ABSTRACT

NIEVES-BERNIER, ELIAS Probing the Rate of Hole Transfer in Oxidized Synthetic Chlorin Dyads via Site-Specific ^{13}C -Labeling. (Under the direction of Dr. Jonathan S. Lindsey.)

Understanding electronic communication among interacting constituents of multicomponent molecular architectures is important for rational design in diverse fields including artificial photosynthesis and molecular electronics. One strategy for examining ground-state hole/electron transfer in oxidized tetrapyrrolic arrays relies on analysis of the hyperfine interactions observed in the EPR spectrum of the π -cation radical. This strategy has been previously employed to probe the hole/electron-transfer process in oxidized multiporphyrin arrays of normal isotopic composition, wherein ^1H and ^{14}N serve as the hyperfine “clocks,” and in arrays containing site-specific ^{13}C -labels, which serve as additional hyperfine clocks. Herein, the hyperfine-clock strategy is applied to dyads of dihydroporphyrins (chlorins). Chlorins are more closely related structurally to chlorophylls than are porphyrins. A de novo synthetic strategy has been employed to introduce a ^{13}C label at the 19-position of the chlorin macrocycle, which is a site of large electron/hole density and is accessible synthetically beginning with ^{13}C -nitromethane. The resulting dyad contains a diphenylethyne linker spanning the 10-positions of two zinc chlorins, one of which contains the single ^{13}C label. EPR studies of the monocations of both the natural abundance and ^{13}C -labeled chlorin dyads and benchmark monomers reveal that the time scale for hole/electron transfer is in the 4-7 ns range, which is 5-10-fold longer than that in analogous porphyrin arrays. The slower hole/electron transfer rate observed for the chlorin versus porphyrin dyads is attributed to the fact that the HOMO is a_{1u} -like for the chlorins versus a_{2u} -like for the porphyrins; the a_{1u} -like orbital exhibits little (or no) electron/hole density at the site of linker

attachment whereas the a_{2u} -like orbital exhibits significant electron/hole density at this site. Collectively, the studies of the chlorin and porphyrin dyads provide insights into the structural features that influence the hole/electron-transfer process.

Probing the Rate of Hole Transfer in Oxidized Synthetic Chlorin Dyads via Site-Specific
¹³C-Labeling

by
Elías Nieves-Bernier

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Chemistry

Raleigh, North Carolina

03/22/2011

APPROVED BY:

Alexander Deiters

Christian Melander

Jonathan S. Lindsey
Chair of Advisory Committee

DEDICATION

This thesis is dedicated to my father Elias Nieves-Nieves and my mother Luz M. Bernier-Amaro. Even though they are far away from me physically they have always been with me in thoughts and spirit. Their unconditional and everlasting support has been a key factor in my success as both a student as well as a person. Despite the obstacles found along the way, they have always been there to help me get through.

I also want to dedicate my thesis to my two brothers Luis E. Nieves-Bernier and Pedro E. Nieves-Bernier and my sister Elia M. Nieves-Bernier. I have learned important things from them such as to never give up despite the adversities and to fight for what I want until the end. They were an important factor in my comeback to finish my Master's Degree after I took a leave of absence. Part of my motivation to keep going comes from the fact that they see me as a model to imitate since I am the eldest brother.

Last but not least I want to dedicate my thesis to all the friends I have made both as an undergraduate and graduate student. During my journey that started almost nine years ago, they have seen me grow not only as a student but as a person. My mother told me once that my friends are my family when my immediate family is not present. That is how important all of you are to me. Thank you for all the support that I received from all of you and for being there for me through the good times as well as the bad. My thoughts are always with all of you, always have and always will be.

Esta tesis está dedicada a mis padres Elías Nieves-Nieves y Luz M Bernier-Amaro. A pesar de la distancia, siempre los llevo en mis pensamientos y en mi corazón. Su apoyo incondicional e infinito ha sido un factor importante en mi progreso tanto como estudiante y como persona. A pesar de los obstáculos encontrados en el camino, ellos siempre han estado ahí para mí para ayudarme a pasar a través de estos.

También quiero dedicar mi tesis a mis hermanos Luis E. Nieves-Bernier, Pedro E Nieves-Bernier y a mi hermana Elia M. Nieves-Bernier. De todos ellos he aprendido varias cosas importantes tales como a nunca darme por vencido en momentos de dificultad y a luchar por lo que quiero hasta el final. Ellos fueron un factor importante en mi regreso a la universidad para terminar mis estudios graduados después de haberme tomado una licencia temporal de mis estudios post graduados. Parte de mi motivación para seguir adelante viene del hecho de que ellos me ven como un modelo a imitar por ser el hermano mayor en la familia.

Por ultimo pero no menos importante quiero dedicar esta tesis a todos mis amigos que han estado conmigo desde que comencé en este viaje hace casi 9 años. Tanto a los amigos que conocí en Puerto Rico cuando fui estudiante sub graduado como a los que conocí cuando llegué a Estados Unidos para continuar mis estudios postgraduados. Todos ellos han visto de cerca mi crecimiento tanto como de estudiante y como persona a través de todos estos años. Una vez mi madre me dijo que mis amigos iban a ser mi segunda familia cuando mi familia no estuviese presente físicamente. Eso es cuán importante todos ustedes son para mí. Gracias a todos ustedes por su apoyo y por haber estado conmigo tanto en las buenas como en las malas. Siempre los llevo en el corazón, siempre los he llevado y siempre los llevaré.

BIOGRAPHY

I was born on August 8th 1984 in Arroyo, Puerto Rico. I am the eldest of four children. My parents are Elias Nieves-Nieves and Luz M. Bernier Amaro. During my childhood I excelled in math. I participated in several math competitions winning twice, one in elementary school and the other when I was a freshman in college. I entered college in the fall of 2002 at the University of Puerto Rico at Cayey majoring in Math Pedagogy. In the spring 2004 I realized I no longer had the passion for math I used to have and I decided to take on a challenge and embark on a new journey. I decided to try something in the science field. It wasn't until the fall of 2004 when I was taking Organic Chemistry that I realized that I wanted to pursue it as a career. It was then that I switched my major to chemistry. In 2006 I was nominated by my college to enter a contest to determine the best chemistry student in Puerto Rico. This competition was sponsored by the *Colegio de Quimicos de Puerto Rico* (College of Chemists of Puerto Rico). I finished in 4th place. In June of 2007 I obtained my bachelor's degree with magna cum laude honors in science and a concentration in chemistry. The following fall I entered graduate school at North Carolina State University in the chemistry program. I started working with Dr. Brent Gunnoe's group. In the spring semester of 2008 Dr. Gunnoe decided to move to the University of Virginia with his research group. I was the only one who decided to stay at NC State. It was then that I joined Dr. Jonathan Lindsey's group and worked there for the next two years. On March 22nd 2011, I had my master's thesis defense. I defended it with success and in the process obtained my Master's Degree in Organic Chemistry. As for my future goals, I have two main goals that I want to

achieve. One of them is to become an Organic Chemistry professor. The other is to obtain my Ph.D in Chemistry.

TABLE OF CONTENTS

LIST OF FIGURES	vii
LIST OF SCHEMES	viii
LIST OF CHARTS	ix
LIST OF TABLES	x
Introduction	
Porphyrins and Hydroporphyrins	1
Ground-State Hole-Transfer	4
Excited-State Energy and Charge Transfer	6
Probing the Rate of Hole Transfer in Oxidized Synthetic Chlorin Dyads via Site-Specific ¹³ C-Labeling	
Introduction	8
Results and Discussion	
Site Specific Labeling Considerations	14
Synthesis	16
Characterization	22
EPR Studies	23
Summary and Outlook	27
Experimental Section	28
References	37

LIST OF FIGURES

Figure 1.	Representative absorption spectra of a porphyrin (chlorophyll <i>c</i> [blue line]), chlorin (chlorophyll <i>a</i> [green line]), and bacteriochlorin (bacteriochlorophyll <i>a</i> [red line])	3
Figure 2.	Absorption spectra of chlorophyll <i>a</i> (green line) and chlorophyll <i>d</i> (red line) in diethyl ether at room temperature	4
Figure 3.	Room temperature EPR spectra of the monocations of the unlabeled chlorin monomer and unlabeled chlorin dyad	25
Figure 4.	Room temperature EPR spectra of the monocations of the ¹³ C-labeled chlorin monomer and ¹³ C-labeled chlorin dyad	26

LIST OF SCHEMES

Scheme 1.	Synthetic Considerations for Site-Specific Labeling	16
Scheme 2.	Synthesis of the ^{13}C -labeled Western Half	17
Scheme 3.	Synthesis of the Eastern Halves	19
Scheme 4.	Formation of Chlorin Building Blocks and ^{13}C -Labeled Dyad	21

LIST OF CHARTS

Chart 1.	Porphyrins and Hydroporphyrins with Examples	1
Chart 2.	Porphyrin Dyads with One Meso- ^{13}C Label or Two α - ^{13}C Labels	10
Chart 3.	Metalloporphyrin a_{2u} and a_{1u} Orbitals	11
Chart 4.	HOMO for a Chlorin	12
Chart 5.	Site-Specifically ^{13}C -Labeled Chlorin Dyad and Unlabeled Dyad	14
Chart 6.	Unlabeled Chlorin Monomer	24

LIST OF TABLES

Table 1.	^{13}C NMR Chemical Shifts of Labeled Compounds	23
----------	--	----

Introduction

Porphyrins and Hydroporphyrins

Chlorophylls are the most abundant biological pigments¹ which are vital in photosynthesis due to their unique photophysical properties. The macrocycle of chlorophylls is the basis for their characteristic spectral features. Around 100 chlorophylls are known today, and all of them can be divided into three major groups according to their macrocycle type: porphyrins, chlorins and bacteriochlorins (Chart 1).

