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Meso-^{13}C-Labeled Porphyrins for Studies of Ground-State Hole Transfer in Multiporphyrin Arrays

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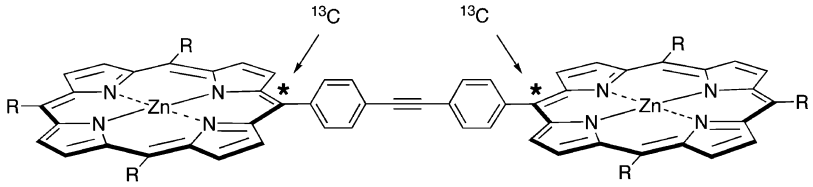

Understanding electronic communication among interacting chromophores provides the foundation for a variety of applications. The ground-state electronic communication in diphenylethyne-linked zinc-porphyrin dyads has been investigated by a novel molecular design strategy that entails introduction of a ^{13}C-atom (*) at specific sites of the porphyrins where there is substantial electron density in the relevant frontier (highest occupied) molecular orbital. The site of ^{13}C substitution is at a meso-position, either the site of attachment of the linker (proximal, "P") or the site trans to the linker (distal, "D"). The substituents (R) at the non-linking meso-positions are mesityl, tridec-7-yl ("swallowtail"), or *p*-tolyl groups. Altogether five isotopically labeled porphyrin dyads have been prepared. The hole/electron-transfer properties of one-electron oxidized dyads have been examined by electron paramagnetic resonance (EPR) spectroscopy. The introduction of the meso-^{13}C label provides a "clock" (via the hyperfine interactions) that allows investigation of a time scale for hole transfer that is 3−4 times shorter than that provided by the natural abundance ^{14}N nuclei of the pyrrole nitrogen atoms. The EPR studies indicate that the hole transfer, which has been previously shown to be fast on the time scale of the ^{14}N hyperfine clock (∼220 ns), remains fast on the time scale of the ^{13}C hyperfine clock (∼50 ns).

Introduction

Understanding electronic communication between the individual components of multicomponent molecular architectures is essential for the rational design and tailoring of such materials for use in molecular electronic and/or photonic devices. Toward this goal, we have investigated a variety of porphyrin-based arrays wherein the individual components are covalently linked and electronic communication is primarily through-bond via the linker.[1] One objective of these studies has been to design arrays that might function both as light-harvesting complexes and as solar-energy transduction systems.[2] In these arrays, the porphyrinic components are arranged such that excited-state energy and ground-state holes flow in opposite directions.[2] Energy flow is toward the anode where electron injection occurs and hole flow is toward the cathode where electrons and holes recombine to complete the circuit. Such a design should enhance solar-energy-conversion efficiency because the energy-hole rectification process mitigates deleterious charge-recombination reactions at the anode.

One approach that we have employed to investigate the time scale of ground-state hole-transfer in multiporphyrin arrays has been to monitor the hyperfine splittings in the EPR spectra of singly oxidized arrays such as **Dyad-1** and **Dyad-2** (Chart 1). This approach does not explicitly yield the rate of hole transfer but rather elucidates whether hole transfer is fast or slow on the time scale defined by the hyperfine coupling. The basic

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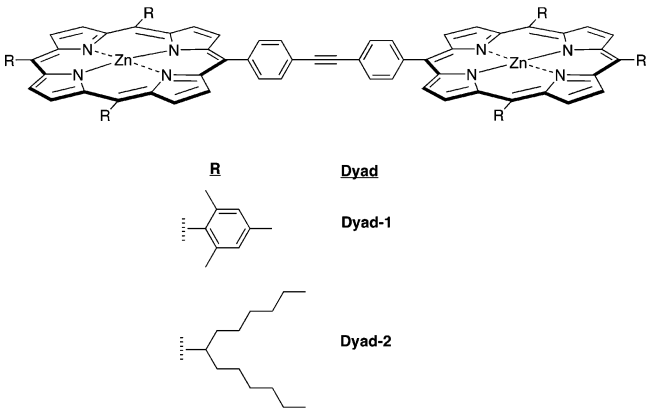
CHART 1



concept is as follows. If hole transfer is slow on the EPR time scale, the measured hyperfine coupling in a singly oxidized array is similar to that of a singly oxidized monomeric porphyrin. As the rate of hole transfer approaches the time scale defined by the hyperfine coupling, the hyperfine splittings in the EPR spectra are attenuated; as hole transfer becomes rapid, the splittings collapses to 1/*n* of the value observed in a monomer, where *n* is the number of centers over which the hole is delocalized.

In typical porphyrin π-cation radicals, the only nuclei that exhibit hyperfine interactions with the unpaired electron are ^{1}H and ^{14}N.[3] The relative magnitude of the interactions for the two types of nuclei depends on the type of porphyrin π-cation radical. In most meso-substituted porphyrins (which constitute the bulk of the complexes we have investigated[1]), the unpaired electron (and hole) resides in the $a_{2u}(\pi)$ HOMO; in other words, the ground state of the monocation is $^2A_{2u}$.[3] This ground state is characterized by substantial ^{14}N hyperfine interactions and minimal ^{1}H interactions due to the distribution of spin density in the $a_{2u}(\pi)$ orbital, which is primarily at the meso-carbon and pyrrole nitrogen atoms, with minimal density at the β-pyrrole carbon atoms. A typical ^{14}N hyperfine coupling for a porphyrin π-cation with a $^2A_{2u}$ ground state is ~1.6 G, the equivalent of ~4.5 MHz. Thus, the ^{14}N hyperfine interactions serve as a clock that provides information as to whether hole transfer is fast or slow on a time scale of ~220 ns.

In most of the porphyrin arrays we have studied to date, hole transfer is fast on the 220 ns time scale of the ^{14}N hyperfine coupling;[1] thus, it would be desirable to have a faster hyperfine clock. Practical considerations severely restrict the types of porphyrin isotopomers that (1) can be prepared and (2) have the requisite hyperfine coupling characteristics. All things considered, ^{13}C incorporation is the best choice for isotopic substitution. In $^2A_{2u}$ porphyrin π-cation radicals, the spin density at the meso-carbon atoms is much larger than at the pyrrole nitrogen atoms.[3] As a result, the hyperfine coupling for meso-^{13}C is ~5.7 G (or ~16 MHz), affording the opportunity to monitor events on the ~60 ns time scale in $^2A_{2u}$ radicals.[4] Furthermore, ^{13}C incorporation affords essentially the only means of monitoring hole transfer in porphyrin π-cation radicals with $^2A_{1u}$ ground states. The latter situation occurs for β-pyrrole- versus meso-substituted porphyrins (for which the HOMO is the a_{1u} versus the a_{2u} orbital) because the spin density in the $^2A_{1u}$ ground state is localized primarily on the α- and β-pyrrole carbon atoms.

The majority of ^{13}C-labeled porphyrins that have been prepared are labeled analogues of naturally occurring porphyrins and have been prepared via biosynthetic procedures using labeled precursors.[5] By contrast, relatively few non-natural porphyrins bearing ^{13}C-labels in the macrocycle have been prepared since the first examples nearly 30 years ago.[4,6−16] *meso*-Tetraphenylporphyrin,[4,7,11] *meso*-tetra-*p*-tolylporphyrin,[6] and *meso*-tetramesitylporphyrin[14] bearing four meso ^{13}C-labels have been prepared by condensation of pyrrole and the labeled aldehyde. *meso*-Tetraphenylporphyrin bearing four pairs of adjacent ^{13}C-labeled pyrrole α- and β-carbons, or ^{13}C labels at all β-carbons, has been prepared by reaction of the labeled pyrrole and benzaldehyde.[7] Octaethylporphyrin bearing four meso ^{13}C-labels has been prepared by condensation of ^{13}C-labeled paraformaldehyde and 3,4-diethylpyrrole.[12] An *N*-confused porphyrin (2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin) bearing ^{13}C-labels at each α- and β-pyrrole position (16 labels altogether) was prepared by condensation of per-^{13}C-labeled pyrrole and benzaldehyde.[16] A mixture of etioporphyrin isomers wherein each pyrrole contains one ^{13}C label has been prepared through use of the labeled pyrrole.[13] Synthetic porphyrins bearing ^{13}C labels at one or two specific meso-positions have been prepared through use of labeled dipyrromethanes. A *trans*-A_2B_2-porphyrin bearing two ^{13}C labels (at trans meso-positions) was prepared by self-condensation of a labeled 1-acyldipyrromethane.[15] A protoporphyrin analogue bearing a single meso-^{13}C label has been prepared through use of a meso-labeled dipyrromethane.[8] Labeled analogues of other naturally occurring porphyrins (bearing 8 β-substituents) have been prepared from 1-methyl or 1-iminomethyl ^{13}C-labeled bilenes[9] or a,c-biladienes.[10]

In this Article, we report the preparation and characterization of five different porphyrin dyads and companion benchmark monomers in which a ^{13}C label is incorporated at one of the

