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Neocuproine-Extended Porphyrin Coordination Complexes

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The possibility of incorporating porphyrin dimers and oligomers into novel materials has drawn considerable research interest. These materials have widespread optical and electronic applications.[1−5] Desired properties of these systems include enhanced electronic conjugation and/or excitonic communication between the porphyrin units. Additional advantageous features are that the system be easily accessible synthetically and readily modifiable. The vast majority of systems previously studied connect the porphyrins covalently through the meso positions via an aryl linker.[1,5−9] Such a structural motif tends to have disrupted π overlap between the subunits.[7] Another way to assemble multichromophore systems is to fuse a π system directly onto the porphyrin fragment through the β-pyrrole positions.[10−13] Herein we present a report on a compound in which the porphyrin π system is effectively extended beyond the inner conjugated macrocycle into a neocuproine[14] molecule fused at the β-pyrrole positions.

Although most porphyrin arrays are connected via covalent linkages, noncovalent assembly offers a multitude of advantages.[2,6,8,11,15−24] Our research approach utilizes coordination chemistry to assemble the systems studied below. Modulation of the system's electronic and optical properties can be easily achieved by changing the coordinating metal (vide infra). This communication details an investigation of the spectroscopic properties of **1** and its Zn^{II} and Cu^{I} complexes, **2** and **3**, respectively (Figure 1). Although Cu^{I} and Zn^{II} are isoelectronic, marked differences in the optical and photophysical properties of **2** and **3** are observed.

Compound **1** is structurally similar to Crossley and co-worker's "molecular alligator clip".[11] Crossley's molecule has a phenanthroline moiety separated from a *meso*-tetraaryl porphyrin by three fused six-membered rings.[11] These units in **1**, however, are separated by only one six-membered ring. This design feature is expected to enhance the electronic coupling between the porphyrin and the metal-binding phenanthroline group, and to improve the solubility of **1** relative to Crossley's molecule. The phenanthroline moiety of **1** has methyl groups at its 2 and 9 positions, thus limiting the conformational ambiguity at the central metal. The 2,9 positions of the phenanthroline unit are easily modifiable synthetically and sterically influence the coordination geometry in bis(phenanthroline) metal complexes.[25−27] By varying these substituents, we can thus carefully study the effect that changes in geometry about the linker metal ion have on interactions between the chromophores − a feature not accessible in similar systems studied to date.[2,11,17]

The synthetic strategy used to prepare **1** is similar to that employed by Crossley[11] and Pandey,[28] where a Schiff base condensation affords the fused system. The free-base monomer, *meso*-tetramesitylporphyrinneocuproine (H_2TMPNc, **1**) was synthesized in five steps from Cu(II) *meso*-tetramesitylporphyrin, CuTMP (see Supporting Information).[29] The compound H_2TMPNc was characterized by ^{1}H NMR[30] and FAB MS. Compounds **2** and **3** are formed cleanly upon addition of $[Zn(OAc)_2]\cdot 2H_2O$ or $[Cu(MeCN)_4(PF_6)]$ to a solution of **1**. Complexes **2** and **3** were identified by ESI MS.[31]

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(30) ^{1}H NMR ($CDCl_3$) [δ(ppm)], **1**: 1.824 (12H, s, *ortho*-aryl-C-$\mathbf{H_3}$), 1.903 (12H, s, *ortho*-aryl-C$\mathbf{H_3}$), 2.642 (6H, s, *para*-aryl-C$\mathbf{H_3}$), 2.887 (6H, s, *para*-aryl-C$\mathbf{H_3}$), 3.053 (6H 2,9-phen-C$\mathbf{H_3}$), 7.300 (4H, s, *meta*-aryl-**H**), 7.470 (4H, s, *meta*-aryl-**H**), 7.656 (2H, d, 3,8-phen-**H**), 8.569 (2H, s, pyrrole-β-**H**), 8.837 (4H, dd, pyrrole-β-**H**), 8.927 (2H, d, 4,7-phen-**H**).
(31) Mass spectral data: FAB, **1**, observed *m/z* 1015 $(M + H)^+$ and 1147 $(M + Cs)^+$, calcd for $C_{70}H_{62}N_8$, 1014; ESI pos, **2**, observed *m/z* 2094 $(M + e)^+$, calcd for $C_{140}H_{124}N_{16}Zn$, 2094; **3**, observed *m/z* 2093 $(M)^+$, calcd for $C_{140}H_{124}N_{16}Cu$, 2093.