Chart 1. Porphyrins and Hydroporphyrins with Examples.

Porphyrins are essential for oxygen transport and storage in blood in the form of porphyrin-protein complexes hemoglobin and myoglobin.² A porphyrin is an 18 π -electron aromatic tetrapyrrole. Chlorins and bacteriochlorins differ from the basic porphyrin in having one or two pyrrole rings reduced at the β -position(s), respectively. Porphyrins and

hydroporphyrins are aromatic and obey Hückel's rule of aromaticity. The degree of saturation of the tetrapyrrole determines the difference in absorption properties of chlorophylls. Porphyrins strongly absorb in the blue spectral region, and only moderately in the red region around 620 nm. The dihydroporphyrin macrocycle, chlorin, is present in chlorophylls *a*, *b*, *d* and *e* and in bacteriochlorophylls *c*, *d*, and *e* of green bacteria. Thus, the fully unsaturated porphyrin macrocycle is present in the c-type chlorophylls of some algae and prokaryotes. These chlorin macrocycles pigments have characteristic absorption bands of similar intensity at 440 and 660 nm. Tetrahydroporphyrin macrocycle, bacteriochlorin, is present in bacteriochlorophylls of purple bacteria and absorbs in the near ultraviolet and near infrared spectrum region (Figure 1). The unique spectral and photophysical properties of porphyrins and hydroporphyrins have been exploited for use in biomedical applications, solar energy conversion, and molecular information storage.^{3,4,5}

Figure 1. Representative absorption spectra of a porphyrin (chlorophyll *c* [blue line]), chlorin (chlorophyll *a* [green line]), and bacteriochlorin (bacteriochlorophyll *a* [red line]).⁶

The presence of specific substituents at sites along the perimeter of the chlorophyll macrocycle can have significant effects on spectral, electronic, and photochemical properties. Changing even one substituent can significantly alter the spectral properties of chromophores. Thus, chlorophyll *a* and chlorophyll *d* (Chart 1) vary only in a single substituent at the 3-position, but this slight change results in profound difference in spectral properties⁷ (Figure 2).

Figure 2. Absorption spectra of chlorophyll *a* (green line) and chlorophyll *d* (red line) in diethyl ether at room temperature.⁶

Ground-State Hole Transfer

A detailed understanding of ground-state hole migration in molecular architectures is essential for the design and construction of solid-state molecular-based solar-energy conversion systems. In traditional liquid-junction solar cells, the holes are transported by the anode by exogenous diffusive carriers in the medium subsequent to photo-induced injection of an electron into the cathode. The combination of these processes completes the circuit that converts solar flux into electrical energy. In any type of all solid-state cell, hole-transport mediated by diffusive carriers is not a viable mechanism. One design that addresses this constraint is an all-molecular light harvesting/electron injection system wherein the gradient for excited-state energy flow is opposite that for the ground-state hole transport. Diffusive carriers are not required in this construct owing to the fact that hole migration occurs along the molecular backbone. The facile transport of holes away from the charge-injection unit

mitigates deleterious charge-recombination processes that compromise the efficiency of the cell.

Ground-state hole transfer has been much less studied than excited-state electron transfer despite the fundamental importance of the former. As noted above, ground-state hole-transfer are central to the design of solar cells or indeed any type of system that requires meta-stabilization or charge separated states and/or the effective elimination of charge recombination. Precluding charge recombination would permit the facile directing of holes to specific sites for detection, injection or storage.

A primary motivation for our early studies of ground-state hole/electron transfer was to gain insight into the rates of excited state charge-transfer processes that might occur. The rates of excited state interporphyrin charge transfer were not directly measurable because these processes are extremely inefficient in systems that were explicitly designed for highly efficient energy transfer. It should be emphasized that the hole-transfer rates in the electronic ground states of the oxidized arrays are not expected to be equal to the charge-transfer rates in the excited states of the neutral arrays; however, the former rates provide a qualitative measure of the factors that control the latter process. Here we have extended a new strategy that employs the use of isotopic label to access hyperfine interactions, and thereby clock the rates of hole transfer. The strategy relies on placement of a labeled nucleus at a site where substantial spin density exists in the cation radical formed upon oxidation. We previously have used ^{13}C labels in porphyrins; here we extend this approach to hydroporphyrins (chlorins).

Excited-State Energy and Charge Transfer

Excited-state energy transfer is the key process in light-harvesting systems for the capture of photons and the delivery of the excitation energy to a specific site for storage or utilization. In most energy-conversion schemes, ground-state hole transfer would then follow these excited-state processes in order to move charge from one place to another, such as in the completion of the circuit to utilize the photon-derived energy in molecular solar cells. We continue our studies on excited-state energy and charge transfer in multichromophore arrays to complement the studies on ground-state hole transfer. As with the studies on ground-state hole transfer, the proposed studies on excited-state processes will focus on hydroporphyrin-based arrays and fundamental mechanistic issues that will underlie the use of such architectures in solar-energy conversion applications.

The majority of work on artificial photosynthetic architectures has employed porphyrins, much less work has been devoted to chlorins, and only a few papers have appeared that incorporate a bacteriochlorin in arrays. The reliance of porphyrins as surrogates for chlorophylls and bacteriochlorophylls has stemmed from ease of synthetic access. The recent synthetic advances in chlorin and bacteriochlorin chemistry now make this reliance unnecessary. Our group have previously prepared light-harvesting arrays composed of tetrapyrrole analogues that absorb in the red or near infrared region, including phthalocyanines, chlorins, and oxochlorins. One finding that emerged concerned the mechanisms of energy transfer. In porphyrin-porphyrin arrays, the dominant mechanism entailed through-bond (TB) rather than through-space (TS) energy transfer. In the one chlorin-containing dyad (joined via the 10-positions) that was examined by our group, the TB

contribution was strongly diminished whereas the TS contribution was only slightly enhanced. It is of fundamental interest to assess the contributions of the TB and TS pathways in chlorin dyads wherein the linker is located at a variety of positions at the perimeter of the macrocycle, given that the HOMO has a node at the 10 position and therefore, a sizable TB contribution is not expected.

In addition to energy transfer, it is of fundamental interest to characterize and understand any charge-transfer processes that also occur in hydroporphyrin arrays. Here the issues of interest include the redox potentials of the constituents in the array, the molecular orbital characteristics and the TB pathway that supports the hole-transfer process. Gaining a deep understanding of energy and charge transfer in hydroporphyrin arrays is of fundamental interest for the rational design of molecular materials for use in solar-energy conversion applications.

This report describes the synthesis of a site specific ^{13}C -labeled zinc dyad to determine the rate of energy transfer. This project was done in collaboration with Dr. Bocian and Dr. Holten groups.

Probing the Rate of Hole Transfer in Oxidized Synthetic Chlorin Dyads via Site-Specific ^{13}C -Labeling.

Introduction

Understanding electronic communication among interacting chromophores is essential for the rational design of molecular architectures for artificial photosynthetic light-harvesting and energy conversion. Porphyrinic macrocycles have been widely employed in the construction of synthetic light-harvesting arrays owing to their attractive and versatile physical properties and amenability to synthetic control.⁸⁻²³ An effective light-harvesting array absorbs intensely and transfers the resulting electronic excited-state energy to a specific site with high efficiency. Conversion of the harvested excited-state energy to electrical energy then requires efficient electron injection into the anode followed by efficient ground-state hole migration away from the anode, thereby preventing charge recombination. Accordingly, understanding hole mobility in prototypical light-harvesting and charge-separation systems is of fundamental interest.

Over the past decade or more, our groups have investigated ground-state hole/electron transfer in oxidized porphyrinic arrays using EPR spectroscopy.²⁰ More recently, we have developed transient-absorption spectroscopic approaches for examining the ground-state hole/electron-transfer process.²⁴ While the transient optical methods have the advantage of providing detailed insights into the hole/electron-transfer process, these methods have the disadvantage of a complex experimental and data-interpretation protocol. The simplicity of the EPR methods has prompted us to explore other strategies for capitalizing on this method for probing ground-state hole/electron transfer.

The use of EPR techniques to examine ground-state hole/electron transfer relies on the measurement of the modulation of hyperfine interactions via the hole/electron-transfer process. In this regard, our early EPR studies utilized porphyrinic arrays of natural isotopic composition, thereby restricting the studies to measurements of ^{14}N and/or ^1H interactions.^{20,25-27} The reliance on ^{14}N and ^1H hyperfine interactions is a severe constraint because these couplings are relatively small in porphyrin π -cation radicals.²⁸ As a consequence, the exact rates of hole/electron transfer could not be extracted from the data; it could only be determined whether the process is fast or slow on the EPR time scale. More recently, we have attempted to mitigate the limitations of the EPR method by embarking on molecular design strategies that entail introduction of a ^{13}C label at specific sites in the porphyrin macrocycle where there is substantial hole/electron density in the relevant frontier (highest occupied) molecular orbital (HOMO).^{29,30} The incorporation of ^{13}C labels has two advantages: (1) The ^{13}C hyperfine interactions in porphyrin π -cation radicals are typically larger than those of ^{14}N or ^1H .^{28,31} (2) The introduction of an additional hyperfine coupling affords more accurate simulations of the EPR spectra.

