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

Elías J. Nieves-Bernier,[†] James R. Diers,[‡] Masahiko Taniguchi,[†] Dewey Holten,*[,§] David F. Bocian,*[,‡] and Jonathan S. Lindsey*[,†]

[†]*Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204,* [‡]*Department of Chemistry, University of California, Riverside, California 92521-0403, and* [§]*Department of Chemistry, Washington University, St. Louis, Missouri 63130-4889*

holten@wuchem.wustl.edu; david.bocian@ucr.edu; jlindsey@ncsu.edu

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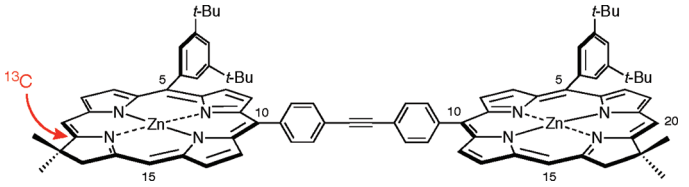

Understanding electronic communication among interacting constituents of multicomponent molecular architectures is important for rational design in diverse fields including artificial photosynthesis and molecular electronics. One strategy for examining ground-state hole/electron transfer in an oxidized tetrapyrrolic array 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 ^{1}H 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 singly ^{13}C-labeled chlorin was coupled with an unlabeled chlorin to give a dyad wherein a diphenylethyne linker spans the 10-positions of the two zinc chlorins. EPR studies of the monocations of both the natural abundance and ^{13}C-labeled zinc chlorin dyads and benchmark zinc chlorin 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.

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 physical properties and amenability to synthetic control.[1−16] An effective light-harvesting array absorbs intensely and transfers

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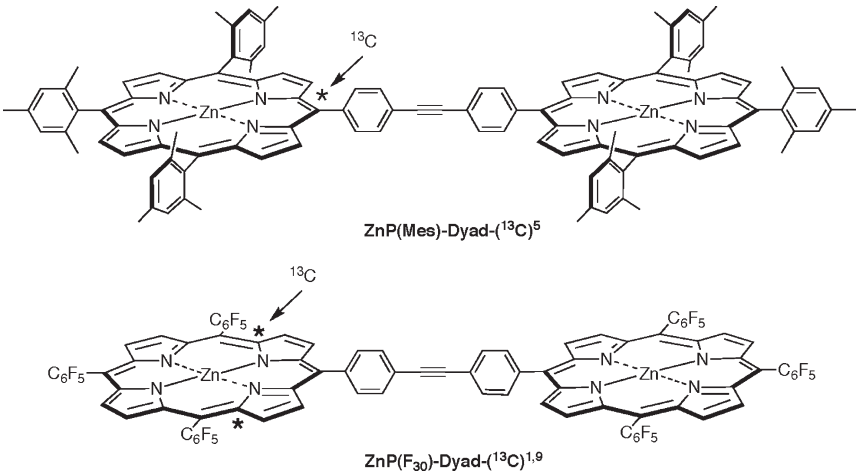
CHART 1. Porphyrin Dyads with One Meso-^{13}C Label or Two α-^{13}C Labels



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.[13] More recently, we have developed transient-absorption spectroscopic approaches for examining the ground-state hole/electron-transfer process.[17] While the transient optical methods have the advantage of providing detailed insights into the hole/electron-transfer process, these methods have the disadvantage of complex experimental and data-interpretation protocols. 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 ^{1}H interactions.[13,18−20] The reliance on ^{14}N and ^{1}H hyperfine interactions is a severe constraint because these couplings are relatively small in porphyrin π-cation radicals.[21] 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).[22,23] 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 ^{1}H.[21,24] (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(F$_{30}$)-Dyad-(^{13}C)^{1,9}**] the ^{13}C label is introduced at selected α-pyrrolic positions. (The dyads were previously termed **Zn$_2$D-Mes(5-^{13}C)** and **Zn$_2$D-F$_{30}$(1,9-^{13}C)**, respectively.[22,23]) 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 2). Accordingly, these locations for the ^{13}C labels yield the largest hyperfine

