

# Porphyrins Linked Directly to the 5,5' Positions of 2,2'-Bipyridine: A New Supramolecular Building Block and Switch

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The synthesis and coordination chemistry of two porphyrin dimers linked either at the 5,5' or the 4,4' positions of 2,2'-bipyridine are described. These compounds, which may serve as molecular tectons for the construction of a variety of supramolecular arrays of diverse function, reveal that the ground- and excited-state electronic communication between the chromophores is only moderately affected by the complexation state of the bipyridyl moiety. The nature of the metal ion chelated by the bipyridine only slightly perturbs the ground-state spectra, and differences observed in the excited state are largely ascribed to the heavy atom effect. This work also shows that conformational changes in structural subunits, in this case induced by bipyridyl complexation of various metal ions, do not necessarily require reorganization of supramolecular systems.

## Introduction

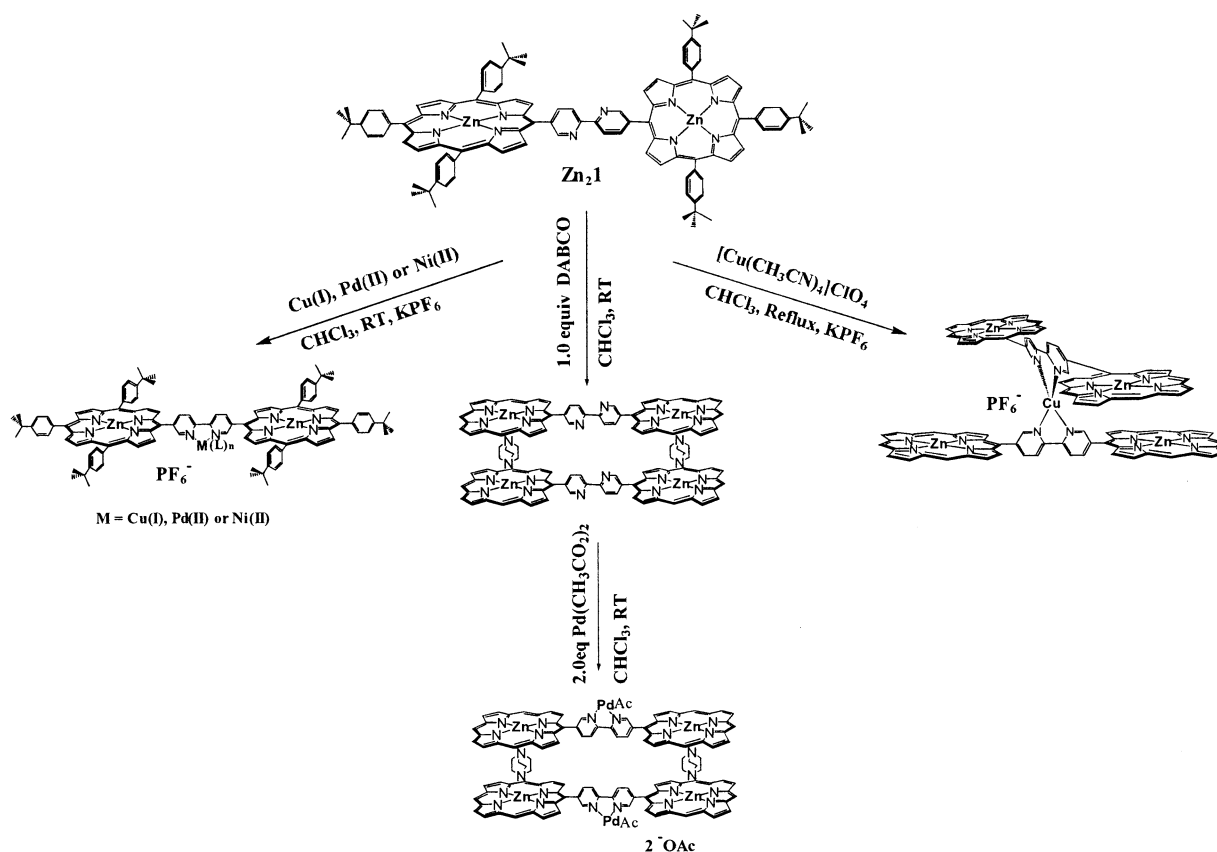
With the rapidly developing field of molecular-based materials, the preparation of supramolecular organic photonic devices is an important research area in view of both fundamental science and applications development.<sup>1</sup> The practical applications of supramolecular photonics<sup>2</sup> include solar energy conversion into electrical or chemical energy<sup>3–7</sup> and as components of nanoscaled devices.<sup>1,8–10</sup> Porphyrins are appealing subunits for materials<sup>11–15</sup> because they can

efficiently harvest light due to their strong absorption bands, they are remarkably robust considering their rich photochemical and redox properties, and there are a variety of means to fine-tune these properties via peripheral substituent modifications or metal complexation. Since their discovery at the end of the 19th century, bipyridines such as 2,2'-bipyridine (BiPy) and their coordination chemistry have been well studied for many of the same reasons.<sup>2,16</sup> The combination of porphyrins and BiPy tectons<sup>17–20</sup> continues to develop in the arena of molecular-scale information processing systems, such as in highly conjugated porphyrin-based assemblies.<sup>21–23</sup> Terpyridyl and similar ligands appended to porphyrins are of continuing interest in the formation of

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Scheme 1<sup>a</sup>

<sup>a</sup> Upon chelation by many transition metal ions, the 2,2'-bipyridine moiety becomes rigid and planar, thus making the two porphyrins at the 5,5' positions in **1** or **Zn<sub>2</sub>**1**** coplanar on average, and somewhat increases the electronic communication between the chromophores (left). The 2,2'-bipyridyl moieties of two **1** or **Zn<sub>2</sub>**1**** species can bind to a tetrahedral metal ion (right) or metals with different coordination geometries. The axial coordination of the zinc ions of two **Zn<sub>2</sub>**1**** species by two DABCO moieties creates a supramolecular square (center), which maintains its structural integrity upon metal ion binding by the two 2,2'-bipyridines (bottom), thus demonstrating that conformational changes in a component need not alter supramolecular structure. For clarity, the *t*-butylphenyl groups are not shown.

catenanes and other topologically complex structures, and there are a variety of other approaches to self-assembled porphyrin systems.<sup>11,21–23</sup> Certainly, one of the most exploited methods to assemble porphyrin arrays, layers, and crystals is to use pyridyl porphyrins and transition metals. The 60°, 120°, or 180° direction of the respective 2-, 3-, or 4-pyridyl nitrogens, combined with the various coordination geometries of transition metals, and the axial positions of metal derivatives, can result in a very large number of porphyrinic materials, both discrete and polymeric.<sup>11,23,24</sup> Therefore, one of the central issues in supramolecular porphyrin chemistry is the role of the pyridyl–metal–pyridyl linker in mediating electron and energy transfer among the chromophores.<sup>25</sup>

To develop new building blocks that also address the role of the linker in the photophysics of supramolecular porphyrin