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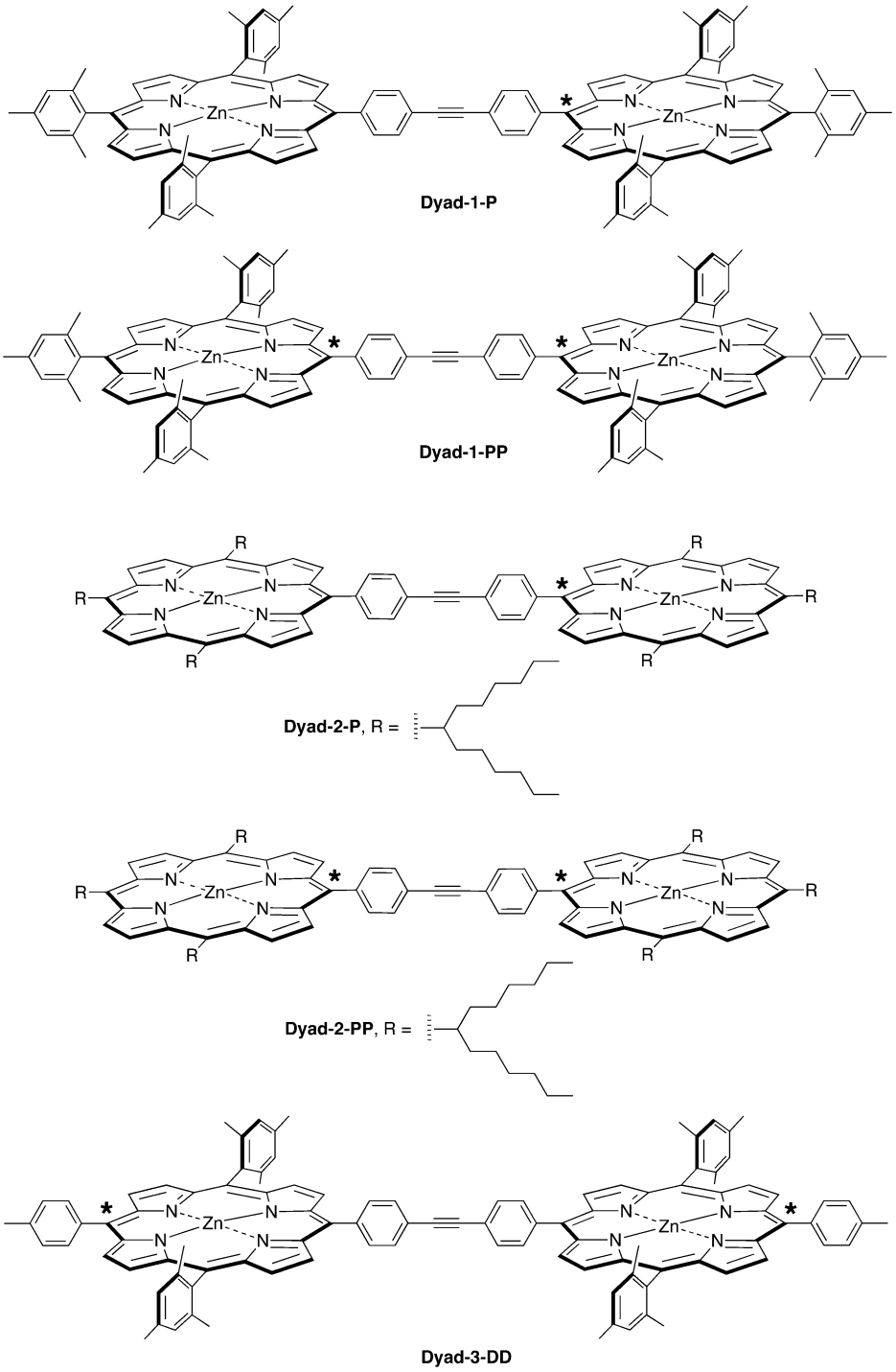
CHART 2

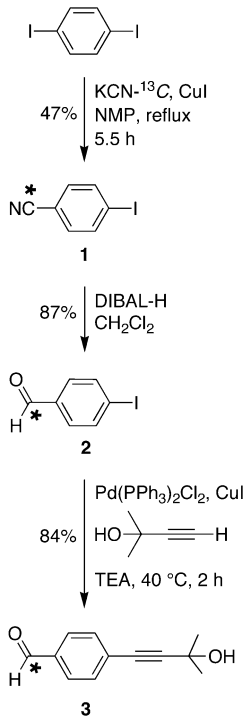


four meso-positions of the porphyrin macrocycle. The new dyads are shown in Chart 2. Two such isotopic substitutions were investigated: the meso-position where a linker is appended (proximal "P") and the meso-position opposite to that where the linker is appended (distal "D"). The rationale for preparing singly ^{13}C-labeled species is that the EPR spectra are less complicated than those that would be observed for a porphyrin in which all meso-carbon atoms are ^{13}C-labeled.[4] The types of dyads investigated include unsymmetrical isotopomers, wherein the ^{13}C is incorporated in only one of the two constituent porphyrins of the dyad, and symmetrical isotopomers, wherein ^{13}C is incorporated in both porphyrins. Collectively, the studies illustrate a novel molecular design strategy wherein modified hyperfine clocks are employed for studies of hole transfer in multiporphyrin arrays.

Results and Discussion

I. Synthesis. 1. Strategy. Each target porphyrin dyad bears a diphenylethynyl interporphyrin linkage and one or two ^{13}C labels (Chart 2). Hence, Sonogashira coupling of an iodo-porphyrin monomer and an ethynyl-porphyrin monomer is the reaction of choice for joining the porphyrin constituents.[17,18] A ^{13}C atom is present at one or both of the linking meso-positions

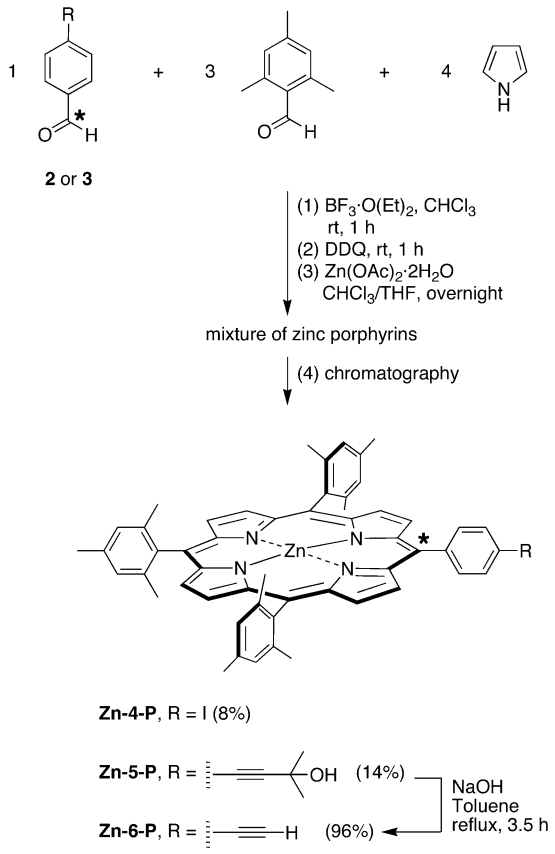
SCHEME 1



in four dyads (**Dyad-1-P**, **Dyad-1-PP**, **Dyad-2-P**, and **Dyad-2-PP**), and at the non-linking, distal meso-positions of the **Dyad-3-DD**. The substituents at the non-linking meso-positions include mesityl, swallowtail, and *p*-tolyl groups. Mesityl[17,18] and swallowtail[19,20] groups provide facial encumbrance and thereby increase the solubility of porphyrins and accompanying multiporphyrin arrays. The porphyrins in **Dyad-1-P** and **Dyad-1-PP** or **Dyad-2-P** and **Dyad-2-PP** are of the A_3B-type and include three mesityl or three swallowtail groups. The porphyrins in **Dyad-3-DD** are of the *trans*-AB_2C type and include two mesityl groups at the flanking ("winged") positions and a *p*-tolyl group at the site distal to the interporphyrin linker.

Rational synthetic methods are available for the synthesis of porphyrins bearing up to four different meso-substituents.[21,22] The methods accommodate a variety of substituents, but are not yet compatible with three mesityl or three swallowtail groups. Accordingly, the A_3B-porphyrins bearing mesityl or swallowtail groups (required for the synthesis of **Dyad-1P**, **Dyad-1PP**, **Dyad-2P**, and **Dyad-2PP**) were prepared via statistical methods. In each case, the singly ^{13}C-labeled A_3B-porphyrin was prepared through use of a non-linking "A" aldehyde and the labeled "B" aldehyde. The *trans*-AB_2C-porphyrin required for the synthesis of **Dyad-3-DD** was prepared via a rational route where the labeled unit was introduced via 9-acylation of a 1-acyldipyrromethane.

SCHEME 2



2. Labeled Porphyrin Monomers. The preparation of an aldehyde precursor is shown in Scheme 1. The ^{13}C atom was introduced by cyanation of 1,4-diiodobenzene with 1.1 equiv of KCN-^{13}C in the presence of CuI[23] in 1-methyl-2-pyrrolidinone[24] to give the labeled cyano derivative **1** in 47% yield. Reduction of the latter using DIBALH followed by Pd-coupling of the resulting aldehyde **2** with 2-methylbut-3-yn-2-ol gave aldehyde **3**. These two ^{13}C-labeled aldehydes were used in the syntheses of the precursors of the target dyads.