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CHART 2. Metalloporphyrin a_{2u} and a_{1u} Orbitals

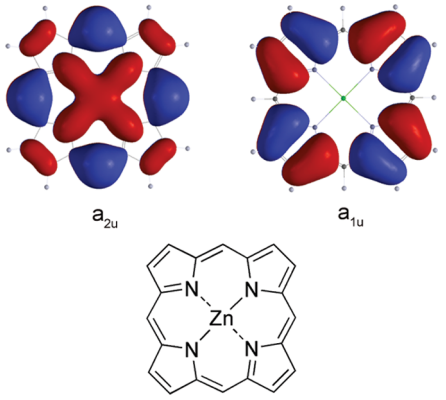
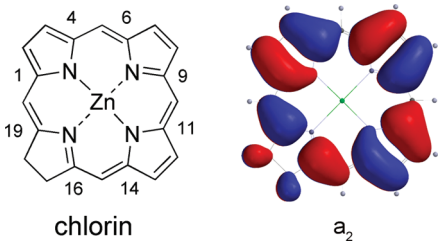


CHART 3. HOMO for a Chlorin



interactions in porphyrin π-cation radicals that exhibit $^2A_{2u}$ and $^2A_{1u}$ ground states, respectively.[22,23]

Hydroporphyrins (e.g., chlorins) are structurally more similar to natural photosynthetic pigments (e.g., chlorophylls) than porphyrins; these structural features impart important photophysical properties to the molecules.[25] In particular, chlorins contain one reduced pyrrole (i.e., pyrroline) 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 3), and therefore, the largest hole/electron density is located on the α-carbons (versus the β- or meso-carbons).[21] 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 3; however, calculations show that the electron density at 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.

The introduction of ^{13}C-isotopes into tetrapyrrole macrocycles has largely served as a means to elucidate tetrapyrrole biosynthetic pathways[26−29] and to prepare labeled porphyrins for spectroscopic studies.[30−32] 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 $^{13}CH_3{}^{13}COONa$ (or $^{13}CO_2$) or $NaH^{13}CO_3$ in various cell types has afforded per-^{13}C-labeled chlorophyll *a*[33,34] or per-^{13}C-labeled bacteriochlorophyll *c*,[35,36] respectively. Studies with more advanced precursors such as site-specifically labeled δ-aminolevulinic acid[37] or glutamic acid have provided chlorophyll *a* labeled at multiple sites.[38]

(2) The *semisynthesis* approach entails chemical modification of chlorophylls and has been used to prepare a wide variety of chlorophyll analogues.[39] Regioselective ^{18}O-labeling at the 3-formyl, 3-hydroxymethyl, and 13-keto groups has been achieved upon treatment with acidic $H_2{}^{18}O$,[40−42] but the semisynthesis approach apparently has not been employed to introduce ^{13}C atoms to the chlorophyll skeleton.

(3) The *de novo synthesis* approach to prepare chlorin isotopologues has generally relied on routes to tetraphenylchlorin or octaethylchlorin. Thus, zinc(II)tetraphenylchlorin bearing ^{13}C-labels at the four meso positions has been prepared by synthesis of the meso-^{13}C-labeled free base tetraphenylporphyrin, diimide reduction[43] to give the corresponding free base chlorin and metalation to give the zinc chelate.[44] Octaethylchlorin has been prepared with per-^{15}N-labeling (beginning with $Na^{15}NO_2$ in an established synthesis of octaethylporphyrin[45] followed by reduction[46,47]) or deuterium labeling at some or all of the meso positions (by isotopic

