

Synthesis, Characterization, and Preliminary Host–Guest Binding Studies of Porphyrinic Molecular Squares Featuring *fac*-Tricarbonylrhenium(I) Chloro Corners

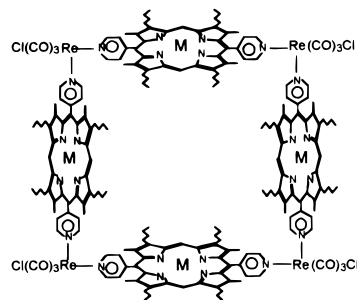
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The stoichiometric combination of rigid or semirigid difunctional ligands with appropriate cis-coordinating metal centers has been shown to produce macrocyclic tetrametallic assemblies ("molecular squares") in remarkably high yield. The 30 or so available squares have been constructed from platinum, palladium, nickel, tungsten, and rhenium precursors and have been assembled in both homometallic and heterometallic form.^{1–3} Depending on cavity size and overall charge, selected molecular squares are capable of functioning as solution-phase hosts for either complex anionic guests^{3a} or neutral aromatic guests where binding is achieved, respectively, via coulombic or hydrophobic interactions. While host–guest binding is typically monitored via NMR spectroscopy, detection based on host luminescence has also been demonstrated.³ Particularly versatile in this respect are molecular squares derived from $\text{Re}(\text{CO})_5\text{Cl}$. These emit from comparatively long-lived metal-to-bridging-ligand charge-transfer (MLCT) excited states. The available square cavity sizes (i.e., minimum van der Waals diameters) range from ca. 3 Å (pyrazine bridged species)^{3a} to ca. 16 Å (1,4-phenyl bis(picolinoate)-bridged species).^{3c} We reasoned that even larger cavity sizes could be accessed by utilizing 5,15-meso-substituted porphyrins as bridging ligands. If tricarbonylrhenium(I) chloro moieties are used as corners, the resulting squares should remain luminescent but with emission coming from porphyrin-localized excited states. We additionally reasoned that porphyrin metalation would provide a basis for single or multipoint guest binding via axial ligation. We note that squares based on 5,10- and 5,15-substituted porphyrins and Pd(II) corners have been reported by Lehn and Drain.⁴ In addition, flexible alkyne-linked tetraporphyrin assemblies have been reported by Anderson.^{5a} In the presence of appropriate guests, these can adopt complementary tub-shaped geometries.

Compound **1** was obtained as a maroon microcrystalline powder in high yield by combining 169 mg (0.227 mmol) of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl)-porphyrin,^{6,7} **2**, with 82 mg (0.227 mmol) of $\text{Re}(\text{CO})_5\text{Cl}$ dissolved in 100 mL of freshly distilled 4:1 tetrahydrofuran–



1 ($\text{M} = 2\text{H}^+$), **3** ($\text{M} = \text{Zn}^{\text{II}}$)

toluene as solvent and heated to reflux for 48 h under $\text{N}_2(\text{g})$. Following cooling, 100 mL of hexanes was added to encourage product precipitation. The product was isolated at 86% yield by vacuum filtration, washed with hexanes, and dried *in vacuo*. ^1H NMR indicates complete coordination of available pyridyl fragments. Elemental analysis and FAB mass spectrometry (Supporting Information) were used to verify that tetraporphyrin species are formed.

The analogous tetrazinc(II)-metalated square, **3**, was obtained in nearly quantitative yield by first dissolving **1** in a minimum volume of CH_2Cl_2 , adding a 5 mL volume of saturated Zn^{II} acetate in methanol, and stirring for 4 h. **3** was precipitated by adding a large volume of methanol/water mixture. The product was isolated by vacuum-filtration, washed with water and then ether, and dried *in vacuo*. ^1H NMR, elemental analysis, and mass spectral results are all in agreement (Supporting Information) with formation of the metalated porphyrin square.

The tetraporphyrin squares are highly soluble in CHCl_3 , tetrahydrofuran, and CH_2Cl_2 but insoluble in water. These squares also are enormously chromophoric, especially in the porphyrin Soret region (~ 400 – 420 nm). Square formation induces a bathochromic shift of ca. 6 nm in the Soret region, consistent with net removal of electron density from the porphyrin π system upon rhenium–pyridine bond formation. Near-UV fluorescence excitation studies (MLCT region) established that rhenium corners serve only a structural, rather than a direct photophysical, role within the square framework. Single photon counting experiments yielded excited state lifetimes of 3.0 ns for **1** and 2.4 ns for **3**. In contrast, the analogous tetrarhenium cyclophane species typically exhibit excited state (MLCT) lifetimes of ca. 100 ns.^{3b,c} The difference is potentially significant for luminescence-based molecular recognition and sensing applications: The short-lived porphyrin square excited states will tend to respond only to species bound internally or externally as guests. The longer lived cyclophane excited states, on the other hand, also have the potential to interact with putative guests via nonspecific diffusional encounters.

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(7) The alkyl groups are essential for both porphyrin ligand and square solubility.

