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Twisted Schiff-base macrocycle showing excited-state intramolecular proton-transfer (ESIPT): assembly and sensing properties

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A Schiff-base macrocyclic host (MH) showing ESIPT and AIEE is reported for the first time, the fluorescent macrocycle that exhibited good pH tolerance and could serve as a probe for Cu^{2+} and Fe^{3+} ion sensing and removal. In addition, a series of size-tunable nanoparticles was fabricated by the self-assembly of free MH and its coordination complex with Fe^{3+} in THF/water solution.

Excited-state intramolecular proton transfer (ESIPT)¹ refers to photo-induced proton tautomerization, where by an enol tautomer is converted into the keto form. Remarkable dualfluorescence emission with large Stokes shifts can be generated by ESIPT through drastic electronic and structural changes.² From a structural viewpoint, the prerequisite for ESIPT is the presence of an intramolecular hydrogen bond between a proton donor (-OH or -NH₂) and a proton acceptor (=N- or -C=O), that is to say, these groups have to be in close proximity within a molecule.³ Reports have indicated that the spectral properties of ESIPT fluorophores are strongly dependent on hydrogen bonding,⁴ rotamerization,⁵ solvents,⁶ and the acidity/basicity of the surrounding medium.⁷ Because of their unique photophysical properties, ESIPT fluorophores have been widely applied in various fields, including fluorescent probes and logic gates,⁸ fluorescence imaging,⁹ and solid organic lightemitting diodes.¹⁰

Generally, most of the reported ESIPT molecules have been highly emissive in dilute solution in nonpolar media, but weakly emissive at high concentration, in polar solvents, and in the solid state,¹¹ which has greatly limited their further application. Therefore, various strategies, including aggregation-induced emission (AIE),¹² aggregation-induced enhanced emission (AIEE),¹³ dendrimer encapsulation,¹⁴ and restriction of intramolecular rotation (RIR),¹⁵ have been devised with the aim of improving ESIPT emission quality. Herein, we report a twisted Schiff-base macrocycle-supported ESIPT emitter for the first time, which emitted yellow fluorescence not only in dilute solution, but also in the solid state. In particular, because of the rigid three-dimensional (3D) skeleton of the twisted macrocyclic scaffold, the ESIPT-based fluorophore exhibits AIEE.



Fig. 1 Chemical (a) and X-ray (b) structure of MH.

The macrocycle host (**MH**; Fig. 1) was obtained by a simple one step Schiff-base reaction in methanol solution at room temperature. Our recent studies suggested that a series of coreshell-based organic micro/nanospheres, including their intermediate forms, could be directly precipitated from the reaction solution.¹⁶ The X-ray crystal structure of solid **MH** clearly revealed that the macrocycle adopted a twisted 3D helical form, involving multiple intramolecular hydrogenbonding interactions. Interestingly, as shown in Fig. 1b, a rigid coplanar arrangement (C1, C2) between the phenol and aromatic phenyl groups, fixed by hydrogen bonds O3-N3 and O7-N8, was observed in both side chains of the twisted **MH**,

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⁺ Footnotes relating to the title and/or authors should appear here.

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along with further coplanar arrangements (C3, C4) between the phenol and aromatic phenyl moieties (hydrogen bonds O4-N4, and O8-N9) with dihedral angles of 34° and 38° (Fig. S1), respectively. The relevant hydrogen-bond distances are between 2.55 and 2.61 Å, implying that classical ESIPT emission could be triggered by the coplanar moieties in **MH**.



A UV-vis absorption spectrum in THF solution revealed that the absorption of the twisted **MH** appeared in the region 250-400 nm (Fig.S2). The broad absorption wavelength range was due to the formation of intramolecular hydrogen bonds in MH. As shown in Fig. 2a, the macrocycle produced a yellow emission with a maximum at 553 nm upon excitation at 395 nm in DMF or DMSO solution at room temperature. The emission intensity was increased in THF or CH₂Cl₂ solution, and enhanced dualemission was clearly observed for MH in CHCl₃, CH₃OH, and CH₃CH₂OH solutions, which is characteristic of ESIPT. The enol form emitted at a shorter wavelength and the keto form emits at a longer wavelength. The accompanying enhanced fluorescence intensity of the dual-emission was ascribed to the poor solubility of $\mathbf{M}\mathbf{H}$ in these solvents, in which its planarity and rigidity were enforced. This result indicated that the macrocyclic-scaffold-supported ESIPT was AIEE-active. For example, the process of the coplanar arrangement of C3 and C4 like the coplanar from C1, and C2 in less solvating media is the cause of the AIEE (Fig. S1).