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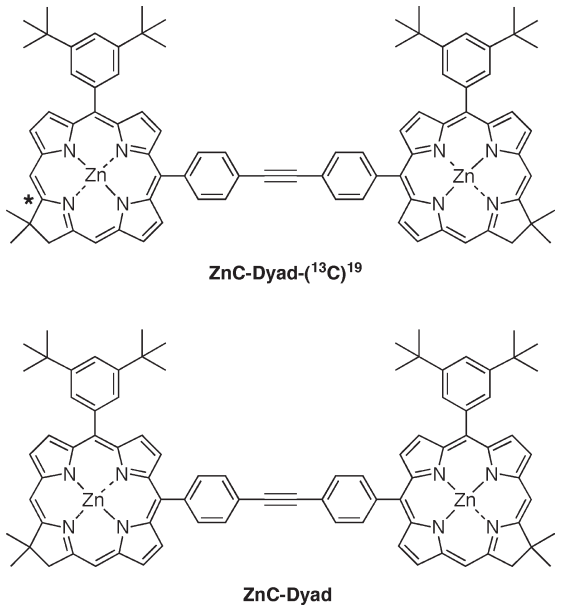
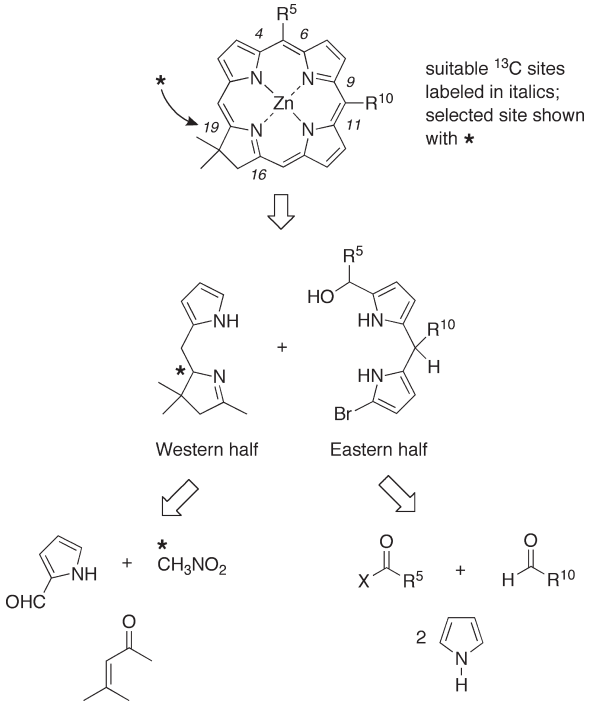
CHART 4. Site-Specifically ^{13}C-Labeled Chlorin Dyad and Unlabeled Dyad



exchange under acidic conditions[46,48−51]) but ^{13}C 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 ^{13}C-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 ^{13}C atoms have been little explored given the requirement to begin the synthesis with isotopically labeled precursors to pyrroles.[23,52−54] 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-^{13}C-labeled bacteriochlorophyll *c* pigments to elucidate their organization in self-assembled light-harvesting antennas.[35,36] 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.[55] Herein, we employ the de novo synthetic route for the preparation of a site-specifically ^{13}C-labeled chlorin dyad [**ZnC-Dyad-(^{13}C)^{19}**, Chart 4] 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 iodophenylchlorin and ethynylphenylchlorin building blocks.[56]

SCHEME 1. Synthetic Considerations for Site-Specific Labeling



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-tetrahydrodipyrrin (Western half) and a 5-aryl-9-bromodipyrromethane-1-carbinol (Eastern half).[55] The Western half contains a pyrrole ring and a *gem*-dimethyl-substituted pyrroline ring; the latter becomes the pyrroline ring of the chlorin. The presence of the geminal dimethyl group stabilizes the chlorin against 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,[23,57] the requirement to construct the pyrroline 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.

