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#### meso, meso-Linked Porphyrin Arrays\*\*

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Owing to the central importance of multiporphyrin assemblies in photosynthetic reaction centers and light-harvesting antenna complexes, considerable attention has been focused on the development of covalently linked porphyrin arrays as effective biomimetic models. Systematic studies on these models will aid also in the development of new photonic materials and molecular devices.<sup>[1-6]</sup> In these model studies a variety of bridges that connect porphyrin chromophores have been examined in their abilities to facilitate electron and photon connectivity or to perturb the spectral properties of the porphyrin chromophores. As an extension, a bridgeless, directly coupled porphyrin array may be a fascinating, ultimate candidate for exploring novel connectivity.

Here we report on a novel, very facile oxidative coupling reaction of zinc(II) 5,15-di(3,5-di-tert-butylphenyl)porphyrin (1) to give porphyrin dimer 2 and porphyrin trimer 3 as the first example of meso, meso-coupled multiporphyrins. Treatment of a chloroform solution of 1 with  $AgPF_6$  (0.5 equiv) dissolved in acetonitrile for 5 h gave 2 and 3; NMR analysis revealed the distribution of products: 1 (47%), 2 (27%), and 3 (4%). Although these products were difficult to separate over standard silica gel columns, they were separated by size exclusion chromatography,<sup>[7]</sup> by which the products are eluted in the order of molecular weight: first, higher oligomers and trace amounts of tetramer 4 > 3 > 2 > 1. The yields of isolated compounds were 25% for 2 and 4% for 3, based on the amount of 1 used. Reaction of 2 under analogous conditions (0.5 equiv AgPF<sub>6</sub>) gave 4 in 23% yield. The regioselectivity of the coupling was quite high.[8]

Compounds 2-4 were fully characterized by <sup>1</sup>H NMR spectroscopy (500 MHz) and FAB mass spectrometry. <sup>1</sup>H NMR analysis revealed the presence of one *meso*- and two, four, six, and eight  $\beta$ -protons in 1-4, respectively (Scheme 1). In the spec-

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Scheme 1. Structures of 1-5. NMR chemical shifts of the *meso-* and  $\beta$ -protons (CDCl<sub>3</sub>) are indicated. Ar = 3,5-tBu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

trum of **2** the signals of the inner  $\beta$ -protons are shifted upfield by  $\Delta \delta = 1.33$  and 0.46 ppm relative to those of **1**, reflecting the ring current effect of the second porphyrin ring, while the signals of the outer  $\beta$ -protons appear nearly at the same chemical shifts. Similar features are observed for **3** and **4**. These data, analyzed in terms of the ring current model, suggest an approximate perpendicular arrangement of the neighboring porphyrins.

AgClO<sub>4</sub> and AgBF<sub>4</sub> were similarly effective in this coupling, but the use of AgNO<sub>2</sub> led to meso-nitration, giving 5 almost quantitatively. The coupling reaction was accelerated by addition of  $I_2$ ; under these conditions the reaction was complete within 5-10 min.<sup>[9]</sup> In the I<sub>2</sub>-promoted reactions use of one or more equivalents of the  $Ag^{I}$  salt and  $I_{2}$  led to lower yields of 2 and 3, under otherwise the same reaction conditions.<sup>[10]</sup> Most probably, the initial generation of radical cation 1<sup>•+</sup> followed by nucleophilic attack by a molecule of neutral 1 results in the formation of 2, in analogy to the related meso-substitution reaction of porphyrins.<sup>[11]</sup> Thus, the nitrite ion traps 1<sup>++</sup> to give 5 in the reaction of  $AgNO_2$ , and an excess of strong oxidant ( $I_2/Ag^1$ salt) converts a large portion of 1 to 1<sup>++</sup>, thereby suppressing the formation of 2. The concurrent formation of 2 and 3 can be explained by the fact that 1 and 2 have nearly the same oxidation potentials.<sup>[12, 13]</sup> Consistent with this mechanism, treatment of a chloroform solution of 1 with tris(4-bromophenyl)aminium hexachloroantimonate, a typical one-electron oxidizing agent, provided 2 (8%) and 3 (2%).