The AIEE properties of MH were further evaluated in THF/water mixtures with different water fractions (f_w) , which enabled fine-tuning of the solvent polarity and the extent of solute aggregation (Fig. 1b). MH in pure THF solution exhibited a moderate yellow fluorescence with an emission maximum at 553 nm. Upon gradual addition of water to THF from $f_w = 0$ to 90 vol.%, the emission intensity increased steadily. From $f_w = 90$ to 99 vol.%, the emission decreased slightly due to some precipitation owing to the poor solubility of MH in aqueous media. The precipitate from 99% water was collected by filtration as a pale yellow powder. Fluorescence spectral analysis of the solid indicated that the MH exhibited yellow fluorescence with a maximum emission wavelength around 560 nm in the solid state (Fig. S3). The above results strongly supported the occurrence of AIEE-based ESIPT emission in MH. Most interestingly, SEM and TEM images demonstrated that the precipitate collected from THF/water (1:99, v/v) was composed of numerous discrete solid organic particles with diameters around 500 nm (Fig. 4a, c). This was very different from the

core-shell-based particles of MH directly precipitated from the the supramolecular assembly MH has potential applications in fabricating diverse organic nanoparticles. Moreover, pH titration experiments suggested that the macrocyclic-scaffoldsupported ESIPT had high pH tolerance. As shown in Fig. S4, MH displayed strong yellow emission (ESIPT) at pH < 12 in water/THF solution, and a titration jump at pH >12 with a blueshift of its emission from 553 to 500 nm. In the reference compound hemi-MH (L), which lacked the support of the rigid macrocyclic scaffold (Scheme S1), the ESIPT was only observed in the pH range 5–9 (Fig. S5). The emission changes of MH and L at high pH could be attributed to deprotonation of the phenolic O–H rather than decomposition the C=N bonds (Figs. S6-S9). In addition, L exhibited a classical AIE-based ESIPT property. As shown in Fig. S10, no fluorescence emission was observed for L in pure THF solution and in THF/water mixtures with f_w lower than 50%, and the fluorescence emissions enhanced remarkably when the f_w were between 60% - 90%. This result implied that the twisted macrocyclic scaffold played a key role in the stability of the Schiff-based-derived AIEE based ESIPT of MH.



Fig. 3 UV-vis and fluorescence spectra of **MH** (20.0 μ M) in THF/H₂O (1:4, v/v) in presence of increased concentration of Cu²⁺ (a, c) and Fe³⁺ions (b, d). (λ_{ex} = 395 nm)

To further exploit the macrocycle-supported AIEE-based ESIPT in a fluorescent probe, the selectivity of **MH** towards metal ions was evaluated. The nitrogen-containing Schiff-base bond and the hydroxyl moiety together formed an ideal coordination motif for transition metal and heavy metal cations.¹⁷ Fig. S11 shows the UV-vis spectra of **MH** in THF/H₂O (1:4, v/v) solution in the presence of various metal ions. No significant changes were observed in the spectra, except in the cases of Cu²⁺ and Fe³⁺ ions. The addition of Cu²⁺ and Fe³⁺ produced new red-shifted absorption bands at around 450 nm, such that the initially colourless solution became yellow or pale-yellow. These changes could be easily discerned by the naked eye. The intensities of the new red-shifted absorption bands of **MH** increased as a function of the Cu²⁺ and Fe³⁺ concentrations (Fig. 3a, b). Essentially, these red-shifted bands were due to

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metal-coordination-induced intramolecular charge-transfer (ICT)¹⁸ transitions.