Following the published procedure for preparing the non-labeled analogues,[25,26] a mixed-condensation of mesitaldehyde, pyrrole, and aldehyde **2** in the presence of BF_3−ethanol cocatalysis[27] (BF_3·$O(Et)_2$ in $CHCl_3$ containing ethanol) followed by DDQ oxidation afforded the mixture of free base porphyrins. A mixture composed of porphyrins bearing substituents that give a graded degree of steric hindrance is more easily separable upon conversion to the zinc chelates versus the free base species given the affinity of the apical zinc site for adsorption chromatographic media.[17] Thus, metalation with zinc acetate gave the corresponding zinc porphyrins, which upon chromatography on silica gave the ^{13}C-containing iodo-porphyrin **Zn-4-P** in 8% yield (Scheme 2). Analogous reaction with aldehyde

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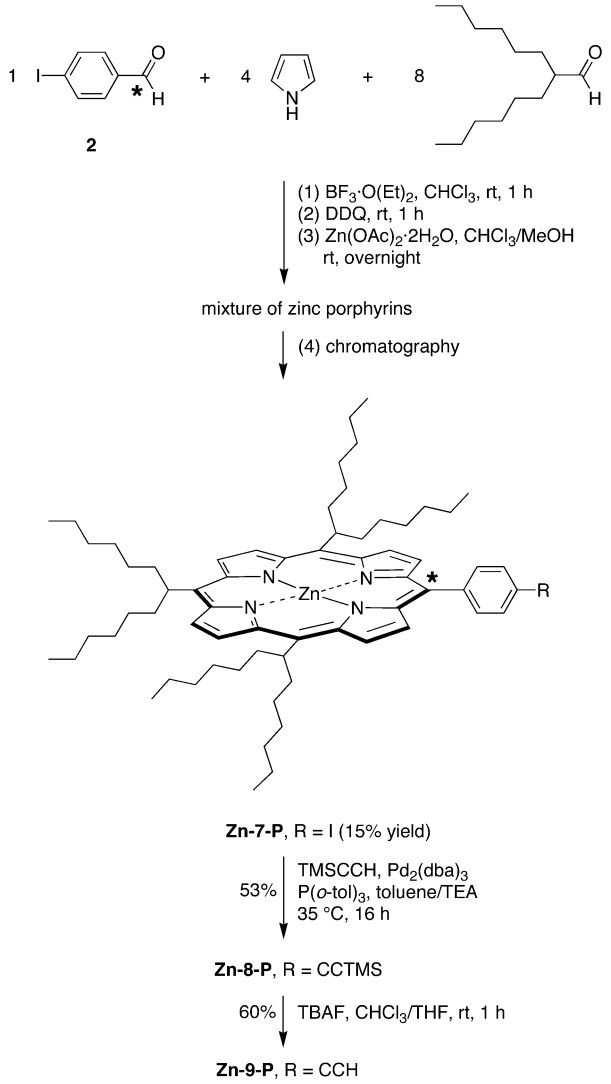
SCHEME 3

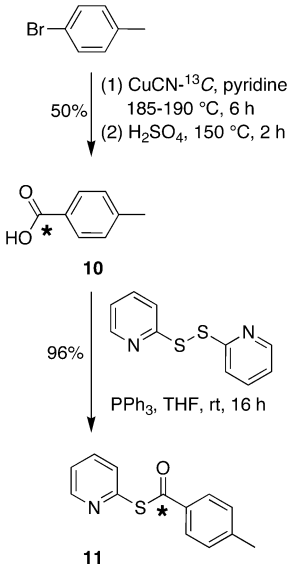


3 gave TMS-ethynyl-porphyrin **Zn-5-P** in 14% yield. Deprotection of **Zn-5-P** with NaOH in refluxing toluene gave ethynyl-porphyrin **Zn-6-P** in 96% yield.

In a similar manner,[19] condensation of pyrrole, aldehyde **2**, and 7-formyltridecane[28] followed by DDQ oxidation gave the mixture of free base porphyrins. Zinc metalation and chromatographic separation gave iodo-porphyrin **Zn-7-P** in 15% yield (Scheme 3). Pd-coupling of the latter with (trimethylsilyl)-acetylene led to TMS-ethynyl-porphyrin **Zn-8-P**, which upon TMS-deprotection with TBAF gave ethynyl-porphyrin **Zn-9-P**.

Following a procedure for the synthesis of unlabeled *p*-toluic acid,[29] *p*-bromotoluene underwent cyanation with KCN-^{13}C and CuI[23] in pyridine[30] followed by 75% aqueous H_2SO_4 to obtain labeled *p*-toluic acid **10** in 50% yield (Scheme 4). Reaction[31] of the latter with 2,2′-dipyridyl disulfide in the presence of PPh_3 afforded benzothioate **11** in 96% yield. The latter was employed

SCHEME 4



as an acylating reagent for the preparation of a porphyrin monomer to be used in the synthesis of **Dyad-3-DD**.

The synthesis of the porphyrin building blocks bearing two mesityl groups, one *p*-tolyl group attached to a ^{13}C-labeled meso site, and an iodophenyl or ethynylphenyl unit, is shown in Scheme 5. 5-Mesityldipyrromethane (**12**)[32] was acylated previously under standard Grignard-mediated conditions with iodobenzothioate **13a**[21] and TMS-ethynylbenzothioate **13b**[21] to give the known compounds **14** and **15**.[21] 1-Acyldipyrromethanes streak extensively upon chromatography and afford amorphous solids, rendering purification difficult. We recently developed methodology wherein a dialkylboron complex is prepared of the 1-acyldipyrromethanes, affording nonpolar crystalline solids.[33] Accordingly, the resulting 1-acyldipyrromethane was readily isolated in the form of a dialkylboron complex (**Bu_2B-14**[33] or **Bu_2B-15**) in 89% or 63% yield, respectively.

The Grignard-mediated 9-acylation[34] of dialkylboron complex **Bu_2B-14** or **Bu_2B-15** with benzothioate **11** led to the labeled 1,9-diacyldipyrromethane-dialkylboron complex **Bu_2B-16** or **Bu_2B-17** in 41% or 45% yield, respectively. Reduction of complex **Bu_2B-16** or **Bu_2B-17** with $NaBH_4$ gave the corresponding dipyrromethane-1,9-dicarbinol, which upon condensation with dipyrromethane **12** in the presence of Yb(OTf)$_3$,[21,35] oxidation with DDQ, and metalation of the resulting porphyrin with $Zn(OAc)_2$·$2H_2O$ gave zinc iodo-porphyrin **Zn-18-D** or zinc TMS-ethynyl-porphyrin **Zn-19-D** in 13% or 18% yield, respectively. TMS-cleavage from **Zn-19-D** with TBAF gave ethynyl-porphyrin **Zn-20-D** in 98% yield.

3. Unlabeled Porphyrin Monomers. Several porphyrin monomers required for the synthesis of the singly labeled dyads were synthesized previously. The monomers include iodo-porphyrin **Zn-21**,[25] TMS-ethynyl-porphyrin **Zn-22**,[19] and ethynyl-porphyrin **Zn-23**,[19] which are shown in Chart 3.

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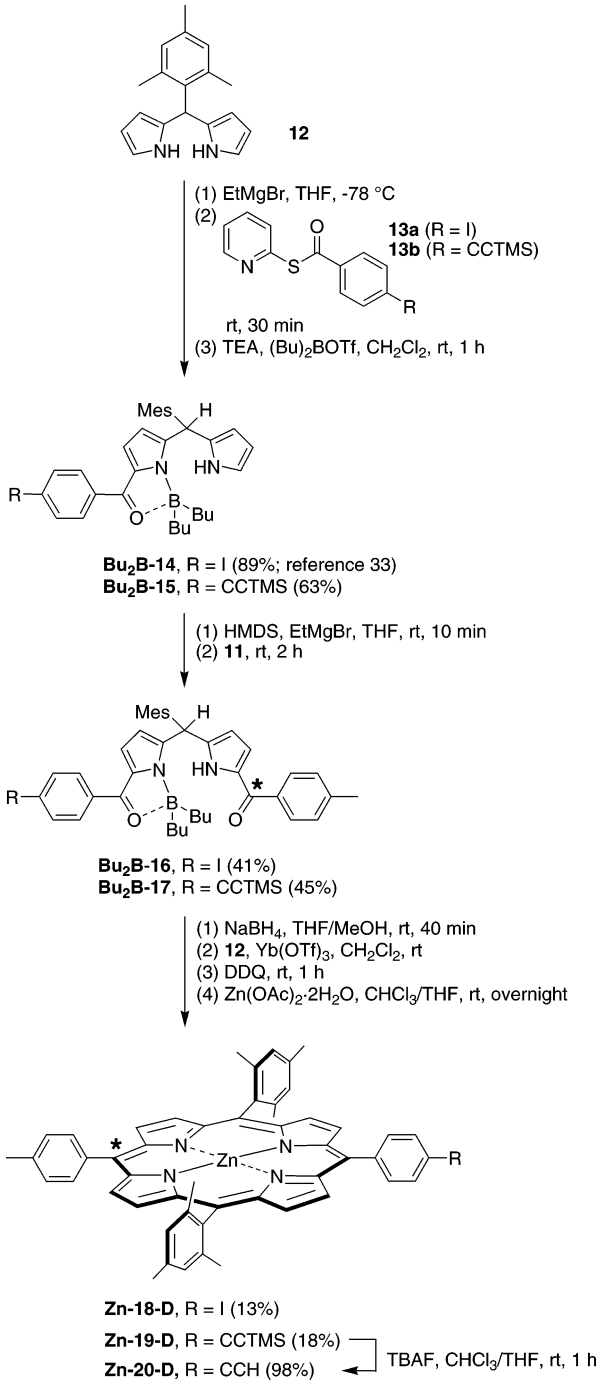
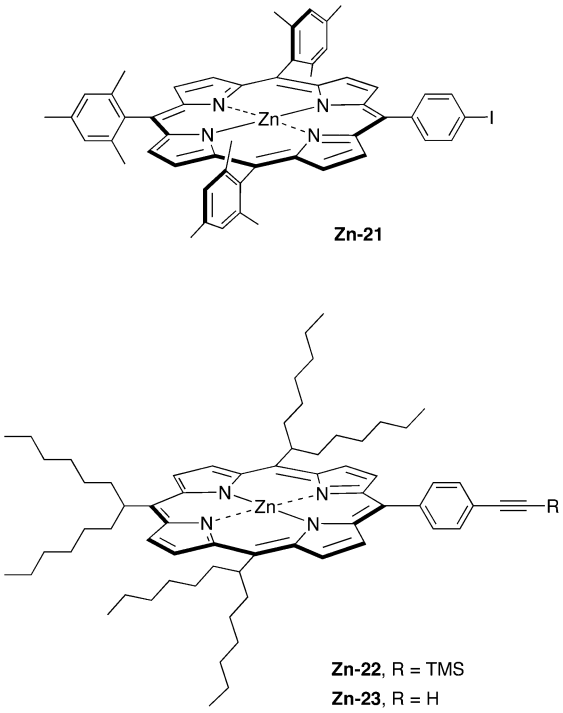
SCHEME 5



