunction is nodal at the bridgehead carbon and its one-electron occupancy does not directly contribute to the observed spin density at this carbon. This is noteworthy, because the role of the Ph-NN(HOMO) $\rightarrow$ Ph-NN(LUMO) excited state is important in our discussion of the electronic origin of the observed antiferromagnetic exchange in 1-mPh.
Two additional transitions contribute to the intensity of band c. The first is calculated to possess moderate intensity and is assigned as the \([\text{NN(SOMO)} \rightarrow \text{Ph-NN(LUMO)} + \text{Ph-NN(HOMO)} \rightarrow \text{NN(SOMO)}]\) transition with enhanced intensity due to the additive nature of the two transition dipoles for the two one-electron contributions to the transition. Band c is obviously more intense in 1-mPh than the corresponding band in 1-pPh which is most likely due to the presence of a very intense charge transfer band in this spectral region that can be assigned as the \(\text{SQ(SOMO)} \rightarrow \text{SQ-Ph(e2, LUMO)}\) transition which is primarily localized on the SQ chromophore but possesses SQ \(\rightarrow\) Ph(e2) charge transfer character. In contrast to the SQ \(\rightarrow\) Ph-NN(e1) charge transfer character observed in 1-pPh, the phenylene (bridge) orbital of e2 symmetry possesses nodal character at the carbon atoms that attach to the SQ and NN.
fragments in $1\text{-}p\text{Ph}$, and therefore is essentially nonbonding in character with respect to the SQ and NN frontier orbitals of $1\text{-}p\text{Ph}$ (Figure IV-15, right). Differences in the charge transfer spectra between $1\text{-}m\text{Ph}$ and $1\text{-}p\text{Ph}$ reveal different interactions between SQ and NN frontier orbitals and the Ph(e1) and Ph(e2) bridge orbitals, and this highlights the effects of connectivity differences between para- and meta-substituted benzene rings in these biradicals. The dominant SQ(SOMO) $\rightarrow$ Ph(e2) charge transfer band in $1\text{-}m\text{Ph}$ is also fully consistent with a distinct reduction in the SQ(SOMO)$\rightarrow$Ph-NN(e1, LUMO) charge transfer that contributes to the efficient donor to acceptor ferromagnetic pathway responsible for strong ferromagnetic coupling in $1\text{-}p\text{Ph}$ (Figure IV-15, right).

As we've seen, the charge transfer band is unique to the biradical electronic absorption spectrum and thus we can use this transition to watch for changes in intensity as a function of temperature. As discussed previously, the $\sim 27,000$ cm$^{-1}$ $\pi\rightarrow\pi^*$ transition in $1\text{-}m\text{Ph}$ is dramatically more intense compared to the same region in $1\text{-}p\text{Ph}$. We have shown through calculations that the charge transfer band for $1\text{-}m\text{Ph}$ is dramatically reduced so we can look at the SQ(SOMO) to Ph(e2) $\pi\rightarrow\pi^*$ transition in $1\text{-}m\text{Ph}$ instead. We can watch the intensities of this band as a function of temperature. As shown in Figure IV-16, the variable temperature electronic absorption spectra shows an increase in intensity of the 27,500 cm$^{-1}$ band with a decrease in intensity in the 25,000 cm$^{-1}$ and 31,000 cm$^{-1}$ bands as the temperature is swept from 298K down to 5K. Importantly, there are also multiple isosbestic points at $\sim 26,000$ cm$^{-1}$, $\sim 26,500$ cm$^{-1}$, $28,500$ cm$^{-1}$, and $\sim 29,500$ cm$^{-1}$ indicating only two distinct species in solution: the singlet species and the triplet species.
When the ground state singlet and triplet are split, it follows that there can be thermal population of the higher state provided $|2J| < k_B T$. By lowering the temperature we can see a decrease in intensity of parts the nominal $\pi\rightarrow\pi^*$ band and increases in others. From this we can conclude the existence of multiple bands due to a thermally populated excited state related to the splitting of the ground state. As with both magnetometry and variable temperature EPR, we are still looking at the population of the singlet versus the triplet as a function of temperature. This means we can again use a Boltzmann population to model the changes in intensity of the electronic absorption spectra. Since we know from magnetometry that 1-mPh is a ground state singlet, we can assume that as temperature decreases from 298K to 5K the decreases in intensity are due to the triplet state being thermally depopulated and the increases in intensity a manifestation of the re-population of the singlet state.
These assignments allow us to compare the normalized intensity of select absorptions to a theoretical plot of using $2J_{DA} = -64 \text{ cm}^{-1}$ for the singlet and triplet population as a function of temperature. The intensity dependence on temperature directly correlates with the singlet-triplet gap ($2J_{DA} = -64 \text{ cm}^{-1}$) determined from solid-state magnetic susceptibility studies (Figure IV-10). Thus both the VT-EPR and the VT-EAS provide compelling evidence that the average solution conformation is very similar to that observed in the X-ray structure.\textsuperscript{102}

By knowing the Boltzmann population of the singlet and triplet at any given temperature (Figure IV-17), we can deconvolute the electronic absorption spectra into a representation of what a pure singlet ($^1\text{GC} \rightarrow ^1\text{EC}$) and pure triplet ($^3\text{GC} \rightarrow ^3\text{EC}$) spectrum would look like and is shown in Figure IV-18.
Figure IV-18. Deconvoluted pure singlet (blue) and pure triplet (red) electronic absorption spectra for \textit{1-mPh} by variable temperature electronic absorption spectroscopy.

The similarity of the singlet and triplet component spectra indicate that there is no dramatic change in the GS and ES orbital character as a function of spin. It is also clear that the observed transitions between \(\sim 24,000 - 32,000 \text{ cm}^{-1}\) occur at lower energy for the triplet configuration than for the singlet configuration. For the intense singlet and triplet transitions in the \(\sim 27,500 \text{ cm}^{-1}\) region, the oscillator strength of the singlet transition is greater than that of the triplet transition and the \(^3\)ES is stabilized by \(\sim 500 \text{ cm}^{-1}\) relative to the singlet state (Figure IV-18).

In order to explain the manifestation of the antiferromagnetic exchange in \textit{1-mPh}, we must explore all possible reasons for the \(^1\)GC to be lower in energy than the \(^3\)GC. For \textit{1-pPh}, the dominant mechanism for ferromagnetic exchange involves configurational mixing of an SQ(SOMO) \(\rightarrow\) Ph-NN(e1, LUMO) intraligand charge transfer configuration (\(^3\)CTC2, Figure IV-19) into the ground configuration (\(^3\)GC, Figure IV-19).\(^4\) In \textit{1-mPh}, the decrease in
SQ(SOMO) → Ph-NN(e1, LUMO) charge transfer intensity comes directly from the cross-conjugated phenylene bridge connectivity. The effect of this reduction is produces reduced excited state ferromagnetic exchange contributions to the ground state and allows antiferromagnetic contributions to dominate. Therefore, the observation of ground state antiferromagnetic exchange coupling in 1-mPh is important because it reveals the fact that other orbital pathways are providing the non-zero exchange between SQ and NN. In order to understand the nature of the magnetic exchange pathways in 1-mPh and correlate these pathways with spectroscopic observables, we can construct electronic configurations that result from one-electron promotions to the Ph-NN(HOMO), NN(SOMO), Ph-NN(e1, LUMO) and SQ(SOMO) frontier molecular orbitals to form the EC and CTCs of Figure IV-19. These orbitals represent a minimum number required to understand how singlet and triplet ECs and CTCs mix into the GS to promote antiferromagnetic exchange coupling of the NN and SQ spins.
Figure IV-19. Possible electronic configurations contributing for 1-mPh. (Left) The GC and EC of 1-mPh. Double-headed arrows indicate exchange interaction. (Middle) Singlet and triplet charge transfer configurations (CTCs) that result from one-electron promotions from the GC. (Right) Closed-shell configurations that derive from one-electron promotions from CTCs. Note that DEC2 and DEC4 can also result from direct SQ(SOMO)→NN(SOMO) and NN(SOMO)→SQ(SOMO) kinetic exchange contributions. Since the <SQ(SOMO)|NN(LUMO)> overlap integral is essentially zero, the kinetic exchange term is also expected to be zero for 1-mPh.\textsuperscript{94}

Configurational mixing of the EC and CTCs depicted in Figure IV-19 with the GC stabilize both the 1GS and 3GS.\textsuperscript{203} The previous analysis of the electronic absorption spectrum for 1-mPh provides evidence for the formation of all the singly excited configurations depicted in Figure IV-19. As is the case in 1 and 1-pPh, configurational mixing of CTC1 and CTC2 with the GC will result in preferential stabilization of the 3GS since the single site (NN) exchange integral ($K_0$) is anticipated to be large ($K_0 = 2,275$ cm$^{-1}$ for 1).\textsuperscript{7} In fact, we have
experimentally determined that ~4% of an $^3$CTC2 type configuration is admixed into the $^3$GS of 1 resulting in the observation of strong GS ferromagnetic exchange ($J_{\text{SQ-NN}} \approx +550$ cm$^{-1}$).

There is some support for admixture of CTC1 and CTC2 into the $^3$GS of $\text{1-mPh}$. This comes from the computed spin density description for the $^3$GS which shows an increase in spin density on the NN fragment (1.04) compared to the SQ fragment (0.96). Spin population transfer between the SQ and NN fragments$^{48}$ derives from the fact that none of the spins in CTC1 and CTC2 are localized on the SQ fragment since the SQ(SOMO) is either doubly occupied or vacant in these triplet configurations and therefore possesses no net spin density.

One possible way for the $^1$GS to be stabilized with respect to the $^3$GS is by configurational mixing of excited configurations that lack a triplet counterpart with the $^1$GC to stabilize the $^1$GS. Excited state configurations that lack a triplet counterpart are closed-shell configurations. The closed shell double excited configurations (DECs) shown in Figure IV-19 (right) can configurationally mix with the GC in fourth order to selectively stabilize the $^1$GS.$^{203}$ The double excited states DEC2 and DEC4 are identical to the states that result from a direct Anderson type kinetic exchange contribution involving the SQ and NN SOMOs and resemble the metal-to-metal charge transfer (MMCT) states of transition metal dimers.$^{203}$ However, due to the lack of direct orbital overlap between the SQ(SOMO) and the NN(SOMO) the kinetic exchange term is expected to be negligible in $\text{1-mPh}$. DEC1 and DEC3 are double excitations from the Ph-NN (HOMO) to the two SOMOs and to the Ph-NN (LUMO), respectively. The role of DECs in the stabilization of the $^1$GS is well documented,$^{203,204}$ and was recently suggested to be important for the stabilization of the $^1$GC in meta-poly-acene (n > 3) bridged Cr(III) dimers.$^{205}$
Even though there is precedence for the role of DECs in contributing to ground state antiferromagnetic exchange, there is no direct experimental evidence that they contribute to $^1$GS stabilization in 1-mPh. If DECs were responsible for stabilization of the singlet ground state, then the singlet only spectrum in Figure IV-18 should be lower in energy than the triplet spectrum, which is not the case. Also, band a in singlet 1-mPh and triplet 1-pPh are identical which means there is no major change to the SQ and NN SOMOs and provides no support for DECs as the primary reason for the singlet stabilization. The fundamental difference in the electronic absorption spectra of 1-mPh and 1-pPh occurs in the region of band b. The SQ(SOMO) $\rightarrow$ Ph-NN(LUMO) transition that results in ground state ferromagnetic exchange in 1-pPh is dramatically reduced in intensity for 1-mPh. Thus, it would appear that excited state antiferromagnetism, which contributes to GS antiferromagnetic exchange through CI mixing of DECs with the $^1$GC via $^1$ECs, likely only contributes to a reduction in excited state ferromagnetic contributions to the GS exchange.

Spin unrestricted broken-symmetry DFT calculations on 1-mPh indicate a large (~0.75eV) exchange splitting between the spin-up and spin-down orbitals of the Ph-NN(HOMO) orbital resulting from strong exchange interactions between the spin-up and spin-down electrons in the Ph-NN(HOMO) and the unpaired electron spins in the NN(SOMO) and the SQ(SOMO). A spin polarization mechanism can therefore be invoked in order to explain how the $^1$GS is stabilized with respect to the $^3$GS, and we start with a simple spin polarization analysis of occupied Ph-NN(HOMO) orbitals using the four HMO fragment orbitals depicted in Figure IV-20. Configurational mixing of the $^{1,3}$ECs (Figure
IV-19) into the ground state result in a spin polarization of the doubly occupied Ph-NN(HOMO) orbital shown in the center of Figure IV-20. The electron-electron repulsion between these spin polarized core electrons and the NN(SOMO) and SQ(SOMO) spins result in a stabilization of the singlet ground configuration ($^1$GC) over the triplet with an antiparallel orientation of the NN(SOMO) and SQ(SOMO) spins. This spin polarization argument also allows one to predict the signs of the atomic spin populations in 1-mPh, and these are in excellent agreement with those computed from a spin-unrestricted DFT calculation of the $^1$GS (Figure IV-20, right). This analysis underscores the importance of the $^1$EC to the observed magnetic exchange, which arises from a Ph-NN(HOMO)$\rightarrow$Ph-NN(LUMO) one-electron promotion with appreciable contributions from the meta-phenylene bridge. This analysis can be more quantitatively evaluated in the context of MC-SCF calculations. We initially performed MC-SCF calculations on 1-mPh using an active space spanning just the NN(SOMO) and SQ(SOMO) orbitals. The results of this calculations yield a triplet ground state comprised solely of the $^3$GC depicted in Figure IV-19 and a small ferromagnetic singlet-triplet splitting of $2J_{DA} = +0.4 \text{ cm}^{-1}$. Increasing the active space to include the Ph-NN(HOMO), SQ(HOMO), NN(SOMO), SQ(SOMO), Ph-NN(e1, LUMO), and Ph(LUMO) orbitals yields a $^1$GS stabilized by $2J_{DA} = -35 \text{ cm}^{-1}$ (~50% the experimental value) with respect to the $^3$GS, in good agreement with the experimental results ($2J_{DA} = -64 \text{ cm}^{-1}$). The $^1$GS wavefunction is found to be dominantly comprised of the $^1$GC (88%) listed in Figure IV-19 with CI mixing of the $^1$EC (Figure IV-19; 7%) and a small degree (3%) of an excited configuration resulting from promotion of both Ph-NN(HOMO) electrons to the Ph-NN(e1, LUMO). Interestingly, no closed-shell singlet DECs were observed to contribute to
the $^1$GS in the MC-SCF calculations within a cutoff of 1%. The large contribution of the EC (Figure IV-19) to the ground state exchange is precisely what we derived from the molecular orbital spin polarization analysis detailed above, and provides a key state description of the spin density derived from the spin-unrestricted DFT calculations.

**Figure IV-20.** Spin polarization in 1-mPh. (Left) Fragment 1-mPh HMOs from Figure IV-15. (Middle) Double Spin Polarization in Ph-NN fragment via the EC mixed into GC. (Right) In-phase Ph-NN spin polarization and SQ spin delocalization supporting antiferromagnetic alignment of SQ and NN fragments.

Based on the HMO diagrams (Figure IV-15), there should not have been any appreciable exchange coupling between SQ and NN in this cross-conjugated biradical due to the nodal nature of the meta-phenylene bridge. If we were to view this system in a molecular version of Hund's rule (Figure I-3), there would have been no preference between the singlet and triplet ground states. However, we have shown how a cross-conjugated system can have an appreciable amount of electronic coupling through both excited state analysis in Figure
IV-19 and the spin polarization results in Figure IV-20. Essentially, spin polarization of the cross-conjugated $\pi$-system combined with suppressed ferromagnetic interactions due to lack of a SQ to NN CT provides a D-B-A system where a molecular version of Hund's rule cannot be applied to predict the sign nor strength of the exchange interaction.

3. Direct Comparison of Electronic Coupling Between Conjugated and Cross-Conjugated D-B-As and the Relationship to Quantum Interference Effects

By confirming the origin of the surprisingly strong antiferromagnetic exchange in 1-mPh in the previous section, we can provide the fundamental comparisons of electronic coupling between conjugated and cross-conjugated D-B-A systems that only differ in the location of the connection of donor and acceptor on the bridge. Similar cross-conjugated systems studied by Wasielewski\textsuperscript{23} and Bardeen\textsuperscript{22} have shown a factor of ~30 decrease in charge separation rate compared to conjugated systems which in turn suggests an attenuation of $(30)\approx 5.4$ in $H_{DA}$. However, there has been no report of a direct comparison of $H_{DA}$ values for meta- and para-phenylene. The VBCI approach to exchange coupling in 1-mPh presented here allows for this comparison. The relationship between electronic- and exchange coupling can be approximated using Eq. (IV.2).\textsuperscript{208}

\[ 2J_{DA} = \frac{H_{eff}^2}{\Delta E} \]  

IV.2

By using 25,750 cm\(^{-1}\) for $\Delta E$ (NN-Ph (HOMO) $\rightarrow$ NN-Ph (LUMO) energy; Table IV-1) with $|2J| = 64$ cm\(^{-1}\) in Eq. (IV.2), we can calculate an effective $H_{DA}$ ($H_{eff}$) of 1284 cm\(^{-1}\). This value may be compared with an $H_{eff} \approx 664$ cm\(^{-1}\) from 1-pPh obtained by dividing $H_{DA} = 3632$ cm\(^{-1}\) for 1-pPh\textsuperscript{21} by $(30)\approx 5.4$. This estimation of $H_{eff}$ for 1-mPh from 1-pPh can then be
compared to the determined value of $H_{DA}$ for 1-mPh and is nearly twice the value predicted by the square root of the ratio of charge separation rates in the nonadiabatic regime reported by Wasielewski$^{23}$ and Bardeen.$^{23}$ However, there are distinctly different CI mechanisms which contribute to the electronic/exchange coupling in 1-mPh compared to 1-pPh such that orbital contributions to $H_{eff}$ are quite different from those described by the $H_{DA}$ value determined for 1-pPh. The different CI mechanisms are illustrated schematically in Figure IV-21. 1-mPh electronic/exchange coupling is activated by the generation of an electron/hole pair involving the Ph-NN HOMO and LUMO. 1-pPh electronic/exchange coupling is a consequence of D→A/SQ→Ph-NN(e1, LUMO) charge transfer.

**Figure IV-21.** Cartoon descriptions of the dominant CI mechanisms for antiferromagnetic exchange coupling of SQ and NN spins in cross-conjugated 1-mPh (left) and ferromagnetic exchange coupling in conjugated 1-pPh (right).