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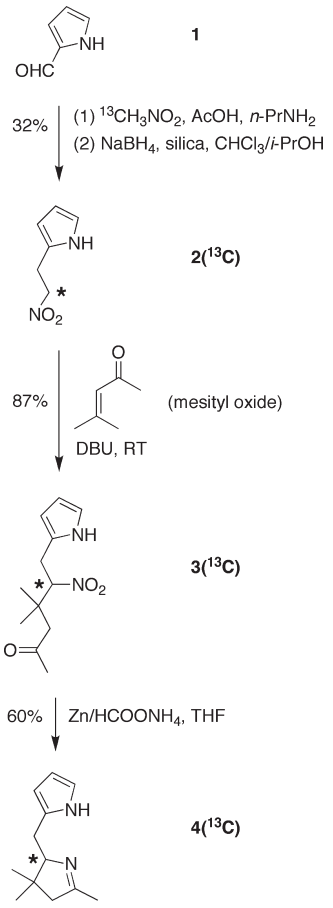
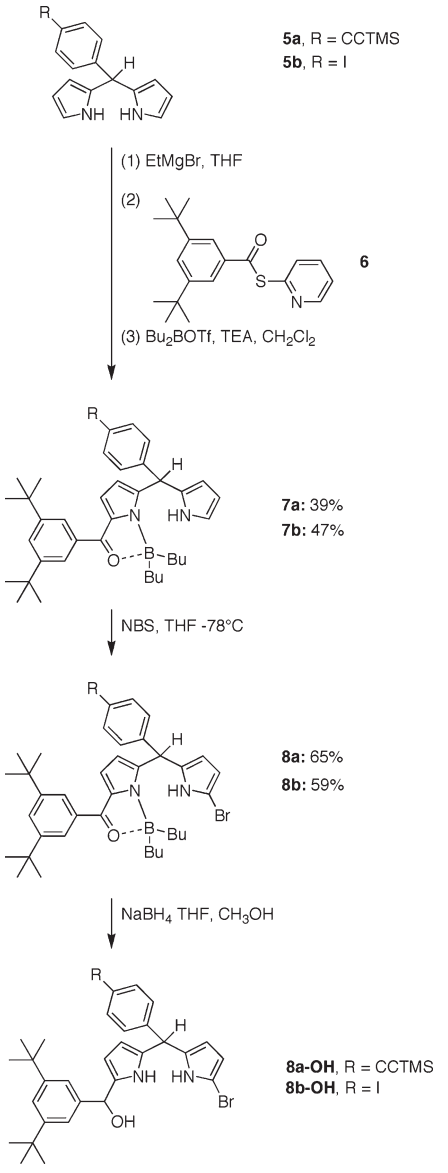
SCHEME 2. Synthesis of the ^{13}C-Labeled Western Half



Synthesis. The unlabeled dyad was prepared over 7 years ago.[56] Since then, refined procedures have been developed for multiple steps in the synthesis of Eastern halves[58−60] and the Western half.[61] 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 tetrahydrodipyrrin [Western half, **4**(**^{13}C**)] in 60% yield.

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[56] and were prepared here via refined procedures (Scheme 3). The known (TMS-ethynylphenyl)dipyrromethane (**5a**)[62]

SCHEME 3. Synthesis of the Eastern Halves



and iodophenyldipyrromethane (**5b**),[63] prepared via a streamlined synthesis,[60] were treated with EtMgBr followed by the known Mukaiyama reagent (**6**)[55] 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.[59] Accordingly, treatment with Bu_2BOTf gave the dibutylboron complexes **7a** and **7b** in 39% and 47% overall yield, respectively. Bromination[58] 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 dipyrromethanecarbinols but were used immediately in chlorin formation.

