

Electronic Supplementary Information (ESI)

Aggregation-induced emission enhancement (AIEE)-active
tetraphenylethene (TPE)-based chemosensor for Hg²⁺ with
solvatochromism and cell imaging characteristics

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1. Experimental section

Materials and measurements

All operations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. The starting materials 7-bromopyrido[2,3-*b*]pyrazine, diphenylmethane, 4-bromobenzophenone and *p*-toluenesulfonic acid were purchased from J&K Chemicals used as received. The solutions of metal ions (0.1 mol L⁻¹) were prepared by the dissolution of their respective metal nitrates in distilled water, except for K⁺, and Ba²⁺ (all of their counter ions were chloride ions). Other raw materials and reagents were obtained as analytical-grade from variety commercial providers and used without further purification. Compound **a**¹ and **a-1**¹ were prepared by procedures described in the corresponding literatures. ¹H NMR (400 MHz) and ¹³C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ¹H NMR spectra are reported as followed: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constant (Hz). ¹³C NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77 ppm. Mass spectra were obtained on a Bruker AmaZon SL Ion Trap Mass spectrometer. Elemental analyses (C, H, N) were carried out with a PE CHN 2400 analyzer. The absorption spectra were measured on an Agilent 8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded on

a Hitachi-F-4600 fluorescence spectrophotometer. The acetonitrile-water mixtures with various water fractions were prepared by tardily adding ultra-pure water into the acetonitrile solution of samples. The aggregate behavior of the compound was investigated by NanoBrook 90 plus. Absolute luminescence quantum yields were measured by HAMAMATSU ABSOLUTE PL QUANTUM YIELD SPECTROMETER C11347. Column chromatographic separations were carried out on silica gel (200-300 mesh). TLC was performed by using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm.

General procedure for the synthesis of luminogen 1

A mixture of compound **b** (2.4 mmol, 0.5 g), **a-1** (2.5 mmol, 0.94 g), K_2CO_3 (10 mmol), $Pd(PPh_3)_4$ (0.2 mmol) were stirred in THF (50 ml) and H_2O (5 ml) for two days under an argon atmosphere at 80°C. After completion of present reaction, the mixture was extracted with dichloromethane (3 × 30 mL), and the combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues were purified by column chromatography using 3:2:1 petroleum ether: dichloromethane: ethyl acetate as eluent, affording the expected white solid product in a yield of 65.6%. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.36 (s, 1H), 8.98 (d, $J = 4$ Hz, 1H), 8.89 (s, 1H), 8.50 (s, 1H), 7.47 (d, $J = 8$ Hz, 2H), 7.16 (d, $J = 8$ Hz, 2H), 7.09-6.97 (m, 15H). ^{13}C

NMR (100.6 MHz, CDCl₃): δ (ppm) = 153.5, 150.2, 147.3, 146.6, 145.0, 143.4, 143.3, 142.1, 139.9, 138.4, 138.0, 134.8, 133.7, 132.5, 131.4, 131.3, 131.3, 127.9, 127.9, 127.7, 126.8, 126.7, 126.7. MS-ESI (m/z): 484.1[M + Na]⁺ (calcd 461.19). Anal. Calcd. For C₃₃H₂₃N₃: C, 85.87; H, 5.02; N, 9.10. Found: C, 85.93; H, 4.94; N, 9.17.

2. Reference

1. Z. Zhao, C. Y. K. Chan, S. Chen, C. Deng, J. W. Y. Lam, C. K. W. Jim, Y. Hong, P. Lu, Z. Chang, X. Chen, P. Lu, H. S. Kwok, H. Qiu and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 4527-4534.

3. Figs. S1-S9

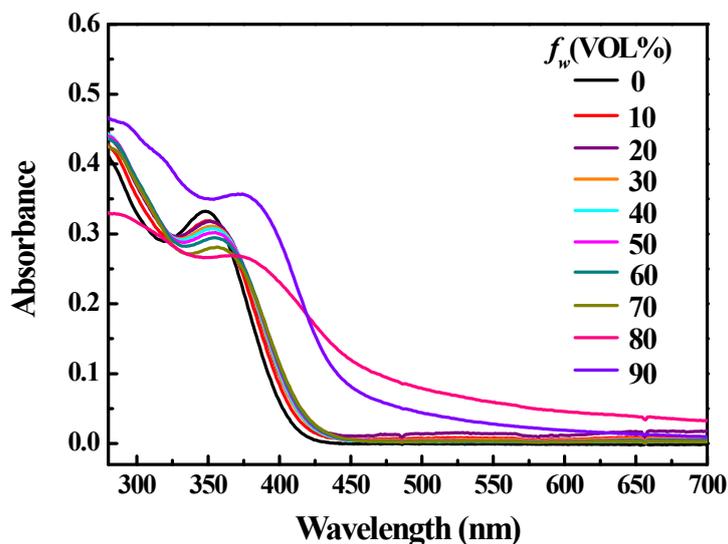


Fig. S1 UV-visible absorption spectra of luminogen **1** (2.0×10^{-5} mol L⁻¹) in acetonitrile-water mixtures with different water content (0-90%).

