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Calix[2]-*m*-benzo[4]phyrin with Aggregation-Induced Enhanced-Emission Characteristics: Application as a Hg^{II} Chemosensor

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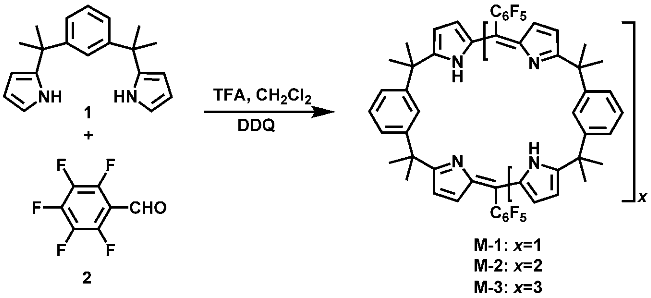
In recent years, solid-state fluorescent materials have received much attention in diverse fields, such as fluorescent biological labels, sensors, and light-emitting diodes.[1] Many conjugated organic luminophores are highly emissive in dilute solutions, however, when fabricated into thin films, they suffer an aggregation-caused quenching (ACQ) effect, which limits their practical applications.[1] To solve this problem, recently, some organic molecules, which show an intense emission in the aggregated state, whereas they exhibit almost no or weak emission in dilute solutions, were reported. This unique phenomenon is widely researched as aggregation-induced emission (AIE)[2] and aggregation-induced enhanced emission (AIEE).[3] However, the potential utility of this phenomenon has not been explored in macrocycles. On the other hand, molecular sensors for Hg^{II} ions have received considerable attention due to the extremely toxic impact exerted by Hg^{II} on our environment.[4] Many efforts have been made to design various chemosensors specific to Hg^{II} ions.[5] The major challenges involved in the creation of Hg^{II} sensors are lack of selectivity and specificity.

Calixphyrins, polypyrrolic macrocycles, are known for the coordination chemistry,[6] but reports on metal-ion sensing are very rare. Herein, we wish to report the AIEE characteristic of a calixbenzophyrin-derivative, **M-1**, and utilize this novel property for probing Hg^{II} ions both in aqueous solution and in the solid state.

The syntheses of calixbenzophyrins are outlined in Scheme 1. The synthetic methodology followed here is basically an acid-catalyzed condensation reaction. Stirring a solution of **1**[7] with pentafluorobenzaldehyde in dichloromethane in the presence of trifluoroacetic acid (TFA) followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) resulted in calix[*n*]-*m*-benzo[*m*]phyrins ($n=2,3,4$; $m=4,6,8$) in 20% (**M-1**), 10% (**M-2**), and 5% (**M-3**) yield, respectively. All the macrocycles were fully characterized by electronic, FAB-MS, and NMR spectral studies, and the structure of **M-1** was finally confirmed by single-crystal X-ray-diffraction analysis.[8] All the derivatives are soluble in common organic solvents, but insoluble in water.



Scheme 1. Syntheses of calix[*n*]-*m*-benzo[*m*]phyrins.

A solution of **M-1** in dilute acetonitrile shows an absorption band at 434 nm, which arises from the π–π* transition of the dipyrrin moiety.[8] The emission spectrum shows a band at 539 nm. We observed an anomalous behavior in the emission spectrum of **M-1** upon addition of various percentages of water (0–90%), upon which the band at 539 nm is intensified with a bathochromic shift to 550 nm (Figure 1, left). Because water is not a good solvent for **M-1**, addition of water promotes efficient calixphyrin self-aggregation, which enhances the emission; in other words, **M-1** is AIEE active. The trajectory of the intensity change suggests that the molecularly dissolved **M-1** starts to congregate at a water fraction of 50% and the population of the aggregate continues to increase as the water fraction increases from 50 to 90% (Figure 1, left, inset). To have a quantitative picture, we estimated the photoluminescence (PL) quantum yields (Φ_F) of **M-1** in pure acetonitrile and in a 1:9 acetonitrile/