4. Labeled Porphyrin Dyads. The Sonogashira coupling of an iodo-porphyrin and an ethynyl-porphyrin was carried out to give the target dyads. The coupling was performed under copper-free conditions in the presence of $Pd_2(dba)_3$ and P(*o*-tol)$_3$ in toluene/TEA at 35 °C.[25] The reaction was monitored by analytical size exclusion chromatography (SEC), which showed the complete consumption of the monomer after 22 h. The reaction mixtures were purified by a three-column sequence consisting of adsorption chromatography and preparative SEC. The dyads were obtained in reasonable yield, with the exception of **Dyad-1-PP** where, due to the poor solubility of the compound, the reaction mixture could not be completely redissolved after the complete removal of the solvent. The results are summarized in Table 1.

CHART 3



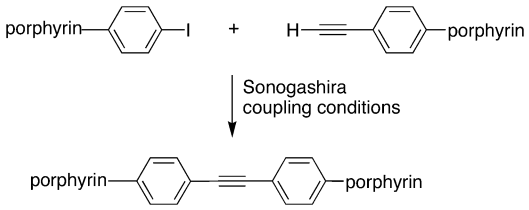
5. Chemical Characterization of the Labeled Porphyrins and Dyads. Each labeled porphyrin was characterized by absorption spectroscopy, fluorescence spectroscopy, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and mass spectrometry. The latter included laser desorption mass spectrometry (LD-MS) without a matrix[36] and high-resolution FAB-MS. The dyads were similarly characterized including use of analytical SEC to establish purity but without FAB-MS given their higher mass. The availability of ^{13}C-labeled porphyrins, porphyrin precursors, and porphyrin dyads provides a valuable set of data for unambiguous assignment of ^{13}C NMR resonances for these compounds. A table of such data is provided in the Supporting Information.

II. EPR Spectra and Hole-Transfer Characteristics of the Dyads. The EPR spectra of the monocation radicals of all of the ^{13}C-labeled monomers and dyads were examined. Ambient-temperature spectra of selected monomers and dyads are shown in Figures 1 and 2, respectively. In both figures, the top trace is the spectrum of the monocation radical of an unlabeled analogue of one of the labeled complexes. The complexes for which spectra are shown in the figures were chosen because the monocation radicals of these species exhibit the full complement of spectral features observed for all of the singly oxidized complexes.

The EPR spectrum of the unlabeled complex, **[Zn-22]**$^+$, exhibits the characteristic nine-line hyperfine pattern due to interaction of the four ^{14}N nuclei with the unpaired electron (Figure 1, top trace).[2−4] The spectra of the two ^{13}C-labeled complexes, **[Zn-8-P]**$^+$ and **[Zn-19-D]**$^+$, exhibit this same pattern superimposed on each member of the doublet that results from interaction of the single ^{13}C nucleus with the unpaired electron. The ^{13}C hyperfine splittings for both of the labeled complexes

(36) (a) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291. (b) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99.

TABLE 1. Synthesis of Labeled Porphyrin Dyads[a]



	iodo-porphyrin			ethynyl-porphyrin				
entry	no.	R^{10}, R^{20}	R^{15}	no.	R^{10}, R^{20}	R^{15}	product	yield
1	**Zn-4-P**	Mes	Mes	**Zn-6-P**	Mes	Mes	**Dyad-1-PP**	23%
2	**Zn-21**	Mes	Mes	**Zn-6-P**	Mes	Mes	**Dyad-1-P**	80%
3	**Zn-7-P**	SWT	SWT	**Zn-9-P**	SWT	SWT	**Dyad-2-PP**	71%
4	**Zn-7-P**	SWT	SWT	**Zn-23**	SWT	SWT	**Dyad-2-P**	73%
5	**Zn-18-D**	Mes	*p*-Tol	**Zn-20-D**	Mes	*p*-Tol	**Dyad-3-DD**	51%

[a] Mes = mesityl; SWT = swallowtail (7-tridecyl); *p*-Tol = *p*-tolyl.

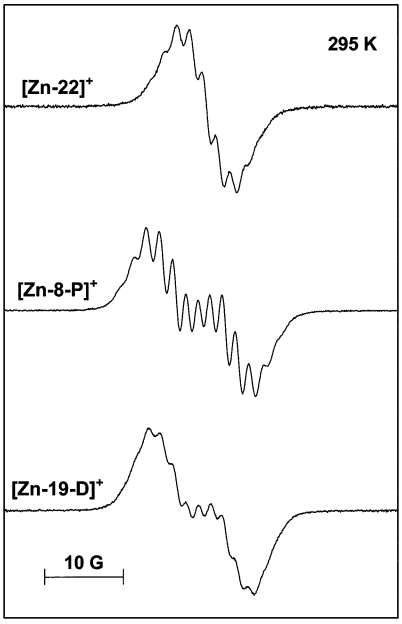


FIGURE 1. Ambient temperature EPR spectra of **[Zn-22]**$^+$, **[Zn-8-P]**$^+$, and **[Zn-19-D]**$^+$.

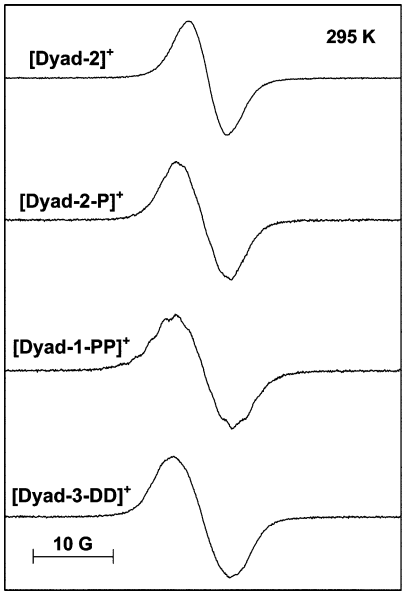


FIGURE 2. Ambient temperature EPR spectra of **[Dyad-2]**$^+$, **[Dyad-2-P]**$^+$, **[Dyad-1-PP]**$^+$, and **[Dyad-3-DD]**$^+$.

are ∼6.2 G, which is much larger (as expected[4]) than the ^{14}N hyperfine splittings, which are ∼1.5 G. [Note that the meso-^{13}C hyperfine couplings observed for **[Zn-8-P]**$^+$ and **[Zn-19-D]**$^+$ are slightly larger than those observed for the monocation radical of zinc tetraphenylporphyrin (∼5.7 G).[2]] The ^{14}N hyperfine pattern for **[Zn-8-P]**$^+$ is much better resolved than that for **[Zn-19-D]**$^+$. This difference is not due to the slightly larger ^{14}N hyperfine couplings for complexes that contain swallowtail
(**[Zn-8-P]**$^+$ ∼1.7 G) versus aryl (**[Zn-19-D]**$^+$ ∼1.5 G) non-linker substituents, but rather to a difference in line width that appears to be characteristic of placement of the ^{13}C label proximal versus distal to the appended linker. This assessment is based on the fact that **[Zn-5-P]**$^+$ and **[Zn-6-P]**$^+$, each of which contains a proximal ^{13}C label and aryl non-linker substituents, exhibit well-resolved spectra similar to that observed for **[Zn-8-P]**$^+$. We have no explanation for this difference in line widths.

The EPR spectrum of the unlabeled dyad, **[Dyad-2]**$^+$, does not exhibit any resolved ^{14}N hyperfine splittings (Figure 2, top trace) because of collapse of these splittings due to rapid hole transfer.[2] As expected, the EPR spectra of the three different ^{13}C-labeled dyads, **[Dyad-2-P]**$^+$, **[Dyad-1-PP]**$^+$, **[Dyad-3-DD]**$^+$, also fail to exhibit resolved ^{14}N hyperfine splittings. More importantly, the spectra of the three dyads also fail to exhibit resolved ^{13}C hyperfine splittings. Spectral simulations indicate that the ^{13}C splittings have been reduced from ∼6.2 to ∼3.1 G. This result is consistent with hole transfer remaining fast on the time scale defined by the ^{13}C hyperfine interactions (∼50 ns).

