ABSTRACT

HONG, YOUNG-RAE Structure-Property Relationships for Electron Transfer Kinetics in Metal Tris(bipyridine) Core Dendrimers (under the direction of Dr. Christopher B. Gorman)

Structure-property relationships in the redox-active core dendrimers were systematically studied by probing the rate and driving force for electron transfer. An isostructural series of redox-active, metal tris(bipyridine) core dendrimers were synthesized for this purpose. Various synthetic routes were attempted to introduce the bulky dendritic moieties to the bipyridine units with high yields. Heterogeneous electron transfer kinetics was studied by electrochemical methods. In the second generation of these dendrimers, a large attenuation of electron transfer rate was observed qualitatively. A newly designed thin layer electrode was constructed and utilized to study heterogeneous electron transfer kinetics in the second generation dendrimers. In the finite condition, the slow heterogeneous electron transfer kinetics in second generation dendrimers could be studied by computer simulation. Homogeneous electron self-exchange kinetics was studied by nuclear magnetic resonance spectroscopy. The rate attenuation of electron transfer with dendrimer generation was not the same as the behavior found in heterogeneous, electrochemical electron transfer rate determinations. While a large attenuation was observed between the zeroth and first generation, the attenuation of electron transfer between the first and second generation was insignificant. This was rationalized by the concept of core mobility. The redox core in slow exchange limit can move in a non-rate
limiting fashion toward a neighboring redox core with the result that the structural effect of the dendrimer is reduced and electron transfer is facilitated in larger dendrimers. For further studies, thermodynamic activation parameters were also obtained by variable temperature nuclear magnetic resonance studies.
Structure-Property Relationships for Electron Transfer Kinetics in Metal Tris(bipyridine) Core Dendrimers

By

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A Dissertation Submitted to the Graduate Faculty of North Carolina State University in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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July 1, 2005

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Graduate School Representative
To my loving parents, Hyun Joung, and Celine

사랑하는 나의 부모님, 나의 아내 현정, 그리고 딸 세린에게
Biography

Young-Rae Hong was born in Incheon, Korea on December 4, 1972 to Soong Koon Hong and Kyung Myo Chun. He received his primary and secondary education from the local schools where he met his future wife, Hyun Joung. After graduating from the high school in 1991, he attended Dankook University and received a B.S. in chemistry in 1995. In 1996, he began the graduate study in Korea University under the direction of Dr. Jung-Il Jin and received a M.S. in organic chemistry in 1999. For pursuing more challenges in chemistry and life, he decided to study abroad and moved to Raleigh, North Carolina in July 2000 to attend graduated school in chemistry at North Carolina State University. Young-Rae pursued a Ph.D. under the direction of Dr. Christopher B. Gorman and received his Ph.D. in chemistry in July 2005.
Acknowledgements

First and foremost, I would like to acknowledge my parents. Without their lifelong supports and love throughout my life, I would not be the person who I am today. I would especially like to thank my wife, Hyun Joung and five month old daughter, Celine. They always be there and believe in me whenever I need them.

I would like to acknowledge Dr. Christopher B. Gorman for his support and guidance throughout my research career. He showed me how to access scientific problems and find a right solution. His hospitality for me as well as scientific knowledge made me successfully complete Ph.D. program here in NC State.

I would like to acknowledge past and present members of the Gorman group; I met Syzmon Dembowy and Aneta Dembowa here in NC State and they became my best friends. We talked a lot about science and many other issues and spent lots of time together. I can not forget those valuable times with you guys. I also would like to thank Jennifer Areys, Matthew Lewis and Anil Sharma. They spent lots of their valuable time for reviewing my dissertation. I also would like to thank Dr. Drew Wassel, Dr. Stephan Kraemer, and Dr. Tyson Chasse. They gave me many advice and helps about science and life in US. I will miss you guys. Namjin Kim is my Korean lab mate. We and our family spent lots of time together. It was great time with you Namjin ‘HYUNG’.
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Chapter 1

Introduction and Overview of Dendritic Encapsulation
1.1. Introduction

Understanding the structure-property relationships of functional materials is important because it not only provides fundamental knowledge of a material but also makes it possible to precisely control its properties. The structural and conformational effects on the properties of functional materials can be studied by observing property changes with systematic variation of molecular structures.

One of the most interesting molecules for this purpose is a dendrimer. The dendrimer is the highly branched globular shape molecule. It has a unique structure which can be systematically varied in several ways, most simply by variation in the numbers of layers of the repeating unit (e.g. the generation of the dendrimer). Functionalities with measurable properties can be introduced via chemical synthesis in several distinct places throughout the dendrimer structure and the effects of systematic structural variation on the original properties can be studied by various analytical techniques.1-7

Encapsulation of a functional core by bulky dendritic moieties recently has received great attention in various research fields such as molecular electronics and bio-mimetic systems.7-10 As the layer of bulky dendritic unit is increased, the functional core is shielded from the outside environments such as solvents, small molecules, and electrons (Figure 1.1).1, 4, 6
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Figure 1.1. Schematic illustration for the concept of dendritic encapsulation.

This molecular encapsulation of the functional core has shown various interesting effects on the original properties such as electron transfer attenuation,\textsuperscript{6, 10} and luminescence enhancement.\textsuperscript{11}

One goal of this Chapter is to review these behaviors and establish rationale for the new structure-property studies that will be described in subsequent chapters.

1.2. Dendrimer structure and synthetic approaches

Before discussing the properties of dendrimers, a short description of their structure and general methods for their synthesis are given. Dendrimers are globular shape macromolecules which have branched repeating units. Three distinct structural units can be distinguished within a dendrimer: a core or focal unit, layers of branched repeating units, and periphery units (Figure 1.2). The core is the central unit of the dendrimer from
which layers of repeating units emanate. The repeat units are the branched moieties which generate the topographic layers within the dendrimer (generation). Finally, the peripheral units cap each branch.

![Dendrimer Structure](image)

**Figure 1.2.** The example structure of a dendrimer: the second generation is shown here.

Two general methodologies used for the synthesis of dendrimers are divergent and convergent approaches (Figure 1.3). The divergent approach was first developed by Tomalia\textsuperscript{12, 13} and Newkome\textsuperscript{14} in the mid 1980s. In this approach, growth is initiated from the core and continues outward by the repetition of coupling and activation cycles. However, as the generation of dendrimer increases, the number of reactions required at
the periphery increases exponentially. Because of this large increase, incomplete reactions (even with excess reagent) and side reactions will eventually occur during the reaction causing structural flaws and polydispersity in higher generation dendrimers.

Figure 1.3. General methodologies for dendrimer synthesis.
To overcome these problems, an alternative synthetic strategy, called the convergent approach, was developed by Hawker and Frèchet in late 1980s. In this approach, the growth starts at the periphery of the dendrimer and continues inward to the central core by a stepwise fashion. After stepwise synthesis of the dendritic wedge or dendron, the focal group of the dendron is finally activated and attached to the central core completing the construction of the dendrimer. Because the intermediate products can be purified after each step, the resulting dendrimers have high monodispersity. However, as the growth continues, steric hindrance limits another addition of monomer to the buried focal point resulting in low yields and difficulties in synthesizing very large dendrimers. In spite of these limitations, this method provides relatively easy control over structure by stepwise reactions, the ability to precisely introduce functionalities throughout the structure, and high purity making it an attractive approach for designing of functional materials.

1.3. Dendrimers with Functional Core

Although various molecular fragments are available for the dendrimer synthesis, units with measurable properties have received the most attention. Molecular encapsulation by bulky dendritic units can be studied by observing the variation of photophysical or electrochemical properties of the core as a function of dendrimer generation. Thus, many dendrimers with photoactive or redox-active core have been prepared and intensively studied.
1.3.1 Encapsulation Effects on Photoactive core dendrimers

The bulky dendritic units in photoactive core dendrimers can enhance the solubility and processibility of the core resulting in more flexibility for device fabrication. However, most studies with photoactive dendrimers have been concentrated on the effects of the site isolation of the photoactive core.

Intermolecular interaction between chromophores and with small molecule quenchers such as triplet oxygen, has resulted in undesirable luminescent quenching leading to a low luminescent efficiency in many molecular dyes. By radial encapsulation of the chromophore core with bulky dendritic units, these can be reduced and luminescent efficiency can be increased.

The first photophysical probe for the microenvironment near the dendritic core was synthesized and studied by Hawker and co-workers. The absorption maximum shift of 4-(N-methylamino)-1-nitrobenzene core moiety was studied as a function of dendrimer generation. The absorbance maximum in chloroform shifted dramatically between the third and fourth generations (from 372 nm to 379 nm), consistent with the core residing in a more polar microenvironment generated by polar polyether dendron. This result suggested that only large dendrimers can efficiently encapsulate their core shielding it from the exterior environment.

Inoue and co-workers prepared dendritic “caged” porphyrin-zinc complexes up to the fourth-generation (Figure 1.4). The zinc porphyrin core was encapsulated by aryl ether dendrons with methoxy group on the periphery and their fluorescence was studied. Fluorescence of the fourth generation dendrimer was more efficiently quenched by small
quencher, vitamin K₃, while the fluorescence quenching by the first generation free base
dendrimer as a large quencher was completely blocked. It was suggested that the
dendritic repeating unit in the fourth generation behaved as a steric shield against access
of a larger quencher to the core, but served as a trap for small molecules.

Figure 1.4. Aida’s zinc porphyrin core dendrimers.

Aida and co-workers prepared also zinc porphyrin core dendrimers with
carboxylic groups on the periphery (Figure 1.4).²⁴ The UV-vis absorption spectrum of the
second and fourth generation dendrimers showed that the absorbance of the smaller
dendrimer was strongly influenced by the addition of methyl viologen (MV²⁺) or
negatively charged naphthalene sulfonate (NS⁻) electron acceptor, while the absorbance
of the higher generation dendrimer was not affected by the addition of these electron
acceptors. Fluorescence quenching studies also showed the fluorescence of the lower
generation dendrimers was more efficiently quenched by MV²⁺ than the fourth generation.
dendrimer. This behavior suggested that the lower generation dendrimer has more open structure compared with the higher generation dendrimer and allows the access of electron acceptors to the core.

Aida and co-workers also extended the generation of zinc porphyrin core dendrimers up to the fifth generation and studied their properties (Figure 1.4).\textsuperscript{24, 25} The Soret band of these dendrimers became solvent independent as the generation increased. This result again suggested that the core was more shielded from solvent molecules by dendrons in higher generations.

Vögtle, Balzani and co-workers utilized bidentate bipyridine ligands and a ruthenium metal as a core unit and synthesized Ru(bpy)\textsubscript{3}\textsuperscript{2+} core dendrimers up to the third generation (Figure 1.5).\textsuperscript{26}

\textbf{Figure 1.5.} Vögtle and Balzani’s Ru(bipyridine) core dendrimers

\begin{center}
\includegraphics[width=\textwidth]{image.png}
\end{center}

\textit{R = -OCH\textsubscript{3}}
The emission of the higher generation dendrimer core was more intense and exhibited a longer excited-state lifetime compared with the reference Ru(bpy)$_3^{2+}$ in oxygenated solutions. This result can be explained by dendritic shielding effects of the core from dioxygen quenching.

Frèchet and Kawa prepared Lanthanide core dendrimers up to the fourth generation utilizing the ionic interaction between carboxylate groups and a trivalent lanthanide ion (Er$^{3+}$, Eu$^{3+}$, or Tb$^{3+}$). The luminescent properties of these dendrimers were investigated in both solution and bulk film and enhanced luminescence was observed as dendrimer generation increased. This enhancement is attributed to both the ‘antenna effect’, the excitation energy transfer from nonconjugated aryl ether dendritic units to the Ln$^{3+}$ core, and the site isolation of Ln$^{3+}$ core preventing their self-quenching.

The concept of encapsulation has been utilized in the field of organic light-emitting diodes. Freeman and coworkers prepared a family of emissive, hole-transporting dendrimers. They showed that site isolation can inhibit intermolecular energy transfer between two different core chromophores enabling simultaneous emissions. This example can be applied toward a potential color tunable OLED device which can be fabricated by simply adjusting the ratio of dendritic chromophores in the device.

Lupton and co-workers showed that dendritic encapsulation could be adapted to balancing charge transport in OLED device The dendron branching controlled the separation between the chromophores and the charge mobility was reduced by two orders of magnitude as the size of the molecule doubled with increased branching or dendrimer generation. Additionally, an increase in chromophore separation also resulted in a
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reduction of intermolecular interactions, which reduced the red emission tail in film photoluminescence.

1.3.2 Encapsulation Effects on Redox-active core Dendrimers

Another interesting core for dendritic encapsulation studies is a redox-active unit. Like photoactive cores, the properties of redox-active cores are also influenced by dendritic encapsulation. In nature, metalloproteins are a good example of molecular encapsulation. The protein controls the rate and driving force of electron transfer to and from the redox unit via a structurally specific encapsulation of the unit by polypeptide ligands. However, detailed structural information that explicates this precise control of electron transfer by nature is not yet available. Thus, redox-active core dendrimers could be a useful probe to study nature’s ability. Moreover, better understanding of electron transfer would be useful for investigating new functional materials for molecular electronics.

It is well established that dendritic encapsulation leads to the attenuation of electron transfer rates due to the non-conducting branched dendritic shells between a redox core and an electrode surface. The effect of dendritic structure on the redox potential, however, is not well understood. The microenvironmental polarity near the redox core strongly influences its redox potential. Thus, the solvation of the core and the properties of the dendritic unit could stabilize or destabilize a redox core affecting the redox potential.

Various redox active core dendrimers have been prepared to study the effect of
molecular encapsulation on their electrochemical properties. Diederich and co-workers prepared a series of zinc porphyrin core dendrimers with ether amide repeating units.16 These molecules served as a model for electron transfer proteins such as cytochrome \( c \) and chlorophylls. Computer simulation on the third generation of this dendrimer suggested that it has a globular shape with a diameter of 4 nm. The size and shape of this molecule resemble the heme protein cytochrome \( c \) which also has a porphyrin redox center. The electrochemical properties of these dendrimers were studied by cyclic voltammetry. The zinc porphyrin based redox potential for the first reduction process shifted to more negative values as the dendrimer generation increased. This result is interpreted to mean that the negative charge build-up at the porphyrin core is less thermodynamically favored in the dendritic environment compared to the solvent. More specifically, microenvironment generated by the dendritic unit was more electron rich than the solvent. This microenvironment also makes the oxidation of the porphyrin core thermodynamically favored and displayed the negative shift of the redox potential for the first oxidation process of the core. The electrochemical data for these dendrimers also showed the rate of electron transfer becomes slower as the dendrimer generation increases.

A series of iron porphyrin core dendrimers were also prepared by Diederich and co-workers.49 These dendrimers had hydrophilic ethylene glycol units at the periphery providing solubility in polar solvent such as water. The electrochemical data indicated that the polarity of the solvent strongly influenced the redox potential of the core. In methylene chloride, both the first and second generation dendrimers displayed only a
small difference in the redox potential of the core. In water, however, a larger shift in redox potential of the iron porphyrin core was observed between the first and the second generation. In organic solvents such as methylene chloride, both the first and second generation dendrimers are exposed to similar microenvironments resulting in small difference in the redox potential of the core. In aqueous solution, however the loosely packed first generation dendrimers with hydrophilic units in the periphery allow the access of polar water molecules near the core while the more densely packed second generation dendrimers hindered the aqueous solvation of the core. The lack of polar water molecules near core caused destabilization of the oxidized form shifting the redox potential to a more positive value.

Frèchet and co-workers prepared zinc porphyrin core dendrimers up to the fourth generation (Figure 1.6).\textsuperscript{50} This series of dendrimers nicely displayed the effect of dendritic encapsulation on the rate of electron transfer. The qualitative electrochemical data illustrated that encapsulation of a porphyrin core with even a small generation dendrimer can significantly lower the rate of electron transfer reaction between the core and electrode surface (Figure 1.7). The attenuation of the electron transfer rate was more pronounced as larger generation dendrimers were employed. This result was explained by the increase of distance between the core and electrode surface by site isolation of the core.

Chow and co-workers reported the synthesis of terpyridine based iron core dendrimers up to the fourth generation.\textsuperscript{51}
Chapter 1: Dendrimers with functional cores

Figure 1.6. Fréchet’s zinc porphyrin core dendrimers.

Figure 1.7. Cyclic voltammograms for Fréchet’s zinc porphyrin dendrimers; Oxidation (left) and Reduction (Right) currents in mA scale.
Cyclic voltammetry studies also displayed similar attenuation behavior of electron transfer kinetics as on iron-terpyridine core was shielded by higher generation dendritic units.

More recently, Kaifer and co-workers illustrated the effect of molecular orientation on the rate of electron transfer using unsymmetrical dendrimers and a modified electrode (Figure 1.8). They prepared asymmetric ferrocene core dendrimers with carboxylic acid groups at the periphery. The pKa of the carboxylic acid in these dendrimers is in the range 4.5-6 and multiple negative charges could build up at the dendrimer periphery in neutral pH. These charges could be utilized to orient the unsymmetric dendrimers at the electrode surface. Cystamine was immobilized at the electrode surface to give a positively charged surface through an experimental pH range of 3-7. At low pH, the peripheral carboxylic acid groups were protonated and the ferrocene core could be freely oriented toward the electrode surface resulting in fast electron transfer. At neutral pH, however, interaction between the negative charged carboxylic group and the positive charged electrode surface forced the ferrocene core to orient so that the distance from electrode surface was maximized resulting in very slow electron transfer. This example nicely illustrates the importance of dendrimer conformation and core position as well as dendrimer structures for effective encapsulation.

