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We demonstrate a unique negative solvatochromic emission (NSE) process from a conformational change of a coordination cage in response to solvent composition. The cationic cage contains two tetra-(4-pyridylphenyl) ethylene (TPPE) luminogens on two opposite faces, linked by $Pt(PEt_3)_2$ and isophthalate. When the solvent changes from acetone/acetonitrile/methanol to water, the emission of single cages gradually shifts to short wavelength (NSE) with a drastic value of ~ 60 nm. Small angle X-ray scattering (SAXS) measurements indicate a molecular conformational change during the process and intramolecular π-π stacking and hydrophobic interaction between the TPPE planes could be the driving forces. As a comparison, a cage with a longer inter-fluorophore distance does not have such strong intramolecular interactions and only shows regular positive solvatochromic emission (PSE) under the same condition.

Fluorescent compounds are of great importance in biological sensing and imaging,[1-4] optoelectronic systems,[5, 6] and stimuli responses[7, 8]. They are sensitive to environmental change, responding by either intensity or wavelength change of the emission.[9-11] In solution, fluorophores could interact with solvent molecules and show a tunable emission color.[12] In most cases, a red-shifted emission with increasing solvent polarity based on charge transfer mechanism is observed, as higher solvent polarity promotes charge separation and induces a low-energy emission with longer wavelength (positive solvatochromic emission, PSE).[13, 14]

This situation might change if other interactions are involved. Aggregation and precipitation introduce strong intermolecular interaction that may induce a blue-shifted emission in a more polar environment.[15-17] Recently, aggregation-induced emission (AIE)[18-21] has received tremendous attention as it greatly expands fluorescence to aggregation/solid state. AIE phenomenon is often observed in certain organic molecules, which consume energy by molecular motion in solution but emit with restricting molecular motion in aggregation/solid state. A particularly interesting system is tetraphenylethene (TPE). Many functional materials are synthesized with exhibiting various interesting features when incorporating TPE fluorophores.[22-29]

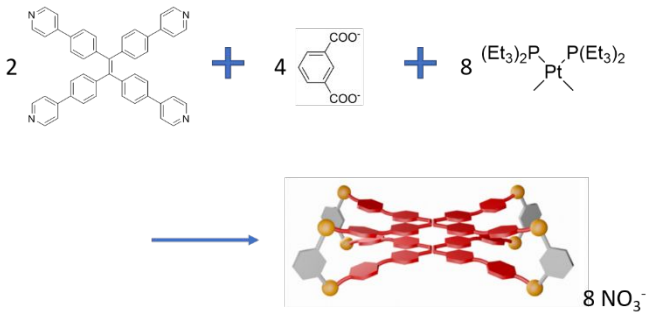

Figure 1 Molecular structure of **Cage 1** (2.5 × 2.0 × 1.5 nm^3). Red: TPPE; gray: isophthalate; yellow: bis(triphenylphosphine) platinum(II). Triphenylphosphine and eight nitrate counterions have been omitted for clarity.

One of the examples is metal-organic cage[30-34]. Along with their well-defined shapes, metal-organic cages can be delicately designed and functionalized with additional groups. Huang and Stang et al. designed a Pt-based molecular cage with two tetra-(4-pyridylphenyl) ethylene (TPPE) AIE luminogens.[35] This type of cages exhibits emission in both dilute solution and aggregation states,[36-38] as the rotation of TPPE ligands were restricted by either cage frame or assembly/aggregation. Upon aggregation, the cage is capable to show tunable visible-light emission, most likely based on the charge transfer mechanism.[39, 40]

In this study, we synthesized a Pt-cage (**Cage 1**, Figure 1) similar to Huang and Stang's work[35] by replacing eight triflate anions (OTf^-) counterions with eight nitrate (NO_3^-) ions. The structure is characterized by ^{1}H-NMR (Figure S2), ^{31}P-NMR

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(Figure S4), 2D DOSY NMR (Figure S6), and small angle X-ray scattering (SAXS, Figure S25) measurements. Similarly, **Cage 1** shows enhanced fluorescence when aggregating in solvents with low dielectric constants, such as THF and hexane, by following the AIE mechanism. The counterion replacement greatly improves **Cage 1** solubility in polar solvents, making it well dissolved in water, DMF, acetonitrile, acetone and methanol. No large structures were observed in these dilute solutions, as confirmed by very low scattered intensity from static light scattering (SLS). The SAXS data from **Cage 1** in acetonitrile matches with the simulated result from proposed model and support the intact cages (Figures 2a &2b).