The temperature dependence of the EPR spectra of the monocations of the various dyads was also examined. The spectra of a selected (and representative) dyad, **[Dyad-2-P]**$^+$, obtained in the 120−295 K range are shown in Figure 3. As the temperature is lowered from 295 to 190 K, near the freezing point of the solvent, the hyperfine splittings become slightly better resolved; however, the overall spectral line width remains approximately constant. This observation indicates that hole transfer remains fast on the time scale of the ^{13}C (and ^{14}N) clock at reduced temperature. The line width is appreciably broadened at 120 K, where the solvent is frozen; however, no hyperfine splittings are resolved. This result is consistent with previous

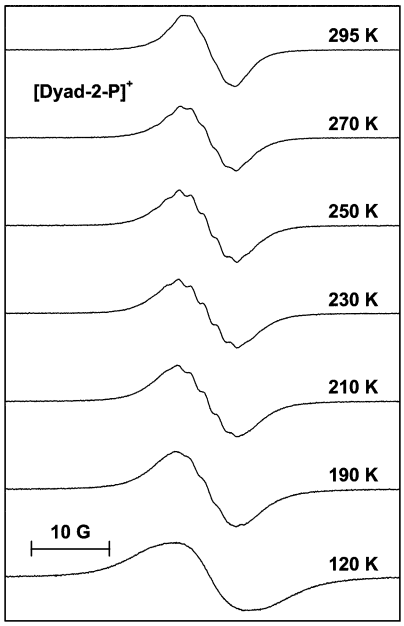


FIGURE 3. Temperature dependence of the EPR spectrum of **[Dyad-2-P]**$^+$.

studies of unlabeled dyads, which indicate that hole transfer becomes slow on the EPR time scale upon freezing of the solvent.[37] These previous studies have also revealed that the slowing of hole transfer occurs abruptly upon solvent freezing, similar to the behavior observed herein. The abrupt slowing of hole transfer is attributed to the significantly higher reorganization energy of the frozen versus liquid solvent.

Experimental Section

Electrochemistry. The electrochemical measurements were performed using techniques and instrumentation previously described.[38] The solvent was CH_2Cl_2, CH_2Cl_2/THF (9:1), or CH_2Cl_2/*o*-dichlorobenzene (9:1), depending on the solubility of the complex, containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. The bulk oxidized complexes were prepared in a glove box. Upon oxidation, the samples were transferred to an EPR tube and sealed in the glove box.

EPR Spectroscopy. The EPR spectra were recorded on an E-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 at both ambient and cryogenic temperatures. The microwave power and magnetic field modulation amplitude were typically 5.7 mW and 0.32 G, respectively.

4-Iodobenzonitrile-*cyano*-^{13}*C* (1). Following a standard procedure[24] with slight modification, a mixture of 1,4-diiodobenzene (5.00 g, 15.2 mmol), KCN-^{13}*C* (1.10 g, 16.7 mmol), and CuI (1.44 g, 7.56 mmol) in NMP (38 mL) was refluxed in a Schlenk flask for 5.5 h. After the mixture was cooled to room temperature, ethyl acetate (200 mL) was added. The resulting reaction mixture was washed with several solutions in the following sequence: aqueous $FeCl_3$ (2 × 250 mL, 10 w/v %), water (250 mL), aqueous $Na_2S_2O_3$ (2 × 250 mL, 10 w/v %), water (250 mL), and saturated NaCl (250 mL). After drying over Na_2SO_4, the solvent was evaporated. Flash column chromatography [silica, hexanes → hexanes/CH_2Cl_2 (2:1)] afforded a white solid (1.65 g, 47%): mp 124−125 °C; ^{1}H NMR (400 MHz) δ 7.38 (dd, J = 8.4 Hz, J = 5.2 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 118.2 (enh), 133.1, 133.2, 138.45, 138.51. Anal. Calcd for $C_6{}^{13}CH_4IN$: C, 36.98; H, 1.75; N, 6.09. Found: C, 37.04; H, 1.73; N, 5.94.

4-Iodobenzaldehyde-*formyl*-^{13}*C* (2). A solution of **1** (3.00 g, 13.0 mmol) in CH_2Cl_2 (43 mL) was cooled in an ice bath and slowly treated with DIBAL-H (15.65 mL, 1.0 M in hexanes). The ice bath was removed. The reaction mixture was stirred at room temperature. After 3 h, the mixture was poured into a mixture of crushed ice (100 g) and 6 N HCl (250 mL) and stirred for 1 h. The organic phase was separated, washed with 5% $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography [silica, CH_2Cl_2/hexanes (1:2)], resulting in a white solid (2.64 g, 87%): mp 77−78 °C; ^{1}H NMR (400 MHz) δ 7.60 (dd, J = 8.0 Hz, J = 4.8 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 9.96 (d, J = 175.2 Hz, 1H); ^{13}C NMR δ 130.78, 130.82, 138.37, 138.42, 191.4 (enh). Anal. Calcd for $C_6{}^{13}CH_5O$: C, 36.51; H, 2.16. Found: C, 36.21; H, 2.08.

4-(3-Methyl-3-hydroxybut-1-yn-1-yl)benzaldehyde-*formyl*-^{13}*C* (3). A mixture of **2** (500 mg, 2.15 mmol), $Pd(PPh_3)_2Cl_2$ (151 mg, 0.215 mmol), and CuI (21.0 mg, 0.110 mmol) was degassed in a Schlenk flask. Dry TEA (4.3 mL) was added, and the resulting mixture was treated with 2-methylbut-3-yn-2-ol (250 μL, 2.58 mmol). The reaction mixture was heated to 40 °C and stirred for 2 h. After being cooled to room temperature, the mixture was filtered. The filtered material was washed with diethyl ether. The filtrate was concentrated to dryness and purified by column chromatography (silica, CH_2Cl_2) to obtain a yellow oil, which solidified upon cooling (342 mg, 84%): ^{1}H NMR (400 MHz) δ 1.64 (s, 6H), 2.35 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.80 (dd, J = 8.0 Hz, J = 4.8 Hz, 2H), 9.99 (d, J = 174.8 Hz, 1H); ^{13}C NMR δ 31.3, 65.6, 81.3, 97.8, 129.1, 129.4, 129.5, 132.09, 132.14, 135.1, 135.6, 191.5 (enh); FAB-MS obsd 190.0941, calcd 190.0949 [(M + H)$^+$, M = $C_{11}{}^{13}CH_{12}O_2$].

5-(4-Iodophenyl)-10,15,20-trimesitylporphinatozinc(II)-(*5*-^{13}*C*) (Zn-4-P). Following a standard procedure,[25] a mixture of pyrrole (346 mg, 5.16 mmol), mesitaldehyde (572 mg, 3.86 mmol), and **2** (300 mg, 1.29 mmol) in $CHCl_3$ (515 mL) was degassed for 5 min and treated with $BF_3{\cdot}O(Et)_2$ (215 μL, 1.70 mmol) at room temperature. After 1 h, DDQ (875 mg, 3.85 mmol) was added. The reaction mixture was stirred for 1 h, and then TEA (0.50 mL) was added. The mixture was passed through a silica pad (CH_2Cl_2) to give the mixture of porphyrins. The solvent was removed. The resulting crude mixture was dissolved in $CHCl_3$ (40 mL) and treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (1.37 g, 6.24 mmol) in methanol (10 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4), and concentrated to dryness. Column chromatography [silica, CH_2Cl_2/hexanes (1:4)] afforded the title compound as the second purple band (100 mg, 8%): ^{1}H NMR (400 MHz, THF-d_8) δ 1.84 (s, 12H), 1.85 (s, 6H), 2.63−2.64 (m, 9H), 7.28−7.29 (m, 6H), 7.96 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H), 8.08 (d, J = 8.4 Hz, 2H), 8.71 (s, 4H), 8.77 (d, J = 4.8 Hz, 2H), 8.84 (d, J = 4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 21.5, 21.66, 21.75, 119.0 (enh), 127.6, 130.75, 130.81, 131.15, 131.22, 131.71, 131.79, 131.81, 135.58, 135.63, 136.0, 136.1, 137.4, 137.7, 138.87, 138.95, 139.2, 149.00, 149.04, 149.7, 149.8, 149.9, 150.0; LD-MS obsd 929.2 [M$^+$], 1734.2 [(2M − I)$^+$]; FAB-MS obsd 919.1989, calcd 919.2014 ($C_{52}{}^{13}CH_{45}IN_4Zn$); λ_{abs} 423, 549, 593 nm; λ_{em} (λ_{ex} = 550 nm) 594, 645 nm.

5-[4-(3-Methyl-3-hydroxybut-1-yn-1-yl)phenyl]-10,15,20-trimesitylporphinatozinc(II)-(*5*-^{13}*C*) (Zn-5-P). Following a standard procedure,[26] a mixture of pyrrole (355 mg, 5.29 mmol), mesitaldehyde (587 mg, 3.96 mmol), and **3** (250 mg, 1.32 mmol) in $CHCl_3$ (72 mL) was degassed for 5 min and treated with $BF_3{\cdot}O(Et)_2$ (164 μL, 1.29 mmol) at room temperature for 1 h. DDQ (901 mg, 3.97 mmol) was added, and the reaction mixture was stirred for 1 h.

(37) (a) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578−10592. (b) Seth, J.; Palaniappan, V.; Wagner, R. W.; Johnson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 11194−11207.

(38) 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*, 117−47.