Kaifer and Balzani independently studied the electrochemical behavior of 4,4’-bipyridinium core dendrimers up to the third generation.
Figure 1.8. Illustration of interfacial orientation of Kaifer’s dendrimers(right) and their experimental and simulated SWV.

Quantitative electrochemical data showed no evidence of significant attenuation of electron transfer rate as the dendrimer generation increased. This anomalous behavior could be rationalized by considering the relatively open structure of these dendrimers. Two extended dendrons and low molecular weight compared with previous dendrimers result in a more open conformation facilitating the electron transfer.
Over the past few years, more quantitative and systematic studies for dendritic encapsulation have been done by Gorman and co-workers using an iron-sulfur cluster core. In nature, iron-sulfur proteins give a good example for molecular encapsulation showing the precise control of redox properties of iron-sulfur cluster. Thus, iron-sulfur core dendrimers are the best candidate to mimic nature’s complex structures and understand how nature precisely controls the properties of its redox centers by polypeptide based encapsulation.

For this purpose, two series of iron-sulfur core dendrimers were prepared up to the fourth generation.\textsuperscript{8,55-58} One series had “flexible” architectures carrying Frèchet’s aryl ether repeating units while the other series had relatively “rigid” architectures carrying Moore’s phenylacetylene repeating units (Figure 1.9 and 1.10). Quantitative electrochemical data to probe the effects of dendritic encapsulation were obtained using these two series of dendrimers. The rate of heterogeneous electron transfer versus molecular weight was attenuated more effectively at the “rigid” series of dendrimer compared with the “flexible” series of dendrimers. This result was rationalized by computer modeling. Simulation results indicated that the iron-sulfur core is more mobile in the flexible series of dendrimers resulting in the increased possibilities of locating the core near the periphery. Meanwhile, the relatively immobile iron-sulfur core of the “rigid” series of dendrimers is located on average near the center of dendrimers. Thus, the distance for electron transfer between the core and electrode surface is shorter in the “flexible” series compared with in the “rigid” series leading to a faster rate of electron transfer.
Figure 1.9. Gorman’s ‘flexible’ series of iron-sulfur dendrimers.
Figure 1.10. Gorman’s ‘rigid’ series of dendrimers.
The rate of electron transfer versus molecular radius, however, showed quite the opposite behavior (Figure 1.11). Electron transfer through the larger, rigid series of dendrimers was more efficient than in the smaller, flexible series of dendrimers. Although the phenylacetylene repeating units provides the larger distance between the core and electrode surface for electron transfer in the rigid series of dendrimers, the cross-conjugate $\pi$ system facilitates the through-bond electron transfer compared with relatively saturated flexible series of dendrimers.

**Figure 1.11.** Heterogeneous electron transfer rate vs molecular weight (left) and molecular size (right).

Thus, the dendritic medium as well as the distance for electron transfer has to be considered to study the effect of dendritic encapsulation in redox-active dendrimers.

Although thermodynamic redox potentials of these series of dendrimers were not strongly influenced in solution by dendrimer generation (Figure 1.12B), a large change in redox potential was observed with dendrimer generation in bulk film studies (Figure 1.12A). In bulk films, dendritic fragments exclude solvent molecules and dilute the effective concentration of counter ions generating a less polar microenvironment near the
iron-sulfur core. This nonpolar microenvironment leads to a negative shift in redox potential as the dendrimer generation increases. In contrast to the large variation in redox potentials, little change in the kinetics of charge transfer was observed with generation in dendrimer films (Figure 1.2A). This can be rationalized by introducing the concept of core mobility. A mobile redox core can permit the close approach of redox cores between dendrimers over the time scale of electron hopping through the film.

Figure 1.12. Cyclic Voltammograms of iron-sulfur dendrimers in bulk film (A and C) and solution (B).
Thus, the effective distance for electron hopping is not strongly influenced by dendrimer generation. The importance of core mobility was further supported by employing rigid dendrimers in which core mobility was limited. Both the kinetics and thermodynamics of electron transfer were influenced by generation in rigid dendrimer films (Figure 1.12C). Another interesting approach by Gorman and co-workers was studying synthetically driven conformational effects on the dendritic encapsulation. Three pairs of constitutional isomers of the second generation iron-sulfur core dendrimer were prepared (Figure 1.13). By varying the substitution pattern of repeating unit, the backfolded isomers were synthesized. The electrochemical data showed that iron-sulfur cores were more effectively encapsulated in the backfolded isomers compared with their extended counterparts. A more hydrophobic microenvironment generated by backfolded conformations make the backfolded isomers more difficult to reduce than their extended isomeric counterparts. This structural difference results in a negative redox potential shift. Longitudinal proton relaxation times indicated that backfolded isomers have a smaller and more compact conformation. These results showed that the core mobility and position in dendrimers affects the effective electron transfer distance (Figure 1.14). To determine the electron transfer rate attenuation as the results of dendritic encapsulation, the effective electron transfer distance rather than the dendrimer size plays an important role.
Figure 1.13. Gorman’s three pairs of iron-sulfur dendrimer isomers.
1.4. Summary and Outlook

For the past decade, rapid progress has been made in the field of dendrimer chemistry. Electro-active and photoactive core dendrimers are the most intensively studied functional dendrimers because of their wide range of potential application. By probing the effects on their properties of dendritic encapsulation, the structure-property relationships for functional core dendrimers can be established. This would play an important role in designing future functional materials.

Photoactive core dendrimers have displayed the effects of dendritic encapsulation such as shifts in optical absorption bands and luminescent quenching. However, recently, most work has been concentrated on a variety of energy harvesting and conversion materials. On the other hand, electro-active core dendrimers have been intensively
studied in a variety ways to understand the encapsulation effects on their electron transfer behavior. Generally, the rate of heterogeneous electron transfer between the redox-core and electrode surface is attenuated as dendrimer generation increases. Various work on electron transfer attenuation in redox-active core dendrimers have been done and this phenomenon is becoming better understood. However, the effect of dendritic encapsulation on thermodynamic redox potential of the redox core is not well established yet. The polarity of the microenvironment near core plays an important role determining the redox potential. This can be influenced by solvation of the core, the dendritic building block, and the electrolyte, making it difficult to generalize the effect of encapsulation on the redox potential.

Although tremendous work has been performed to understand the effects of the dendritic encapsulation on electron transfer, a significant amount of research is still required before we obtain a firm understanding the structure property relationship for the rate and driving force of electron transfer in redox-active core dendrimers.
1.5. References


Chapter 2

Synthetic Approaches to an Isostructural Series of Redox-Active, Metal Tris(bipyridine) Core Dendrimers

Part of this work was the subject of a publication, Hong, Y.R.; Gorman, C.B., J. Org. Chem., 2003, 68(23), 9019-9025.
2.1. Introduction

There have been various approaches to understand how dendritic units encapsulate the functional core and change its original properties.\textsuperscript{1-4} Redox-active core dendrimers are one of the most intensively studied molecules for this purpose because electron transfer between electrode and redox-active core buried in dendrimer structures can be easily studied by simple electrochemical techniques such as cyclic voltammetry. Several types of redox-active core dendrimers have been prepared and studied to better understand this encapsulation behavior by probing the rate and driving force for electron transfer.\textsuperscript{5-34} These include the illustration of the effects of dendrimer architecture\textsuperscript{1, 3, 35, 36}, conformational effects biased by dendrimer isomer\textsuperscript{37}, and the behavior of unsymmetrical dendrimers on modified electrode\textsuperscript{38}. Mostly these studies focused on the effect of dendron structures and conformation for electron transfer between redox-active core and electrode.

It is of interest to systematically vary the redox potential of the core without significant change of dendrimer structure and conformation. This would enable us to study the effects of differences in redox potential in redox-active core dendrimers while excluding those due to conformational differences between dendrimers. It also makes it possible to study homogeneous electron transfer kinetics between two different cores or electron self exchange kinetics between two different oxidation states.

To this end, a series of isostructural dendrimers carrying metal tris(bipyridine) type cores are synthesized and studied. Poly pyridine based metal complexes have been used in various dendrimers.\textsuperscript{37, 39-53} However, few synthetic methodologies are available for
introducing bulky dendrons to a bipyridine core moiety with an acceptable yield. Throughout this chapter, all synthetic efforts for a series of isostructural dendrimers are described, including an efficient route for introducing bulky dendrons to a bipyridine moiety.

2.2. Results and Discussion

2.2.1 Dendrimer Containing a Bipyridine-O-R linkage

Bis(phenoxy)isovalerate-based first generation dendritic mesylate (5) was readily available from previous studies and synthesized again with slightly modified procedure in large scale (Scheme 1).

Scheme 2.1. a

\[ X = \text{CO}_2\text{H}, 97\% \\
X = \text{CO}_2\text{CH}_3, 96\% \\
X = \text{CH}_2\text{OH}, 95\% \\
X = \text{CH}_2\text{OSO}_2\text{CH}_3, 90\% \]

\[ \text{Reagents and conditions: i) SOCl}_2, \text{MeOH}; \text{ii) benzyl chloride, K}_2\text{CO}_3, \text{18-crown-6, acetone}; \text{iii) LiAlH}_4, \text{THF}; \text{iv) MsCl, DMAP, TEA, CH}_2\text{Cl}_2. \]

The mesyl group has been known as a good leaving group for nucleophilic substitution reaction and simple SN2 reaction was thought to be an attractive way for coupling between a dendritic mesylate and a bipyridine moiety (Scheme 2.2). To introduce nucleophilic groups to a bipyridine, 4,4’-dimethoxy bipyridine (6) was treated with
HBr/acetic acid at reflux resulting in 4,4'-dihydroxy bipyridine (7) in acceptable yield. This molecule was then converted to first generation dendron (8) in excellent yield.

Scheme 2.2. 

\begin{align*}
\text{6} & \quad \xrightarrow{i} \quad 67\% \\
\text{7} + \text{5} & \quad \xrightarrow{ii} \quad 93\% \\
\text{6 (G0)} & \quad \xrightarrow{iii \text{ or } iv \text{ or } v} \quad [\text{M(6)}_3]([\text{PF}_6])_2 \\
\text{8 (G1)} & \quad \xrightarrow{iii \text{ or } iv} \quad [\text{M(8)}_3]([\text{PF}_6])_2
\end{align*}

\begin{align*}
9, \text{ M} = \text{Ru}, 40\% \\
10, \text{ M} = \text{Fe}, 82\% \\
11, \text{ M} = \text{Co}, 81\%
\end{align*}

\begin{align*}
12, \text{ M} = \text{Ru}, 22\% \\
13, \text{ M} = \text{Fe}, 39\%
\end{align*}

\(^a\) Reagents and conditions: i) HBr, AcOH; ii) K\textsubscript{2}CO\textsubscript{3}, 18-crown-6, acetone; iii) RuCl\textsubscript{3}·xH\textsubscript{2}O, NH\textsubscript{4}PF\textsubscript{6}, various solvents; iv) (NH\textsubscript{4})\textsubscript{2}Fe(SO\textsubscript{4})·6H\textsubscript{2}O, NH\textsubscript{4}PF\textsubscript{6}, various solvents; v) Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, NH\textsubscript{4}PF\textsubscript{6}, EtOH.

The candidates for core metals were selected from literature studies along with simple model complexations with 2,2'-bipyridine and several metal salts. General concerns for selection of metals were preferably mild complexation conditions, quasi-reversible
electrochemical behavior for corresponding complexes and distinct redox potentials. As the result of prescreening, ruthenium, iron and cobalt were thought to be the best candidates for core metals. Thus, both 4,4’-dimethoxy bipyridine (6, G0) and compound (8, G1) were converted to corresponding metal complexes (Scheme 2.2) and electrochemical properties of these molecules are examined by cyclic voltammetry (Figure 2.1).

![Cyclic voltammograms of compounds 9, 10, and 11 (left, G0) and 12 and 13 (right, G1) (scan rate 200 mV/s, argon-purged acetonitrile solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode).](image)

Figure 2.1. Cyclic voltammograms of compounds 9, 10, and 11 (left, G0) and 12 and 13 (right, G1) (scan rate 200 mV/s, argon-purged acetonitrile solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode).

Although the ruthenium and iron cores showed quasi-reversible electrochemical behavior for both generations (G0 and G1), the cobalt complex (11, G0) displayed irreversible metal centered oxidation. From a synthetic point of view, this route was very attractive because all reactions involved were very efficient and could be synthesized on a relatively large scale.
However, the goal of obtaining at least three dendrimer series with quasi-reversible redox behavior at distinct redox potentials could not be satisfied with this series of dendrimers.

### 2.2.2 Dendrimer Containing a Bipyridine –CH₂-OR linkage

Although the 4,4’-dimethoxy bipyridine ligand based cobalt complex (11) failed to show quasi-reversible electrochemical behavior, both 2,2’-bipyridine and 4,4’-dimethyl bipyridine based metal complexes showed electrochemical behavior desired at

![Cyclic voltammograms of metal complexes based on three different bipyridine ligands](image)

**Figure 2.2.** Cyclic voltammograms of metal complexes based on three different bipyridine ligands (scan rate 200 mV/s, argon-purged acetonitrile solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode).
three different redox potentials (Figure 2.2).

It was thought that the alkoxy group on the bipyridine ligand caused the poor electrochemical behavior for the cobalt complex. Thus, another linkage between bipyridine and dendritic fragment was sought. The criteria for this linkage are as follows. First, the linkage should be synthetically feasible using available dendritic molecules such as a dendritic alcohol (4). Second, reasonable yield is required to utilize the same scheme throughout generations. Third, the linkage has to be electrochemically inert at interested metal centered oxidation potential window. It was thought that if a methylene group was introduced between the bipyridine and dendritic alkoxy group, the resulting dendritic bipyridine ligand would give a cobalt complex which shows the desired electrochemical behavior. Two different approaches were adapted to this end (Scheme 2.3). First, a dendritic alcohol (4) was used as a nucleophile and an electrophile was introduced to the bipyridine moiety by Fraser’s method (Scheme 2.3). 4,4’-Dimethyl bipyridine (14) was converted to the electrophilic dihalomethyl derivatives (16 and 17) via TMS protected dicarbanion (15). A nucleophilic substitution reaction between the dendritic alcohol (4) and dibromomethyl bipyridine (16) was attempted varying the hydride (NaH vs KH) and the solvent (DMF vs THF), and the catalyst (18-crown-6). However, the reaction yield was unacceptably low (32%) for the preparation of higher generation dendrons.

The other approach involved the switching of the roles of the nucleophile and electrophile moieties in case above.
Scheme 2.3. a

Reagents and conditions: i) LDA, TMSCl, THF; ii) BrF₂CCF₂Br, CsF, DMF; iii) Cl₃CCCl₃, CsF, DMF; iv) K₂Cr₂O₇, H₂SO₄; v) H₂SO₄, EtOH; vi) NaBH₄, EtOH; vii) KH, 18-crown-6, THF; viii) NaH, 15-crown-5, DMF
A bipyridine derivative was used as a nucleophile and a dendritic mesylate (5) was used as an electrophile (Scheme 2.3). Although the nucleophilic bipyridine derivative (20) could be synthesized on relatively large scale with a good yield, the final coupling reaction with dendritic electrophile (5) did not give improved yields compared with the previous route. Thus, both of these routes were not pursued further.

### 2.2.3 Dendrimer Containing a Bipyridine-CH₂-R linkage

Another possible route for introducing dendritic units to the bipyridine ligand involved the direct deprotonation of 14 followed by reaction with an electrophile. Although dialkyl bipyridine could be synthesized from alkyl halides using LDA, a similar approach employing the dendritic mesylate (5) was not successful. Model studies with alkyl mesylate or triflate showed that they were not good electrophiles like the alkyl halide for LDA reaction. Thus, the bulkiness of dendrons could not be blamed for poor results.

As another approach, the dendritic alcohol (5) was converted to the dendritic chloride as a dendritic halide and reacted with 14 resulting in similar poor results (Scheme 2.4). Thus, dendritic bromide was thought to be the best candidate for an electrophile and two different synthetic approaches were attempted (Scheme 2.5). Although CBr₄ or PBr₃ has been frequently used in the literature for direct conversion of a dendritic alcohol to a dendritic bromide, it was found that in our hands, yields were variable and column chromatography was required to get pure samples.
Scheme 2.4.  

\[
\begin{align*}
\text{5, } X &= -\text{OSO}_2\text{CH}_3 \\
\text{23, } X &= -\text{OSO}_2\text{CH}_3 \\
\text{22, } X &= -\text{OH} \\
\text{24, } X &= -\text{OSO}_2\text{CF}_3 \\
\text{25} \quad &+ \quad 14 \quad \xrightarrow{\text{LDA, THF}} \quad \text{X} \\
\text{MsCl, TEA, DMAP} \quad &+ \quad \text{CH}_2\text{Cl}_2, 83\% \\
\text{Tf}_2\text{O, TEA, DMAP} \quad &+ \quad \text{CH}_2\text{Cl}_2, 63\% \\
\text{27, } X &= -\text{CH}_2\text{Cl}, 75\% \\
\end{align*}
\]
Instead of this time consuming route, a high yielding, two step reaction sequence was employed to obtain dendritic bromide. The dendritic alcohol (4) could be converted to the dendritic mesylate (5) with excellent yield (Scheme 2.1). The dendritic mesylate (5) was then converted to the dendritic bromide (36) using sodium bromide and phase transfer catalyst, tetrabutylammonium bromide. However, the coupling reaction between 14 and 36 using LDA gave the desired product (37) with unacceptably low yields (30%) and reactions with higher generation dendrons (G2 and G3) were not successful.