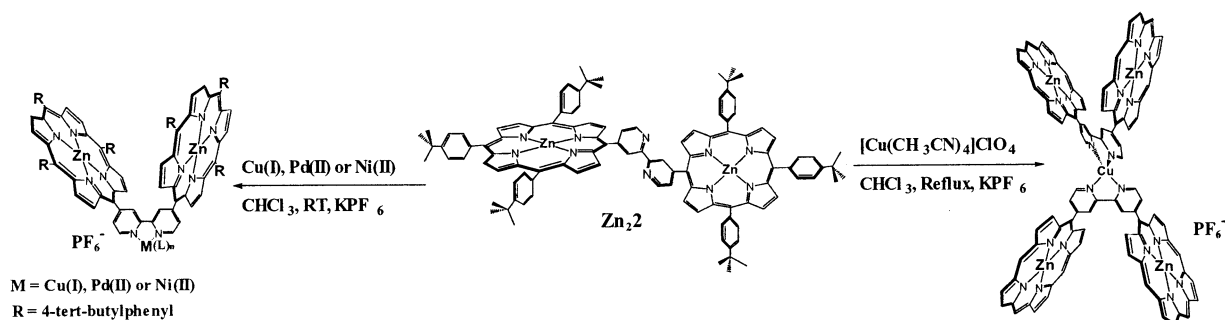
arrays, herein we report the synthesis, characterization, and functionality of 5,5'-bis[5'-(10,15,20-(4-*tert*-butylphenyl)porphyrinyl)]-2,2'-bipyridine, **1**, wherein the porphyrins are appended 180° from each other in any conformation of the BiPy (Scheme 1). In this system, the covalent bond between the 2 and 2' positions is conjugated to the 5,5' positions where the porphyrins are attached and the pyridyl nitrogens are not conjugated to the 5 positions. The spectral properties of this supramolecular tecton are compared to 4,4'-bis[5'-(10,15,20-(4-*tert*-butylphenyl)porphyrinyl)]-2,2'-bipyridine, **2**, wherein the relative angle between the porphyrin planes changes with the conformation of the BiPy moiety (Scheme 2). A meso alkyl derivative of **2** was reported earlier.<sup>26</sup> In contrast, the covalent bond in this latter system is not conjugated to the 4,4' positions bearing the porphyrins, but the pyridyl nitrogens are. As in all meso aromatic porphyrin compounds, the dihedral angle between the porphyrin macrocycle and the meso pyridyl substituent is on average 90° and can vary ±~60° in solution. The orthogonality of the porphyrins to the pyridines minimizes conjugation; nevertheless, it is well-known that the wavelengths of the Q and B bands in the ground-state electronic spectra of meso

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Scheme 2<sup>a</sup>

<sup>a</sup> Upon chelation by many transition metal ions, the 2,2'-bipyridine moiety becomes rigid and planar, thus locking the two porphyrins at the 4,4' positions in **2** or **Zn<sub>2</sub>2** in a syn conformation (left), and also somewhat increases the electronic communication between the chromophores. Similar to **1**, the BiPy unit can bind a variety of metal ions, but the resultant geometry of the macrocycles is quite different (right). For clarity, the t-butylphenyl groups are not shown.

4-pyridyl porphyrins are shifted by several nanometers upon pyridyl coordination to a variety of metal ions.<sup>25,27,28</sup> Also, metalation of the porphyrin significantly alters the basicity of the para pyridyl nitrogen. These are clear indications that there is significant electronic communication between the macrocycle and the pyridyl subunits.

The BiPy moiety is normally not planar, but it adopts a planar conformation upon metal ion binding. The planar structure electronically couples, via conjugation, the two aromatic pyridine systems with the atomic orbitals of the metal contributing to varying degrees toward the overall molecular orbitals of the complex. As such, the complexation of a metal ion by the BiPy moiety results in increased electronic coupling between the two 5,5' attached chromophores because the BiPy becomes planar. Thus, the BiPy moiety serves as a metal-gated switch to electronically couple the porphyrins (Scheme 1). When the BiPy unit of compound **2** binds a metal, the two porphyrins rotate from an average anti-like conformation to lock into a syn-like conformation so that they are on the same side of the BiPy and can serve as receptor to ditopic ligands of appropriate size and orientation (Scheme 2). For **2**, electronic communication is mediated also by the adoption of a planar structure by the BiPy, but the nitrogens of the bis chelate are conjugated to the point of attachment of the macrocycles.

The primary goals of the present work are (1) to compare the ground- and excited-state spectra of these two structural isomers when the bipyridyl linker is coordinated to various metal ions in order to gain insights into the role of this motif in the photophysical properties of supramolecular porphyrin arrays assembled by exocyclic coordination to metal ions, and (2) to design and characterize a new tecton for the self-assembly of porphyrinic materials. To this end, we have examined the electronic absorption and emission spectra of **1** and its zinc metalloporphyrin derivative, **Zn<sub>2</sub>1**, and compared these results to those of **2** and **Zn<sub>2</sub>2**. These reactions are summarized in Schemes 1 and 2.

In most supramolecular systems, a conformational change in one of the structural elements results in a substantial change in the structure of the supermolecule<sup>29–31</sup> or even

disassembly, as well demonstrated by tecton **2** and its derivatives, whereas in compound **1** the conformational changes resulting upon binding of a metal ion by the BiPy moiety leave the structure of a supramolecular assembly intact. This latter feature is demonstrated by the observation that the structural integrity of a supramolecular square composed of two **Zn<sub>2</sub>1** moieties and two 1,2-diazabicyclo-[2,2,2]octane (DABCO) units (Scheme 1) remains intact even though the 2,2'-bipyridine moieties change conformation upon binding transition metals.

## Experimental Section:

**Reagents and Physical Measurements.** All solvents were distilled using standard methods. Silica gel (Baker, 60  $\mu\text{m}$  average particle size) and alumina (Fisher, 80–200 mesh) were used for column chromatography. The  $\text{CHCl}_3$  was reagent grade and used directly. The methyl-THF was of reagent grade and used as obtained. The THF was freshly distilled from Na, and methanol was distilled from  $\text{CaH}_2$  or  $\text{P}_2\text{O}_5$ . 2,2'-Bipyridine-4,4'-dicarboxaldehyde was purchased from Aldrich Chemical Co., and 2,2'-bipyridine-5,5'-dicarboxaldehyde was prepared according to the literature.<sup>32,33</sup>  $^1\text{H}$  NMR spectroscopy was performed at 300 MHz on a Varian U-300 spectrometer using chloroform-*d* solvent as internal reference. UV-vis spectra were recorded on a Varian Bio-100 spectrometer. Electrospray mass spectroscopy spectra were obtained from a Hewlett-Packard HP-1100 LC/MS in positive-ion mode.

Schemes, procedures, and characterization of the intermediates for the unsuccessful directed synthesis of **2** are presented in the Supporting Information. In general for titration experiments, an aliquot of the solution containing the given metal ion was added to the porphyrin solution, the mixture was stirred at room temperature for  $\sim 15$  min (for the Pd(II) compounds, the mixture was heated to  $\sim 50$   $^\circ\text{C}$ ), and spectra were recorded at  $\sim 20$   $^\circ\text{C}$ . Under the conditions described for the titrations, and consistent with known BiPy chemistry, plots of either absorption intensity or chemical shifts versus mole ratio indicate a 1:1 stoichiometry of the porphyrin derivatives to the metal ion coordinated to the BiPy unit.

