

# Tetrakis-heteroleptic Complexation at Porphyrins: A Convenient Route to Diversely Functionalized Aggregates<sup>†</sup>

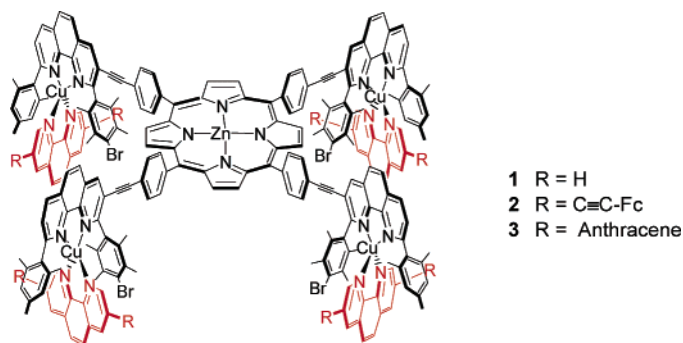
Michael Schmittel\* and R. S. K. Kishore

Center of Micro and Nanochemistry and Engineering (Cu), Organic Chemistry I,  
Universität Siegen, Adolf-Reichwein-Strasse, D-5708 Siegen, Germany

*schmittel@chemie.uni-siegen.de*

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## ABSTRACT



Using a novel tetraphenanthroline porphyrin building block and heteroleptic bisphenanthroline complexation, copper-instructed multicomponent assemblies exhibiting distinct electrochemical and photoactive behavior were accessed.

One of the important prerequisites to realize complex systems characterized by interdependence and emergence is to bring together functional constituents within appreciable spatial proximity, thus enabling interaction and possible amplification of desired functions. Dendritic and supramolecular approaches have addressed this issue by clustering functional units into large molecules to control communication among the components, thus leading to high end functions such as catalysis,<sup>1</sup> light harvesting,<sup>2</sup> and molecular switching and gating.<sup>3</sup> Since the construction of multiple covalent bonds

poses a considerable challenge, often requiring long synthetic sequences, metal-instructed supramolecular assembly is now being looked at as an effective alternative to build supramolecular aggregates with well-defined geometry and orientation.<sup>4,5</sup>

In the past few years, we have been exploring a novel approach (HETPHEN approach) to heteroleptic bisphenan-

\* Fax: + (49)271-740320.

<sup>†</sup> This article is dedicated to Prof. Dr. H.-D. Lutz (Universität Siegen) on the occasion of his 70th birthday.

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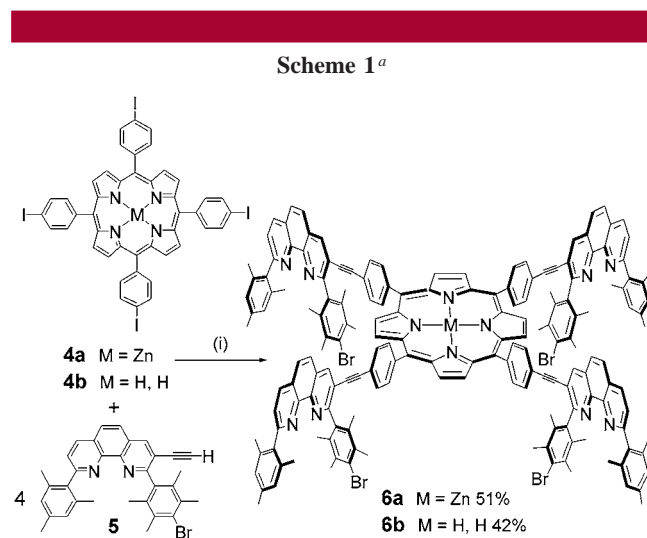
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throline complexation at various metal centers,<sup>6</sup> which has been exploited to build supramolecular nanoscaffolds, ring-in-ring structures, and nanogrids.<sup>7</sup> Herein, we demonstrate the utility of our approach to access peripherally functionalized porphyrins that may have applications as electronic switches in energy gating and harvesting processes. Our intention in studying copper(I) phenanthroline-appended porphyrins stems from the interesting photophysical behavior of copper(I) phenanthrolines as cheap substitutes to ruthenium complexes.<sup>8</sup> Tetraruthenated porphyrins have been reported earlier.<sup>9</sup> Exploring 1,10-phenanthrolines in conjunction with porphyrins could be fruitful in getting closer to viable molecular devices.<sup>10</sup> Herein, we describe the synthesis and characterization of the tetraphenanthrolinated porphyrins<sup>11</sup> **6a** and **6b** as supramolecular synthons and their Cu(I)-instructed assemblies **1–3**.