Two previously prepared porphyrin dyads that contain ^{13}C labels at specific sites in the macrocycle are shown in Chart 1. In the dyad containing electron-rich trimesityl-substituted porphyrins [**ZnP(Mes)-Dyad-(^{13}C)⁵**], the ^{13}C label is introduced at the meso position; in the dyad containing electron-deficient pentafluorophenyl-substituted porphyrins [**ZnP(F₃₀)-Dyad-(^{13}C)^{1,9}**] the ^{13}C label is introduced at the α -position(s) of the pyrrole rings. The rationale for these choices of ^{13}C label location is that the HOMO for the trimesityl-substituted porphyrin is a_{2u} whereas the HOMO for the pentafluorophenyl-substituted

porphyrin is a_{1u} (D_{4h} symmetry labels). The former HOMO is characterized by large hole/electron density at the meso positions, whereas the latter is characterized by substantial electron/hole density at the α -position(s) of the pyrrole rings (Chart 3). Accordingly, these locations for the ^{13}C labels yield the largest hyperfine interactions in porphyrin π -cation radicals that exhibit $^2A_{2u}$ and $^2A_{1u}$ ground states, respectively.^{29,30}

Chart 2. Porphyrin Dyads with One Meso- ^{13}C Label or Two α - ^{13}C Labels.

Chart 3. Metalloporphyrin a_{2u} and a_{1u} Orbitals.

Hydroporphyrins (chlorins) are structurally more similar to natural photosynthetic pigments (i.e., chlorophylls) than porphyrins; these structural features impart important photophysical properties to the molecules.³² In particular, chlorins contain one reduced pyrrole ring. Pyrrole-ring saturation results in a greatly enhanced oscillator strength in the long-wavelength absorption relative to porphyrins. Accordingly, hydroporphyrins are potentially more attractive for use as light-harvesting elements in photoconversion systems. An additional characteristic of hydroporphyrins is that the HOMO is the a_{1u} -like orbital (a_2 in C_{2v} symmetry; Chart 4) and therefore the largest hole/electron density is located on the α -carbons (versus the β - or meso-carbons).²⁸ In chlorins the hole/electron density is large and of comparable magnitude at the 4, 6, 9, 11, 16, and 19 positions; less density resides at the remaining two α -carbons (1, 14). [Note that the lower electron density at the 1 and 14 positions is not particularly obvious from the chlorin HOMO electron-density diagram in

Chart 4; however, calculations show that the electron density at each of the 1 or 14 position is less than half that at the 4, 6, 9, 11, 16, or 19 position]. This characteristic of chlorins prompted us to pursue a chlorin dyad containing one unlabeled chlorin and one chlorin containing a single ^{13}C label at one of the aforementioned six higher-electron-density α -positions.

Chart 4. HOMO for a Chlorin.

The introduction of ^{13}C -isotopologues into tetrapyrrole macrocycles has largely served as a means to elucidate tetrapyrrole biosynthetic pathways³³⁻³⁶ and to prepare labeled porphyrins for spectroscopic studies.³⁷⁻³⁹ Studies devoted to the preparation of isotopologues of chlorins are far fewer and have typically employed three distinct approaches.

(1) The *biosynthesis* approach entails labeling of naturally occurring chlorins upon feeding labeled precursors to photosynthetic cells or plants. Thus, use of $^{13}\text{CH}_3$ $^{13}\text{COONa}$ (or $^{13}\text{CO}_2$) or $\text{NaH}^{13}\text{CO}_3$ in various cell types has afforded per- ^{13}C -labeled chlorophyll *a*^{40,41} or per- ^{13}C -labeled bacteriochlorophyll *c*,^{42,43} respectively. Studies with more advanced precursors such as site-specifically labeled δ -aminolevulinic acid⁴⁴ or glutamic acid have provided chlorophyll *a* labeled at multiple sites.⁴⁵

(2) The *semisynthesis* approach entails chemical modification of chlorophylls and has been widely used to prepare a wide variety of chlorophyll analogues.⁴⁶ Regioselective ¹⁸O-labeling at the 3-formyl, 3-hydroxymethyl and 13-keto groups has been achieved upon treatment with acidic H₂¹⁸O,⁴⁷⁻⁴⁹ but the semisynthesis approach apparently has not been employed to introduce ¹³C atoms to the chlorophyll skeleton.

(3) The *de novo synthesis* approach to prepare chlorins isotopologues has generally relied on routes to tetraphenylchlorin or octaethylchlorin. Thus, zinc(II)tetraphenylchlorin bearing ¹³C-labels at the four meso positions has been prepared by synthesis of the meso-¹³C-labeled free base tetraphenylporphyrin, diimide reduction⁵⁰ to give the corresponding free base chlorin and subsequent zinc metalation.⁵¹ Octaethylchlorin has been prepared with per-¹⁵N-labeling (beginning with Na¹⁵NO₂ in an established synthesis of octaethylporphyrin⁵² followed by reduction^{53,54}) or deuterium labeling at some or all of the meso positions (by isotopic exchange under acidic conditions^{53,55-58}) but ¹³C labeling apparently has not yet been reported.

While each of the above methods has merit, to our knowledge no prior syntheses have placed a single ¹³C-label at the α -position of the chlorin macrocycle. In general, even synthetic porphyrins wherein the α - or β -carbon framework is labeled with one or more ¹³C atoms have been little explored given the requirement to begin the synthesis with isotopically labeled precursors to pyrroles.^{30,59-61} Regardless, *de novo* syntheses of site-specifically labeled chlorin isotopologues are expected to be of considerable value. One example of their utility is suggested by NMR studies of partially or per-¹³C-labeled bacteriochlorophyll *c* pigments to elucidate their organization in self-assembled light-harvesting antennas.^{42,43} We

have developed a de novo synthetic route to chlorins that in principle enables location of one or more ^{13}C labels at any designated site.⁶² Herein, we employ a de novo synthetic route for the preparation of a site-specifically ^{13}C -labeled chlorin dyad [**ZnC-Dyad- $(^{13}\text{C})^{19}$** , Chart 5] and examine its hole/electron-transfer characteristics using EPR spectroscopy. The dyad contains a diphenylethyne linker that is identical to that in the isotopically labeled porphyrin dyads shown in Chart 1. The ^{13}C label was placed at the 19-position owing to considerations of (1) HOMO hole/electron density, and (2) synthetic facility. The synthesis of the unlabeled dyad (**ZnC-Dyad**) was achieved previously by Sonogashira coupling of iodophenyl and ethynylphenylchlorin building blocks.⁶³

Chart 5. Site-Specifically ^{13}C -Labeled Chlorin Dyad and Unlabeled Dyad.

Results and Discussion

Site-Specific Labeling Considerations. The de novo synthesis of chlorins entails the reaction of a 1,3,3-trimethyl-2,3,5,6-tetrahydropyrrin (Western half) and a 5-aryl-9-

bromodipyrromethane-1-carbinol (Eastern half).⁶² The Western half contains a pyrrole ring and a geminal-dimethyl-substituted pyrroline ring; the latter becomes the pyrroline ring of the chlorin. The presence of the geminal dimethyl group stabilizes the chlorin to adventitious dehydrogenation. The six possible locations of the ^{13}C label are the 4, 6, 9, 11, 16 and 19 positions (Scheme 1). The introduction of a ^{13}C label at the 4, 6, 9, or 11 positions would entail labeling of an α -carbon in a pyrrole derivative. Although such an approach is feasible,^{30,64} the requirement to construct the pyrrole ring regardless of labeling site, versus use of commercially available pyrrole as starting material in the syntheses, led to focus on positions 16 and 19 (which constitute the α -positions of the reduced, pyrroline ring). Among these, labeling the 16-position would require synthesis of mesityl oxide bearing a ^{13}C label at the carbonyl carbon, whereas the 19-position can be labeled upon use of ^{13}C -labeled nitromethane, a commercially available compound. In this regard, among all eight α -positions and eight β -positions of the chlorin macrocycle, the 19-position is conveniently the most accessible synthetically with regards to introduction of a single ^{13}C label. This synthetic convenience is felicitous given that the 19-position has electron density comparable to or greater than that at the other α -positions considered for location of the label.

Scheme 1. Synthetic Considerations for Site-Specific Labeling.

Synthesis. The unlabeled dyad was prepared over seven years ago.⁶³ Since then refined procedures have been developed for multiple steps in the synthesis of Eastern halves⁶⁵⁻⁶⁷ and the Western half.⁶⁸ The refined procedures were used here to prepare the labeled and unlabeled Western halves and both of the Eastern halves. The synthesis of the labeled Western half is shown in Scheme 2. Nitro-aldol condensation of pyrrole-2-carboxaldehyde (**1**) and ^{13}C -nitromethane followed by reduction with NaBH_4 afforded 2-(2-nitroethyl)pyrrole-(2- ^{13}C) [**2**(^{13}C)] in 32% yield. Michael addition of **2**(^{13}C) and mesityl oxide afforded the corresponding labeled nitrohexanone **3**(^{13}C) in 87% yield. Reductive cyclization of **3** using Zn and HCOONH_4 afforded the labeled tetrahydrodipyrin [Western half, **4**(^{13}C)] in 60% yield.

