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Synthesis of Strapped Porphyrins: Toward Isolation of the Chromophore on Semiconductor Surfaces

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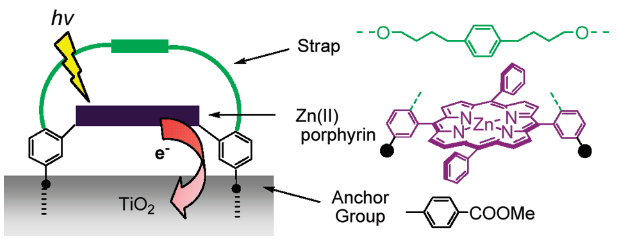

Strapped porphyrins, designed to bind planar to semiconductor surfaces, were synthesized as model dyes to study the sensitization processes on metal oxide semiconductor nanoparticles surfaces. The strap was added to limit porphyrin−porphyrin stacking and contacts with the semiconductor, while constraining the anchoring groups' orientation. Diester **ZnPorOMe$_2$** (**2b**) was made of a Zn(II) 5,10,15,20-tetraphenylporphyrin (ZnTPP) with the 5 and 15 *meso*-phenyl groups tethered by a 1,4-phenylenebis(butyl-4-oxy) unit (the strap) and carrying a methylbenzoic ester (the anchoring group) in the *meta* position. The synthesis involved a useful intermediate, dibromide **ZnPorOBr$_2$** (**2a**). The X-ray structure of the corresponding metal-free **H$_2$PorOBr$_2$** shows that, in the crystal, the strap is located on one side above the macrocycle and tilted with respect to the porphyrin plane. The characterization included ^{1}H−^{1}H COSY, ^{1}H−^{13}C HMQC, and DEPT. The spectroscopic and electrochemical properties of **2b** varied little when compared to ZnTPP, suggesting that the properties are not greatly influenced by the tether or the anchor groups. The HOMO−LUMO gap for **2b**, at 2.14 V, was typical for a ZnTPP derivative. Compound **2b** was bound to TiO$_2$ and ZrO$_2$ nanoparticle films. On TiO$_2$, the fluorescence emission was fully quenched, while the emission on insulating ZrO$_2$ was similar to the solution spectra.

Introduction

The study of porphyrins as sensitizing dyes for wide band gap metal oxide semiconductor nanoparticles (typically TiO$_2$, SnO$_2$, or ZnO) has attracted much interest in view of the potential technological applications for renewable energy.[1] Porphyrins are excellent sensitizers from a practical and fundamental standpoint because they possess favorable photophysical properties, including excellent light harvesting in the visible, and are photostable.[2] In addition, the porphyrin macrocycle can host a variety of metal ions,[3] and its synthetic versatility is ideal for the design of model compounds of varying complexity. For instance, porphyrin oligomeric arrays are studied for numerous applications, ranging from antennae for artificial photosynthesis to light-harvesting arrays in renewable energy projects.[1,4−8]

More recently, anchor−spacer−porphyrin systems[1b,d,e,i,5,9−13] have been developed as model dyes to understand the kinetics of the sensitization process of semiconductors used in dye-sensitized solar cells (DSSCs). For instance, we reported that DSSCs prepared from tetrachelated Zn(II) tetraphenylporphyrin (ZnTPP) derivatives **1a**−**c**, Figure 1, designed to bind planar to the semiconductor surface, were more efficient than those prepared from rigid-rod ZnTPP models designed to bind perpendicularly.[10,11a,13a,13b] This was observed on cells prepared from TiO$_2$ nanoparticles[13b] as well as from TiO$_2$ nanotube[13a] electrodes. For example, IPCE values at the Q bands of **1a** (*m*-ZnTCPP) and **1b** were 20-fold higher with respect to the IPCE values observed in the same region for *p*-ZnTCPP, which is binding normal to the surface, Figure 1.[13a] Additionally, *p*-ZnTCPP and porphyrin rigid-rods aggregated considerably, even at low surface coverage.[11a,13a,13b] The orientation effect on DSSCs efficiencies for *m*- and *p*-ZnTCPP was first probed by Officer and co-workers.[1b]

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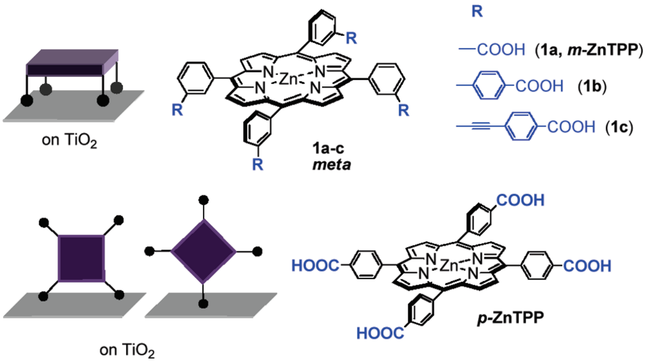

FIGURE 1. Tetrachelate porphyrins **1a**−**c** bind planar to the semiconductor surface. The calculated height increases from 3.6 Å (**1a**) to 7.1 Å (**1b**) to 9.1 Å (**1c**).[13b]

Recent charge-transfer and computational studies[14] of the tetrachelated ZnTPP compounds, however, suggest that it is necessary to design an improved generation of models to (a) inhibit porphyrin stacking, (b) limit the conformational mobility of the phenyl rings carrying the anchor group, and (c) decrease the possibility of direct contacts with the semiconductor in mesoporous films (i.e., head-down binding or "shorting" contacts[10] with adjacent nanoparticles). To improve the design, we have now synthesized ZnTPP porphyrins **2** and **3**,[15] designed to bind planar to the surface of the semiconductor and having the top plane of the ring protected by a single tether (strap) or a double tether (cap), respectively, Figure 2. The main goal is to use such model compounds to study charge-transfer kinetics on TiO_2 or ZnO, as **2** and **3** may provide better control over the binding geometry, and, ultimately, to a better understanding of injection and recombination dynamics. The strap was added to limit or prevent porphyrin−porphyrin stacking and contacts with the semiconductor while providing a constraint on the conformation of the *meso*-phenyl rings.

One attractive aspect of this design is that the phenyl ring in the strap (or cap) could eventually be replaced by a photo- or redox-active unit (i.e., an electron donor, for instance). We have followed Lindsey's classification[16] and named **2** as "strapped" and **3** as "capped" porphyrins. We recently reported the synthesis of milligram amounts of metal-free **3**.[15] Typically, however, the syntheses of capped porphyrins similar to **3** require long and low-yielding pathways.[17]

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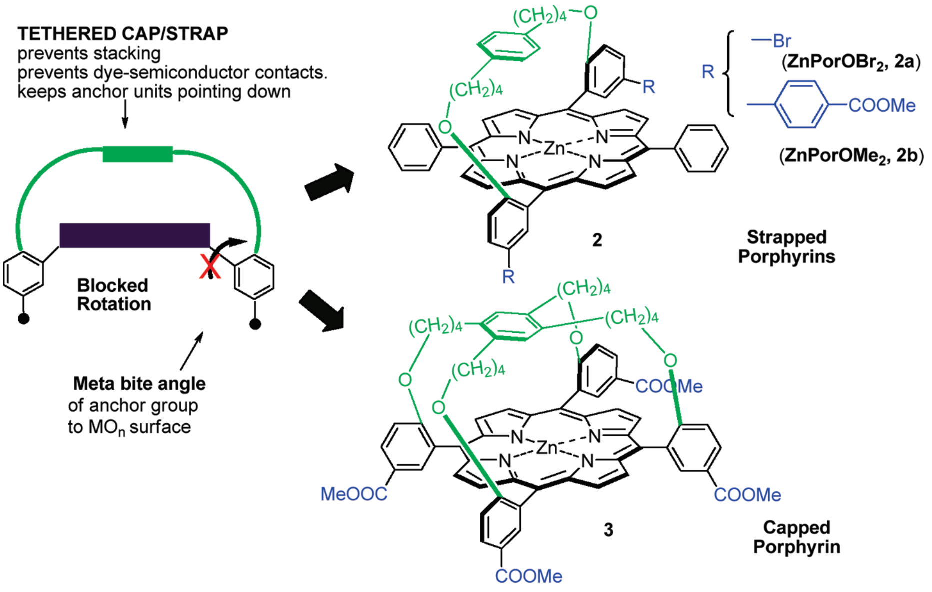

FIGURE 2. *Meso*-strapped and *meso*-capped porphyrins.

In this paper, we describe a practical synthesis of strapped porphyrins **2a** and **2b**, their characterization, and properties in solution and bound. Porphyrin dibromide **2a** does not have anchor units to bind to a semiconductor surface but is a useful precursor, as the Br group can be used in cross-coupling reactions to introduce a variety of anchor units.

While the synthetic complexity of **2** and **3** prevents their use for purely practical applications, our interest is to develop novel model compounds for fundamental charge transfer studies and that are designed to decrease binding heterogeneity and aggregation and to achieve better control over the porphyrin/semiconductor interface. We do not anticipate an improvement in DSSCs efficiencies, rather in improved binding geometry control and, possibly, less complex injection and recombination dynamics. Recent years have seen an increased effort toward the synthesis of model anchor−spacer−dyes to tune the HOMO−LUMO gap, the spacer's length and conjugation, and the orientation of the dye unit on the semiconductor surface because such structural variations influence key parameters of DSSCs devices and the dyes' properties.[18] The design of porphyrin dyes **1**−**3** is part of our continuing effort to achieve a greater control and understanding over this important interface. In addition, it will be interesting to determine to what extent the cap and tether unit can protect the chromophoric macrocycle on the semiconductor surface, in what can be called an "isolation effect". This approach, which is little explored, involves the study of dyes[19] or redox active[20] molecules encapsulated in host macrocycles and bound to semiconductors.