The strategy conceived to obtain target molecules **6a,b** was to attach a highly modified phenanthroline substrate **5** to the *meso* position of the porphyrins **4a,b**, (Scheme 1)



<sup>a</sup> Conditions: (i) Pd<sub>2</sub>(dba)<sub>3</sub>, AsPh<sub>3</sub>, pyridine, 40 °C, 4 h.

through an acetylene linker at the 3-position of the 1,10-phenanthroline. The basic unit **5** has been used by us previously<sup>12</sup> as a component of ligands in supramolecular assemblies.<sup>7</sup> Apart from stabilizing Cu<sup>+</sup> complexes against oxidation<sup>13</sup> and enhancing the photophysical properties,<sup>14</sup> the

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2,9-aryl substitution on the phenanthroline additionally circumvents solubility problems common to many multiple 1,10-phenanthroline systems.

Thus, **5** was attached to porphyrins **4a,b**<sup>15</sup> via a Sonogashira cross-coupling protocol.<sup>16</sup> Purification was achieved by preparative size exclusion chromatography using BioRad Bio-Beads SX-1 under gravity flow. **6a** and **6b** were obtained in 51 and 43% yields, respectively, and characterized by <sup>1</sup>H and <sup>13</sup>C NMR, electrospray mass and absorption spectroscopy, and elemental analysis.

The absorption spectrum of **6a** displayed a marginal bathochromic shift of 8 nm of the B band as compared to 420 nm in ZnTPP (zinc tetraphenylporphyrin). Besides, the oxidation potentials of **6a** obtained by cyclic voltammetry were not different from those of ZnTPP<sup>17</sup> (Table 1). This

**Table 1.** Cyclic Voltammetric Data<sup>a</sup>

	$E_{1/2}/V$ (Fc/Fc <sup>+</sup> )	$E_{1/2}/V$ (Cu <sup>+</sup> /Cu <sup>2+</sup> )	$E_{1/2}/V$ (Por/Por <sup>+</sup> )	$E_{1/2}/V$ (Por <sup>+</sup> /Por <sup>2+</sup> )
<b>1</b>		0.76	0.90 ( $E_{pa}$ = 0.94)	1.23
<b>2</b>	0.56	0.73		
<b>6a</b>			0.85 ( $E_{pa}$ = 0.87)	1.12
<b>8</b>	0.53			
<b>ZnTPP</b>			0.81 ( $E_{pa}$ = 0.85)	1.10
<b>11</b>	0.57			

<sup>a</sup>  $E_{1/2}$  vs SCE in CH<sub>2</sub>Cl<sub>2</sub> with *n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M); scan rate 100 mV s<sup>-1</sup>.

suggests the absence of any strong electronic interaction between the porphyrin ring and the phenanthrolines and insignificant perturbation of the HOMO of the porphyrin unit by the phenanthroline appendages.

UV–vis titration of **6a** against Cu(I) revealed that the low-energy shoulder of the  $\pi$ – $\pi^*$  band of the phenanthroline moved bathochromically (with an isosbestic point at 361 nm). With increasing addition of Cu(I) was also noticed a decrease in the intensity of the Soret band accompanied by broadening. This enhanced interaction between the porphyrin chromophore and the Cu<sup>+</sup>-loaded phenanthrolines could be due to the MLCT interaction between Cu(I) and the phenanthroline units forcing a shift of electron density from the porphyrin core toward the periphery.

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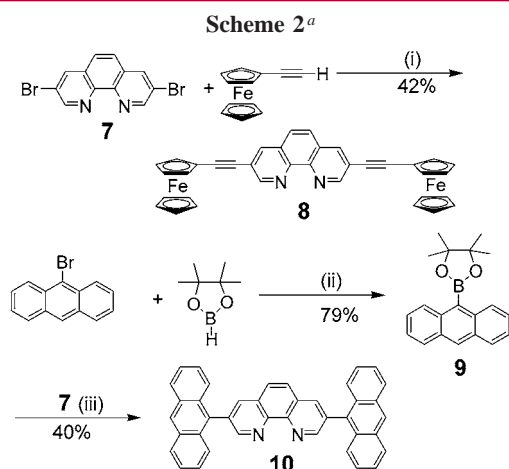
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The coordination behavior of **6a** was explored by its reaction with 4 equiv of 1,10-phenanthroline in the presence of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ , yielding exclusively **1** as a tetrakis-heteroleptic porphyrin phenanthroline aggregate. The proton NMR of **1** revealed an upfield shift of 0.9 ppm (from  $\delta$  6.97 ppm in **6a** to  $\delta$  6.00 ppm in **1**) for the 3'' and 5'' protons at the mesitylene due to the shielding effect of the aromatic  $\pi$  cloud of the complexed parent 1,10-phenanthroline.

When the reaction was performed in a sequential manner, it was possible to isolate and characterize  $\mathbf{6a}\cdot(\text{Cu})_4^{4+}$ , a Cu(I)-loaded species, by  $^1\text{H}$  NMR, ESI MS, and UV. The proton NMR of  $\mathbf{6a}\cdot(\text{Cu})_4^{4+}$  revealed a downfield shift of all the phenanthroline protons due to the coordination to Cu(I).