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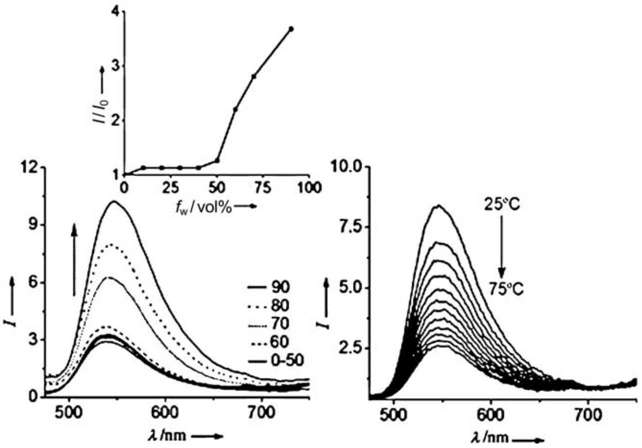

Figure 1. Left: Emission spectra of **M-1** (8.7 μm) in acetonitrile/water mixtures with different fractions of water ($f_w = 0–90$ vol %). The inset shows the changes in emission intensities (I) of **M-1** with increased water contents. I_0 = intensity in pure acetonitrile. Right: Temperature effect on the emission peak intensity of **M-1** in acetonitrile/water (1:9 v/v, λ_{ex} = 440 nm).

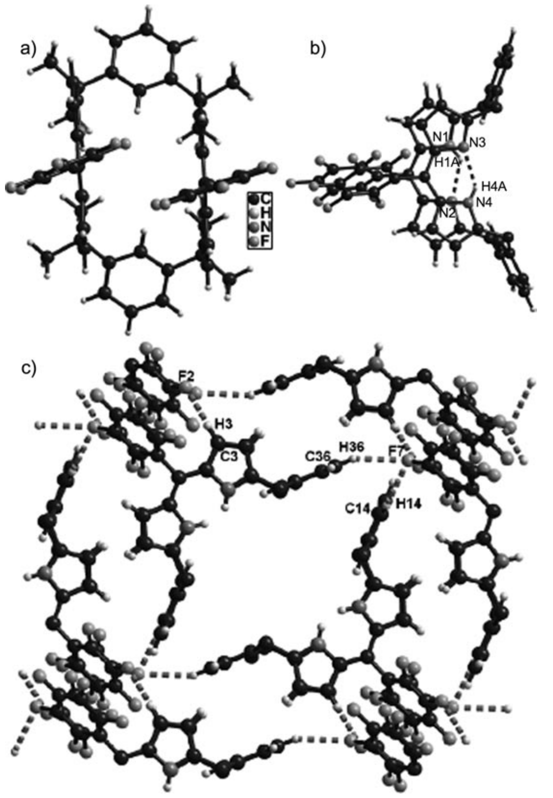

Figure 2. Single-crystal X-ray structure of **M-1**. a) Top view, b) side view, and c) 2-D array.

water mixture. The Φ_F values were found to be 0.8×10^{-3} and 3.36×10^{-3}, respectively, which is 4.2 fold higher than that in a pure acetonitrile. A similar trend was observed in the previously studied AIEE systems.[9] Basically, when the water content is increased to 50%, it reaches a critical point, at which addition of a small amount of water significantly weakens the solvating power of the solvent mixture. This greatly populates the aggregates and leads to rapid increase in the emission intensity. The enhancement in emission also eliminates the possible formation of delocalized excitons or excimers, which usually quenches the emission.[9]

Further, the temperature effect on the fluorescence spectra of **M-1** in an acetonitrile/water mixture (1:9 v/v) was also investigated (Figure 1, right). Upon increasing the temperature, the aggregate state of the compound at low temperatures changed to a monomer-like state at high temperatures. This proves that aggregation restricts intramolecular rotations (IMR) of the pentafluorophenyl group; this rigidifies the molecule and hence makes it more emissive. The single-crystal X-ray studies further confirm that the IMRs in **M-1** have indeed been restricted during aggregation.