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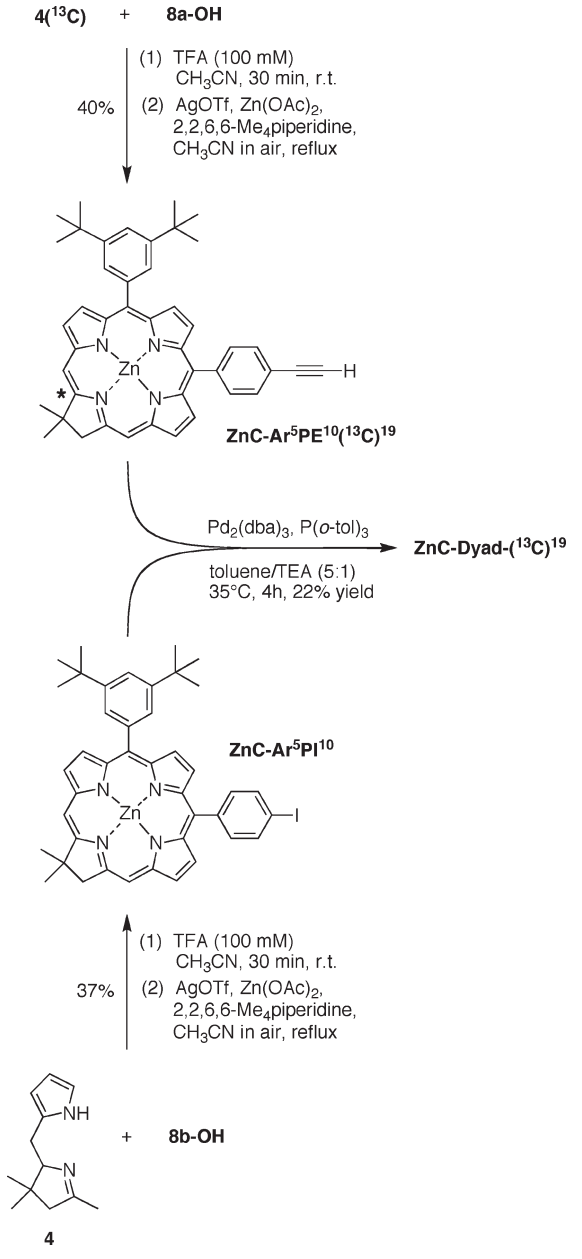
SCHEME 4. Formation of Chlorin Building Blocks and ^{13}C-Labeled Dyad



The synthesis of chlorins[55] 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-ethynylphenyl Eastern half **8a-OH** and labeled Western half **4**(**^{13}C**) gave the ethynylphenylchlorin bearing a single ^{13}C label [**ZnC-Ar^5-PE^{10}(**^{13}**C)^{19}**] in 40% yield. The TMS group was cleaved during the reaction of **8a-OH** and **4**(**^{13}C**). The analogous reaction of iodophenyl Eastern half **8b-OH** and unlabeled Western half **4**[61] gave the iodophenylchlorin **ZnC-Ar^{5}PI^{10}** in 37% yield.

The dyad was prepared via Pd-mediated coupling under copper-free conditions[64] of the two chlorin building blocks, ethynylphenyl **ZnC-Ar^{5}PE^{10}(**^{13}**C)^{19}** and iodophenylchlorin **ZnC-Ar^{5}PI^{10}**. Some difficulties were encountered upon purification of the resulting dyad **ZnC-Dyad-(**^{13}**C)^{19}**. The purification process consisted of a three-column sequence:[65] 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 ^{1}H NMR spectroscopic examination. Suspension of the mixture in methanol and sonication followed by decanting the supernatant afforded the target dyad with purity >95% (by ^{1}H NMR spectroscopy) and expected dominant peak due to the molecular ion in the mass spectrum.

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-Ar^{5}PE^{10}(^{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.

Chemical Characterization. All synthetic compounds were characterized by mass spectrometry and by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR spectra of the labeled compounds **2**(**^{13}C**)−**4**(**^{13}C**) exhibited expected additional coupling with the proton(s) bonded to the ^{13}C atom. The ^{13}C NMR spectra exhibited strongly enhanced intensity of the peak due to the ^{13}C atom versus that of the natural abundance analogues (**2**−**4**).[61] The chemical shifts of the ^{13}C atom of the labeled compounds are shown in Table 1. The ^{13}C NMR spectrum of the dyad [**ZnC-Dyad-(**^{13}**C)^{19}**] was not characterized in detail, but the signal from the ^{13}C atom was observed as expected upon comparison with that of the labeled Zn-chlorin monomer [**ZnC-Ar^{5}PE^{10}(**^{13}**C)^{19}**].