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**5,5'-Bis[5'-(10,15,20-tri-4-*tert*-butylphenyl)porphyrinyl]-2,2'-bipyridine (1).** A mixture of 2,2'-bipyridine-5,5'-dicarboxaldehyde (25 mg, 0.12 mmol) and pyrrole (0.07 mL, 0.96 mmol) in a 15 mL solvent mixture of acetic acid and nitrobenzene (3:2 v/v) was refluxed for 15 min, and then, 4-*tert*-butylbenzaldehyde (0.12 mL, 0.72 mmol) was added to the reaction mixture. The final mixture was refluxed in air for 18 h at 140 °C. Then, the excess solvent was removed by vacuum distillation. The crude dark solid was dissolved in chloroform and filtered through a pad of silica (5% EtOH in chloroform). The filtrate was concentrated, redissolved in CHCl<sub>3</sub>, and chromatographed (silica 37 g, chloroform). The second purple band was collected. Four-fifths of the solvent was removed, and the crude product was crystallized with acetonitrile at 0 °C, affording a purple precipitate that was centrifuged and the pellet dried in vacuo (3.7 mg, 2%). <sup>1</sup>H NMR (chloroform-*d*): δ 9.71 (d, *J* = 2.5 Hz, 2H, H6 in 2,2'-bipyridyl), 9.22 (d, *J* = 8 Hz, 2H, H3 in 2,2'-bipyridyl), 9.03 (d, *J* = 5 Hz, 4H, pyrrole-Hβ), 8.99 (d, *J* = 5 Hz, 4H, pyrrole-Hβ), 8.93 (s, 8H, pyrrole-Hβ), 8.87 (dd, *J*<sub>1</sub> = 2.5 Hz, *J*<sub>2</sub> = 8 Hz, 2H, H4 in 2,2'-bipyridyl), 8.19 (m, 12H, H2 in 4-*tert*-butylphenyl), 7.80 (m, 12H, H3 in 4-*tert*-butylphenyl), 1.65 (s, 54H, CH<sub>3</sub> in 4-*tert*-butylphenyl), -2.66 (br s, 4H, inner-NH). UV-vis (methyl-THF): λ<sub>max</sub> = 422, 516, 552, 594, 650 nm. ESMS obsd 1566.8, calcd 1566.0 (C<sub>110</sub>H<sub>104</sub>N<sub>10</sub>).

**5,5'-Bis[5'-(10,15,20-tri-4-*tert*-butylphenyl)porphyrinatozinc(II)]-2,2'-bipyridine (Zn<sub>2</sub> 1).** Compound **1** (3.0 mg, 1.9 μmol) was dissolved in 10 mL of CHCl<sub>3</sub>, and then, 6 drops of saturated Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> in methanol was added to the solution. The resulting porphyrin solution was allowed to reflux for 15 min (the process was monitored by UV-vis spectroscopy). The reaction was quenched by adding 10 mL of water, and then, the layers were separated. The organic layer was dried (MgSO<sub>4</sub>), and concentrated to 1/5 of the volume. The resulting porphyrin solution was crystallized from acetonitrile at 0 °C to afford a reddish precipitate. The solid was centrifuged and the pellet dried in vacuo (3.1 mg, 95%). <sup>1</sup>H NMR (chloroform-*d*/THF-*d*<sub>8</sub> 6:1): δ 9.63 (d, *J* = 2.5 Hz, 2H, H6 in 2,2'-bipyridyl), 9.14 (d, *J* = 8 Hz, 2H, H3 in 2,2'-bipyridyl), 8.99 (m, 8H, pyrrole-Hβ), 8.89 (s, 8H, pyrrole-Hβ), 8.78 (dd, *J*<sub>1</sub> = 2.5 Hz, *J*<sub>2</sub> = 8 Hz, 2H, H4 in 2,2'-bipyridyl), 8.13 (m, 12H, H2 in 4-*tert*-butylphenyl), 7.72 (m, 12H, H3 in 4-*tert*-butylphenyl), 1.59 (s, 36H, CH<sub>3</sub> in 4-*tert*-butylphenyl), 1.58 (s, 18H, CH<sub>3</sub> in 4-*tert*-butylphenyl). UV-vis (methyl-THF): λ<sub>max</sub> = 430, 558, 599 nm. ESMS obsd 1694.3, calcd 1693.0 (C<sub>110</sub>H<sub>100</sub>N<sub>10</sub>Zn<sub>2</sub>).

**4,4'-Bis[5'-(10,15,20-tri-(4-*tert*-butylphenyl)porphyrinyl)]-2,2'-bipyridine (2).** A sample of 2,2'-bipyridine-4,4'-dicarboxaldehyde (25 mg, 0.12 mmol) was treated identically as for **1**, affording 5.6 mg (3%) of reddish purple solid. <sup>1</sup>H NMR (chloroform-*d*): δ 9.64 (s, 2H, H3 in 2,2'-bipyridyl), 9.07 (d, *J* = 4.8 Hz, 2H, H6 in 2,2'-bipyridyl), 8.98 (s, 8H, pyrrole-Hβ), 8.92 (s, 8H, pyrrole-Hβ), 8.24 (dd, *J*<sub>1</sub> = 1.4 Hz, *J*<sub>2</sub> = 4.0 Hz, 2H, H5 in 2,2'-bipyridyl), 8.18 (d, *J* = 8.1 Hz, 12H, H2 in 4-*tert*-butylphenyl), 7.78 (d, *J* = 8.1 Hz, 12H, H3 in 4-*tert*-butylphenyl), 1.63 (s, 54H, CH<sub>3</sub> in 4-*tert*-butylphenyl), -2.68 (br s, 4H, inner-NH). UV-vis (methyl-THF): λ<sub>max</sub> = 422, 515, 550, 593, 648 nm. ESMS obsd 1566.8, calcd 1566.0 (C<sub>110</sub>H<sub>104</sub>N<sub>10</sub>).

**4,4'-Bis[5'-(10,15,20-tri-(4-*tert*-butylphenyl)porphyrinatozinc)]-2,2'-bipyridine (Zn<sub>2</sub> 2).** A sample of compound **2** (5.0 mg, 3.2 μmol) was treated identically as for Zn<sub>2</sub>1, affording 5.1 mg (95%) of a reddish solid. <sup>1</sup>H NMR (chloroform-*d*): δ 9.63 (s, 2H, H3 in 2,2'-bipyridyl), 9.06 (d, *J* = 4.8 Hz, 2H, H6 in 2,2'-bipyridyl), 9.03 (s, 8H, pyrrole-Hβ), 8.97 (s, 8H, pyrrole-Hβ), 8.23 (dd, *J*<sub>1</sub> = 1.4 Hz, *J*<sub>2</sub> = 4.0 Hz, 2H, H5 in 2,2'-bipyridyl), 8.17 (d, *J* = 8.1 Hz, 12H, H2 in 4-*tert*-butylphenyl), 7.76 (d, *J* = 8.1 Hz, 12H, H3 in 4-*tert*-butylphenyl), 1.63 (s, 54H, CH<sub>3</sub> in 4-*tert*-butylphenyl). UV-

vis (methyl-THF): λ<sub>max</sub> = 430, 557, 597 nm. ESMS obsd 1694.3, calcd 1693.0 (C<sub>110</sub>H<sub>100</sub>N<sub>10</sub>Zn<sub>2</sub>).