The results of this work suggest that CI mixing of specific ECs into the ground state may be important for controlling electronic communication and electron transport mediated by cross-conjugated bridges. As discussed in chapter I, the conductance ($g$) of a molecular junction is related to the transmission probability evaluated at the Fermi energy according to Eq. (I.40) and is related to frontier molecular orbital theory through the Green’s function
matrix element by Eq. (I.41).\textsuperscript{209,210} For cross-conjugated bridge molecules, Eq. (I.40) predicts strong antiresonances\textsuperscript{68,71,187–189,191,211–213} near the Fermi energy that result in a dramatic reduction in the transmission probability. If we consider SQ and NN as molecular analogs of biased electrodes, and use only the spin density coefficients for the quaternary carbons of the SQ(SOMO) and NN(SOMO) frontier molecular orbitals that connect to the meta-phenylene bridge in 1-mPh, we would expect the transmission at $E_F$ to be zero due to three of the values being equal to zero (Figure IV-20, left). However, it is important to note that the conductance described by Eq. (I.40) and Eq. (I.41) is a sum over all filled and empty orbitals and not simply the frontier orbitals. The anticipated value of zero for the transmission mediated by the frontier molecular orbitals is related to the magnitude of the magnetic exchange interaction ($J_{DA} \sim 0$) that we calculate for 1-mPh in the active-electron approximation,\textsuperscript{40} where the active space in the MC-SCF calculations is restricted to the NN(SOMO) and the SQ(SOMO) orbitals. Only through CI mixing of higher energy configurations do we obtain a spin density description of 1-mPh that spans the entire molecule with non-zero spin populations on the carbons that connect to the meta-phenylene bridge, and obtain a magnetic exchange interaction that is non-zero. To the extent that CI similarly affects electron transport in cross-conjugated molecule-bridged systems, a state description of electron transport may provide greater insight into important molecular design concepts for control of electron transport in the quantum interference regime.\textsuperscript{213–215} The inclusion of excited configurations in transport calculations, which is in line with our description of the magnetic exchange in 1-mPh, may have the effect of modulating the magnitude of antiresonance contributions to the electron transport by increasing $\pi$-type electronic communication. This
idea may also transfer to modulating photoinduced electron transfer rates in cross-conjugated D-B-A systems as well.\textsuperscript{23}

C. **Electron Rich Cross-Conjugated Thiophene Biradicals**

In the previous section, we focused on a simple \textit{meta}-phenylene bridge to understand the basics of antiferromagnetic coupling through a cross-conjugated system.\textsuperscript{145} As we saw with \textit{1-mPh}, being able to understand and control the coupling through a bridge by changing how the donor and acceptor are attached to the bridging ring provides greater insight into electron transport in the quantum interference regime.\textsuperscript{213–215} However, as we saw in chapter III, \textit{para}-phenylene-bridged D-B-As provide a weaker electronic coupling between donor and acceptor compared to 2,5-thiophene-bridges D-B-As. Since thiophene, and similar chalcogenophenes, are common bridge types in PET\textsuperscript{123,150,170} and MMM conductance\textsuperscript{58,59,125,165,167,180} studies, it is also important to understand the effects of cross-conjugation in this molecular archetype. Figure IV-22 illustrates the effects of placing the donor and acceptor in different positions on a labeled thiophene ring. When the donor and acceptor are in the 2 and 5 positions of the thiophene ring, a direct conjugative pathway can be seen by the direct interaction of the two radicals. However, if either the donor and acceptor are in the 2 and 4 positions, the two radicals can no-longer interact, just as they cannot in cross-conjugated systems like \textit{meta}-phenylene. From this description, we will call these connection patterns on the thiophene "\textit{meta}" to each other and the 2,5-thiophene connection pattern "\textit{para}".
**Figure IV-22.** Resonance effect of various donor and acceptor positions on a thiophene ring. If two radicals are conjugated to each other, they can annihilate to form a bond (left). However, if the radicals are cross-conjugated (middle and right), the two radicals will not be able to interact with each other through the π-system.

While there are some nitronyl nitroxide homospin biradical studies\(^{24,25,216,217}\) and a recent MMM conductance study by Stary,\(^{26}\) the effect of cross-conjugation in *meta*-thiophene on electronic coupling has not been well explored. Specifically, there has been no direct comparison of the electronic coupling between 2,5-thiophene- and 2,4-thiophene-bridged D-B-As. Furthermore, there has been no studies on the effect of the placement of the donor and acceptor relative to the sulfur atom in thiophene. Figure IV-23 shows line bond drawings of three SQ-B-NN biradicals synthesized to explore these cross-conjugated effects:

\[
\text{Tp}^{\text{Cum}}\text{MeZn(SQ-(2,5-thiophene)-NN)} (2-(2,5)T), \text{Tp}^{\text{Cum}}\text{MeZn(SQ-(3,5-thiophene)-NN)} (2-(3,5)T) \text{ and } \text{Tp}^{\text{Cum}}\text{MeZn(SQ-(2,4-thiophene)-NN)} (2-(2,4)T).\]

Due to the asymmetric nature of the SQ-B-NN system and the direct synthetic control we have over the construction of the biradical, we have been able to place the donor and acceptor at specific positions on the bridging ring allowing us to study the difference in electronic coupling between these D-B-A biradicals.
1. Synthesis of Cross-Conjugated Thiophenes

For the synthesis of 2-(3,5)T, as shown in Error! Reference source not found., commercially available thiophene 64 was reacted with 16 under Suzuki conditions to yield 65. Phenol 65 was oxidized with IBX to form quinone 66 followed by reduction with ascorbic acid to catechol 67. Compound 67 was reacted with BHA to form compound 68 followed by oxidation with I₂ to form nitronylnitroxide 69. Catechol-nitronylnitroxide 69 was finally reacted with Zn(OH)Tp Cum,Me under standard conditions⁷,96,102 to yield biradical 2-(3,5)T.

Figure IV-23. Line bond drawing of 2-(2,5)T, 2-(3,5)T, and 2-(2,4)T.
Scheme IV-2. Synthesis of 2-(3,5)T.

For the synthesis of 2-(2,4)T, as shown in Error! Reference source not found.,

hiophene 70\(^{218}\) was reacted with 16 under Suzuki conditions to yield 71. Phenol 71 was then oxidized to quinone 72 with IBX then reduced with ascorbic acid to catechol 73. Using BHA, compound 73 was transformed into 74 in concentrated methanol. Using I\(_2\), 74 was oxidized to nitronyl nitroxide 75. Under standard conditions,\(^{7,96,102}\) catechol-nitronyl nitroxide 75 and Zn(OH)Tp\(^{\text{Cum,Me}}\) were reacted to form biradical complex 2-(2,4)T.
2. Discussion of Results for Cross-Conjugated Thiophenes

As in the last two chapters, structural evidence of the SQ and NN radicals can be obtained through comparison of bond lengths of crystallographic studies to previous work. Thermal ellipsoid plots with hydrogen atoms and cumenyl groups removed for clarity of 2-(2,5)T, 2-(3,5)T, and 2-(2,4)T are shown in Figure IV-24. Structural parameters of 2-(2,5)T were discussed in chapter 3 and are reproduced here for comparison purposes. Structures presented for 2-(3,5)T and 2-(2,4)T are preliminary structures which require refinement but provide enough information about the core SQ-B-NN structure to confirm some structural parameters. The bond lengths for the \( \alpha \)-SQ and NN components in 2-(3,5)T and 2-(2,4)T fall within typical values. The structural deviation parameters for these radicals are summarized.
in Table IV-3. In each case, structural deviations of $\Sigma|\Delta_i| \approx 0.01\AA$ for the $o$-SQ component and $\Sigma|\Delta_i| \approx 0.02\AA$ for the NN component are small when compared to previously reported SQ-B-NN biradicals.$^{102,142}$ The noticeably larger deviations in 2-(2,4)\T are a manifestation of lower structure quality and should fall in line with 2-(2,5)\T and 2-(3,5)\T with a more refined structure. Finally, the ZnO\N coordination sphere is identical to other $\text{Tp}^{\text{Cum,MeZn(SQ-}}$Bridge-NN) biradical complexes.$^{4,47,142,145}$

Similarly to chapter II, the torsion between D-B-A fragments has a strong effect on the SQ-NN exchange/electronic coupling and will modulate the donor-acceptor interaction.$^{10,13,61,75,148}$ Table IV-2 displays select torsion angles for the three complexes in Figure IV-24. These torsion angles were determined by the mean plane defined by the ortho-
SQ ring, the mean plane of the thiophene ring, and the mean plane of the O-N-C-N-O atoms of the NN. The SQ-B torsion angles in 2-(3,5)T and 2-(2,4)T are more twisted than 2-(2,5)T by 24° and 17° respectively. The larger SQ-B torsion angle in 2-(3,5)T is most likely due to two flanking hydrogen atoms on the 2 and 4 positions on the thiophene ring of 2-(3,5)T compared to the single flanking hydrogen on the 3 position at 2-(2,4)T and 2-(2,5)T. The same effect can possibly be seen in the B-NN torsion of 2-(2,4)T (8°) compared to 2-(2,5)T (4°) and 2-(3,5)T (2°). The more planar nature of 2-(2,5)T compared to 2-(3,5)T and 2-(2,4)T could also be due to the conjugated nature of the para-thiophene and the strong electronic coupling determined in chapter III\textsuperscript{94} whereas the cross-conjugated nature of the meta-thiophenes lack this strong coupling.

**Table IV-2.** Select torsion angles for 1-mPh,\textsuperscript{145} 2-(2,5)T,\textsuperscript{94} 2-(3,5)T, and 2-(2,4)T.

<table>
<thead>
<tr>
<th>Complex</th>
<th>SQ-Bridge Torsion Angle (°)</th>
<th>Bridge-NN Torsion Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-mPh</td>
<td>23.9</td>
<td>5.9</td>
</tr>
<tr>
<td>2-(2,5)T</td>
<td>11.4</td>
<td>1.9</td>
</tr>
<tr>
<td>2-(3,5)T</td>
<td>28.8</td>
<td>3.5</td>
</tr>
<tr>
<td>2-(2,4)T</td>
<td>35.4</td>
<td>8.4</td>
</tr>
</tbody>
</table>

As discussed earlier in this chapter, intermolecular interactions through oxygen-oxygen close contacts can contribute to the overall observed antiferromagnetic exchange coupling.\textsuperscript{200} The closest intermolecular contact for these oxygen atoms in 2-(2,5)T, 2-(3,5)T, and 2-(2,4)T are given in Table IV-3. The values for 2-(2,5)T and 2-(3,5)T are outside the range for significant intermolecular contributions to the measured magnetic exchange
However, the nitronyl nitroxide oxygen-oxygen distance in \(2-(2,4)T\) is within the range for significant intermolecular antiferromagnetic interactions.

**Table IV-3.** Structural Deviation Parameters and NN oxygen-oxygen intermolecular distances for \(2-(2,5)T\), \(2-(3,5)T\), and \(2-(2,4)T\).

| Complex   | \(o-SQ \sum|\Delta i| \) (Å) | NN \(\sum|\Delta i| \) (Å) | Intermolecular O-O Distance (Å) |
|-----------|-------------------------------|------------------------------|---------------------------------|
| \(2-(2,5)T\) | 0.008                         | 0.026                        | 4.604                           |
| \(2-(3,5)T\) | 0.007                         | 0.014                        | 5.095                           |
| \(2-(2,4)T\) | 0.018                         | 0.014                        | 3.685                           |

In magnetic and crystallographic studies of intermolecular NN interactions, we see the antiferromagnetic intermolecular interaction occurs between the spin containing oxygen atoms of the NN that are between 3.3 Å and 4.0 Å.\(^{146,147,219}\) If we look at a section of the \(2-(2,4)T\) unit cell (Figure IV-25), we can see the closest NN oxygen-oxygen interaction is \(~3.68 \text{ Å}\) which is within the range for possible, but not guaranteed, intermolecular interactions. However, this distance carries an unknown amount of error due to the preliminary nature of the current structure.
Figure IV-25. Oxygen-oxygen close contact in 2-(2,4)T preliminary crystal structure. Hydrogen atoms and cumenyl groups have been removed for clarity.

Magnetometry on single crystal 2-(3,5)T and microcrystalline 2-(2,4)T are shown in Figure IV-26 and fit with the HDVV expression in Eq. (1.28) to give $J_{DA} = -22 \text{ cm}^{-1}$ for 2-(3,5)T and $J_{DA} = -18 \text{ cm}^{-1}$ for 2-(2,4)T. Both meta-thiophene bridged biradicals show antiferromagnetic exchange coupling, just as 1-mPh does, which indicates the suppression of the ferromagnetic pathway through the cross-conjugated bridge. The fit for 2-(3,5)T is excellent ($R^2 = 0.999$) but the fit for 2-(2,4)T shows a small amount of over-estimation for data points in the 5-50 K region which is potentially caused by neglecting to fit crystal packing interactions within the microcrystalline 2-(2,4)T sample. Unfortunately, the current preliminary structure cannot give us a full, accurate picture with which to attempt a correction to this fit. Therefore, we can at a minimum conclude that 2-(2,4)T has antiferromagnetic coupling, indicating cross-conjugated behavior, which is on the same order of magnitude as 2-(3,5)T.
As with 1-mPh,\textsuperscript{145} we can support the measured solid-state exchange coupling with a series of frozen solution VT-EPR measurements while removing any possible intermolecular interactions contributing to $J_{DA}$. Of course, the downside of this technique is the addition of more possible confirmers in solution by a statistical distribution of torsion angles between SQ-B and B-NN in the frozen solution. The left side of Figure IV-27 shows an example EPR spectrum for the $\Delta m_s = 2$ transition used to create the Curie plot on the right side of Figure IV-27. By fitting the Curie plot for 2-(3,5)T with Eq. (IV.1), we obtain $J_{DA} = -13 \text{ cm}^{-1}$ for a solution phase exchange coupling. Due to the reasonably good fits of the Curie plot and magnetometry data, both exchange couplings for 2-(3,5)T are valid and reflect the change in environment around the biradical. Since there are no obvious intermolecular interactions contributing to the antiferromagnetic exchange in the magnetometry data, the large difference in $J_{DA}$ for 2-(3,5)T must come from significant torsions in frozen solution reducing the
overall average exchange coupling measured by VT-EPR. A variable temperature EPR experiment using the same conditions as Figure IV-27 is currently planned for 2-(2,4)T when the instrument is available again. Ideally, VT-EPR data for 2-(2,4)T will solidify the measured difference in exchange coupling between 2-(3,5)T and 2-(2,4)T through frozen solution measurements.

Interestingly, both 2-(3,5)T and 2-(2,4)T show less antiferromagnetic (more ferromagnetic) coupling than 1-mPh (\(J_{DA} = -32\) cm\(^{-1}\) for magnetometry, \(J_{DA} = -19\) cm\(^{-1}\) for VT-EPR).\(^{145}\) The reduction in antiferromagnetic coupling may be due to either larger SQ-B and B-NN torsion angles in 2-(3,5)T and 2-(2,4)T compared to 1-mPh (see Table IV-2) or that possibly the antiferromagnetic pathways in thiophene are inherently weaker than those in phenylene. Confirmation of one, both, or neither of these theories requires excited state
analysis with TDDFT similar to that performed on 1-mPh as well as a series of sterically hindered cross-conjugated biradicals in order to determine the effect of torsion on antiferromagnetic coupling.

Evidence of the cross-conjugated nature of these meta-thiophenes should manifest itself in the electronic absorption spectra just as it did with the dramatic reduction of the SQ (SOMO) → NN (LUMO) CT band in 1-mPh compared to 1-pPh. In Figure IV-28 we see and overlay of 2-(2,5)T, 2-(3,5)T, and 2-(2,4)T in DCM. Each of these spectra show characteristic SQ and NN bands in the 10,000 cm⁻¹ to 16,000 cm⁻¹ region confirming the presence of both donor and acceptor radicals spectroscopically. The two peaks at ~21,000 cm⁻¹ and 23,000 cm⁻¹ in the 2-(2,5)T spectrum (green) correspond to the SQ (SOMO) → NN (LUMO) CT which is clearly attenuated in the spectra for 2-(3,5)T (blue) and 2-(2,4)T (red). We can then apply the same argument used for the presence of strong antiferromagnetic coupling in 1-mPh to 2-(3,5)T and 2-(2,4)T. Since the ferromagnetic CT band is attenuated, this opens up alternative weaker antiferromagnetic coupling pathways for these meta-thiophenes. It is also interesting to note the drastic difference in absorption profile for 2-(3,5)T versus 2-(2,4)T in the 24,000 cm⁻¹ to 30,000 cm⁻¹ region. The bands in the meta-thiophene spectra do not obviously resemble any bands in the para-thiophene spectrum which suggests that there are new, intense bands solely due to the difference in location of donor and acceptor on the thiophene ring.
Figure IV-28. Electronic absorption spectra of 2-(2,5)T (green), 2-(3,5)T (blue), and 2-(2,4)T (red) with expansion of 10,000 cm\(^{-1}\) to 20,000 cm\(^{-1}\) region (inset).

The dramatic reduction in the CT band for 2-(3,5)T and 2-(2,4)T suggests the strong antiferromagnetic coupling in these biradicals must come from a similar spin polarization mechanism as 1-mPh. Figure IV-29 shows the same four relevant HMO fragments for 2-(3,5)T and 2-(2,4)T as was shown in 1-mPh: T-NN (HOMO), NN (SOMO), SQ (SOMO), and T-NN (LUMO). Unlike 1-mPh, both meta-thiophene SQ-B-NNs do not have an obvious node on the thiophene ring preventing significant CT interactions. NN (SOMO) and SQ (SOMO) still do not interact due to the node on the bridging carbon of NN (SOMO), but there is significant overlap between T-NN (HOMO) and SQ (SOMO) as well as between SQ (SOMO) and T-NN (LUMO). These transitions may be the cause of the higher energy bands in the electronic absorption spectra of 2-(3,5)T and 2-(2,4)T and could possibly contribute to the preference of the antiferromagnetic exchange coupling.
Figure IV-29. (Top) Important fragment HMOs for $2-(3,5)T$ (left) and $2-(2,4)T$ (right) where red is positive and blue is negative. (Bottom) Spin polarization of the $\pi$-system for $2-(3,5)T$ (left) and $2-(2,4)T$ (right) where blue is (+) spin and green is (-) spin.

Due to the number of overlapping transitions in the 24,000 cm$^{-1}$ to 30,000 cm$^{-1}$ region of the meta-thiophenes, it is unlikely that a comparison of the electronic absorption of donor-bridge and bridge-acceptor fragment molecules could deconvolute the electronic absorption spectra of $2-(3,5)T$ and $2-(2,4)T$. While the differences in the electronic absorption spectra of $2-(2,5)T$, $2-(3,5)T$, and $2-(2,4)T$ are very interesting, without spectral assignment through TDDFT it is difficult to comment on the origin of the higher energy transitions and thus pin
down the exact manifestation of the antiferromagnetic exchange as was done with \textit{1-mPh}.\textsuperscript{145} We suspect spin polarization plays a major role in the negative sign in $J_{DA}$, but being able to determine which configurations impart polarization on which transitions will go a long way in truly understanding cross-conjugated thiophene bridges. Work on these calculations has begun in the Kirk group and are still in progress.

\textbf{D. Gating Quantum Interference: Substituent Effects on Electronic and Exchange Coupling in Cross-Conjugated Donor-Bridge-Acceptor Biradical Complexes

1. Introduction to substituent effects on cross-conjugated donor-bridge-acceptor biradical complexes}

As we discussed earlier in this chapter, cross-conjugated systems have limited communication, compared to conjugated systems, from one end of the molecule to the other due to a node at the connection point (Figure IV-30, left). This node is formed from destructive interference of two wavefunctions which is also known as quantum interference. There have been studies of many different kinds of single molecule cross-conjugated devices such as quantum interference effect transistors (QuIETs),\textsuperscript{27,28} spin filters,\textsuperscript{220} molecular switches,\textsuperscript{187} and molecular logic devices.\textsuperscript{33,34,221} The most closely related device to our SQ-B-NN system is likely the QuIET, which has no experimental model. It has shown through calculations on QuIETs that by applying an electric current (L3) \textit{ortho} to one connection (L1) and \textit{para} to the other (L2), it is possible to modulate the transmittance across the system (Figure IV-30, right).\textsuperscript{27,28,222}
Figure IV-30. (Left) Frontier orbitals for a para- and meta-coupled phenylene ring. (Right) A cartoon of a quantum interference effect transistor (QuiET). L1 and L2 are covalent connections to donor and acceptor electrodes whereas L3 is a mobile probe capable of modulating the electronic coupling between L1 and L2.

Figure IV-31. Line bond drawings of 1-mPh, 1-NO$_2$, 1-OMe, 1-CN, and 1-Me.

D-B-A biradical complexes studied in this section are presented in Figure IV-31. These biradicals are designed as single molecule models of gated cross-conjugated devices described by Cardamone$^{27,28}$ where electron donating and withdrawing capabilities of various substituents are used as the “bias voltage” (L3 in Figure IV-30 right) for the coupling between cross-conjugated SQ and NN. Our results provide the molecular basis for
understanding and future design of single-molecule devices, like QuIETs, through the addition of electron withdrawing and electron donating substituents at the L3 position of a cross-conjugated SQ-meta-phenylene-NN system where L1 is SQ and L2 is NN (see Figure IV-30).