The single-crystal X-ray structure of **M-1** is shown in Figure 2. The dipyrrin units contain both the amine and imine pyrrole nitrogen atoms that form intramolecular hydrogen-bonding interactions with the distance and angles of N1–H1A···N2 and N3···H4A–N4 are 2.08 Å, 130° and 2.02 Å, 135°, respectively (Figure 2b). The *m*-phenyl units and the *meso*-pentafluorophenyl groups are deviated from the mean dipyrrin plane by 89.92 and 71.9°, respectively.[8] The fluorine atoms in the *meso*-pentafluorophenyl groups generate intermolecular hydrogen-bonding interactions, in which F2 interacts with the pyrrolic β-CH to form a self-assembled dimer (C3–H3···F2: 2.57 Å and 154°). In addition to the self-assembled dimer, F7 generates a 1-D array. To generate such interactions, three molecules of **M-1** are involved: F7 in the first molecule interacts both with C14–H14 in one of the *m*-phenyl units present in the second molecule, to form the second self-assembled dimer, and further with C36–H36 in the *m*-phenyl group of the third molecule to form the 1-D array with the distance and angles of 2.62 Å, 146° and 2.66 Å, 155°, respectively.[8] By combining these two self-assembled dimers and the 1-D array, **M-1** generates the 2-D supramolecular assembly shown in Figure 2c. Overall, the *meso*-pentafluorophenyl groups are effectively packed by the intermolecular hydrogen-bonding interactions; this restricts the intramolecular rotation of these units in the solid state and leads to further emission enhancement, as observed in the aggregated state.

The efficient emission of **M-1** in the aggregated state prompted us to explore the potential application as chemosensors. All the spectroscopic measurements were carried out in 90% aqueous acetonitrile solutions at pH 7.4 (10 mm phosphate buffer containing 2 mm NaCl). Compound **M-1** was treated with ten equivalents of various metal ions, such as Cu^{II}, Cd^{II}, Co^{II}, Cr^{III}, Fe^{III}, K^{I}, Li^{I}, Ni^{II}, Pb^{II}, Mn^{II}, Zn^{II}, and Hg^{II}, to test the sensing ability. Among the tested metal ions, only Hg^{II} exhibited effective fluorescence quenching (Figure 3a). To have a quantitative picture, various equivalents of Hg^{II} ions were gradually added to the **M-1** solution. As the concentration of Hg^{II} ions was increased, the emission intensity gradually quenches (Figure 3b). Also, the competitive-recognition studies reveal that Hg^{II} ions could