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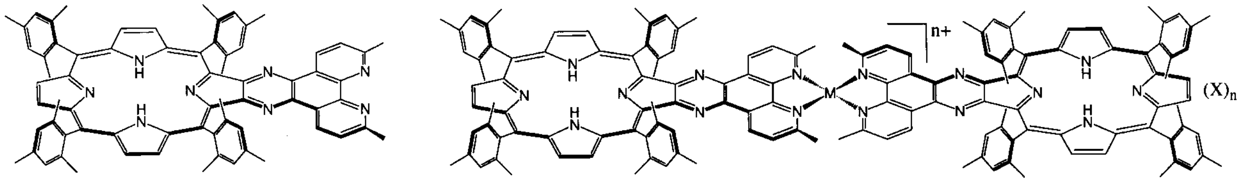

1; H_2TMPNc

2; M = Zn, n = 2, X = OAc^-
3; M = Cu, n = 1, X = PF_6^-

Figure 1. Schematic depiction of the molecules investigated.

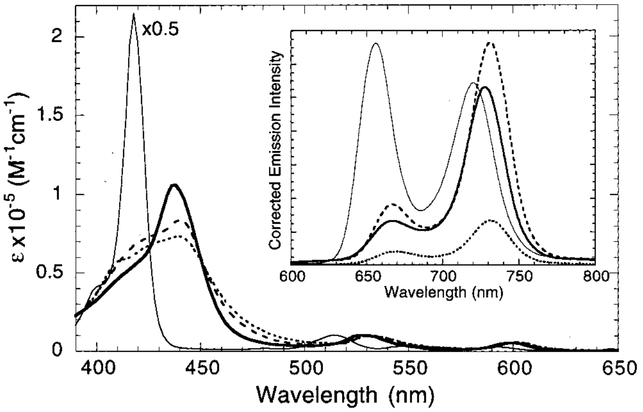

Figure 2. Absorption spectra in CH_2Cl_2 at room temperature for compounds H_2TMP (thin solid line), **1** (thick solid line), **2** (long dashes), and **3** (short dashes). Inset: Corrected emission spectra in CH_2Cl_2 at room temperature (same line-type assignments). Emission intensities are normalized to identical OD values at excitation wavelength.

Relative to free-base *meso*-tetramesitylporphyrin (H_2TMP), there are notable differences observed in the absorption spectrum of **1** (Figure 2). Upon fusing the neocuproine moiety to the porphyrin, the entire visible spectrum shifts to lower energy, the high-energy shoulder adjacent to the *B* band increases in intensity, and the *Q*(0,0) transitions are diminished in intensity relative to the *Q*(1,0) bands. The shift to lower energy is largest in the *B* transition (1092 cm^{-1}), while the $Q_y(1,0)$ and the $Q_x(1,0)$ bands red shift by 444 and 227 cm^{-1} respectively. The shape and red shift observed in the *B* band region is indicative of increased delocalization of the porphyrin π system.[3,5,10,23] The low intensity of the *Q*(0,0) transitions of **1** may result from a change in the ordering of the b_1 and b_2 orbitals.[32] It is evident from these data that the porphyrin chromophore is well-coupled electronically to the neocuproine π system.