As we saw for these complexes, the Ph-NN (HOMO) → Ph-NN (LUMO) excitation pathway is responsible for the antiferromagnetic (AFM) coupling through spin polarization of the π-framework. We can use the known Ph-NN (HOMO) → Ph-NN (LUMO) relationship to attempt to predict how the exchange coupling should vary with different substituents. As electron density in the bridge is increased through electron donating groups, we would expect the coupling to become less AFM by increasing both the Ph-NN (HOMO) and Ph-NN (LUMO) energies making AFM coupling less energetically accessible. Similarly, as electron density in the bridge is reduced through electron withdrawing groups, we expect the coupling to become more AFM through lowering the energy of the Ph-NN HOMO to Ph-NN LUMO transition and making AFM coupling more energetically accessible.

We can attempt to correlate our findings to macroscopic effects by comparing our substituted cross-conjugated D-B-As to field effect transistors. A field effect transistor has three terminals: a source electrode (donor), a drain electrode (acceptor), and a gate electrode (substituent). When a gate voltage is applied in a field effect transistor, more current (stronger electronic coupling) is allowed to flow through the transistor by lowering the conduction band (LUMO) making the transmission of electrons more facile through shrinking the gap. Using our D-B-A biradical complexes as models of molecular transistors similar to those described by Cardamone, we can think of the energy required
to promote and electron from Ph-NN (HOMO) to Ph-NN (LUMO) as the voltage required to pass from the source terminal to the drain terminal of a field effect transistor where the SQ donor is the source electrode, the NN acceptor is the drain electrode, and the substituent ortho to the SQ and para to the NN is the gate electrode. The electron donating and withdrawing capabilities of the substituents on the bridge should act as varying amounts of voltage being applied at a gate electrode and thus be able to modulate the electronic coupling between the donor (SQ) and acceptor (NN).

2. Discussion of Results for Substituted meta-Phenylenes

i. Synthesis and Characterization

For the synthesis of 1-NO₂, as shown in Error! Reference source not found., compound 76 was prepared as reported²²⁴ and reacted with 16 under Suzuki conditions to yield 77. Protected aldehyde 77 was immediately deprotected with weak acid to yield phenol-aldehyde 78. Phenol 78 was oxidized with IBX to quinone 79 then reduced to catechol 80 with ascorbic acid. Using BHA, 80 was transformed to 81 then oxidized with I₂ to catechol-nitronylnitroxide 82. Under standard conditions,²⁷,⁹⁶,¹⁰² Zn(OH)Tp⁸⁶,M₆ and 82 were reacted to form biradical complex 1-NO₂.
Scheme IV-4. Synthesis of 1-NO₂.

For the synthesis of 1-OMe, as shown in Scheme IV-5, commercially available 83 and compound 16 were reacted under Suzuki conditions to yield phenol 84. Using IBX, phenol 84 was oxidized to quinone 85 then reduced to catechol 86 with ascorbic acid. Compound 86 was reacted with BHA to form 87 then oxidized to catechol-nitronylnitroxide 88. Compound 88 and Zn(OH)TpCum,Me were reacted under standard conditions to form biradical complex 1-OMe.
For the synthesis of 1-CN, as shown in Scheme IV-6, commercially available 89 was reacted with NBS and BPO to form 90 then oxidized with AgNO₃ to benzaldehyde 91. To avoid a detrimental Cannizzaro reaction under basic conditions, aldehyde 91 was protected with trimethoxymethane to form compound 92. Compounds 9 and 92 were reacted under Suzuki conditions to form 93 which was immediately deprotected to catechol-aldehyde 94 under acidic conditions. Using BHA, 94 was transformed to 95 then oxidized to 96 with I₂. Under standard conditions, 7,47,96 96 and Zn(OH)TpCum,Me were reacted to form biradical complex 1-CN.
Scheme IV-6. Synthesis of 1-CN.

For the synthesis of 1-Me, as shown in Scheme IV-7, commercially available 97 was reacted with 16 under Suzuki conditions to yield 98. Using IBX, phenol 98 was oxidized to quinone 99 then reduced with ascorbic acid to catechol 100. Compound 100 was reacted with BHA to yield compound 101 which was then oxidized to catechol-nitronylnitroxide 102. Compound 102 and Zn(OH)Tp\textsuperscript{Cum,Me} were reacted under standard conditions\textsuperscript{7,47,96} to yield biradical complex 1-Me.
Scheme IV-7. Synthesis of 1-Me.

**ii. Structural and magnetic properties of substituted cross-conjugated biradicals**

Thermal ellipsoid plots of 1-mPh, 1-NO₂, 1-OMe, 1-Me, and 1-CN are shown in Figure IV-32 with hydrogen atoms and cumenyl groups removed for clarity. Torsion angles were determined using the mean plane of the o-SQ ring, bridge aromatic ring, O-N-C-N-O atoms of the nitronylnitroxide, and atoms of the substituent respectively and are listed in Table IV-4.
In this series of complexes, the bridge-NN dihedral angles are relatively unchanged while the SQ-bridge dihedral angles are dependent on the substituent ortho to the semiquinone ring. Interestingly, 1-OMe, 1-NO2, and 1-CN share similar SQ-bridge dihedral angles around 48° while 1-mPh is more planar at 24° and 1-Me nearly orthogonal at 88°. The variance in dihedral angles in these complexes leads to a cosine dependence of the exchange coupling, similar to that which was discussed in chapter II, and is discussed below.

Table IV-4. Select torsion angles for 1-mPh, 1-NO2, 1-OMe, 1-CN, and 1-Me. Due to the nature of the substituent, also included are substituent-bridge torsion angles for 1-NO2 and 1-OMe. Oxygen-oxygen intermolecular interactions are given between spin containing oxygen atoms on the NN ring.

<table>
<thead>
<tr>
<th>Complex</th>
<th>SQ-Bridge Angle (°)</th>
<th>Bridge-NN Angle (°)</th>
<th>Substituent-Bridge Angle (°)</th>
<th>Closest Oxygen-Oxygen Intermolecular Contact (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-mPh</td>
<td>23.83</td>
<td>0.82</td>
<td>---</td>
<td>5.10</td>
</tr>
<tr>
<td>1-NO2</td>
<td>47.03</td>
<td>12.68</td>
<td>44.87</td>
<td>4.40</td>
</tr>
<tr>
<td>1-CN</td>
<td>49.22</td>
<td>18.28</td>
<td>---</td>
<td>4.54</td>
</tr>
<tr>
<td>1-OMe</td>
<td>46.28</td>
<td>10.99</td>
<td>0.98</td>
<td>5.63</td>
</tr>
<tr>
<td>1-Me</td>
<td>87.99</td>
<td>14.09</td>
<td>---</td>
<td>9.80</td>
</tr>
</tbody>
</table>
Oxygen-oxygen intermolecular distances listed in Table IV-4 are the closest distances between spin-containing oxygen atoms on two different NN rings. All measured distances fall outside the range of significant intermolecular magnetic interactions and thus measured solid-state exchange coupling is due to intramolecular interactions between the SQ donor and NN acceptor.\(^{24,216}\)

Magnetometry data for these cross-conjugated biradical complexes were fit with Eq. (I.28) and are plotted as \(\chi_{\text{Para}}\) versus temperature in Figure IV-33. Without looking at the fit parameters, we can immediately tell the significant shift in exchange coupling across the series by looking at the peak maxima. The peak of 1-mPh at the highest temperature tells us that it is the strongest AFM coupling of the five complexes and 1-Me, being the lowest temperature peak, is the weakest AFM coupling. This analysis is then confirmed by the excellent fits to the data showing \(J_{DA} = -32\) cm\(^{-1}\) for 1-mPh and \(J_{DA} = -5\) cm\(^{-1}\) for 1-Me. The parameters for the remaining complexes, as well as \(R^2\) values for each fit are given in Figure IV-33.
Figure IV-33. Magnetometry stack plot for 1-mPh (red), 1-NO₂ (blue), 1-OMe (green), 1-CN (purple), and 1-Me (black).

If we look at the crystal structures in Figure IV-32, we can see significant torsional effects due to the addition of substituents on the bridge ortho to the SQ ring. As discussed in chapter II, there is dramatic torsional dependence on the electronic coupling between donor and acceptor which must be addressed in these cross-conjugated complexes.
In Figure IV-34, we show the relationship between solid-state exchange coupling and crystallographic torsion angles through a contour plot. Figure IV-34A shows us graphically
that the torsion angles between the bridge and NN rings are all very similar and fall between 0° and 15°. Figure IV-34B shows a more dramatic picture with a wide variation in the torsion angle between the SQ and bridge rings. However, we can immediately see in Figure IV-34C that the torsion angles between the SQ and bridge rings for 1-NO₂, 1-CN, and 1-OMe all fall very close to 47.5° which is fortuitous for comparison of substituent effects. With this fact combined with a line drawn between the 1-mPh and 1-Me data points in Figure IV-34, we can see that the difference in $J_{DA}$ values for 1-NO₂, 1-OMe, and 1-CN are not just due to torsional effects of the donor and the bridge. However, it should be noted that the value of the exchange coupling for 1-Me ($J_{DA} = -5$ cm⁻¹) is approaching the limitation of the instrument and thus has a larger uncertainty than the other values. Although this is not reflected in the $R^2$ value, it is evident by the visual quality of the fit to the low temperature data points. The implication of this is thus the lines drawn in Figure IV-34 have a large uncertainty and cannot be used to accurately predict the exchange coupling for an unsubstituted cross-conjugated biradical with $\phi_{SQ} = 47.5°$.

Now that we have shown that the difference in $J_{DA}$ for 1-NO₂, 1-OMe, and 1-CN are not torsional effects, we can compare the exchange couplings of these three complexes to see that 1-OMe has weaker AFM coupling and 1-CN has stronger AFM coupling as predicted. However, 1-NO₂ has approximately the same exchange coupling as 1-OMe according to our results. This can be explained by the substituent torsion angle of the -NO₂ group (see Figure IV-32 and Table IV-4). The strong withdrawing capacity of the -NO₂ substituent is dependent on the interaction between the -NO₂ orbitals and the aromatic orbitals of the bridging ring. Since the -NO₂ group is twisted by almost 45°, we can assume the electron
withdrawing capacity of the \(-\text{NO}_2\) group on \(1\text{-NO}_2\) is reduced and is thus making the observed exchange coupling weaker (less AFM) than it would be if the \(-\text{NO}_2\) plane to bridge plane torsion angle were 0°.

In order to eliminate any potential intermolecular interactions as well as confirm the relative magnitude of measured exchange couplings for these cross-conjugated biradical complexes, VT-EPR experiments were performed. A stack plot of the doubly integrated spectra versus inverse temperature is show in Figure IV-35 with the intensity normalized and shifted vertically to easily compare each set of data.

![Figure IV-35](image)

**Figure IV-35.** Variable-temperature electron paramagnetic resonance stack plot of \(1\text{-mPh}\), \(1\text{-NO}_2\), \(1\text{-OMe}\), \(1\text{-CN}\), and \(1\text{-Me}\). Intensities normalized and shifted vertically for comparison purposes.

Each set of VT-EPR data has a notably lower \(R^2\) value than the solid-state magnetometry measurements due to the less accurate measurement of temperature inside the
cavity and additional variation in signal-to-noise ratios for each data point. These VT-EPR experiments also have fewer low temperature data points than magnetometry experiments due to limitations of the heater inside the cavity. However, even with all of these instrumental factors, we have an excellent agreement between solid-state and solution exchange coupling values. Exchange coupling parameters determined by magnetometry and VT-EPR for 1-NO₂, 1-OMe, and 1-CN all agree within 1 cm⁻¹ suggesting the overall molecular structure of the solid-state and frozen solution are very similar, if not identical, and lack any significant intermolecular exchange coupling. The large difference in exchange coupling parameters for 1-Me (J_DA = -5 cm⁻¹ for magnetometry versus J_DA = -14 cm⁻¹ for VT-EPR) is likely due to a decrease in ϕSQ to a more planar structure in frozen solution further confirming the presence of a torsional aspect to the observed exchange coupling.

**iii. Spectroscopy and electrochemistry of substituted cross-conjugated D-B-As**

The electronic effects caused by the substituents on the bridge of these cross-conjugated meta-phenylenes is also observed by the shift of the Ph-NN (HOMO) → Ph-NN (LUMO) transition in the electronic absorption spectra. A stack plot of extinction coefficients for 1-mPh, 1-NO₂, 1-CN, 1-OMe, and 1-Me is shown in Figure IV-36. Through the effects of adding substituents to the bridges of these D-B-As, the previously hidden charge transfer band in the electronic absorption spectrum of 1-mPh appears to be moved away from bridge centered π → π* transitions. The noticeable decrease in intensity of the band around ~28,000 cm⁻¹ in complexes 1-NO₂, 1-OMe, 1-CN, and 1-Me is partially due to torsional influences of the bridge substituents similar to the effect on the methyl group on 1-MePh in chapter II.
However, twisting of the bridge fragments does not account for the new bands at ~25,500 cm\(^{-1}\) in 1-CN and ~32,000 cm\(^{-1}\) in 1-NO\(_2\).

![Figure IV-36](image_url)

**Figure IV-36.** Electronic absorption stack plot for 1-mPh (red), 1-NO\(_2\) (blue), 1-OMe (green), 1-CN (purple), and 1-Me (black). Inset is an expansion of the 10,000 cm\(^{-1}\) to 20,000 cm\(^{-1}\) region.

Assuming the band at ~28,000 cm\(^{-1}\) in 1-mPh is the Ph-NN (HOMO) → Ph-NN (LUMO) transition, it appears that the same transition in 1-OMe is ~120 cm\(^{-1}\) higher in energy than 1-mPh while the same transition in 1-NO\(_2\) is ~895 cm\(^{-1}\) lower in energy than 1-mPh and 1-CN is ~1253 cm\(^{-1}\) lower in energy than 1-mPh. It should be noted that the broadened transitions in 1-NO\(_2\) likely due to free rotation of the nitro group causing a wider energy distribution of transitions in that complex. Unfortunately, without calculations it is difficult to say for sure what each transition is and thus the above analysis may just be circumstantial. Thankfully, these calculations are planned for the near future through our
collaboration with the Kirk group so that we may better understand the effect of the substituents on the electronic absorption spectra for these complexes.

Through the utility of cyclic voltammetry, we can also observe the effect of the substituents on the oxidation and reduction potentials for these SQ-B-NN complexes. By analyzing the shift in potential of observable NN/NN', Catecholate$^{2-}$/SQ$^-$ (Cat/SQ), SQ$^-$/Quinone$^0$ (SQ/Q) and NN/NN$^+$ redox couples, we see how the substituents raise and lower the energy required to oxidize or reduce the donor and acceptor as shown in Table IV-5. Included in Table IV-5 are the redox potentials for the donor by itself (via Tp$^{Cum,MeZn(SQ)}$) and the acceptor by itself (via Ph-NN) in order to assign the observed redox couples in the biradical complexes. By the addition of electron withdrawing groups in 1-NO$_2$ and 1-CN the donor and acceptor require larger potentials to oxidize (SQ/Q and NN/NN$^+$) compared to 1-mPh and thus are more difficult to oxidize. Conversely, the addition of an electron donating group in 1-OMe causes the donor and acceptor to require smaller potentials compared to 1-mPh and thus is easier to oxidize. These results actually reinforce the argument for the primary mechanism of AFM coupling being through Ph-NN (HOMO) → Ph-NN (LUMO) and not some form of SQ (SOMO) → NN (LUMO) CT. If the SQ (SOMO) were involved in determining the strength of the AFM exchange coupling, these electrochemical results suggest that the trend observed would be the opposite of what was observed. Since we see no obvious relation between the relative potential of the SQ/Q redox potential and the measured AFM exchange coupling, we can reaffirm that the source of the AFM coupling must come from spin polarization of the Ph-NN (HOMO) → Ph-NN (LUMO) as described in the first section of this chapter.
Table IV-5. Cyclic voltammetry redox potentials for 1-mPh, 1-NO2, 1-CN, 1-OMe, 1-Me, Tp^{Cum,MeZn}(SQ), and Ph-NN in DCM with a scan rate of 40 mV/s.

<table>
<thead>
<tr>
<th>Complex</th>
<th>NN/NN’ (mV)</th>
<th>Cat/SQ (mV)</th>
<th>SQ/Q (mV)</th>
<th>NN/NN’+ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-mPh</td>
<td>-1424</td>
<td>-997</td>
<td>+115</td>
<td>+416</td>
</tr>
<tr>
<td>1-NO2</td>
<td>n.a.</td>
<td>-897</td>
<td>+217a</td>
<td>+518</td>
</tr>
<tr>
<td>1-CN</td>
<td>n.a.</td>
<td>-927</td>
<td>+171a</td>
<td>+481</td>
</tr>
<tr>
<td>1-OMe</td>
<td>n.a.</td>
<td>-1091</td>
<td>+8</td>
<td>+373</td>
</tr>
<tr>
<td>1-Me</td>
<td>-1586a</td>
<td>-1043</td>
<td>+121</td>
<td>+394</td>
</tr>
<tr>
<td>Tp^{Cum,MeZn}(SQ)</td>
<td>-----</td>
<td>-1191</td>
<td>+27</td>
<td>-----</td>
</tr>
<tr>
<td>Ph-NN</td>
<td>-1297</td>
<td>-----</td>
<td>-----</td>
<td>+428</td>
</tr>
</tbody>
</table>

\(^a\)Value is at the peak of the observed current for the irreversible couple.  
\(^b\)Not observed.

Interestingly, the SQ/Q redox couple in 1-NO2 and 1-CN are irreversible while all of the other SQ/Q redox couples in Table IV-5 are reversible. Figure IV-37 shows a stack plot of 1-mPh, 1-NO2, 1-OMe, and Tp^{Cum,MeZn}(SQ) with its line bond drawing on the right side. The black lines represent the redox potentials reported in Table IV-5 for each shown complex. The irreversibility of the SQ/Q redox couple in 1-NO2 and 1-CN suggests that the electron withdrawing nature of the -NO2 and -CN groups pull enough electron density out of the quinone formed, causing the quinone to be a weaker Lewis base compared to the same quinone formed in the other complexes, and allows the quinone-bridge-NN to disassociate from the Tp^{Cum,MeZn} metal center.
Figure IV-37. Oxidation half of cyclic voltammetry for 1-mPh, 1-NO$_2$, 1-OMe, and Tp$^{Cum,Me}$Zn(SQ) referenced to Fc/Fc$^+$ couple. Black lines indicate Q/SQ redox potential. The oxidations at more positive potential in 1-mPh, 1-NO$_2$, and 1-OMe are the NN/NN$^+$ redox couple. Black arrows indicate direction of scan.

E. Experimental

General Considerations. Reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer at room temperature. $^1$H and $^{13}$C chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. Infrared spectra were recorded on a Brüker Vertex 80v spectrometer with Brüker Platinum ATR attachment. Elemental analyses were performed by Atlantic Microlabs, Inc. High-resolution mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility. Single crystal XRD structures were determined by Roger Sommer at NCSU. Compounds 5,$^{92,93}$ 9,$^{88}$ 16,$^{109}$ 70,$^{218}$ 76,$^{224}$ o-iodoxybenzoic acid (IBX),$^{89}$ 2,3-dimethyl-2,3-
bis(hydroxyamino)butane (BHA), Zn(OH)Tp\textsuperscript{Cum,Me}, Tp\textsuperscript{Cum,Me}Zn(SQ), and Ph-NN\textsuperscript{225} were prepared according to published procedures.