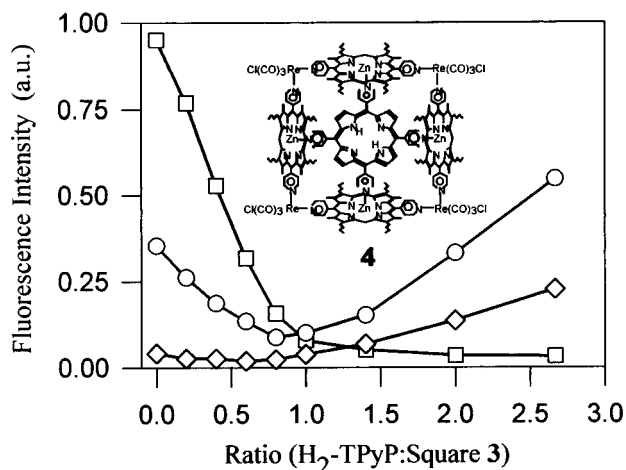


Figure 1. Fluorescence emission curves of pentaporphyrin host-guest complex **4** formation in CH_2Cl_2 solution. $[\mathbf{3}] = 1 \times 10^{-6} \text{ M}$. Curves correspond to host emission at 586 nm (\square), host-guest mixed emission at 654 nm (\circ), and guest fluorescence at 710 nm (\diamond) with excitation at 426 nm.

Luminescence measurements show that both squares are unresponsive to millimolar additions of toluene. Millimolar additions of pyridine, on the other hand, lead to significant red shifts in the fluorescence of **3**. From the known fluorescence response of (monomeric) Zn^{II} porphyrin species⁸ and the lack of response by **1** to pyridine addition, the effect observed for **3** is clearly associated with axial ligation of porphyrin-bound zinc by pyridine.

The dimensions, pre-organization, and multiple binding site availability of **3** suggest the possibility of strong host-guest complex (**4**) construction. The notion is further supported by (1) modeling studies that suggest open-ended box type conformations for **1** and **3** (i.e. pairs of approximately cofacial porphyrins) and (2) related multi- Zn^{II} porphyrin studies which demonstrate dramatic enhancements in host-guest binding strength based on multipoint guest ligation.⁵ The results of a fluorescence titration of a micromolar Zn^{II} porphyrin square solution with 5,10,15,20-tetrapyrrolylporphyrin ($\text{H}_2\text{-TPyP}$) are shown in Figure 1. Addition of $\text{H}_2\text{-TPyP}$ results in a loss of fluorescence intensity from **3**. Intensity quenching at the fluorescence maximum for **3** (586 nm) is virtually complete ($\sim 90\%$) for a 1:1 guest-host ratio, as one would expect for efficient interior binding of $\text{H}_2\text{-TPyP}$.⁹ When this ratio is exceeded, a pronounced growth in free $\text{H}_2\text{-TPyP}$ fluorescence at 654 and 710 nm is observed. From additional measurements at lower host concentrations, the host-guest association constant is $4 \times 10^7 \text{ M}^{-1}$.¹⁰ In contrast, binding constants typically are

on the order of 10^3 M^{-1} for assemblies which can form only one pyridine/ Zn -porphyrin bond (as would be the case, for example, for $\text{H}_2\text{-TPyP}$ binding to the square exterior).

Further insight into $\text{H}_2\text{-TPyP}/\mathbf{3}$ binding is provided by electronic absorption measurements. At micromolar concentrations, 1:1 mixtures exhibit an essentially complete loss of host Q band features at 542 and 576 nm. These are replaced, however, by host-derived Q-band absorbances at 550 and 584 nm. The absorption studies are consistent, therefore, with a binding geometry which entails pyridine ligation of all available Zn^{II} sites.^{5,8,10} Spectral changes in the Soret region, while less well resolved, also are indicative of complete ligation.

Finally, absorption and emission studies of **3** in the presence of **2** provide compelling evidence for formation of another pentaporphyrin assembly, **5** (see synopsis). Fluorescence quenching studies in the micromolar range in CH_2Cl_2 as solvent establish the host:guest stoichiometry as 1:1 ($K = 3 \times 10^6 \text{ M}^{-1}$). Consistent with a proposed structure involving only two-point binding, stoichiometric host-guest complex formation quenches only about half the host luminescence. Further quenching (presumably associated with exterior binding) is encountered only when the guest concentration is increased to the millimolar level.

We intend to report shortly on sensing and molecular recognition applications involving higher order assemblies of the porphyrin molecular squares, **1** and **3**. We additionally suggest, however, that all-porphyrin guest-host assemblies such as **4** and **5** may prove useful as model systems for excited-state energy transfer applications (e.g., artificial photosynthetic systems).

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Supporting Information Available: A table of data for the characterization of **1** and **3**, low-resolution fast atom bombardment (FAB) mass spectra of squares **1** and **3**, electronic absorption spectra of **1** and **3**, and fluorescence curves for formation of **4** and **5** (6 pages). Ordering information is given on any current masthead page.

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(9) Although large, the binding constant obtained for $\text{H}_2\text{-TPyP}$ within this cavity is significantly smaller than the value obtained for binding to the flexible cavity described in ref 5a. One likely cause of this difference is the inherent rigidity of the transition metal square assembly. We suggest that $\text{H}_2\text{-TPyP}$ experiences a tight, but not perfect, fit within the sterically constrained square cavity, with consequent diminution of the binding affinity.

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