Scheme 2. Synthesis of the ^{13}C -labeled Western Half

The Eastern half contains the functional group (iodophenyl, ethynylphenyl) that serves to form the linker joining the chlorins. Both Eastern halves have been prepared previously,⁶³ and were prepared here via refined procedures (Scheme 3). The known ethynylphenyldipyrromethane (**5a**)⁶⁹ and iodophenyldipyrromethane (**5b**),⁷⁰ prepared via a streamlined synthesis,⁶⁸ were treated with EtMgBr followed by the known Mukaiyama reagent (**6**)⁶² to give the corresponding 1-acyldipyrromethanes. 1-Acyldipyrromethanes afford amorphous foams and are prone to streak upon attempted chromatography, but

typically give crystalline solids upon dialkylboron complexation.⁶⁶ Accordingly, treatment with Bu₂BOTf gave the dibutylboron complexes **7a** and **7b** in 39 and 47% overall yield, respectively. Bromination⁶⁵ of **7a,b** using NBS gave Eastern half precursors **8a,b** in 65 and 59% yield, respectively. Intermediates **7a,b** and **8a,b** are new compounds. Reduction of the carbonyl group afforded the Eastern halves **8a-OH** and **8b-OH**, which were not isolated owing to the typical instability of dipyrromethane-carbinols, but were used immediately in chlorin formation.

Scheme 3. Synthesis of the Eastern Halves

The synthesis of chlorins⁶² entails a two-step procedure of acid-catalyzed condensation of the Eastern half and the Western half followed by metal-mediated oxidative

cyclization (Scheme 4). The reaction of TMS-protected ethynylphenyl Eastern half **8a-OH** and labeled Western half **4**(¹³C) gave the ethynylphenylchlorin bearing a single ¹³C label [**ZnC-Ar⁵PE¹⁰(¹³C)¹⁹**] in 40% yield. The TMS group was cleaved during the acid-catalyzed condensation of **8a-OH** and **4**(¹³C). The analogous reaction of iodophenyl Eastern half **8b-OH** and unlabeled Western half **4**⁶⁸ gave the iodophenylchlorin **ZnC-Ar⁵PI¹⁰** in 37% yield.

Scheme 4. Formation of Chlorin Building Blocks and ¹³C-Labeled Dyad

The dyad was prepared via Pd-mediated coupling under copper-free conditions⁷¹ of the two chlorin building blocks, ethynylphenyl **ZnC-Ar⁵PE¹⁰(¹³C)¹⁹** and iodophenylchlorin

ZnC-Ar⁵PI¹⁰. Some difficulties were encountered upon purification of the resulting dyad **ZnC-Dyad-(¹³C)¹⁹**. The purification process consisted of a three column sequence:⁷² silica gel chromatography to remove the monomers, size exclusion chromatography (SEC) to remove high molecular weight material, and silica gel chromatography to remove particles derived from the SEC column. The resulting crude dyad showed some impurities in the aromatic region upon ¹H NMR spectroscopic examination. Suspension of the mixture in methanol and sonication followed by decanting the supernatant afforded the target dyad with purity >95% (by ¹H NMR spectroscopy) and expected dominant peak due to the molecule ion in the mass spectrum.

Characterization. All synthetic compounds were characterized by mass spectrometry and by ¹H NMR and ¹³C NMR spectroscopy. ¹H NMR spectra of the labeled compounds **2(¹³C)-4(¹³C)** exhibited expected additional coupling with the proton bonded to the ¹³C atom. The ¹³C NMR spectra exhibited strongly enhanced intensity of the peak due to the ¹³C atom versus that of the natural abundance analogues (**2-4**). The chemical shifts of the ¹³C atom of the labeled compounds are shown in Table 1. The ¹³C NMR spectrum of the dyad [**ZnC-Dyad-(¹³C)¹⁹**] was not characterized but it showed the presence of the ¹³C atom as expected upon comparison with that of the labeled Zn-chlorin monomer [**ZnC-Ar⁵PE¹⁰(¹³C)¹⁹**].

Table 1. ^{13}C NMR Chemical Shifts of Labeled Compounds

Compound	Type of bond	δ , ppm (in CDCl_3)
2(^{13}C)		75.4
3(^{13}C)		94.9
4(^{13}C)		80.3
ZnC-Ar⁵PE¹⁰(^{13}C)¹⁹		170.9
ZnC-Dyad-(^{13}C)¹⁹		170.6 ^a

^a ^{13}C NMR spectrum in toluene- d_8 at room temperature.

EPR Studies. The EPR spectra of the monocations of the unlabeled chlorin monomer⁷³ (**ZnC-T⁵M¹⁰**, Chart 6) and unlabeled chlorin dyad (**ZnC-Dyad**, Chart 5) are shown in Figure 3 (left traces). The spectrum of the monocation of the monomer exhibits a three-line pattern due to hyperfine interactions with the two H atoms ($I(^1\text{H}) = \frac{1}{2}$) on the reduced pyrrole ring. In contrast, the spectrum of the monocation of the dyad exhibits a (poorly resolved) five-line pattern indicative of rapid hole/electron transfer on the time scale

of the H-atom hyperfine clock. Simulations of the EPR spectra of the monocations of the monomer and dyad are also shown in Figure 3 (right traces). The spectrum of the monocation of the monomer is fit with an ^1H hyperfine coupling of ~ 6.2 G. This value is comparable to that measured previously for the ^1H hyperfine coupling in monocations of other types of chlorins.²⁸ Simulations of the EPR spectrum of the monocation of the dyad are reasonably well accounted for (see below for additional discussion) with a rate constant for hole/electron transfer, $k_{\text{HT}} \sim 2.6 \times 10^8 \text{ s}^{-1}$ (time constant, $\tau_{\text{HT}} \sim 3.8$ ns).

Chart 6. Unlabeled Chlorin Monomer.

Figure 3. Room temperature EPR spectra of the monocations of the unlabeled chlorin monomer and unlabeled chlorin dyad.

The EPR spectra of the monocations of the α - ^{13}C -labeled chlorin monomer **ZnC-Ar⁵PE¹⁰(^{13}C)¹⁹** and labeled dyad **ZnC-Dyad-(^{13}C)¹⁹** are shown in Figure 4 (left traces). The spectrum of the monocation of the monomer exhibits additional structure due to hyperfine interactions with the single ^{13}C ($I(^{13}\text{C}) = \frac{1}{2}$) nucleus. The monocation of the labeled dyad exhibits a line shape that is less well resolved than that of the unlabeled dyad. Simulations of the EPR spectra of the monocations of the ^{13}C -labeled monomer and dyad are also shown in Figure 4 (right traces). The spectrum of the monocation of the monomer is fit with a ^{13}C hyperfine coupling of ~ 4.8 G in addition to the ^1H hyperfine coupling of ~ 6.2 G. Simulations of the EPR spectrum of the monocation of the dyad are reasonably well accounted for with a rate constant for hole/electron transfer, $k_{\text{HT}} \sim 1.4 \times 10^8 \text{ s}^{-1}$ (time constant, $\tau_{\text{HT}} \sim 7.1 \text{ ns}$).

Attempts to obtain a more self-consistent fit of the EPR spectra of the monocations of the labeled versus unlabeled dyads were unsuccessful. The simulations shown represent the best compromise for self-consistent fits of the spectra of the two dyads. Regardless, the collective simulations of the EPR spectra of both the labeled and unlabeled dyads establish that the time scale for hole/electron transfer is in the 4-7 ns range.

Figure 4. Room temperature EPR spectra of the monocations of the ^{13}C -labeled chlorin monomer and ^{13}C -labeled chlorin dyad.

The time scale for the hole/electron transfer process in the monocations of the prototypical chlorin dyad (4-7 ns) is significantly longer than that measured (via optical techniques) for the analogous process in the monocation of a prototypical porphyrin dyad (~ 0.8 ns) that contains the same linker (diphenylethyne) and linker attachment site (meso carbon position).⁷⁴⁻⁷⁶ As noted in the Introduction, a key difference between porphyrins (with the types of meso substituents present on the monomers and dyads investigated herein)

and chlorins is that the HOMO in the former molecule is a_{2u} , whereas the HOMO in the latter is the a_{1u} -like a_2 orbital. Thus, the hole/electron density at the site of linker attachment is much larger for the porphyrin dyad than the chlorin dyad (Chart 4). The resulting larger through-bond electronic coupling in the porphyrin versus chlorin dyads is consistent with the faster rates of hole/electron transfer in the monocations of the former dyads. In this connection, previous studies of excited-state energy transfer in neutral Zn-free base analogues of the bis-Zn porphyrin and chlorin dyads have shown that the time constant for the energy-transfer process is ~5-fold shorter in the porphyrin (24 ps) versus chlorin (110 ps) dyads.⁶³ Accordingly, the relative time scales for excited-state energy transfer in the neutral porphyrin versus chlorin dyads are in a similar range as those for ground-state hole/electron transfer in the monocations of the same dyads.