Another attempt involved introducing a simple protecting group at the end of the first generation dendron in order to skip low yield LDA reactions for higher generation (Scheme 2.6). However, even first generation dendron could not be synthesized with this route.

Variation of end group halide, temperature, adding additives like TMEDA, and the use of strong base like dimysyl anion did not give improved results (Table 1). According to these results and previous model studies (Scheme 2.4), it was thought that the structure and reactivity of the biscarbanion along with the leaving group play an important role in this reaction. Indeed, when potassium diisopropyl amide was used, dramatic increased yields were observed (Table 1). Although this route was not successful for a further reaction (because solubility of 34), KDA reaction could be adapted to previous route (Scheme 2.5) resulting in the first generation dendron with excellent yields.
Scheme 2.5.  

Reagents and conditions: i) CBr₄, PPh₃, CHCl₃/CH₃CN; ii) PBr₃/toluene; iii) NaBr, (n-Bu)₄NBr, acetone; iv) LDA, THF, -78°C to r.t.; v) KDA, THF, -78°C.
Scheme 2.6. 

Reagents and conditions: i) CH$_3$I, K$_2$CO$_3$, 18-Crown-6, acetone; ii) LiAlH$_4$, THF; iii) MsCl, DMAP, TEA, CH$_2$Cl$_2$; iv) NaBr, (n-Bu)$_4$NBr, acetone; v) NaI, (n-Bu)$_4$NI, acetone; vi) see text; vii) HBr, AcOH; viii) K$_2$CO$_3$, 18-crown-6, DMF.
Table 2.1.

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<sup>a</sup>The mixture of starting material and product and low yields made impossible to separate products from mixture.

For higher generation (G2 and G3), bis(phenoxo)isovaleric acid (1) was reduced to the corresponding alcohol (38) and reacted with the mesylate (5 or 40) to give the dendritic alcohol (39 or 42) which could be converted to the mesylate (40 or 43) (Scheme 2.7). The second and third generation mesylates (40 and 43) could be converted to corresponding dendritic bromide (41 and 44) with high yields. The KDA reaction was also employed to the second and third generation dendrons resulting in each generation of dendritic bipyridine ligands (35 and 45) with excellent yields (Scheme 2.8). Each of the metal complexations was conducted up to the second generation to give a series of metal tris(bipyridine) core dendrimers (Scheme 2.9). It was later discovered that significant amounts of each generation dendrimer is needed to measure the homogeneous electron transfer kinetics which are discussed in Chapter 4.
Scheme 2.7.

1 \[\rightarrow\] HO[CH\_2\_OH] \[\xrightarrow{\text{i}}\] X[\(\xrightarrow{\text{ii}}\)] 38, X=-CH\_2\_OH, 95%

1 \[\rightarrow\] HO[CH\_2\_OH] \[\xrightarrow{\text{i}}\] X[\(\xrightarrow{\text{ii}}\)] 39, X=-CH\_2\_OH, 98%

1 \[\rightarrow\] HO[CH\_2\_OH] \[\xrightarrow{\text{i}}\] X[\(\xrightarrow{\text{ii}}\)] 40, X=-CH\_2\_OSO\_2\_CH\_3, 96%

1 \[\rightarrow\] HO[CH\_2\_OH] \[\xrightarrow{\text{i}}\] X[\(\xrightarrow{\text{ii}}\)] 41, X=-CH\_2\_Br, 93%

ii + iii

38 + 40 \[\xrightarrow{\text{ii}}\] 42, X=-CH\_2\_OH, 92%

ii + iii

38 + 40 \[\xrightarrow{\text{ii}}\] 43, X=-CH\_2\_OSO\_2\_CH\_3, 96%

ii + iii

38 + 40 \[\xrightarrow{\text{ii}}\] 44, X=-CH\_2\_Br, 97%

\(^a\) Reagents and conditions: i) LiAlH\_4, THF; ii) K\_2CO\_3, 18-crown-6, acetone; iii) MsCl, DMAP, TEA, CH\_2\_Cl\_2; iv) NaBr, (n-Bu)\_4NBr, acetone.
To synthesize a large amount of material requires considerable time and materials and it was decided that although the third generation dendron was available in ~500mg quantities, synthetic efforts would be concentrated on the first two generation.

Although harsh reaction conditions were required, osmium complexes up to the first generation were added to the series in later studies because of the instability of chemically oxidized ruthenium(III) complexes (Scheme 2.9) and a detailed discussion is included in Chapter 4.
Scheme 2.9.

\[
\begin{align*}
14 \text{ (G0)} & \xrightarrow{i, ii, iii, or iv} [M(G0)_3](PF_6)_2 \\
37 \text{ (G1)} & \xrightarrow{i, ii, iii, or iv} [M(G1)_3](PF_6)_2 \\
35 \text{ (G2)} & \xrightarrow{i, ii, or iii} [M(G2)_3](PF_6)_2
\end{align*}
\]

46, \( M = \text{Ru}, 76\% \\
47, \( M = \text{Fe}, 84\% \\
48, \( M = \text{Co}, 75\% \\
49, \( M = \text{Os}, 67\% \\
50, \( M = \text{Ru}, 34\% \\
51, \( M = \text{Fe}, 77\% \\
52, \( M = \text{Co}, 97\% \\
53, \( M = \text{Os}, 48\% \\
54, \( M = \text{Ru}, 69\% \\
55, \( M = \text{Fe}, 91\% \\
56, \( M = \text{Co}, 75\% \\

^a \text{Reagents and conditions: i) RuCl}_3\cdot x\text{H}_2\text{O}, \text{NH}_4\text{PF}_6, \text{various solvents; ii) (NH}_4\text{)}_2\text{Fe(SO}_4\text{)}_2\cdot 6\text{H}_2\text{O}, \text{NH}_4\text{PF}_6, \text{various solvents; iii) Co(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}, \text{NH}_4\text{PF}_6, \text{various solvents iv) (NH}_4\text{)}_2\text{OsCl}_6, \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH.}

Electrochemical behavior of both the G0 and G1 ruthenium, iron and cobalt complexes was examined by cyclic voltammetry and all showed the quasi-reversible redox wave desired (Figure 2.3). As hypothesized, a methylene linkage between the bipyridine and the dendritic unit avoids the slow electrochemical kinetics found in the alkoxy substituted cobalt tris(bipyridine) complexes. It is hypothesized that the electron donating alkoxy group on the cobalt complexes weakens the ligand fields as has been observed for alkoxy terpyridine cobalt complexes\(^{59}\) and makes it possible to undergo rate limiting spin crossover upon oxidation resulting in irreversible wave on cyclic voltammogram\(^{60}\).

In the following chapter, electrochemical behavior of these molecules will be discussed in more detail.
Figure 2.3. Cyclic voltammograms of metal complexes based on three different bipyridine ligands (scan rate 200 mV/s, argon-purged acetonitrile solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode).

2.2.4 Characterization of synthesized materials

The selected characterization data are summarized in Table 2. All three structures of dendrons verified using $^1$H-NMR and elemental analysis. MALDI usually gave successful results for ruthenium and osmium complexes. However, iron and cobalt complexes could not be characterized by MALDI possibly due to weaker binding of the dendritic ligand to the metal core compared to ruthenium or osmium complexes. FAB-
MS could be an alternative ionization technique up to the first generation. However, the molecular weight of the second generation dendrimers was out of the instrument’s available molecular range. Acceptable elemental analyses were obtained for the second generation iron and cobalt core dendrimers. Measured elemental percentage differed slightly from those calculated for ruthenium. This result was attributed to trace impurities and/or the tendency toward solvent inclusion. The presence of water or other solvents perhaps contained within the dendritic cavities leads to errors in the analyses. Overall, multiple characterization techniques confirmed all dendritic structure satisfactorily for further studies.
Table 2.2. The selected characterization data

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<th>1H-NMR</th>
<th>Mass Spectroscopy</th>
<th>Elemental Analysis</th>
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<tr>
<td>G1</td>
<td>s</td>
<td>NA$^a$</td>
</tr>
<tr>
<td>G2</td>
<td>s</td>
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<tr>
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<td>s</td>
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<tr>
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<td>s</td>
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<tr>
<td>Fe(G0)</td>
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<tr>
<td>Fe(G1)</td>
<td>s</td>
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<tr>
<td>Fe(G2)</td>
<td>s</td>
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<tr>
<td>Co(G0)</td>
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<td>Os(G0)</td>
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<tr>
<td>Os(G1)</td>
<td>s</td>
<td>3494.6, 3349.6</td>
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$^a$ not measured. $^b$ NMR data was satisfied with published data. $^c$ MALDI data. $^d$ FAB-MS data. $^e$ see text. $^f$ Mass data was satisfied. s : satisfied
2.2.5 General considerations of metal complexation

Although metal complexation was achieved via the methods described in following experimental section, there were several problems encountered along the way. A general problem encountered during metal complexation was the solubility of metal salts and ligands. As the generation of the dendron increased, it required less polar solvent such as methylene chloride or chloroform for solubility. However, such a solvent could not dissolve metal salts and a solvent mixture was needed to dissolve both of starting materials and products. Although DMF is often used as the solvent in various ruthenium or osmium poly pyridine complexation, it did not give the desired products in this case. An EtOH/CH₃Cl mixture is a commonly used solvent to synthesize metal poly pyridine complexes. The disadvantage of this solvent system is its low boiling point (~70°C) and long reaction time. This could be overcome by switching the solvent to high-boiling alcohol such as 2-methoxy ethanol or 2-(2-methoxyethoxy)ethanol (Table 3). The use of high boiling point solvents along with a microwave reactor dramatically decreased the reaction time to form the ruthenium complexes. However, it could not be used for the synthesis of the second generation dendrimers because of the insolubility of the dendron even at high temperature. Generally, ruthenium and osmium complexes have the similar reaction conditions and purification methods except osmium complexes require solvents with higher boiling point (Table 3). The only successful complexation of osmium was in 2-(2-methoxyethoxy)ethanol. Column chromatography with both ruthenium and osmium dendrimers always gave better results when it was performed before ion exchange. The use of a microwave reactor gave dramatically decreased reaction time for the zeroth
Chapter 2: Results and Discussion

generation, but it didn’t give such an improvement for higher generation dendrimers.

Complexation with iron was somewhat different. It did not require high boiling point solvents (Table 3). The reaction was usually completed at room temperature or with gentle heating. However, the solubility of the starting metal salt was worse than others and required a highly polar solvent like ethanol or water. The mixed solvent system could be used and yielded satisfactory results in all cases.

Table 2.3. a

<table>
<thead>
<tr>
<th>core</th>
<th>ligand</th>
<th>reagent</th>
<th>solvent</th>
<th>temp (°C)</th>
<th>heating</th>
<th>time</th>
<th>results</th>
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<td>RuCl3·xH2O</td>
<td>EtOH/CH3Cl</td>
<td>70</td>
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<td>5days</td>
<td>s</td>
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<tr>
<td></td>
<td></td>
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<td>ME</td>
<td>124</td>
<td>o.b.</td>
<td>12hrs</td>
<td>s</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>DMF</td>
<td>120</td>
<td>m.w.</td>
<td>1hrs</td>
<td>e</td>
</tr>
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<td>EtOH/CH3Cl</td>
<td>70</td>
<td>o.b.</td>
<td>5days</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ME</td>
<td>124</td>
<td>o.b.</td>
<td>12hrs</td>
<td>s</td>
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<td></td>
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<td>DMF</td>
<td>120</td>
<td>m.w.</td>
<td>5hrs</td>
<td>e</td>
</tr>
<tr>
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<td>RuCl3·xH2O</td>
<td>EtOH/CH3Cl</td>
<td>70</td>
<td>o.b.</td>
<td>5days</td>
<td>s</td>
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<tr>
<td></td>
<td></td>
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<td>DMF</td>
<td>120</td>
<td>o.b.</td>
<td>12hrs</td>
<td>s</td>
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<tr>
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<td></td>
<td></td>
<td>DMF</td>
<td>150</td>
<td>o.b.</td>
<td>12hrs</td>
<td>p</td>
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<td>Fe</td>
<td>G0</td>
<td>(NH4)2Fe(SO4)2</td>
<td>EtOH or H2O</td>
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<td>o.b.</td>
<td>1hrs</td>
<td>s</td>
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<td>g.h.</td>
<td>o.b.</td>
<td>1hrs</td>
<td>s</td>
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<tr>
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<td>n.a.</td>
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<tr>
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<td>194</td>
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<td></td>
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<td>70</td>
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<td>7days</td>
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<tr>
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<td>MEE</td>
<td>194</td>
<td>m.w.</td>
<td>4hrs</td>
<td>p</td>
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</tr>
</tbody>
</table>

a ME: 2-methoxyethanol; MEE: 2-(2-methoxyethoxy)ethanol; g.h: gentle heat; o.b: oil bath; m.w.: micro wave; e: excellent; s: satisfactory (but long reaction time); p: poor.

2.3. Experimental Section
**General Considerations.** Chemicals were purchased from Aldrich or Acros and were used as received unless otherwise indicated. Ruthenium(III) chloride hydrate was purchased from Strem chemicals. THF was purified by distillation over sodium/benzophenone. Column chromatography was carried out with silica gel 60Å, 32-63 µm (Sorbent technologies). Nuclear magnetic resonance characterization was performed at 300MHz or 400MHz for $^1$H and 75Mz and 100MHz for $^{13}$C on Varian spectrometers. MALDI-MS investigations were carried out using a Bruker Proflex + (Bruker Daltonics, Billerica, MA) linear MALDI-TOF instrument with a 1.2 m flight tube. DHB (2,5-dihydroxy benzoic acid) or dithranol was used as matrix. For FAB-MS investigations, a JEOL HX-110 (JEOL USA, Inc. Peabody, MA) sector instrument was used and NBA (3-nitrobenzyl alcohol) was used as matrix. Elemental analysis was performed by Atlantic Microlaboratories. Electrochemical experiments were carried out on Bioanalytical Systems CV-50W Voltammetric Analyzer. The three-electrode cell consisted of a Pt disk working electrode (area of 0.0201 cm$^2$), a Pt auxiliary electrode, and a homemade, nonaqueous Ag/AgNO$_3$ reference electrode (Ag wire contacting a acetonitrile solution of 0.01M AgNO$_3$ and 0.1M supporting electrolyte, tetrabutylammonium tetrafluoroborate, TBABF$_4$). Millimolar concentrations of the analytes were dissolved in argon-purged acetonitrile, which contained 0.1M tetrabutylammonium tetrafluoroborate, TBABF$_4$ supporting electrolyte. All electrochemical experiments were carried out in argon-purged acetonitrile solutions at room temperature.

[2,2’] Bipyridinyl-4,4’-diol (7). To a solution of 4,4’-dimethoxy-2,2’-bipyridine (6)
(2.95 g, 14 mmol) in 170 mL of glacial acetic acid was added 48 wt % HBr solution in water (24 mL, 140 mmol). The mixture was refluxed overnight. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in water and neutralized by adding aqueous ammonium hydroxide. This produced a white solid which was filtered and dried. This was used for the next step without further purification. Yield: 67% (1.76 g).

**G1-OBpy (8).** To a suspension of 7 (0.50 g, 2.66 mmol) in 60 mL of dry acetone were added G1-OMs (5) (3.13 g, 5.9 mmol), anhydrous potassium carbonate (1.1 g, 7.98 mmol) and a catalytic amount of 18-crown-6. The mixture refluxed and stirred vigorously for 36 hrs. After cooling to room temperature, the solid residue was filtered and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography with CH₂Cl₂ followed by 2:1 ethyl acetate: hexane eluent. Yield: 93% (2.62 g); ¹H NMR (CDCl₃) δ (ppm) 1.50-1.80 (m, 10H), 2.22 (m, 4H), 4.06 (t, 4H), 5.03 (s, 8H), 6.80 (br, 2H), 6.89 (d, 8H, J = 6.9 Hz), 7.20 (d, 8H, J = 6.9 Hz), 7.30-7.50 (m, 20H), 7.94 (s, 2H), 8.47 (br, 2H, J = 4.7 Hz); ¹³C NMR (CDCl₃) δ (ppm) 25.03, 28.34, 38.57, 45.13, 68.81, 70.29, 107.20, 111.53, 114.43, 127.75, 128.13, 128.46, 128.76, 137.33, 142.02, 150.18, 156.90, 157.75, 166.29.