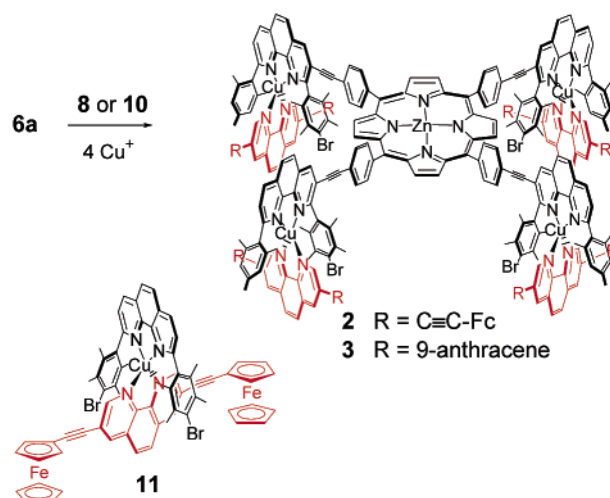
<sup>a</sup> Conditions: (i)  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ , CuI, DIPA, benzene, 80 °C, 48 h. (ii)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{NEt}_3$ , benzene 80 °C, 12 h. (iii)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{NEt}_3$ ,  $\text{Na}_2\text{CO}_3$ , 80 °C, 48 h

Since it was possible to readily assemble four heteroleptic copper complexes quantitatively in a single step, we decided to prepare the novel phenanthrolines **8** and **10** to add a functional periphery to **1**. Thus, bis(ferrocenyl-ethynyl)phenanthroline (**8**) was synthesized by a Sonogashira cross-coupling reaction from ferrocene acetylene and 3,8-dibromophenanthroline (**7**) in 42% yield. Bisanthryl phenanthroline **10** was prepared from 9-anthryl boronic ester **9** coupled to **7** via a Suzuki coupling reaction in 40% yield. Subsequent complexation of **8** and **10** in the presence of Cu(I) ions afforded **2** and **3** as peripherally functionalized tetrakis-heteroleptic complexes. They were characterized by ESI MS,  $^1\text{H}$  NMR, UV-vis spectroscopy, and elemental analysis. The presence of a four-charged species was unequivocally proven by the isotopic splitting from the molecular ion in the ESI MS. The experimental isotopic distributions fit perfectly with the calculated ones.

The upfield chemical shifts of the 3'' and 5'' mesitylene protons are a reliable indicator for the extent of shielding these protons receive due to the orthogonally coordinated 1,10-phenanthroline. The smallest upfield shift was found for those in **3** ( $\delta$  6.39 ppm) followed by those in **2** ( $\delta$  6.14 ppm), and the largest upfield shift was found for those in **1** ( $\delta$  6.00 ppm).

Complex **2** contains 13 redox centers in the form of eight peripheral ferrocenes, four Cu(I) phenanthroline units, and a Zinc porphyrin core and is akin to many first-generation ferrocene dendrimers reported earlier.<sup>18</sup> A study of its electrochemical properties revealed two reversible oxidation waves at 0.56 and 0.73  $V_{\text{SCE}}$ . Quantification experiments and simulation showed that the former wave was a four-electron wave, while the latter involved two electrons. A straightforward assignment of all waves could be made on the basis of electrochemical studies on **1**, **8**, and model complex **11**, which is a simple heteroleptic copper(I) complex of **8** with 2,9-bis(bromoduryl) phenanthroline.

**Scheme 3.** Representation of complexes **2**, **3**, and model complex **11**



Phenanthroline **8** and model complex **11** exhibited single oxidation waves at 0.53 and 0.57  $V_{\text{SCE}}$ , respectively. Current quantification established that only one electron was oxidatively transferred both in **8** and **11**, indicating considerable communication among the two- and three-metal centers of **8** and **11**, respectively. Such mixed valence behavior of multiple metal centers has been well established.<sup>19</sup>

With complex **1**, a reversible oxidation wave at 0.76  $V_{\text{SCE}}$  due to the  $\text{Cu}^{\text{I/II}}$  couple<sup>20</sup> and two reversible waves at 0.90 and 1.23  $V_{\text{SCE}}$  ascribable to porphyrin ring oxidation were observed. However, measuring the relative current intensity in **1** revealed that only two of the four  $\text{Cu}^{\text{I}}$  centers were oxidized. The more anodic potential of the ring oxidation in **1** as compared to that of **6a** is most likely due to the decrease in  $\pi$  electron density on the ring arising from the peripheral copper complexation.