Summary and Outlook

The studies reported herein establish the methodology for preparation of chlorins that contain a ^{13}C label selectively placed at the 19-position of the macrocycle. EPR studies of the monocations of both the labeled and unlabeled dyads establish that the time constant for hole/electron transfer is in the 4-7 ns range. This general approach can be extended to chlorin analogues, particularly 17-oxochlorins.⁷⁷ The incorporation of the ^{13}C label is essential for studies of hole/electron transfer in the 17-oxochlorins because H atoms are not present on the pyrroline ring of these macrocycles. Thus, the ^1H hyperfine clock that is present in the chlorins (owing to the methylene at the 17-position) is absent in the oxochlorins. The collective studies of the porphyrins, chlorins, oxochlorins, and ultimately

bacteriochlorins (two saturated pyrrole rings) will elucidate how the structural features of the different macrocycles modulate the hole/electron-transfer rates in the monocations of dyads (and larger arrays) of these molecular architectures.

Experimental Section

Electrochemistry. The electrochemical measurements were performed using techniques and instrumentation previously described.⁷⁸ The solvent was CH₂Cl₂ containing 0.1 M Bu₄NPF₆ as the supporting electrolyte. The bulk oxidized complexes were prepared in a glove box using techniques previously described.⁷⁸ Upon oxidation, the samples were transferred to an EPR tube and sealed in the glove box.

EPR Spectroscopy and Simulations. The EPR spectra were recorded on an X-band spectrometer (Bruker EMX) equipped with an NMR gaussmeter and microwave frequency counter. The EPR spectra were obtained on samples that were typically 0.2 mM. The microwave power and magnetic field modulation amplitude were typically 5.7 mW and 0.32 G, respectively.

The EPR spectra of the monocations of the chlorin monomers were simulated with the WinSim program.⁷⁹ The hyperfine coupling constants obtained from these simulations were then used as parameters in the simulations of the EPR spectra of the monocations of the dyads. The hole/electron-transfer rates for the monocations of the dyads were obtained from these simulations using the ESR-EXN program.⁸⁰

2-(2-Nitroethyl)pyrrole-(2-¹³C) (2(¹³C)). Following a general procedure,⁶⁸ a stirred solution of acetic acid (0.69 mL, 12 mmol) in methanol (1.3 mL) under argon at 0 °C was treated dropwise

with *n*-propylamine (0.90 mL, 11 mmol). The resulting *n*-propylammonium acetate mixture was stirred at 0 °C for 5 min, then added dropwise to a stirred solution of **1** (1.90 g, 20.0 mmol) in ¹³C-nitromethane (99% ¹³C; 1.10 mL, 20.0 mmol) at 0 °C. The resulting mixture was stirred at 0 °C. After 15 min, the cooling bath was removed and stirring was continued at room temperature. The color changed from yellow to dark orange during the course of reaction. After 2 h, CHCl₃ (100 mL) was added and the organic phase was washed with water and brine. Then 2-propanol (33 mL) was added to the crude mixture of 2-(2-nitrovinyl)pyrrole, to which silica (18 g) was added. The mixture was stirred vigorously and NaBH₄ (1.51 g, 40.0 mmol) was added in one batch. After 1 h, the mixture was filtered. The filter cake was washed with CH₂Cl₂. The filtrate was concentrated and the resulting dark oil was filtered through a silica pad (CH₂Cl₂) to afford an orange oil (890 mg, 32%): ¹H NMR δ 3.30–3.34 (m, 2H), 4.61 (dt, ¹J(¹³C-¹H) = 147 Hz, ³J = 6.6 Hz, 2H), 6.00–6.02 (m, 1H), 6.13–6.16 (m, 1H), 6.71–6.72 (m, 1H), 8.07–8.22 (br, 1H); ¹³C NMR δ 25.3, 25.7, 75.4 (¹³C), 107.0, 108.9, 117.9; ESI-MS obsd 141.0615, calcd 141.0619 [(M + H)⁺, M = C₅C¹³H₈N₂O₂].

3,3-Dimethyl-2-nitro-1-(2-pyrrolyl)-5-hexanone-(2-¹³C) (3**(¹³C)).** Following a general procedure,⁶⁸ a mixture of **2**(¹³C) (890 mg, 6.4 mmol) and mesityl oxide (0.81 mL, 7.0 mmol) was treated with DBU (2.92 g, 19.2 mmol). The temperature rose immediately and the reaction mixture darkened. The reaction mixture was stirred at room temperature for 24 h, diluted with ethyl acetate (100 mL) and washed with water. The organic layer was dried (Na₂SO₄) and concentrated. Excess mesityl oxide was removed under high vacuum. The resulting oil was dissolved in a minimal amount of CH₂Cl₂ and filtered through a silica pad [ethyl acetate/hexanes (1:3)] to afford a light brown oil (1.32 g, 87%): ¹H NMR (CDCl₃) δ 1.12 (s, 3H), 1.25 (s, 3H), 2.15 (s, 3H), 2.41 (AB, *J* = 17.4 Hz, 1H), 2.59 (AB, *J* = 17.4 Hz, 1H), 3.04 (ABX, ³*J* = 2.4 Hz, ²*J* = 15.4 Hz, 1H), 3.35 (ABX, ³*J* = 11.6 Hz, ²*J* = 15.4 Hz, 1H), 5.13 (ddd, ¹J(¹³C-¹H) = 152 Hz, ³*J* = 11.6 Hz, ³*J* = 2.4 Hz, 1H), 5.95–5.99 (m,

1H), 6.08–6.10 (m, 1H), 6.65–6.67 (m, 1H), 8.10–8.13 (br, 1H); ^{13}C NMR δ 24.3, 24.6, 26.8, 32.1, 36.9, 51.6, 94.9 (^{13}C), 107.5, 108.9, 118.0, 126.2, 207.2; ESI-MS obsd 239.1349, calcd 239.1351 [(M + H) $^+$, M = C₁₁C¹³H₁₈N₂O₃].

2,3,4,5-Tetrahydro-1,3,3-trimethyldipyrin-(4- ^{13}C) (4(^{13}C)). Following a general procedure,⁶⁸ a stirred suspension of HCOONH₄ (4.73 g, 75.0 mmol) and nitrohexanone **3**(^{13}C) (0.715 g, 3.00 mmol) in THF (12 mL) was treated in one portion with zinc dust (9.76 g, 75.0 mmol). The resulting mixture was stirred vigorously at room temperature. After 2 h, ethyl acetate (40 mL) was added and the mixture was filtered. The filter cake was washed with ethyl acetate. The filtrate was washed with water, brine and dried (Na₂SO₄). The solvent was concentrated to afford a light brown oil, which slowly solidified upon standing. The crude product (1.65 g) was chromatographed (silica, ethyl acetate) to afford a light brown oil which solidified to a pale yellow-orange solid (0.345 g, 60%): mp 55–56 °C (lit.⁶⁸ 53–54 °C for **4**); ^1H NMR δ 0.94 (s, 3H), 1.11 (s, 3H), 2.03 (s, 3H), 2.27 (AB, J = 16.8 Hz, 1H), 2.37 (AB, J = 16.8 Hz, 1H), 2.57 (ABX, 3J = 11.6 Hz, 2J = 14.8 Hz, 1H), 2.77 (ABX, 3J = 3.2 Hz, 2J = 14.8 Hz, 1H), 3.62 (dm, $^1J(^{13}\text{C}-^1\text{H})$ = 138 Hz, 1H), 5.92–5.94 (m, 1H), 6.08–6.11 (m, 1H), 6.69–6.71 (m, 1H), 9.75–9.83 (br, 1H); ^{13}C NMR δ 20.5, 22.8, 27.3, 28.2, 41.7, 54.4, 80.3 (^{13}C), 105.2, 107.3, 116.4, 131.7, 174.2; ESI-MS obsd 191.1505, calcd 191.1503 [(M + H) $^+$, M = C₁₁C¹³H₁₈N₂].

S-2-Pyridyl 3,5-di-*tert*-butylbenzothioate (6).⁶² Following a general procedure,⁶⁵ a solution of 2-mercaptopyridine (2.78 g, 25.0 mmol) in THF (10 mL) was treated with 3,5-di-*tert*-butylbenzoyl chloride (6.31 g, 25.0 mmol) in THF (15 mL) over 30 min. The organic phase was isolated, washed with water, then dried (Na₂SO₄) and the solvent was removed to afford a yellow solid. The solid was recrystallized from hexanes to afford a yellow solid

(5.10 g, 62%): mp 73–77°C (lit.⁶² 73–74 °C); ¹H NMR δ 1.37 (s, 18H), 7.32–7.35 (m, 1H), 7.69–7.70 (m, 1H), 7.74–7.82 (m, 2H), 7.86–7.88 (m, 2H), 8.67–8.69 (m, 1H); ¹³C NMR δ 32.0, 35.7, 122.6, 124.2, 128.9, 131.4, 136.9, 137.7, 151.1, 152.3, 152.5, 190.8; Anal. Calcd for C₂₀H₂₅NOS: C, 73.35; H, 7.69; N, 4.28. Found: C, 73.46; H, 7.69; N, 4.28.