Strapped porphyrins have been reported before, although only a few carry functional groups on the tethered *meso* rings. They are divided into two main categories: β-strapped,[21] with the tethers attached to the pyrrole units, and *meso*-strapped (as in **2**), with the tethers attached to the *meso*-phenyl rings. We selected the latter design to build models that are directly comparable to the ZnTPP models that we studied previously[11] and to determine the influence of the conformational restriction of the strap on the *meso*-phenyl rings carrying the anchor groups (Figure 2).[14] In addition, since the *meso*-phenyl rings are electronically decoupled from the chromophore,[11] the presence of the strap would not result in large spectroscopic changes.

Meso-strapped porphyrins were used to model the photosynthetic center,[22] to mimic the catalytic activity of naturally occurring iron porphyrins,[17d,f,23] and to develop new types of polymers,[24] self-assembled monolayers,[25−27] and light harvesting arrays.[28,29] They also have found use in molecular

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recognition,[30] ion sensing,[31] host−guest complex[32] studies, and other applications.[31b,33−35] *Meso*-strapped porphyrins were made with a variety of connections of the tethers: *trans*-[23,28,30,31a,32a,33c,33d] or *cis*-[36] connected single straps, *cis*-αα- or αβ-straps,[35a,b,37] *trans*-αα-[38] or αβ-straps,[24,31a,39,40] and so-called gyroscope straps.[41] The tethers were made from a variety of chains, including alkanes,[24,31a,36,42] ethylene oxides,[26,28,29] diimides,[43] disulfides,[27] and peptides.[44] In some cases, in the tethers were embedded aromatic rings (pyridine,[45] phenyl,[31a,33a,33d,46] biphenyl[23]), chromophores (binaphthyl,[17n,35a,35b,35d] fullerene,[47] phenanthroline,[17r,s,32b,48,57] anthracene,[17e] porphyrin[49]), or coordinating hosts (crown[32c]/aza-crown ethers,[40,50] TREN,[51] and calix/cavitands[17k,14l,32a]). Fewer had functional groups on the *meso*-phenyl rings, as the compounds described in Figure 2.[24,25,28,30,34a,41,46] Strapped porphyrins with substituent groups on the tethered *meso*-phenyl rings are more rare.

The main general strategies for the syntheses of strapped porphyrins are illustrated in Figure 3. The formation of the porphyrin ring is achieved by condensation of tethered tetra-aldehydes and pyrrole, as in Figure 3, routes A−C and E. Alternatively, the tether is added to a porphyrin ring using substitution or condensation reactions of ester,[17d,m] azide,[52] or amide[23,38] groups, Figure 3, route D.[53]

Here, we report the synthesis and preliminary spectroscopic and electrochemical studies of novel strapped porphyrins **2a**−**c** in solution and semiconductor-bound and the crystal structure of **2a**. The synthetic route described here is practical, as it proceeds through a useful intermediate, bromo derivative **2a**, that is amenable to synthetic modifications to attach the anchor units, and it proceeds in satisfactory yields, leading to half-gram amounts of products.

Results and Discussion

a. Synthesis. For the synthesis of **2b**, our strategy followed route B in Figure 3, and involved the condensation of the brominated, tethered bis(dipyrrolylmethylphenyl) compound **8** (Scheme 1) with benzaldehyde. The reaction conditions were based on recent work by Crooks and co-workers.[54] The strap is made of a benzene ring tethered in *para* through two C4 saturated alkyl chains, and attached to the tetraphenyl porphyrin macrocycle (TPP) through an ether group ($\mathrm{Ph}[-(\mathrm{CH_2})_4\mathrm{O}-]_2$-TPP). The use of an ether to attach the tether was a compromise. Groups such as esters, ketones, or amides, although in some cases synthetically more convenient, were avoided because they could physisorb or bind to metal oxides, leading to unwanted binding interactions with the surface. Conversely, the synthesis of a nonreactive, and chemically more robust, tether made of methylene units ($\mathrm{Ph}[-(\mathrm{CH_2})_n]_2$TPP) would have been considerably complex.[42] The tether's length was carefully selected. Shorter chains inhibit the cyclization step necessary to form the porphyrin ring,[55] while longer chains would have promoted intermolecular reactions and would not provide the conformational constrain needed in the final product. The anchoring PhCOOMe groups in **2b** were placed in the *meta*-position on the *meso* ring to ensure a better bite angle to the metal oxide surface.[56]

The synthesis of **8** is shown in Scheme 1. Commercially available 1,4-diiodobenzene was reacted with excess

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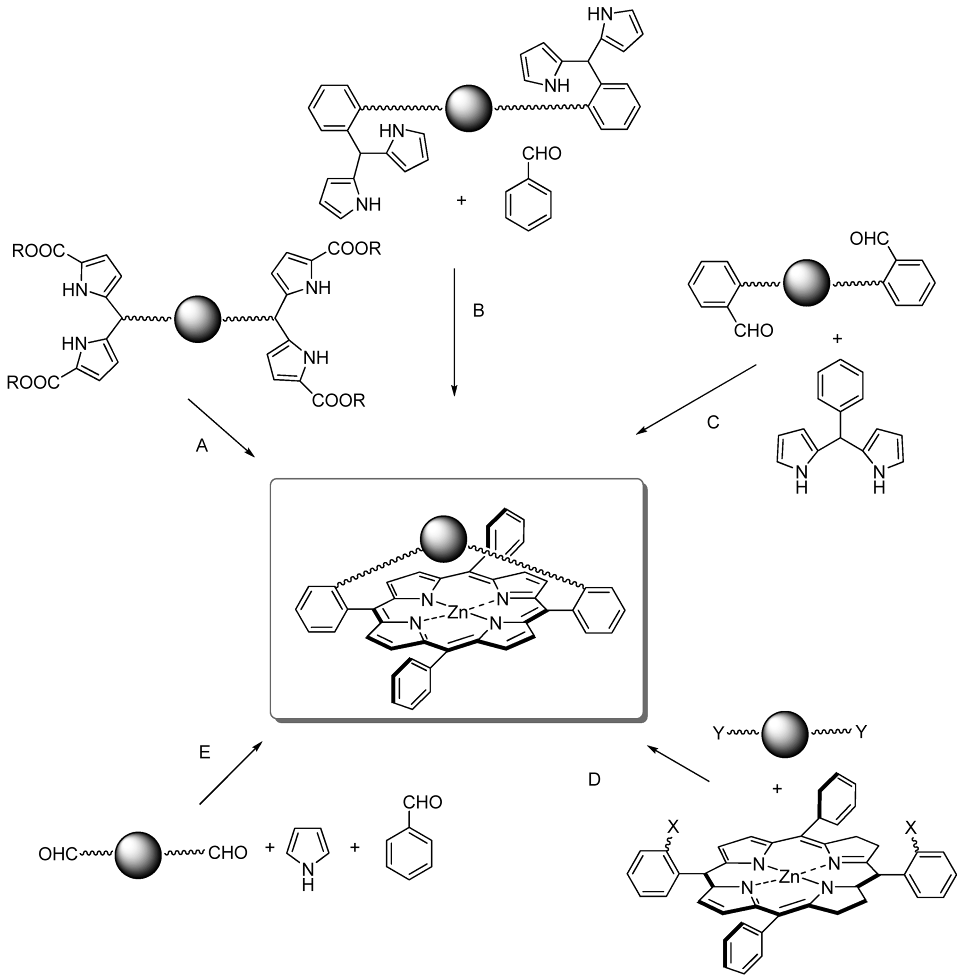

FIGURE 3. General strategies for the synthesis of strapped porphyrins.

3-butyn-1-ol in Sonogashira Pd-catalyzed cross coupling conditions to yield 4,4′-(1,4-phenylene)dibut-3-yn-1-ol (**4**) in excellent (92%) yields. White, needle-like crystals of **4** were obtained by crystallization from THF/MeOH. After crystallization, **4** became stable in the presence of air and light.

Hydrogenation of **4** in the presence of 10% Pd/C at room temperature and atmospheric pressure yielded 4,4′-(1,4-phenylene)dibutan-1-ol (**5**) in 76% yield. Diol **5** was reacted with carbon tetrabromide and triphenylphosphine to prepare the corresponding dibromide, 1,4-bis-(4-bromobutyl)benzene (**6**), in 81% yield. Nucleophilic substitution of **6** with excess 5-bromo-2-hydroxybenzaldehyde in the presence of potassium carbonate in DMF led to **7** in excellent yields (96%). Tethered dialdehyde **7** was reacted with excess pyrrole in the presence of a catalytic amount of trifluoroacetic acid in CH_2Cl_2 to yield the tethered bis(dipyrrolylmethylphenyl) units[24] **8** in 64% yields, Scheme 1. The bromine groups in **8** are necessary to introduce the anchor groups on the phenyl rings after formation of the porphyrin.

The one-pot cyclization and metalation of the highly insoluble **8** was done in propinoic acid/methylene chloride solvent mixture, with excess benzaldehyde, and in the presence of zinc acetate dihydrate and oxidizing agent DDQ,[57] Scheme 2. The brominated Zn(II) porphyrin **ZnPorBr$_2$** (**2a**) was obtained in 27% yields, together with a small amount of the corresponding metal-free porphyrin **H$_2$PorBr$_2$** (typically less than 10%), Scheme 2. Metalation of the **H$_2$PorBr$_2$**/**ZnPorBr$_2$** mixture with zinc acetate dihydrate in refluxing chloroform/methanol yielded quantitatively **ZnPorBr$_2$** (**2a**). Suzuki coupling of dibromide **2a** with 4-methylcarboxyphenylboronic acid in the presence of a catalytic amount of $Pd(PPh_3)_4$ and Na_2CO_3 led to diester **ZnPorOMe$_2$** (**2b**), a purple solid which was soluble in common organic solvents.

Alternatively, metal-free porphyrin dibromide **H$_2$PorBr$_2$** was synthesized directly from **8** and then metalated to yield **2a** (Scheme 2) or, using the same Suzuki coupling conditions, reacted with 4-methylcarboxyphenylboronic acid to afford metal-free **H$_2$PorOMe$_2$**. The latter was then metalated in the presence of zinc acetate to yield **2b** in excellent yields. In conclusion, Zn(II) and metal-free strapped porphyrins were accessible through various approaches, as shown in Scheme 2.