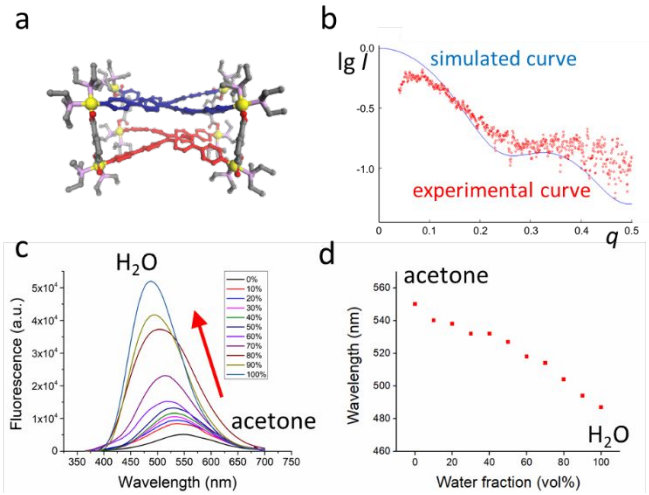

Figure 2. Optimised 3D structure of **Cage 1** (a) and its simulated/experimental SAXS curves (b). Fluorescence spectra and (c) wavelength of the maximum fluorescence (d) of **Cage 1** in water/acetone mixed solvents with different water fractions (0.05 mg/mL) excited at 355 nm.

Due to the cage frame that limits the molecular motion of TPPE ligands, single **Cage 1** in good solvents is still able to show fluorescence. It is interesting that, **Cage 1** can show different emission colors in different solvents: weak yellow fluorescence in good organic solvents like methanol (550 nm), acetonitrile (552 nm), acetone (550 nm), but very strong blue emission in water (487 nm). This interesting phenomenon does not follow the regular solvatochromism that shows red-shifted emission when solvent polarity increases (PSE); instead, it is referred as the negative solvatochromic emission (NSE) effect. In addition, the current NSE effect must be related to the unique cage structure which limits the rotation of the TPPE ligands, because for individual TPPE molecule in water/acetone mixed solvents, it shows enhanced and red-shifted emission with increasing water content – the PSE effect (TPPE would aggregate when water fraction > 50%, Figure S13). This is because the TPPE ligands tend to exhibit AIE that is accompanied with twisted intramolecular charge transfer (TICT) process.[13, 39]

To further understand this phenomenon, **Cage 1** was dissolved in acetone/water mixed solvents with different solvent compositions. In all solvent compositions, **Cage 1** can be dissolved easily and does not form any aggregation, supported by the solvent-level light scattered intensity from SLS measurements (Table S2). Therefore, any observed emission change should be attributed to the change on individual **Cage 1**. When excited at 355 nm, the acetone solution of **Cage 1** (0.05 mg/mL) generates a weak emission. With higher water fraction in solvent, the emission becomes considerably stronger (Figure 2c) and finally reaches the maximum in pure water. Considering that the mechanism for AIE is the limitation of molecular motion, the enhanced emission suggests that the cages, or more specifically, the TPPE moieties, become more rigid in water. At the same time, when changing solvent from acetone-d6/D_2O mixed solvent to D_2O, 1D ^{1}H-NMR spectra (Figure S7) show that the resonance signals from aromatic protons are almost completely lost, which indicates that the relaxation of the single cage greatly increases. Moreover, the signals from ethyl groups (close to Pt ions) are also suppressed. Because the ethyl groups are on the periphery of the cage and pointing out to the solution, their motions were affected less. Detection of the NMR signals from the ethyl group is consistent with the assumption that no aggregation is formed. Results from the NMR study also support the assumption that, the enhanced fluorescence might be due to the hydrophobicity of **Cage 1**, whose interaction with surrounding water molecules greatly limits the free rotation of TPPE ligands.

Along with the enhanced emission, a gradual blue-shift in the wavelength of the maximum emission is also observed when water fraction increases. The emission color changes from yellow in acetone (550 nm) to cyan in water/acetone mixed solvents, and finally to blue in water (487 nm, Figure 2d). From acetone to water, the emission wavelength decreases monotonically with a large span of 63 nm, showing a negative solvatochromic emission (NSE) effect. Similar phenomena have also been observed in water/methanol and water/acetonitrile mixed solvents (Figures S15-S16, S20-S21).