**Electronic Structure Calculations.** Spin unrestricted gas-phase geometry optimizations were performed at the density functional level of theory using the Gaussian 03 software package.\textsuperscript{226} All calculations employed the B3LYP hybrid functional, and a 6-31G(d’p’) basis set, a split valence basis set with polarization functions was used for all atoms. Input files were prepared using the molecule builder function in the Gaussview software package and the t-buty1 substituent on the semiquinone was modeled/represented as a methyl group. Frontier molecular orbitals (MOs) were generated for the optimized ground states. Optical excitation energies and oscillator strengths were calculated using time-dependent DFT methods. These time-dependent DFT calculations were performed on the optimized ground-state geometries, and the first 25 excited states were calculated. Electron density difference maps (EDDMs) were constructed utilizing custom in-house software. Complete-active space self-consistent field (CASSCF) calculations, which are based on a multiconfigurational approach, were carried out in the ORCA SCF-MO program. The CASSCF calculations employed a def2-TZVP triple zeta basis set with added polarization functions, and a convergence tolerance for the orbital gradient of 1e\textsuperscript{-4}. The energy of was optimized for the singlet and triplet ground state with respect to the coefficients of the configurations that contribute to each state as well as the molecular orbital coefficients of the spin restricted orbitals.

**Electron Paramagnetic Resonance.** EPR spectra were recorded on either a JEOL JES-FA100 EPR spectrometer or a Bruker EleXsys EPR with low temperature spectra
recorded by use of an ARS-LTR continuous flow cryostat or an Oxford ESR900 continuous flow cryostat. A 2 mM sample was prepared in freshly distilled 2-methyl-tetrahydrofuran, degassed, and the spectra collected in a J. Young tube or standard quartz EPR tube sealed with a rubber septum. Collected variable temperature data was fit using the Curie Law and a Boltzmann distribution of $S = 1$ to $S = 0$ ground states.

**Magnetic Susceptibility.** Magnetic susceptibility measurements were collected on a Quantum Design MPMS-XL7 SQUID magnetometer with an applied field of 0.7 T. A microcrystalline sample (~10-20 mg) was loaded into a gelcap/straw sample holder and mounted to the sample rod with Kapton tape for variable temperature measurements. Collected raw data was corrected with a straight line for diamagnetic response of sample container and molecular diamagnetism using Pascal's constants as a first approximation, where the slope of the line represents the residual diamagnetic correction.

**Electronic Absorption Spectroscopy.** Low-temperature electronic absorption spectra were obtained on a Hitachi U-3501 UV-Vis-NIR spectrometer capable of scanning a wavelength region between 185 and 3200 nm using a double-beam configuration at 2.0 nm resolution. The instrument was calibrated to the 656.1 nm deuterium line using the corresponding Hitachi software option. Variable-temperature electronic absorption measurements required the removal of the cuvette holder assembly in order to accommodate the cryostat in the sample chamber. A custom designed Janis STVP-100 continuous flow cryostat was mounted in the sample holder allowing for variable temperature electronic absorption data to be conveniently collected in the 5 K – 300 K temperature range. Sample temperature was monitored with a Lakeshore silicon-diode (PT-470) and regulated by a
combination of helium flow and dual heater assemblies. Solid-solution spectra were collected on thin polystyrene (MW = 280,000) polymer films prepared by evaporation of saturated polystyrene solutions cast on glass plates.

3′-(tert-butyl)-4′-hydroxy-[1,1′-biphenyl]-3-carboxaldehyde (59) To a 50 mL Schlenk flask, 1.00 g (4.36 mmol) 4-bromo-2-tert-butylphenol, 5, was added with 782 mg (5.23 mmol) (3-formylphenyl)boronic acid, 58, and 273 mg (0.24 mmol) Pd(PPh₃)₄, with ~15 mL tetrahydrofuran under nitrogen atmosphere. A 2 M solution of potassium carbonate was degassed and 7.6 mL was added to the reaction vessel via syringe. The reaction was refluxed 16 hours and checked by thin layer chromatography (TLC)(75% ethyl acetate in hexanes) to ensure product formation. The reaction was cooled to room temperature and stopped by addition of ~10 mL deionized water with stirring in air for 30 minutes. The reaction was transferred to a separatory funnel and washed with saturated sodium bicarbonate then extracted with dichloromethane. The dichloromethane extractions were dried over sodium sulfate and the solvent was removed under reduced pressure. The resulting brown oil was dissolved in diethyl ether and approximately an equal volume of petroleum ether was added then filtered through medium porosity sintered glass. The solvent was removed under reduced pressure yielding a yellow solid which was recrystallized from warm ethyl acetate to yield 721 mg of compound 59 (65% yield). ¹H NMR (DMSO-d₆, δ): 10.07 (s, 1H), 9.64 (s, 1H), 8.08 (t, ³J 1.6 Hz, 1H), 7.91 (dt, ³J 7.7 Hz, ⁴J 1.6 Hz, 1H), 7.79 (dt, ³J 7.7 Hz, ⁴J 1.6 Hz, 1H), 7.62 (t, ³J 7.7 Hz, 1H), 7.46 (d, ³J 2.2 Hz, 1H), 7.39 (dd, ³J 8.2 Hz, ⁴J 2.2 Hz, 1H), 6.91 (d, ³J 8.2, 1H), 1.41 (s, 9H). ¹³C NMR (DMSO-d₆, ppm): 193.97, 156.88, 142.42, 137.40, 136.45, 132.66, 130.25, 129.95, 127.98, 127.40, 125.95, 125.61, 117.43, 35.05, 29.92. IR
(solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3310 (br, vO-H), 1690 (s, vC=O). Elemental analysis: Calculated (C: 80.28, H: 7.13), Found: (C: 79.99, H: 7.09).

$5^\prime$-(tert-butyl)-3',4'-dioxo-3',4'-dihydro-[1,1'-biphenyl]-3-carboxaldehyde (60) To
a 50 mL pear shaped flask, 593 mg (2.33 mmol) 59 and 1.33 g (4.75 mmol) IBX were added
with 2 mL DMF and stirred shielded from light for 30 hours. After about 30 minutes, the
solution changed color from light yellow to dark green. Reaction progress is monitored by
TLC (50% ethyl acetate in hexanes) and $^1$H-NMR. Once all of 59 had been consumed, the
reaction was poured into 100 mL water, transferred to a separatory funnel and extracted with
ethyl acetate. The organic phase was washed three times with saturated sodium bicarbonate
solution then twice with half saturated sodium chloride solution. The organic phase was then
collected, dried over sodium sulfate, and the solvent removed under reduced pressure to yield
460.7 mg of compound 60 (70% yield). $^1$H NMR (CDCl$_3$, $\delta$): 8.05 (s, 1H), 7.95 (d, $^3$J 7.9 Hz,
1H), 7.83 (d, $^3$J 7.9 Hz, 1H), 7.64 (t, $^3$J 7.9 Hz, 1H), 7.16 (d, $^3$J 2.0 Hz, 1H), 6.49 (d, $^3$J 2.0
Hz, 1H), 1.24 (s, 9H). $^{13}$C NMR (CDCl$_3$, ppm): 191.31, 180.14, 179.26, 151.59, 150.36,
137.98, 136.86, 134.05, 132.07, 131.95, 130.01, 127.10, 124.33, 35.71, 29.08. IR (solid) $\nu_{\text{max}}$
(cm$^{-1}$): 1702 (s, vC=O), 1653 (s, vC=O). Elemental analysis: Calculated (C: 71.82, H: 5.67),
Found (C: 72.01, H: 5.67).

$3^\prime$-(tert-butyl)-4',5'-dihydroxy-[1,1'-biphenyl]-3-carboxaldehyde (61) Quinone 60
was dissolved in 10 mL tetrahydrofuran and transferred to a separatory funnel. To a 25 mL
Erlenmeyer flask, 328 mg (1.86 mmol) ascorbic acid was added and dissolved in 10 mL
deionized water. The ascorbic acid was added to the separatory funnel containing 60 and
shaken. The green color of 60 instantly changed to light yellow. Saturated sodium chloride
solution was added and the product was extracted by ethyl acetate. The organic phase was
dried over sodium sulfate and the solvent removed under reduced pressure. The product is
purified by flash chromatography (20% ethyl acetate in hexanes) to yield 401 mg of
compound 61 (86% yield). \(^1\)H NMR (DMSO-\(d_6\), \(\delta\)): 10.08 (s, 1H), 9.64 (s, 1H), 8.33 (s, 1H),
8.02 (s, 1H), 7.83 (m, 2H), 7.64 (t, \(^3\)J 7.7 Hz, 1H), 7.02 (s, 1H), 6.97 (s, 1H), 1.40 (s, 9H). \(^1^3\)C
NMR (DMSO-\(d_6\), ppm): 193.47, 145.61, 144.48, 142.00, 136.76, 136.17, 132.02, 129.71,
128.78, 127.121, 126.99, 115.71, 111.33, 34.51, 29.41. IR (solid) \(\nu_{\text{max}}\) (cm\(^{-1}\)): 3140 (br, \(\nu_{\text{O-H}}\), 1678 (s, \(\nu_{\text{C=O}}\)). Mass Spectrometry (\(m/z\)): 271.1327 (M+H)+

2-(3\(^\prime\)′-( tert-buty l)-4\(^\prime\)′,5\(^\prime\)′-dihydroxy-[1,1\(^\prime\)′-biphenyl]-3-yl)-4,4,5,5-
tetramethylimidazolidine-1,3-diol (62) To a 10 mL pear-shaped flask 331 mg (1.22 mmol)
61 and 279 mg (1.88 mmol) BHA were added with a magnetic stir bar. A Schlenk adapter
was attached and sealed with a thick septum. The system was then attached to a Schlenk line
and pump/purged with nitrogen 5 times. In a 50 mL Schlenk flask 15 mL methanol was
degassed and 2 mL was added to the reaction flask. The reaction mixture was stirred for 24
hours at room temperature. The resulting opaque white solution was vacuum filtered to
collect a white solid that was collected into a sample vial and dried under reduced pressure
yielding 339 mg of compound 62 (80% yield). \(^1\)H NMR (DMSO-\(d_6\), \(\delta\)): 9.52 (br s, 1H), 8.14
(br s, 1H), 7.77 (s, 2H), 7.62 (s, 1H), 7.35 (m, 2H), 6.95 (s, 1H), 6.89 (s, 1H), 4.53 (s, 1H),
1.38 (s, 9H), 1.08 (d, \(^3\)J 4.4 Hz, 12H). \(^1^3\)C NMR (DMSO-\(d_6\), ppm): 145.22, 143.55, 142.22,
140.47, 135.78, 130.56, 127.77, 126.40, 126.32, 124.81, 90.32, 66.03, 34.29, 29.35, 24.25,
17.06.
2-(3’-(tert-butyl)-4’,5’-dihydroxy-[1,1’-biphenyl]-3-yl)-4,4,5,5-
tetramethylimidazolidine-3-oxide-1-oxyl (63) To a 100 mL round bottom flask, 49 mg (0.12 mmol) 62 was added with 20 mL diethyl ether, 10 mL fresh pH 7 buffer, and magnetically stirred at 0°C. To a 60 mL separatory funnel, 47 mg (0.18 mmol) I$_2$ was added with 30 mL diethyl ether and shaken. The solution of I$_2$ was added dropwise with stirring to the reaction mixture. After all of the iodine was added, the reaction stirred for 15 minutes then 100 mL pH 7 buffer was added. The reaction was transferred to a separatory funnel and washed with 50 mL saturated thiosulfate solution twice followed by 50 mL saturated sodium chloride solution. The organic phase was collected, dried over magnesium sulfate, and the solvent removed under reduced pressure to yield 53 mg of 63 (>95% yield). IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3300 (br, $\nu$O-H). EPR (X-band, 298K): pentet (1:2:3:2:1), $a_N = 7.6$ G. Mass Spectrometry ($m/z$): 383.2322 (M+H-O)$^+$. 

Tp$^{\text{Cum,Me}}$Zn(SQ-meta-phenylene-NN) (1-mPh) To a 25 mL oven dried Schlenk flask, 42 mg (0.11 mmol) 63 and 69 mg (0.10 mmol) Zn(OH)Tp$^{\text{Cum,Me}}$ were added with a stir bar. The reaction vessel was pump/purged with nitrogen and about 5 mL methanol distilled over calcium hydride was added via purged syringe. The reaction was stirred under inert atmosphere for 2 hours. Afterward, the reaction was opened to air, stirred overnight, then filtered through slow filter paper. The filter paper containing the product was placed in a beaker and the olive green solid was dissolved in dichloromethane. The new solution was filtered again to remove any salts and yielded 27 mg of 1-mPh (25% yield). The product was crystallized by slow evaporation of n-hexane and a few drops of dichloromethane. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2546 (w, -BH). Mass spectrometry ($m/z$): 1068.5226 (M+H)$^+$. 
Synthesis of 4-(3-(tert-butyl)-4-hydroxyphenyl)thiophene-2-carboxaldehyde (65).

To a 100 mL Schlenk flask, 1.193 g (4.32 mmol) of 16 was added with 751 mg (3.93 mmol) of 64, 360 mg (0.31 mmol) Pd(PPh₃)₄, and 20 mL THF under inert atmosphere. The reaction flask was attached to a nitrogen line, 6.5 mL of 2M K₂CO₃ was added via purged syringe, and a condenser attached under nitrogen purge. During heating to reflux over 3 days, the reaction was monitored by TLC (25% EtOAc in hexanes) and stopped when no starting material remained. The reaction was opened to air, 20 mL DI-H₂O was added, and the mixture transferred to a separatory funnel. The organic phase was diluted with 20 mL EtOAc and washed with saturated NaHCO₃ solution once followed by NaCl saturated solution twice. The organic layer was collected, dried over Na₂SO₄, and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO₂, 25% EtOAc in hexanes) to yield 464 mg (46%) of 65. ¹H NMR (400 MHz, DMSO-d₆, δ): 9.96 (s, 1H), 9.60 (s, 1H), 8.36 (s, 1H), 8.22 (s, 1H), 7.47 (s, 1H), 7.40 (d, J = 8.2 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 1.39 (s, 9H). ¹³C NMR (100 MHz, DMSO-d₆, δ): 184.3, 155.3, 143.6, 143.5, 136.1, 135.7, 128.3, 124.7, 124.3, 116.6, 34.4, 29.3. IR (solid) v max (cm⁻¹): 3244 (br, -OH), 1655 (s, -C=O). Mass spectrometry (m/z): calculated for C₁₅H₁₆O₂S (M+H)⁺: 261.0944, found: 261.0945 (M+H)⁺.

Synthesis of 4-(5-(tert-butyl)-3,4-dioxocyclohexa-1,5-dien-1-yl)thiophene-2-carboxaldehyde (66). To a 25 mL round bottom flask, 416 mg (1.60 mmol) of 65, 1.00 g (3.57 mmol) of IBX, and 10 mL DMF was added and placed under inert atmosphere. The reaction was shielded from light and allowed to stir at room temperature for 4 days. The reaction was monitored by ¹H-NMR and once 65 had been completely consumed, the
reaction was stopped by addition of saturated NaHCO$_3$ solution. After transferring the 
reaction to a separatory funnel, the reaction was diluted with EtOAc, washed three times with 
saturated NaHCO$_3$ solution followed by two washed of saturated NaCl solution. The organic 
phase was collected, dried over Na$_2$SO$_4$, and the solvent removed to yield 359 mg (82%) of 
66. $^1$H NMR (400 MHz, CDCl$_3$, δ): 10.01 (d, J = 1.3 Hz, 1H), 8.14 (m, 1H), 8.04 (d, J = 1.8 
Hz, 1H), 7.18 (d, J = 2.2 Hz, 1H), 6.63 (d, J = 2.2 Hz, 1H), 1.34 (s, 9H). $^{13}$C NMR (100 
MHz, CDCl$_3$, δ): 182.4, 180.3, 179.3, 152.1, 145.6, 144.0, 139.5, 134.2, 133.2, 132.8, 122.3, 
35.8, 29.2. IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 1661 (s, =C=O), 1647 (s, =C=O).

**Synthesis of 4-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophene-2-carboxaldehyde** 
(67). To a 250 mL round bottom flask, 359 mg (1.31 mmol) of 66 and 318 mg (1.78 mmol) 
of ascorbic acid was added with 50 mL THF and 50 mL DI-H$_2$O and stirred for 30 min in air. 
To this mixture, 50 mL saturated NaCl solution was added to separate the organic and 
aqueous layers then the reaction was poured into a separatory funnel. The organic layer was 
diluted with 50 mL EtOAc and washed with half saturated NaCl solution three times. The 
organic phase was collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced 
pressure to yield 377 mg (>95%) of 67. $^1$H NMR (400 MHz, DMSO-$d_6$, δ): 9.97 (d, J = 1.3 
Hz, 1H), 9.60 (s, 1H), 8.28 (d, J = 1.3 Hz, 1H), 8.12 (m, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.99 
(d, J = 2.0 Hz, 1H), 1.38 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$, δ): 184.4, 145.4, 144.3, 
143.8, 143.7, 136.1, 128.3, 124.1, 115.3, 110.9, 106.9, 34.4, 29.4. IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 3201 
br, -OH).

**Synthesis of 2-(4-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophen-2-yl)-4,4,5,5-
tetramethylimidazolidine-1,3-diol** (68). To a 10 mL round bottom flask, 281 mg (1.02
mmol) of 67 was added with 366 mg (2.08 mmol) of BHA and pump/purged with nitrogen 5 times. Using a purged syringe, 2.5 mL of dry, degassed MeOH was added and the reaction heated gently to dissolve the starting materials. The reaction was then allowed to stir at room temperature, shielded from light and under inert atmosphere, for 3 days. Once the reaction showed an absence of an aldehyde by $^1$H-NMR and IR, the reaction was stopped by removing the solvent under reduced pressure to yield 556 mg (>95%) of crude 68 which was used directly in the synthesis of 69. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3233 (br, -OH). Mass spectrometry ($m/z$): calculated for C$_{21}$H$_{30}$N$_2$O$_4$S (M+H)$^+$: 407.1999, found: 407.1987 (M+H)$^+$.

**Synthesis of 2-(4-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophen-2-yl)-4,4,5,5-tetramethylimidazolidine-3-oxide-1-oxyl (69).** To a 250 mL round bottom flask, 419 mg (1.03 mmol) of 68 was added with 30 mL Et$_2$O, 10 mL buffer (pH = 7), and chilled to 0°C in an ice-water bath. To a 125 mL separatory funnel, 391 mg (1.54 mmol) of I$_2$ was added with 40 mL Et$_2$O. The solution of I$_2$ was added dropwise to the stirring reaction mixture while shielded from light. Once all of the I$_2$ solution was added, 50 mL buffer (pH = 7) was added and the reaction mixture was transferred to a separator funnel. The organic phase was washed with Na$_2$S$_2$O$_3$ to remove any excess I$_2$ followed by saturated NaCl solution. The organic layer was collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure to yield 411 mg (>95%) 69. EPR (X-Band, 298K, DCM): pentet (1:2:3:2:1), $a_N = 7.45$ G. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3100 (br, -OH). Mass spectrometry ($m/z$): calculated for C$_{21}$H$_{27}$N$_2$O$_4$S (M+H)$^+$: 404.1764, found: 404.1757 (M+H)$^+$.

**Synthesis of Tp$^{\text{Cum,Me}}$Zn(SQ-(3,5)-thiophene-NN) (2-(3,5)T).** To a 25 mL oven dried Schlenk flask, 75 mg (0.19 mmol) of 69 was added with 205 mg (0.32 mmol)
**Zn(OH)Tp_{Cum,Me}** and pump/purged with nitrogen 5 times. Using a purged syringe, 10 mL of a dried and degassed solution of MeOH/DCM (1:1) was added. The reaction was stirred for 0.5 h then opened to air to stir in the dark overnight. The next morning, the solvent was removed under reduced pressure and the product purified by column chromatography (Basic Alumina, 33% EtOAc in hexanes) to yield 128 mg (63%) of 2-(3,5)T. Diffusion crystallizations were setup in a minimal amount of DCM in a small vial with MeOH in an outer vial. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2547 (w, -BH). Mass spectrometry ($m/z$): calculated for $\text{C}_{60}\text{H}_{71}\text{BN}_8\text{O}_4\text{SZn (M+H)}^+$: 1075.4776, found: 1075.4793 (M+H)$^+$.  