TEA (0.50 mL) was added. The mixture was passed through a short silica column (CH_2Cl_2), affording a first band (faint, containing *meso*-tetramesitylporphyrin) and a second band (intense, containing a mixture of A_3B, A_2B_2, AB_3, and B_4 free base porphyrins). The solvent was removed. The resulting crude purple material was dissolved in $CHCl_3$ (40 mL) and treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (1.45 g, 6.61 mmol) in methanol (10 mL) at room temperature. The reaction mixture was washed with water and dried (Na_2SO_4). Column chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded the title compound as the first purple band. The resulting solid was suspended in methanol; the suspension was sonicated and then decanted to afford a purple solid (165 mg, 14%): ^{1}H NMR (400 MHz, THF-d_8) δ 1.77 (s, 6H), 1.84 (s, 12H), 1.86 (s, 6H), 2.37 (s, 1H), 2.64 (s, 9H), 7.28 (s, 6H), 7.81 (d, J = 8.0 Hz, 2H), 8.18 (dd, J = 8.0 Hz, J = 3.6 Hz, 2H), 8.71 (s, 4H), 8.76 (d, J = 4.4 Hz, 2H), 8.83 (d, J = 4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 21.5, 21.7, 21.8, 31.6, 119.1 (enh), 127.6, 129.74, 129.78, 129.82, 130.68, 130.73, 130.8, 131.1, 131.2, 131.75, 131.79, 131.81, 131.83, 134.28, 134.3, 137.40, 137.45, 137.47, 139.0, 139.2, 139.3, 149.1, 149.7, 149.9, 150.0; LD-MS obsd 885.3 [M^+]; FAB-MS obsd 885.3508, calcd 885.3466 ($C_{57}{}^{13}CH_{52}N_4OZn$); λ_{abs} 423, 550, 592 nm; λ_{em} (λ_{ex} = 550 nm) 595, 645 nm.

5-(4-Ethynylphenyl)-10,15,20-trimesitylporphinatozinc(II)-(5-^{13}*C*) (Zn-6-P). A solution of **Zn-5-P** (100 mg, 113 μmol) in toluene (7.5 mL) was treated with powdered NaOH (76.6 mg, 1.92 mmol) under reflux. After 3.5 h, TLC analysis showed the complete consumption of **Zn-5-P**. The reaction mixture was passed through a silica pad (toluene) whereupon the title compound eluted as the first band. Removal of the solvent led to a purple solid (90 mg, 96%): ^{1}H NMR (400 MHz, THF-d_8) δ 1.85 (s, 12H), 1.86 (s, 6H), 2.64 (s, 9H), 3.32 (s, 1H), 7.29 (s, 6H), 7.88 (d, J = 8.0 Hz, 2H), 8.20 (dd, J = 8.4 Hz, J = 4.0 Hz, 2H), 8.72 (s, 4H), 8.77 (d, J = 4.4 Hz, 2H), 8.84 (d, J = 4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 21.5, 21.67, 21.75, 118.9 (enh), 121.1, 127.6, 130.27, 130.32, 130.7, 130.8, 131.1, 131.2, 131.7, 131.8, 134.29, 134.30, 137.4, 138.9, 139.0, 139.2, 149.0, 149.7, 149.8, 149.90, 149.93, 149.95, 150.0; LD-MS obsd 827.3 [M^+]; FAB-MS obsd 827.3045, calcd 827.3047 ($C_{54}{}^{13}CH_{46}N_4Zn$); λ_{abs} 423, 550, 592 nm; λ_{em} (λ_{ex} = 550 nm) 595, 645 nm.

5-(4-Iodophenyl)-10,15,20-tris(tridec-7-yl)porphinatozinc(II)-(5-^{13}*C*) (Zn-7-P). Following a standard procedure,[19] a mixture of pyrrole (411 mg, 6.13 mmol), 7-formyltridecane (2.60 g, 12.3 mmol), and **2** (357 mg, 1.53 mmol) in $CHCl_3$ (613 mL) was degassed for 5 min and treated with $BF_3{\cdot}O(Et)_2$ (257 μL, 2.03 mmol) at room temperature. After 1 h, DDQ (1.04 g, 4.60 mmol) was added, and the mixture was stirred for 1 h. TEA (0.50 mL) was added. The reaction mixture was filtered through a silica pad (CH_2Cl_2). The resulting mixture of free base porphyrins was dissolved in $CHCl_3$ (48 mL) and treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (1.68 g, 7.66 mmol) in methanol (12 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4), and concentrated to dryness. Column chromatography [silica, CH_2Cl_2/hexanes (1:8)] afforded the title compound as the second purple band (263 mg, 15%): ^{1}H NMR (400 MHz) δ 0.70−0.75 (m, 18H), 1.02−1.64 (m, 48H), 2.71−2.84 (m, 6H), 2.88−3.02 (m, 6H), 5.14−5.27 (m, 3H), 7.93 (dd, J = 8.0 Hz, J = 3.6 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 8.84−8.90 (m, 2H), 9.60−9.84 (m, 6H); ^{13}C NMR δ 13.9, 22.5, 29.6, 29.7, 29.8, 29.9, 31.7, 42.5, 42.6, 47.1, 47.2, 47.3, 47.5, 116.9 (enh, t, J = 70.5 Hz), 124.3, 124.5, 129.1, 129.3, 129.6, 130.0, 130.3, 130.6, 131.0, 131.3, 135.5, 136.0, 142.7, 143.2, 146.6, 146.8, 147.1, 147.5, 148.6, 148.8, 149.0, 149.4, 149.6, 151.0, 151.1, 151.6; LD-MS obsd 1121.6; FAB-MS obsd 1121.6035, calcd 1121.5770 ($C_{64}{}^{13}CH_{93}IN_4Zn$); λ_{abs} 425, 555, 593 nm; λ_{em} (λ_{ex} = 550 nm) 602, 652 nm.

5-[4-[2-(Trimethylsilyl)ethynyl]phenyl]-10,15,20-tris(tridec-7-yl)porphinatozinc(II)-(5-^{13}*C*) (Zn-8-P). Following a standard procedure[19] with modification,[18] a mixture of **Zn-7-P** (200 mg, 178 μmol), $Pd_2(dba)_3$ (24.4 mg, 26.6 μmol), and $AsPh_3$ (66.2 mg, 216 μmol) in dry toluene/TEA (72 mL, 5:1) was placed in a Schlenk flask followed by (trimethylsilyl)acetylene (30.4 μL, 307 μmol). After reaction at 35 °C for 16 h, the reaction mixture was concentrated to dryness and purified by column chromatography [silica, CH_2Cl_2/hexanes (1:9)], affording a purple solid (90 mg, 53%): ^{1}H NMR δ 0.43 (s, 9H), 0.70−0.76 (m, 18H), 1.02−1.66 (m, 48H), 2.75−2.86 (m, 6H), 2.88−3.00 (m, 6H), 5.14−5.30 (m, 3H), 7.88 (dd, J = 7.8 Hz, 2H), 8.15 (dd, J = 7.8 Hz, J = 3.6 Hz, 2H), 8.82−8.98 (m, 2H), 9.58−9.88 (m, 6H); ^{13}C NMR δ 0.1, 13.9, 22.5, 29.6, 29.7, 29.8, 29.9, 31.7, 42.5, 42.6, 47.1, 47.2, 47.4, 47.5, 95.0, 105.4, 117.7 (enh, t, J = 69.0 Hz), 122.0, 124.1, 124.3, 124.6, 129.1, 129.3, 129.4, 130.07, 130.11, 130.4, 130.6, 130.9, 131.0, 131.2, 131.3, 134.2, 143.5, 144.2, 146.9, 147.5, 148.8, 149.5, 149.6, 151.2, 151.7; LD-MS obsd 1092.2; FAB-MS obsd 1091.6882, calcd 1091.7199 ($C_{69}{}^{13}CH_{102}N_4SiZn$); λ_{abs} 425, 555, 593 nm; λ_{em} (λ_{ex} = 550 nm) 604, 654 nm.

5-(4-Ethynylphenyl)-10,15,20-tris(tridec-7-yl)porphinatozinc-(II)-(5-^{13}*C*) (Zn-9-P). A solution of **Zn-8-P** (70.0 mg, 64.0 μmol) in $CHCl_3$/THF (7.0 mL, 3:1) was treated with a solution of TBAF (96.0 μL, 96.0 μmol, 1.0 M in THF) at room temperature over 1 h. The reaction mixture was washed with 10% $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated to dryness. The resulting crude product was purified by column chromatography [silica, CH_2Cl_2/hexanes (1:8)] to obtain a purple solid (40 mg, 60%): ^{1}H NMR (400 MHz) δ 0.69−0.74 (m, 18H), 1.02−1.64 (m, 48H), 2.72−2.84 (m, 6H), 2.87−3.01 (m, 6H), 3.33 (s, 1H), 5.16−5.26 (m, 3H), 7.89 (d, J = 7.6 Hz, 2H), 8.16 (dd, J = 7.6 Hz, J = 4.0 Hz, 2H), 8.81−8.90 (m, 2H), 9.48−9.84 (m, 6H); ^{13}C NMR δ 13.9, 22.5, 29.6, 29.8, 29.9, 31.7, 42.5, 42.6, 47.1, 47.2, 47.3, 47.5, 77.8, 84.0, 117.5 (enh, t, J = 68.1 Hz), 124.0, 125.1, 129.1, 129.3, 129.5, 130.21, 130.25, 130.6, 131.0, 131.3, 134.2, 143.8, 144.5, 146.8, 147.2, 147.5, 148.7, 149.0, 149.5, 149.7, 150.5, 151.0, 151.10, 151.18, 151.24; LD-MS obsd 1021.3; FAB-MS obsd 1019.7037, calcd 1019.6803 ($C_{66}{}^{13}CH_{94}N_4Zn$); λ_{abs} 425, 555, 593 nm; λ_{em} (λ_{ex} = 550 nm) 605, 653 nm.