UV-Vis spectra of **Cage 1** (Figure S11) revealed consistent evidence. The absorption of **Cage 1** revealed two absorption bands in methanol and acetonitrile, with $\lambda_{max} \approx 278$ nm and 324 nm. In water, the low energy absorption peak was notably blue-shifted to $\lambda_{max} \approx 312$ nm. This blue-shifted UV-Vis absorption indicates that the conjugation degree of TPPE ligands in **Cage 1** decreases in water, in comparison with that in a non-aqueous solution (e.g. in methanol and acetonitrile).

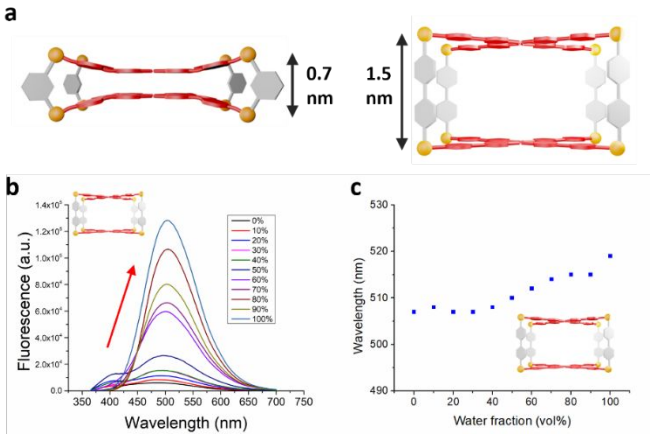

Figure 3. (a) Proposed conformations of **Cage 1** and **Cage 2**. The heights of two cages (in Pt-Pt distance) are 0.7 nm and 1.5 nm in water, respectively; (b) fluorescence spectra and (c) wavelength of the maximum fluorescence, of **Cage 2** in water/acetone mixed solvents with different water fractions (0.05 mg/mL) excited at 355 nm.

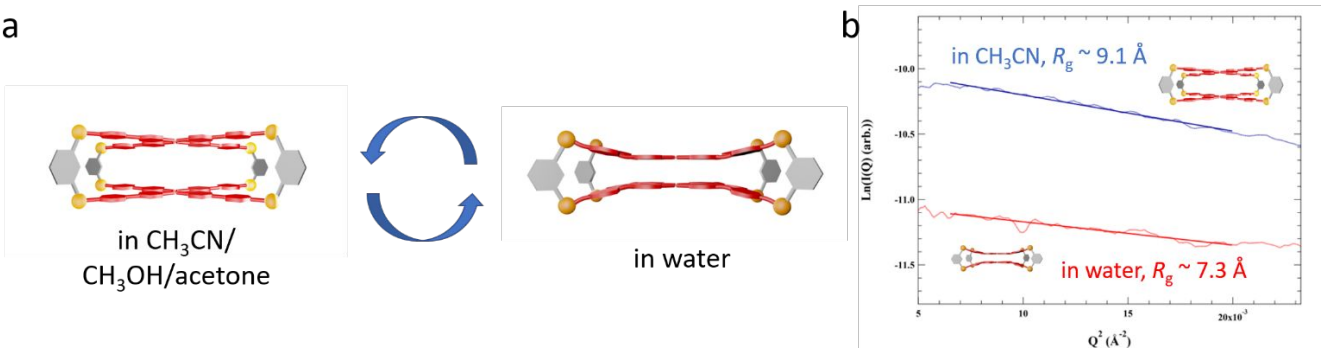

Figure 4. (a) Illustration of the proposed conformational change of **Cage 1** in different solvents. The single bonds in TPPE ligands might be twisted but not shown here. (b) Guinier analysis on **Cage 1** in the aqueous solution (red, R_g ~ 7.3 Å) and acetonitrile solution (blue, R_g ~ 9.1 Å).

In **Cage 1**, the two TPPE ligands are very close to each other (0.7 nm between Pt ions shown in Figure 3a), where the inter-TPPE distance could be even shorter according to our computer simulation. Within 0.5 nm, intramolecular interaction might be involved, such as hydrophobic interaction and π-π stacking. Therefore, there could be two possible explanations for the optical property changes: (1) TPPE ligands are fixed to a certain degree due to their hydrophobic nature, and the phenyl rings are in a less conjugated conformation in water because of single bond rotation; (2) Two TPPE ligands are more curved with more water based on the strong intramolecular hydrophobic interaction and their conjugation degree decreases accordingly.