Purple, needle-shaped crystals of **H$_2$PorBr$_2$** were grown by layering MeOH over a $CHCl_3$ solution of **H$_2$PorBr$_2$**. A picture of the structure of **H$_2$PorBr$_2$** obtained by small-angle X-ray diffraction is shown in Figure 4.[58]

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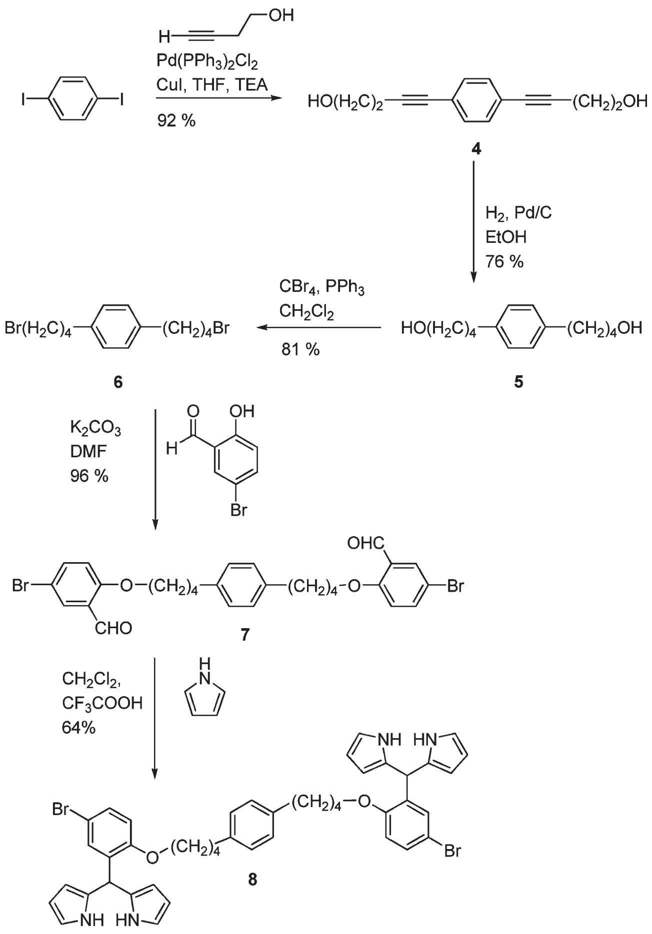
(58) Lee, C.-H.; Lalancette, R.; Galoppini, E. Manuscript in preparation.

SCHEME 1. **Synthesis of the Brominated, Tethered Bis(Dipyrrolylmethylphenyl) Derivative 8**



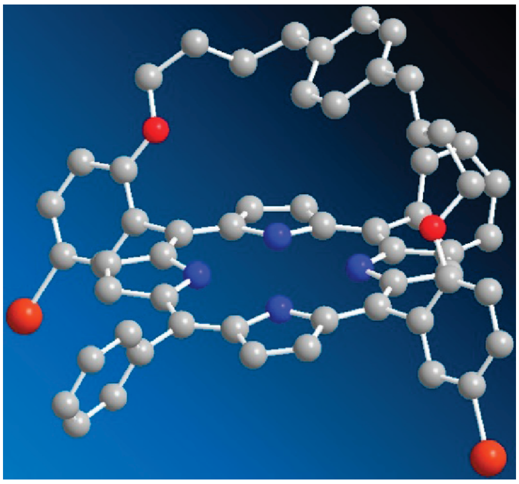
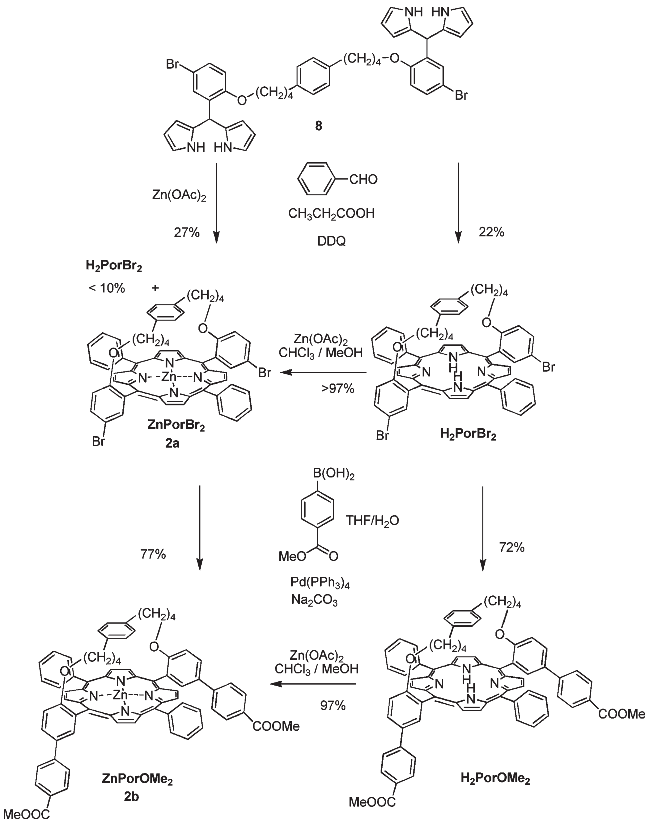


FIGURE 4. Single-crystal X-ray structure of metal-free porphyrin dibromide **H_2PorBr_2**.

SCHEME 2. **Synthesis of Strapped Porphyrin $ZnPorOMe_2$**



Although there are examples of crystal structures of strapped porphyrins,[21a,23,32b,32c,33c,33d,37b,43,48a,48d,49,50b,59,60] to the best of our knowledge, this is the first example a crystal structure of a strapped porphyrin with substituent group on the tethered *meso*-phenyl rings. The X-ray structure indicates that, at least in the crystal packing, the phenyl group of the strap is not centered above the porphyrin and is tilted with respect to the porphyrin plane at a 66° angle. The data (collected at 100 K) indicate that the alkyl chain is disordered as the result of conformational mobility. In summary, the structure in Figure 4 is not representative of the solution conformation (see NMR). The structure shows that, in the crystal, the metal-free macrocyclic ring is not significantly distorted from planarity.[61] Two chloroform molecules (not shown) were trapped in each unit cell, and the crystal lattice was characterized by channels.[58] The two porphyrinato hydrogens were shared almost equally between the four pyrrole units, and the nitrogens of the pyrrole units were identical.

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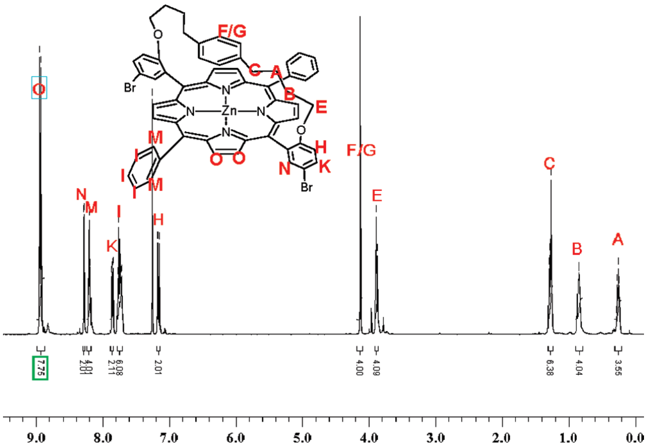

FIGURE 5. ^{1}H NMR ($CDCl_3$) spectrum of $ZnPorOBr_2$ and assignments (see the Supporting Information).

b. NMR Study of 2a and 2b. Figure 5 shows the ^{1}H NMR spectrum of **2a** with the corresponding assignments.

The assignments for dibromide **2a** were determined by 2D-NMR, specifically ^{1}H$-^1$H COSY (Figure S19, Supporting Information) and ^{1}H$-^{13}$C HMQC (Figure S20, Supporting Information) in $CDCl_3$. The ^{1}H$-^1$H COSY spectrum indicates that signal **O** (8 H) belongs to the pyrrole units protons and that **M** (4 H) and **I** (6 H), which are correlated, belong to the aromatic protons of the unsubstituted *meso*-phenyl rings. Signals **H**, **K**, and **N** (each 2 H) were assigned to the bromo-substituted *meso*-phenyl rings. Signal **K** is a double of doublet (J_1 = 2.4, J_2 = 8.8 Hz) split by **H** (d, J = 8.9 Hz) and **N** (d, J = 2.4 Hz). The coupling constant of *ortho* aromatic protons is typically 6−10 Hz, and long-range coupling in aromatics is 1−3 Hz (*meta*) and 0−1 Hz (*para*).[62] This suggests that signal **N** can be assigned to the isolated proton of the bromo-substituted phenyl ring, with a long-range coupling and weak correlation to **K**, and that **K** and **H**, which are strongly coupled, are *ortho* to each other. In the ^{1}H$-^{13}$C HMQC spectrum, the **F/G** signal is correlated to a carbon at 125.7 ppm in the Ph proton region and was assigned to the protons of the phenyl ring of the strap.

Interestingly, the **F/G** protons are considerably shifted upfield by the porphyrin ring current, an observation consistent with literature available on capped porphyrins.[17f,j,35c,46] Protons **A**, **B**, **C**, and **E** were assigned to the CH_2 groups of the tether units ($Ph[-CH_2CH_2CH_2CH_2O]_2-$). Methylenic protons **E** were observed at 3.9 ppm, with the corresponding carbon (^{1}H$-^{13}$C HMQC spectrum) at 68.8 ppm. **E** was therefore assigned to the CH_2 bound to the oxygen. Signal **C**, which is shifted downfield with respect to **A** and **B**, was assigned to the $PhCH_2-$ on the tether. Signal **E** correlates only with **B**, while **A** is correlated with **B** and **C**. In summary, the assignment of the methylenic units of the tether is as follows: $Ph[-CH_{2\mathbf{C}}CH_{2\mathbf{A}}\text{-}CH_{2\mathbf{B}}CH_{2\mathbf{E}}O]_2$.