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The one-electron oxidation reactions of metalloporphyrins have been extensively studied in view of their important roles in electron transfer and oxidation processes in biological systems.<sup>[14]</sup> Interestingly, cations such as  $[Mg(oep)]^+$  and  $[Zn-(oep)]^+$  (oep 0 2,3,7,8,12,13,17,18-octaethylporphyrin dianion) were reported to dimerize at low temperature,<sup>[15]</sup> and later the structure of a dimeric product,  $[{Zn(oep)}_2]$ , was determined by X-ray analysis to be a noncovalently bound, stacked dimer.<sup>[16]</sup> In a few examples the formation of bis(tetrapyrroles) (from 5,15-dioxoporphodimethene and oxophlorin (2-hydroxyporphyrin)) with similar direct *meso,meso* linkage have been reported upon oxidation of [Zn(oep)] with Tl(OTf)<sub>3</sub><sup>[17]</sup> and on oneelectron oxidation of *meso*-hydroxyl-substituted [Ni<sup>II</sup>(oep)].<sup>[18]</sup> However, **2**–**4** are the first examples of *meso,meso*-coupled arrays of the porphyrin chromophore.

The meso-positions of porphyrins have been known to be the most reactive centers towards both electrophilic and nucleophilic reagents,<sup>[19]</sup> but these reactivities are usually masked in tpp (tpp = tetraphenylporphyrin) and oep derivatives because of the *ipso*-phenyl groups in the former and the severe steric congestion due to the neighboring  $\beta$ -ethyl substituents in the latter. In this respect, 5,15-diarylporphyrins, which lack  $\beta$ pyrrolic substituents, are good substrates for exploring the intrinsic high reactivity of the meso-position, particularly towards sterically demanding reagents.<sup>[20]</sup> It seems probable that steric congestion around the meso,meso linkage in the previously studied bis(tetrapyrroles)<sup>[17, 18]</sup> suppresses the formation of meso,meso-linked porphyrins, in which the planarity of porphyrin would increase the steric hindrance. In this regard, 1 is also a good substrate for this coupling.

As shown in Figure 1, the direct *meso,meso* connectivity in 2-4 results in large excitonic splitting in the Soret bands ( $S_2$  state), but the spectral changes in the Q-band region ( $S_1$  state)



Figure 1. Absorption spectra of 1-4 in THF ( $c = 1.0 \times 10^{-6}$  M)

are rather modest. When the exciton splitting energies in the Soret bands,  $\Delta E$ , were plotted versus  $2\cos[\pi/(N+1)]$ ,<sup>[21]</sup> we obtained a line with a slope of  $E_0 = 2100 \text{ cm}^{-1}$ . This value, which corresponds to the exciton coupling energy between the neighboring porphyrins, is certainly larger than that found for 1,4-phenylene-bridged linear porphyrin arrays (ca.  $800 \text{ cm}^{-1})^{[22]}$  but seems to be small considering the direct linkage of the porphyrin  $\pi$ -systems. The fluorescence emission spectrum of 1 displays two bands (584 and 634 nm), which are characteristic of a zinc porphyrin monomer; the spectra of 2-4

exhibit slightly broadened emissions with peak maxima of 613, 626, and 633 nm, respectively. The fluorescence quantum yields of 1-4 determined in THF relative to Zntpp  $(0.03)^{[23]}$  are 0.036, 0.025, 0.036, and 0.033, respectively. The symmetric structural feature **2** is reminiscent of that of 9,9'-bianthryl, which undergoes solvent-induced symmetry breaking, thereby promoting the population of the charge transfer states.<sup>[24]</sup> But significant reduction of the fluorescence quantum yield was not observed for **2**–**4** even in polar solvents such as DMF and acetonitrile. We interpret the observed small electronic interactions in the ground and  $S_1$  states as evidence that the porphyrins in **2**–**4** lie approximately orthogonal to each other, in line with the results of the <sup>1</sup>H NMR analyses.