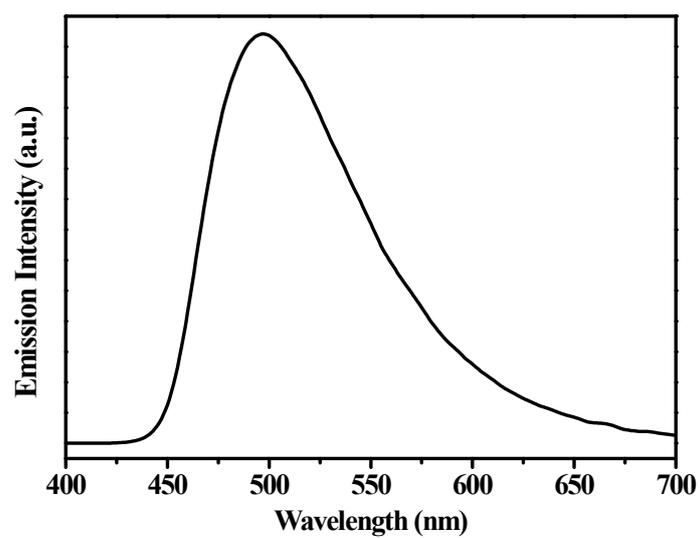


Fig. S2 Solid-state fluorescence spectrum of luminogen **1** (Excitation wavelength: 365 nm).

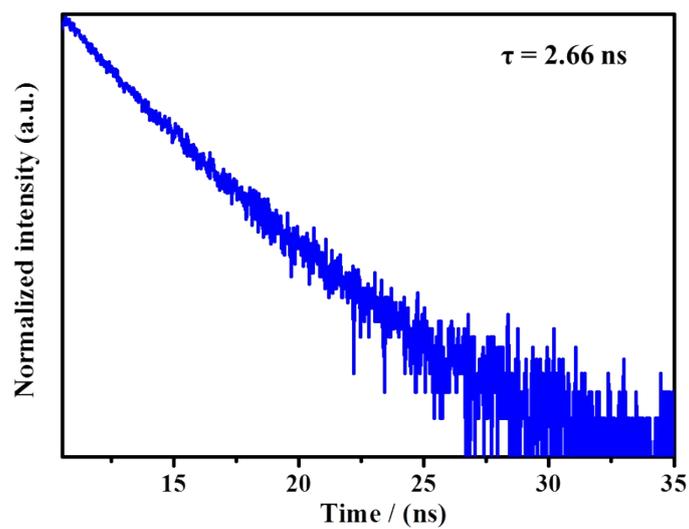


Fig. S3 The fluorescence lifetime of solid-state luminogen **1** (Excitation wavelength: 375 nm).

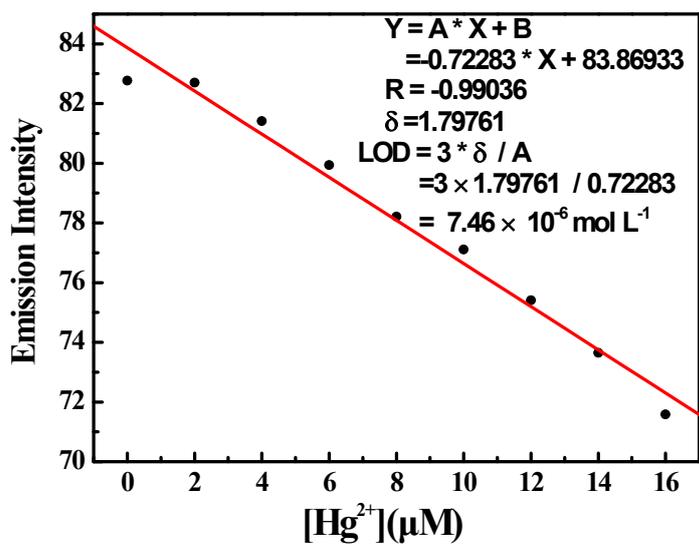


Fig. S4 The limit of detection (LOD), LOD is 7.46×10^{-6} M.