**Synthesis of 5-(3-(tert-butyl)-4-hydroxyphenyl)thiophene-3-carboxaldehyde (71).** To a 50 mL Schenk flask, 675 mg (2.44 mmol) of 16, 467 mg (2.44 mmol) of 70, 160 mg (0.14 mmol) Pd($\text{PPh}_3)_4$, and 20 mL THF was added under inert atmosphere. The reaction vessel was attached to a nitrogen line, 4.5 mL of a 2M K$_2$CO$_3$ solution added via purged syringe, and a condenser attached under nitrogen purge. Throughout refluxing the reaction for 4 days, the reaction was monitored by TLC (25% EtOAc in hexanes) and finally stopped when no starting material remained. The reaction was stopped by the flask being opened to air and 20 mL DI-H$_2$O added. After being transferred to a separatory funnel, the organic layer was diluted with EtOAc and washed with saturated NaCl solution twice. The organic phase was then collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO$_2$, 25% EtOAc in hexanes) to yield 233 mg (46%) of 71. $^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$): 9.84 (s, 1H), 9.74 (s, 1H), 8.46 (s, 1H), 7.59 (s, 1H), 7.41 (s, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 6.85 (d, $J = 8.2$ Hz, 1H), 1.38 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$, $\delta$): 186.1, 156.5, 146.6, 143.5, 136.8,
135.9, 124.6, 124.2, 123.4, 118.0, 116.8, 34.3, 29.1. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3233 (br, -OH), 1652 (s, -C=O). Elemental Analysis: Calculated for C$_{15}$H$_{16}$O$_2$S: (C: 69.20, H: 6.19), found: (C: 69.00, H: 6.35).

**Synthesis of 5-(5-(tert-butyl)-3,4-dioxocyclohexa-1,5-dien-1-yl)thiophene-3-carboxaldehyde** (72). To a 15 mL round bottom flask, 230 mg (0.88 mmol) of 71 was added with 496 mg (1.77 mmol) of IBX and 5 mL DMF. The reaction was then stirred in the dark and under inert atmosphere for 4 days while being monitored by $^1$H-NMR. Once all of 71 had been consumed, the reaction was stopped by pouring the mixture into 50 mL saturated NaHCO$_3$ solution. The mixture was then transferred to a separatory funnel, the organic layer diluted with EtOAc, washed with saturated NaHCO$_3$ solution three times, and finally washed with saturated NaCl solution twice. The organic phase was collected, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure to yield 190 mg (78%) of crude 72 which was used directly in the synthesis of 73. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 1682 (s, -C=O), 1641 (s, -C=O).

**Synthesis of 5-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophene-3-carboxaldehyde** (73). To a 250 mL separatory funnel, 190 mg (0.70 mmol) of 72 and 289 mg (1.62 mmol) of ascorbic acid were dissolved in 20 mL THF and 20 mL DI-H$_2$O. The mixture was shaken for 5 minutes then 20 mL saturated NaCl solution was added to separate the layers. The organic layer was diluted with EtOAc, washed with saturated NaCl, and collected. After being dried over Na$_2$SO$_4$, the solvent of the organic phase was removed under reduced pressure. The product was purified by column chromatography (SiO$_2$, 50% EtOAc in hexanes) to yield 125 mg (65%) of 73. $^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$): 9.83 (s, 1H), 9.72 (s, 1H), 8.46 (s, 1H), 8.45 (d, $J = 1.3$ Hz, 1H), 7.49 (d, $J = 1.3$ Hz, 1H), 6.97 (d, $J = 2.2$ Hz, 1H), 6.95 (d, $J = 2.2$ Hz, 1H), 6.95 (d, $J = 2.2$ Hz, 1H).
Hz, 1H), 1.37 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$, $\delta$): 186.1, 160.4, 154.1, 146.9, 145.5, 144.8, 143.4, 136.3, 133.6, 117.8, 110.4, 34.4, 29.2. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3444 (m, -OH), 3200 (br, -OH), 1644 (s, -C=O).

Mass spectrometry ($m/z$): calculated for C$_{15}$H$_{16}$O$_3$S (M+H)$^+$: 277.0898, found: 275.0805 (M-H)$^-$. 

**Synthesis of 2-(5-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophen-3-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (74).** To a 10 mL round bottom flask, 116 mg (0.42 mmol) of 73 and 149 mg (0.85 mmol) of BHA were added and pump/purged with nitrogen 5 times. Using a purged syringe, 2 mL of dry and degassed MeOH was added and the reaction mixture heated gently to dissolve the starting materials. The reaction was then allowed to stir at room temperature, in the dark and under inert atmosphere, for 2 days. Once all of 73 had been consumed, as determined by IR and $^1$H-NMR, the reaction was stopped by removing the solvent under reduced pressure to yield 240 mg (>95%) of crude 74 which was used directly in the synthesis of 75. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3233 (br, -OH).

**Synthesis of 2-(5-(3-(tert-butyl)-4,5-dihydroxyphenyl)thiophen-3-yl)-4,4,5,5-tetramethylimidazolidine-3-oxide-1-oxyl (75).** To a 100 mL round bottom flask, 170 mg (0.42 mmol) of 74 was added with 25 mL Et$_2$O, 10 mL buffer (pH = 7), and chilled to 0°C in an ice-water bath. To a 125 mL separatory funnel, 160 mg (0.63 mmol) of I$_2$ was added and dissolved in 30 mL Et$_2$O. The solution of I$_2$ was added dropwise to the cold solution of 74 in the dark. Once all of the I$_2$ solution was added, the reaction was stopped by the addition of 20 mL buffer (pH = 7) and then transferred to a separatory funnel. The organic phase was washed with saturated Na$_2$S$_2$O$_3$ solution followed by saturated NaCl solution. The organic phase was collected, dried over Na$_2$SO$_4$, and the solvent removed under
reduced pressure to yield 149 mg (88%) of 75. EPR (X-Band, 298K, DCM): pentet 
(1:2:3:2:1), aN = 7.48 G. IR (solid) νmax (cm⁻¹): 3133 (br, -OH). Mass spectrometry (m/z): 
calculated for C₂₁H₂₇N₂O₄S (M+H)+: 404.1764, found: 404.1754 (M+H)+.

Synthesis of TpCum,MeZn(SQ-(2,4)-thiophene-NN) (2-(2,4)T). To a 25 mL oven 
dried Schlenk flask, 63 mg (0.16 mmol) of 75 was added with 115 mg (0.17 mmol) of 
Zn(OH)TpCum,Me and pump/purged with nitrogen 5 times. Using a purged syringe, 10 mL of 
a dry and degasses MeOH/DCM solution (1:1) was added under inert atmosphere to the 
reaction mixture and stirred for 30 min. The reaction was then opened to air, shielded from 
light, and stirred overnight. The next morning, the reaction was stopped by removing the 
solvent under reduced pressure. The produce was purified by column chromatography (Basic 
alumina, 33% EtOAc in hexanes) to yield 157 (93%) of 2-(2,4)T. Diffusion crystallizations 
were setup in inert atmosphere at 5°C using a minimal amount of benzene in a small vial 
with MeOH in an outer vial. IR (solid) νmax (cm⁻¹): 2544 (w, -BH).

3'-tert-butyl)-4'-hydroxy-6-nitro-[1,1'-biphenyl]-3-carboxaldehyde (78). To a 100 
ml Schlenk flask in a nitrogen atmosphere, 2.00 g (7.27 mmol) of 76, 2.03g (7.35 mmol) of 
16, and 92mg Pd(PPh₃)₄ were added with 15 mL tetrahydrofuran. From a nitrogen bubbled 
solution, 11 mL of 2M K₂CO₃ was added via purged syringe and a condenser attached under 
nitrogen purge. The reaction was heated to reflux in the dark for 3 days then cooled to room 
temperature and stirred with 20 mL water for 30 min. The mixture was transferred to a 
separatory funnel, diluted with ethyl acetate, washed twice with saturated NaCl solution, the 
organic layer dried over Na₂SO₄, and the solvent removed under reduced pressure. The crude 
reaction mixture was purified by column chromatography (SiO2, 20% EtOAc in Hexanes).
\(^1\)H NMR of the collected product showed a mixture of 77 and 78 indicating the aldehyde was being partially deprotected under the purification conditions. The product mixture was dissolved in 10 mL acetone, transferred to a 50 mL round bottom flask, and a few crystals of \(p\)-toluenesulfonic acid added. The reaction was capped with a septum and allowed to stir in the dark overnight. The reaction was transferred to a separatory funnel, washed with saturated NaCl solution, the organic layer dried over Na\(_2\)SO\(_4\), and the solvent removed under reduced pressure to yield 1.87 g (>95%) of 78, a light yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 10.15 (s, 1H), 8.00 (s, 1H), 7.98 (d, \(J = 8.1\) Hz, 1H), 7.89 (d, \(J = 8.1\) Hz, 1H), 7.29 (s, 1H), 7.11 (d, \(J = 8.1\) Hz, 1H), 6.77 (d, \(J = 8.1\) Hz, 1H), 1.45 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 190.3, 155.1, 138.0, 137.0, 133.1, 128.2, 127.1, 126.5, 124.4, 117.1, 34.7, 29.5. IR (solid) \(\nu_{\text{max}}\) (cm\(^{-1}\)): 3472, 2959, 2914, 2873, 1683, 1605, 1583, 1531, 1508, 1483, 1468, 1408, 1392, 1358, 1307, 1297, 1281, 1263, 1245, 1194, 1182, 1142, 1102, 1084, 1046, 891, 838, 824, 765, 750, 641, 598, 576, 554, 526, 493, 467, 420, 403, 391. Mass spectrometry (\(m/z\)): 298.1085 (M-H\(^-\)).

3\(^{'-}\)(tert-butyl)-4\(^{'-}\),5\(^{'-}\)-dihydroxy-6-nitro-[1,1\(^{'-}\)-biphenyl]-3-carboxaldehyde (80). To a 50 mL round bottom flask, 1.87 mg (6.25 mmol) of 78 was added with 20 mL N,N-dimethylformamide followed by 2.64 g (9.43 mmol) IBX. The mixture was sealed with a septum, shielded from light, and allowed to stir at room temperature for 3 days. The reaction was monitored by \(^1\)H-NMR and stopped when all of 78 had been transformed to 79. The reaction was poured into 100 mL water, diluted with ethyl acetate, and transferred to a separatory funnel where it was washed with saturated NaHCO\(_3\) solution followed by saturated NaCl solution. The organic layer was dried over Na\(_2\)SO\(_4\) and the solvent removed.
under reduced pressure yielding 1.49 g (76%) of crude 79, a dark green solid. Quinone 79 was found to be unstable during initial attempts at purification so the crude material was dissolved in 20 mL tetrahydrofuran and placed in a separatory funnel with a water solution of 489 mg (2.75 mmol) ascorbic acid. Upon shaking the mixture, the organic layer quickly changed color from green to yellow indicating the reduction of quinone 79 to catechol 80. The organic layer was then washed with saturated NaCl solution, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO$_2$, 20% EtOAc in Hexanes) to yield 1.49 g (>95%) of catechol 80, a yellow solid. $^1$H NMR (400 MHz, DMSO-$d_6$, δ): 10.13 (s, 1H), 9.78 (s, 1H), 8.52 (s, 1H), 8.00 (m, 3H), 6.71 (s, 1H), 6.67 (s, 1H), 1.34 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 192.9, 152.8, 146.1, 145.7, 138.7, 136.9, 136.3, 133.5, 128.4, 125.5, 125.1, 117.4, 112.8, 35.1, 29.9. IR (solid) ν$_{\text{max}}$ (cm$^{-1}$): 3483, 3185, 2958, 2921, 2870, 1682, 1616, 1539, 1348, 1326, 1271, 1268, 1235, 1180, 1154, 1106, 1084, 1044, 982, 945, 853, 747, 696, 659, 633, 545. Mass spectrometry (m/z): 316.1181 (M+H$^+$). Elemental analysis: Calculated (C: 62.43, H: 6.38, N: 9.50), Found: (C: 61.60, H: 6.79, N: 9.93).

2-(3’-(tert-butyl)-4’,5’-dihydroxy-6-nitro-[1,1’-biphenyl]-3-yl)-4,4,5,5-
tetramethylimidazolidine-1,3-diol (81). To a 15 mL round bottom flask, 163 mg (0.52 mmol) of 80 and 160 mg (1.08 mmol) of BHA was added and pump purged with nitrogen 5 times. Using a purged syringe, 2 mL dry and degassed methanol was added to the reaction mixture under nitrogen with stirring and light heat to dissolve the reactants. The reaction was covered from light and allowed to stir under nitrogen in the dark for 5 days. An aliquot was taken from the reaction mixture to monitor the disappearance of the aldehyde proton at 10.13
211 ppm in DMSO-\textit{d}_6. Once all of 7 was consumed, the reaction was stopped by removal of the solvent under reduced pressure to yield 210 mg (91\%) of crude 81 which was used directly in the synthesis of 82. \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6, \delta): 7.80 (d, J = 8.1 Hz, 1H), 7.59 (m, 2H), 6.69 (s, 1H). 6.69 (1H), 4.69 (s, 1H), 1.33 (s, 9H), 1.09 (m, 12H). IR (solid) \nu_{\text{max}} (\text{cm}^{-1}): 3237, 2959, 2925, 2874, 1587, 1528, 1462, 1433, 1422, 1367, 1301, 1257, 1216, 1161, 1066, 1022, 958, 941, 923, 868, 846, 802, 758. Mass spectrometry (\textit{m}/\textit{z}): 446.2295 (M+H).\

2-(3\''-(\text{tert-butyl})-4',5'-dihydroxy-6-nitro-[1,1'-biphenyl]-3-yl)-4,4,5,5,-
etramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (82). To a 300 mL round bottom flask, 210 mg (0.47 mmol) of 81 with 30 mL diethyl ether and 10 mL of buffer (pH = 7) was chilled to 0\(^\circ\)C and shielded from light. To a 125 mL separatory funnel, 179 mg (0.71 mmol) \textsubscript{I}2 was added with 30 mL diethyl ether and added dropwise to the stirring reaction mixture. After all of the \textsubscript{I}2 solution was added, the reaction was stirred for 15 min then 100 mL buffer (pH = 7) was added and the mixture transferred to a separatory funnel. The reaction was washed with Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} followed by saturated NaCl solution, the organic layer dried over Na\textsubscript{2}SO\textsubscript{4}, and the solvent removed under reduced pressure to yield 94 mg (45\%) of 82, a light green solid. IR (solid) \nu_{\text{max}} (\text{cm}^{-1}): 3223, 3101, 2959, 2927, 2866, 1661, 1601, 1576, 1529, 1429, 1355, 1319, 1294, 1258, 1216, 1162, 1134, 1101, 1062, 1023, 959, 923, 866, 838, 806, 759, 724, 695, 663, 634, 606, 542. EPR (X-Band, 298 K): pentet (1:2:3:2:1), \alpha_N = 7.44 G. Mass spectrometry (\textit{m}/\textit{z}): 428.2188 (M+H).\

\textsubscript{Tp}\textsuperscript{Cum,MeZn(SQ-\textit{m}Ph-\textit{o}NO\textsubscript{2}-NN) (1-NO\textsubscript{2})}. To a 25 mL oven dried Schlenk flask, 74 mg (0.17 mmol) of 82 and 149 mg (0.22 mmol) of \textsubscript{Tp}\textsuperscript{Cum,MeZn(OH)} were added and pump purged with nitrogen 5 times. Using a purged syringe, 5 mL dry and nitrogen purged
methanol was added to the reaction mixture under a nitrogen atmosphere. The reaction was
allowed to stir under nitrogen for 2 hours then was opened to air and allowed to stir overnight
where the solution changed color from green to brown. The reaction was checked by EPR to
ensure formation of the biradical product then the solvent removed under reduced pressure.
The product was purified by column chromatography (Basic alumina, 50% EtOAc in
Hexanes) to yield 169 mg (90%) of 1-NO₂, a light brown solid. Crystals of 1-NO₂ were
obtained by slow evaporation of a dichloromethane/methanol mixture in air at room
temperature. IR (solid) νmax (cm⁻¹): 2962, 2929, 2870, 2547, 1741, 1631, 1605, 1550, 1521,
1440, 1367, 1301, 1242, 1172, 1099, 1062, 1022, 982, 835, 787, 747, 710, 648, 637, 560,
512. EPR (ca. 0.2 mM in 2-methyltetrahydrofuran): apparent aN = 3.26 G. Mass spectrometry
(m/z) calculated for C₆₂H₇₂BN₉O₆Zn: 1114.5063 (M+H)⁺, found: 1114.5071 (M+H)⁺.

3′-(tert-butyl)-4′-hydroxy-6-methoxy-[1,1′-biphenyl]-3-carboxaldehyde (84). To a
100 mL oven dried Schlenk flask, 1.325 g (4.79 mmol) of 16, 1.004 g (4.67 mmol) of 83, 150
mg (0.13 mmol) of Pd(PPh₃)₄ and 20 mL tetrahydrofuran was added in a nitrogen
environment. From a nitrogen bubbled solution, 8 mL of 2M K₂CO₃ was added with a
purged syringe. A condenser was fit to the reaction flask under nitrogen purge and the
reaction heated to reflux while shielded from light for 2 days. The reaction was monitored by
TLC and when complete was stopped by cooling the flask to room temperature and adding
30 mL water. The reaction was transferred to a separatory funnel, diluted with ethyl acetate,
and washed twice with saturated NaCl solution. The organic layer was dried over Na₂SO₄
and the solvent removed under reduced pressure. The product was purified by column
chromatography (SiO₂, 15% EtOAc in Hexanes) to yield 759 mg (57%) of 84, a light yellow
solid. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 9.94 (s, 1H), 7.84 (m, 2H), 7.44 (d, $J = 2.2$ Hz, 1H), 7.27 (dd, $J = 8.2$ Hz, $J = 2.2$ Hz, 1H), 7.08 (d, $J = 9.0$ Hz, 1H), 6.73 (d, $J = 9.0$ Hz, 1H), 3.92 (s, 3H), 1.45 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 191.2, 161.7, 154.1, 136.0, 132.3, 128.6, 128.2, 116.5, 111.2, 56.1, 34.83, 29.8. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3424, 2999, 2958, 2918, 2848, 1686, 1591, 1513, 1480, 1440, 1378, 1345, 1290, 1257, 1198, 1175, 1143, 1088, 1051, 1018, 941, 897, 861, 824, 868, 641, 597, 560, 538, 501, 497, 439, 410. Mass spectrometry ($m$/z): 285.1482 (M+H)$^+$. Elemental analysis: Calculated (C: 76.03, H: 7.09), Found: (C: 75.56, H: 7.06).

5'-($\text{tert}$-butyl)-6-methoxy-3',4'-dioxo-3',4'-dihydro-[1,1'-biphenyl]-3-carboxaldehyde ($85$). To a 100 mL round bottom flask, 759 mg (2.67 mmol) of $84$ was added with 10 mL N,N-dimethylformamide followed by 1.60 g (5.71 mmol) IBX sealed with a septum and stirred in the dark for 3 days. Once the reaction was complete, it was poured into 100 mL water and diluted with ethyl acetate. The mixture was transferred to a separatory funnel and washed with saturated NaHCO$_3$ solution three times followed by saturated NaCl solution twice. The organic layer was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure to yield 676 mg (85%) of $85$, a dark green solid. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 9.95 (s, 1H), 8.00 (dd, $J = 8.6$ Hz, $J = 2.1$ Hz, 1H), 7.89 (d, $J = 2.1$ Hz, 1H), 7.15 (d, $J = 8.6$ Hz, 1H), 7.02 (d, $J = 2.1$ Hz, 1H), 6.48 (d, $J = 2.1$ Hz, 1H), 4.01 (s, 3H), 1.30 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 190.0, 180.5, 161.8, 150.5, 150.0, 136.4, 133.9, 130.8, 130.3, 128.1, 127.3, 118.6, 111.9, 56.4, 35.6, 29.4. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2962, 2874, 2841, 2738, 1763, 1737, 1686, 1656, 1623, 1598, 1495, 1462, 1436, 1370, 1356, 1312, 1260, 1172, 1136, 1015, 916, 868, 824, 798, 773, 622, 589, 417. Mass spectrometry ($m$/z):
299.1276 (M+H)+. Elemental analysis: Calculated (C: 72.47, H: 6.08), Found: (C: 71.12, H: 6.18).