Figure 6 (top) and Figure 7 (top) show two regions of the ^{1}H NMR spectrum of **2b** with the corresponding assignments. Diester **2b** was characterized by ^{1}H$-^1$H COSY (Figure 6, bottom and Figure 7, bottom), ^{1}H$-^{13}$C HMQC (Figure 8), and DEPT (Figure 9), and the spectral assignments for **2b** were done following the spectral assignments of **2a**. For instance, **M** (4 H) and **I** (6 H) were assigned to the protons from the unsubstituted *meso*-phenyl ring of the porphyrin.

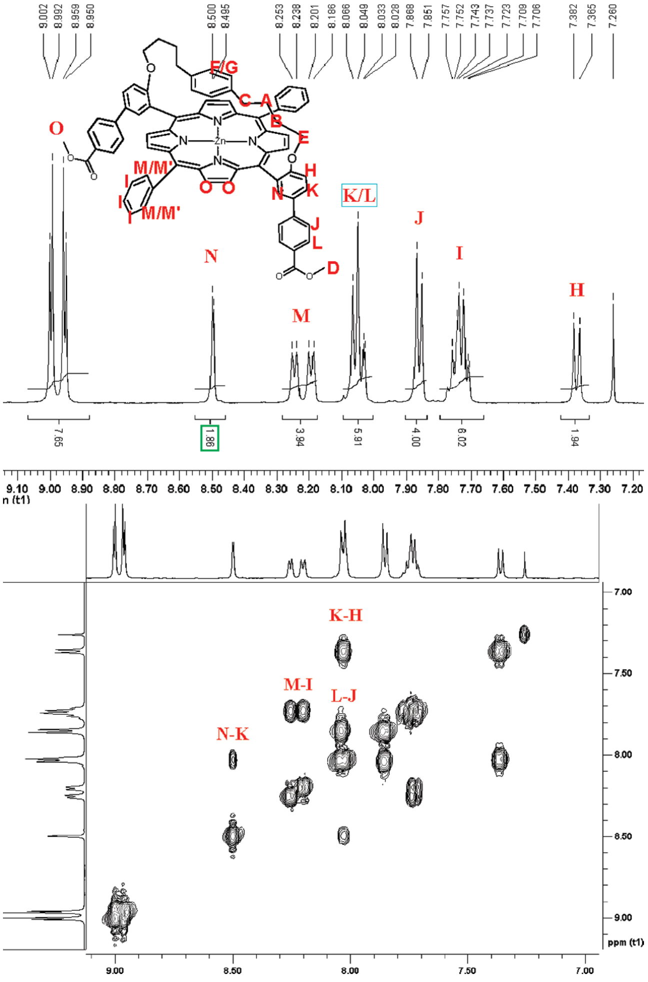

FIGURE 6. NMR spectra of **2b** ($CDCl_3$). The 9−7 ppm region of the ^{1}H (top) and ^{1}H$-^1$H COSY (bottom) spectra.

Signals **K** and **L** are overlapping (4 + 2 H), with **K−H** and **L−J** correlations. **L** and **J** were assigned to the protons from the additional phenyl rings (PhCOOMe) added in the Suzuki coupling step. **H**, **K**, and **N** were assigned as aforementioned. The protons **F/G** (4 H) in the ^{1}H$-^1$H COSY in Figure 7 were assigned to the protons on the phenyl ring of the cap as **F/G** correlates to the Ph carbon at 125.8 ppm in the ^{1}H$-^{13}$C HMQC in Figure 8. Signal **D** (6 H), the only primary carbon in the ^{13}C/DEPT (Figure 9), was readily assigned to the methyl group of the ester ($COOCH_3$). The assignment of the methylenic unit of the tether was $PhCH_{2\mathbf{C}}CH_{2\mathbf{A}}CH_{2\mathbf{B}}\text{-}CH_{2\mathbf{E}}O$, following the same assignment for **2a**. The pyrrolic protons of **$ZnPorBr_2$ (2a)** and **$ZnPorOMe_2$ (2b)** were split into double doublets (J = 4.6, 11.5 Hz for **2a** and J = 4.6, 19.8 Hz for **2b**). However, for **$H_2PorOMe_2$**, the pyrrolic proton was split into two sets of double doublets at 8.94−9.00 (dd, J = 4.6, 23.0 Hz, 4H) and at 8.83−8.90 (dd, J = 4.2, 27.5 Hz, 4H). This splitting may be due to some distortion of the metal-free porphyrin ring. Also, most notably, the

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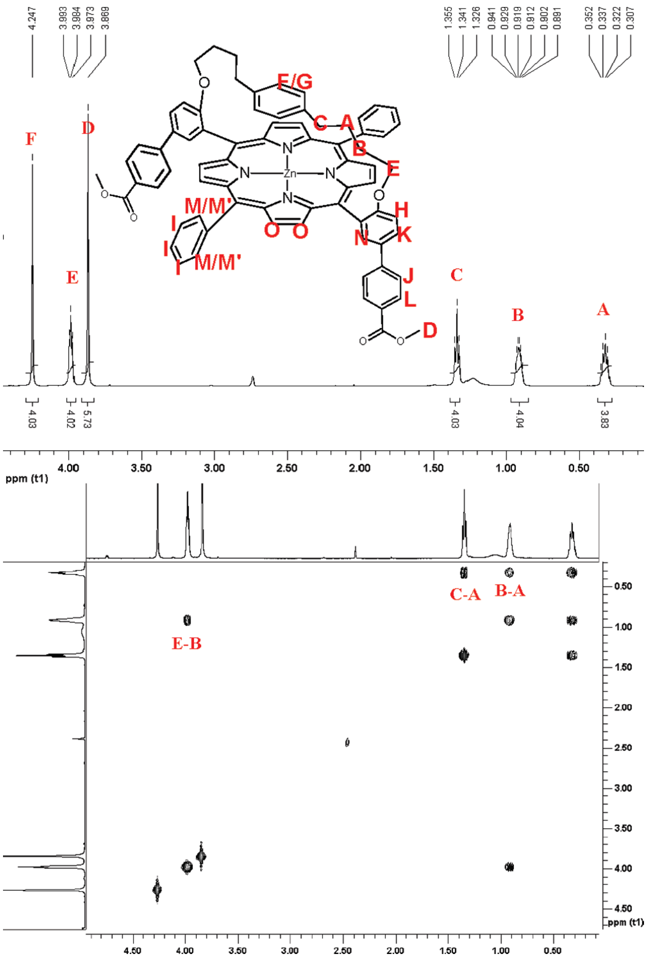

FIGURE 7. NMR spectra of **2b** ($CDCl_3$). The aliphatic region of the ^1H (top) and $^1H-^1H$ COSY (bottom).

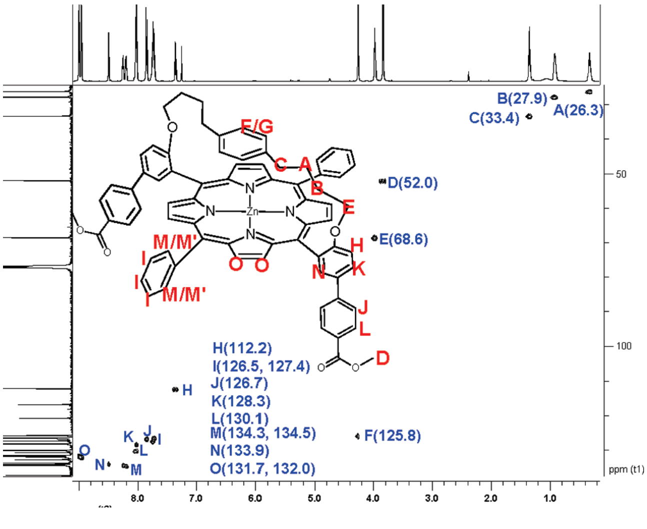

FIGURE 8. 2D $^1H-^{13}C$ HMQC NMR spectrum of **2b**.

coupling constant in $\mathbf{H_2PorOMe_2}$ and $\mathbf{ZnPorOMe_2}$ (~20 Hz) was considerably larger compared to that of $\mathbf{ZnPorBr_2}$. Comparisons between selected signals in the ^1H NMR spectra of **2a** and **2b** are listed in Table 1.

c. Electrochemistry. The electrochemical properties of **2b** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) and were compared to data obtained for the parent compound ZnTPP as the reference, Figure 10 and Table 2.

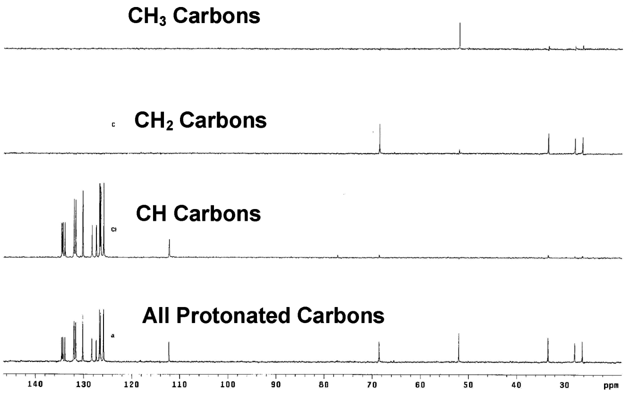

FIGURE 9. ^{13}C/DEPT NMR spectrum of **2b**.

The formation of the radical cation was observed at 0.8 V vs SCE, and the dication at about 1.1 V vs SCE. In the negative potential region, three irreversible/quasireversible reduction processes were observed in the range −1.31 to −1.78 V vs SCE.[64] The reduction processes were more clearly discernible by DPV. The electrochemical data indicate that ZnTPP and **2b** have very similar electrochemical properties, and the HOMO−LUMO gap was calculated to be 2.14 V.

d. Absorption and Emission Properties in Solution and Bound to TiO_2. The solution ($CHCl_3$) UV−vis and steady-state fluorescence emission spectra of **2a** and **2b** are shown in an overlay in Figure 11, and their selected photophysical properties are listed in Table 3.