10-(Dibutylboryl)-1-(3,5-di-*tert*-butylbenzoyl)-5-{4-[2-(trimethylsilyl)ethynyl]-phenyl}dipyrromethane (7a). Following a general procedure,⁶⁶ EtMgBr (10.0 mL, 1.0 M in THF) was added to a solution of **5a** (1.59 g, 5.00 mmol) in dry THF (10 mL) at room temperature under argon. The mixture was stirred at room temperature for 10 min and then cooled to –78 °C. A solution of **6** (1.64 g, 5.00 mmol) in dry THF (10 mL) was added. The reaction mixture was maintained at –78 °C for 10 min, then the cooling bath was removed. After 1 h, the reaction was quenched with 50 mL of saturated aqueous NH₄Cl. The reaction mixture was extracted with ethyl acetate, washed with water, and then dried (Na₂SO₄) and concentrated under reduced pressure to give a dark foam. The crude product was dissolved in CH₂Cl₂ (10 mL) and then treated with TEA (1.67 mL, 12.0 mmol) followed by Bu₂BOTf (10.0 mL, 1.0 M in CH₂Cl₂), with stirring at room temperature. After 1 h the mixture was poured onto a pad of silica eluting with hexanes/CH₂Cl₂ (1:1). Column chromatography [silica packed with hexanes/CH₂Cl₂ (4:1),] afforded a yellow amorphous solid (1.55 g, 47%): mp 80°C (dec); ¹H NMR δ 0.25 (s, 9H), 0.46–0.62 (m, 4H), 0.66 (t, *J* = 7.3 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H), 0.78–0.99 (m, 4H), 1.06–1.19 (m, 4H), 1.40 (s, 18H), 5.60 (s, 1H), 5.84–5.85 (m, 1H), 6.14–6.16 (m, 1H), 6.41 (d, *J* = 4.0 Hz, 1H), 6.70–6.72 (m, 1H), 7.20–7.22 (m, 3H), 7.40–7.43 (m, 2H), 7.74 (t, *J* = 1.8 Hz, 1H), 7.77–7.83 (br, 1H), 8.03 (d, *J* = 1.8 Hz, 2H); ¹³C NMR δ 14.12, 14.23, 22.4, 22.6, 26.0, 26.9, 27.2, one of the butyl groups was not

observed perhaps owing to overlap, 31.3, 35.1, 43.9, 94.2, 104.9, 107.9, 108.6, 117.4, 117.7, 118.9, 121.9, 124.0, 128.5, 128.7, 130.0, 131.5, 132.2, 134.5, 141.8, 149.0, 151.9, 177.9. Anal. Calcd for $C_{43}H_{59}BN_2OSi$: C, 78.39; H, 9.03; N, 4.25. Found: C, 78.26; H, 9.06; N, 4.24.

10-(Dibutylboryl)-1-(3,5-di-*tert*-butylbenzoyl)-5-(4-iodophenyl)dipyrromethane

(7b). Following a general procedure,⁶⁶ EtMgBr (20.0 mL, 1.0 M in THF) was added to a solution of **5b** (3.48 g, 10.0 mmol) in dry THF (10 mL) at room temperature under argon. The mixture was stirred at room temperature for 10 min and then cooled to $-78\text{ }^{\circ}\text{C}$. A solution of **6** (3.27 g, 10.0 mmol) in dry THF (10 mL) was added. The reaction mixture was maintained at $-78\text{ }^{\circ}\text{C}$ for 10 min, then the cooling bath was removed. After 1 h, the reaction was quenched with 50 mL of saturated aqueous NH_4Cl . The reaction mixture was extracted with ethyl acetate, washed with water, and then dried (Na_2SO_4) and concentrated under reduced pressure to give a dark foam. The crude product was dissolved in CH_2Cl_2 (20 mL) and then treated with TEA (3.34 mL, 24.0 mmol) followed by Bu_2BOTf (20.0 mL, 20.0 mmol, 1.0 M in CH_2Cl_2) with stirring at room temperature. After 1 h the mixture was poured onto a pad of silica eluting with hexanes/ CH_2Cl_2 (1:1). Column chromatography [silica packed with hexanes/ CH_2Cl_2 (4:1)] afforded a yellow amorphous solid (2.68 g, 39%): mp $145\text{--}146\text{ }^{\circ}\text{C}$; ^1H NMR δ 0.34–0.61 (m, 4H), 0.65 (t, $J = 7.3\text{ Hz}$, 3H), 0.74 (t, $J = 7.3\text{ Hz}$, 3H), 0.81–0.98 (m, 4H), 1.01–1.20 (m, 4H), 1.40 (s, 18H), 5.54 (s, 1H), 5.83–5.85 (m, 1H), 6.13–6.18 (m, 1H), 6.41 (d, $J = 4.4\text{ Hz}$, 1H), 6.70–6.72 (m, 1H), 7.00–7.04 (m, 2H), 7.20 (d, $J = 4.1\text{ Hz}$, 1H), 7.62–7.66 (m, 2H), 7.66–7.68 (br, 1H), 7.74 (t, $J = 1.8\text{ Hz}$, 1H), 8.02 (d, $J = 1.9\text{ Hz}$, 2H); ^{13}C NMR δ 14.10, 14.19, 22.3, 22.6, 25.95, 26.00, 26.9, 27.2, 31.3, 35.1, 43.6, 92.5,

107.9, 108.6, 117.5, 117.6, 118.7, 124.0, 128.8, 129.9, 130.6, 131.3, 134.5, 137.6, 141.2, 148.9, 151.9, 178.0; Anal. Calcd for C₃₈H₅₀BiN₂O: C, 66.29; H, 7.32; N, 4.07. Found: C, 66.49; H, 7.57; N, 4.04.

1-Bromo-10-(dibutylboryl)-9-(3,5-di-*tert*-butylbenzoyl)-5-{4-[2-(trimethylsilyl)-ethynyl]phenyl}dipyrromethane (8a). Following a general procedure,⁶⁵ a solution of **7a** (1.32 g, 2.00 mmol) in 30 mL of dry THF was cooled to –78 °C under argon. NBS (356 mg, 2.00 mmol) was added, and the reaction mixture was stirred for 1 h at –78 °C. Hexanes (20 mL) and water (20 mL) were added and the mixture was allowed to warm to room temperature. Et₂O was added. The organic phase was separated and dried (Na₂SO₄) and the solvent was removed under reduced pressure without heating. Column chromatography [silica; hexanes/CH₂Cl₂ (2:1)] afforded a light brown powder (950 mg, 65%): mp 55 °C (dec.); ¹H NMR δ 0.24 (s, 9H), 0.46–0.61 (m, 4H), 0.66 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H), 0.79–0.98 (m, 4H), 1.01–1.17 (m, 4H), 1.40 (s, 18H), 5.54 (s, 1H), 5.77 (t, *J* = 2.9 Hz, 1H), 6.07 (t, *J* = 2.9 Hz, 1H), 6.41 (d, *J* = 4.0, 1H), 7.21 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.75 (s, 2H), 8.03 (d, *J* = 1.8 Hz, 1H); a ¹³C NMR spectrum could not be acquired due to decomposition in CDCl₃, acetone-*d*₆, THF-*d*₈, or CD₂Cl₂. Anal. Calcd for C₄₃H₅₈BBrN₂OSi: C, 70.01; H, 7.92; N, 3.80. Found: C, 69.87; H, 7.89; N, 3.72.

1-Bromo-10-(dibutylboryl)-9-(3,5-di-*tert*-butylbenzoyl)-5-(4-iodophenyl)-dipyrromethane (8b). Following a general procedure,⁶⁵ a solution of **7b** (2.07 g, 3.00 mmol) in 30 mL of dry THF was cooled to –78 °C under argon. NBS (534 mg, 3.00 mmol) was added, and the reaction mixture was stirred for 1 h at –78 °C. Hexanes (20 mL) and

water (20 mL) were added and the mixture was allowed to warm to room temperature. Et₂O was added. The organic phase was separated and dried (Na₂SO₄) and the solvent was removed under reduced pressure without heating. Column chromatography [silica; hexanes/CH₂Cl₂ (4:1)] afforded a light brown powder (1.35 g, 59%): mp 55 °C (dec.); ¹H NMR δ 0.43–0.60 (m, 4H), 0.66 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H), 0.79–0.97 (m, 4H), 1.09–1.15 (m, 4H), 1.40 (s, 18H), 5.48 (s, 1H), 5.75–5.77 (m, 1H), 6.06–6.08 (m, 1H), 6.40 (d, *J* = 4.4 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.75 (t, *J* = 1.8 Hz, 2H), 8.03 (d, *J* = 1.8 Hz, 1H); a ¹³C NMR spectrum could not be acquired due to decomposition in CDCl₃, acetone-*d*₆, THF-*d*₈, or CD₂Cl₂. Anal. Calcd for C₃₈H₄₉BBrIN₂O: C, 59.47; H, 6.44; N, 3.65. Found: C, 59.43; H, 6.47; N, 3.56

Zn(II)-17,18-Dihydro-10-(4-ethynylphenyl)-18,18-dimethyl-5-(3,5-di-*tert*-butylphenyl)porphyrin-(19-¹³C) (ZnC-Ar⁵PE¹⁰(¹³C)¹⁹). Following a standard procedure,⁶² a sample of **8a** (737 mg, 1.00 mmol) was reduced with NaBH₄ (757 mg, 20.0 mmol) in 10 mL of anhydrous THF/methanol (3:1). The resulting **8a-OH** was dissolved in 10 mL of anhydrous CH₃CN, then **4**(¹³C) (190 mg, 1.00 mmol) and TFA (78 μL, 1.0 mmol) were added. The reaction mixture was stirred at room temperature for 30 min and 551 mg of crude tetrahydrobilene were obtained. Then 215 mg of the obtained crude tetrahydrobilene were treated with AgOTf (385 mg, 1.50 mmol), Zn(OAc)₂ (826 mg, 4.50 mmol) and 2,2,6,6-tetramethylpiperidine (0.76 mL, 4.5 mmol) in CH₃CN (30 mL). The resulting mixture was refluxed for 18 h. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed [silica, hexanes/CH₂Cl₂ (2:1)], affording a blue solid (84 mg, 40%). ¹H NMR δ 1.49 (s, 18H), 2.02 (s, 6H), 3.26 (s, 1H), 4.50 (s, 2H), 7.72 (t, *J* = 1.5 Hz,