3'(tert-butyl)-4',5'-dihydroxy-6-methoxy-[1,1'-biphenyl]-3-carboxaldehyde (86).
In a 250 mL separatory funnel, 652 mg (2.19 mmol) 85 was dissolved in 20 mL tetrahydrofuran and a water solution of 389 mg (2.19 mmol) of ascorbic acid was added. The mixture changed color upon mixing from dark green to light yellow indicating quinone 85 had been reduced to catechol 86. The mixture was washed three times with saturated NaCl solution, the organic layer dried over Na2SO4, and the solvent removed under reduced pressure to yield 656 mg (>95%) of 86, a yellow solid. 1H NMR (400 MHz, DMSO-d6, δ): 9.91 (s, 1H), 9.48 (s, 1H), 8.19 (s, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.74 (s, 1H), 7.27 (d, J = 7.5 Hz, 1H), 6.88 (s, 1H), 6.77 (s, 1H) 3.88 (s, 3H), 1.37 (s, 9H). 13C NMR (100 MHz, DMSO-d6) δ (ppm): 191.5, 161.0, 144.4, 143.6, 135.1, 131.2, 130.2, 129.5, 126.4, 117.9, 114.0, 111.9, 55.9, 34.3, 29.4. IR (solid) νmax (cm⁻¹): 3328, 2958, 2874, 2844, 1799, 1733, 1675, 1594, 1572, 1499, 1462, 1440, 1418, 1370, 1308, 1257, 1205, 1176, 1136, 1070, 1018, 974, 938, 864, 817, 776, 758, 674, 622, 472. Mass spectrometry (m/z): 301.1429 (M+H)+.

2-(3'(tert-butyl)-4',5'-dihydroxy-6-methoxy-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (87). To a 10 mL oven dried round bottom flask, 631 mg (2.10 mmol) 86 was added with 625 (4.22 mmol) BHA and pump purged with nitrogen five times. Using a purged syringe, 2 mL dry and nitrogen bubbles methanol was added with light heat and stirring to dissolve the reactants. The reaction mixture was allowed to stir in the dark under nitrogen for 2 days. The opaque reaction mixture was filtered to collect a white precipitate yielding 933 mg (>95%) 87 which was used directly in the synthesis of 88. 1H
NMR (300 MHz, DMSO-$d_6$, $\delta$): 9.35 (s, 1H), 8.03 (s, 1H), 7.71 (s, 2H), 7.34 (s, 1H), 7.29 (d, $J = 8.3$ Hz, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 6.87 (s, 1H), 6.75 (s, 1H), 4.46 (s, 1H), 3.73 (s, 3H), 1.35 (s, 9H), 1.06 (s, 6H), 1.04 (s, 6H). IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 3486, 3241, 2981, 2951, 2903, 2866, 2840, 1605, 1499, 1461, 1436, 1365, 1315, 1300, 1250, 1178, 1156, 1141, 1094, 1072, 1028, 1008, 994, 979, 937, 921, 904, 865, 824, 800, 755, 740, 687, 658, 634, 610, 574, 532, 512, 486. Mass spectrometry ($m/z$): 431.2542 (M+H)$^+$. 

2-(3'-(tert-butyl)-4',5'-dihydroxy-6-methoxy-[1,1'-biphenyl]-3-yl)-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (88). To a 250 mL round bottom flask, 933 mg (2.17 mmol) 14 was added with 45 mL diethyl ether, 15 mL buffer (pH = 7), chilled to 0°C and shielded from light. In a 125 mL separatory funnel, 829 mg (3.28 mmol) I$_2$ was added with 45 mL diethyl ether and added dropwise to the reaction mixture. Once all of the I$_2$ solution was added, the reaction was allowed to stir for 15 minutes then 100 mL buffer solution (pH = 7) was added. The reaction mixture was transferred to a separatory funnel and washed first with Na$_2$S$_2$O$_3$ followed by saturated NaCl solution three times. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure to yield 603 mg (65%) of 88, a blue solid. IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 3182, 2955, 2869, 1657, 1602, 1486, 1438, 1345, 1256, 1204, 1155, 1129, 1074, 1022, 958, 921, 865, 813, 758, 732, 698, 665, 631, 601, 542, 471, 449. EPR (X-Band, 298 K): pentet (1:2:3:2:1), $a_N$ = 7.60 G. Mass spectrometry ($m/z$): 413.2445 (M+H)$^+$. 

Tp$^{\text{Cum,Me}}$Zn(SQ-Ph-oOMe-NN) (1-OMe). To a 25 mL oven dried Schlenk flask, 102 mg (0.24 mmol) 88 was added with 165 mg (0.24 mmol) Zn(OH)Tp$^{\text{Cum,Me}}$ and pump purged with nitrogen five times. Using a purged syringe, 5 mL dry and nitrogen bubbles
methanol was added under a nitrogen atmosphere. The resulting blue solution was stirred under nitrogen for 2 hours then opened to air to stir overnight. The solvent of the resulting dark green solution was removed under vacuum and the product purified by column chromatography (Basic alumina 50% EtOAc in Hexanes) to yield 188 mg (73%) of 1-OMe, a green solid. Crystals were obtained by slow evaporation of a dichloromethane/methanol solution in air at room temperature. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 2958, 2927, 2868, 2549, 1736, 1632, 1602, 1550, 1482, 1439, 1410, 1382, 1361, 1332, 1319, 1296, 1257, 1176, 1128, 1062, 1020, 984, 835, 790, 746, 643, 634, 558, 512. EPR: (ca. 0.2 mM in 2-methyltetrahydrofuran): apparent $a_N = 3.94$ G. Mass spectrometry ($m/z$): 1099.5325 (M+H$^+$).

**2-bromo-4-(dibromomethyl)benzonitrile (90).** To a 100 mL round bottom flask, 3.06 g (15.6 mmol) of 89, 8.34 g (46.9 mmol) of N-bromosuccinimide, and 379 mg (1.56 mmol) of benzoyl peroxide was added with 50 mL of carbon tetrachloride and a condenser attached. The reaction was attached to a nitrogen line and refluxed for 2 days. The reaction was monitored by TLC (1:15 Ethyl Acetate:Hexanes) and when complete, the reaction was allowed to cool to room temperature, filtered into a separatory funnel, and diluted with diethyl ether. The organic layer was washed with Na$_2$S$_2$O$_3$ followed by two washes of NaCl. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO$_2$, 5% Ethyl Acetate in Hexanes) to yield 2.74 g (50%) of solid 90. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.06 (t, $J = 1.5$ Hz, 1H), 8.03 (dd, $J = 8.1$ Hz, $J = 1.56$ Hz, 1H), 7.82 (dt, $J = 8.2$ Hz, $J = 1.7$ Hz, 1H), 7.39 (d, $J = 1.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 148.7, 136.3, 131.2, 127.5, 125.2, 117.3, 116.1, 39.7. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3058, 3006, 2233, 1913, 1673, 1591, 1547, 1477, 1460, 1398,
Mass spectrometry (m/z): 277.9781 (M+Na). Elemental analysis: Calculated (C: 27.16, H: 1.14, N: 3.96), Found: (C: 27.43, H: 1.23, N: 3.96).

2-bromo-4-formylbenzonitrile (91). To a 250 mL round bottom flask, 4.05 g (11.5 mmol) of 90 was added with 100 mL of acetonitrile. In a separate flask, 8.03 g (47.3 mmol) of silver nitrate was dissolved in 50 mL deionized water and added to the reaction mixture. A condenser was attached, the reaction refluxed in air overnight, and monitored by TLC (25% Ethyl Acetate in Hexanes). Once the reaction was complete, the reaction flask was allowed to cool then filtered into a separatory funnel where the mixture was diluted with diethyl ether. The organic layer was washed with saturated NaCl solution until no further AgCl precipitated. The organic layer was dried over Na2SO4 and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO2, 25% Ethyl Acetate in Hexanes) to yield 1.15 g (48%) of 91, a yellow solid. 1H NMR (400 MHz, CDCl3, δ): 9 (s, 1H). 13C NMR (100 MHz, CDCl3) δ (ppm): 190.0, IR (solid) νmax (cm⁻¹): 3369, 3069, 3060, 3034, 2229, 1692, 1656, 1596, 1551, 1470, 1409, 1368, 1281, 1208, 1185, 1140, 1127, 1044, 1015, 972, 903, 835, 747, 731, 669, 595, 567, 552, 469, 417. Mass spectrometry (m/z): 207.9395 (M-H). Elemental analysis: Calculated (C: 45.75, H: 1.92, N: 6.67), Found: (C: 45.76, H: 1.95, N: 6.65).

2-bromo-4-(dimethoxymethyl)benzonitrile (92). To a 50 mL round bottom flask, 1.11 g (5.26 mmol) of 91, 1.6 mL (14.6 mmol) of trimethoxymethane, and 22 mg (0.12 mmol) p-toluenesulfonic acid were added with 25 mL dichloromethane. The reaction flask was fit with a condenser, refluxed overnight, and monitored by TLC (25% Ethyl Acetate in
Hexanes). Once the reaction was complete, the mixture was transferred to a separatory funnel where 50 mL NaCl solution was added and the product extracted with dichloromethane. The organic layer was dried over Na₂SO₄ and the solvent removed under reduced pressure to yield 1.32 g (98%) of 92, a yellow oil. ¹H NMR (400 MHz, CDCl₃, δ): 7.96 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.57 (d, J = 8.5 Hz, 1H), 5.47 (s, 1H), 3.27 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 146.1, 135.6, 131.7, 127.2, 125.1, 117.7, 115.0, 101.6, 53.7. IR (solid) ν_max (cm⁻¹): 2937, 2832, 2230, 1601, 1553, 1444, 1384, 1346, 1280, 1263, 1194, 1102, 1057, 989, 918, 881, 832, 780, 676, 577, 547, 481, 448. Elemental analysis: Calculated (C: 46.90, H: 3.94, N: 5.47), Found: (C: 47.00, H: 4.04, N: 5.36).

3'(tert-butyl)-5-(dimethoxymethyl)-4',5'-bis(methoxymethoxy)-[1,1'-biphenyl]-2-carbonitrile (93). To a 100 mL oven dried Schlenk flask, 1.25 g (4.86 mmol) of 92, 2.17 g (5.71 mmol) of 9, and 420 mg (0.36 mmol) of Pd(PPh₃)₄ were added with 40 mL tetrahydrofuran under a nitrogen atmosphere. Using a purged syringe, 8 mL 2M K₂CO₃ was added and a condenser was attached to the reaction vessel under nitrogen purge. The reaction was refluxed in the dark and under nitrogen for 4 days. Once complete by TLC, the reaction was cooled to room temperature, opened to air, and 30 mL water was added. The mixture was then transferred to a separatory funnel and diluted with ethyl acetate. The organic layer was washed with saturated NaCl solution, dried over Na₂SO₄, and the solvent removed under reduced pressure. The product showed decomposition of the methoxymethoxy protecting groups and was carried on to the next step as a crude product.

3'(tert-butyl)-5-formyl-4',5'-dihydroxy-[1,1'-biphenyl]-2-carbonitrile (94). To a 50 mL round bottom flask, 853 g (1.97 mmol) of 93 and a catalytic amount of p-
toluenesulfonic acid was dissolved in 20 mL acetone and allowed to stir at 45°C under nitrogen for 14 h. Once the reaction was complete by TLC, the mixture was diluted with ethyl acetate and transferred to a separatory funnel where the organic layer was washed twice with saturated NaCl solution. The organic layer was then dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure to yield 586 mg (59%) of 94. $^1$H NMR (400 MHz, CDCl$_3$, δ): 10.09 (s, 1H), 9.80 (s, 1H), 8.55 (s, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.99 (s, 1H), 7.88 (d, $J = 7.9$, 1H), 6.93 (s, 1H), 6.91 (s, 1H), 1.34 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 193.3, 146.8, 146.1, 146.0, 139.5, 136.6, 135.5, 131.3, 127.1, 127.0, 118.9, 118.7, 114.9, 113.7, 35.2, 29.9. IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3351, 2956, 2228, 1697, 1597, 1561, 1483, 1433, 1416, 1365, 1286, 1253, 1223, 1153, 1065, 969, 937, 828, 803, 759, 678, 639, 495. Mass spectrometry (m/z): 294.1136 (M-H$^-$).

$3'$-(tert-butyl)-5-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidin-2-yl)-4',5'-dihydroxy-[1,1'-biphenyl]-2-carbonitrile (95). To a 15 mL round bottom flask, 110.5 mg (0.37 mmol) of 94 was added with 132.5 mg (0.75 mmol) BHA and pump purged with nitrogen five times. Using a purged syringe, 2 mL of dry and nitrogen bubbled methanol was added with light heat to dissolve the reactants. The reaction was allowed to stir under nitrogen and shielded from light for 2 days. Once complete by $^1$H NMR, the solvent was removed under reduced pressure to yield 159 mg (>95%) of crude 95 which was used directly in the synthesis of 96. $^1$H NMR (400 MHz, CDCl$_3$, δ): 8.47 (s, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.48 (m, 2H), 6.90 (s, 1H), 4.45 (s, 1H), 1.37 (s, 9H), 1.08 (s, 6H), 1.06 (s, 6H). (s, 1H). IR (solid) $\nu_{\text{max}}$ (cm$^{-1}$): 3263, 2955, 2223, 1658, 1594, 1417, 1366, 1318, 1251, 1156, 1066, 1026, 999, 954, 908, 864, 800, 664, 638, 605, 530, 494.
3'-(*tert*-butyl)-5-(4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl)-4',5'-
dihydroxy-[1,1'-biphenyl]-2-carbonitrile (96). To a 250 mL round bottom flask, 223 mg
(0.52 mmol) of 95 was added with 30 mL diethyl ether, 10 mL buffer (pH = 7) solution, and
chilled to 0°C. To a 125 mL separatory funnel, 199 mg (0.78 mmol) I2 was added with 30
mL diethyl ether and added dropwise while shielded from light to the stirring reaction
mixture. After all of the I2 solution was added, the reaction was allowed to stir for 15 min
before 100 mL buffer (pH = 7) solution was added and the mixture transferred to a separatory
funnel. The organic layer was washed with saturated Na2S2O3 solution followed by saturated
NaCl solution then dried over Na2SO4 and the solvent removed under reduced pressure to
yield 143 mg (65%) of 96, a green solid. IR (solid) νmax (cm⁻¹): 3197, 2954, 2919, 2868,
2224, 1714, 1662, 1593, 1428, 1362, 1316, 1283, 1254, 1204, 1159, 1131, 1066, 1013, 959,
922, 865, 826, 802, 759, 729, 693, 667, 632, 603, 577, 539, 501, 475, 447. EPR (X-band,

TpCum,MeZn(SQ-mPh-oCN-NN) (1-CN). To an oven dried 25 mL Schlenk flask,
48.2 mg (0.11 mmol) of 96 was added with 76 mg (0.11 mmol) Zn(OH)TpCum,Me and pump
purged with nitrogen five times. Using a purged syringe, 10 mL of a 1:1 mixture of dry and
nitrogen bubbled methanol and dichloromethane was added under a nitrogen atmosphere.
The reaction was stirred for 2 h then opened to air and allowed to stir shielded from light
overnight. The solvent was removed under reduced pressure and the product purified by
column chromatography (Basic alumina, 50% EtOAc in Hexanes) to yield 58 mg (47%) of 1-
CN, a dark green solid. Crystals of 1-CN were grown from slow evaporation of a
methanol/dichloromethane mixture in air at room temperature. IR (solid) νmax (cm⁻¹): 2958,
2925, 2866, 2547, 1635, 1520, 1440, 1360, 1173, 1062, 982, 835, 786, 742, 644, 555, 511. EPR: (ca. 0.2 mM in 2-methyltetrahydrofuran): apparent $a_N = 3.71$ G. Mass spectrometry ($m/z$) calculated for C$_{63}$H$_{72}$BN$_9$O$_4$Zn: 1094.5165 (M+H)$^+$, found: 1094.5164 (M+H)$^+$.

3'-(tert-butyl)-4'-hydroxy-6-methyl-[1,1'-biphenyl]-3-carboxaldehyde (98). To a 100 mL Schlenk flask, 1.40 g (5.07 mmol) of 16, 1.00 g (5.02 mmol) of 97, and 400 mg (0.35 mmol) of Pd(PPh$_3$)$_4$ were added with 20 mL tetrahydrofuran under a nitrogen atmosphere. Using a purged syringe, 8 mL of a nitrogen bubbled 2M K$_2$CO$_3$ solution was added to the reaction mixture. Under nitrogen purge, a condenser was attached to the reaction vessel and the reaction was heated to reflux while shielded from light for 3 days. Once the reaction was complete by TLC, the mixture was cooled to room temperature and 30 mL water was added. The reaction was then diluted with ethyl acetate and transferred to a separatory funnel where the organic layer was washed with saturated NaCl solution, dried over Na$_2$SO$_4$, and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO$_2$, 20% EtOAc in Hexanes) to yield 1.41 g (>95%) of 98, a light yellow solid. $^1$H NMR (400 MHz, DMSO-d$_6$, δ): 9.98 (s, 1H), 9.54 (s, 1H), 7.73, (dd, $J = 7.8$ Hz, $J = 1.6$ Hz, 1H), 7.69 (d, $J = 1.6$ Hz, 1H), 7.48 (dd, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 2.2$ Hz, 1H), 7.04 (dd, $J = 8.1$ Hz, $J = 2.2$ Hz, 1H), 6.87 (d, $J = 8.1$ Hz, 1H), 2.32 (s, 3H), 1.36 (s, 9H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ (ppm): 193.4, 155.9, 143.3, 143.1, 135.7, 135.1, 131.8, 131.7, 130.8, 127.9, 127.6, 116.7, 35.0, 30.0, 21.5. IR (solid) $v_{\text{max}}$ (cm$^{-1}$): 3390, 3341, 2994, 2956, 2864, 2938, 2748, 1676, 1598, 1506, 1482, 1405, 1389, 1367, 1304, 1283, 1257,

5′-(tert-butyl)-6-methyl-3′,4′-dioxo-3′,4′-dihydro-[1,1′-biphenyl]-3-carboxaldehyde (99). To a 10 mL round bottom flask, 1.40 g (5.24 mmol) of 98 was added with 3 mL N,N-dimethylformamide followed by 2.94 g (10.51 mmol) of IBX. The reaction was sealed with a stopper and allowed to stir in the dark for 2 days. Once the reaction was complete by 1H NMR, the reaction was poured into 100 mL water, diluted with ethyl acetate, and transferred to a separatory funnel. The organic layer was washed three times with saturated NaHCO₃ solution, twice with saturated NaCl solution, dried over Na₂SO₄, and the solvent was removed under reduced pressure to yield 1.35 g (91%) of 99, a dark green solid. 1H NMR (400 MHz, DMSO-d₆, δ): 10.01 (s, 1H), 7.89 (m, 2 H), 7.58 (d, J = 7.6 Hz, 1H), 6.85 (d, J = 2.1 Hz, 1H), 6.38 (d, J = 2.1 Hz, 1H), 2.46 (s, 3H), 1.23 (s, 9H). 13C NMR (100 MHz, DMSO-d₆) δ (ppm): 193.0, 180.4, 179.6, 152.1, 150.1, 143.1, 139.5, 136.4, 135.1, 132.5, 130.2, 129.9, 128.0, 35.7, 29.6, 21.1. IR (solid) νₘₐₓ (cm⁻¹): 2965, 2923, 2867, 1686, 1660, 1622, 1600, 1560, 1480, 1464, 1367, 1352, 1311, 1265, 1244, 1198, 1167, 1134, 1013, 961, 938, 917, 866, 830, 800, 772, 727, 695, 654, 603, 541, 494, 457, 421. Elemental analysis: Calculated (C: 76.57, H: 6.43), Found: (C: 73.27, H: 6.55).