**[Ru(6)₃](PF₆)₂ (9).** To a solution of 4,4’-dimethoxy-2,2'-bipyridine (6) (0.50 g, 2.3 mmol) in 30 mL of pure ethanol was added Ruthenium-trichloride hydrate (40 – 43 % Ru) (0.15 g, 0.72 mmol) in 5 mL of pure ethanol. The reaction mixture was refluxed for five days. The solvent was removed in vacuo. The residue was dissolved in CH₂Cl₂ and a solution of NH₄PF₆ (1.18g, 7.23 mmol) in a small amount of methanol was added
dropwise with stirring. The mixture was stirred for 2h and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of CH$_2$Cl$_2$ and added dropwise with stirring to 150 mL of petroleum ether. The orange precipitate was filtered, washed with ethanol, and dried. Yield: 40 % (0.30 g); $^1$H NMR (CD$_3$CN) $\delta$ (ppm) 3.99 (s, 6H), 6.94 (d, 2H), 7.52 (d, 2H), 7.98 (s, 2H); $^{13}$C NMR (CD$_3$CN) $\delta$ (ppm) 57.65, 111.89, 114.63, 153.26, 159.46, 167.85. MALDI-TOF MS (matrix: DHB); m/z Calcd 895.14 (M-PF$_6$); found 892.68. FAB-MS (matrix: NBA); m/z Calcd 895.14 (M-PF$_6$); found 895.10. Anal. Calcd for C$_{36}$H$_{36}$F$_{12}$N$_6$O$_6$P$_2$Ru: C, 41.59; H, 3.49; N, 8.08; found: C, 41.48; H, 3.34; N, 8.11.

$[\text{Fe(6)}_3](\text{PF}_6)_2$ (10). To a solution of 4,4’-dimethoxy-2,2’-bipyridine (6) (0.50 g, 2.3 mmol) in 30 mL of pure ethanol was added FeSO$_4$·(NH$_4$)$_2$SO$_4$·6H$_2$O (0.28 g, 0.72 mmol) in 5 mL of water. The reaction mixture was refluxed for 24 hrs. The solvent was removed in vacuo. The residue was dissolved in CH$_2$Cl$_2$ and a solution of NH$_4$PF$_6$ (1.18g, 7.23 mmol) in a minimum amount of methanol was added dropwise while stirring. The mixture was stirred for 2hrs and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure. The residue was dissolved in a minimum amount of CH$_2$Cl$_2$ and added dropwise while stirring to 150 mL of petroleum ether. The orange precipitate was filtered, washed with ethanol, and dried. Yield: 82 % (0.59 g); $^1$H NMR (CD$_3$CN) $\delta$ (ppm) 4.01 (s, 6H), 6.98 (d, 2H), 7.23 (d, 2H), 8.06 (s, 2H); $^{13}$C NMR (CD$_3$CN) $\delta$ (ppm) 57.69, 111.89, 115.04, 155.59, 161.36, 169.06. MALDI-TOF MS (matrix: DHB); m/z Calcd 849.17 (M-PF$_6$); found 847.20. FAB-MS (matrix: NBA); m/z Calcd 849.17 (M-PF$_6$); found 849.20. Anal. Calcd for
Chapter 2: Experimental Section

C₃₆H₃₆F₁₂FeN₆O₆P₂: C, 43.48; H, 3.65; N, 8.45; found: C, 43.40; H, 3.62; N, 8.42.

[Co(6)₃](PF₆)₂ (11). To a solution of 4,4′-dimethoxy-2,2′-bipyridine (6) (0.50 g, 2.3 mmol) in 30 mL of pure ethanol was added Co(NO₃)₂·6H₂O (0.21 g, 0.72 mmol) in 5 mL of ethanol. The reaction mixture was heated to reflux under Ar for 24 hrs. The solvent was removed *in vacuo*. The residue was dissolved in CH₂Cl₂ and a solution of NH₄PF₆ (1.18g, 7.23 mmol) in a minimum amount of methanol was added dropwise while stirring. The mixture was stirred for 2 hrs and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure. The residue was dissolved in a minimum amount of CH₂Cl₂ and added dropwise while stirring to 150 mL of petroleum ether. The orange precipitate was filtered, washed with ethanol, and dried. Yield: 81 % (0.58 g); ¹H NMR (CD₃CN) δ (ppm). 6.66 (s, 6H), 40.79 (s 2H), 77.08 (s, 2H), 91.96 (br, 2H). MALDI-TOF MS (matrix: DHB); m/z Calcd 852.17 (M-PF₆); found 852.21. FAB-MS (matrix: NBA); m/z Calcd 852.17 (M-PF₆); found 852.21. Anal. Calcd for C₃₆H₃₆CoF₁₂N₆O₆P₂: C, 43.34; H, 3.64; N, 8.42; found: C, 43.47; H, 3.64; N, 8.48.

[Ru(8)₃](PF₆)₂ (12). This complex was prepared analogous to 9, alternatively using chloroform/ethanol solvent mixture (2:1 v/v). Purified by neutral alumina column chromatography with 10:1 CH₂Cl₂: methanol eluent. Yield: 24 % (0.11 g); ¹H NMR (Acetone-d₆) δ (ppm) 1.50-1.80 (m, 10H), 2.24 (m, 4H), 4.16 (t, 4H), 5.03 (s, 8H), 6.90(d, 8H), 7.02(d, 2H), 7.13 (d, 8H), 7.10-7.43 (m, 20H), 7.74 (d, 2H), 8.24 (br, 2H); ¹³C NMR (Acetone-d₆) δ (ppm) 24.65, 27.47, 37.93, 44.72, 69.70, 70.00, 111.47, 114.36, 127.72, 127.74, 128.00, 128.38, 128.64, 137.76, 141.97, 152.44, 157.08, 158.72, 166.35. MALDI-TOF MS (matrix: DHB); m/z Calcd 3416.39 (M-PF₆); found 3413.55. FAB-MS
(matrix: NBA); m/z Calcd 3416.39 (M-PF₆); found 3418.4. Anal. Calcd for C₂₁₆H₂₀₄F₁₂N₆O₁₈P₂Ru: C, 72.81; H, 5.77; N, 2.36; found: C, 72.60; H, 5.93; N, 2.34.

\[ \text{[Fe(8)₃]}(\text{PF₆})₂ \] (13). This complex was prepared analogous to 10 alternatively using chloroform/ethanol solvent mixture (2:1 v/v). The purple solid was dissolved in a minimum amount of CH₂Cl₂ and added dropwise while stirring to 150 mL of toluene. The purple precipitate was filtered, washed with ethanol, and dried. Yield: 39 % (0.22 g); ¹H NMR (Acetone-d₆) \( \delta \) (ppm) 1.59-1.70 (br, 10H), 2.20-2.30 (m, 4H), 4.15-4.20 (br, 4H), 5.03 (s, 8H), 6.90 (d, 8H, \( J = 7.2 \) Hz), 7.05-7.14 (m, 10H), 7.25-7.45 (m, 22H), 8.30 (s, 2H); ¹³C NMR (Acetone-d₆) \( \delta \) (ppm) 24.63, 27.46, 37.92, 44.72, 69.70, 70.04, 111.44, 114.36, 127.73, 127.75, 128.00, 128.39, 128.64, 137.76, 141.96, 154.78, 157.07, 160.63, 167.51. FAB-MS (matrix: NBA); m/z Calcd 3370.42 (M-PF₆); found 3372.20.

\text{G1-O-CH₂Bpy} (21). To a suspension of KH (0.14 g, 3.5 mmol) and a catalytic amount of 18-crown-6 in 20 mL of dry THF at 0 °C was added G1-OH (4) (0.8 g, 1.77 mmol) in 10ml of dry THF. After 1h, 4,4'-bis-bromomethyl -2,2'-bypridinyl (16) (0.2 g, 0.58 mmol) in 5 ml of dry THF was added and allowed to warm to room temperature. After 12hrs, ethanol was added slowly to quench the reaction followed by water. The solution was extracted with ethyl acetate three times and the combined organic layers were evaporated to dryness under reduced pressure. The crude product was purified by column chromatography with CH₂Cl₂ followed by ethyl acetate eluents. Yield: 32 % (0.2 g); ¹H NMR (CDCl₃) \( \delta \) (ppm) 1.40-1.50 (m, 4H), 1.50-1.70 (m, 6H), 2.10-2.20 (m, 4H), 3.50 (t, 4H), 4.53 (s, 4H), 5.01(s, 8H), 6.87 (d, 8H), 7.13 (d, 8H), 7.28-7.46 (m, 22H), 8.30 (s, 2H), 8.65 (d, 2H)
**n-Octyl mesylate (23)** To a solution of n-octyl alcohol (3.0 g, 23 mmol), triethylamine (9.7 mL, 69 mmol), and a catalytic amount of 4-dimethylaminopyridine in CH$_2$Cl$_2$ at 0 °C was added methanesulfonyl chloride (5.3 g, 46 mmol). The mixture was stirred for 1 hr, and then allowed to warm to room temperature. After additional 2 hrs, water was added to quench the reaction. The solution was extracted with CH$_2$Cl$_2$ two times and the combined organic layers were evaporated to dryness under reduced pressure. The crude product was purified by plug column chromatography with CH$_2$Cl$_2$ eluent. Yield: 83% (4.25 g); $^1$H NMR (CDCl$_3$) δ (ppm) 0.90 (t, 3H), 1.20-1.85 (m, 12H), 3.00 (s, 3H), 4.20 (t, 2H). This spectrum matched that published previously.$^{61}$

**n-Octyl triflate (24)** To a solution of n-octyl alcohol (3.0 g, 23 mmol), triethylamine (9.7 mL, 69 mmol), and a catalytic amount of 4-dimethylaminopyridine in CH$_2$Cl$_2$ at 0 °C was added trifluoromethanesulfonic anhydride (13 g, 46 mmol). After 2 hrs, water was added to quench the reaction. The solution was extracted with CH$_2$Cl$_2$ two times and the combined organic layers were evaporated to dryness under reduced pressure. The crude product was purified by plug column chromatography with pentane eluent. Yield: 63% (4 g); $^1$H NMR (CDCl$_3$) δ (ppm) 0.90 (t, 3H), 1.30-1.88 (m, 12H), 4.54 (t, 2H, J = 6.6 Hz). This spectrum matched that published previously.$^{62,63}$

**G1-Br (36).** To a solution of G1-OMs (5) (1.0 g, 1.88 mmol) in 50 mL of dry acetone were added NaBr (0.58 g, 5.64 mmol) and a catalytic amount of tetrabutylammonium bromide. The mixture was refluxed for 36 hrs. After cooling to room temperature, the solid residue was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ and extracted with water two times. The
combined organic layers were dried with Na$_2$SO$_4$ and evaporated to dryness under reduced pressure. Yield: 93 % (0.90 g); $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 1.60-1.80 (m, 5H), 2.10 (br, 2H), 3.36 (t, 2H), 5.04 (s, 4H), 6.89 (d, 4H, J = 8.7 Hz), 7.11 (d, 4H, J = 8.7 Hz), 7.30-7.50 (m, 10H). This spectrum matched that published previously.$^{64}$

**G1-Bpy (37).** To a solution of potassium tert-butoxide (1 M in THF, 6.24 mL, 6.24 mmol) and diisopropylamine (0.93 mL, 6.65 mmol) in 20 mL of THF cooled to -78 °C under Ar was added n-butyllithium (1.6 M in hexane, 3.64 mL, 5.82 mmol). The mixture was stirred for 1 hr at -78 °C, and then, a solution of 4,4’-dimethyl-2,2’-bipyridyl (14) (0.38 g, 2.08 mmol) in 10 mL of THF was added over 1 min. The mixture was stirred at -78 °C for 1h and a solution of G1-Br (36) (3.0 g, 5.82 mmol) in 10 mL of THF was added and stirring at -78 °C was continued for additional 2 hrs. The reaction was quenched with methanol (2 mL) and added to 20 mL of saturated aqueous NH$_4$Cl (20 mL). The THF was removed *in vacuo*, and the residue was extracted with CH$_2$Cl$_2$. The combined organic layers were evaporated under reduced pressure and the crude product was purified by column chromatography with CH$_2$Cl$_2$ followed by 10:0.2 CH$_2$Cl$_2$:ethyl acetate eluents. Yield: 96% (2.10 g); $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 1.20-1.31 (m, 4H), 1.59 (s, 6H), 1.64-1.71(m, 4H), 2.08 (m, 4H), 2.63 (t, 4H J = 6 Hz), 5.03 (s, 8H), 6.89 (d, 8H, J = 6.6 Hz), 7.07-7.12 (m, 10H), 7.31-7.46 (m, 20H), 8.24 (s, 2H), 8.53 (d, 2H, J = 3.9 Hz); $^{13}$C NMR (CDCl$_3$) $\delta$ (ppm) 24.76, 28,10, 31.34, 35.56, 42.01, 45.15, 70.16, 114.28, 121.49, 124.11, 127.77, 128.13, 128.44, 128.76, 137.38, 142.47, 149.06, 153.05, 156.12, 156.84; . Anal. Calcd for C$_{74}$H$_{72}$N$_2$O$_4$: C, 84.38; H, 6.89; N, 2.66; found: C, 84.49; H, 6.92; N, 2.76.
**G2-Bpy (35).** This complex was prepared analogous to 37. Yield: 92% (1.79 g); $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 1.2 (m, 4H), 1.5-1.8 (br, 30H), 2.1-2.4 (m, 12H), 2.6 (t, 4H), 3.9 (t, 8H), 5.0 (s, 16H), 6.8 (d, 8H), 6.9 (d, 16H), 7.0-7.2 (m, 24H), 7.3-7.6 (m, 42H), 8.2 (s, 2H), 8.6 (d, 2H). Anal. Calcd for C$_{170}$H$_{168}$N$_2$O$_{12}$: C, 83.99; H, 6.97; N, 1.15; found: C, 83.75; H, 6.83; N, 1.32.

**G3-Bpy (45).** This complex was prepared analogous to 37. Yield: 84% (1.38 g); $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 1.2 (br, 28H), 1.5-1.8 (m 80H), 2.2 (br, 28H), 2.6 (t, 4H), 3.9 (br, 24H), 5.0 (32H), 6.7 (d, 24H), 6.9 (d, 32H), 7.0-7.2 (m, 56H), 7.3-7.6 (m, 82H), 8.2 (s, 2H), 8.5 (br, 2H). Anal. Calcd. for C$_{362}$H$_{360}$N$_2$O$_{28}$: C, 83.83; H, 7.00; N, 0.54; found: C, 83.60; H, 7.00; N, 0.54.

**[Ru(14)$_3$](PF$_6$)$_2$ (46).** This complex was prepared analogous to 9. Yield: 76 % (0.63 g); $^1$H NMR (Acetone-d$_6$) $\delta$ (ppm) 2.56 (s, 6H), 7.38 (d, 2H, J = 4.2 Hz), 7.83 (d, 2H, J = 4.2 Hz), 8.67 (s, 2H); $^{13}$C NMR (Acetone-d$_6$) $\delta$ (ppm) 20.51, 125.21, 128.71, 150.21, 151.03, 157.09. MALDI-TOF MS (matrix: DHB); m/z Calcd 799.17 (M-PF$_6$); found 799.58. FAB-MS (matrix: NBA); m/z Calcd 799.17 (M-PF$_6$); found 799.10.

**[Fe(14)$_3$](PF$_6$)$_2$ (47).** This complex was prepared analogous to 10. Yield: 84 % (0.66 g); $^1$H NMR (Acetone-d$_6$) $\delta$ (ppm) 2.58 (s, 6H), 7.39 (d, 2H, J = 3.9 Hz), 7.51 (d, 2H, J = 4.2 Hz), 8.69 (s, 2H). $^{13}$C NMR (CD$_2$Cl$_2$) $\delta$ (ppm) 21.32, 124.72, 128.75, 151.50, 152.85, 158.69. FAB-MS (matrix: NBA); m/z Calcd 753.20 (M-PF$_6$); found 753.30.

**[Co(14)$_3$](PF$_6$)$_2$ (48).** To a solution of Co(NO$_3$)$_2$·6H$_2$O (0.24 g, 0.81 mmol) in 30 mL of ethanol was added 4,4’-dimethyl-2,2’-bipyridyl (14) (0.50 g, 2.3 mmol). The reaction mixture was refluxed under Ar for 24 hrs. The solution was then allowed to cool to room
temperature and filtered to remove any insoluble impurities. The solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ and added dropwise with stirring to 150 mL of petroleum ether. The yellow precipitate was filtered, washed with ether and petroleum ether several times. The yellow precipitate was dissolved in water and extracted with diethyl ether several times. To the combined aqueous layers was added a solution of KPF$_6$ (1.49 g, 8.14 mmol) in a small amount of water. The produced yellow precipitate was filtered, dissolved in CH$_2$Cl$_2$, and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure. Yield: 75 % (0.55 g); $^1$H NMR (Acetone-d$_6$) $\delta$ (ppm) 0.36 (s, 6H), 44.77 (s, 2H), 81.55 (s, 2H), 91.48 (br, 2H). $^{13}$C NMR failed to show all of the expected signals, presumably due to fast nuclear relaxation by the paramagnetic cobalt. FAB-MS (matrix: NBA); m/z Calcd 756.20 (M-PF$_6$); found 756.20. Anal. Calcd for C$_{36}$H$_{36}$CoF$_{12}$N$_6$P$_2$: C, 47.96; H, 4.02; N, 9.32; found: C, 47.94; H, 4.09; N, 9.30.