**5-Mesityldipyrromethane (3).** A mixture of pyrrole (18.8 mL, 271 mmol) and mesitaldehyde (2 mL, 13.5 mmol) was flushed with nitrogen for 15 min and then treated with TFA (0.11 mL, 2.5 mmol), and the mixture was stirred under nitrogen at room temperature for 1 h and then quenched with triethylamine (0.5 mL). Toluene (100 mL) was added, and the organic phase was washed with brine (2 × 50 mL) and dried (MgSO<sub>4</sub>). The solvent was removed under vacuum to give a black oil. Vacuum distillation removed the excess pyrrole to yield a highly colored solid that was washed with ethyl acetate. The solvent was evaporated until a solid began to form. Then, 50 mL of cyclohexanes was added to precipitate a yellow solid that was filtered and recrystallized from ethanol/water (10:1) to give yellow crystals (0.88 g, 25%). <sup>1</sup>H NMR (chloroform-*d*): δ 7.95 (br, 2H), 6.87 (s, 2H), 6.67 (m, 2H), 6.19 (m, 2H), 6.02 (m, 2H), 5.93 (s, 1H), 2.29 (s, 3H), 2.07 (s, 6H).

**5,5'-Bis(2,2'-dipyrromethyl)-2,2'-bipyridine (4).** A mixture of pyrrole (6.5 mL, 94 mmol) and 2,2'-bipyridine-5,5'-dicarboxaldehyde (200 mg, 0.94 mmol) was flushed with nitrogen for 15 min and treated with TFA (0.06 mL, 0.75 mmol). The solution darkened, and the mixture was stirred for 15 min. Aqueous NaOH (0.1 N, 20 mL) and 20 mL of ethyl acetate were added, and the layers were separated. The organic layer was washed with water (2 × 20 mL). The combined organic layers were washed with brine and dried (MgSO<sub>4</sub>), and vacuum distillation removed the excess pyrrole. Precipitation from hexane/CH<sub>2</sub>Cl<sub>2</sub> gave a yellow solid, which was filtrated and dried in vacuo (0.25 g, 60%). <sup>1</sup>H NMR (chloroform-*d*/DMSO-*d*<sub>6</sub>): δ 9.20 (br, 4H), 8.40 (s, 2H), 8.16 (d, *J* = 8 Hz, 2H), 7.52 (dd, *J*<sub>1</sub> = 2 Hz, *J*<sub>2</sub> = 8 Hz, 2H), 6.61 (m, 4H), 5.99 (m, 4H), 5.77 (s, 4H), 5.45 (s, 2H).

## Results and Discussion

**Synthesis.** Compounds **1** and **2** were synthesized by mixed aldehyde condensations based on a modified Adler synthesis<sup>34</sup> in ~3% yield (Scheme 3) using the respective 2,2'-bipyridine-5,5'-dicarboxaldehyde and 2,2'-bipyridine-4,4'-dicarboxaldehyde. The directed synthesis of each using a MacDonald-type 2 + 2 coupling strategy (compounds **3** and **4** in Scheme 4) was unsuccessful using a variety of reaction conditions with either the 4-*tert*-butylbenzaldehyde or the mesityl aldehyde.<sup>35–39</sup> While the precursors and their intermediates for both **1** and **2** were readily synthesized and characterized according to literature methods, these reaction sequences failed in the porphyrinogen/porphyrin forming step as was observed earlier for a compound similar to **2**.<sup>26</sup> The mesityl aldehydes are reported to minimize scrambling and increase the solubility (i.e., reactivity) of the intermediates, yet the synthesis of these derivatives also fails at the crucial porphyrin-forming step. The previous synthesis of a meso alkyl version of **2** involved the directed synthesis of a

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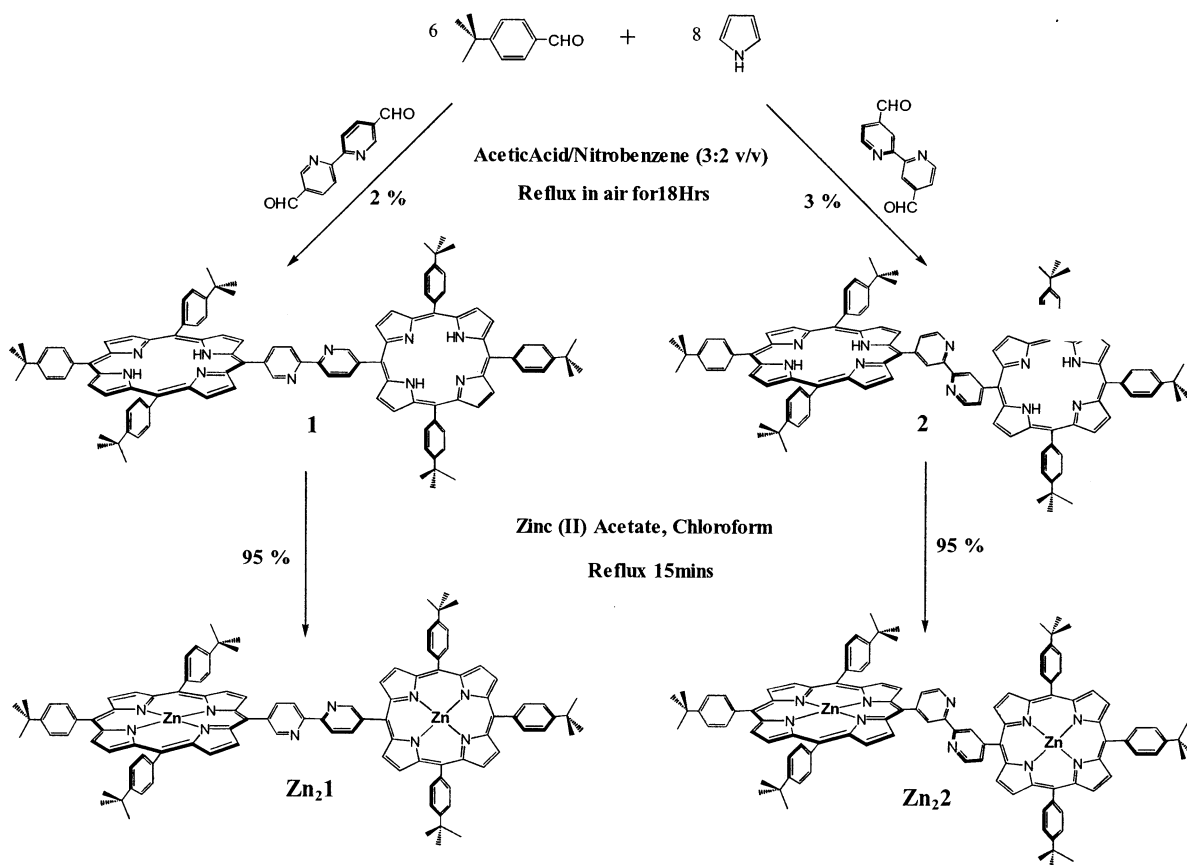
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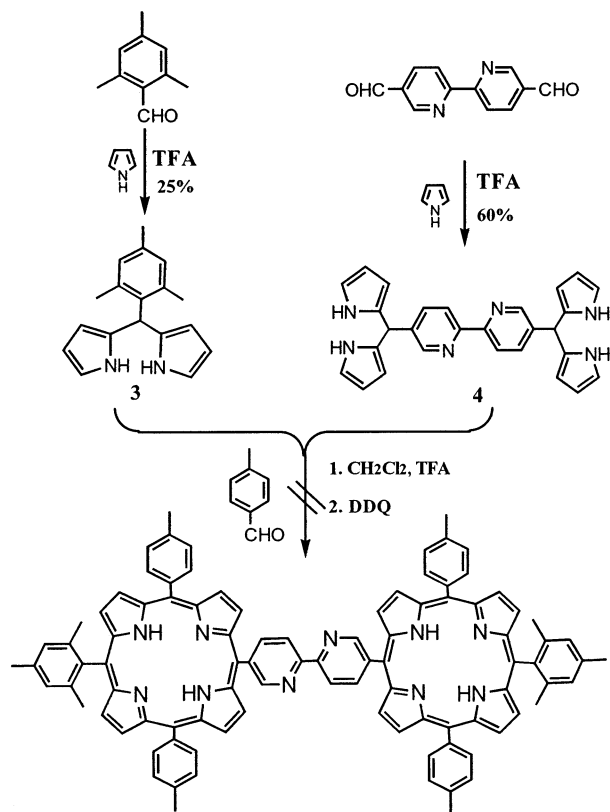
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Scheme 3