3′-(tert-butyl)-4′,5′-dihydroxy-6-methyl-[1,1′-biphenyl]-3-carboxaldehyde (100). To a 250 mL separatory funnel, 1.35 g (4.78 mmol) of 99 was added with 20 mL tetrahydrofuran and 1.11 g (6.24 mmol) of ascorbic acid dissolved in 20 mL water. The mixture was shaken for 5 minutes and the mixture changed color from dark green to yellow indicating quinone 99 was reduced to catechol 100. The organic layer was washed with
saturated NaCl solution, dried over Na₂SO₄, and the solvent was removed under reduced pressure to yield 1.36 g (>95%) of 100, a golden yellow solid. ¹H NMR (400 MHz, DMSO-


d₆, δ): 9.98 (s, 1H), 9.56 (s, 1H), 8.23 (s, 1H), 7.73 (dd, J = 7.7 Hz, J = 1.6 Hz, 1H), 7.67 (d, J = 1.6 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 6.69 (d, J = 2.1 Hz, 1H), 6.61 (d, J = 2.1 Hz, 1H), 2.33 (s, 3H), 1.36 (s, 9H). ¹³C NMR (100 MHz, DMSO-


d₆) δ (ppm): 193.5, 145.5, 144.9, 143.5, 143.0, 136.1, 135.0, 131.8, 131.5, 130.3, 127.7, 118.4, 114.2, 35.0, 30.1, 21.4. IR (solid) νmax (cm⁻¹): 3326, 2955, 2868, 1808, 1675, 1598, 1567, 1483, 1416, 1364, 1314, 1247, 1227, 1198, 1179, 1153, 1123, 1066, 1041, 964, 864, 820, 770, 675, 643, 607, 453.

Elemental analysis: Calculated (C: 76.03, H: 7.09), Found: (C: 71.77, H: 6.89).

2-(3’-(tert-butyl)-4’,5’-dihydroxy-6-methyl-[1,1’-biphenyl]-3-yl)-4,4,5,5-

tetramethylimidazolidine-1,3-diol (101). To an oven dried 25 mL round bottom flask, 1.28 g (4.50 mmol) of 100 was added with 1.33 g (8.97 mmol) BHA and pump purged with nitrogen five times. Using a purged syringe, 6 mL of dry and nitrogen bubbled methanol was added with light heat to dissolve the reactants. The reaction was allowed to stir under nitrogen and shielded from light at room temperature for 5 days. Once the reaction was complete by ¹H NMR, the solvent was removed under reduced pressure to yield 1.87g (>95%) crude 101, which was used directly in the synthesis of 102. ¹H NMR (400 MHz, DMSO-


d₆, δ): 7.74 (br s, 1H), 7.27 (m, 2H), 7.17 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 2.1 Hz, 1H), 6.57 (d, J = 2.1 Hz, 1H), 4.49 (s, 1H), 2.23 (s, 3H), 1.36 (s, 9H), 1.07 (s, 6H), 1.04 (s, 6H). ¹³C NMR (100 MHz, DMSO-


d₆) δ (ppm): 145.3, 143.5, 141.9, 139.9, 135.7, 133.9, 132.1, 130.3, 130.1, 127.3, 118.4, 114.3, 90.8, 66.7, 62.2, 49.2, 34.97, 30.2, 25.0, 21.4, 20.7, 17.8.
2-(3'(tert-butyl)-4',5'-dihydroxy-6-methyl-[1,1'-biphenyl]-3-yl)-4,4,5,5,-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (102). To a 250 mL round bottom flask, 1.87 g (4.51 mmol) of 101 was added with 50 mL diethyl ether, 20 mL buffer (pH = 7) solution, and chilled to 0°C. To a 125 mL separatory funnel, 1.73 g (6.82 mmol) I2 was added with 60 mL diethyl ether and added dropwise to the reaction mixture shielded from light. Once all of the I2 solution was added, the reaction was allowed to stir for 15 minutes before 100 mL buffer (pH = 7) solution was added. The mixture was transferred to a separatory funnel where the organic layer was washed once with Na2S2O3 followed by saturated NaCl solution three times. The organic layer was dried over Na2SO4 and the solvent removed under reduce pressure to yield 1.86 g (>95%) of 102, a blue solid. IR (solid) νmax (cm⁻¹): 3119, 2953, 2867, 1594, 1483, 1423, 1347, 1315, 1287, 1200, 1154, 1117, 1069, 1014, 958, 865, 819, 801, 757, 734, 692, 665, 632, 540, 516, 477, 450. EPR (X-Band, 298 K): pentet (1:2:3:2:1), aN = 7.36 G. Mass spectrometry (m/z): 410.2221 (M-H)⁻.

TpCum,MeZn(SQ-mPh-oMe-NN) (1-Me). To an oven dried 25 mL Schlenk flask, 95 mg (0.23 mmol) of 102 was added with 156 mg (0.23 mmol) Zn(OH)TpCum,Me and pump purged with nitrogen five times. Using a nitrogen purged syringe, 5 mL of dry and nitrogen bubbled dichloromethane was added to the reaction mixture under a nitrogen atmosphere. The reaction was stirred under nitrogen for 3 hours the opened to air overnight. The solvent was removed under reduced pressure and the product purified by column chromatography (Basic alumina, 50% EtOAc in Hexanes) to yield 165 mg (67%) of 1-Me, a green solid. Crystals of 1-Me were grown from slow evaporation of a methanol/dichloromethane solution in air at room temperature. IR (solid) νmax (cm⁻¹): 3182, 2955, 2869, 1657, 1602, 1486, 1438,
1345, 1256, 1204, 1155, 1129, 1074, 1022, 958, 921, 865, 813, 758, 732, 698, 665, 631, 601, 542, 471, 449. EPR: (ca. 0.2 mM in 2-methyltetrahydrofuran): apparent $a_N = 3.63$ G. Mass spectrometry ($m/z$) calculated for C$_{63}$H$_{75}$BN$_8$O$_4$Zn: 1083.5368 (M+H)$^+$, 1083.5386 (M+H)$^+$. 
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Appendix A: Valence Tautomers for Device Applications, Crystal Solvation Studies, and Solution Phase Valence Tautomerism

In this appendix, we will show how valence tautomers are potential candidates for molecular spintronics in the form of spin logic devices\textsuperscript{227,228} as depicted in Figure A-1. In both cases, the electronic properties of the synthesized molecules have potential utility and/or applications for molecular electronics.

![Diagram of a Spin Valve in a circuit turning on a light. By applying a field, B, the ferromagnetic (FM) components become aligned and spin is injected into the semiconductor, completing the circuit.]

Figure A-1

1. Cobalt Valence Tautomers and Molecular Spintronics

As D-B-A systems can be considered for molecular electronics, so too can valence tautomers be considered for their potential for molecular spintronics.\textsuperscript{227} Spintronics is a field of study that focuses on spin-transport-electronics that classically uses ferromagnetic / antiferromagnetic transition metal layers.\textsuperscript{229,230} However, there are many different types and uses for spintronic devices that even include molecular spintronics.\textsuperscript{228} Cobalt based valence
tautomers have a unique stability through their $ hs$-$ Co^{II}$ and $ ls$-$ Co^{III}$ forms that make them ideal for molecular spintronics.

Valence tautomers are defined as a class of compounds that undergo intramolecular electron transfer coupled to a spin crossover. Even though valence tautomer complexes containing Mn, Ir, and Rh have been studied, only cobalt dioxolene valence tautomeric complexes will be considered here. These tautomer in particular have been studied extensively by Abakumov, Pierpont, Dei, and Shultz.

Before jumping into valence tautomerism, it is important to understand what it means for a compound to be mixed valent. The most commonly known mixed valent compound is the Creutz-Taube ion. Even though most mixed valent systems studied consist of two metals connected by a bridging ligand, there are types of systems where the metal center is the bridge between two mixed valent organic ligands. There are three classes of mixed valent compounds as shown in Figure A-2 using a metal-ligand-metal example. It is important to use a mixed valent ligand set that has redox potentials close to the redox active valence shell of the cobalt center to facilitate the redox conversion of the metal center. For this reason, quinonate ligands have been used since the energy of the catecholate and semiquinonate redox active orbitals are very close to the d-orbitals of cobalt which allow electron transfer between the ligands and the metal center. The result of this interaction is a favorable and relatively small positive $\Delta H^0$ for the complex. The valence tautomers studied by the Shultz Group use 3,5-di-tert-butylsemiquinonate (DBSQ) and 3,5-di-tert-butylcatecholate (DBCat) as redox active ligands.
Figure A-2. The three classes of mixed valence molecules.\textsuperscript{231} Class I has no interaction between metal center charges where $\Delta Q$ is the difference in nuclear coordinate (left). Class II has a weak interaction between two metal centers where $E_{TH}$ is a thermal barrier and $\beta_{12}$ (equivalent to $H_{DA}$) is the electronic coupling matrix element (middle). Class III fully delocalizes the charges of each metal center (right).

Along with the conversion between Co$^{\text{II}}$ and Co$^{\text{III}}$ comes the d-electron reorganization required to minimize electron interaction energy in the d-orbitals of cobalt. The electron configuration of the cobalt d-block for Co$^{\text{II}}$ and Co$^{\text{III}}$ as well as an orbital diagram of the cobalt d-orbitals can be found in Figure A-3. When the valence tautomer is in the high spin Co$^{\text{II}}$ form, d-electrons are placed in the anti-bonding e$_g$ orbitals. This causes the bond order between the ligands and the metal center to decrease. Since the transition to $h$s-Co$^{\text{II}}$ increases the bond lengths of the cobalt-dioxolene bonds by occupying the e$_g$ orbitals, it also incurs a relatively large positive $\Delta S^0$ for the system because there are now more vibrational states than there were in $l$s-Co$^{\text{III}}$. Dei\textsuperscript{245} has shown this through infrared spectroscopy and DFT calculations. Transient infrared spectroscopy shows a significant difference between stretching frequencies for the Co$^{\text{II}}$ and Co$^{\text{III}}$ forms of a valence tautomer. Figure A-4 shows a comparison between a cobalt-catecholate complex with a cobalt-semiquinonate complex.
Figure A-3. Diagram of d-orbitals for cobalt d-electrons for an O₆ metal center interacting with dioxolene oxygen atom p-orbitals (left). Electron configuration of the cobalt d-block for hs-Co²⁺ and ls-Co³⁺.

Figure A-4 Infrared spectra of Co³⁺(DBCat)(tpa) (top) and Co²⁺(DBSQ)(Me₃tpa) (bottom) where tpa is tris(2-pyridylmethyl)amine and Me₃tpa is tris(6-methyl-2-pyridylmethyl)amine. Black spectra are experimental and colored spectra are calculated via DFT. Stars accentuate major differences between the two spectra. The stretch above 1600 cm⁻¹ is attributed to tpa ring breathing modes.

Thus, we can use ΔG⁰ to relate the thermodynamic properties of the system to the equilibrium between ls-Co³⁺ and hs-Co²⁺ using Eq. (A.1)
\[-RT \ln K_{VT} = \Delta G^o = \Delta H^o - T\Delta S^o\]  \hspace{1cm} \text{(A.1)}

where $K_{VT}$ is the equilibrium constant between $hs$-$Co^{II}(DBSQ)_2$ and $ls$-$Co^{III}(DBSQ)(DBCat)$. Recall that due to matching the redox potentials of the dioxolene ligands to the metal center, $\Delta H^0$ is small yet positive. Also recall that the population of the antibonding $e_g$ state in $hs$-$Co^{II}$ causes $\Delta S^0$ for the system to be large and positive. The consequence of these two facts shows that with high enough temperature, the conversion from $ls$-$Co^{III}$ to $hs$-$Co^{II}$ becomes spontaneous (sign of $\Delta G^0 = f(T)$). The temperature at which $[ls$-$Co^{III}] = [hs$-$Co^{II}]$ is $T_{1/2}$ and can be used to describe the effect of ancillary ligands on the transition.\(^{240}\) In Figure A-5\(^{240}\) we can see the relative concentrations of $ls$-$Co^{III}$ and $hs$-$Co^{II}$ based on the magnetic susceptibility for a set of cobalt valence tautomers where $\chi T = 0.475$ for $hs$-$Co^{II}$ and $\chi T = 0.375$ for $ls$-$Co^{III}$ based on Eq. (A.2)

\[\chi T = \frac{n}{8} (n + 2)\]  \hspace{1cm} \text{(A.2)}

\textbf{Figure A-5.} Magnetic susceptibility plots for Co$^{II}$(DBSQ)$_2$(4-$x$-pyridyl)$_2$ ($x$ = cyano, bromo, nitro) $C_{2h}$ symmetric valence tautomers.\(^{246}\)
where \( n \) is the number of unpaired electrons. Even though temperature is the main factor that causes the valence tautomeric transition, other external stimuli can also cause the transformation. It has been shown that valence tautomers can be converted from one form to another with the use of light\(^{240}\) or pressure.\(^{247}\)

2. **Solution Phase Valence Tautomerism**

In all previously studied \( C_{2h} \) symmetric valence tautomers, the transition between Co\(^{II}\) and Co\(^{III}\) valence tautomers were studied using crystalline samples via X-ray diffraction and magnetometry.\(^{240,241,248}\) As part of determining the viability of valence tautomers in spintronics devices (where crystalline samples are unlikely to be used due to device fabrication requirements), it was important to determine if previously studied tautomers would go through their transition as a solution. Devices were to be made of spun coat valence tautomers which would result in amorphous, solution-like conditions. Unpublished work by Shultz has shown valence tautomers incorporated into a polymer backbone can affect the amount of current allowed through a cast film as seen in Figure A-6.
As a model for amorphous films, Co$^{II}$\((3,5$\text{-}$$t$-$t$-$e$t$-t$-$e$t$-$b$-$u$-$t$-$y$-$-$o$-$-$s$-$e$m$i$-$q$-$i$n$-$o$-$n$o$-$n$ate$)_2$(4-$c$-$y$n$-$a$n$-$o$-$a$n$yl$)$\((4$-$c$-$y$n$-$a$n$-$o$-$a$n$yl)\) ("4-CNpyVT") was chosen for its well studied valence transition, EPR activity of the low spin tautomter, and the expressed desire to use this particular valence tautomer for differential current experiments. Synthesis of 4-CNpyVT is shown in Scheme A-1.$^{240,241}$

$$
\text{Scheme A-1. Synthesis of Co}^{II}(3,5$-$d$-$t$-$e$t$-$t$-$e$t$-$b$-$u$-$t$-$y$-$o$-$s$-$e$m$i$-$q$-$i$n$-$o$-$n$o$-$n$ate)_2$(4-$c$-$y$n$-$a$n$-$o$-$a$n$yl)_2$ (4-CNpyVT).
$$
Initial attempts at performing solution phase studies of $C_{2h}$ symmetric valence tautomers ran into trouble when they decomposed upon exposure to air. Proof of instability as a solution came from a simple experiment using a pure sample of 4-CNpyVT infrared spectroscopy. An initial spectrum was taken of the 4-CNpyVT record stretching frequencies associated with the pure valence tautomer. Less than 10 mg was then dissolved in DCM and shaken in air for 1 minute. The olive green solution was then drop cast and a second spectrum was recorded. The two spectra are displayed, offset for comparison in Figure A7, where a peak clearly appears at 1660 cm$^{-1}$ for the sample exposed to air.

![Figure A-7](image)

**Figure A-7.** (Left) Line bond drawing depicting aerobic decomposition of 4-CNpyVT. (Right) FTIR of 4-CNpyVT as a solid (red) and as a film cast from an aerobic solution (blue) showing the quinoidal stretching of a decomposed valence tautomer.
This stretch is attributed to the C=O stretch of an orthoquinone which arises from a decomposed valence tautomer. As oxygen binds to the cobalt center, the dioxolene ligands are displaced and form 3,5-di-tert-butyl-o-quinone. For completeness, a solution of 4-CNpyVT was prepared and drop cast on a NaCl IR plate under inert atmosphere. An IR of the dried film showed absolutely no evidence of the band at 1660 cm\(^{-1}\) which proves oxygen will destroy the compound in solution.

By preparing all solutions under inert atmosphere, initial variable temperature EPR studies were performed in a toluene solution shown in Figure A-8. While this shows an expected significant increase in 8-line cobalt hyperfine signal of the Co\(^{III}\) form of the valence tautomer.

![Figure A-8](image.png)

**Figure A-8.** Variable temperature EPR of 4-CNpyVT in toluene. Nominal \(a_{Co} = 20\) G.
The softening point of toluene causes a visible change between solution phase spectra and
frozen solution spectra. Since we only want to look at the valence tautomer as an amorphous
solution, we decided a MW 250,000 polystyrene matrix would allow us to have a greater
range in which the solution matrix would stay constant. The first attempt produced a dark
green flexible film that showed an EPR signal like the frozen solution spectra. Upon closer
inspection of the film, it was evident that there were crystallites that had formed at the edges
of the film during evaporation of solvent. When the film was placed in liquid nitrogen, the
outside rim changed from olive green to dark purple which is indicative of Co$^{III}$. The green
color for the inner, non-crystallite containing center failed to change colors. To ensure the
spectra collected were free of any crystalline material, a less concentrated solution of the
valence tautomer was made and a film was produced at about 4% (w/w) valence tautomer
loading. After a thorough visual inspection using a simple light microscope, it was concluded
that there were no crystallites present in the new film. Before recording an EPR experiment,
the film was first submerged in liquid nitrogen to check for a color change.
After sitting at 77 K for several minutes, it was evident that the color did not visibly change for the new polystyrene film. EPR at 300 K and 77 K of this same film was taken and the results shown in Figure A-9. Even though there is no color change for the polystyrene matrix, it is still valence tautomeric as evident by the anisotropic 8-line hyperfine pattern of the Co\textsuperscript{III} form. To prove the anisotropic signal is coming from lower temperature and polystyrene matrix, a model compound, displayed in Figure A-10 with its corresponding EPR spectra at 298 K and 77 K, was also suspended in polystyrene. Clearly, the low temperature causes the significant dipolar interactions even as a polystyrene matrix so polystyrene is not the cause of the anisotropy.
Figure A-10. EPR spectra of Co(III)(L)(DBSQ) at 298 K (red) and 77 K (blue) in a polystyrene matrix.

Figure A-11. Variable temperature EPR from 4 K (purple) to 280 K (black) in 20 K intervals on a polystyrene film containing 4-CNpyVT as a 4% (w/w) solution. Nominal $a_{Co} = 20$ G.