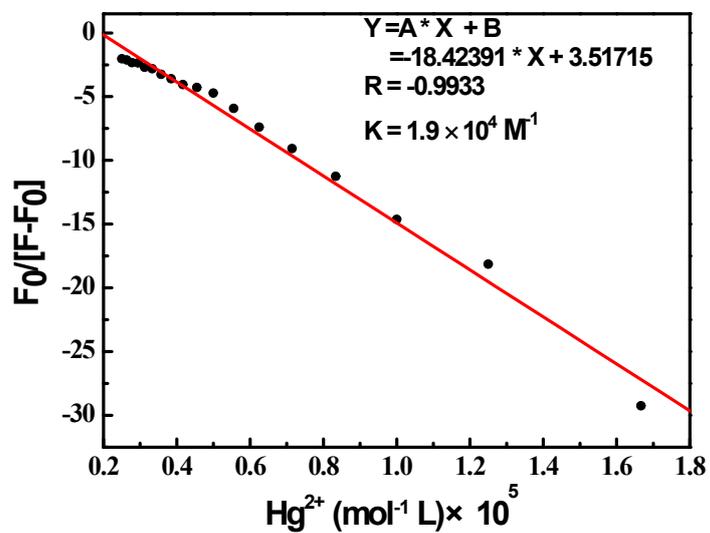


Fig. S5 Hildebrand-Benesi plot based on the 1 : 1 ratio for luminogen **1** and Hg²⁺, the binding constant is $1.9 \times 10^4 \text{ M}^{-1}$.

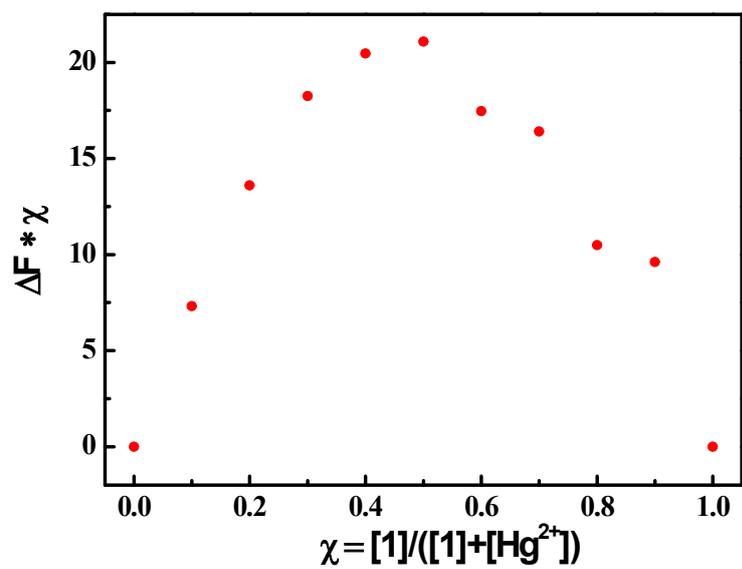


Fig. S6 Job's Plot of luminogen **1** with Hg^{2+} showing 1:1 stoichiometry.