By comparison with **11**, the oxidation of **2** at 0.56  $V_{\text{SCE}}$  could be assigned to the  $\text{Fc}/\text{Fc}^+$  couple. The wave arising at

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(20) Assignment is based on similar values obtained by us for analogous Cu(I) heteroleptic complexes: Schmittel, M.; Michel, C.; Liu, S.-X.; Schildbach, D.; Fenske, D. *Eur. J. Inorg. Chem.* **2001**, 1155–1166.

0.73 V was ascribed to the Cu<sup>III</sup> couple analogously to that in **1**. In contrast to **1**, no waves for porphyrin oxidation were detectable in **2**. It is noteworthy that only four out of eight ferrocenes and only two out of four Cu<sup>+</sup> centers were oxidized. Obviously the Cu<sup>+</sup>(8) units in **2** form a mixed valence system of two ferrocenes with the Cu<sup>+</sup> center not being involved (unlike in **11**). The oxidation of altogether only two Cu<sup>+</sup> centers in **1** and **2**, respectively, reveals an enhanced communication across the core porphyrin upon metal complexation.

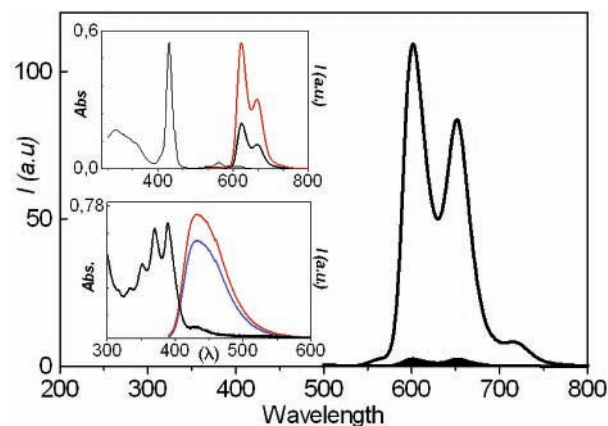
Complex **3**, being an assembly of eight anthracene units and a porphyrin chromophore, was investigated for its emission properties. Studies of the emission properties of bisanthryl phenanthroline **10** showed a single emission maximum at 431 nm irrespective of excitation at the anthracene or phenanthroline chromophores, suggesting that the anthracene chromophores interact with the phenanthroline unit producing a single emission.

Fluorescence studies of **6a** in CH<sub>2</sub>Cl<sub>2</sub> revealed that excitation at 429 nm, corresponding to the Soret absorption of the zinc porphyrin chromophore, led to emission at 605 nm with a shoulder at 649. Importantly, excitation at 279 nm (excitation of the phenanthroline chromophore) in **6a** also led to an emission at 605 and 649, amounting to an energy transfer from the phenanthroline chromophore to the porphyrin core.

In complex **3**, it was found that excitation at both the anthracene and the phenanthroline chromophores revealed no emission. Moreover, a 96% decrease in the intensity of the porphyrin emission was observed when the heteroleptic Cu(I) complex **3** was excited at 429 nm (Soret absorption). While this decrease is certainly due to quenching by CuNN<sup>+</sup> as reported earlier,<sup>21</sup> the fluorescence quenching of the anthracene chromophore in addition suggests the occurrence of a more complex process. Thus, an effective switching occurs when ligand **6a** (showing emission of the porphyrin center: ON) coordinates to phenanthrolines furnishing complex **3** (showing a quenching of the porphyrin emission: OFF).

As our approach also allows for the use of other metals (silver, zinc) in heteroleptic bisphenanthroline complex formation, the interesting road maps of switching behavior (cf. in **3**) and electronic communication (cf. in **2**) as a function of other metals are currently being investigated.

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**Figure 1.** Emission spectra of **6a** and **3** (shaded black) excited at 429 nm. Inset (top): Absorption spectrum of **6a** in CH<sub>2</sub>Cl<sub>2</sub> (black) and emission of **6a** excited at 429 nm (red) and 279 nm (black). Inset (bottom): Absorption spectrum of **10** (black) and emission spectra of **10** excited at 279 nm (red) and 369 nm (blue).

In conclusion, the new tetraphenanthroline porphyrins **6a,b** emerge as promising supramolecular synthons for the preparation of the heteroleptic multicomponent assemblies **1–3**. Given the considerable interest that CuNN<sup>+</sup> systems are receiving due to their photophysical and electronic properties, this approach should allow for rapid exploration of a wide variety of heteroleptic porphyrin aggregates such as **2** and **3**. In particular, it will be enticing to see whether the nature or the oxidation state of metal ions at the phenanthroline coordination site or in the center of the porphyrin can open/close the communication between the peripheral units and the porphyrin in order to generate gated electronic devices.

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**Supporting Information Available:** (1) ESI MS spectra with isotopic distributions, (2) fluorescence and UV spectra, (3) cyclic voltammograms, and (4) NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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