EPR Studies. The chlorin monocations were prepared in a glovebox via quantitative coulometric bulk electrolysis at a Pt electrode (see the Experimental section). The EPR spectra of the monocations of the unlabeled chlorin monomer[66] (**ZnC-T^{5}M^{10}**, Chart 5) and unlabeled chlorin dyad (**ZnC-Dyad**, Chart 4) are shown in Figure 1 (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}H) = 1/2] on the pyrroline ring. In contrast, the spectrum of the monocation of the dyad exhibits a (poorly resolved) five-line pattern indicative of rapid hole/electron

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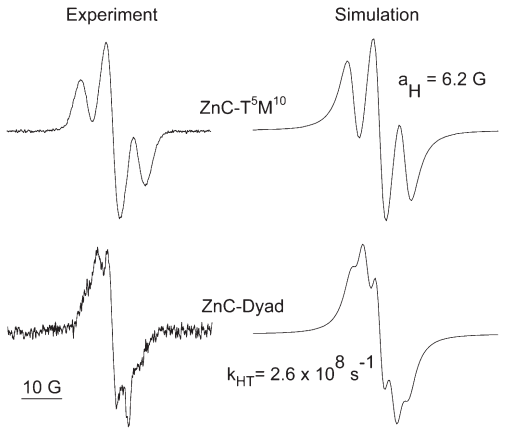
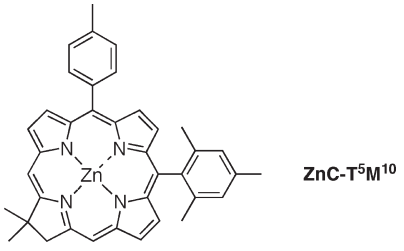


FIGURE 1. Room-temperature EPR spectra of the monocations of the unlabeled chlorin monomer and unlabeled chlorin dyad.

CHART 5. Unlabeled Chlorin Monomer



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 1 (right traces). The spectrum of the monocation of the monomer is fit with an ^{1}H hyperfine coupling of ~6.2 G. This value is comparable to that measured previously for the ^{1}H hyperfine coupling in monocations of other types of chlorins.[21] 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, $k_{HT} \sim 2.6 \times 10^8$ s^{-1} (time constant, $\tau_{HT} \sim 3.8$ ns).

The EPR spectra of the monocations of the α-^{13}C-labeled chlorin monomer **ZnC-Ar^{5}PE^{10}(^{13}C)^{19}** and labeled dyad **ZnC-Dyad-(^{13}C)^{19}** are shown in Figure 2 (left traces). The spectrum of the monocation of the monomer exhibits additional structure due to hyperfine interactions with the single ^{13}C [$I(^{13}C) = 1/2$] 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 2 (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 ^{1}H 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, $k_{HT} \sim 1.4 \times 10^8$ s^{-1} (time constant, $\tau_{HT} \sim 7.1$ 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

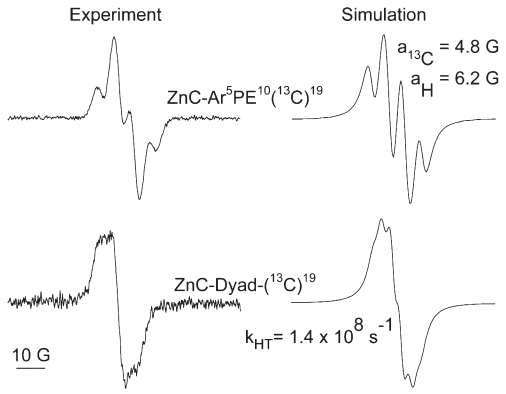


FIGURE 2. Room temperature EPR spectra of the monocations of the ^{13}C-labeled chlorin monomer and ^{13}C-labeled chlorin dyad.

dyads establish that the time scale for hole/electron transfer is in the 4−7 ns range.