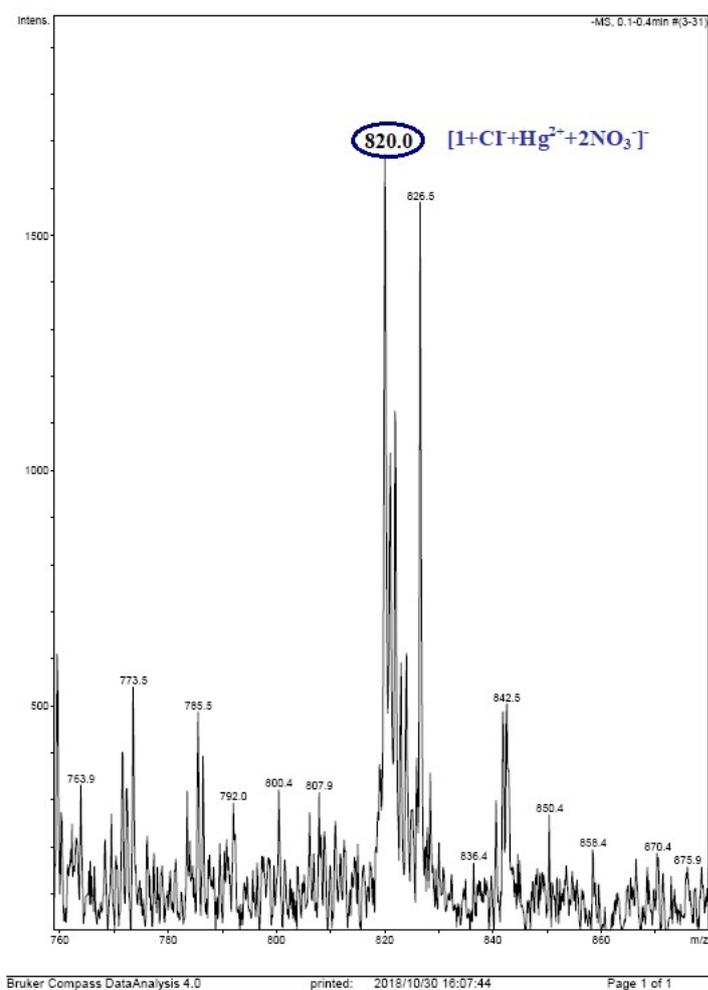


Fig. S7 Mass spectrum of luminogen 1 with Hg²⁺.

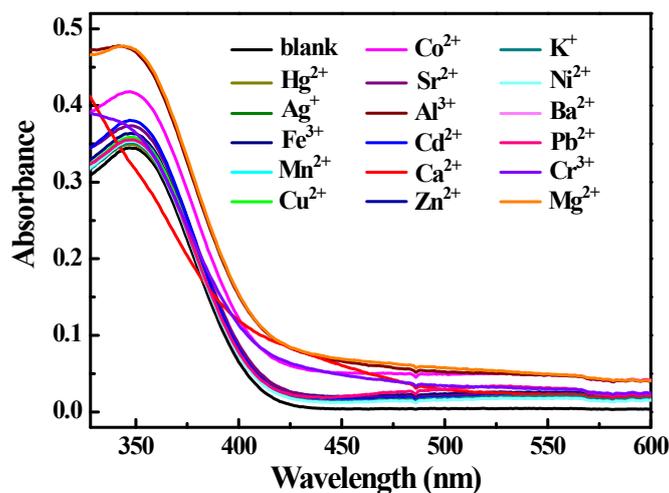


Fig. S8 The UV-Vis absorption spectra of luminogen **1** (2.0×10^{-5} mol L⁻¹) towards various cations including Zn²⁺, Cd²⁺, Hg²⁺, Ba²⁺, Sr²⁺, Mn²⁺, Mg²⁺, Ca²⁺, Pb²⁺, Ni²⁺, Co²⁺, Cu²⁺, Al³⁺, Fe³⁺, Cr³⁺ Ag⁺ and K⁺.

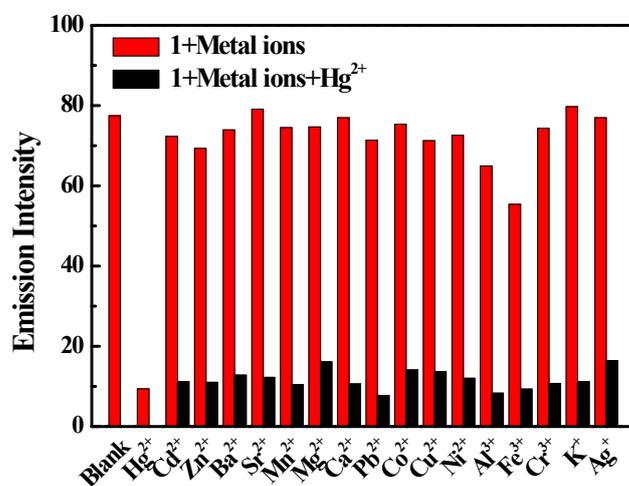


Fig. S9 Fluorescence response of luminogen **1** to various metal ions (including Zn²⁺, Cd²⁺, Hg²⁺, Ba²⁺, Sr²⁺, Mn²⁺, Mg²⁺, Ca²⁺, Pb²⁺, Ni²⁺, Co²⁺, Cu²⁺, Al³⁺, Fe³⁺, Cr³⁺ Ag⁺ and K⁺). Red bars represent the addition of 7.0 equiv. of the appropriate metal ions to a solution of luminogen **1** (2.0×10^{-5} mol L⁻¹ in acetonitrile). Black bars represent the

addition of 7.0 equiv. of Hg^{2+} to the solutions containing luminogen **1** (2.0×10^{-5} mol L^{-1} in acetonitrile) and the appropriate metal ions (7.0 equiv.). Excitation wavelength = 380 nm.

4. Copies of NMR spectra and Mass spectrum