To test our hypothesis, a larger cage (**Cage 2**, Figure 3a) was synthesized with a longer distance between the two TPPE ligands, by using biphenyl-4,4'-dicarboxylate ligands. **Cage 2** remains the cuboid-like structure with eight positive charges and can be dissolved in polar solvents. The distance between the two TPPE ligands in **Cage 2** is calculated as 1.5 nm, which is too far for any intramolecular hydrophobic or π-π interaction. In water/acetone mixed solvents, **Cage 2** (0.05 mg/mL, excited at 355 nm) also shows higher fluorescence intensity when gradually increasing the water fraction (Figure 3b). However, different from **Cage 1**, the wavelength of the maximum emission gradually (but slightly) shifts from 507 nm in acetone to 519 nm in aqueous solution (Figure 3c). This red-shifted emission with increasing solvent polarity (PSE) matches well with the charge transfer mechanism (either TICT from TPPE ligand or metal-to-ligand charge transfer from the coordination bond) and induces the emission of **Cage 2** with lower energy (i.e., longer wavelength).

Similar PSE phenomena have also been found when **Cage 2** was dissolved in water/acetonitrile (Figures S17-S18) and water/methanol (Figures S22-S23) mixed solvents. In addition, the UV-Vis spectra of **Cage 2** (Figure S11) show slight red-shifted absorption or almost no shift when the solvent changes from acetonitrile (329 nm) or methanol (334 nm) to water (335 nm), consistent with our fluorescence results. It indicates the conjugation degree of TPPE in **Cage 2** has almost no change, which shows a reverse trend compared to **Cage 1**. In both cages, the TPPE ligands should follow the same mechanism to interact with water molecules based on their hydrophobicity but show completely different fluorescence and UV-Vis absorption shifts. Therefore, the explanation of the less conjugation degree of TPPE in cages based on TPPE-solvent interaction can be excluded. As a consequence, the emission change in **Cage 1** can only be attributed to the strong intramolecular interaction based on the short inter-TPPE distance (Figure 4a).

The inter-TPPE intramolecular interaction will lead to significant inward bending of the two TPPEs in more polar solvents. To prove our speculation, small angle X-ray scattering (SAXS) measurements were applied to monitor the conformational changes in cages with changing solvent composition. Because SAXS measurements require high concentration, water and acetonitrile were selected as the solvents. For **Cage 1**, only intact molecules were detected in both water and acetonitrile solutions (Figure S25). The R_g values determined from Guinier analysis[41] are 9.1 Å in acetonitrile and 7.3 Å in water (Figure 4b). This decrement in R_g values indicates that **Cage 1** shrinks greatly from acetonitrile to water, which should be caused by the strong intramolecular hydrophobic interaction between two TPPE ligands in **Cage 1** as the ligands are poorly solvated. Compared to **Cage 1**, concentrated **Cage 2** solutions (20 mg/mL) shows similar SAXS curves in both water and acetonitrile with a small portion of aggregation. Therefore, Moore mothed,[42] instead of Guinier analysis, was used to obtain their R_g information (Figure S26). The result shows that when the solvent is changed from acetonitrile (R_g, 12.6 Å) to water (R_g, 12.9 Å), **Cage 2** almost keeps the same conformation and the TPPE ligands do not interact with each other.

It is also interesting to notice that in acetone, **Cage 1** shows yellow emission (550 nm) but **Cage 2** shows cyan emission (507 nm), indicating a higher conjugation degree of TPPE ligands in **Cage 1**. This is probably due to the intramolecular π-π stacking in **Cage 1**, as the distance between the two ligands is close to the maximum effective distance for π-π stacking (0.5 nm)[43]. Consequently, a high degree of conjugation leading to longer-wavelength emission was obtained.

Conclusions

As a summary, we demonstrated that with two paralleling, closely placed planar fluorophores in a single macromolecular cage, it can demonstrate an unusual negative solvatochromic emission (NSE) effect due to conformational change based on

intramolecular hydrophobic interaction and π-π stacking, supported by fluorescence, UV-Vis absorption and small angle X-ray scattering. The emission decreases with increasing solvent polarity from acetone/acetonitrile/methanol to water. The cages might be used as delicate indicators to caliber the strength of non-covalent interaction in solution, which regulates most of the structures and phase transitions in complex fluids. On the other hand, the drastic change of emission fluorescence with changing external environment also makes such cages potential systems as sensors for the change of solvent quality and/or ionic strength. The same idea can be easily applied in other systems to create fluorophores sensitive to various changes of environment.

Conflicts of interest

There are no conflicts to declare.

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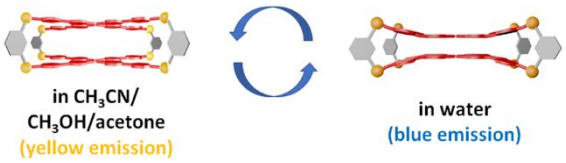

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