***p*-Toluic-*carboxy*-^{13}*C* Acid (10).** Following a known procedure,[29] a solution of CuCN-^{13}*C* (2.41 g, 26.6 mmol) in pyridine (1.82 mL, 22.5 mmol) at 150−155 °C was treated with 4-bromotoluene (3.50 g, 20.5 mmol). The reaction mixture was refluxed at 185−190 °C for 6 h. After the mixture cooled to room temperature, 75% aqueous H_2SO_4 (12 mL) was added, and the mixture was stirred at 150 °C for 2 h. The reaction mixture was poured into ice−water (20 mL) and subsequently treated with 5% aqueous NaOH (30 mL), resulting in a yellow precipitate. After being stirred at room temperature for 15 min, the mixture was filtered. The filtrate was acidified with 50% aqueous HCl until pH < 4 was obtained. A colorless precipitate was collected and dissolved in ethyl acetate (50 mL). The ethyl acetate solution was dried (Na_2SO_4) and concentrated to dryness, affording a white solid (1.41 g, 50%): mp 180 °C; ^{1}H NMR δ 2.44 (s, 3H), 7.29 (d, J = 8.1 Hz, 2H), 8.02 (dd, J = 8.1 Hz, J = 4.2 Hz, 2H); ^{13}C NMR δ 21.8, 126.1, 127.0, 129.17, 129.23, 130.2, 144.6, 172.2 (enh). Anal. Calcd for $C_7{}^{13}CH_8O_2$: C, 70.06; H, 5.88. Found: C, 70.05; H, 5.94.

***S*-2-Pyridyl 4-Methylbenzo-*carbonyl*-^{13}*C* Thioate (11).** Following a standard procedure,[31] a solution of **10** (0.750 mg, 5.47 mmol), 2,2′-dipyridyl disulfide (2.41 g, 10.9 mmol), and PPh_3 (2.84 g, 10.9 mmol) in dry THF (8 mL) was stirred at room temperature for 16 h. After removal of the solvent, the resulting yellow oil was chromatographed [silica, ethyl acetate/hexanes (1:1)] to afford a colorless solid (1.21 g, 96%): mp 61 °C; ^{1}H NMR δ 2.44 (s, 3H), 7.28−7.36 (m, 3H), 7.72−7.82 (m, 2H), 7.93 (dd, J = 8.4 Hz, J = 4.5 Hz, 2H), 8.68−8.69 (m, 1H); ^{13}C NMR δ 21.7, 123.5, 127.6, 127.7, 129.4, 129.5, 130.9, 133.5, 134.4, 137.1, 144.9, 150.5, 151.5, 188.9 (enh). Anal. Calcd for $C_{12}{}^{13}CH_{11}NO_2S$: C, 67.80; H, 4.81; N, 6.08. Found: C, 67.57; H, 4.77; N, 6.03.

10-(Dibutylboryl)-5-mesityl-1-[4-[2-(trimethylsilyl)ethynyl]-benzoyl]dipyrromethane (Bu_2B-15). Following a standard procedure,[33] a solution of **12** (550 mg, 2.08 mmol) in dry THF (2.10 mL) was treated with EtMgBr (4.2 mL, 4.2 mmol, 1.0 M in THF) at room temperature for 10 min. The reaction mixture was cooled

to −78 °C and treated with a solution of **13b** (650 mg, 2.09 mmol) in THF (2.10 mL). The cooling bath was removed, and the reaction mixture was stirred at room temperature for 30 min. Standard workup including treatment with TEA (695 μL) and dibutylboron triflate (4.16 mL, 4.16 mmol, 1.0 M in CH_2Cl_2) followed by flash column chromatography [silica, hexanes/CH_2Cl_2 (3:1) → CH_2Cl_2] afforded a yellow solid (771 mg, 63%): mp 55 °C (dec); ^{1}H NMR δ 0.29 (s, 9H), 0.56−1.26 (m, 18H), 2.16 (s, 6H), 2.27 (s, 3H), 5.89 (s, 1H), 5.90−5.94 (m, 1H), 6.19 (dd, J = 4.5 Hz, J = 1.8 Hz, 1H), 6.49 (d, J = 3.3 Hz, 1H), 6.68−6.72 (m, 1H), 6.83 (s, 2H), 7.19 (d, J = 3.3 Hz, 1H), 7.61 (dd, J = 4.8 Hz, J = 1.5 Hz, 2H), 7.83 (brs, 1H), 8.12 (d, J = 6.3 Hz, 2H); ^{13}C NMR δ −0.2, 14.0, 14.3, 20.7, 21.5, 25.9, 26.0, 27.1, 27.3, 39.9, 99.2, 103.9, 107.8, 108.7, 116.5, 116.8, 122.4, 128.6, 129.3, 129.9, 130.1, 130.4, 132.4, 134.6, 135.3, 136.7, 137.0, 152.5, 174.4; LD-MS obsd 588.1 [M$^+$]. Anal. Calcd for $C_{38}H_{49}BN_2OSi$: C, 77.53; H, 8.39; N, 4.76. Found: C, 77.27; H, 8.39; N, 4.73.

10-(Dibutylboryl)-9-(4-iodophenyl)-5-mesityl-1-(4-methylbenzoyl-*carbonyl*-^{13}*C*)dipyrromethane (Bu_2B-16). Following a standard procedure,[34] a solution of **Bu_2B-14** (853 mg, 1.38 μmol) and HMDS (288 μL, 1.38 μmol) in dry THF (2.76 mL) was treated with EtMgBr (2.8 mL, 2.8 mmol, 1.0 M in THF) at room temperature for 10 min. The reaction mixture was treated with a solution of **11** (635 mg, 2.76 mmol) in THF (2.76 mL) and stirred at room temperature for 2 h. Standard workup followed by flash column chromatography [silica, CH_2Cl_2/hexanes (1:1) → CH_2Cl_2] afforded a yellow solid (420 mg, 41%): mp 89−90 °C (dec); ^{1}H NMR δ 0.30−1.26 (m, 18H), 2.16−2.17 (m, 6H), 2.28 (s, 3H), 2.44 (s, 3H), 5.95−6.01 (m, 2H), 6.46 (dd, J = 4.2 Hz, J = 3.0 Hz, 1H), 6.82−6.84 (m, 1H), 6.86 (s, 1H), 7.20 (d, J = 3.9 Hz, 1H), 7.24 (d, J = 4.2 Hz, 1H), 7.29 (s, 1H), 7.56−7.61 (m, 1H), 7.65−7.70 (m, 1H), 7.79 (dd, J = 8.1 Hz, J = 3.9 Hz, 2H), 7.89−7.96 (m, 2H), 8.20−8.23 (m, 1H), 9.07 (brs, 1H); ^{13}C NMR δ 14.1, 14.2, 20.7, 21.5, 26.0, 27.0, 27.4, 40.0, 102.0, 111.0, 117.2, 119.8, 121.5, 121.9, 124.7, 128.9, 129.0, 129.1, 129.7, 130.6, 130.8, 133.4, 134.0, 135.4, 136.1, 137.0, 137.2, 137.3, 138.5, 139.0, 139.3, 142.2, 149.2, 149.9, 183.9 (enh); LD-MS obsd 613.5 [(M − I)$^+$]; FAB-MS obsd 738.2826, calcd 738.2809 [(M + H)$^+$, M = $C_{40}{}^{13}CH_{46}BIN_2O_2$].

10-(Dibutylboryl)-5-mesityl-1-(4-methylbenzoyl-*carbonyl*-^{13}*C*)-9-[4-[2-(trimethylsilyl)ethynyl]benzoyl]dipyrromethane (Bu_2B-17). Following a standard procedure,[34] a solution of **Bu_2B-15** (771 mg, 1.31 mmol) and HMDS (273 μL, 1.31 mmol) in dry THF (2.60 mL) was treated with EtMgBr (2.6 mL, 2.6 mmol, 1.0 M in THF) at room temperature for 10 min. The reaction mixture was treated with a solution of **11** (603 mg, 2.62 mmol) in THF (2.76 mL) and stirred at room temperature for 2 h. Standard workup followed by column chromatography [silica, CH_2Cl_2/hexanes (1:1) → CH_2Cl_2] gave a yellow solid (420 mg, 45%): mp 100−101 °C (dec); ^{1}H NMR (400 MHz) δ 0.29 (s, 9H), 0.30−1.26 (m, 18H), 2.17 (s, 6H), 2.28 (s, 3H), 2.44 (s, 3H), 5.95−6.01 (m, 2H), 6.46−6.47 (m, 1H), 6.83−6.84 (m, 1H), 6.86 (s, 2H), 7.20 (d, J = 3.3 Hz, 1H), 7.29 (s, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.78−7.81 (m, 2H), 8.14 (d, J = 8.0 Hz, 2H), 9.07 (brs, 1H); ^{13}C NMR δ −0.2, 14.1, 14.2, 20.7, 21.1, 21.55, 21.58, 26.0, 27.0, 27.4, 40.0, 99.4, 103.9, 111.0, 117.2, 120.0, 121.7, 129.0, 129.4, 129.9, 132.4, 133.3, 135.5, 137.0, 137.2, 139.2, 142.2, 149.2, 149.6, 175.2, 183.9 (enh); LD-MS obsd 597.5 [(M − 2(*n*-butyl))$^+$], 653.5 [(M − *n*-butyl)$^+$], 708.1 [M$^+$]; FAB-MS obsd 708.4280, calcd 708.4238 [(M + H)$^+$, M = $C_{45}{}^{13}CH_{55}BN_2O_2Si$].