The absorption spectra were typical of a Zn(II) tetraphenylporphyrin with the strong Soret absorption band at ~421 nm corresponding to the $S_0 \rightarrow S_2$ transition and the Q bands corresponding to the two vibrational modes of the $S_0 \rightarrow S_1$ transition at ~550 nm (Q(1,0)) and ~590 nm (Q(0,0)), Figure 12. The absorption and emission spectra of dibromide **2a** exhibited a modest (~ 4 nm) red shift compared to the spectra of diester **2b**. Significant spectral changes upon substitution on the *meso* phenyl rings are not observed in tetraphenylporphyrins,[12a,13b] but a very modest (few nm) red shift upon substitution with electron-withdrawing groups, such as a Br group, has been reported before.[24,65]

The emission bands at 605 nm (0−0 emission) and 650 nm (0−1 emission) in the fluorescence spectra of **2** are typical of ZnTPP derivatives. The stacking of Zn porphyrins produces typical shifts in the absorption and emission spectra,[66] and the lack of spectral shifts in solution spectra collected in $CHCl_3$ at varying concentrations (Figure S15, Supporting Information) indicated that, as anticipated, **2a** and **2b** do not aggregate in solutions of a polar solvent.

The TiO_2 and ZrO_2 films were prepared according to previously reported procedures.[11a] The films were immersed in 0.4 mM CH_2Cl_2 solutions of **2a** and **2b** for variable periods of time (30 min to 24 h) and rinsed with neat solvent until

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TABLE 1. Comparison of Selected Signals (in ppm) in the ^{1}H NMR Spectra and Coupling Constants J (in Hz) of 2a and 2b

porphyrin	D	F/G	H	I	J	K, L	M	N	O	
ZnPorBr$_2$ 2a		4.14 s 4 H	7.17 d $J = 8.9$ 2 H	7.71–7.78 m 6 H		7.85–7.87 dd $J_1 = 2.4$ $J_2 = 8.8$ 2 H	8.19–8.21 m 4 H	8.28 d $J = 2.4$ 2 H	8.92–8.95 dd $J_1 = 4.6$ $J_2 = 11.5$ 8 H	
H$_2$PorOMe$_2$	3.91–3.92 d $J = 3.7$ 6 H	4.03–4.23 m 4 H	7.35–7.38 d $J = 7.8$ 2 H	7.70–7.77 m 6H	7.87–7.88 d $J = 8.5$ 4 H	8.03–8.06 dt $J_1 = 2.5$ $J_2 = 8.6$ 6 H	8.17–8.24 m 4 H	8.50–8.51 dd $J_1 = 2.5$ $J_2 = 8.9$ 2 H	8.83–8.90 dd $J_1 = 4.2$ $J_2 = 27.5$ 4H	8.94–9.00 dd $J_1 = 4.6$ $J_2 = 23.0$ 4H
ZnPorOMe$_2$ 2b	3.87 s 6 H	4.25 s 4 H	7.37 d $J = 8.7$ 2 H	7.71–7.76 m 6H	7.86 d $J = 8.6$ 4 H	8.03–8.07 m 6 H	8.19–8.25 dd $J_1 = 7.5$ $J_2 = 26.7$ 4 H	8.50 d $J = 2.3$ 2 H	8.95–9.00 dd $J_1 = 4.6$ $J_2 = 19.8$ 8 H	

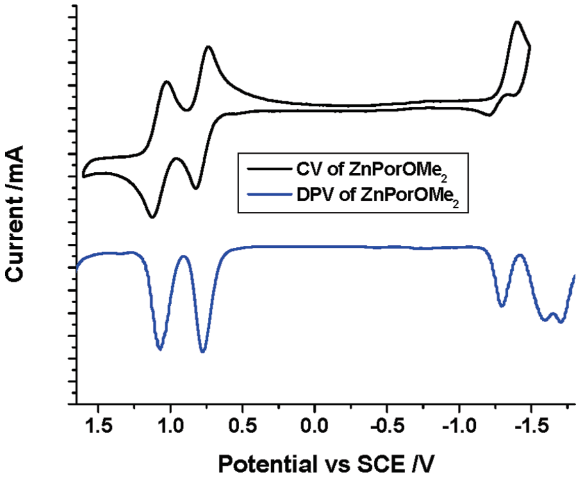

FIGURE 10. CV (black solid line) and DPV (blue solid line) of **ZnPorOMe$_2$** (**2b**) vs SCE.

TABLE 2. Solution Redox Potentials of Porphyrin Methyl Esters in Dichloromethane Reported vs SCE (V)

	oxidation (V)		reduction(V)		
	1st	2nd	1st	2nd	3rd
ZnTPP[63]	0.82	1.14	−1.3	−1.70	−1.78
ZnTPP (exp)	0.79	1.10	−1.32	−1.68	−1.78
2b	0.79	1.08	−1.31	−1.59	−1.71

UV–vis spectra of the solvent showed no leaching of the dye. The absorption spectra in Figure 12, with binding times up to 1 h, show that dibromide **2a**, which does not have an anchor group, did not bind or physisorb significantly to the surface of the semiconductor. Diester **2b** did bind, again indicating that the methyl ester of a carboxylic acid can be an effective anchor group for TiO$_2$ nanoparticles. The binding of methyl esters on metal oxides nanoparticle films has been observed before.[67] The most notable features in the absorption spectra on TiO$_2$ films were the *red* shift (~10 nm) of the Soret band observed upon binding and the general broadening of the spectrum, Figure 12. Broadening of the absorption spectra are a typically observed in dyes bound to metal oxide nanoparticle surfaces.

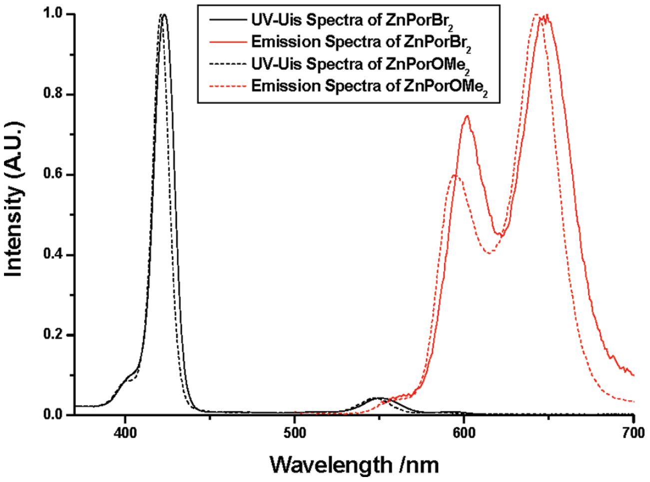

FIGURE 11. Normalized UV–vis (black) and steady-state fluorescence (red) spectra of CHCl$_3$ solutions of **2a** (**ZnPorOBr$_2$**, 2×10^{-6} M, solid lines) and **2b** (**ZnPorOMe$_2$**, 1×10^{-6} M, dotted lines), $\lambda_{ex} = 410$ nm.

The origin of the observed shift is not clear. The simplest explanation of the red shift would be a side-by-side interaction of the porphyrin rings (J-aggregates), since the formation of H-aggregates (face to face stacking) between porphyrin molecules leads to *blue* shifts.[11a,68,66a] Longer binding times (12 h, not shown) produced very intensely colored films, but no changes in the observed shift and broadening. The spectral shift may indicate that the single strap is not sufficient to completely avoid dye–dye interaction. We suppose that, since **2b** is a dichelate (binds through two anchoring groups), the porphyrin rings are tilted on the surface, leading to some degree of *J*-overlap. A second possible explanation is that the strap leads to conformationally constrained and geometrically distorted geometry upon binding. The synthesis of capped tetrachelate **3**, still in progress, should clarify this point. In addition,

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(67) (a) Wang, D.; Mendelsohn, R.; Galoppini, E.; Hoertz, P. G.; Carlisle, R. A.; Meyer, G. J. *J. Phys. Chem. B* **2004**, *108*, 16642–16653. (b) Galoppini, E.; Guo, W.; Zhang, W.; Hoertz, P. G.; Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 7801–7811. (c) Piotrowiak, P.; Galoppini, E.; Qei, Q.; Meyer, G. J.; Wiewiór, P. *J. Am. Chem. Soc.* **2003**, *125*, 5278–5279. (d) Clark, C. C.; Meyer, G.; Wei, Q.; Galoppini, E. *J. Phys. Chem. B* **2006**, *10*, 11044–11046. (e) Hoertz, P. G.; Carlisle, R. A.; Meyer, G. J.; Wang, D.; Piotrowiak, P.; Galoppini, E. *Nano Lett.* **2003**, *3*, 325–330. (f) Galoppini, E.; Guo, W. *J. Am. Chem. Soc.* **2001**, *123*, 4342–4343.

(68) Aratani, N.; Osuka, A.; Cho, H. S.; Kim, D. J. *Photochem. Photobiol. C: Photochem. Rev.* **2002**, *3*, 25–52.

TABLE 3. Selected Photophysical Properties of 2a, 2b, and Reference Compound 1a

porphyrin	Soret λ_{max}, nm ($\varepsilon \times 10^5$, M^{-1} cm^{-1})	Q(1,0) λ_{max}, nm ($\varepsilon \times 10^4$, M^{-1} cm^{-1})	Q(0,0) λ_{max}, nm ($\varepsilon \times 10^4$, M^{-1} cm^{-1})	Q(0,0)*, Q(0,1)* λ_{max}, nm	E_{0-0}, eV
ZnPorOBr$_2$ (2a)	423 (4.16)	550 (1.95)	593 (0.43)	600, 645	2.22
ZnPorOMe$_2$ (2b)	421(4.19)	548 (1.87)	584 (0.33)	595, 643	2.24
***m*-ZnTCPP**[a] **(1a)**,[1111a]	423 (4.44)	558 (2.09)	597 (0.66)	604, 657	2.07

[a] Acquired from the triethylammonium salt in methanol.