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).[67−69] 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 3). 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.[56] 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.[70] The

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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 ^{1}H 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.[71] The samples were contained in a three-compartment cell equipped with a Pt wire working electrode, a Pt mesh counter electrode, and a Ag/Ag+ (butyronitrile) reference electrode. The solvent was CH_2Cl_2 containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. The bulk-oxidized complexes were prepared in a glovebox via quantitative coulometric bulk electrolysis at a Pt mesh electrode. The integrity of the samples was checked by cyclic voltammetry after each successive oxidation. Upon oxidation, the samples were transferred to an EPR tube and sealed in the glovebox.

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.[72] 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.[73]

2-(2-Nitroethyl)pyrrole-(2-^{13}C) (2(^{13}C)). Following a general procedure,[61] 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 and then added dropwise to a stirred solution of **1** (1.90 g, 20.0 mmol) in ^{13}C-nitromethane (99% ^{13}C; 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 the reaction. After 2 h, $CHCl_3$ (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 $NaBH_4$ (1.51 g, 40.0 mmol) was added in one batch. After 1 h, the mixture was filtered. The filter cake was washed with CH_2Cl_2. The filtrate was concentrated, and the resulting dark oil was filtered through a silica pad (CH_2Cl_2) to afford an orange oil (890 mg, 32%): ^{1}H NMR (300 MHz) δ 3.30−3.34 (m, 2H), 4.61 (dt, $^{1}J(^{13}C-^{1}H)$ = 147 Hz, ^{3}J = 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); ^{13}C NMR δ 25.3, 25.7, 75.4 (^{13}C), 107.0, 108.9, 117.9; ESI-MS obsd 141.0615, calcd 141.0619 [$(M + H)^+$, M = $C_5C^{13}H_8N_2O_2$].

3,3-Dimethyl-2-nitro-1-(2-pyrrolyl)-5-hexanone-(2-^{13}C) (3(^{13}C)). Following a general procedure,[61] a mixture of **2**(^{13}C) (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 (Na_2SO_4) and concentrated. Excess mesityl oxide was removed under high vacuum. The resulting oil was dissolved in a minimal amount of CH_2Cl_2 and filtered through a silica pad [ethyl acetate/hexanes (1:3)] to afford a light brown oil (1.32 g, 87%): ^{1}H NMR (400 MHz) 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, $^{1}J(^{13}C-^{1}H)$ = 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 = $C_{11}C^{13}H_{18}N_2O_3$].

2,3,4,5-Tetrahydro-1,3,3-trimethyldipyrrin-(4-^{13}C) (4(^{13}C)). Following a general procedure,[61] a stirred suspension of HCO_2NH_4 (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 (water, brine) and dried (Na_2SO_4). 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.[61] mp 53−54 °C for **4**); ^{1}H NMR (300 MHz) 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, ^{3}J = 11.6 Hz, ^{2}J = 14.8 Hz, 1H), 2.77 (ABX, ^{3}J = 3.2 Hz, ^{2}J = 14.8 Hz, 1H), 3.62 (dm, $^{1}J(^{13}C-^{1}H)$ = 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 = $C_{11}C^{13}H_{18}N_2$].

***S*-2-Pyridyl 3,5-Di-*tert*-butylbenzothioate (6).** Following a general procedure,[58] 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, and dried (Na_2SO_4). The solvent was removed to afford a yellow solid, which upon recrystallization (hexanes) afforded a yellow solid (5.10 g, 62%): mp 73−77 °C (lit.[55] mp 73−74 °C); ^{1}H NMR (400 MHz) 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); ^{13}C 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 $C_{20}H_{25}NOS$: 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,[59] 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, and then the cooling bath was removed. After 1 h, the reaction was quenched with 50 mL of saturated aqueous NH_4Cl. The