1H), 7.81 (d, $J = 8.1$ Hz, 2H), 7.92 (t, $J = 1.5$ Hz, 2H), 8.03 (d, $J = 8.1$ Hz, 2H), 8.35 (d, $J = 4.5$ Hz, 1H), 8.45 (d, $J = 4.5$ Hz, 1H), 8.58 (s, 1H), 8.59–8.62 (m, 2H), 8.64 (s, 1H), 8.66 (d, $J = 4.5$ Hz, 1H), 8.72 (d, $J = 4.5$ Hz, 1H); ^{13}C NMR δ 30.9, 31.7, 34.7, (d, 44.9 and 45.3), 50.2, 77.8, 83.9, (d, 94.4 and 95.1), 96.7, 120.8, 122.9, 126.1, 126.86, 126.91, 128.2, 128.9, 129.2, 130.4, 131.4, 131.8, 133.5, 133.8, 141.3, 143.3, 145.7, 146.3, 146.9, 147.7, 148.6, 153.5, 154.1, 159.7, 170.9 (^{13}C). ESI-MS obsd 691.2713, calcd 691.2734 [(M + H) $^+$, M = $\text{C}_{43}\text{C}^{13}\text{H}_{42}\text{N}_4\text{Zn}$].

Zn(II)-17,18-Dihydro-10-(4-iodophenyl)-18,18-dimethyl-5-(3,5-di-*tert*-butylphenyl)porphyrin ($\text{ZnC-Ar}^5\text{PI}^{10}$). Following a standard procedure,⁶² a sample of **8b** (767 mg, 1.00 mmol) was reduced with NaBH_4 (757 mg, 20.0 mmol) in 10 mL of anhydrous THF/methanol (3:1). The resulting **8b-OH** was dissolved in 10 mL of anhydrous CH_3CN , then **4** (190 mg, 1.00 mmol) and TFA (78 μL , 1.0 mmol) were added. The reaction mixture was stirred at room temperature for 30 min, and then the reaction mixture was diluted with 100 mL of CH_3CN . AgOTf (771 mg, 3.00 mmol), $\text{Zn}(\text{OAc})_2$ (2.75 g, 15.0 mmol) and 2,2,6,6-tetramethylpiperidine (2.55 mL, 15.0 mmol) were added. The resulting mixture was refluxed for 18 h. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed [silica, hexanes/ CH_2Cl_2 (2:1)], affording a blue solid (292 mg, 37%): ^1H NMR δ 1.49 (s, 18 H), 2.03 (s, 6H), 4.51 (s, 2H), 7.72 (t, $J = 1.5$ Hz, 1H), 7.80 (d, $J = 8.1$ Hz, 2H), 7.91 (t, $J = 1.5$ Hz, 2H), 8.01 (d, $J = 8.1$ Hz, 2H), 8.35 (d, $J = 4.5$ Hz, 1H), 8.44 (d, $J = 4.5$ Hz, 1H), 8.58 (s, 1H), 8.61–8.63 (m, 2H), 8.65–8.69 (m, 2H), 8.72 (d, $J = 4.5$ Hz, 1H); ^{13}C NMR δ 30.9, 31.7, 35.0, 45.1, 50.3, 93.5, 94.8, 96.8, 120.8, 122.4, 126.4, 126.90, 127.03, 128.1, 128.7, 129.2, 132.9, 133.8, 135.2, 135.8, 141.3, 142.1, 145.7, 146.3,

146.9, 147.7, 148.6, 153.6, 154.1, 159.8, 170.9. ESI-MS obsd 792.1639, calcd 792.1662 [(M + H)⁺, M = C₄₄C¹³H₄₁IN₄Zn].

10-[4-[2-[4-[17,18-Dihydro-18,18-dimethyl-5-(3,5-di-*tert*-butylphenyl)porphinatozinc(II)-10-yl]phenyl]ethynyl]phenyl]-17,18-dihydro-18,18-dimethyl-5-(3,5-di-*tert*-butylphenyl)porphinatozinc(II)-(19-¹³C) (ZnC-Dyad-(¹³C)¹⁹).

Following a reported procedure,^{63,71} samples of **ZnC-Ar⁵PE¹⁰(¹³C)¹⁹** (23.0 mg, 33.0 μmol) and **ZnC-Ar⁵PI¹⁰** (26.3 mg, 33.0 μmol) were coupled using Pd₂(dba)₃ (4.5 mg, 4.95 μmol) and P(*o*-tol)₃ (11.0 mg, 36.3 μmol) in toluene/triethylamine (5:1, 12 mL) at 35 °C under argon in a Schlenk flask. Analytical SEC showed that the reaction had leveled off after 4 h. The product was purified by a three column chromatography sequence, without complete evaporation of solvent from intermediate fractions. After removal of the solvent, the resulting reaction mixture was passed through a silica column [hexanes/CH₂Cl₂ (1:1)]. The second purple band was collected and concentrated to obtain a solution of minimal volume. Preparative SEC (THF) gave the compound as the second band. The product solution was concentrated but not to dryness, and used directly for silica gel column chromatography (CH₂Cl₂). The resulting product was suspended in methanol, the suspension was sonicated and then filtered to afford a purple solid (10 mg, 22%): ¹H NMR (toluene-*d*₈) δ 1.53 (s, 36H), 1.88 (s, 12H), 4.17 (s, 4H), 7.95 (t, *J* = 1.7 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 4H), 8.13 (d, *J* = 8.0 Hz, 4H), 8.30 (d, *J* = 1.7 Hz, 4H), 8.43 (s, 2H), 8.45 (s, 2H), 8.57–8.61 (m, 6H), 8.75 (d, *J* = 4.4 Hz, 2H), 8.85 (d, *J* = 4.4 Hz, 2H), 8.98 (d, *J* = 4.4 Hz, 2H); MALDI-MS (matrix of 1,4-bis(5-phenyloxazol-2-yl)benzene)⁸¹ obsd 1355.0, 1354.52 calcd (C₈₆H₈₂N₈Zn₂).

References

- (1) Scheer, H. In *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications; Advances in Photosynthesis and Respiration*; Grimm, B.; Porra, R. J.; Rüdiger, W.; Scheer, H., Eds.; Springer: Dordrecht, The Netherlands, 2006, Vol. 25, pp 2–26.
- (2) Milgrom, L. R. How do they do it?-Coping with oxygen. *Colors of Life*; Oxford University Press: New York, 1997.
- (3) Dougherty, T. J.; Gomer, C. J.; Henderson, B. W.; Jori, G.; Kessel, D.; Korbelik, M.; Moan, J.; Peng, Q. *J. Natl. Cancer Inst.* **1998**, *90*, 889–905.
- (4) Guldi, D. M. *Chem. Soc. Rev.* **2002**, *31*, 22–36.
- (5) Liu, Z. M.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543.
- (6) “Photochemcad 2. A Refined Program with Accompanying Spectral Databases for Photochemical Calculations,” Dixon, J. M.; Taniguchi, M.; Lindsey, J.S. *Photochem. Photobiol.* **2005**, *81*, 212–213.
- (7) Strain, H. H.; Thomas, M. R.; Katz, J. J. *Biochim. Biophys. Acta* **1963**, *75*, 306–311.
- (8) Maretina, I. A. *Russ. J. Gen. Chem.* **2009**, *79*, 1544–1581.
- (9) Aratani, N.; Kim, D.; Osuka, A. *Acc. Chem. Res.* **2009**, *42*, 1922–1934.
- (10) Flamigni, L. *J. Photochem. Photobiol. C: Photochem. Rev.* **2007**, *8*, 191–210.
- (11) Nakamura, Y.; Aratani, N.; Osuka, A. *Chem. Soc. Rev.* **2007**, *36*, 831–845.
- (12) Lo, P.-C.; Leng, X.; Ng, D. K. P. *Coord. Chem. Rev.* **2007**, *251*, 2334–2353.
- (13) Kobuke, Y. *Struct. Bond.* **2006**, *121*, 49–104.
- (14) Iengo, E.; Scandola, F.; Alessio, E. *Struct. Bond.* **2006**, *121*, 105–143.
- (15) Balaban, T. S. *Acc. Chem. Res.* **2005**, *38*, 612–623.
- (16) Balaban, T. S.; Tamiaki, H.; Holzwarth, A. R. *Top. Curr. Chem.* **2005**, *258*, 1–38.
- (17) Imahori, H. *J. Phys. Chem. B* **2004**, *108*, 6130–6143.

