Supporting Information

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

Qing Yu, Xiaodong Zhang, Shou-Ting Wu, Huaiyu Chen, Qi-Long Zhang, Hong Xu, Ya-Li Huang, Bi-Xue Zhu and Xin-Long Ni

Synthesis of the hemi-MH (L): 5,5'-methylene-bis-salicylaldehyde (256.0 mg, 1 mmol) and phenylamine (93.0 mg, 1 mmol) were dissolved in methanol solution (40.0 mL) in a round bottomed flask for 10 min, and conc. H₂SO₄ (12 µL) was added to the solution. The resulting mixture was stirred at room temperature for 4 h. Then, the reaction mixture was filtered to give the crude solid product, and the residue was washed with methanol three times to afford a light yellow solid compound L (345 mg, 85%). Single crystals were obtained from a crystal grown by evaporation of L (50.0 mg) in a solution of CHCl₃. CCDC1969906. ¹H NMR (400 MHz, DMSO-d₆) δ 12.88 (s, 2H), 8.87 (s, 2H), 7.47 (d, J = 16 Hz, 2H), 7.41 (s, 2H), 7.39 (d, J = 12 Hz, 4H), 7.34 (d, J = 8 Hz, 4H), 7.30-7.22 (m, 6H), 6.88 (d, J = 12Hz, 2H), 3.87 (s, 2H) ppm. ¹³C NMR (100 MHz, DMSO-d₆) δ 163.84, 159.14, 148.68, 134.34, 132.60, 132.49, 129.99, 127.45, 121.90, 119.66, 117.25, 39.36 ppm.

![Scheme S1](image)

Scheme S1 Synthetic route to the hemi-MH (L), and the X-ray structure.
**Fig. S1** X-ray structure of **MH**: (a) dihedral angle between C3 and C4 linked by hydrogen bonds O4-N4, (b) dihedral angle between C3 and C4 linked by hydrogen bonds O8-N9, (c, d) plausible rotation tendency between the C3 and C4, (e) top view of the coplanar arrangement of C1 and C2.

**Fig. S2** UV-vis absorption spectra of **MH** (20.0 µM) in THF solution.
Fig. S3 Fluorescence spectra of MH in the solid state. ($\lambda_{ex} = 395$ nm)

Fig. S4 Fluorescence spectra of MH (20.0 µM) in the range from pH = 2 to 14 in THF/water solution (1:1, v/v). ($\lambda_{ex} = 395$ nm)

Fig. S5 Fluorescence spectra of L (20.0 µM) in the range from pH = 2 to 14 in THF/water solution (1:1, v/v). ($\lambda_{ex} = 395$ nm)
Fig. S6 $^1$H NMR spectra of MH (1.0 mM, DMSO-$d_6$) in the presence of DCl and NaOD.

Fig. S7 $^1$H NMR spectra of L (1.0 mM, DMSO-$d_6$) in the presence of DCl and NaOD.

Fig. S8 $^1$H NMR spectra (DMSO-$d_6$) of the mixture precursors (aldehyde and amine) of MH.
Fig. S9 Fluorescence spectra of MH, L and their precursors in THF/water solution (1:1, v/v) at pH 2.0 and pH 14, respectively.

Fig. S10 Fluorescence spectra of L (20.0 µM) with different water fractions (f_w). (λ_ex = 395 nm)
**Fig. S11** UV-vis spectra of MH probe (20.0 µM) with addition of nitrate salts of Li⁺, Co²⁺, Cr³⁺, K⁺, Cd²⁺, Pb²⁺, Ca²⁺, Hg²⁺, Ba²⁺, Cu²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Al³⁺ and Fe³⁺ (150 µM) in THF/water solution (1:4, v/v).

**Fig. S12** Fluorescence spectra of MH probe (20.0 µM) with addition of nitrate salts of Li⁺, Co²⁺, Cr³⁺, K⁺, Cd²⁺, Pb²⁺, Ca²⁺, Hg²⁺, Ba²⁺, Cu²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Al³⁺ and Fe³⁺ (150 µM) in THF/water solution (1:4, v/v). (λ<sub>ex</sub> = 395 nm)
Fig. S13 Fluorescence spectra of L probe (20.0 µM) in presence of various metal ions (150 µM) (a), and in the presence of increasing concentration of Al^{3+} ions in THF/water solution (1:1, v/v). (λex = 395 nm)
Fig. S14 Job plot of MH toward Cu²⁺(a) and Fe³⁺(b).

Fig. S15 The 1:2 binding constants ($K_a$) of MH with Cu²⁺ and Fe³⁺ was calculated (using the soft of KaleidaGraph 4.0) to be $1.10 \times 10^3$ M⁻¹ and $3.68 \times 10^6$ M⁻¹ for Cu²⁺ and $1.21 \times 10^3$ M⁻¹, and $2.36 \times 10^6$ M⁻¹ for Fe³⁺, respectively. The red solid line was obtained from the non-linear curve-fitting.

Fig. S16 Bar diagram of the competitive experiments of various metal cations on the fluorescence intensity of the probe / Cu²⁺ complex (a) and the probe / Fe³⁺ complex (b).
Fig. S17 SEM (a) and TEM (b) images of the precipitate of MH/Fe$^{3+}$ from THF/H$_2$O (1:4, v/v).
Fig. S18 SEM (a) and TEM (b) images of the precipitate of MH from THF/H$_2$O (1:99, v/v).
Fig. S19 SEM (a) and EDS (b) images of the precipitate of MH/Cu²⁺ from THF/H₂O (1:4, v/v).

Fig. S20. MS spectrum of L.
Fig. S21 $^1$H NMR (400 MHz, DMSO-$d_6$) of L.

Fig. S22 $^{13}$C NMR (100 MHz, DMSO-$d_6$) of L.