$[\text{Ru}(37)]_3(\text{PF}_6)_2$ (50). To a solution of 37 (0.54 g, 0.51 mmol) in 40 mL of ethylene glycol/DMF (1/2 v/v) was added Ruthenium-trichloride hydrate (40 – 43 % Ru) (0.15 g, 0.72 mmol) in 5 mL of DMF. The reaction mixture was refluxed for 24 hrs. The solution was allowed to cool to room temperature and filtered to remove any insoluble impurities. The solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ and added dropwise with stirring to 150 mL of petroleum ether. The orange precipitate was filtered, washed with ether and petroleum ether several times. The orange precipitate was dissolved in a minimum amount of acetone and added while stirring to 200 mL of water. A solution of KPF$_6$ (0.3 g, 1.65 mmol) in a minimum amount of water was then added to
the resulting orange red solution. This produced an orange precipitate, which was subsequently filtered, dissolved in CH$_2$Cl$_2$, and extracted with water two times. The combined organic layers were evaporated under reduced pressure and the crude product was purified by column chromatography with CH$_2$Cl$_2$:ethyl acetate 10:0.2 eluent. Yield: 34 % (0.20 g); $^1$H NMR (CD$_2$Cl$_2$) $\delta$ (ppm) 1.22-1.27 (br, 4H), 1.54-1.65 (br, 10H), 2.08-2.12 (br, 4H), 2.72 (t, 4H, J = 8.4 Hz), 4.99 (s, 8H), 6.85 (d, 8H, J = 9Hz), 7.08-7.15 (m, 10H), 7.31-7.46 (m, 20H), 8.08 (s, 2H); $^{13}$C NMR (CD$_2$Cl$_2$) $\delta$ (ppm) 25.01, 27.68, 30.99, 35.47, 41.76, 70.10, 114.24, 123.91, 127.76, 127.99, 128.12, 128.39, 128.70, 137.49, 142.45, 150.73, 154.67, 156.63, 156.87. MALDI-TOF MS (matrix: DHB); m/z Calcd 3404.52 (M-PF$_6$); found 3410.46. FAB-MS (matrix: NBA); m/z Calcd 3404.52 (M-PF$_6$); found 3405.70. Anal. Calcd for C$_{222}$H$_{216}$F$_{12}$N$_6$O$_{12}$P$_2$Ru: C, 75.09; H, 6.13; N, 2.37; found: C, 74.87; H, 6.23; N, 2.34.

[Fe(37)$_3$](PF$_6$)$_2$ (51). This complex was prepared analogous to 10 alternatively using chloroform/ethanol solvent mixture (2:1 v/v). Yield: 77 % (0.40 g); $^1$H NMR (CD$_2$Cl$_2$) $\delta$ (ppm) 1.22 (br, 4H), 1.54-1.65 (m, 10H), 2.10 (m, 4H), 2.73 (t, 4H, J = 6.6 Hz), 4.99 (s, 8H), 6.86 (d, 8H, J = 6.6Hz), 7.09-7.13 (m, 10H), 7.31-7.41 (m, 22H), 8.11 (s, 2H); $^{13}$C NMR (CD$_2$Cl$_2$) $\delta$ (ppm) 25.14, 27.82, 31.03, 35.47, 41.86, 45.13, 70.16, 114.23, 127.70, 127.87, 128.06, 128.34, 128.64, 137.42, 142.36, 153.15, 155.64, 156.78, 158.68. FAB-MS (matrix: NBA); m/z Calcd 3358.55 (M-PF$_6$); found 3360.30. Anal. Calcd for C$_{222}$H$_{216}$F$_{12}$FeN$_6$O$_{12}$P$_2$: C, 75.09; H, 6.13; N, 2.40; found: C, 75.50; H, 6.17; N, 2.34.

[Co(37)$_3$](PF$_6$)$_2$ (52). This complex was prepared analogous to 48 alternatively using chloroform/ethanol solvent mixture (2:1 v/v). Yield: 97 % (0.77 g); $^1$H NMR is shown in
the supplementary material. Additional peaks were always observed in these spectra despite repeated attempts to purify this compound by silica gel and alumina chromatography, reverse phase chromatography, selective precipitation and gel permeation chromatography. It is suspected that these may be perhaps due to paramagnetic shifting of certain nuclei due to the presence of the cobalt as acceptable elemental and mass spectral analyses were obtained. $^{13}$C NMR failed to show all of the expected signals, presumably due to fast nuclear relaxation by the paramagnetic cobalt.

FAB-MS (matrix: NBA); m/z Calcd 3361.55 (M-PF$_6$); found 3362.60. Anal. Calcd for C$_{222}$H$_{216}$F$_{12}$CoN$_6$O$_{12}$P$_2$: C, 75.99; H, 6.20; N, 2.40; found: C, 75.86; H, 6.31; N, 2.35.

$[^{Os(14)}_3](PF_6)_2$ (49). This complex was prepared analogous to 9 alternatively using 2-(2-methoxyethoxy)ethanol as a solvent. Yield: 67 % (0.32 g); $^1$H NMR (Acetonitrile-d$_3$) $\delta$ (ppm) 2.56 (s, 6H), 7.1 (d, 2H), 7.4 (d, 2H), 8.2 (s, 2H).

$[^{Os(37)}_3](PF_6)_2$ (53). This complex was prepared analogous to 50 alternatively using 2-(2-methoxyethoxy)ethanol as a solvent and microwave reactor( 100 W, 194°C, 5hrs run). Yield (48%) (0.11g); $^1$H NMR (CD$_2$Cl$_2$:CD$_3$CN=5:1 mixture) $\delta$ (ppm) 1.1-1.2 (br, 4H), 1.54-1.65 (br, 10H), 2.0 (br, 4H), 2.7 (t, 4H), 4.9 (s, 8H), 6.85 (d, 8H), 6.9-7.1 (m, 10H), 7.1-7.4 (m, 20H), 8.1 (s, 2H). MALDI-TOF MS (matrix: dithranol); m/z Calcd 3494.6 (M-PF$_6$); found 3494.1.

$[^{Ru(35)}_3](PF_6)_2$ (54). This complex was prepared analogous to 50 alternatively using chloroform/ethanol solvent mixture (2:1 v/v). Yield: 98% (0.28g); $^1$H NMR (CD$_2$Cl$_2$:CD$_3$CN=5:1 mixture) $\delta$ (ppm) 1.2 (m, 4H), 1.4-1.6 (br, 30H), 2.0-2.4 (m, 12H), 2.6 (t, 4H), 3.7 (t, 8H), 4.9 (s,16H), 6.7 (d, 8H), 6.8 (d, 16H), 6.9-7.1 (m, 26H), 7.2-7.4
(m, 42H), 8.0 (s, 2H). MALDI-TOF MS (matrix: dithranol); m/z Calcd 7534.7 (M-PF₆); found 7535.1. Anal. Calcd for C₅₁₀H₅₀₄F₁₂RuN₆O₃₆P₂: C, 79.71; H, 6.61; N, 1.09; found: C, 79.43; H, 7.63; N, 1.08.

[Fe(35)](PF₆)₂ (55). This complex was prepared analogous to 51. Yield: 91 % (0.48 g); ¹H NMR (CD₂Cl₂) δ (ppm) 1.2 (m, 4H), 1.4-1.6 (br, 30H), 2.0-2.4 (m, 12H), 2.6 (t, 4H), 3.7 (t, 8H), 5.0 (s,16H), 6.7 (d, 8H), 6.8 (d, 16H), 6.9-7.1 (m, 26H), 7.2-7.4 (m, 42H), 8.2 (s, 2H). Anal. Calcd for C₅₁₀H₅₀₄F₁₂FeN₆O₃₆P₂: C, 80.18; H, 6.65; N, 1.10; found: C, 80.13; H, 6.67; N, 1.08.

[Co(35)](PF₆)₂ (56). This complex was prepared analogous to 52. Yield: 94% (0.45g). Anal. Calcd for C₅₁₀H₅₀₄F₁₂CoN₆O₃₆P₂: C, 80.15; H, 6.65; N, 1.10; found: C, 80.07; H, 6.65; N, 1.10.
2.4. References


Chapter 3

Electrochemical Behavior of Metal Tris(bipyridine) Core Dendrimers: Encapsulation Effects on Heterogeneous Electron Transfer Kinetics
3.1. Introduction

Dendritic encapsulation of a redox core is one of the most intensively studied subjects in the field of dendrimer chemistry. By probing the rate and driving force for electron transfer to and from the encapsulated redox core, one can rationalize how the primary dendrimer structure can influence its conformation and affect the redox properties of the core. A better understanding of dendritic structure property relationships would help us to interpret existing biological systems and to design and fabricate modern nano electrical devices.\textsuperscript{1-3}

Various redox-active cores and repeating units have been employed to construct dendrimers and their structural and conformational effects on the rate and driving force for electron transfer have been widely studied. The thermodynamic redox potentials of those dendrimers broadly spread out roughly around a ±2 V range and many different dendritic building blocks have been utilized.\textsuperscript{1-6} Because there are several variables involved, it is difficult to understand the role of thermodynamic redox potential on the rate attenuation for electron transfer.

Thus, it is of interest to systematically vary the redox potential of dendrimer cores while maintaining the same structural and conformational features. The results of this variation would allow us to understand how the thermodynamic barrier for electron transfer can affect the kinetic behavior, that is, the attenuation of heterogeneous electron transfer between generations.
This chapter describes electro-analytical efforts for determining the rate of heterogeneous electron transfer for a series of isostructural tris(bipyridine) core dendrimers. Preliminary data is shown and possible solutions for problems encountered are proposed.

### 3.2. Results and Discussion

**Determination of thermodynamic redox potential and heterogeneous ET rate constant**

Cyclic voltammetry is a tool normally employed to study the redox behavior of dendrimers. Qualitative kinetic information can be drawn out from the separation between anodic and cathodic peak potentials, and the thermodynamic redox potential can determined from the half wave potential of both of peaks. More quantitative analysis in quasi-reversible systems can be done using the Nicholson method which is based on relationships between the standard heterogeneous electron transfer rate constant \( k_o \) and the peak separation \( (\Delta E_p) \).

\[
\Delta E_p = \psi \left( \frac{\pi D_o \nu}{RT} \right)^{1/2} \left( \frac{D_R}{D_o} \right)^{\alpha/2} 
\]

where \( \psi \) is the kinetic parameter related to \( \Delta E_p \), \( D_o \) is the diffusion coefficient \((\text{cm}^2/\text{s})\), \( \nu \) is the scan rate \((\text{V/s})\), \( n \) is the number of electrons passed, \( F \) is Faraday’s constant, \( R \) is the gas constant, and \( T \) is the cell temperature. (assuming \( D_o = D_R \))

However, for very fast and slow kinetic regimes, this method may produce erroneous results. For very fast electron transfer kinetics, \( \Delta E \) only slightly differs from
the reversible value and uncompensated cell resistance and the resulting voltage drop (IR drop) becomes an important effect on the peak separation. On the other hand, in the very slow electron transfer kinetic regime, it is difficult to determine peak potential because of peak broadening.\textsuperscript{10}

A more sensitive technique to study electron transfer kinetics is Osteryoung square wave voltammetry. This technique employs a square wave superimposed on staircase wave which can reduce background charging current giving improved sensitivity compared with cyclic voltammetry. Its current-voltage response can be fitted iteratively to deduce the standard heterogeneous electron transfer rate constant, which can be calculate from the following relationship

\[
\log(\kappa\sqrt{t_d}) = \log\left(\frac{k_o}{\sqrt{D_o}}\right)\sqrt{I_d} \quad \text{for quasi-reversible system}
\]

where \(t_d\) is the experimental pulse period, \(D_o\) is the molecular diffusion coefficient, and \(\kappa\) is the reduced rate constant.\textsuperscript{11} Net current is iteratively fitted using FSQPLT software\textsuperscript{12} to yield \(E_{1/2}\), \(\alpha\), and \(\log(\kappa/(t_d)^{1/2})\).

For systematically studying the electrochemical behavior of a series of isostructural dendrimers, it is important to have a potential window wide enough to accommodate the thermodynamic redox potentials of all the dendrimers synthesized in Chapter 2. Redox potentials of these dendrimers spread out in the range between -10 to 1000 mV (vs Ag/AgNO\textsubscript{3} in acetonitrile). Acetonitrile is normally employed for this
potential region because of its high dielectric constant and wide potential window especially in the positive region. Although acetonitrile could be successfully employed as a solvent for G0 to G1 (Chapter 2), it could not be used for the 2nd generation dendrimers because of its inability to dissolve these dendrimers. N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) could dissolve all dendrimer generations and exhibit high dielectric constants, but produced large background currents near 1000 mV (vs Ag/AgNO3) which was not acceptable for ruthenium core dendrimers which have redox potential at ca. 1000 mV (vs Ag/AgNO3). Propylene carbonate has a wider positive potential range but its low dielectric constant requires a high concentration (~300 mM) of electrolyte to show redox peaks of ruthenium dendrimers. Additionally, the 2nd generation dendrimers were not soluble in this electrolyte concentration. Methylene chloride could dissolve all generations of dendrimers in the presence of such high electrolyte concentrations but did not exhibit a satisfactory positive potential limit for ruthenium core dendrimers. The redox potentials of dendrimers were positively shifted around 120mV in propylene carbonate and methylene chloride compared to their values in acetonitrile. This shift required an even greater window limit in order to study the redox behavior of ruthenium core dendrimers. A mixture of acetonitrile and methylene chloride was thus adapted to study the redox behavior of a whole series of dendrimers by utilizing both the wide potential window associated with acetonitrile and the solubilizing power of methylene chloride. In a 1:1 (v/v) mixture of these solvents, all dendrimers synthesized were soluble enough for electrochemical studies and their redox potentials were located in analyzable potential window.
Qualitative electrochemical studies of all dendrimers synthesized are displayed in Figures 1 through 4. In initial studies, a noticeable faradaic current response was not observed in the cyclic voltammograms of the second generation dendrimers due to attenuation of the electron transfer rates. Difficulties associated with the quantitative analysis of the 2nd generation dendrimers using electrochemical methods prompted the homogeneous electron transfer studies described in Chapter 4. After completing the project described in Chapter 4, this project was reassessed and re-evaluated qualitatively and quantitatively.

Both the cyclic voltammograms and Osteryoung square wave voltammograms in Figure 3.1 through 3.4 at the end of this section showed qualitatively the attenuation of electron transfer as the dendrimer generation increased. The attenuation of electron transfer was monitored by the decrease in current and the increase in peak separation. Surprisingly, in the 2nd generation dendrimer, electron transfer slowed down dramatically giving a very weak current response. To our knowledge, this is the first example showing such a big attenuation of electron transfer in the second generation of redox active core dendrimers. This is probably because six dendrons near the metal tris(bipyridine) core more efficiently encapsulates the core compared with the analogous dendrimer carrying just four dendrons. Additionally, thermodynamic redox potentials were positively shifted around 30mV from G0 to G1. On the other hand, redox potentials for the second generations determined by Osteryoung square wave voltammetry were not changed much from values of the first generations. This can be rationalized by the fact that the first and second generation dendrimer produced a much more different microenvironment near the
tris(bipyridine) core compared with free dendron complex G0.

For more quantitative approaches, diffusion coefficients for these dendrimers were measured by chronoamperometry. This electrochemical technique employs a potential step to generate a diffusion limited current response as a function of time. Time dependent current is plotted versus $t^{-1/2}$ by BAS CW50 software and a diffusion coefficient is calculated from the slope of this plot (Cottrell plot).\(^{10}\)

\[
i(t) = \frac{nFAD_{D}^{1/2}C_{O}}{\pi^{1/2}t^{1/2}} \quad \text{Cottrell equation}
\]

Heterogeneous electron transfer rate constants for all dendrimers were measured by cyclic voltammetry and Osteryoung square wave voltammetry. A plot of peak current versus the square root of the scan rate in their cyclic voltammograms displayed linear behavior indicating no adsorption of these species onto the electrode (Figure 3.5). However, measured rate constants and diffusion coefficients showed a very broad range of values (Table 1) even for G0 complexes. Large background current, impurities in samples, and/or electrode surface can cause this problem. Another problem was the solvent mixture. During the experiments, methylene chloride evaporated to slightly change the ratio of solvent. This also would be a problem for further studies because ca. 120 mV difference in the redox potential of dendrimers was observed between acetonitrile and methylene chloride. Therefore, changes in the ratio would give erroneous thermodynamic redox potential and electron transfer kinetic data. For more detailed
studies, a new solvent system and more careful measurement of electrochemical behavior are required. Use of solvent systems like propionitrile, 1,2-dichloroethane/acetonitrile mixture and tetrachloroethane/acetonitrile mixture might be a solution to these problems. Heterogeneous electron transfer rate constants for 2nd generation dendrimers have to be acquired from Osteryoung square wave voltammetry because cyclic voltammetry does not have enough sensitivity to measure such a small current response. For fitting square wave data to a quasi-reversible model, the Gorman group has used FSQPLT software which gives $E_{1/2}$ and $\log(\kappa/t_d)$ as the result of fitting. To calculate heterogeneous electron transfer rate constants, separately measured diffusion coefficients are required. However, a lack of current response from chronoamperometry of the second generation dendrimers hampered the electrochemical measurement of diffusion coefficients. In future studies, a PFG-SE NMR technique could potentially be utilized to measure diffusion coefficients. However, in preliminary PFG-SE experiments, diffusion coefficients calculated for Fe(G0)$_2$(PF$_6$)$_2$ were much smaller than expected based upon a reasonable hydrodynamic radius ($4.6 \times 10^{-6}$ cm$^2$/s in CH$_2$Cl$_2$). When one is using a square pulse longer than 2ms (4-5ms was used for the iron core dendrimers), distortion at percentage above 70% was occurred in pulse shape. Thus, one would get more power at 40 %/2 ms than one get at 70%/ 4 ms. More studies have to be done to work with this non linear gradient at longer gradient pulse.