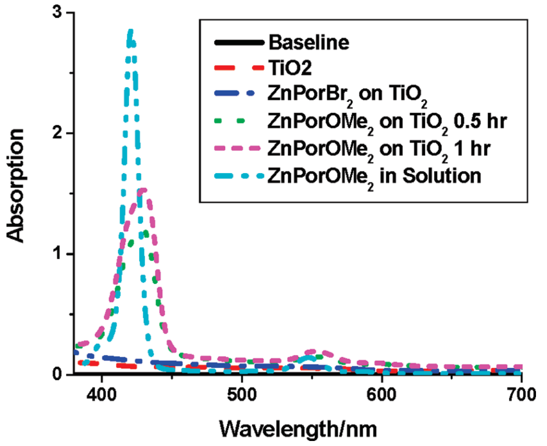

FIGURE 12. Selected UV–vis spectra of zinc-strapped porphyrins in solution and bound.

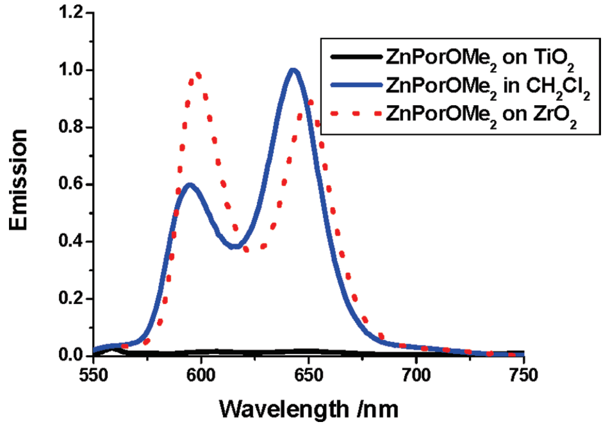

FIGURE 13. Normalized emission spectra of ZnPorOMe$_2$ bound to TiO$_2$ (black) and ZrO$_2$ surfaces (red, dotted line) and in CH$_2$Cl$_2$ (blue); λ_{exc} = 420 nm.

binding studies on TiO$_2$ (rutile) planar crystal surfaces with **2b** and the corresponding acid will help characterize the binding.[69]

The fluorescence emission spectra of diester **2b** bound to TiO$_2$ and ZrO$_2$ films are shown in Figure 13, in an overlay with the solution emission spectrum. Because of the much wider bandgap (E_{bg} ~5 eV for ZrO$_2$, compared to ~3 eV for TiO$_2$), ZrO$_2$ behaves as an insulator preventing electron injection and quenching. Therefore, ZrO$_2$ films are an excellent substrate to study the emission of dyes bound to a semiconductor surface with morphology very similar to the TiO$_2$ films. The fluorescence emission on ZrO$_2$ resembled the solution spectra, and the dramatic spectral changes (merging of the two emission bands) that are associated with porphyrin aggregation[11a,13c] were not observed.

The decrease in intensity of one of the two emission bands, the 605 nm $S_1(0-0)$ emission, has been observed before in our previous study of tetrachelated porphyrins bound to ZrO$_2$.[13b] The bound spectrum (**2b**/ZrO$_2$) in Figure 13 also exhibits a moderate blue shift (few nm) upon binding. Similar changes in intensity in the 0–0 and 0–1 emission bands and blue shifts have been observed in Zn(II) tetraphenylporphyrin "compartmentalized" in highly constraining polymer microenvironments,[70] where the polymer chains imposed conformational distortions on the molecule resulting in a high energy excited state. We speculate that the contraints imposed by the tether and the binding may result in a similar effect. Forthcoming photophysical studies of **2b** will address this question.

The fluorescence emission of **2b** bound to TiO$_2$ was fully quenched, Figure 13. Prior results with **1a–c** and other porphyrins suggest that quenching is indicative of efficient electron injection into the semiconductor.[10,11,13] This result suggests that it will be possible to carry out charge transfer and DSSCs studies with the more soluble esters, rather than the carboxylic acids.

Conclusions

Novel strapped ZnTPP porphyrins model dyes, with functional or anchoring groups at the *meta* position on the *meso*-phenyl rings connected by the tether, were synthesized and characterized by 2D NMR, electrochemistry, MS, and X-ray crystallography. Their UV–vis and fluorescence emission spectra were recorded in solution and bound to TiO$_2$ and ZrO$_2$ films. Diester **2b** did bind efficiently to TiO$_2$ or ZrO$_2$ surfaces, and the fluorescence emission was fully quenched on TiO$_2$ nanoparticles films. The spectral data suggested that there is no significant aggregation on the surface of semiconductor nanoparticles films, but some degree of dye–dye interaction may be present. The electrochemical and spectral properties of strapped porphyrin **2b** were very similar to the properties of ZnTPP, indicating that the modifications of the two *meso*- phenyl rings connected by the strap do not influence significantly the properties of the chromophoric unit. DSSCs and charge transfer studies of **2b** are in progress.

Experimental Section

General Methods. Air- and moisture-sensitive reactions were carried out in flame-dried glassware under nitrogen atmosphere. THF was freshly distilled over sodium/benzophenone. Dichloromethane and Et$_3$N were distilled over calcium hydride. Propinoic acid and other solvents were used as received. Commercially available chemicals, including 5-bromo-2-hydroxybenzaldehyde and 1,4-diiodobenzene, were used as such or purified. Melting points were uncorrected. Flash column chromatography was performed

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(69) Bartynski, R. Private communication.

(70) Morishima, Y.; Saegusa, K.; Kamachi, M. *Macromolecules* **1995**, *28*, 1203–1207. In this case, however, the emission spectra exhibited a blue-shift.

with silica gel (230−400 mesh) and TLC on aluminum-backed silica gel (200 μm thick). ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra (1D or 2D) were collected on an NMR spectrometer operating at 499.896 MHz for ^{1}H, and 125.711 MHz for ^{13}C at room temperature in $CDCl_3$, THF-d_8, or acetone-d_6, as noted. Chemical shifts were reported relative to the central line of the solvent: $CDCl_3$ (δ 7.26 ppm), THF-d_8 (δ 1.73 ppm) or acetone-d_6 (δ 2.05 ppm) for ^{1}H spectra, and $CDCl_3$ (δ 77.0 ppm), THF-d_8 (δ 25.37 ppm) or acetone-d_6 (δ 29.92 ppm) for ^{13}C spectra. Infrared (IR) spectra were obtained at room temperature on a FT-IR spectrometer using KBr in pellets. MS data are reported for the molecular ion or the protonated molecular ion. GC−MS data were collected from a gas chromatograph with a MS detector. High-resolution mass spectra (ESI) were recorded on the departmental FTMS facility. Elemental analyses were determined by a commercial facility.

Spectroscopic Measurements. Absorption spectra were collected at room temperature on a UV−vis spectrophotometer. Emission spectra were recorded at room temperature on a fluorescence spectrophotometer. The excited-state oxidation potentials $E_{1/2}$ (P^+/P^*) of all porphyrins in MeOH were calculated from eq 1

$$E_{1/2}(P^+/P^*) = E_{1/2}(P^+/P) - E_{0-0} \qquad (1)$$

where $E_{1/2}$ (P^+/P) is equivalent to the first oxidation potential of the ground-state porphyrin chromophore and E_{0-0} is the zero−zero excitation energy.[71] E_{0-0} was calculated from the intersection of the porphyrin absorption spectrum with the fluorescence emission spectrum in MeOH at normalized absorption/emission intensity.

Electrochemistry. The electrochemical properties of reference compound **ZnTPP** and of diester **2b** were studied by cyclic voltammetry on a potentiostat. All cyclic voltammograms were measured at room temperature at 0.1 or 0.05 V/s in dichloromethane with 0.1 M Bu_4NClO_4 electrolyte. The measurements were carried out with potential calibration using the ferricenium/ferrocene redox couple, i.e., E_0 (Fe^{3+}/Fe^{2+}) in CH_2Cl_2 as +0.45 V (ref to SCE) in 0.1 M Bu_4NClO_4 solution at room temperature under Ar using a three-electrode system: Ag/AgCl electrode (auxiliary), glassy carbon (working), and Pt (reference). The half-wave redox potentials ($E_{1/2}$) were determined according to eq 2

$$E_{1/2} = (E_{pa} + E_{pc})/2 \qquad (2)$$

where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. All potentials were referenced to SCE. When $E_{1/2}$ could not be calculated, due to irreversible oxidation or reduction processes, E_{pa} and E_{pc} are reported, respectively. All redox processes were also studied by differential pulse voltammetry (DPV), using the relationship in eq 3

$$E_{1/2} = E_{max} + \Delta E/2 \qquad (3)$$

where E_{max} is the peak maxima in the DPV scan and ΔE is the pulse amplitude.[72]

Synthesis. 4,4′-(1,4-Phenylene)dibut-3-yn-1-ol (4). To a stirring solution of 1,4-diiodobenzene (15.0 g, 45 mmol) in THF (250 mL) were added 3-butyn-1-ol (15.9 g, 227 mmol), $PdCl_2(PPh_3)_2$ (3.19 g, 4.5 mmol), copper(I) iodide (1.73 g, 9.1 mmol), triphenylphosphine (2.38 g, 9.1 mmol), and triethylamine (150 mL) under nitrogen. The reaction mixture was stirred for 2 days at 50 °C under nitrogen. The mixture was concentrated in vacuo and partitioned between $CHCl_3$ and water. The organic layer was then separated and dried over Na_2SO_4. The crude product was purified by column chromatography (silica gel, gradient from hexane to THF) to yield **1** as a pale yellow powder. The solid was crystallized in THF/MeOH to yield white needle-like crystals (9.0 g, 92%). Before crystallization, **4** degraded when stored at ambient temperature and exposed to light. The crystals of **4** were stable: mp 207−208 °C; ^{1}H NMR (acetone-d_6, δ 2.05) 7.34 (s, 4H), 3.99−4.01(t, J = 5.5 Hz, 2H), 3.70−3.74 (dd, J = 6.5, 13.5 Hz, 4H), 2.59−2.62 (t, J = 6.5 Hz, 4H); ^{13}C NMR (acetone-d_6, δ 29.92) 132.3, 124.3, 90.3, 81.7, 61.4, 24.5; HRMS (ESI$^+$-TOF) m/z calcd for $C_{14}H_{14}O_2^+$ 214.0994, found 214.0990 $[M]^+$; IR (cm^{-1}) ν 3400 (broad), 2946, 2882, 2231, 1484, 1403, 1330, 1264, 1183, 1030, 891, 842, 777, 639. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.85; H, 6.17.

