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ON/OFF Red Emission from Azaporphine in a Coordination Cage in Water

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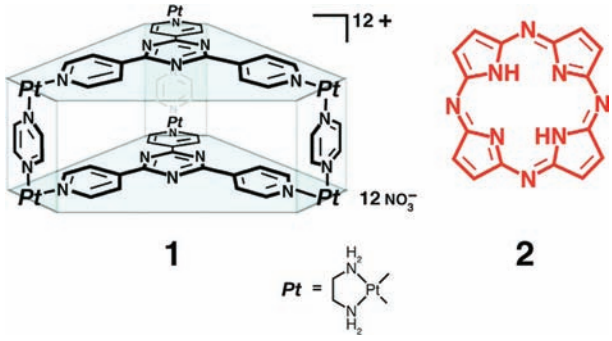
The utility of many organic dyes as chemosensors, biological labels, and light-emitting materials is limited by poor solubility and, in the case of fluorescent applications, the formation of nonemissive aggregates.[1] Sequestering dyes in protective host molecules is not only an effective method of enhancing the photo-optical properties but can also increase the effective solubility, especially in aqueous solution. Whereas common organic cages (e.g., cyclodextrins,[2] calix[*n*]arenes,[3] and cucurbiturils[4]) can form emissive host−guest complexes, coordination cages, such as columnar host **1**, effectively quench guest emission. The hydrophobic cavity of cage **1** and its derivatives accommodates a variety of emissive guests,[5,6] but the host−guest complexes remain nonemissive. As the major nonradiative pathway involves energy transfer from electron-rich aromatic guests to the low-lying LUMO of the triazine ligand panels,[7] we employed an electron-deficient fluorophore to prevent charge-transfer (CT) interactions.



Tetraazaporphine (TAP) (**2**) is the fundamental porphine derivative intermediate between porphyrins and phthalocyanines, which are important supramolecular components because of their robust and useful photophysical and electrochemical properties.[8] Unlike its more famous siblings, TAP has seen little use, but it displays similar properties and has considerable potential in functional materials.[9−11] We have found that, in striking contrast to porphyrin guests, **2** strongly fluoresces when in the cavity of **1**. Additionally, encapsulation within the highly cationic host enhances the acidity of the interior protons, so simple addition of NEt_3 quenches the TAP emission via deprotonation.

When purple **2** (3 molar equiv) was suspended in a colorless D_2O solution of **1** (10 mM) and heated at 80 °C for 6 h, the solution dramatically changed to dark-red-purple, indicating the formation of the host−guest complex **1**⊃**2**. After filtration of excess **2**, the

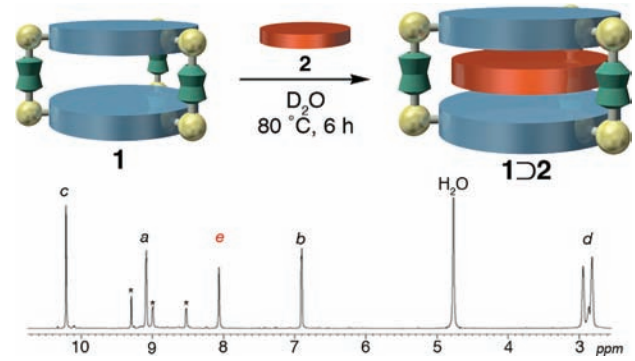


Figure 1. (top) Schematic illustration of the formation of **1**⊃**2** and (bottom) ^{1}H NMR spectrum (500 MHz, rt) of **1**⊃**2** in D_2O. Signal assignments for **1**⊃**2**: *a* = PyH_α; *b* = PyH_β; *c* = pyrazine; *d* = en; *e* = **2**, and * = residual empty cage **1**.

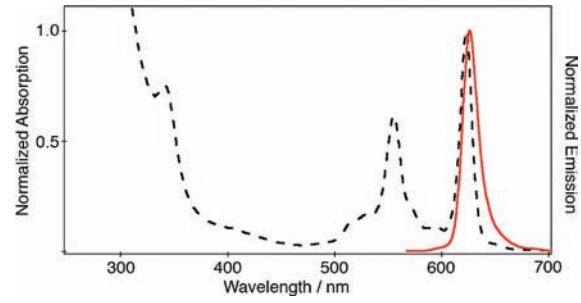


Figure 2. UV−vis (dashed line) and emission (red line) spectra of **1**⊃**2** in H_2O.

^{1}H NMR spectrum of the dark-red-purple solution revealed that the signals from the eight TAP protons were highly upfield-shifted ($\Delta\delta \approx 1.5$ ppm) as a result of shielding by the cage aromatic panels (Figure 1). The guest protons appeared as a singlet, as the TAP can rotate within the confines of the D_{3h}-symmetric host. The single band observed in a diffusion-ordered spectroscopy (DOSY) NMR experiment (log $D = -9.74$) emphasizes that **2** remains within **1** and that **1**⊃**2** diffuses as a single molecular entity. ^{1}H NMR integration and coldspray ionization mass spectrometry (CSI-MS) confirmed that **1**⊃**2** was formed in 75% yield.