In summary, the Ag<sup>I</sup>-promoted oxidative coupling of zinc(II) 5,15-diarylporphyrins provides an easy entry to a new class of *meso,meso*-linked multiporphyrin arrays, which will offer new opportunities for studying the electronic interactions in porphyrin arrays with direct links, and for exploring intramolecular, long-range electron- and energy-transfer systems across these directly linked porphyrin arrays.

#### **Experimental Section**

To a solution of 1 (60 mg, 80 mmol) in 40 mL of CHCl<sub>3</sub> was added all at once a solution of AgPF<sub>6</sub> (10.3 mg, 40 mmol) in acetonitrile. The reaction mixture protected from light and stirred at room temperature for 5 h. The mixture was filtered, diluted with water, and extracted with CHCl3. The organic layer was removed, washed with water, and dried over anhydrous Na2SO4. A saturated solution of Zn(OAc)2 in methanol (1 mL) was added, and the resulting solution was refluxed for 1 h, diluted with water, and extracted with CHCl3. The organic layer was removed and dried over  $Na_3SO_4$ . The product mixture was separated by preparative size exclusion chromatography (BioRad Bio-Beads SX-1 packed in benzene in a  $4.8 \times 60$  cm gravity-flow column; flow rate 4 mL min<sup>-1</sup>). Elution with benzene yielded four major fractions in the following order: higher oligomers along with a trace amount of tetramer 4, trimer 3, dimer 2, and the starting monomer 1. Because separation of 3 and 2 was difficult, chromatographic separations were repeated on the same column. UV spectroscopy was very effective in checking the fractions. The trimer 3 (2.4 mg, 4%) and the dimer 2 (15 mg, 25%) were obtained in pure form from the second and the third fractions, respectively, and the starting monomer 1 (20 mg, 33 %) was recovered from the fourth fraction. The tetramer 4 was prepared in 23% yield from the analogous reaction of 2 (45 mg, 30 mmol) in 60 mL of CHCI,

1: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.57 (s, 36 H, *t*Bu-H), 7.84 (t, *J* = 1.8 Hz, 2H, Ar-4-H), 8.15 (d, *J* = 1.8 Hz, 4H, Ar-2.6-H), 9.20 (d, *J* = 4.9 Hz, 4H,  $\beta$ -H), 9.45 (d, 4H, *J* = 4.9 Hz,  $\beta$ -H), 10.34 (s, 2H, *meso*-H); FAB MS: *m*/z: 748.5 (calcd for C<sub>48</sub>H<sub>52</sub>N<sub>4</sub>Zn: 748.3); UV/Vis (THF):  $\lambda_{max}(\varepsilon) \approx$  413 (550 000), 543 (20 000), 580 nm (4170).

2: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.45$  (s, 72 H, *t*Bu-H), 7.71 (t, J = 1.8 Hz, 4H, Ar-4-H), 8.11 (d, J = 1.8 Hz, 8H, Ar-2.6-H), 8.12 (d, J = 4.9 Hz, 4H,  $\beta$ -H), 8.74 (d, J = 4.9 Hz, 4H,  $\beta$ -H), 9.18 (d, J = 4.9 Hz, 4H,  $\beta$ -H), 9.49 (d, J = 4.9 Hz, 4H,  $\beta$ -H), 10.39 (s, 2H, *meso*-H); FAB MS: m/z: 1498.6 (calcd for C<sub>98</sub>H<sub>102</sub>N<sub>8</sub>Zn<sub>2</sub>: 1498.7); UV/Vis (THF):  $\lambda_{max}$  ( $\varepsilon$ ) = 416 (234000), 451 (229000), 559 (50100), 594 nm (5890).