Diffusion coefficients and heterogeneous electron transfer rate constants can be estimated at the same time by fitting experimental data to a digital simulation of Osteryoung square wave voltammogram. For this purpose, free software such as ESP
and DigiElch\textsuperscript{16} were utilized. However, first attempts to fit the data were not successful with either software package even if the background current was measured separately and subtracted from the data. More careful measurement of background and faradaic currents is required for further studies.\textsuperscript{17}
Figure 3.1. Cyclic voltammograms (left) and Osteryoung square wave voltammograms (right) for ruthenium core dendrimers (scan rate 100 mV/s for CV and 40mV/s for OSWV, argon-purged acetonitrile/methylene chloride (1:1 v/v) solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode). Counter ions were PF$_6^-$.
Figure 3.2. Cyclic voltammograms (left) and Osteryoung square wave voltammograms (right) for iron core dendrimers (scan rate 100 mV/s for CV and 40mV/s for OSWV, argon-purged acetonitrile/methylene chloride (1:1 v/v) solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode). Counter ions were PF$_6^-$ . Inset in the second generation in OSWV shows expanded y-axis to illustrate the peak.
Figure 3.3. Cyclic voltammograms (left) and Osteryoung square wave voltammograms (right) for cobalt core dendrimers (scan rate 100 mV/s for CV and 40mV/s for OSWV, argon-purged acetonitrile/methylene chloride (1:1 v/v) solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode). Counter ions were PF$_6^−$. G1 dendrimer was expended in previous studies and was unavailable for this experiment.
Figure 3.4. Cyclic voltammograms (left) and Osteryoung square wave voltammograms (right) for osmium core dendrimers (scan rate 100 mV/s for CV and 40mV/s for OSWV, argon-purged acetonitrile/methylene chloride (1:1 v/v) solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode). Counter ions were PF$_6^-$.
Figure 3.5. Plots of current versus the square root of scan rate. This linear relationship indicates a freely diffusing species.
Table 3.1.

<table>
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<tr>
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<th>$E_{1/2}$ (mV)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$D_o$ x 10^-3 cm^2/s</th>
<th>$\kappa$ x 10^-3 cm/s</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CV</td>
<td>OSWV</td>
<td>CV</td>
<td>OSWV</td>
<td>CV</td>
</tr>
<tr>
<td>Ru(G0)</td>
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<td>918</td>
<td>74</td>
<td>7.6</td>
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<tr>
<td>Ru(G1)</td>
<td>949</td>
<td>948</td>
<td>110</td>
<td>5.1</td>
<td>4.91</td>
</tr>
<tr>
<td>Fe(G0)</td>
<td>691</td>
<td>688</td>
<td>81</td>
<td>12</td>
<td>19.9</td>
</tr>
<tr>
<td>Fe(G1)</td>
<td>721</td>
<td>722</td>
<td>89</td>
<td>5.6</td>
<td>9.56</td>
</tr>
<tr>
<td>Os(G0)</td>
<td>460</td>
<td>468</td>
<td>74</td>
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</tr>
<tr>
<td>Os(G1)</td>
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<td>500</td>
<td>88</td>
<td>3.8</td>
<td>7.90</td>
</tr>
<tr>
<td>Co(G0)</td>
<td>-8</td>
<td>-10</td>
<td>94</td>
<td>12</td>
<td>11.8</td>
</tr>
</tbody>
</table>

*a* determined by chronoamperometry.

**Thin Layer Cyclic Voltammetry**

Recently, Nierengarten and co-workers quantitatively showed that thin layer cyclic voltammetry dramatically improved the current response from higher generation dendrimers at a slow scan rate, 2 mV/s.$^{18}$ At such a small scan rate, the diffusion layer in a bulk solution will grow much further from the electrode compared to that in a faster scan. Consequently, the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates resulting in lower current response. However, in a thin layer cell, the diffusion layer can not grow any larger than the thickness of the cell and a higher current response is expected compared to that obtained with a regular electrochemical cell.$^{10}$ Using thin layer cyclic voltammetry with a slow scan rate (1mV/s), electron transfer rate constants down to 10^-6 cm/s can be observed.$^{18}$

Initial electrode fabrication with Heineman’s design was not successful because
Teflon tape spacer swelled with methylene chloride and made the cell leak.\textsuperscript{19} Thus, modified electrodes were constructed. A gold slide was masked with scotch tape as shown Figure 3.6 and etched with aqua regia. This reduces radial diffusion from a bulk solution to the slide edge. A scotch tape was again used for spacer and for bonding two slides. This electrode is much easier to fabricate and to clean.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_6.png}
\caption{Schematic diagram of thin layer cell: Au (upper) and Pt (lower)}
\end{figure}

A platinum thin layer electrode was also constructed as shown in Figure 3.6. Platinum foil and a gold slide were utilized for cell fabrication. The electrochemical cell was constructed by immersing the thin layer electrode in a sample solution with a counter electrode (Pt wire) and reference electrode. As can be seen in Figure 3.7, ferricyanide
displayed desirable finite diffusion behavior in these thin layer cells. The second generation cobalt dendrimers displayed a nice and well resolved quasi reversible signal shown in Figure 3.8 utilizing the gold thin layer electrode. However, the gold thin layer electrode could not be used for iron and ruthenium dendrimers because the gold electrode oxidized at ca. 900mV vs Ag/AgNO₃. The modified platinum thin layer electrode gave a signal for the second generation iron dendrimers but gold oxidation was also observed inevitably because of cell design. Platinum foil was placed on the etched gold surface to make contact with the potentiostat and a scotch tape spacer was used so that the gold surface did not come in contact with the sample solution (Figure 3.6). However, the sample solution permeated through the gap between the platinum foil and the spacer, coming in contact with gold surface below platinum foil. Thus, a more careful cell design is required for further studying of ruthenium and iron dendrimers.

Aforementioned Digielch software has a simulation option available for the finite diffusion condition. This data can be fitted to a simulation curve to estimate diffusion coefficients and heterogeneous electron transfer coefficients. However, care should be taken to fit experimental data because the thin layer cell normally carries its reference and counter electrode outside of cell resulting in large IR drops. The preliminary fitting data are shown in Figure 3.9.
Figure 3.7. Cyclic voltammograms in regular cell (a) and thin layer cell (b and c) for K₃Fe(CN)₆ (scan rate 100mV for a, 1 mV/s for b and c; argon-purged aqueous solution, 2 M potassium chloride supporting electrolyte). b. with gold thin layer electrode; c. platinum thin layer electrode.
Figure 3.8. Cyclic voltammograms in regular cell (left) and thin layer cell (right) for 2\textsuperscript{nd} generation dendrimers of iron (upper) and cobalt (lower) (scan rate 1 mV/s, argon-purged acetonitrile/methylene chloride (1:1 v/v) solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte). Counter ions were PF\textsubscript{6}\textsuperscript{−}. 
Figure 3.9. Experimental (after background correction, continuous line) and simulated (circles) thin layer cyclic voltammogram for $\text{Co(G2)}_{3}^{2+/3+}$. The deduced parameters are shown.

$E_{1/2} = 20\text{mV}$

$\alpha = 0.56$

$k_0 = 2.80 \times 10^5 \text{ cm/s}$

$D_0 = 3.43 \times 10^{-7} \text{ cm}^2/\text{s}$
3.3. Concluding remarks

The attenuation of the electron transfer rate of metal tris(bipyridine) core dendrimers was qualitatively shown here. Dramatic rate attenuation was observed between the first and second generations. However, more quantitative efforts are necessary for a better understanding of the dendritic encapsulation effects on electron transfer in this series of molecules. To accommodate all redox potentials of dendrimers, a wider potential window is required. Potential windows are sensitive to moisture, impurities, electrolyte and solvent. Propionitrile would be the best candidate for an alternate solvent. It shares the same functionality (nitrile) with acetonitrile and has high dielectric constant (27) comparable to acetonitrile (36). However, solubility cannot be guaranteed. Alternatively, a high boiling point solvent such as 1,2-dichloroethane and tetrachloroethane can be employed for the substitution of methylene chloride. This mixture will not evaporate easily and can hold its volume ratio with acetonitrile during experiments. With this solvent system, the thermodynamic redox potential as well as heterogeneous electron transfer rate constant can be measured more accurately. PFG-SE NMR and electrochemical simulation packages can be used to estimate the attenuation of electron transfer rate in this series of dendrimers especially for the 2nd generation dendrimer which show too weak of a current response to utilize electrochemical diffusion coefficient measurement.
3.4. References


12. FSQPLT software was provided by John J. O'Dea of the J. Osteryoung Group.


Chapter 4

Electron Self-Exchange Dynamics in Metal Tris(bipyridine) Core Dendrimers: Encapsulation Effects on Homogeneous Electron Transfer
4.1. Introduction

There have been many interesting approaches to understand how nature controls the rate and driving force for electron transfer in redox proteins.\textsuperscript{1-11} These include various studies with redox-active core dendrimers.\textsuperscript{12-15} Dendrimers serve as a simplified model for nature’s complex systems. Their synthetically controllable structures allow us to systematically study how the structural and conformational difference of redox active dendrimer affects the rate and driving force for electron transfer.

Although most biological processes occur in homogeneous conditions, current studies for dendritic encapsulation of redox cores have employed heterogeneous electrochemical methods such as cyclic voltammetry. Electrochemical methods are powerful, convenient, and relatively fast analyzing techniques for studying redox species. There are, however, several disadvantages to using electrochemical methods for dendritic encapsulation studies. First, the apparent heterogeneous electron transfer rate is quite sensitive to the nature and history of the electrode.\textsuperscript{16} Thus, a somewhat different rate constant may be obtained depending on the material, size or pretreatment of the electrode.\textsuperscript{16-18} Second, more frequently, electrode adsorption of analytes during the experiments causes difficulties in obtaining quantitative data especially for high generation dendrimers.\textsuperscript{19, 20} Irreversible behavior of redox dendrimers can also be a problem for quantitative analysis.\textsuperscript{21} Current voltage response from redox dendrimers in an electrochemical cell decreases and broadens as dendrimer generation increased. Thus, slow electron transfer kinetics observed for high generation dendrimers could not be quantitatively evaluated.\textsuperscript{21} Finally, large concentrations of electrolyte are normally
employed in electrochemical experiments to reduce cell resistance. This can affect heterogeneous electron transfer and careful analysis of data is required to study structural effects excluding electrolyte effects.

It is thus of interest to know how dendritic encapsulation influences homogeneous electron transfer kinetics in solution. Although many studies have been conducted for heterogeneous electron transfer kinetics of redox-active core dendrimers, systematical studies of encapsulation effects on homogeneous electron transfer kinetics have not been conducted yet. Moreover, this approach can avoid most problems encountered in electrochemical approaches. Specifically, the measurable rate range can be dramatically expanded with the help of modern spectroscopic techniques. Although heterogeneous and homogeneous electron transfer rates cannot be directly compared, the wider range of rates accessible for homogeneous electron transfer would help us to better understand the structure-property relationships for electron transfer in redox-active core dendrimers, especially for dendrimers showing slow electron transfer kinetics. Throughout this chapter, the first systematic efforts to determine homogeneous electron self-exchange rate constant in the redox active dendrimers utilizing nuclear magnetic resonance spectroscopy are described.

4.2. Results and Discussion

4.2.1 Homogeneous vs Heterogeneous Electron Transfer

The electrochemically measured rate of electron transfer is the rate between the electrode surface and redox-active molecules in the solution adjacent to the electrode
surface (Figure 4.1). In this heterogeneous process, the electrode is just virtual partner for
electron transfer from/to redox species and simply acts as a source(reduction) or
sink(oxidation) for electron(s).

\[ \text{ML}_{x}^{z^{+}} + e^{-} \rightarrow \text{ML}_{x}^{(z-1)^{+}}, \text{ first order rate constant } k_{0} \text{ (cm/s)} \]

On the other hand, if the electrode is substituted with another redox species in solution,
electron(s) would be transferred or exchanged between two different redox species in
homogeneous solutions (Figure 4.1). This rate can be measured by spectroscopic
techniques such as UV-vis and NMR spectroscopy.

\[ \text{ML}_{x}^{z^{+}} + \text{ML}_{x}^{(z-1)^{+}} \rightarrow \text{ML}_{x}^{(z-1)^{+}} + \text{ML}_{x}^{z^{+}}, \text{ 2nd order rate constant } k_{0} \text{ (M}^{-1}\text{s}^{-1}) \]

Both heterogeneous and homogeneous electron transfer can occur by outer-sphere or
inner-sphere mechanism (Figure 4.1). In inner-sphere mechanism, there are strong
interactions such as adsorption of the redox species onto the electrode and a ligand bridge
between redox species in the activated complex, while original coordination spheres are
maintained in outer-sphere mechanism. Outer-sphere electron transfers can be treated in a
more general way compared with inner-sphere process, where more complex
interpretation of data is required. For this reason, outer-sphere electron transfer kinetics is
more widely studied in homogeneous and heterogeneous system.
4.2.2 Dynamic NMR: Measurement of Electron Self-Exchange Kinetics

Homogeneous electron transfer kinetics can be studied via two different electron transfer schemes. One is the electron transfer between two different redox species. This electron transfer reaction is called the cross reaction and normally measured by monitoring absorption intensities of both redox species utilizing UV-vis spectroscopy. The other scheme is the electron self-exchange reaction between the same redox species of two different oxidation states and the rate of this reaction is measure by NMR spectroscopy.
Dynamic NMR techniques are normally employed to study electron self-exchange kinetics. This technique deals with time-dependent phenomena such as reaction or exchange kinetics. The exchange processes include chemical exchange such as inter or intramolecular proton/electron transfer, and conformational changes such as the boat-chair interconversion of cyclic structures or the hindered rotation of molecular fragments.

There are three exchange rate regimes in NMR time scale, which are fast, intermediate, and slow exchange. For fast and slow exchange rate limit, approximate equations are available to facilitate the analysis of data while for intermediate rate limit, more complicated mathematical treatment is required.

Second order electron transfer kinetics between two redox species is considered as two site exchange model (Figure 4.2). If the exchange rate is very slow compared to the chemical shift difference between two sites, the rate is in slow exchange regime. In this case, the two resonances are distinctly separated with narrow line width, and the relative fractions of molecules in the two sites are given by the relative integrated areas. The intermediate exchange rate results in broadened and/or convoluted resonances in which the resonance positions change toward a weighted average position. If the exchange rate is very fast compared to the chemical shift difference between two sites, a single sharp resonance is observed at a position that is the weighed average of the individual resonances.
Figure 4.2. Chemical exchange line shapes. (a) symmetric exchange with $p_1 = p_2 = 0.5$. (b) exchange with skewed populations $p_1 = 0.75$ and $p_2 = 0.25$.\textsuperscript{55}
4.2.3 **Determination of homogeneous electron self-exchange rate constants**

Electron transfer between oxidized species (3+) and reduced species (2+) of dendrimers are measured by NMR spectroscopy in partially oxidized dendrimer solutions. Dendrimers employed in this study have iron, ruthenium, and osmium tris(bipyridine) cores which showed large paramagnetic contact shifts when oxidized (Figure 4.3).