Upon sequestration of TAP within cage **1**, the complex **1**⊃**2** was highly water-soluble and emitted red fluorescence with quantum yield $\phi_f = 0.17$ (Figure 2). **2** usually suffers from poor solubility and is prone to quenching from aggregation.[9] Within cage **1**, the emission was red-shifted by 8 nm relative to that in $CHCl_3$ but remained sharp ($\Delta\lambda_{1/2} \approx 16$ nm). The excitation spectra of **1**⊃**2** and free **2** are effectively identical, indicating that cage **1** is not involved in the emission process. Previously, guest emission has

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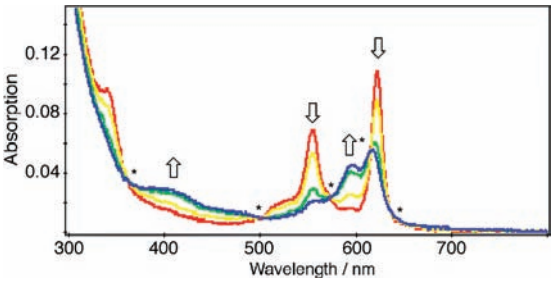

Figure 3. UV−vis titration of **1**⊃**2** with NEt_3 in H_2O. The red, yellow, green, and blue curves are for addition of 0, 55, 555, and 5555 equiv of NEt_3, respectively. Isosbestic points are indicated by asterisks.

always been severely or completely quenched upon encapsulation by coordination cages.[6] Efficient energy transfer into host−guest CT states is a major pathway in the relaxation of excited guest fluorophores,[7] but for **2**, host−guest CT interactions are minimal, as evidenced by the lack of spectral broadening or CT bands in the absorption and emission spectra [Figure 2; also see the Supporting Information (SI)]. Within the protecting confines of cage **1**, the emission lifetime of **2** increases to 5.9 ns, indicating potential applications in "supramolecular radiative decay engineering".[12]

Upon addition of NEt_3, the emission of **1**⊃**2** in H_2O was strongly quenched. The quenching by NEt_3 took place only in **1**⊃**2**, whereas noticeable quenching for free **2** was not observed in $CHCl_3$. The quenching did not follow bimolecular Stern−Volmer kinetics and, more importantly, was accompanied by significant UV−vis spectral changes (Figure 3). The solution color changed from purple to blue as the two Q bands at 623 and 556 nm were reduced in intensity and a new band appeared at 597 nm, corresponding to an increase in the TAP symmetry from D_{2h} to D_{4h}.[11] Such symmetry changes are typical upon metal complexation or deprotonation. Several isosbestic points were clearly visible in the UV−vis spectra, evidencing a one-to-one transformation.[13] Stabilization of the TAP anion, presumably through electrostatic interactions with highly cationic (12+) **1**, enhances the acidity of the interior TAP protons, giving rise to new host−guest CT bands at 450 and 675 nm. ^{1}H NMR analysis of the blue solution further indicated that the TAP anion remained inside cage **1** (Figure S18 in the SI). The deprotonated anionic TAP has high symmetry, D_{4h}, and the TAP protons appeared as a single singlet but were highly upfield-shifted ($\Delta\delta \approx 0.6$ ppm) as a result of the increased electron density. Addition of HNO_3 turned the solution back to purple and restored the red TAP emission.[14] The acid/base ON/OFF switching of **1**⊃**2** fluorescence was repeatable (Figure S19 in the SI)

In contrast to NEt_3, encapsulation of **2** by coordination cage **1** reduced the quenching of TAP emission by DMF and DMSO. DMF and DMSO are known fluorescence quenchers and efficiently quenched **2** in $CHCl_3$ following biomolecular Stern−Volmer kinetics ($k_q = 1.2 \times 10^8$ and 1.4×10^8, respectively; see Figure S13 and Table S1 in the SI). When **2** was protected inside cage **1**, direct contact between the excited TAP and quencher was obstructed, and the quenching rate constants decreased ($k_q = 1.6 \times 10^7$ and 4.4×10^7, respectively).

Molecular modeling of **1**⊃**2** (Figure S6 in the SI) emphasized the lack of solvent access to the faces of TAP but also showed open side portals. In the case of NEt_3, the interior protons are fully protected, so it is likely that **2** partially or fully dissociates from **1** before deprotonation.

In summary, sequestering the red-fluorescent dye tetraazaporphine **2** within coordination cage **1** endowed high water solubility and prevented dye aggregation in the solution and solid state (see the SI). Unlike typical aromatic hydrocarbon guests, the electron-deficient TAP did not form a CT complex with cage **1** and remained emissive. The highly cationic cage **1** protected TAP from small-molecule quenching but facilitated the deprotonation of **2**. The present results demonstrate that coordination cages can be suitable hosts for fluorescent dye molecules and envision their application as new red-emissive materials.

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Supporting Information Available: Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Further addition of base did not result in a second change, and it is unclear whether one or both of the TAP protons were removed.
(14) HNO_3 was used, as NO_3^- anions are requisite for the water solubility of cage **1**. Other bases, such as NaOH, were employed and displayed similar acid/base properties with respect to deprotonation of caged TAP.

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