3: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.33 (s, 36 H, *t*Bu-H), 1.49 (s, 72 H, *t*Bu-H), 7.57 (t, J = 1.8 Hz, 2 H, Ar-4-H), 7.75 (t, J = 1.8 Hz, 4 H, Ar-4-H), 8.07 (d, J = 1.8 Hz, 4 H, Ar-2.6-H), 8.15 (d, J = 1.8 Hz, 8 H, Ar-2.6-H), 8.17 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.29 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.72 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.83 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.72 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.83 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 9.20 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 9.51 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 10.40 (s, 2 H,  $\beta$ -H), FAB MS: *m/z*: 2245.1 (calcd for C<sub>144</sub>H<sub>132</sub>N<sub>12</sub>Zn<sub>3</sub>: 2247.0); UV/Vis (THF):  $\lambda_{max}$  ( $\varepsilon$ ) = 413 (355000), 475 (309000), 570 (91200), 611 nm (12300).

**4**: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.37$  (s, 72 H, *t*Bu-H), 1.50 (s, 72 H, *t*Bu-H), 7.61 (t, J = 1.8 Hz, 4 H, Ar-4-H), 7.75 (t, J = 1.8 Hz, 4 H, Ar-4-H), 8.11 (d, J = 1.8 Hz, 8 H, Ar-2.6-H), 8.16 (d, J = 1.8 Hz, 8 H, Ar-2.6-H), 8.19 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.31 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.33 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.33 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.40 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.24 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 8.25 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 9.52 (d, J = 4.9 Hz, 4 H,  $\beta$ -H), 10.41 (s, 2 H, meso-H); FAB MS: m/z 2996.1 (caled for  $C_{1.92}H_{2.02}N_{16}Zn_4$ : 2995.3); UV/Vis (THF):  $\lambda_{max}(\varepsilon) = 413$  (479000), 486 (447000), 575 (151000), 616 nm (20000).

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# X-ray Structure of [Ru(bpy)<sub>3</sub>]<sup>0</sup>: An Expanded Atom or a New Electride?\*\*

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Dedicated to Professor Waldemar Adam on the occasion of his 60th birthday

We recently prepared and chemically characterized single crystals of electroneutral  $[M(bpy)_3]^0$  complexes (where bpy is 2,2'-bipyridine and M is Fe, Ru, and Os).<sup>[1]</sup> These materials had been previously reported as powders.<sup>[2]</sup> Herein we present the X-ray crystal structure characterization of the  $[Ru(bpy)_3]^0$  complex; the transport and magnetic properties of this material have been previously discussed.<sup>[3]</sup>

The compound  $[Ru(bpy)_3]^0$  (1) is conceptually similar to the first crystalline cryptatium (2), which was described in 1991.<sup>[4]</sup>



For the latter neutral, "expanded-atom" type species **2**, formed by reductive electrocrystallization of sodium tris(bipyridine) cryptate, the crystal structure analysis provides clear evidence that the unpaired electron density is mainly localized on only one of the bpy subunits.<sup>[4]</sup> This observation is consistent with MO calculations for bpy, which show that the LUMO (2,2'bond) is bonding and thus that its occupation by an added electron would tend to flatten the bpy subunit.<sup>[5]</sup> Both compounds may be compared, at least conceptually, to endohedral fullerenes, since in all three cases there are central metal cations surrounded by organic ligands that effectively delocalize the negative charge to afford overall electroneutral species.<sup>[6]</sup>

 $[Ru(bpy)_3](PF_6)_2$  and  $[Ru(bpy)_3](PF_6)_3$  were recently structurally characterized.<sup>[7a]</sup> The latter was the first report of the structure of the Ru<sup>3+</sup> complex, while the structure of the Ru<sup>2+</sup> complex had been described before (see citation in reference [6]). The results presented here for 1 are mainly compared to those for  $[Ru(bpy)_3]^{2+.[7a]}$ 

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