Scheme 4



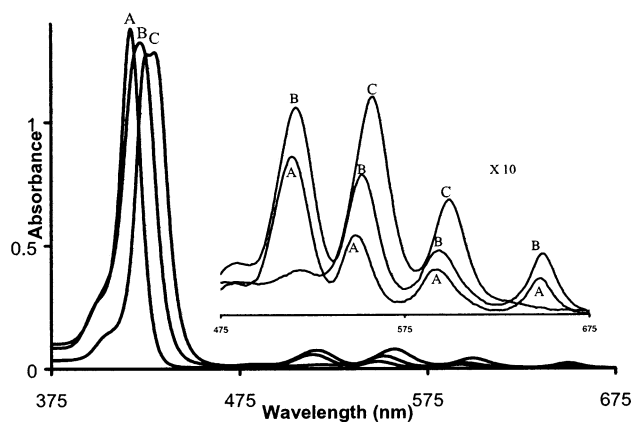
monopyridylporphyrin followed by a coupling reaction to form the pyridyl moiety.<sup>26</sup> Though more elegant from a

synthetic point of view, this method for **2** both is more time-consuming and provides a comparable overall yield from the starting aldehydes. As noted with similar synthetic procedures that use the Adler method to make porphyrins bearing both heterocyclic and phenyl moieties, allowing the less reactive heterocyclic aldehyde to react with the pyrroles for ~15 min before addition of the arylaldehyde significantly increases the yield of the porphyrins bearing the heterocyclic groups.<sup>40,41</sup> The yield from the Adler-based synthesis is somewhat less than the expected ~4% estimated from the statistical reaction of the aldehydes based on stoichiometry, and a 25% yield for each porphyrin. However, this is greatly ameliorated by the ease of scale-up of the one-step synthesis. We obtain only traces of porphyrin using the five-step reaction sequence outlined in Scheme 4 which would have an overall yield of ~2% had the two porphyrin-forming reactions occurred with 25% yields each.

**Electronic Spectra.** The two halves of free 2,2'-bipyridine are not coplanar, and the nitrogens generally point away from each other; therefore, there is little conjugation between the two pyridyl rings. Meso aryl groups on porphyrins are also noncoplanar with the macrocycle, but the effects of substitutions on the aryl ring are readily observed in the electronic spectra, indicating some degree of electronic coupling between the two. Therefore, we expected and observed that

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(41) Drain, C. M.; Shi, X.; Milic, T.; Nifati, F. *Chem. Commun.* **2001**, 287–288.

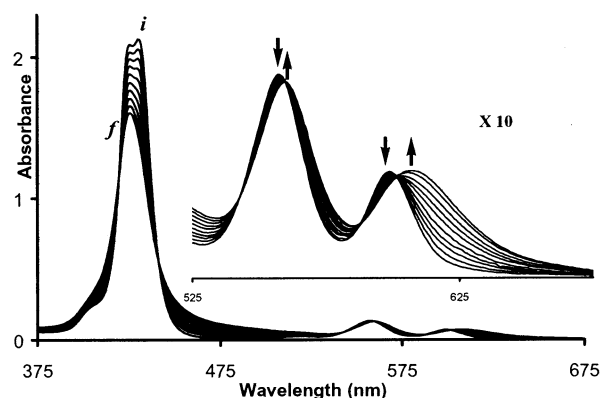
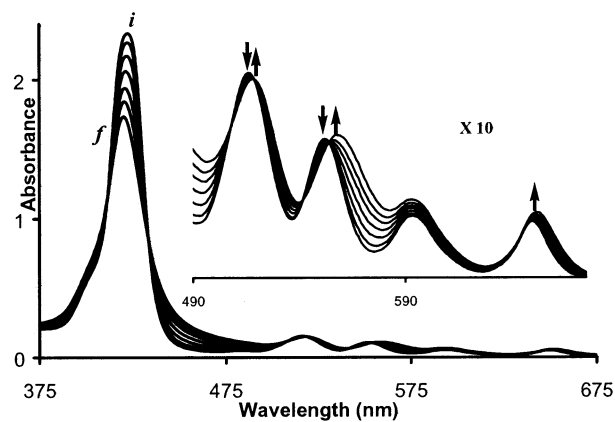


**Figure 1.** UV-vis spectra of 5-(4-pyridyl)-10,15,20-tri(4-*tert*-butylphenyl)porphyrin (A), **1** (B), and **Zn<sub>2</sub>1** (C) in 2-methyl-THF (4  $\mu$ M).

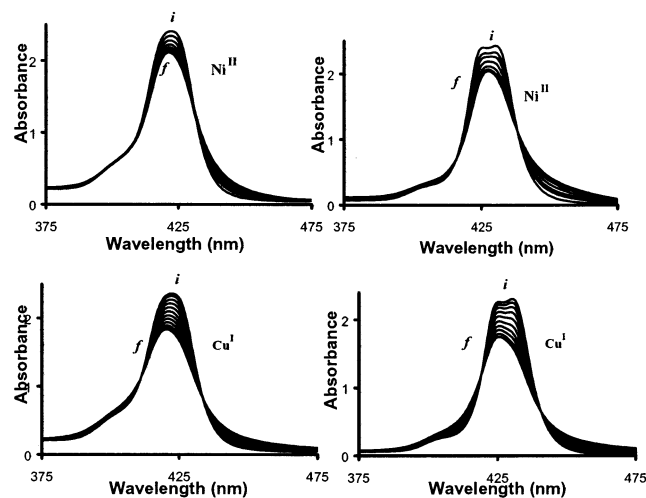
the two free-base porphyrins of both compounds **1** and **2** linked by the free-base 2,2'-bipyridine are reasonably electronically isolated. There is a  $\sim 5$  nm red shift and  $\sim 50\%$  increase in fwhm of the Soret band of **1**, and for **2**, the broadening is only  $\sim 25\%$ , both versus a monopyrindylporphyrin analogue. These are somewhat greater than most simple substituent effects for porphyrinic systems (Figure 1). The UV-vis spectrum indicates compound **1** has an increased proclivity to aggregate compared to **2**.