**Chemical oxidation of Metal cores**

To study homogeneous electron self-exchange kinetics, it is imperative to chemically oxidize the central core. Partially oxidized dendrimer solutions for measuring electron self-exchange rate can be made by mixing reduced and oxidized dendrimers together or *in situ* partial oxidation of dendrimers in solution. Various chemical oxidants are available for this purpose such as lead (IV) oxide, ceric (IV) ammonium nitrate, nitrosonium ion, and chlorine gas. 4,4’-Dimethyl-2,2’-bipyridine metal complexes could be oxidized by lead (IV) oxide in acidic aqueous solutions and separated from the reaction mixture. Partially oxidized solutions for these complexes were made by mixing two different oxidation states of dendrimer solutions (Scheme 4.1). However, oxidation for higher generation dendrimers has to be done in nonaqueous solution because of solubility. Moreover, separation of oxidized dendrimers from reaction mixture can easily cause some loss of material.
Figure 4.3. Dendrimers employed to Homogeneous electron self-exchange study.
This is undesirable because of limited sample amounts of higher generation dendrimers and the instability of the oxidized form. Thus, *in situ* partial oxidation method was used for preparing samples for higher generation dendrimers. Nitrosonium salts (e.g., NOPF₆) and chlorine gas are the best candidates for the oxidant for higher generation dendrimers. These reagents do not require specific purification steps to remove its reduced form after oxidation reaction because it has gas phase (NO(g)) or serves as a counter ion (Cl⁻ or PF₆⁻) for oxidized dendrimers. However, chlorine gas could not be used because of difficulties in quantitative measure of used amounts. Thus, nitrosonium salt was initially used for chemical oxidation of higher generation dendrimers. However, noticeable decomposition of dendrons was observed during experiments. Model studies showed that valerate based dendrons can be decomposed to some extent by nitrosonium ions (Table 1). As the dendron is intended only as an encapsulating moiety, an alternate, milder oxidant was required. Fortunately, it was determined that unsubstituted metal tris(bipyridine), (M(bpy)₃²⁺/³⁺) had a slightly higher redox potential compared to the methyl substituted metal complex (M(G0-bpy)₃²⁺/³⁺) and, upon addition of M(bpy)₃³⁺ to M(Gn)₃²⁺ (n = 1, 2) the former oxidized the latter (Scheme 4.1). The redox potential difference between these two species (ca. 150 mV in CH₃CN) provided a very mild route to prepare the oxidized dendrimers (Figure 4.4). Moreover, the resulting M(bpy)₃²⁺ did not interfere with the spectroscopic observation of the desired, line broadened signals (ca. 2.5ppm) and was much more stable toward reduction at room temperature compared with the nitrosonium ion.
Scheme 4.1.

\[
\begin{align*}
\text{M(Gn)}^2+ + \text{M(bpy)}^3+ \xrightarrow{\text{PbO}_2, \text{H}^+, \text{aq}} \text{oxidants} \\
\text{M(G0)}^2+ + \text{M(bpy)}^3+ \xrightarrow{\text{NOBF}_4(\sim 2\text{eq})} \text{r.t dark yellow} \text{ yes} \\
\text{M(G0)}^2+ + \text{M(bpy)}^3+ \xrightarrow{\text{Fe(bpy)}^3+} \text{NA} \text{ b no} \\
\text{M(G0)}^3+ + \text{M(bpy)}^3+ \xrightarrow{-78^\circ} \text{NA} \text{ a no} \\
\end{align*}
\]

1, X= -CH$_2$Ph, Y= -CH$_2$ Br

2, X= -CH$_3$, Y=-CH$_2$I

3, X= -CH$_2$Ph, Y= -CH$_2$ OCH$_3$

4, X=-CH$_3$, Y= -CH$_2$OCH$_3$

**Table 4.1.** Stability of valerate based dendrons for nitrosonium ion.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>temp($^\circ$C)</th>
<th>color change</th>
<th>decom.$^a$ (NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NOBF$_4(\sim 2\text{eq})$</td>
<td>r.t dark yellow</td>
<td>yes</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>yes</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>yes</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>yes</td>
</tr>
<tr>
<td>3</td>
<td>&quot; -78</td>
<td>&quot;</td>
<td>NA</td>
</tr>
<tr>
<td>4</td>
<td>&quot; -78</td>
<td>&quot;</td>
<td>NA</td>
</tr>
</tbody>
</table>

$^a$ sign of decomposition in 1H-NMR spectra.

$^b$ Fe(bpy)$_3^{3+}$ has strong red color, thus decomposition can not be evaluated with color.

**Table 4.1.** Stability of valerate based dendrons for nitrosonium ion.
Chapter 4: Results and Discussion

Figure 4.4. Cyclic Voltammetry for $\text{M(bpy)}_3^{2+/3+}$ and $\text{M(G0)}_3^{2+/3+}$ in acetonitrile solution.

Determination of Electron Self-Exchange Rate Constant

It was found that the electron self exchange rate for G0 complexes are near the fast exchange limit as indicated by the linear relationship between the mole fraction of oxidized species, $f_p$, and the chemical shift of proton signal. On the other hand, electron self exchange rate for G1 and G2 complexes are near the slow exchange limit as indicated by line broadening of proton signal without chemical shift movements.

The second order electron self-exchange rate constants were measured by NMR
line broadening techniques. The proton NMR spectra of the partially oxidized dendrimer solutions were interpreted by use of the two-site exchange model between diamagnetic Metal(II) and paramagnetic Metal(III) cores. The approximate Bloch-McConnell equations for the electron self-exchange rate constants in the fast exchange and slow exchange limits were used to calculate the rate constants.\(^{33,39,64}\)

\[
k_{\text{ex}} = \frac{4\pi f_p f_d (\delta\nu)^2}{(W_{DP} - f_d W_D - f_p W_P) C_{\text{tot}}}
\]

in the fast exchange limit \hspace{1cm} (eq. 1)

\[
k_{\text{ex}} = \frac{\pi (W_{DP} - W_D)}{[P]}
\]

in the slow exchange limit \hspace{1cm} (eq. 2)

In the equation, \(\delta\nu\) is the contact shift in Hz (chemical shift movements caused by paramagnetic electrons, that is the chemical shift difference between pure diamagnetic and pure paramagnetic species), \(f_p\) and \(f_d\) are the mole fractions of paramagnetic and diamagnetic species respectively, \(W_p, W_D,\) and \(W_{DP}\) are the peak width (full line width at half-maximum) for paramagnetic species only, diamagnetic species only, and the mixture of two species respectively, \(C_{\text{tot}}\) is total molar concentration and \([P]\) is molar concentration of paramagnetic species. Values for \(f_p\) for the fast exchange system were more precisely determined using the relationship

\[
f_p = \left| \frac{\nu_{dp} - \nu_d}{\delta\nu} \right|
\]
assuming that the chemical shifts vary linearly with mole fraction. \( \nu_d \) and \( \nu_{dp} \) are the resonance frequency of the diamagnetic species and the mixture respectively.

**Near The Fast Exchange Limit: G0 Metal Complexes**

G0 ruthenium and iron complexes could be oxidized chemically by lead(IV) oxide in acidic aqueous solution (Scheme 4.1). The oxidized forms of these complexes were relatively stable toward reduction and could be separated from reaction mixtures. They were stable for a long time period (several months) in dark and cool conditions. \(^1\)H-NMR spectra showed large contact shift for both cases (Figure 4.5 and 4.6). The singlet corresponding to the methyl protons at 2.5 ppm on the methyl-bipyridine ligand was used to calculate the rate constant as it showed sufficient chemical shift movements and line broadening during the experiments (Figure 4.7). Some of protons did not give enough shift movement or showed a peak broadening that was too large to study. Thus, the contact shift and line broadening of methyl proton were monitored throughout experiments. Successive aliquots of solutions of oxidized forms were added to a solution of the reduced forms and a \(^1\)H-NMR spectrum was recorded after each addition. The rate of the electron self-exchange for G0 complexes was found to be in the fast exchange limit, indicated by the linear relationship between the mole fraction, \( f_p \), and the chemical shift. The electron self-exchange rate constant was calculated using approximate equation in the fast exchange limit and is summarized in Table 2 at the end of this chapter.
Figure 4.5. $^1$H-NMR for Fe(G0)$_5^{2+}$ and Fe(G0)$_5^{3+}$.
Figure 4.6. $^1$H-NMR for Ru(G0)$_3^{2+}$ and Ru(G0)$_5^{3+}$.
Figure 4.7. Measured 1H-NMR spectra of partially oxidized dendrimer solution with various fraction \( f_p \) of oxidized complexes at 297K. Initial \( [\text{Fe}^{2+}] \) = 11.13mM and \( [\text{Ru}^{2+}] \) = 10.60 mM
\(^1\)H-NMR spectra were measured in CD\(_2\)Cl\(_2\)/CD\(_3\)CN (5:1, v:v) mixtures throughout the experiments to assure the solubility of all generations (G0, G1, and G2).

**Near The Slow Exchange Limit: the First and Second Generation Dendrimers**

The electron self-exchange rate for the first and second generation of iron tris(bipyridine) core dendrimers were found to be in the slow exchange limit as determined by a lack of noticeable change in chemical shift over the concentration range examined (Figure 4.8). \(^1\)H-NMR line broadening experiment data were fit to the slow exchange equation (eq. 2) and average \(k_{\text{ex}}\) values were determined from slopes of plots \(\pi(W_{\text{DP}}-W_D)\) vs \([\text{Fe}(\text{Gn})_3^{3+}]\) (Figure 4.9). The spin-spin coupling of the observed proton peaks with the methylene protons next to it hampered the determination of the line width. Thus, triplet peaks in pure Fe(Gn)_3\(^{2+}\) (n = 1 and 2) were deconvoluted to determine \(W_D\) values. \(W_{\text{DP}}\) of the sample mixture were measured after line broadening was corrected for this spin-spin coupling. This treatment of data gave more acceptable results for both molecules compared with data without deconvolution, giving an intercept much closer to the expected value of zero (Figure 4.9). Observed electron self-exchange rate constants for all generations were tabulated in Table 2.

Although use of the methylene proton peak (ca. 2.7 ppm) for calculating the electron self-exchange constant was satisfactory, the amounts of sample required were unacceptably large for further study. Kinetic measurements of this partially oxidized solution had to be studied under the pseudo first order kinetic condition, \(k_{\text{obs}} = k_{\text{ex}}[P]\)\(^{41,43,52-54,66}\) and correcting for spin-spin coupling of methylene protons required larger line
Figure 4.8. $^1$H NMR spectra of Fe(G1)$_3^{2+/3+}$ and Fe(G2)$_3^{2+/3+}$ systems at 297K in CD$_2$Cl$_2$/CD$_3$CN (5/1 v/v) mixture. The counter anion was PF$_6^-$ and initial [Fe$^{2+}$] = 8.56 and 8.51mM for G1 and G2 respectively.
Figure 4.9. A plot of line broadening versus the concentration of Fe(Gn)_{3}^{3+} (n = 1, 2).

broadening of the proton signal than splitting of J-coupling. This required large molar concentration of samples (ca. 8.5mM). This was unacceptable because limited amounts of sample are available especially for 2nd generation. Fortunately, there is another signal available near 8.2ppm in 1H-NMR spectra. In the slow exchange limit, this signal showed enough broadening to study electron self-exchange kinetics. Moreover, this did not show any noticeable spin-spin coupling with other protons and enable us to measure small increase of signal broadening compared with triplet signal at 2.7 ppm. Figure 4.10 shows a series of 1H-NMR spectra as successive aliquots of oxidant solution were added to a solution of the reduced form. Signals from the reduced form of oxidant indicated that oxidant itself did not exchange an electron with its reduced form. Otherwise, broadened signals caused by electron exchange of the oxidant have to be observed instead of sharp
Figure 4.10. $^1$H NMR spectra of Fe(G1)$_3^{2+/3+}$ and Fe(G2)$_3^{2+/3+}$ systems at 297K in CD$_2$Cl$_2$/CD$_3$CN (5/1 v/v) mixture. The counter anion was PF$_6^-$ and initial [Fe$^{2+}$] = 1 and 2mM for G1 and G2 respectively.
and well resolved signals. Thus, it is indicated that the cross reaction between the oxidant and dendrimer is not reversible in experimental time scale and it is fast enough to use it as an oxidant for electron self-exchange kinetic study of dendrimers. However, another problem was encountered during experiments with 2nd generation dendrimers. Proton signal at 8.7 ppm slightly move to the upfield compared to the first generation dendrimers. This signal was considerably superimposed on the reduced forms of oxidant causing the difficulties in measuring small variation of line broadening.

A possible solution to this problem was sought by surveying oxidants which have enough thermodynamic driving force to oxidize the dendrimers and have \(^1\)H-NMR signals that do not interfere with the signal from either generation of dendrimers. In literature studies, it was found that phenanthroline (Phen) and 5,5’-dimethyl-2,2’-bipyridine (5-methyl-bpy) make corresponding iron complexes which show slightly higher redox potentials compared to the Fe(G0)\(_{3}^{2+}/3^+\) complex.\(^65, 67\) Thus, Fe(Phen)\(_{3}^{2+}\) and Fe(5-methyl-bpy)\(_{3}^{2+}\) were synthesized (Scheme 4.2) and their \(^1\)H-NMR spectra were compared with both generations of iron core dendrimers (Figure 4.11). However, all compounds showed considerable interference between signals. This situation may be worsened as the peak at ca. 8.2 ppm is broadened as the result of electron exchange.

The other possible solution to the problem of this peak overlap is the use of deuterated bipyridine as a ligand. \(^1\)H-NMR specifically observes the resonance signal from the proton, thus if proton is switched with deuterium, the signal overlap problem would be solved. Scheme 4.3 shows two different approaches that were pursued to synthesize the deuterated bipyridine.\(^68, 69\)
The bipyridine N-oxide route has slightly mild reaction conditions ($150^\circ$C) than the other ($200^\circ$C), thus glass pressure vessel available in the lab could be utilized. However, the final deoxygenation step was unsuccessful and was not pursued further and the second method was pursued in a pressure bomb. The other route was synthetically favored because no particular purification step was required. The $^1$H-NMR spectrum of deuterated bipyridine showed trace $^1$H proton signals as low intensity singlets instead of doublet or triplet (Figure 4.12). This indicates that the possibility of spin-spin coupling with nearby $^1$H proton is low, that is, deuteration reaction was successful (96% conversion calculated by relative integrations). Complexation with iron and oxidation by lead(IV) oxide were also successful as in the case of H$_8$-bipyridine. The deuterated oxidant was stable toward reduction under a cold and dark environment for several months. The $^1$H-NMR line broadening experiments with the deuterated bipyridine oxidant, 15, displayed well resolved successive broadened proton signals at ca. 8.2 ppm.
for both the first and second generation of iron core dendrimers. In the range of employed concentrations of 15, the trace $^1$H proton signals from reduced oxidants, Fe(d$_8$-bpy)$_3^{2+}$ did not considerably interfere with the spectroscopic observation of the desired, line broadened signals (Figure 4.13). Data were fit to the slow exchange equation (eq.2) and average $k_{ex}$ values were determined from slopes of plots $\pi(W_{DP}-W_D)$ vs [Fe(Gn)$_3^{3+}$] and summarized in Table 2.

Figure 4.11. The survey for possible oxidants.
Scheme 4.3.

![Chemical reaction diagram](image)

Figure 4.12. $^1$H-NMR spectra for $^1$H-bipyridine and $^2$H-bipyridine.
Fe(G1)$_3^{2+/3+}$

- [Fe$^{3+}$] = 0.65 mM
- 0.55 mM
- 0.44 mM
- 0.34 mM
- 0.00 mM

Fe(G2)$_3^{2+/3+}$

- [Fe$^{3+}$] = 1.30 mM
- 1.06 mM
- 0.81 mM
- 0.55 mM
- 0.00 mM

Figure 4.13. $^1$H NMR spectra of Fe(G1)$_3^{2+/3+}$ and Fe(G2)$_3^{2+/3+}$ systems at 297K in CD$_2$Cl$_2$/CD$_3$CN (5/1 v/v) mixture. The counter anion was PF$_6^-$ and initial [Fe$^{2+}$] = 2 and 4mM for G1 and G2 respectively.
Meanwhile, complementary data were obtained by using the paramagnetic enhancement of the longitudinal paramagnetic relaxation rate ($R_1$) for electron self-exchange in the slow exchange limit. The line broadening technique described above utilized transverse (spin-spin) relaxation time ($T_2$) to calculate the electron self-exchange rate constant by using the relationship between half height line width signal and transverse relaxation time, $W=(\pi T_2)^{-1}$. The use of line broadening to measure transverse relaxation time ($T_2$) can cause erroneous results because of inhomogeneity of instrument or sample shimming. Thus, it was hypothesized that use of the longitudinal relaxation time can give more reliable data especially in situations where electron self-exchange rate constant is small and the peak broadening by electron exchange can be difficult to determine precisely.
The approximate Bloch-McConnell equation for the slow exchange limit, eq 2 can be re-expressed using the relaxation rate, eq 3. In the slow exchange limit of the exchange system, the observed relaxation rate, \( R_{io} \), of the diamagnetic signal in the partially oxidized sample mixture is given by equation 3.\(^{40-51, 66}\)

\[
R_{io} = R_{id} + k_{ex} c f_p, \quad i = 1, 2 \ (R_i = 1/T_i) \quad \text{(eq. 3)}
\]

Here \( R_{id} \) is the relaxation rate of the diamagnetic site in the absence of exchange, \( f_p \) is the molar fraction of the paramagnetic species, \( k_{ex} \) is the second order electron self-exchange rate constant, and \( c \) is the total concentration of the sample. This equation is given in the general form to indicate the use of the relaxation rate for determining electron self-exchange rate and holds for both the longitudinal (spin-lattice) and transverse relaxation times. A series of conventional 1D \(^1\)H inversion-recovery (IR) experiments were employed to measure the longitudinal relaxation time (Figure 4.15) and a plot of \( R_{io} \) against \( c f_p, [Fe^{3+}] \) gave a straight line with slope of \( k_{ex} \) (Figure 4.16). The electron self-exchange rate constants for G1 and G2 iron core dendrimers are summarized in Table 2.