Fig. 3c, d and Fig. S12 show the fluorescence spectral changes of the ESIPT emission for **MH** (in THF/H₂O, 1:4, v/v) under the same conditions as applied for the UV-vis spectra. As can be seen, among the metal ions tested, no significant fluorescent spectral changes were observed upon addition of most of the cations, but Cu²⁺ and Fe³⁺ ions induced remarkable fluorescence quenching. This fluorescence quenching could be partly ascribed to the coordination of Cu²⁺ and Fe³⁺ breaking the intramolecular hydrogen bond (OH…N) with the imine nitrogen of MH, thereby inhibiting the ESIPT emission at 560 nm, but also partly ascribed to the paramagnetic properties of Cu²⁺ and Fe³⁺ (or the heavy atom effect). The latter involved excitation charge- or energy-transfer from MH to a vacant d-orbital of Cu²⁺ or Fe³⁺, providing a very fast and efficient nonradiative decay pathway for the excited state of MH.¹⁹ Interestingly, when the hemi-MH (L) was tested as a probe for sensing the various metal ions, it was found that the fluorescence of L was also guenched by Cu2+ and Fe3+ ions, but a strong blue-shifted emission was observed in the case of Al³⁺. As shown in Fig. S13, upon gradual addition of Al³⁺ ions to a solution of L, the emission intensity at 541 nm was guenched, and a new emission maximum at 490 nm was significantly increased. We surmise that the coordination of Al3+ removed the phenolic protons, which disrupted and inhibited the ESIPT emission of L at 541 nm, while the increased fluorescence emission intensity at 490 nm could be ascribed to an Al³⁺-coordination-induced ICT normal emission mechanism. Compared to Cu2+ and Fe3+, Al3+ had fully occupied p-orbitals, such that no energy- or charge-transfer processes took place, and hence the ICT emission was not quenched. Notably, the different fluorescence responses of MH and L towards Al³⁺ confirmed that the macrocyclic scaffold facilitated pre-organization of the geometric structure of the ligand for the recognition of specific metal ions.

Job plots for the complexations showed a 1:2 stoichiometry of MH with both cations (Fig. S14). Therefore, on the basis of the UV-vis titration experiments, the two step binding constants $(K_a)^{20}$ of **MH** were determined to be 1.10×10^3 M⁻¹ and $3.68 \times$ $10^6~\text{M}^{-1}$ for Cu²+, and $1.21\times10^3~\text{M}^{-1}$ and $2.36\times10^6~\text{M}^{-1}$ for Fe³+, respectively (Fig. S15). This result implying that the first binding event lead to positive cooperativity for the second association of MH with the cations.²¹ No significant interference in the detection of Cu²⁺ and Fe³⁺ was observed in the presence of other competitive cations (Fig. S16). Furthermore, it was observed that extensive precipitation occurred when Cu2+ or Fe3+ ions were added to a solution of MH after 1h even in the presence of other competitive ions. This result indicated that MH could not only be used as a colorimetric and fluorimetric probe for Cu²⁺ and Fe³⁺ ions, but may also serve as a separation material through adsorption of both cations. Most importantly, SEM and TEM images of the precipitate of MH/Fe³⁺ demonstrated that it was composed of a large amount of solid nanoparticles of sizes in the range 900–1,000 nm (Fig. 4b, d and Fig. S17), larger than the particles of the precipitate of free MH from THF/water solution (Fig. 4a, c and Fig. S18). Elemental mapping analysis of energy-dispersive X-ray spectroscopy (EDS) (Fig. 4e-h) showed

that Fe^{3+} ions were uniformly distributed in the nanoparticles. This observation revealed that **MH** may find broader application as a nanocarrier for Fe^{3+} . On the contrary, no regularly particles were observed in the precipitates of **MH/Cu**²⁺ complex (Fig. S19).



Fig. 4 SEM (a) and TEM (b) images of the precipitate of **MH** from THF/H₂O (1:99, v/v); SEM (c) and TEM (d) images of the precipitate of **MH**/Fe³⁺ from THF/H₂O (1:4, v/v); and the corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping images (e–h). (Scale bar: a, b is 2.0 μ M, c, d is 200 nm, e-h is 500 nm.)

Conclusions

In summary, a twisted Schiff-base macrocycle showing ESIPT has been constructed, and its properties have been evaluated. Experimental results have suggested the macrocyclic-scaffold-induced AIEE-based ESIPT probe not only exhibited good pH tolerance, but may also be utilized as a colorimetric and fluorimetric probe for Cu²⁺ and Fe³⁺ sensing and removal. Interestingly, SEM and TEM studies indicated that a series of size-tunable nanoparticles could be obtained from the self-assembly of free **MH** and its coordination complex with Fe³⁺. This work thus provides new insights for the fabrication of fluorescent-macrocycle-based ESIPT and AIEE probes as well as functional organic nanoparticles.

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Conflicts of interest

There are no conflicts to declare

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