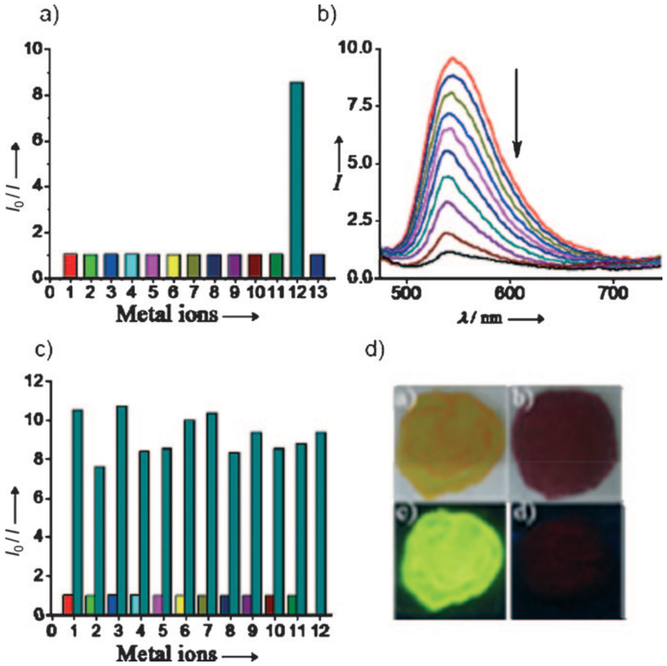

Figure 3. a) Fluorescence response of **M-1** (8.7 μm) in acetonitrile/water (1:9 v/v) at pH 7.4 (10 mm phosphate buffer containing 2 mm NaCl) in the presence of ten equivalents of various metal ions: 1) Cu^{II}, 2) Cd^{II}, 3) Co^{II}, 4) Cr^{III}, 5) Fe^{III}, 6) K^{I}, 7) Li^{I}, 8) Ni^{II}, 9) Pb^{II}, 10) Mn^{II}, 11) Zn^{II}, 12) Hg^{II}, 13) blank. b) The emission changes of **M-1** (8.7 μm) upon titration with Hg^{II} ions in acetonitrile/water (1:9 v/v) at pH 7.4 ($\lambda_{ex}=480$ nm). c) Metal ion selectivity of **M-1** (8.7 μm) in acetonitrile/water (1:9 v/v) at pH 7.4. The small, colored bars represent the changes in the emission intensity of a solution of **M-1** with 100 equivalents of the cation of interest: 1) Cu^{II}, 2) Cd^{II}, 3) Co^{II}, 4) Cr^{III}, 5) Fe^{III}, 6) K^{I}, 7) Li^{I}, 8) Ni^{II}, 9) Pb^{II}, 10) Mn^{II}, 11) Zn^{II}, 12) Hg^{II}. The turquoise bars show the fluorescence change that occurs upon addition of ten equivalents of Hg^{II} to the solution containing **M-1** and the respective cation. d) The solid-state color change of **M-1** upon addition of Hg^{II} ions under visible light (top) and illumination under UV light (bottom, $\lambda_{ex}=365$ nm).

be detected even in the presence of 100 equivalents of other metal ions (Figure 3c). The changes in the emission-spectral data indicate a 1:1 binding mode[8] with an association constant of $4.2\times10^{4}\,\text{M}^{-1}$ and the calculated detection limit is 1.4 ppm. The results were further supported by MALDI-TOF mass-spectral analysis, in which a peak corresponding to the 1:1 complex was observed.[8] The reversibility of the binding mode was examined by the addition of I^- ions.[8] These interesting results encouraged us to investigate the sensing ability of **M-1** in the solid state. Figure 3d shows the color change of **M-1** upon addition of Hg^{II} ions in the solid state. The color of the ligand changes from yellow in the uncoordinated state to brick red in the mercury-bound form. Upon irradiation of UV light, an intense pale green fluorescence, which quenches effectively in the presence of the Hg^{II} ions, was observed. This result proves that **M-1** is an excellent candidate for solid-state detection of Hg^{II} ions.

Finally, the aggregate formation was confirmed by high-resolution (HR)-TEM analysis. The images of **M-1** in the absence and presence of Hg^{II} ions are shown in Figure 4.

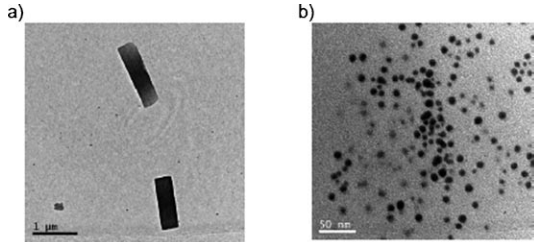

Figure 4. HR-TEM images: a) **M-1** (scale bar = 1 μm) and b) **M-1** in the presence of ten equivalents of Hg^{II} ions (scale bar = 50 nm).

The microrod-shaped aggregates of **M-1** with a length of 2 μm (Figure 4a) dissociate into nanospheres, with a uniform diameter of 12 nm, when ten equivalents of Hg^{II} ions were added to **M-1** (Figure 4b).