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reaction mixture was extracted with ethyl acetate. The organic extract was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to give a dark foam. The crude product was dissolved in CH_2Cl_2 (10 mL) and then treated with TEA (1.67 mL, 12.0 mmol) followed by Bu_2BOTf (10.0 mL, 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 solid (1.55 g, 47%): mp 80 °C (dec.); ^{1}H NMR (400 MHz) 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); ^{13}C 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,[59] 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 °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 °C for 10 min, and then the cooling bath was removed. After 1 h, the reaction was quenched by the addition of 50 mL of saturated aqueous NH_4Cl. The reaction mixture was extracted with ethyl acetate, washed with water, 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 solid (2.68 g, 39%): mp 145−146 °C; ^{1}H NMR (400 MHz) δ 0.34−0.61 (m, 4H), 0.65 (t, J = 7.3 Hz, 3H), 0.74 (t, J = 7.3 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 Hz, 1H), 6.70−6.72 (m, 1H), 7.00−7.04 (m, 2H), 7.20 (d, J = 4.1 Hz, 1H) 7.62−7.66 (m, 2H), 7.66−7.68 (br, 1H), 7.74 (t, J = 1.8 Hz, 1H), 8.02 (d, J = 1.9 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 $C_{38}H_{50}BIN_2O$: 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,[58] 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. The organic phase was extracted with Et_2O and dried (Na_2SO_4). The solvent was removed under reduced pressure without heating. Column chromatography [silica; hexanes/CH_2Cl_2 (2:1)] afforded a light brown powder (950 mg, 65%): mp 55 °C (dec.); ^{1}H NMR (300 MHz) 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 ^{13}C NMR spectrum could not be acquired due to decomposition in $CDCl_3$, acetone-d_6, THF-d_8, or CD_2Cl_2. Anal. Calcd for $C_{43}H_{58}BBrN_2OSi$: 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,[58] 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. The organic phase was extracted with Et_2O and dried (Na_2SO_4). The solvent was removed under reduced pressure without heating. Column chromatography [silica; hexanes/CH_2Cl_2 (4:1)] afforded a light brown powder (1.35 g, 59%): mp 55 °C (dec.); ^{1}H NMR (300 MHz) 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 ^{13}C NMR spectrum could not be acquired due to decomposition in $CDCl_3$, acetone-d_6, THF-d_8, or CD_2Cl_2. Anal. Calcd for $C_{38}H_{49}BBrIN_2O$: 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-^{13}C) (ZnC-Ar^{5}PE^{10}(^{13}C)^{19}). Following a standard procedure,[55] a sample of **8a** (737 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 **8a-OH** was dissolved in 10 mL of anhydrous CH_3CN, and then **4**(**^{13}C**) (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, whereupon 551 mg of the crude tetrahydrobilene intermediate was obtained. Then the crude tetrahydrobilene (215 mg) was 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 CH_3CN (30 mL). 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)] to afford a blue solid (84 mg, 40%): ^{1}H NMR (300 MHz) 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 = $C_{43}C^{13}H_{42}N_4Zn$].

Zn(II)−17,18-Dihydro-10-(4-iodophenyl)-18,18-dimethyl-5-(3,5-di-*tert*-butylphenyl)porphyrin (ZnC-Ar^{5}PI^{10}). Following a standard procedure,[55] 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, and 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), $Zn(OAc)_2$ (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)] to afford a blue solid (292 mg, 37%): ^{1}H NMR (300 MHz) 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 [$(M + H)^+$, $M = C_{44}C^{13}H_{41}IN_4Zn$].

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-^{13}C) (ZnC-Dyad-(^{13}C)^{19}). Following a reported procedure,[56,64] samples of **ZnC-Ar^{5}PE^{10}(^{13}C)^{19}** (23.0 mg, 33.0 μmol) and **ZnC-Ar^{5}PI^{10}** (26.3 mg, 33.0 μmol) were coupled using $Pd_2(dba)_3$ (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. Thus, the concentrated crude reaction mixture was passed through a silica column [hexanes/CH_2Cl_2 (1:1)]. The second purple band was collected and concentrated to obtain a solution of small 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 (CH_2Cl_2). The resulting product was suspended in methanol, the suspension was sonicated and then filtered to afford a purple solid (10 mg, 22%): ^{1}H NMR (300 MHz, 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)[74] obsd 1355.0, 1354.52 calcd ($C_{86}H_{82}N_8Zn_2$).

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Supporting Information Available: General procedures and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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