4,4′-(1,4-Phenylene)dibutan-1-ol (5). To a stirred solution of **4** (3.0 g, 14 mmol) in ethanol (50 mL) was added Pd/C 10% (0.92 g) in 1 portion. The flask was charged with H_2 by three vacuum−hydrogen cycles. The mixture was stirred under H_2 atmosphere overnight. The reaction mixture was filtered through Celite and concentrated in vacuo, and the crude product was purified by column chromatography (silica gel, gradient from hexane, then ethyl acetate/hexane (20/80) and then THF) to yield a white solid as the final fractions (2.36 g, 76%): mp 203−204 °C; ^{1}H NMR ($CDCl_3$, δ 7.26) 7.09 (s, 4H), 3.64 (s, 4H), 2.59−2.62 (t, J = 7 Hz, 4H), 1.65−1.69 (m, 4H), 1.58−1.62 (m, 4H); ^{13}C NMR ($CDCl_3$, δ 77.0) 139.6, 128.3, 62.8, 35.2, 32.3, 27.5; HRMS (ESI$^+$-TOF) m/z calcd for $C_{14}H_{22}O_2^+$ 222.1614, found 222.1620 $[M]^+$; IR (cm^{-1}) ν 3272 (broad), 2930, 2857, 1500, 1478, 1450, 1429, 1348, 1282, 1253, 1191, 1159, 1055, 1029, 1000, 953, 936, 921, 887, 878, 825, 761, 736. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.81; H, 9.87.

1,4-Bis(4-bromobutyl)benzene (6). To a stirring solution of **5** (3.0 g, 14 mmol) in CH_2Cl_2 (600 mL) was added CBr_4 (17.9 g, 54 mmol) at 0 °C. Triphenylphosphine (14.1 g, 36 mmol) was added in small portions. The solution was stirred overnight under nitrogen and then concentrated in vacuo. THF was added, and the precipitate was filtered and discarded. The filtrate was concentrated in vacuo to yield a viscous, yellow oil. The oil was purified by column chromatography (silica gel, hexane, and then gradient to $CHCl_3$). The product was the second band eluting from the column (3.8 g, 81%): ^{1}H NMR ($CDCl_3$, δ 7.26) 7.10 (s, 4H), 3.41−3.44 (t, J = 6.5 Hz, 4H), 2.60−2.63 (t, J = 7.5 Hz, 4H), 1.79−1.88 (m, 4H), 1.74−1.76 (m, 4H); ^{13}C NMR ($CDCl_3$, δ 77.00) 139.3, 128.4, 34.5, 33.7, 32.2, 29.9; HRMS (ESI$^+$) m/z for $[C_{14}H_{20}Br_2 + Na]^+$ 368.9824, found 368.9145 $[M + Na]^+$); IR (cm^{-1}) ν 3011, 2938, 2849, 1508, 1460, 1431, 1333, 1249, 1211, 1187, 1119, 1056, 1019, 970, 902, 815, 750, 736, 698. Anal. Calcd for $C_{14}H_{20}Br_2$: C, 48.30; H, 5.79. Found: C, 48.51; H, 5.81.

6,6′-(4,4′-(1,4-Phenylene)bis(butane-4,1-diyl))bis(oxy)bis(3-bromobenzaldehyde) (7). To a stirred solution of **6** (1.11 g, 3.2 mmol) in dry DMF (20 mL) were added 5-bromo-2-hydroxybenzaldehyde (2.55 g, 12.7 mmol) and K_2CO_3 (3.95 g, 28.6 mmol) under nitrogen. The mixture was stirred at 50 °C for 4 days under nitrogen. The reaction mixture was then poured into water and then filtered. The white solid obtained was used in the next step without further purification (1.8 g, 96%): mp 123−125 °C; ^{1}H NMR(THF-d_8, δ 1.73) 10.37 (s, 2H), 7.81−7.82 (d, J = 2.5 Hz, 2H), 7.64−7.66 (dd, J = 2.5, 9 Hz, 2H), 7.10 (s, 4H), 7.07−7.09 (d, J = 9 Hz, 2H), 4.12−4.14 (t, J = 6.5 Hz, 4H), 2.65−2.68 (t, J = 7.5 Hz, 4H), 1.80−1.87 (m, 8H); ^{13}C NMR (THF-d_8, δ 25.4) 187.6, 161.4, 140.4, 138.8, 131.0, 129.2, 127.5, 116.2, 113.8, 69.7, 35.9, 29.6, 28.8; HRMS(ESI$^+$) m/z calcd for $[C_{28}H_{28}Br_2O_4 + H]^+$ 587.0427, found 587.0402 $[M + H]^+$); IR (cm^{-1}) ν 2938, 1679, 1590, 1519, 1488, 1471, 1405, 1390, 1271, 1250, 1181, 1119, 1031, 1000, 906, 837, 810, 791, 767, 740, 656. Anal. Calcd for $C_{28}H_{28}Br_2O_4$: C, 57.16; H, 4.80. Found: C, 57.32; H, 4.98.

1,4-Bis(4-(4-bromo-2-(di(1*H*-pyrrol-2-yl)methyl)phenoxy)butyl)benzene (8). To a stirring solution of **7** (1.8 g, 3.1 mmol) in pyrrole

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[71] Kuciauskas, D.; Monat, J. E.; Villahermosa, R.; Gray, H. B.; Lewis, N. S.; McCusker, J. K. *J. Phys. Chem. B.* **2002**, *106*, 9347–9358.

[72] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001.

(20 mL) and CH_2Cl_2 (20 mL) under nitrogen and at 0 °C was added trifluoroacetic acid (0.14 mL, diluted with CH_2Cl_2, 2 mL) dropwise. The solution was allowed to stir overnight. The organic solution was extracted with ~1 M $NaOH_{(aq)}$ until the water layer was basic and then with water. The organic layer was separated and then dried over Na_2SO_4 and filtered. The solution was evaporated in vacuo at 50 °C. Addition of hexane led to the formation of a precipitate which was collected by filtration. The crude solid product was purified by column chromatography (silica gel, hexane, then hexane/ethyl acetate (1/1) to yield a brown solid (1.6 g, 64%): mp 154−156 °C; ^{1}H NMR (THF-d_8, δ 1.73) 9.69 (s, 4H), 7.24−7.26 (dd, J = 2.5, 9 Hz, 2H), 7.09 (d, J = 2.5 Hz, 2H), 7.05 (s, 4H), 6.81−6.93 (d, J = 8.5 Hz, 2H), 6.56−6.57 (d, J = 1.5 Hz, 4H), 5.91−5.92 (dd, J = 2.5, 5.5 Hz, 4H), 5.77 (s, 2H), 5.63 (s, 4H), 3.89−3.92 (t, J = 6 Hz, 4H), 2.55−2.58 (t, J = 7 Hz, 4H), 1.65−1.73 (m, 8H); ^{13}C NMR (THF-d_8, δ 25.4) 156.6, 140.4, 136.0, 133.0, 132.7, 130.8, 129.1, 117.6, 114.3, 113.3, 108.0, 107.7, 69.2, 38.1, 36.0, 29.8, 28.6; HRMS (ESI$^+$) m/z calcd for $C_{44}H_{44}Br_2N_4O_2^+$ 818.1826, found 818.1820 $[M]^+$); IR (cm^{-1}) ν 3410, 2930, 2857, 1488, 1468, 1399, 1315, 1280, 1248, 1196, 1171, 1117, 1084, 1030, 955, 809, 794, 717, 650. Anal. Calcd for $C_{44}H_{44}Br_2N_4O_2$: C, 78.48; H, 6.59. Found: C, 78.85; H, 6.17.

H_2PorBr_2 was synthesized directly from **8**, as in Scheme 2: To a stirring solution of **8** (0.50 g, 0.61 mmol) in propinoic acid (50 mL) at 0 °C under nitrogen was added trifluoroacetic acid (0.2 mL, 2.7 mmol). A solution of benzaldehyde (0.19 mL, 1.8 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 1−2 h. under nitrogen. The mixture was stirred at 0 °C for an additional 2 h and then overnight at room temperature, during which time the mixture changed from yellow to purple. The mixture was then refluxed for 2 h, and the purple color intensified. DDQ (0.41 g, 1.82 mmol) was added, and the mixture was stirred for an additional 6 h. The color of the mixture changed from purple to black, and some precipitate formed. Finally, water was added into the solution, and excess $NaHCO_3$ was added in small portions until the aqueous layer was basic. The organic layer was separated and then concentrated in vacuo. The crude product was purified by column chromatography (silica gel, $CHCl_3$) to yield **H_2PorBr_2** as a purple solid (0.13 g, 22%): ^{1}H NMR ($CDCl_3$, δ 7.26) 8.78−8.92 (s, 8H), 8.299−8.303 (d, J = 2.0 Hz, 2H), 8.17−8.19 (t, J = 5.8 Hz, 4H), 7.85−7.87 (dd, J = 2.1, 8.8 Hz, 2H), 7.72−7.77 (m, 6H), 7.13−7.15 (d, J = 8.9 Hz, 2H), 3.97−4.01 (d, J = 17.5 Hz, 4H, Ar-capped), 3.84−3.86 (t, J = 4.8 Hz, 4H), 1.28−1.31 (t, J = 7.0 Hz, 4H), 0.74−0.84 (m, 4H), 0.28−0.36 (m, 4H), −2.61(s, 2H); ^{13}C NMR ($CDCl_3$, δ 77.0) 158.5, 142.1, 137.4, 137.0, 134.6, 134.3, 133.6, 132.6, 127.6, 126.7, 136.6, 125.8, 125.7, 120.0, 114.7, 113.5, 111.8, 68.7, 33.3, 27.7, 25.7, HRMS (ESI$^+$) m/z calcd for $[C_{58}H_{46}Br_2N_4O_2 + H]^+$ 989.2060, found $[M + H]^+$ 989.2044).