15-(4-Iodophenyl)-10,20-dimesityl-5-*p*-tolylporphinatozinc(II)-(*5*-^{13}*C*) (Zn-18-D). Following a standard procedure,[21,35] a solution of **Bu_2B-16** (420 mg, 0.570 mmol) in THF/MeOH (23 mL, 10:1) was treated with $NaBH_4$ (431 mg, 11.4 mmol) at room temperature for 40 min. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (50 mL) and CH_2Cl_2 (50 mL), and then stirred for 10 min. The organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated to dryness. A solution of the resulting foam-like solid and **12** (150 mg, 0.568 mmol) in CH_2Cl_2 (228 mL) was treated with $Yb(OTf)_3$ (453 mg, 0.730 mmol) at room temperature for 15 min, whereupon DDQ (388 mg, 1.71 mmol) was added. After 1 h, TEA (0.50 mL) was added. The mixture was filtered through a silica pad (CH_2Cl_2), and the resulting purple fraction was collected. The resulting crude product was dissolved in $CHCl_3$ (100 mL) and treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (625 mg, 2.85 mmol) in methanol (25 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (1:2)] to afford a purple solid (68 mg, 13%): ^{1}H NMR (THF-d_8) δ 1.84 (s, 12H), 2.53 (s, 9H), 2.61 (s, 3H), 2.68 (s, 3H), 7.29 (s, 4H), 7.54 (d, J = 7.8 Hz, 2H), 7.71−7.73 (m, 2H), 7.97 (d, J = 7.8 Hz, 2H), 8.04−8.11 (m, 4H), 8.17−8.19 (m, 2H), 8.64−8.67 (m, 4H), 8.76 (d, J = 4.5 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H); ^{13}C NMR (THF-d_8) δ 21.7, 22.1, 119.3, 119.5, 121.0, 121.1, 121.4 (enh), 127.2, 127.9, 128.0, 128.2, 128.6, 128.7, 130.71, 130.76, 130.81, 131.1, 132.5, 132.8, 132.9, 133.0, 133.1, 135.4, 135.5, 136.5, 137.3, 137.76, 137.84, 138.17, 138.23, 140.0, 140.8, 140.9, 144.3, 144.7, 150.6, 150.7, 150.9, 151.0, 151.60, 151.64; LD-MS obsd 775.6 [(M − I)$^+$], 901.5 [M$^+$]; FAB-MS obsd 901.1707, calcd 901.1701 ($C_{50}{}^{13}CH_{41}IN_4Zn$); λ_{abs} 423, 549, 593 nm; λ_{em} (λ_{ex} = 550 nm) 596, 644 nm.

10,20-Dimesityl-15-*p*-tolyl-5-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphinatozinc(II)-(*15*-^{13}*C*) (Zn-19-D). Following a standard procedure,[21,35] a solution of **Bu_2B-17** (420 mg, 0.593 mmol) in THF/MeOH (24 mL, 10:1) was treated with $NaBH_4$ (449 mL, 11.9 mmol) at room temperature for 40 min. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (30 mL) and CH_2Cl_2 (30 mL) and stirred for 10 min. The organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated. The resulting crude product was dissolved in CH_2Cl_2 (238 mL), and **12** (157 mg, 0.594 mmol) was added. After a homogeneous solution was obtained, $Yb(OTf)_3$ (472 mg, 0.761 mmol) was added, and the reaction mixture was stirred at room temperature for 15 min. DDQ (405 mg, 1.78 mmol) was added, and stirring was continued for 1 h. TEA (0.50 mL) was added. The mixture was filtered through a silica pad (CH_2Cl_2). The resulting purple crude material was dissolved in $CHCl_3$ (100 mL) and treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (651 mg, 2.97 mmol) in methanol (25 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4), and chromatographed [silica, CH_2Cl_2/hexanes (1:1)]. The resulting solid was suspended in methanol; the suspension was sonicated and then decanted to afford a purple solid (93 mg, 18%): ^{1}H NMR (THF-d_8) δ 0.35 (s, 9H), 1.84 (s, 12H), 2.53 (s, 3H), 2.60 (s, 3H), 2.67 (s, 3H), 7.29 (s, 4H), 7.54 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 8.04−8.08 (m, 2H), 8.17 (d, J = 7.8 Hz, 2H), 8.64−8.66 (m, 4H), 8.76 (d, J = 4.8 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H); ^{13}C NMR (THF-d_8) δ 0.2, 21.6, 22.0, 95.1, 106.4, 110.3, 119.4, 120.8, 121.3 (enh), 121.7, 123.2, 127.8, 127.9, 128.5, 130.7, 130.9, 132.4, 132.9, 133.0, 135.27, 135.35, 137.7, 138.1, 139.9, 140.7, 141.9, 145.1, 150.47, 150.57, 150.64, 150.8, 151.5; LD-MS obsd 871.6 [M$^+$]; FAB-MS obsd 871.3128, calcd 871.3130 ($C_{55}{}^{13}CH_{50}N_4SiZn$); λ_{abs} 425, 552, 593 nm; λ_{em} (λ_{ex} = 550 nm) 602, 648 nm.

5-(4-Ethynylphenyl)-10,20-dimesityl-15-*p*-tolylporphinatozinc-(II)-(*15*-^{13}*C*) (Zn-20-D). A solution of **Zn-19-D** (50.0 mg, 57.2 μmol) in $CHCl_3$/THF (6.4 mL, 3:1) was treated with TBAF (86.0 μL, 86.0 μmol) at room temperature for 1 h. The reaction mixture was washed with 10% aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated to dryness. Purification by column chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a purple solid (45 mg, 98%): ^{1}H NMR (THF-d_8) δ 1.84 (s, 12H), 2.53 (s, 3H), 2.60 (s, 3H), 2.64 (s, 3H), 3.78 (s, 1H), 7.29 (s, 4H), 7.54 (d, J = 7.8 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 8.06 (dd, J = 8.1 Hz, J = 3.6 Hz, 2H), 8.18 (d, J = 7.8 Hz, 2H), 8.65 (t, J = 4.8 Hz, 4H), 8.78 (dd, J = 8.1 Hz, J = 4.5 Hz, 4H); ^{13}C NMR (THF-d_8) δ 21.6, 22.0, 30.7, 79.7, 84.5, 119.4, 119.6, 120.8, 121.3 (enh), 121.7, 122.6, 127.8, 127.9, 128.5, 130.66, 130.70, 130.8, 130.9, 132.4, 132.9, 133.0, 135.3, 135.4, 137.7, 138.1, 139.9, 140.7, 141.2, 145.1,

150.49, 150.58, 150.66, 150.74, 151.5; LD-MS obsd 799.6 [M^+]; FAB-MS obsd 799.2750, calcd 799.2734 ($C_{52}{}^{13}CH_{42}N_4Zn$); λ_{abs} 424, 550, 593 nm; λ_{em} (λ_{ex} = 550 nm) 601, 648 nm.

Dyad-1-P. Following a standard procedure,[25] a mixture of **Zn-6-P** (26.7 mg, 32.2 μmol), **Zn-21** (30.0 mg, 32.2 μmol), $Pd_2(dba)_3$ (4.5 mg, 4.9 μmol), and P(*o*-tol)$_3$ (11.8 mg, 38.8 μmol) in dry toluene/TEA (13 mL, 5:1) was reacted in a Schlenk flask at 35 °C. After 12 h, identical portions of catalyst and ligand were added, and the reaction mixture was stirred for 10 h. The product was purified by a three-column chromatography sequence, without complete evaporation of solvent from intermediate fractions. Thus, after removal of about one-half of the solvent, the resulting reaction mixture was passed through a silica column [CH_2Cl_2/toluene (1:1)]. The first purple band was collected and concentrated to obtain a clear solution of minimal volume (1−2 mL). Preparative SEC (THF) gave the title compound as the second band. After the removal of one-half of the solvent, the resulting purple solution was purified by column chromatography [silica, CH_2Cl_2/hexanes (4:1)]. The resulting product was suspended in methanol; the suspension was sonicated and then decanted to afford a purple solid (34 mg, 80%): ^{1}H NMR (CS_2) δ 1.92 (s, 36H), 2.69 (m, 18H), 7.28 (m, 12H), 8.06 (d, J = 7.8 Hz, 4H), 8.31 (d, J = 8.1 Hz, 4H), 8.73 (s, 8H), 8.80 (d, J = 4.5 Hz, 4H), 8.96 (d, J = 4.8 Hz, 4H); ^{13}C NMR (CS_2) δ 21.5, 22.7, 91.1, 118.5, 118.6, 119.0 (enh), 119.1, 119.2, 119.3, 119.4, 122.4, 127.6, 129.6, 130.5, 130.8, 130.9, 131.9, 134.1, 136.9, 138.5, 138.6, 142.3, 142.7, 143.1, 148.9, 149.3, 149.4, 149.8; LD-MS obsd 1629.0 [M^+], calcd avg mass 1631.7 ($C_{107}{}^{13}CH_{90}N_8Zn_2$); λ_{abs} 426, 550, 589 nm; λ_{em} (λ_{ex} = 550 nm) 596, 646 nm.

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Supporting Information Available: Experimental procedures for the synthesis of four dyads; ^{1}H NMR spectra for selected new compounds; and LD-MS and SEC data for all new porphyrin dyads. This material is available free of charge via the Internet at http://pubs.acs.org.

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