Although the difference between the rate constants determined using \( T_1 \) and \( T_2 \) is considerable, the trend of electron transfer attenuation between generations holds for two different methods (Table 2). However, inversion-recovery experiments require considerable time (ca. 2 to 3 hours) to measure a series of longitudinal relaxation times and further determination of thermodynamic parameters requires more time (c.a 8 to 15
hours) with this method. The partially oxidized samples of dendrimers were not stable enough over such a long experiment time. The observed electron transfer attenuation trend between generations holds for $^1$H-NMR line broadening, thus, inversion-recovery experiments for determining electron self-exchange rate were not used to determine thermodynamic activation parameters.

As can be observed from the data in Table 2, the electron self-exchange rate for the first generation dendrimer was retarded dramatically relative to Fe(G0)$_3^{2+/3+}$ system. The attenuation of the electron self-exchange rate between the first and the second generation dendrimer was insignificant compared to that between Fe(G0)$_3^{2+/3+}$ and Fe(G1)$_3^{2+/3+}$. This result was unexpected as it does not correlate with the “encapsulation” behaviors illustrated in heterogeneous electron transfer studies done previously.15, 21 This result is perhaps even more surprising if one considered that homogeneous electron transfer between the redox centers in Fe(G2)$_3^{2+}$ and Fe(G2)$_3^{3+}$ must occur effectively through four “layers” of repeat units (e.g. two for each molecule). We rationalize these results by considering the possibility of relatively rapid core motion within the dendrimer architecture. Previously, the effects of the core motion were argued to be important in governing the rate of heterogeneous electron transfer in iron-sulfur cluster core dendrimers containing alternately flexible and rigid repeat units and in a series of iron-sulfur cluster core dendrimer constitutional isomers.21, 70, 71 Most notably, in films of these molecules, the rate of the electron hopping through these films was observed to be in the slow exchange regime and no significant variation in the electron self-exchange rate constants was observed with generation.70 Similar explanations may be used to
rationalize the behavior in these systems. Over the time-scale of the slow exchange regime, the redox core unit within the dendrimer can move so as to achieve a relatively close approach with another redox core in a neighboring dendrimer. Thus, the effective distance for electron self-exchange appears to be not strongly affected by dendrimer size in the slow electron exchange regime.
Figure 4.15. A series of inversion recovery experiments for Fe(Gn)$_3^{2+3+}$. The counter anion was PF$_6^-$ and initial [Fe$^{3+}$] = 2mM for G1 and G2. The peak at ca. 8.2ppm shown. $\tau$ was varied ranging from 0.02 to 15s.
Chapter 4: Results and Discussion

1H-NMR line broadening experiments for ruthenium tris(bipyridine) core dendrimers were also conducted. Partially oxidized dendrimer solutions were prepared in a similar fashion to the iron core dendrimers except Ru(bpy)$_3^{3+}$ was used as the oxidant (Scheme 4.1). In several attempts, 1H-NMR line broadening occurred after a considerable amount of oxidant (ca. 0.3 mole fraction) was added. The y-intercept in a line broadening vs [Ru(Gn)$_3^{3+}$] plot was significantly off from its expected value of zero, while keeping its linear behavior in the plot. It was thought that ruthenium complexes are more sensitive for reductive impurities because their relatively high thermodynamic redox potentials. Indeed, Ru(bpy)$_3^{3+}$ is more unstable at room temperature compared with Fe(bpy)$_3^{2+}$. Thus, slightly modified methods were employed to determine the electron self exchange rate for ruthenium core dendrimers. Small volumes of concentrated oxidant, Ru(bpy)$_3^{3+}$ solution were added to dendrimer solution until line broadening occurred. (‘preoxidation’; the concentrated oxidant was used for this step reducing errors from

![Figure 4.16. A plot of $R_{1o}$ versus Fe(Gn)$_3^{3+}$ (n = 1, 2).](image)
Figure 4.17. $^1$H NMR spectra of Ru(G1)$_{2/3+}$ and Ru(G2)$_{2/3+}$ systems at 297K in CD$_2$Cl$_2$/CD$_3$CN (5/1 v/v) mixture. The counter anion was PF$_6^-$ and initial [Ru$^{3+}$] = 4mM for G1 and G2. The spectra are offset; line broadening occurs without significant shifting of peak position.
larger total volume change in following experiments) The oxidized dendrimers produced were unstable toward reduction and reduced to its original oxidation states within around 1 hour (adventitious reduction). Thus, line-broadening by oxidized dendrimers disappeared. After this ‘preoxidation’ step, another line broadening experiment was performed within 20 min. During this time, no considerable line narrowing by adventitious reduction was observed and successive broadened signals were observed giving linearity in a plot of line broadening vs Ru(Gn)$_3^{3+}$ plot. This treatment of data gave more acceptable results for both molecules, giving an intercept much closer to the expected value of zero (Figure 4.18). The observed electron self-exchange rate constants for all generations are tabulated in Table 2.

Figure 4.18. A plot of line broadening versus the concentration of Ru(Gn)$_3^{3+}$ (n = 1, 2).
Determination of Thermodynamic Activation Parameters

In order to obtain further insight into the factors influencing electron self-exchange rate, it is desirable to evaluate activation parameters in addition to rate constants at a single temperature. The temperature dependence of electron self-exchange rate is described by well-known Eyring equation which is theoretically based on the transition state model.

\[
k = \frac{k_B T}{h} \exp \left( -\frac{\Delta G^\ddagger}{RT} \right) = \frac{k_B T}{h} \exp \left( -\frac{\Delta H^\ddagger}{RT} - \frac{\Delta S^\ddagger}{R} \right)
\]

where \( k \) is the second-order rate constant, \( k_B \) is Boltzmann's constant, \( h \) is Planck's constant, \( R \) is the gas constant, \( T \) is the absolute temperature, \( \Delta G^\ddagger \) is the free energy of activation, \( \Delta H^\ddagger \) is the enthalpy of activation, and \( \Delta S^\ddagger \) is the entropy of activation.

Thermodynamic activation parameters for iron core dendrimers (G0, G1 and G2) were obtained by variable temperature NMR studies and are summarized in Table 2. A plot of \( \ln(k_{ce}/T) \) versus \( 1/T \) gave a straight line (Eyring plot, Figure 4.19) and \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) were determined respectively from the slope and the y-intercept of this line. The activation free energy was calculated using the relationship, \( \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \) and changes between generations displayed the similar trends with electron self-exchange attenuation although the difference between G0 and G1 was not big enough to rationalize the large attenuation of electron self exchange. The standard rate constant for outer-sphere ET reactions is given by the Marcus equation and is a function of the activation
barrier $\Delta G^\neq$ and the pre-exponential factor $k_e A$.$^{18, 73, 74}$

$$k^o = k_e A \exp(-\Delta G^\neq/RT)$$

where $k_e$ is the electronic transmission coefficient and $A$ is the nuclear frequency factor. In dendrimer solution, the pre-exponential factors as well as the thermodynamic activation term, $\Delta G^\neq$ play an important role in the kinetics of the electron transfer reaction. Thus, additional contribution from the pre-exponential term can be responsible for large rate attenuation between G0 and G1.$^{18, 35, 58, 70, 73}$

The entropy and enthalpy changes between generations showed somewhat different trends. Although the activation free energy increased from G0 to G1, entropy was decreased. This is probably because the relative solvent free microenvironment for G1 does not require large outer-sphere solvent reorganization energy and dendritic moieties behave analogous to a viscous solvent. Thus, dendritic solvation between two redox states in first generation dendrimers does not require as much rearrangement as solvation of G0 by small solvent molecules. The activation enthalpy increases due to an extended electron transfer distance and causes an increase in the activation free energy compared with the zeroth generation dendrimer. In the case of the first and second generation, enthalpy did not change much within the limits of experimental error but entropy increased slightly. This is probably because the effective distance for electron transfer is similar between generations because of the core mobility.
However, such a rearrangement of the core in the second generation requires more negative entropy change. Thus, the slight increase of activation free energy is mainly due to the entropy change associated with reorganization of the core. However, small changes in activation parameter between generations and uncertainties in the temperature dependence of the rate constants preclude the use of activation parameters to firmly establish the structure-properties relationships for electron self-exchange of dendrimers.

**Figure 4.19.** Eyring plot of self-exchange rate constants for iron tris(bipyridine) core dendrimers.
Further temperature dependence studies of electron self-exchange with ruthenium core dendrimers were hampered by the instability of their oxidized forms and could not be pursued further. A cobalt core could not be used in this study because both of its oxidation states are paramagnetic and cause paramagnetic contact shift and NMR line broadening. Thus, for further study, a new core material was required and osmium was added in a series of metal tris(bipyridine) core dendrimers (Figure 4.20). However, synthetic difficulties prevented the synthesis of the second generation dendrimer and even the first generation dendrimer was not free from impurities and did not give a straight line in the line broadening and [Os\(^{3+}\)] plot. Because, at least, the second generation is required for this study, this route was not pursued further.
Table 4.2.  

<table>
<thead>
<tr>
<th></th>
<th>$k_{ex}$ (M$^{-1}$S$^{-1}$)</th>
<th>$\Delta H^#$ (kcal · mol$^{-1}$)</th>
<th>$\Delta S^#$ (cal · mol$^{-1}$ · K$^{-1}$)</th>
<th>$\Delta G^#$ (J · mol$^{-1}$) 298K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_1$ Aryl</td>
<td>$T_2$ Argy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(G0)</td>
<td>NA$^b$</td>
<td>2.59(0.19) x 10$^7$</td>
<td>NA$^b$</td>
<td>3.09(0.58)</td>
</tr>
<tr>
<td>Fe(G1)</td>
<td>1.48(0.03) x 10$^4$</td>
<td>4.71(0.27) x 10$^4$</td>
<td>5.30(1.01) x 10$^4$</td>
<td>7.75(1.21)</td>
</tr>
<tr>
<td>Fe(G2)</td>
<td>0.56(0.08) x 10$^4$</td>
<td>3.00(0.21) x 10$^4$</td>
<td>2.72(1.03) x 10$^4$</td>
<td>6.37(1.31)</td>
</tr>
<tr>
<td>Ru(G0)</td>
<td>NA$^b$</td>
<td>3.46(0.23) x 10$^7$</td>
<td>NA$^b$</td>
<td>3.20(0.13)</td>
</tr>
<tr>
<td>Ru(G1)</td>
<td>NA$^b$</td>
<td>NA$^b$</td>
<td>7.26(0.89) x 10$^4$</td>
<td>NA$^b$</td>
</tr>
<tr>
<td>Ru(G2)</td>
<td>NA$^b$</td>
<td>NA$^b$</td>
<td>5.70(0.61) x 10$^4$</td>
<td>NA$^b$</td>
</tr>
</tbody>
</table>

$^a$Values in parentheses represent the magnitude of the 90% confidence intervals of these values.

$^b$was not determined.
Figure 4.20. $^1$H-NMR for Os(G0)$_3^{2+}$ and Os(G0)$_3^{3+}$.
4.3. Conclusion

As dendrimers are studied in a greater variety of ways, the idea of dendritic encapsulation is less and less well described by a static dendrimer model. Here, in exploring electron transfer between dendrimers in solution, the simple generational dependence of encapsulation on rate attenuation does not suffice. To understand the effects of encapsulation on electron transfer kinetics, the time-scale of the electron transfer as well as the structure and conformational mobility of the dendrimers are important factors. In this case, a simple rationale for the behaviors observed is that the redox core within these dendrimers in the slow electron self-exchange regime can move in a non-rate limiting fashion toward a neighboring redox core with the result that the structural effect of the dendrimer is reduced and electron transfer is facilitated in larger dendrimers.

4.4. Experimental

NMR kinetic measurements

All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc, dried following standard procedures, and stored in a dry box under nitrogen atmosphere. NMR spectra were obtained using Varian 300MHz NMR or Bruker 500MHz spectrometer. Bruker 500MHz with VT temperature unit was used for variable temperature NMR studies. Sample solutions for NMR measurement were prepared freshly in the dry box prior to use. Solutions of Metal(II) core dendrimers (M = Ru, Fe and Os) in CD$_2$Cl$_2$:CD$_3$CN (5:1 v/v) were prepared and transferred to 5 mm Kontes brand
threaded NMR tubes in the dry box. Aliquots (typically 10uL) of the oxidants (M(G0)₃³⁺ or M(bpy)₃³⁺) in CDCN₃ were added to the NMR tube between each NMR measurements. Line widths were determined by fitting the experimental signals to a Lorenzian function using commercially available NUTs software.

One-dimensional inversion recovery experiments were used to measure the longitudinal $^1$H relaxation rates at 500 MHz. Each experiment consisted of 12 spectra with delay times ranging from 0.02 to 15s. A recovery delay of 10s was applied between scans, and 8 scans were recorded for each spectrum. The relaxation delays were chosen randomly to compensate for possible systematic drift. Integrals of the proton signals versus delay times were plotted and fit to a three-parameter fit using NUTs software.

$$y = A \times \left\{ 1 - \left[ 1 + W \times (1 - \exp(-K/T)) \right] \right\} \times \exp\left(-x/T\right)$$

where $T$ is $T_1$ relaxation time, $A$ is peak integral at time $x >> T$, $K$ is total time between scans in the 180-tau-90 sequence (acquisition time + relaxation delay time), $x$ is delay time $t$ in the 180-tau-90 pulse sequence, and $W$ is -(integral at time $x=0/A$). The parameter $W$ is determined in the fitting process, as inversion in this experiment is not always perfect. This gives better results than assuming that the integral at time $x=0$ is simply the negative of the integral for infinitely long $x$.⁷⁵
Chapter 4: Results and Discussion

Materials

5-methyl-bpy (8).\(^{76}\) A mixture of K\(_2\)CO\(_3\), palladium acetate, tetra-n-butyl ammonium bromide and 3-methylpyridine in DMF was stirred under nitrogen atmosphere for few minutes at 115\(^\circ\)C. Isopropanol was added. The mixture was remained at 115\(^\circ\)C for 4days. After cooling to room temperature, methylene chloride and water were added and filtered. The organic phase was washed with water and dried over MgSO\(_4\). The solvent was evaporated under vacuum. Yield: 35\% (1.87g); \(^1\)H-NMR (CD\(_2\)Cl\(_2\)) \(\delta\) (ppm) 2.4 (s, 6H), 7.6(d, 2H), 8.3(d, 2H), 8.5(d, 2H).

2,2'-Bipyridine N,N-dioxide (12).\(^{77}\) To a solution of 2,2'-bipyridyl (10) (10g) in 75mL of glacial acetic acid was added 30\% hydrogen peroxide (13mL). The mixture was heated at 70-80\(^\circ\)C for 3hrs. An additional 9mL of 30\% hydrogen peroxide was added and the temperature maintained at 70-80\(^\circ\)C for a further 19hrs. On addition of acetone (1L), the product precipitated. This was recrystallized from hot water by the addition of a large excess of acetone, yielding fine white needles. This was used for the next step without further purification. Yield: 85\% (10.2g)

d\(_8\)-2,2’-bipyridyl N,N-dioxide (13).\(^{68}\) 2,2’-Bipyridyl N,N-dioxide (12) in NaOD-D\(_2\)O (1M in NaOD) was heated at 150\(^\circ\)C for 65hrs in a sealed glass tube. From filtered, concentrated, and cooled solution the product separated as colorless needles. This was used for the next step without further purification. However, further reaction was not successful and did not pursue further (see text).

d\(_8\)-2,2’-bipyridyl (11).\(^{69}\) 2,2’-Bipyridyl (10) (2g) was reacted at 200\(^\circ\)C in 20mL of 1M NaOD/D\(_2\)O for 6days. On cooling, the reaction mixture was filtered and air dried. Yield:
73% (1.54g).

**Fe(d-bpy)$_3$(PF$_6$)$_3$**. $^{65}$ d$_8$-2,2'-bipyridyl (10) and FeSO$_4$.7H$_2$O were added to 25mL of H$_2$O and warmed gently until all solid had dissolved. The solution was then filtered into a flask immersed in an ice bath and 2-3mL of 1M H$_2$SO$_4$ added. After further cooling, an excess of PbO$_2$ was added and the solution was mixed thoroughly until all traces of red color had disappeared leaving a blue solution. This solution was filtered into a cold aqueous solution of KPF$_6$ whereupon the blue solid of the desired complex precipitated immediately. The product was filtered, washed first with a small amount of cold water, then chloroform, and dried over P$_2$O$_5$ under vacuum.

**Ru(d-bpy)$_3$(PF$_6$)$_3$**. $^{65}$ d$_8$-2,2'-bipyridyl (10) and RuCl$_3$ were added to 25mL of 2-methoxyethanol. The mixture was heated by microwave reactor and kept at 120°C for 1hrs. The solution was then filtered into a flask immersed in an ice bath and 2-3mL of 1M H$_2$SO$_4$ added. After further cooling, an excess of PbO$_2$ was added and the solution was mixed thoroughly until all traces of orange color had disappeared leaving a emerald green solution. This solution was filtered into a cold aqueous solution of KPF$_6$ whereupon the emerald green solid of the desired complex precipitated immediately. The product was filtered, washed first with a small amount of cold water, then chloroform, and dried over P$_2$O$_5$ under vacuum.
4.5. References


Appendix

The selected $^1$H-NMR Spectra
G1 Dendron (compound 37)
G2 Dendron (compound 35)
G3 Dendron (compound 45)
Fe(G1)$_3$(PF$_6$)$_2$
Fe(G2)_3(PF_6)_2
Ru(G1)$_3$(PF$_6$)$_2$