Upon formation of the complexes **2** and **3**, effects at both the *B* and *Q* spectral regions are observed relative to **1** (Figure 2).[33] The Zn^{II} dimer exhibits intermediate broadening of the *B* band while that of the Cu^{I} dimer is the broadest. The broadness of the *B* band is a measure of the degree of π delocalization in multiporphyrin systems.[3,5] The full-width at half-maximum (fwhm) values for **1**, **2**, and **3** are 1808, 2946, and 3261 cm^{-1}, respectively. Both metal complexes display a *B* band maximum that is slightly lower in energy (104 cm^{-1}) with respect to that of **1**. Although the $[Cu(dmp)_2]^+$ complex[14] displays an MLCT absorption band at 454 nm ($\epsilon = 7950$ M^{-1} cm^{-1}) in CH_2Cl_2,[34] the analogous band in **3** is apparently masked by the large *B* band absorption (Figure 2). The *Q* bands of **2** and **3** do not change shape appreciably compared to those of **1**, but are red shifted by 214 and 111 cm^{-1}, respectively for the *x* and *y* transitions. Studies reported by other researchers on porphyrinic dimers assembled around a central metal ion have demonstrated similar results.[2,35] Such observations are indicative of a further extension of the chromophore's conjugated π system into the transition metal and possibly into the neighboring chromophore.[35] Due to the predicted porphyrin center-to-center distance in **2** and **3** of $\approx$23 Å, excitonic coupling effects are not likely causing the observed spectral phenomena.[36]

The corrected *Q* band emission spectra of H_2TMP and compounds **1**−**3** are shown in Figure 2. Consistent with the absorption spectra, the emission spectrum of **1** is also red shifted relative to H_2TMP.[37] This further supports the hypothesis that there is exocyclic extension of the porphyrin's conjugated π system.[3,5,10] The Cu^{I} dimer displays efficiently quenched emission (integrated intensity 14% of H_2TMP) relative to the parent monomer, **1** (integrated intensity 57% of H_2TMP). Electron transfer was considered as a possible mechanism, however, both oxidative- and reductive-quenching processes are predicted to be thermodynamically uphill by approximately 600 and 240 mV, respectively.[38] Thus, the quenching is assigned to an energy-transfer mechanism between the porphyrin excited state and the $Cu^{I}(dmp)_2$ moiety.[39] At room temperature in CH_2Cl_2, the $[Cu(dmp)_2]^+$ complex is emissive ($\lambda_{em} = 740$ nm; $\tau = 85$ ns)[34] from at least two states that have been assigned as a ^{1}MLCT and a ^{3}MLCT state.[40] Interestingly, the emission of the Zn^{II} dimer (integrated intensity 69% of H_2TMP) is slightly more intense than that of **1**.

A porphyrin-based molecule capable of exocyclic metal binding (**1**) has been prepared utilizing a small number of high-yield reactions. The modular approach used to construct these dimeric complexes can be applied to build higher-order arrays with well-defined structural and tunable optical properties.

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Supporting Information Available: A schematic of the synthesis of **1**, absorption spectra of H_2TMP and **1**, and MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) UV/vis (CH_2Cl_2) [λ_{max} (nm) (log ϵ)] H_2TMP: 418 (5.36), 514 (4.25), 546 (3.74), 590 (3.72), 646 (3.45); **1**, 438 (5.04), 526 (4.00), 598 (3.70); **2**, 440 (4.92), 532 (4.00), 602 (3.70); **3**, 440 (4.86), 532 (4.00), 602 (3.70). Extinction coefficients are ±5%.

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(37) Corrected emission spectra (CH_2Cl_2) [λ_{ex}; λ_{em} (nm)], H_2TMP, 514; 655, 718.5; **1**, 528; 665, 726.5; **2**, 532; 666, 729.5; **3**, 532; 666.5, 730.

(38) Driving forces, $\Delta G°$, were determined as follows: $\Delta G° = [E_{1/2}(D^{\bullet+}/D) - E_{1/2}(A/A^{\bullet-}) - E_{0,0}]$; $E_{0,0}$ was taken as 1.89 eV, and electrochemical measurements in CH_2Cl_2 provide the following values: $[Cu(dmp)_2]^{2+/+} = 0.870$ V; $[Cu(dmp)_2]^{+/0} = -1.390$ V (irrev. in CH_2Cl_2); $[H_2TMPNc]^{\bullet+/0} = 1.100$ V; $[H_2TMPNc]^{0/\bullet-} = -1.260$ V.

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