2a and H_2PorBr_2 Mixture. To a stirred solution of **8** (0.50 g, 0.61 mmol), trifluoroacetic acid (0.54 mL, 7.3 mmol), and $Zn(OAc)_2 \cdot 2H_2O$ (0.53 g, 2.4 mmol) in 50 mL of propinoic acid at 0 °C was added benzaldehyde (0.19 mL, 1.8 mmol) in 20 mL of CH_2Cl_2 dropwise over 1−2 h under nitrogen. The solution was stirred at 0 °C for 2 h and then overnight at room temperature, during which time it changed from yellow to purple and then refluxed for 2 h. The purple color was deeper at the end of the reaction. DDQ (0.41 g, 1.82 mmol) was added, and the mixture was stirred for additional 6 h, during which time the color changed from purple to black and some precipitate formed. Finally, water was added to the mixture, and excess $NaHCO_3$ was added in small portions until the aqueous layer was basic. The organic layer was separated and then concentrated in vacuo. The crude product was purified by column chromatography (silica gel, $CHCl_3$) to yield a purple solid which was a mixture of metal-free **H_2PorBr_2** (from traces to less than 10%) and **$ZnPorBr_2$** (**2a**, 0.17 g, 27%).

2a from H_2PorBr_2. To a stirred solution of **H_2PorBr_2** (0.13 g, 0.13 mmol) in CH_2Cl_2 (20 mL) and MeOH (2 mL) was added $Zn(OAc)_2 \cdot H_2O$ (0.14 g, 0.66 mmol). The solution was refluxed under nitrogen overnight and then dried in vacuo. The solid was partitioned between water and chloroform. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product, a purple powder, was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 1/1) to yield **2a** as a purple solid (0.15 g, 98%): ^{1}H NMR($CDCl_3$, δ 7.26) 8.92−8.95 (dd, J = 4.6, 11.5 Hz, 8H), 8.285−8.290 (d, J = 2.4 Hz, 2H), 8.19−8.21 (m, 4H), 7.85−7.87 (dd, J = 2.4, 8.8 Hz, 2H), 7.71−7.78 (m, 6H), 7.16−7.18 (d, J = 8.9 Hz, 2H), 4.14 (s, 4H, Ar-capped), 3.88−3.90 (t, J = 5.1 Hz, 4H), 1.26−1.30 (m, 4H), 0.83−0.88 (m, 4H), 0.23−0.29 (m, 4H); ^{13}C NMR($CDCl_3$, δ 77.0) 158.4, 150.3, 150.2, 142.8, 137.4, 137.3, 134.5, 134.3, 132.3, 132.1, 131.5, 127.4, 126.5, 125.7, 121.0, 115.7, 113.5, 111.8, 68.8,33.3, 27.7, 26.2; HRMS (ESI$^+$) m/z calcd for $[C_{58}H_{44}Br_2N_4O_2Zn + H]^+$ 1051.1195, found $[M + H]^+$ 1051.0136; IR (cm^{-1}) ν 2913, 2905, 2857, 1249, 1013, 964, 794, 736, 704.

$H_2PorOMe_2$. To a stirring solution of H_2PorBr_2 (0.25 g, 0.25 mmol) in THF (10 mL) were added tetrakis(triphenylphosphine)palladium(0) (29.2 mg, 0.025 mmol), sodium carbonate (0.12 g, 1.1 mmol), 4-methylcarboxyphenylboronic acid (0.14 g, 0.76 mmol), and water (4 mL) under nitrogen. The mixture was refluxed overnight. The reaction mixture was dried in vacuo and then partitioned between water and chloroform. The organic layer was separated and then dried over Na_2SO_4 and filtered. The crude product was purified by column chromatography (silica gel, hexane/CH_2Cl_2 (1:1), then CH_2Cl_2) to yield **2b** as a purple product (0.2 g, 72%): ^{1}H NMR ($CDCl_3$, δ 7.26) 8.94−9.00 (dd, J = 4.6, 23.0 Hz, 4H), 8.83−8.90 (dd, J = 4.2, 27.5 Hz, 4H), 8.50−8.51 (dd, J = 2.5, 3.9 Hz, 2H), 8.17−8.24 (m, 4H) (proton **M**), 8.09−8.12 (m, 4H), 8.03−8.06 (dt, J = 2.5, 8.6 Hz, 42H), 7.87−7.88 (d, J = 8.5 Hz, 4H) (proton **J**), 7.70−7.77 (m, 6H), 7.35−7.38 (d, J = 7.8 Hz, 2H), 4.03−4.23 (4H, Ar-capped), 3.94−3.98 (m, J = 5.1 Hz, 4H), 3.91−3.92 (d, J = 3.7 Hz, 6H), 1.32−1.36 (m, 4H), 0.85−0.90 (m, 4H), 0.31−0.41 (m, 4H), −2.52 (s, 2H); ^{13}C NMR($CDCl_3$, δ 77.00): 167.0, 159.5, 150.4, 150.3, 145.2, 145.1, 143.0, 142.3, 137.3, 137.0, 134.6, 134.5, 134.3, 133.9, 132.8, 132.1, 132.0, 131.6, 130.9, 130.8, 130.2, 128.5, 128.4, 128.3, 127.6, 127.3, 126.7, 126.6, 126.5, 125.8, 120.7, 119.6, 116.8, 115.8, 112.2, 68.5, 67.8, 52.0, 33.4, 29.7, 27.9, 27.8, 26.2, 25.8, 25.5; HRMS (ESI$^+$) m/z calcd for $[C_{74}H_{60}N_4O_6 + H]^+$ 1101.4586, found $[M + H]^+$ 1101.5184; IR (cm^{-1}) ν 1719, 1602, 1490, 1464, 1434, 1273, 1183, 1148, 1109, 1053, 1020, 1000, 969, 831, 798, 770, 750, 729, 716, 701, 663.

2b from $ZnPorBr_2$. To a stirring solution of **2a** (0.10 g, 0.09 mmol) in THF (2 mL) were added tetrakis(triphenylphosphine)-palladium(0) (11 mg, 0.01 mmol), sodium carbonate (45 mg, 0.4 mmol), 4-methyl carboxyphenylboronic acid (51 mg, 0.28 mmol), and water (4 mL). The mixture was refluxed overnight and evaporated in vacuo. The solid residue was partitioned between water and chloroform. The organic layer was separated, dried over Na_2SO_4, and filtered. The crude product was purified by column chromatography (silica gel, hexane/CH_2Cl_2 (1:1), then CH_2Cl_2) to yield **2b** as a purple solid (0.08 g, 77%).

2b from $H_2PorOMe_2$. To a stirred solution of **$H_2PorOMe_2$** (0.19 g, 0.17 mmol) in CH_2Cl_2 (20 mL) and MeOH (2 mL) was added $Zn(OAc)_2 \cdot H_2O$ (0.18 g, 0.84 mmol). The solution was refluxed under nitrogen overnight and then dried in vacuo. The solid was partitioned between water and chloroform. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product, a purple powder, was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 1/1) to yield **2b** as a purple solid (0.19 g, 97%): ^{1}H NMR ($CDCl_3$, δ 7.26) 8.95−9.00 (dd, J = 4.6, 19.8 Hz, 8H), 8.50 (d, J = 2.3, 2H), 8.19−8.25 (dd, J = 7.5, 26.7 Hz, 4H), 8.03−8.07 (m, 6H), 7.85−7.87 (d, J = 8.6 Hz, 4H), 7.71−7.76 (m, 6H), 7.37−7.38 (d, J = 8.7 Hz, 2H), 4.25 (s, 4H, Ar-capped), 3.97−3.99 (t, J = 5.0 Hz, 4H), 3.87 (s, 6H), 1.33−1.36 (t, J = 7.3 Hz, 4H), 0.89−0.94 (m, 4H), 0.31−0.35 (m, 4H); ^{13}C NMR (CDCl$_3$, δ 77.00) 167.0, 159.5, 150.4, 150.2, 154.1, 143.0, 137.4, 134.5, 134.3, 132.8, 132.0, 131.7, 130.8, 130.2, 128.3, 127.4, 126.7, 126.5, 125.8, 120.8, 116.8, 112.2, 68.6, 52.0, 33.4, 27.9, 26.3; HRMS (ESI$^+$) m/z calcd for $C_{74}H_{58}N_4O_6Zn^+$ 1162.3642, found [M]$^+$ 1162.4308); IR (cm^{-1}) ν 2946, 2857, 1711, 1600, 1491, 1460, 1429, 1340, 1273, 1190, 1143, 1109, 1068, 1055, 1021, 998, 904, 852, 834, 808, 800, 769, 754, 728, 717, 702, 670.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of **4**−**8**, H$_2$PorBr$_2$, H$_2$PorOMe$_2$, **2a**, and **2b**; ^{1}H−^{1}H COSY NMR spectra of H$_2$PorBr$_2$, H$_2$PorOMe$_2$, **2a**, and **2b**; ^{1}H−^{13}C HMQC NMR spectra of H$_2$PorBr$_2$, H$_2$PorOMe$_2$, **2a**, and **2b**; UV−vis spectra of H$_2$PorBr$_2$, H$_2$PorOMe$_2$, **2a**, and **2b**; emission spectra of H$_2$PorBr$_2$, H$_2$PorOMe$_2$, **2a**, and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.