Upon metal ion coordination, the two pyridines of 2,2'-bipyridine become coplanar, and the degree of conjugation between the halves increases. The combination of the BiPy and the metal orbitals results in a system that allows greater electronic communication between the porphyrin chromophores. In **1**, the 5 and 5' positions are conjugated to the covalent bond and not with the pyridyl nitrogens. Conversely for **2**, the nitrogens are conjugated to the point of attachment, and the covalent bond is not. As expected, when the BiPy linker is coordinated by a variety of metal ions such as Cu(I), Ni(II), or Pd(II), the UV-vis spectra indicate an increase in the electronic communication between the two porphyrins in **1** (Figures 2 and 3) and **2** (Figure 4). For the Pd(II) adducts of **1** and **2**, this is indicated by a  $\sim 2$  nm blue shift and a further  $\sim 20\%$  broadening of the Soret band, as well as red shifts in the Q-bands (Figure 2). Several isosbestic points are found in the titration experiments for the free-base compounds, indicating the formation of only one product. For comparison, a linear dimer formed from the coordination of two *para* pyridylporphyrins to Pd(II)Cl<sub>2</sub> results in a 2–3 nm red shift and a  $\sim 10\%$  broadening of the Soret band.<sup>27</sup> Thus, in addition to the substituent effects, the ground-state electronic communication between chromophores is mediated by both the covalent bond and by the BiPy chelated metal ion, though the effects are small.

Unexpectedly, when both of the porphyrins are metalated with zinc, the equilibrium between the free-base 2,2'-bipyridine conformations shifts such that a significant population of the coplanar form exists, as observed by the dual Soret bands in the optical spectra for **Zn<sub>2</sub>1** (Figure 1), and to a different extent for **Zn<sub>2</sub>2** (Figure 4, initial spectra). The peak at 430 nm is consistent with the known red shift of porphyrin Soret bands upon Zn(II) coordination, and the

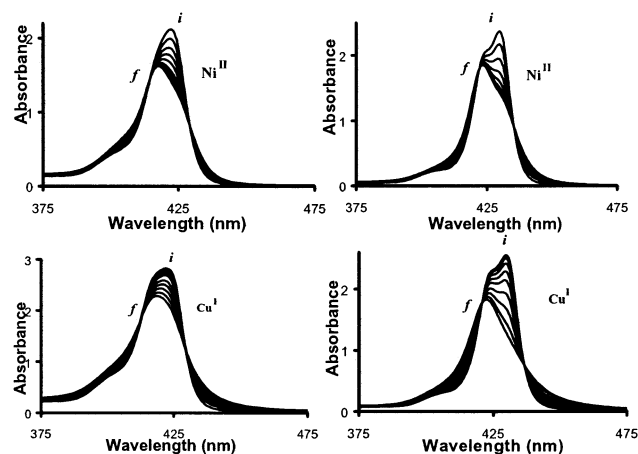


**Figure 2.** UV-visible spectra as 1 equiv (in  $6 \leq 5 \mu\text{L}$  aliquots) of Pd(II)Ac<sub>2</sub> is titrated into 3 mL of a 5  $\mu$ M solution of **1** (top) and **Zn<sub>2</sub>1** (bottom) in 2-methyl-THF.



**Figure 3.** Soret region of the UV-vis spectra as 1 equiv (in  $6 \leq 5 \mu\text{L}$  aliquots) of Ni(II)Ac<sub>2</sub> or Cu(I)ClO<sub>4</sub> is titrated into 3 mL of a 5  $\mu$ M solution of **1** (left), and **Zn<sub>2</sub>1** (right) in 2-methyl-THF; i = initial, f = final.

426 nm band represents the fraction of molecules with the BiPy in a planar conformation. This latter observation also is consistent with the known increase in electron density on the nitrogen(s) of 4 pyridyl porphyrins, as measured by coordination chemistry and basicity, upon zinc metalation.<sup>27,28,40,41</sup> This conclusion is also supported by the observation that when the Pd(II) species is titrated into a solution of **Zn<sub>2</sub>1**, the 430 nm band disappears, to yield a broad Soret band similar to the one found for the free base



**Figure 4.** Soret region of the UV-vis spectra as 1 equiv (in  $6 \leq 5 \mu\text{L}$  aliquots) of  $\text{Ni(II)Ac}_2$  or  $\text{Cu(I)ClO}_4$  is titrated into of 3 mL of  $5 \mu\text{M}$  solutions of **2** (left) and **Zn<sub>2</sub>2** (right) in 2-methyl-THF; i = initial, f = final. The Pd(II) titration can be found in the Supporting Information.

compound upon coordination of this metal by the BiPy subunit. Again, the small red shift of the **Zn<sub>2</sub>1**-Pd(II) complex is due to the zinc metalloporphyrin (Figures 2 and 3). Note that, even at low concentrations ( $< 10 \mu\text{M}$ ) of **Zn<sub>2</sub>1**, the split Soret band remains, so this observation is not due to changes in the aggregation state. Note also that for **2** there is a  $\sim 3$  nm blue shift of the Soret upon complexation of the same set of metal ions (Figure 4). When metal ions bind the BiPy of **Zn<sub>2</sub>2**, the split Soret band also evolves into a broader peak centered to the blue region of that of **Zn<sub>2</sub>2**. Thus, the largest contributor to the observed spectral shifts is the locking-in of the planar conformation of the BiPy by metal ion binding, *vide infra*.