In summary, we have synthesized three hybrid, core-modified, expanded calixphyrins and exploited the AIEE characteristics of **M-1**. To the best of our knowledge, the emission features described herein are hitherto unknown in calixphyrin chemistry. We could utilize this novel property as a probe for the detection of Hg^{II} ions both in solution as well as in the solid state with excellent selectivity over 100 equivalents of other physiologically important metal ions. The emission characteristics and sensing studies are now extended to other expanded calixbenzophyrins and the research is currently underway in our laboratory.

Experimental Section

Synthetic procedure: Pentafluorobenzaldehyde (0.211 mL, 1.71 mmol) was added to a 500 mL flask containing **1** (0.5 g, 1.71 mmol) in dry dichloromethane (400 mL). The reaction mixture was stirred for 10 min at room temperature under a nitrogen atmosphere with light protection. TFA (0.791 mL, 10.27 mmol) was added and the reaction mixture was allowed to stir for 2 h. DDQ (1.164 g, 5.13 mmol) was added. The solution was opened to air and stirred for further 2 h and the solvent was removed under reduced pressure. Column chromatographic purification (basic alumina; 0, 5, and 10% dichloromethane in hexane as eluent) of the residue afforded **M-1**, **M-2**, and **M-3** as yellow solids in 20, 10 and 5% yield, respectively. Crystals suitable for X-ray analysis were obtained in chloroform/*n*-hexane.

Spectral data for M-1: m.p. 210 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=12.39$ (brs, 2H; NH), 7.17 (m, 2H; Ar), 7.10–7.09 (m, 4H; Ar), 7.02–7.01 (d, $J=1.5$ Hz, 2H; Ar), 6.32–6.31 (d, $J=4$ Hz, 4H; pyrrolic-β-CH), 6.23–6.22 (d, $J=4$ Hz, 4H; pyrrolic-β-CH), 1.26 ppm (s, 24H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=166.04$, 147.9, 145.84, 139.19, 128.14, 126.13, 125.28, 123.52, 111.76, 41.27, 29.71, 28.94 ppm. MS (FAB): *m*/*z* (%): 936.56 $[M]^+$ (100); elemental analysis calcd (%) for $C_{54}H_{42}F_{10}N_4$: C 69.22, H 4.52, N 5.98; found: C 69.15, H 4.49, N 5.78.

Spectral data for M-2: m.p. 192 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=12.52$ (brs, 3H; NH), 7.19–7.06 (m, 12H; Ar), 6.25–6.24 (d, $J=4$ Hz, 6H; pyrrolic-β-CH), 6.08–6.07 (d, $J=4.5$ Hz, 6H; pyrrolic-β-CH), 1.25 ppm (s, 36H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta=166.44$, 147.31, 139.13, 128.29, 126.10, 124.53, 124, 120.82, 117.03, 41.32, 32.77, 30.06, 29.72, 29.39, 29.19, 28.87, 22.72, 14.14 ppm. MS (FAB): *m*/*z* (%): 1404.55 $[M]^+$ (100); elemental analysis calcd (%) for $C_{81}H_{63}F_{15}N_6$: C 69.22, H 4.52, N 5.98; found: C 69.11, H 4.41, N 5.87.

Spectral data for M-3: m.p. 176 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta=12.52$ (brs, 4H; NH), 7.20 (s, 4H; Ar), 7.14–7.06 (m, 12H; Ar) 6.24–6.23 (d, $J=4$ Hz, 8H; pyrrolic-β-CH), 6.06–6.05 (d, $J=4.2$ Hz, 8H;

pyrrolic-β-CH) 1.29 ppm (s, 48 H; CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 166.21$, 147.15, 138.81, 127.99, 125.87, 124.09, 116.86, 41.10, 29.46, 28.62, 22.45, 13.88 ppm. MS (FAB): m/z (%): 1874.19 $[M+2]^+$ (80); elemental analysis calcd (%) for $C_{108}H_{84}F_{20}N_8$: C 69.22, H 4.52, N 5.98; found: C 68.99, H 4.47, N 5.76.

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Keywords: calixphyrins · chemosensors · fluoresence · hydrogen bonds · macrocycles

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