- (18) Harvey, P. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2003; Vol. 18, pp 63–250.
- (19) Aratani, N.; Osuka, A. *Chem. Record* **2003**, 3, 225–234.
- (20) Holten, D.; Bocian, D. F.; Lindsey, J. S. *Acc. Chem. Res.* **2002**, 35, 57–69.
- (21) Aratani, N.; Osuka, A. *Macromol. Rapid Commun.* **2001**, 22, 725–740.
- (22) Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, 101, 2751–2796.
- (23) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, 34, 40–48.
- (24) Song, H.-E.; Taniguchi, M.; Diers, J. R.; Kirmaier, C.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Phys. Chem. B* **2009**, 113, 16483–16493.
- (25) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, 116, 10578–10592.
- (26) Seth, J.; Palaniappan, V.; Wagner, R. W.; Johnson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, 118, 11194–11207.
- (27) Yang, S. I.; Lammi, R. K.; Seth, J.; Riggs, J. A.; Arai, T.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Phys. Chem. B* **1998**, 102, 9426–9436.
- (28) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979, Vol. 4, pp 197–256.
- (29) Thamyongkit, P.; Muresan, A. Z.; Diers, J. R.; Holten, D.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2007**, 72, 5207–5217.
- (30) Muresan, A. Z.; Thamyongkit, P.; Diers, J. R.; Holten, D.; Lindsey, J. S.; Bocian, D. F. *J. Org. Chem.* **2008**, 73, 6947–6959.
- (31) Atamian, M.; Wagner, R. W.; Lindsey, J. S.; Bocian, D. F. *Inorg. Chem.* **1988**, 27, 1510–1512.
- (32) Kobayashi, M.; Akiyama, M.; Kano, H.; Kise, H. In *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications; Advances in Photosynthesis and Respiration*, Grimm, B.; Porra, R. J.; Rüdiger, W.; Scheer, H., Eds.; Springer: Dordrecht, The Netherlands, 2006, Vol. 25, pp 79–94.

- (33) Scott, A. I. *Chem. Record* **2001**, *1*, 212–227.
- (34) Battersby, A. R.; Leeper, F. J. *Chem. Rev.* **1990**, *90*, 1261–1274.
- (35) Jordan, P. M. In *Biosynthesis of Heme and Chlorophylls*; Dailey, H. A. Ed.; McGraw-Hill, Inc.: New York, 1990, pp 55–121.
- (36) Scott, A. I. *Acc. Chem. Res.* **1978**, *11*, 29–36.
- (37) Rivera, M.; Caignan, G. A. *Anal. Bioanal. Chem.* **2004**, *378*, 1464–1483.
- (38) (a) Rohrer, A.; Ocampo, R.; Callot, H. J. *Synthesis* **1994**, 923–925. (b) Chen, S.; Lash, T. D. *J. Heterocycl. Chem.* **1997**, *34*, 273–278.
- (39) Procyk, A. D.; Bocian, D. F. *Ann. Rev. Phys. Chem.* **1992**, *43*, 465–496.
- (40) Sashima, T.; Abe, M.; Kurano, N.; Miyachi, S.; Koyama, Y. *J. Phys. Chem. B* **1998**, *102*, 6903–6914.
- (41) Boxer, S. G.; Closs, G. L.; Katz, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 7058–7066.
- (42) Balaban, T. S.; Holzwarth, A. R.; Schaffner, K.; Boender, G.-J.; de Groot, H. J. M. *Biochemistry* **1995**, *34*, 15259–15266.
- (43) Nozawa, T.; Ohtomo, K.; Suzuki, M.; Nakagawa, H.; Shikama, Y.; Konami H.; Wang, Z.-Y. *Photosynth. Res.* **1994**, *41*, 211–223.
- (44) Shrestha-Dawadi, P. B.; Lugtenburg, J. *Eur. J. Org. Chem.* **2003**, 4654–4663.
- (45) Porra, R. J.; Scheer, H. *Photosynth. Res.* **2000**, *66*, 159–175.
- (46) Pavlov, V. Y.; Ponomarev, G. V. *Chem. Heterocycl. Compd.* **2004**, *40*, 393–425.
- (47) Morishita, H.; Tamiaki, H. *Spectrochim. Acta A* **2009**, *72*, 274–279.
- (48) Morishita, H.; Tamiaki, H. *Tetrahedron* **2005**, *61*, 6097–6107.
- (49) Morishita, H.; Tamiaki, H. *Bioorg. Med. Chem.* **2003**, *11*, 4049–4057.
- (50) Whitlock, H. W., Jr.; Hanauer, R.; Oester, M. Y.; Bower, B. W. *J. Am. Chem. Soc.* **1969**, *91*, 7485–7489.

- (51) Blackwood, M. E., Jr.; Lin, C.-Y.; Cleary, S. R.; McGlashen, M. M.; Spiro, T. G. *J. Phys. Chem. A* **1997**, *101*, 255–258.
- (52) Paine, J. B., III; Kirshner, W. B.; Moskowitz, D. W.; Dolphin, D. *J. Org. Chem.* **1976**, *41*, 3857–3860.
- (53) Blackwood, M. E., Jr.; Kumble, R.; Spiro, T. G. *J. Phys. Chem.* **1996**, *100*, 18037–18041.
- (54) Dzilinski, K.; Synyakov, G. N.; Shulga, A. M.; Filatov, I. V.; Gurinovich, G. P. *Radiat. Phys. Chem.* **1995**, *45*, 923–928.
- (55) Procyk, A. D.; Kim, Y.; Schmidt, E.; Fonda, H. N.; Chang, C.-K.; Babcock, G. T.; Bocian, D. F. *J. Am. Chem. Soc.* **1992**, *114*, 6539–6549.
- (56) Blackwood, M. E., Jr.; Spiro, T. G. *J. Phys. Chem. B* **1997**, *101*, 8363–8368.
- (57) Fonda, H. N.; Oertling, W. A.; Salehi, A.; Chang, C.-K.; Babcock, G. T. *J. Am. Chem. Soc.* **1990**, *112*, 9497–9507.
- (58) Terekhov, S. N.; Ksenofontova, N. M.; Gurinovich, I. F.; Grubina, L. A. *J. Appl. Spectrosc.* **1986**, *45*, 812–818.
- (59) Calle, C.; Schweiger, A.; Mitrikas, G. *Inorg. Chem.* **2007**, *46*, 1847–1855.
- (60) Hu, S.; Mukherjee, A.; Piffat, C.; Mak, R. S. W.; Li, X.-Y.; Spiro, T. G. *Biospectroscopy* **1995**, *1*, 395–412.
- (61) Mispelter, J.; Momenteau, M.; Lhoste, J.-M. *J. Chem. Soc. Dalton Trans.* **1981**, 1729–1734.
- (62) Taniguchi, M.; Ra, D.; Mo, G.; Balasubramanian, T.; Lindsey, J. S. *J. Org. Chem.* **2001**, *66*, 7342–7354.
- (63) Taniguchi, M.; Ra, D.; Kirmaier, C.; Hindin, E. K.; Schwartz, J. K.; Diers, J. R.; Knox, R. S.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Am. Chem. Soc.* **2003**, *125*, 13461–13470.
- (64) Mass, O.; Ptaszek, M.; Taniguchi, M.; Diers, J. R.; Kee, H. L.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2009**, *74*, 5276–5289.
- (65) Zaidi, S. H. H.; Muthukumaran, K.; Tamaru, S.-I.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 8356–8365.

- (66) Muthukumaran, K.; Ptaszek, M.; Noll, B.; Scheidt, W. R.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 5354–5364.
- (67) Laha, J. K.; Dhanalekshmi, S.; Taniguchi, M.; Ambroise, A.; Lindsey, J. S. *Org. Process Res. Dev.* **2003**, *7*, 799–812.
- (68) Ptaszek, M.; Bhaumik, J.; Kim, H.-J.; Taniguchi, M.; Lindsey, J. S. *Org. Process Res. Dev.* **2005**, *9*, 651–659.
- (69) Cho, W.-S.; Kim, H.-J.; Littler, B. J.; Miller, M. A.; Lee, C.-H.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 7890–7901.
- (70) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391–1396.
- (71) Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974–2983.
- (72) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166–11180.
- (73) Strachan, J.-P.; O'Shea, D. F.; Balasubramanian, T.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 3160–3172.
- (74) Song, H.-E.; Taniguchi, M.; Kirmaier, C.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *Photochem. Photobiol.* **2009**, *85*, 693–704.
- (75) Song, H.-E.; Kirmaier, C.; Taniguchi, M.; Diers, J. R.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Am. Chem. Soc.* **2008**, *130*, 15636–15648.
- (76) Song, H.-E.; Kirmaier, C.; Diers, J. R.; Lindsey, J. S.; Bocian, D. F.; Holten, D. *J. Phys. Chem. B* **2009**, *113*, 54–63.
- (77) Taniguchi, M.; Kim, H.-J.; Ra, D.; Schwartz, J. K.; Kirmaier, C.; Hindin, E.; Diers, J. R.; Prathapan, S.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 7329–7342.
- (78) Yang, S. I.; Seth, J.; Strachan, J.-P.; Gentemann, S.; Kim, D.; Holten, D.; Lindsey, J. S.; Bocian, D. F. *J. Porphyrins Phthalocyanines* **1999**, *3*, 117–147.
- (79) (a) Duling, D. R. *J. Magn. Reson. B* **1994**, *104*, 105–110. (b) <http://www.niehs.nih.gov/research/resources/software/tools/index.cfm> (accession date, 03/18/2010).

- (80) (a) Heinzer, J. *Mol. Phys.* **1971**, 22, 167–177. (b) Heinzer, J. Quantum Chemistry Program Exchange, No. 209, 1972.
- (81) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, 3, 283–291.