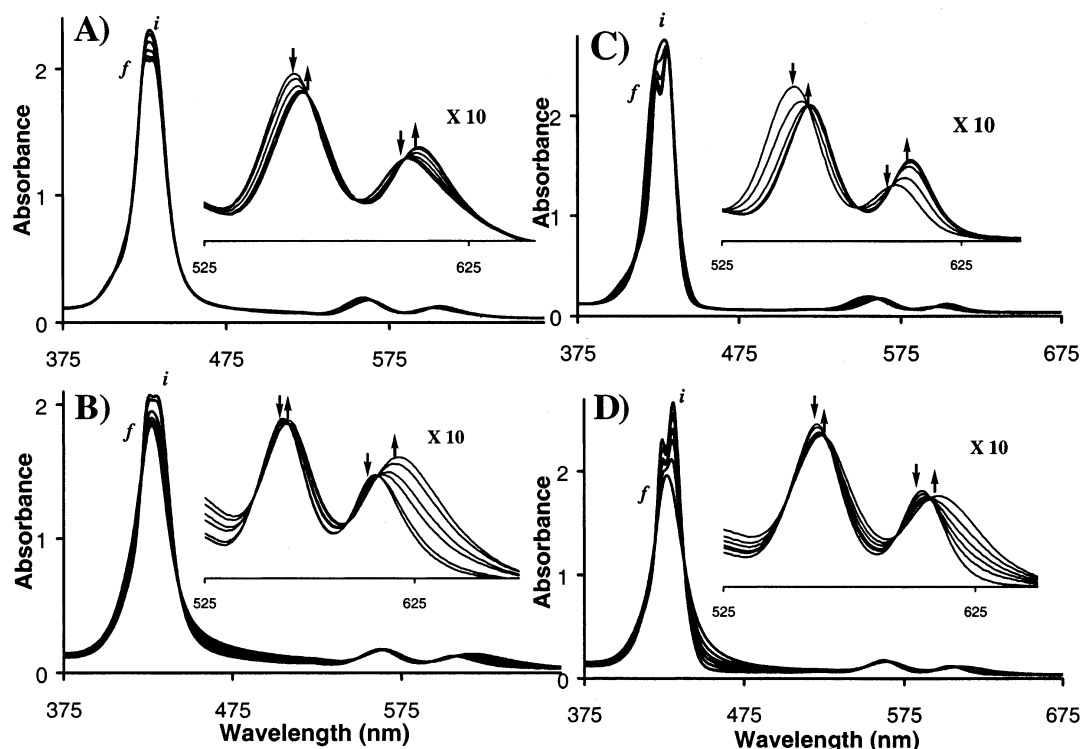
The nature of the metal ion coordinated by the BiPy moiety for both **1** and **2** makes little difference in the ground-state spectra as first row transition metals, second row metals, and divalent and univalent ions result in similar characteristic changes in the optical spectra with only subtle differences between them. The excited-state spectra reveal several features that are worth noting. As expected for virtually any fluorophore, upon coordination of a metal ion by the BiPy moiety, the fluorescence emission spectra decrease in intensity relative to those of the parent compounds due to the heavy atom effect. Second, upon BiPy coordination to some metal ions, there are pronounced differences in both the relative intensities and the energies of the emission bands relative to the unbound species. These differences likely arise from the different redox potentials of the different metal ions rather than enhanced electronic coupling of the chromophores and may represent a means to fine-tune the excited-state properties. The fluorescence emission and excitation spectra for **1**, **Zn<sub>2</sub>1**, **2**, and **Zn<sub>2</sub>2** where the BiPy is complexed to Zn(II) or Pd(II) are essentially similar to those of the uncomplexed species, albeit with reduced intensity due to the heavy atom effect. This latter observation confirms the general conclusion that the conformational changes of the bis-porphyrin BiPy compounds upon coordination to metal ions result in modest electronic coupling of the chromophores.

These observations in the electronic spectra are consistent with the Gouterman four-orbital model.<sup>42</sup> For both **Zn<sub>2</sub>1** and **Zn<sub>2</sub>2**, the largest changes in terms of energetics are observed in the Q(0,0) bands which correspond to the lowest energy  $^1(\pi, \pi^*)$  state. The highest occupied molecular orbitals of zinc porphyrins are  $a_{2u}$  and  $a_{1u}$ , and the former has significant electron density at the meso positions (bearing the BiPy moiety) and the pyrrole nitrogens whereas the latter has electron density on the pyrrole  $\alpha$  and  $\beta$  positions.

**NMR Spectra.** Chelation of Pd(II)Ac<sub>2</sub> by the 2,2'-BiPy subunit for both **1** and **2** was also examined by <sup>1</sup>H NMR titrations whereby 1.5 mg of **1** or **2** was dissolved in 1 mL of CDCl<sub>3</sub> and the spectrum was taken of the initial solution and after each addition of 0.2 equiv of Pd(II)Ac<sub>2</sub> dissolved in CDCl<sub>3</sub>. The highly characteristic shift in the pyridyl protons upon coordination of a palladium ion indicates clean formation of the Pd adducts of **1** and **2**. For **Zn<sub>2</sub>1** in 6:1 CDCl<sub>3</sub>/THF-*d*<sub>8</sub>, the singlet for the pyridyl 6H moves from 9.63 to 9.25 ppm, the doublet for the pyridyl 3H moves from 9.13 to 9.05 ppm, the doublet for the pyridyl 4H moves from 8.78 to 8.65 ppm, and the pyrrole doublet of doublets at 8.98 ppm (which arise from the pyrrole nearest the BiPy unit) changes to complex multiplets at 9.00 and 8.75 ppm. The single pyrrole resonance from the outer pyrroles significantly broadens into three closely spaced peaks, and the *t*-butyl methyls move from 1.59 to 1.61 ppm. Similar <sup>1</sup>H NMR shifts are observed for **2**. The changes in chemical shifts are consistent with those observed for other pyridylporphyrin complexes,<sup>25,27,28</sup> and the increased peak width is likely due to the increased rigidity of the system, and slight increase in molar mass. Significantly, the changes in chemical shift of the pyrrole protons for both **1** and **2** when the BiPy unit binds Pd(II) further indicates the substituent effects, but note that these changes in pyrrole chemical shifts are about the same as those observed when two 5-(4-pyridyl)-10,15,20-tri-(4-*tert*butylphenyl)porphyrins bind the same metal ion. Therefore, the covalent bond between the pyridines in BiPy in **1** and **2** has only minor effects on the ring current of the macrocycles. The predominant causes of the spectral changes are the metal ion and the conformational change of the BiPy induced by metal ion binding.

**Coordination Chemistry.** The coordination chemistry of these two compounds has yet to be fully explored; however, the more than ample precedents in BiPy chemistry indicate that these will be good tectons for a variety of supramolecular arrays and polymers. Control of temperature, relative stoichiometry, and choice of metal ion allow one to design systems wherein these two compounds merely complex the metal ion, such as the work herein, or form higher ordered adducts (such as 2:1 or 3:1).<sup>16</sup> The structure of these complexes will be governed by the metal ion binding properties as well as the steric interactions of the porphyrins. For example, the tetrahedral coordination geometries of some metal ions such as Cu(I) and Zn(II) allow the formation of dimers of **1** or **2** bound together by the coordination of the BiPy moieties to the metal. In these cases, the four chro-

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**Figure 5.** (A) The broad Soret band in the UV-vis spectra of  $\text{Zn}_2\mathbf{1}$  ( $70 \mu\text{M}$  in chloroform, 1 mm path length cuvette) indicates some aggregation, but disaggregation occurs as 1 equiv of DABCO is titrated into the solution to form a supramolecular square (Scheme 1). (B) The addition of 1 equiv of  $\text{Pd}(\text{II})\text{Ac}_2$  per  $\text{Zn}_2\mathbf{1}$  changes the conformation of the BiPy without changing the structure of the supermolecular square. (C) Changes in the optical spectra are nearly complete after only  $\sim 0.5$  equiv of DABCO is added to  $\text{Zn}_2\mathbf{2}$ . (D) The addition of 1 equiv of  $\text{Pd}(\text{II})\text{Ac}_2$  per  $\text{Zn}_2\mathbf{2}$ .

mophores are well separated (Schemes 1 and 2). The optical spectra of both of these simple coordination dimers are unremarkable such that neither dimer displays properties much different from those of the monomers coordinated by the same metal ion. The relative orientation of the porphyrins in coordination oligomers or arrays based on compounds **1** and **2** will be quite different. Coordination of the BiPy moiety of the 5,5' derivative to square planar metal ions will force the macrocycles to be cofacial thereby altering the photophysical properties, as exhibited by further blue shifts in the Soret band. The coordination of the 4,4' derivative to square planar metals leaves the chromophores separated, and the photophysical properties are nearly indistinguishable from the simple monomer coordinated to the same metal ion. The full characterization of self-assembled arrays of these molecules will be reported later.