Using the same batch of non-crystallite containing polystyrene encased 4-CNpyVT, a full variable temperature EPR experiment, shown in Figure A-11 was performed with the help of former group member Dr. Robert Schmidt. By doubly integrating the spectra, an area
versus temperature plot was produced. This plot can be compared with the magnetometry data collected for a solvated crystal of 4-CNpyVT as shown in Figure A-12.\textsuperscript{240} While the magnetometry data and the integrated data do not overlay each other exactly, they both show the same general trend. It could be argued that the polystyrene is providing a greater solvation effect and causing the transition to be even broader than a solvated crystal. The solvation effect in a valence tautomer comes from the fact that the high spin Co\textsuperscript{II} (d\textsuperscript{7}) form has electrons in the e\textsubscript{g} (d\sigma*) orbitals causing the bond order to decrease and the bond lengths between the cobalt center and the dioxolene ligands to expand. Solvation and crystal packing forces play a major role in determining whether or not a given cobalt dioxolene complex is valence tautomeric and the slope of the hs-Co\textsuperscript{II} to and from ls-Co\textsuperscript{III} transition.\textsuperscript{240,241,248}

![Figure A-12. Plot of area under integrated EPR spectra from Error! Reference source not found. vs. magnetic susceptibility data collected by Dr. Robert Schmidt for 4-CNpyVT crystals solvated by toluene (left). Line drawing of 4-CNpyVT valence tautomerism and corresponding cobalt d-electrons in O\textsubscript{h} symmetry (right).]
Clearly, this valence tautomer complex is still valence tautomeric while in a solution state based on the polystyrene matrices studied. This evidence is supported further, although with caution, through crystallographic studies of solvated valence tautomers.\textsuperscript{240,248}

In conclusion, valence tautomers have the potential to become novel spintronic devices through their stable switchable forms. Using a polystyrene matrix, we have seen that valence tautomers will likely retain their tautomeric properties as an amorphous film.

3. Experimental

**General Considerations.** Infrared spectra were recorded on a Bruker Vertex 80v. EPR spectra were recorded on either an IBM Instruments ER 200D-SRC ESR spectrometer or a JEOL JES-FA100 EPR spectrometer. Compounds 103\textsuperscript{235} and 4-C\textsuperscript{241} were synthesized by reported methods.
Appendix B: Crystallographic Data

Complete crystallographic data including experimental procedures for diffraction conditions of the following complexes can be obtained through the NCSU X-ray facility.

$Tpc_{\text{Cum,Me}}Zn(SQ\text{-MePh-NN})$

<table>
<thead>
<tr>
<th>Table B1. Crystal data and structure refinement for $Tpc_{\text{Cum,Me}}Zn(SQ\text{-MePh-NN})$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
</tr>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature/K</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a/Å</td>
</tr>
<tr>
<td>b/Å</td>
</tr>
<tr>
<td>c/Å</td>
</tr>
<tr>
<td>α/°</td>
</tr>
<tr>
<td>β/°</td>
</tr>
<tr>
<td>γ/°</td>
</tr>
<tr>
<td>Volume/Å³</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$/g/cm³</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
</tr>
<tr>
<td>Radiation</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
</tr>
<tr>
<td>Index ranges</td>
</tr>
<tr>
<td>Reflections collected</td>
</tr>
<tr>
<td>Independent reflections</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
</tr>
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</table>
Table B2. Crystal data and structure refinement for $T{p^{Cum,Me}}Zn(SQ{-PhMe{-NN}})$.

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<tr>
<td>Empirical formula</td>
<td>$C_{63}H_{75}BN_8O_4Zn$</td>
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<tr>
<td>Formula weight</td>
<td>1084.49</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>30.9381(10)</td>
</tr>
<tr>
<td>b/Å</td>
<td>11.0948(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>37.0849(12)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>103.7470(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>12364.8(7)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>$\rho_{calc}$/g/cm³</td>
<td>1.165</td>
</tr>
<tr>
<td>$\mu$/mm⁻¹</td>
<td>0.947</td>
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<td>F(000)</td>
<td>4608.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.080 × 0.030 × 0.020</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54178)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>8.496 to 131.93</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-36 ≤ h ≤ 36, -13 ≤ k ≤ 12, -43 ≤ l ≤ 43</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>60342</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>10500 [R$<em>{int}$ = 0.0874, R$</em>{sigma}$ = 0.0585]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>10500/49/742</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.055</td>
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<tr>
<td>Final R indexes [I≥2σ (I)]</td>
<td>R₁ = 0.0699, wR₂ = 0.1550</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.1003, wR₂ = 0.1685</td>
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<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.48/-0.35</td>
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Table B3. Crystal data and structure refinement for Tp\textsuperscript{Cum,Me}Zn(SQ-pXylyl-NN).

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<td>GW2071</td>
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<tr>
<td>Empirical formula</td>
<td>C\textsubscript{128}H\textsubscript{154}B\textsubscript{2}N\textsubscript{16}O\textsubscript{8}Zn\textsubscript{2}</td>
</tr>
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<td>Formula weight</td>
<td>2197.02</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2\textsubscript{1}/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.3325(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>28.3571(7)</td>
</tr>
<tr>
<td>c/Å</td>
<td>34.1400(8)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>100.6200(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å\textsuperscript{3}</td>
<td>12686.3(5)</td>
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<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ\textsubscript{calc}/g/cm\textsuperscript{3}</td>
<td>1.150</td>
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<td>μ/mm\textsuperscript{1}</td>
<td>0.929</td>
</tr>
<tr>
<td>F(000)</td>
<td>4672.0</td>
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<tr>
<td>Crystal size/mm\textsuperscript{3}</td>
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</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54178)</td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
<td>6.12 to 132.968</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-15 ≤ h ≤ 14, -33 ≤ k ≤ 33, -39 ≤ l ≤ 39</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>177913</td>
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<tr>
<td>Independent reflections</td>
<td>21822 [R\textsubscript{int} = 0.0731, R\textsubscript{sigma} = 0.0363]</td>
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<tr>
<td>Data/restraints/parameters</td>
<td>21822/176/1699</td>
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<td>Goodness-of-fit on F\textsuperscript{2}</td>
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<td>Final R indexes [I&gt;2σ(I)]</td>
<td>R\textsubscript{1} = 0.0544, wR\textsubscript{2} = 0.1297</td>
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<td>Final R indexes [all data]</td>
<td>R\textsubscript{1} = 0.0768, wR\textsubscript{2} = 0.1412</td>
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<td>Largest diff. peak/hole / e Å\textsuperscript{3}</td>
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### Table B4. Crystal data and structure refinement for Tp^{Cum,Me}Zn(SQ-PhMe₄-NN).

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<tr>
<td>Empirical formula</td>
<td>C₇₂H₈₇BN₈O₄Zn</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1204.67</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>110.2(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.9485(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>34.5936(13)</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.2895(6)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>108.948(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>6521.5(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ calc / g/cm³</td>
<td>1.227</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.432</td>
</tr>
<tr>
<td>F(000)</td>
<td>2568.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.383 × 0.265 × 0.154</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>3.54 to 61.08</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-19 ≤ h ≤ 19, -49 ≤ k ≤ 49, -20 ≤ l ≤ 20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>138066</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>19942 [R_{int} = 0.0528, R_{sigma} = 0.0392]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>19942/44/813</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.044</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ(I)]</td>
<td>R₁ = 0.0536, wR₂ = 0.1254</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0766, wR₂ = 0.1356</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.57/-0.55</td>
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</table>
**Table B5. Crystal data and structure refinement for Tp\textsuperscript{Cum,Me}Zn(SQ-T\textsubscript{2}-NN).**

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<td>Identification code</td>
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<tr>
<td>Empirical formula</td>
<td>C\textsubscript{64}H\textsubscript{73}BN\textsubscript{8}O\textsubscript{4}S\textsubscript{2}Zn</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1158.60</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>110.2(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2\textsubscript{1}/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>20.6545(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>16.4166(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>21.3372(5)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>108.5680(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å\textsuperscript{3}</td>
<td>6858.3(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ\textsubscript{calc}/g/cm\textsuperscript{3}</td>
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<td>μ/µm\textsuperscript{-1}</td>
<td>0.467</td>
</tr>
<tr>
<td>F(000)</td>
<td>2448.0</td>
</tr>
<tr>
<td>Crystal size/mm\textsuperscript{3}</td>
<td>0.390 × 0.230 × 0.180</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>3.2 to 63.38</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-27 ≤ h ≤ 30, -24 ≤ k ≤ 23, -31 ≤ l ≤ 31</td>
</tr>
<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
<td>23072 [R\textsubscript{int} = 0.0439]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>23072/64/765</td>
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<tr>
<td>Goodness-of-fit on F\textsuperscript{2}</td>
<td>1.027</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ(I)]</td>
<td>R\textsubscript{1} = 0.0474, wR\textsubscript{2} = 0.1288</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R\textsubscript{1} = 0.0730, wR\textsubscript{2} = 0.1437</td>
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<tr>
<td>Largest diff. peak/hole / e Å\textsuperscript{-3}</td>
<td>1.55/-0.74</td>
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</table>
### Table B6. Crystal data and structure refinement for Tp\textsuperscript{Cum,MeZn}(SQ-mPh-NN).

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<td>Empirical formula</td>
<td>C\textsubscript{62}H\textsubscript{73}BN\textsubscript{8}O\textsubscript{4}Zn</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1070.46</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>110</td>
</tr>
<tr>
<td>Space group</td>
<td>P2\textsubscript{1}/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>17.902(4)</td>
</tr>
<tr>
<td>b/Å</td>
<td>17.913(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>22.664(5)</td>
</tr>
<tr>
<td>α/°</td>
<td>90.00</td>
</tr>
<tr>
<td>β/°</td>
<td>128.361(5)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90.00</td>
</tr>
<tr>
<td>Volume/Å\textsuperscript{3}</td>
<td>5699(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ\textsubscript{calc}/g/cm\textsuperscript{3}</td>
<td>1.248</td>
</tr>
<tr>
<td>μ/mm\textsuperscript{-1}</td>
<td>0.485</td>
</tr>
<tr>
<td>F(000)</td>
<td>2272.0</td>
</tr>
<tr>
<td>Crystal size/mm\textsuperscript{3}</td>
<td>0.38 × 0.36 × 0.10</td>
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<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>3.68 to 74.88</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-28 ≤ h ≤ 27, -28 ≤ k ≤ 28, -37 ≤ l ≤ 37</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>581538</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>R\textsubscript{int} = 0.0526</td>
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<tr>
<td>Data/restraints/parameters</td>
<td>25853/0/701</td>
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<td>Goodness-of-fit on F\textsuperscript{2}</td>
<td>1.024</td>
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<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R\textsubscript{1} = 0.0455, wR\textsubscript{2} = 0.1068</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R\textsubscript{1} = 0.0947, wR\textsubscript{2} = 0.1261</td>
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<tr>
<td>Largest diff. peak/hole / e Å\textsuperscript{-3}</td>
<td>0.71/-0.51</td>
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**Table B7. Crystal data and structure refinement for Tp\textsuperscript{Cum,Me}Zn(SQ-(3,5)T-NN).**

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<tbody>
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<td>Empirical formula</td>
<td>C\textsubscript{57.43}BN\textsubscript{9}O\textsubscript{4}SZn</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>Temperature/K</td>
<td>110.48</td>
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<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.2320(9)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.1339(10)</td>
</tr>
<tr>
<td>c/Å</td>
<td>17.6859(13)</td>
</tr>
<tr>
<td>α/°</td>
<td>68.149(2)</td>
</tr>
<tr>
<td>β/°</td>
<td>75.795(3)</td>
</tr>
<tr>
<td>γ/°</td>
<td>88.765(3)</td>
</tr>
<tr>
<td>Volume/Å(^3)</td>
<td>2967.1(4)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) g/cm(^3)</td>
<td>1.1060</td>
</tr>
<tr>
<td>(\mu) mm(^{-1})</td>
<td>0.497</td>
</tr>
<tr>
<td>F(000)</td>
<td>982.5</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo ((\lambda = 0.71073))</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>2.56 to 62.32</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-19 (\leq) h (\leq) 19, -20 (\leq) k (\leq) 20, -25 (\leq) l (\leq) 25</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>133200</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>19114 ([R_{int} = 0.0290, R_{\text{sigma}} = 0.0221])</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>19114/0/793</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.946</td>
</tr>
<tr>
<td>Final R indexes [(I \geq 2\sigma (I))]</td>
<td>(R_1 = 0.1290)</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>(R_1 = 0.1558, wR_2 = 0.4427)</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å(^3)</td>
<td>6.92/-1.08</td>
</tr>
</tbody>
</table>
Table B8. Crystal data and structure refinement for $T_{p}^{Cum,MeZn}(SQ-(2,4)T-NN)$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>rds338_0m</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{165}$B$</em>{29}$O$<em>{15}$S$</em>{4}$Zn$_{4}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>3028.47</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>99.93</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>22.7963(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>33.5026(11)</td>
</tr>
<tr>
<td>c/Å</td>
<td>26.5572(8)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>100.9330(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å$^3$</td>
<td>19914.5(11)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>$\rho$ calc g/cm$^3$</td>
<td>1.010</td>
</tr>
<tr>
<td>μ/mm$^{-1}$</td>
<td>0.573</td>
</tr>
<tr>
<td>F(000)</td>
<td>6008.0</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα ($\lambda = 0.71073$)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>2.188 to 41.804</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-22 ≤ h ≤ 22, -33 ≤ k ≤ 32, -26 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>110992</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>21037 [R$<em>{int} = 0.1187$, R$</em>{sigma} = 0.1152$]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>21037/0/893</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>3.070</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R$_1 = 0.2174$, wR$_2 = 0.5030$</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R$_1 = 0.3322$, wR$_2 = 0.5404$</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å$^{-3}$</td>
<td>1.84/-1.59</td>
</tr>
</tbody>
</table>


### Table B9. Crystal data and structure refinement for Tp\textsuperscript{Cum,Me}Zn(SQ-mPhoNO\textsubscript{2}-NN).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>rds061_0ma</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{65}H\textsubscript{76}BCl\textsubscript{0.12}N\textsubscript{9}O\textsubscript{6}Zn</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1159.95</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>296(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbcn</td>
</tr>
<tr>
<td>a/Å</td>
<td>28.1497(12)</td>
</tr>
<tr>
<td>b/Å</td>
<td>18.2037(9)</td>
</tr>
<tr>
<td>c/Å</td>
<td>25.6416(12)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å\textsuperscript{3}</td>
<td>13139.5(11)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>(\rho_{\text{calc}})/g/cm\textsuperscript{3}</td>
<td>1.173</td>
</tr>
<tr>
<td>(\mu)/mm\textsuperscript{-1}</td>
<td>0.433</td>
</tr>
<tr>
<td>F(000)</td>
<td>4913.0</td>
</tr>
<tr>
<td>Crystal size/mm\textsuperscript{3}</td>
<td>0.55 × 0.46 × 0.24</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoK(\alpha) ((\lambda = 0.71073))</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>3.102 to 61.052</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-40 ≤ h ≤ 24, -25 ≤ k ≤ 25, -36 ≤ l ≤ 36</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>195901</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>20045 [(R_{\text{int}} = 0.0349, R_{\text{sigma}} = 0.0221)]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>20045/0/778</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.783</td>
</tr>
<tr>
<td>Final R indexes ([I \geq 2\sigma (I)])</td>
<td>(R_1 = 0.0644, wR_2 = 0.2167)</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>(R_1 = 0.0886, wR_2 = 0.2353)</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å\textsuperscript{-3}</td>
<td>1.67/-1.43</td>
</tr>
</tbody>
</table>
**TpCum,MeZn(SQ-mPhoOMe-iNN)**

**Table B10. Crystal data and structure refinement for TpZn(SQ-mPhoOMe-iNN).**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>TpZn(SQ-mPhoOMe-iNN)</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₆₃H₇₅BN₈O₅Zn₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1270.34</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>110.2</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>11.8324(4)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.5602(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>19.5064(7)</td>
</tr>
<tr>
<td>α/°</td>
<td>87.785(2)</td>
</tr>
<tr>
<td>β/°</td>
<td>82.487(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>78.794(2)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>3267.9(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρcalc/g/cm³</td>
<td>1.291</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.593</td>
</tr>
<tr>
<td>F(000)</td>
<td>1336.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.210 × 0.200 × 0.200</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>3.88 to 52.74</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14 ≤ h ≤ 13, -18 ≤ k ≤ 18, -23 ≤ l ≤ 24</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>52366</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>13257 [R_{int} = 0.0246]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>13257/0/774</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.038</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R₁ = 0.0490, wR₂ = 0.1370</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0610, wR₂ = 0.1470</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>1.01/-1.50</td>
</tr>
</tbody>
</table>
**Tp\textsuperscript{Cum,Me}Zn(SQ-mPhoCN-NN)**

<table>
<thead>
<tr>
<th>Table B11. Crystal data and structure refinement for Tp\textsuperscript{Cum,Me}Zn(SQ-mPhoCN-NN).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Identification code</strong></td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
</tr>
<tr>
<td><strong>α/°</strong></td>
</tr>
<tr>
<td><strong>β/°</strong></td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
</tr>
<tr>
<td><strong>Volume/Å\textsuperscript{3}</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>ρ\text{calc}/g/cm\textsuperscript{3}</strong></td>
</tr>
<tr>
<td><strong>μ/mm\textsuperscript{-1}</strong></td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
</tr>
<tr>
<td><strong>2Θ range for data collection/°</strong></td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F\textsuperscript{2}</strong></td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;2σ (I)]</strong></td>
</tr>
<tr>
<td><strong>Final R indexes [all data]</strong></td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å\textsuperscript{-3}</strong></td>
</tr>
</tbody>
</table>
Table B12. Crystal data and structure refinement for $\text{Tp}^{\text{Cum,MeZn}(\text{SQ-mPhoMe-NN})}$. 

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>rds132</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>$C_{63}H_{75}BN_8O_4Zn$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1084.49</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>110</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>14.4507(7)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>18.2789(7)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>22.7894(10)</td>
</tr>
<tr>
<td>$\alpha$/°</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>97.460(2)</td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å$^3$</td>
<td>5968.7(5)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$/g/cm$^3$</td>
<td>1.207</td>
</tr>
<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>0.464</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>2304.0</td>
</tr>
<tr>
<td>Crystal size/mm$^3$</td>
<td>$0.600 \times 0.410 \times 0.240$</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα ($\lambda = 0.71073$)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>2.86 to 54.96</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-18 \leq h \leq 18, -23 \leq k \leq 23, -29 \leq l \leq 29$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>105192</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>$R_{\text{int}} = 0.0309$</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>13674/15/714</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.121</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ(I)]</td>
<td>$R_1 = 0.0866, wR_2 = 0.1891$</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>$R_1 = 0.1059, wR_2 = 0.2017$</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å$^{-3}$</td>
<td>1.47/-1.08</td>
</tr>
</tbody>
</table>
Table B13. Crystal data and structure refinement for Tp\textsuperscript{Cum,Me}Zn(SQ-Ph-2-NO\textsubscript{2}).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>rds062_SQPh2NO2</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{123.5}H\textsubscript{135.5}B\textsubscript{2}N\textsubscript{14}O\textsubscript{8}Zn\textsubscript{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>2096.31</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>110.2(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P\textsubscript{2}1/n</td>
</tr>
<tr>
<td>a/Å</td>
<td>22.9383(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.4976(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>39.2156(13)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>92.158(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å\textsuperscript{3}</td>
<td>11234.1(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}})/g/cm\textsuperscript{3}</td>
<td>1.239</td>
</tr>
<tr>
<td>μ/mm\textsuperscript{-1}</td>
<td>0.490</td>
</tr>
<tr>
<td>(F(000))</td>
<td>4434.0</td>
</tr>
<tr>
<td>Crystal size/mm\textsuperscript{3}</td>
<td>0.325 × 0.240 × 0.120</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα ((\lambda) = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>3.52 to 50.24</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-27 ≤ h ≤ 27, -12 ≤ k ≤ 14, -46 ≤ l ≤ 46</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>120808</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>(R_{\text{int}}) = 0.0648</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>19920/151/1422</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.021</td>
</tr>
<tr>
<td>Final R indexes ([I&gt;2\sigma(I)])</td>
<td>(R_1 = 0.0555, wR_2 = 0.1379)</td>
</tr>
<tr>
<td>Final R indexes (\text{all data})</td>
<td>(R_1 = 0.0875, wR_2 = 0.1608)</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å\textsuperscript{-3}</td>
<td>1.71/-0.84</td>
</tr>
</tbody>
</table>