**Supramolecular Squares.** Since the first publications on designed coordination squares of porphyrins,<sup>27</sup> there have been numerous reports on the application of these concepts to the design of functional materials.<sup>24,27,43</sup> In all of the porphyrinic squares, and most supramolecular systems in general, a conformational change in the molecules that constitute the sides either is not possible because they are locked into place or results in the disassembly of the supramolecular system, which may or may not reassemble into a different structure.<sup>30</sup> Compound **1** and its metalloporphyrin derivatives, however, show that this is not a priori

true. As a demonstration, it is possible to form a supramolecular square using two  $\text{Zn}_2\mathbf{1}$  moieties and two DABCO molecules (Scheme 1). At  $70 \mu\text{M}$  in chloroform, the supramolecular square is the predominant species according to well established equilibria and exhibits the characteristic red shift in the electronic spectra upon axial coordination of the zinc porphyrins by nitrogenous ligands<sup>44</sup> (Figure 5). In the process of forming the square, the DABCO disrupts the aggregates of  $\text{Zn}_2\mathbf{1}$  found at this concentration, and note that the Soret band of the final spectrum, "f" (peak maxima at 426, 430, 562, 606 nm) is essentially identical to that of this compound at  $5 \mu\text{M}$ , with one equivalent of piperidine. Note that the nominal Soret bands are essentially the same as that of unligated  $\text{Zn}_2\mathbf{1}$ , but the Q-bands are red shifted by  $\sim 5$  nm. A plot of  $\Delta A$  versus DABCO equivalents confirms the 1:1 stoichiometry. The porphyrins in each  $\text{Zn}_2\mathbf{1}$  unit are now coplanar. This is in contrast to the "average" coplanarity arising from the small oscillations about the pyridyl-porphyrin bonds when the BiPy unit in  $\text{Zn}_2\mathbf{1}$  is bound by metal ions (peak maxima at 426, 560, 607 nm). Then, as the  $\text{Pd}(\text{II})$  species is titrated into the solution containing the square, there is a substantial red shift in the lowest energy Q-band (12 nm), a smaller shift in the intermediate Q-band (3 nm), and the red Soret band at 430 nm disappears. The two BiPy units are now also locked into a planar conformation, and the porphyrins in each subunit in the final structure are not only coplanar but also in register with the opposing subunit. This is further indication that the planar, metal-bound

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state of the BiPy is the main reason for the observed changes in the electronic spectra. On the other hand, with **Zn<sub>2</sub>2**, a plot of  $\Delta A$  versus DABCO equivalents indicates about half an equivalent of DABCO binds per **Zn<sub>2</sub>2**. In this case, the addition of the Pd(II) species shifts the Q-bands to the red, and there is a broadening of the Soret band (Figure 5).

The fluorescence of both the supramolecular square and the **Zn<sub>2</sub>2**–DABCO complex is typical of axial binding of nitrogenous ligands to the Zn(II) centers.<sup>45</sup> As observed in other porphyrin assemblies mediated by Pd(II) coordination,<sup>12,27,28</sup> there are small red shifts in the emission spectra of **Zn<sub>2</sub>1**·Pd(II) and **Zn<sub>2</sub>2**·Pd(II) that reflect the observed shifts in the ground-state spectra. However, note that when two Pd(II) ions bind to the square the fluorescence is quenched by ~50%, but when one Pd(II) binds to the **Zn<sub>2</sub>2**–DABCO complex the emission is quenched by ~80%. The smaller magnitude of the quenching by Pd(II) is consistent with other rigidly assembled porphyrin systems<sup>14</sup> and aggregates.<sup>46</sup>

Taken together the absorption data indicate that the average coplanarity of the chromophores is not the only cause of the spectral shifts, but it is a combination of the planar conformation of the BiPy and the substituent effects caused by metal ion binding to the BiPy. The further red shift of the electronic spectra of the supramolecular square is largely due to the highly rigid structure with the BiPy units locked into a planar conformation.

## Conclusions

The new bis-porphyrin-2,2'-bipyridine system **1** and its Zn complex were synthesized and characterized by UV–vis, NMR and ESI-MS. The rigid architectures of the molecules are in contrast to other porphyrin–bipyridine systems such as **2**, or similar derivatives.<sup>26</sup> When the BiPy subunit binds metal ions, it becomes planar, and facilitates electronic coupling between the chromophores of **1**, **2**, and their metalloporphyrin derivatives. These compounds (**1**, **Zn<sub>2</sub>1**, **2**, and **Zn<sub>2</sub>2**) can serve as sensors for various metal ions with the sensitivity dictated by the binding constant of the BiPy for the given metal ion. In a second functional mode, these compounds can serve as an electronic switch gated by complexation and decomplexation of these ions. Initial studies comparing the ground- and excited-state spectra of supramolecular systems constructed from these com-

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pounds indicate that the spatial arrangement of the porphyrins further dictates the photophysical properties, as expected. Thus, larger and more complex porphyrin arrays may be synthesized by coordinating the appropriate transition metal ions bearing multitopic ligands to the BiPy moiety.<sup>23</sup> These molecules will serve as part of a library of building blocks for the self-assembly of nanoscaled photonic materials.<sup>47–51</sup>

Since the porphyrins only subtly alter the 2,2'-bipyridine metal ion binding properties, the well established coordination chemistry of this subunit can be exploited. However, steric considerations may well prevent or complicate the formation of certain bis- and tris(BiPy) complexes that are well-known in the literature, especially for **1** and its derivatives. Importantly, the results on the ladder complex of **Zn<sub>2</sub>1** demonstrate that there is no a priori requirement that structural rearrangements or reorganization of supramolecular systems will result from structural changes in component molecules, even though these structural perturbations result in significantly different photophysical properties.

**Acknowledgment.** This article is dedicated to Richard W. Franck on the occasion of his 67th birthday. Funding from the National Science Foundation (Grants CHE-0135509 and IGERT DGE-9972892) and the PSC-CUNY fund is gratefully acknowledged. Hunter College Chemistry infrastructure is partially supported by the National Institutes of Health RCMI program, GM3037. Ngee Ai Thai is thanked for her valuable assistance in the preparation of compound **1**.

**Supporting Information Available:** Procedures for the synthesis of the intermediates for the directed synthesis of **2**; <sup>1</sup>H NMR data for the Pd(II) adducts of **Zn<sub>2</sub>1**, **Zn<sub>2</sub>2**, and **2**; UV–vis spectra for the Pd(II) titration into **2** and **Zn<sub>2</sub>2**; fluorescence data for the supramolecular square titrated with Pd(II); and a table of  $\lambda_{\text{max}}$  values for all compounds. This material is available free of charge on the Internet at <http://pubs.acs.org>.

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