Supporting Information

Development of an AIE based fluorescent probe for the detection of nitrate anion in aqueous solution over a wide pH range

Shiyan Chen and Xin-Long Ni*

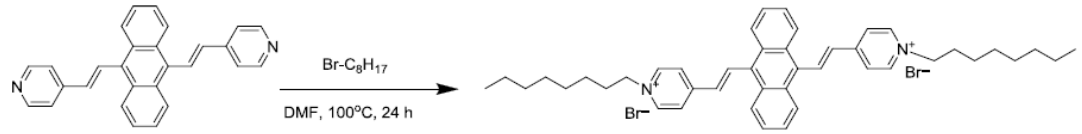
Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China

E-mail: longni333@163.com

General information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were measured on a Varian Nova-500 NMR spectrometer at room temperature using TMS as an internal standard. MALDI-TOF mass spectra were acquired on a time-of-flight mass spectrometer equipped with a nitrogen laser. Fluorescence spectra measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a xenon discharge lamp. Isothermal titration calorimetry (ITC) measurements were carried out using Nano ITC (TA, USA) at 25 ^{o}C. Dynamic light scattering (DLS) experiments were carried out with Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) at 25 ^{o}C, and atomic force microscopy images were obtained on AFM (CSPM 5500) in tapping mode in air at room temperature. Fluorescence microscopy images were taken on an OLYMPUS IX71 fluorescence microscope. A suitable single crystal was determined on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo K_α radiation source (λ = 0.71073 Å, μ = 0.828 mm^{-1}), which was operated in the ω-scan mode at room temperature.

Synthesis of probe 1



9,10-bis((E)-2-(pyridin-4-yl)vinyl)anthracene

probe **1** (80%)

A mixture of 9,10-bis((E)-2-(pyridin-4-yl)vinyl)anthracene (385 mg, 1.0 mmol) and Br-C_8H_{17} (580 mg, 3.0 mmol) in DMF (5 mL) and was heated to 100 ^{o}C for 24 hours. Then the reaction mixture was cooled and an excess amount of acetone (100 mL) was added the solution. The precipitate was filtered and washed with petroleum ether and acetone to give rise to a brown red solid 616 mg (yield 80 %). The X-ray crystals were obtained by slow evaporation of the solvent of probe **1** in CH_3CN solution. ^{1}H NMR (500 MHz, DMSO-$_{d6}$), δ 9.07-9.06 (d, *J*=5 Hz, 4H), 8.97-8.94 (d, *J*=15 Hz, 2H, vinyl-H), 8.52-8.51 (d, *J*=5 Hz, 4H), 8.41-8.39 (m, 4H), 7.64-7.62 (d, *J*=10 Hz, 4H), 7.30-7.27 (d, *J*=15 Hz, 2H, vinyl-H), 4.56-4.52 (t, *J*=20 Hz, 4H), 1.95-1.92 (t, *J*=15 Hz, 4H), 1.29-1.21 (m, 20H), 0.86-0.82 (m, 6H). MALDI-TOF: m/z calcd for $C_{28}H_{20}N_2^{2+}$: 384.47; found: 383.89; elemental analysis calcd (%) for $C_{44}H_{54}N_2Br_2$: C 68.57, H 7.06, N 3.63; found: C 68.49, H 7.14, N, 3.57.

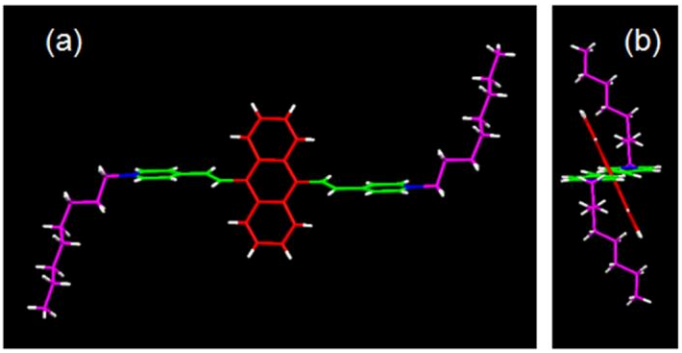


Fig. S1. Crystal structure of **1**: (a) Top view; (b) side view.

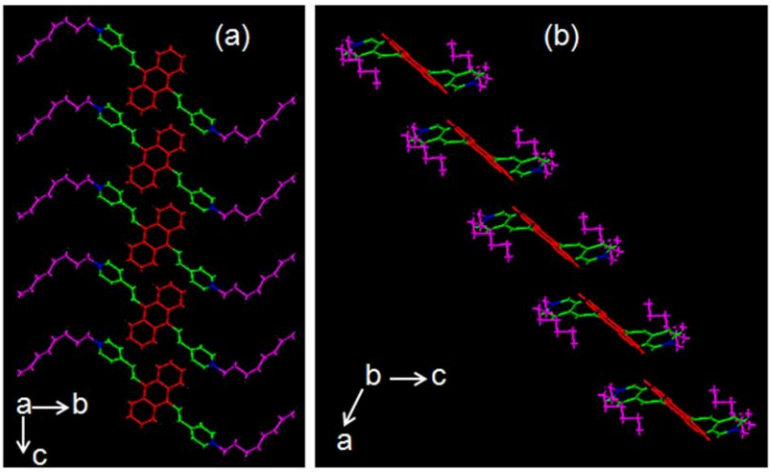


Fig. S2. J-type aggregation of **1** in the solid state in the column: (a) along the *a* axis; (b) along the *b* axis.

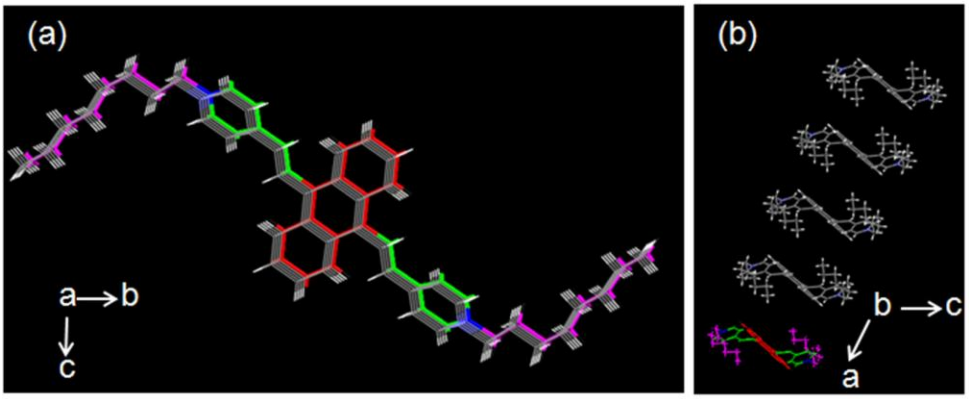


Fig. S3. H-type aggregation of **1** in the solid state in the column: (a) along the *a* axis; (b) along the *b* axis.

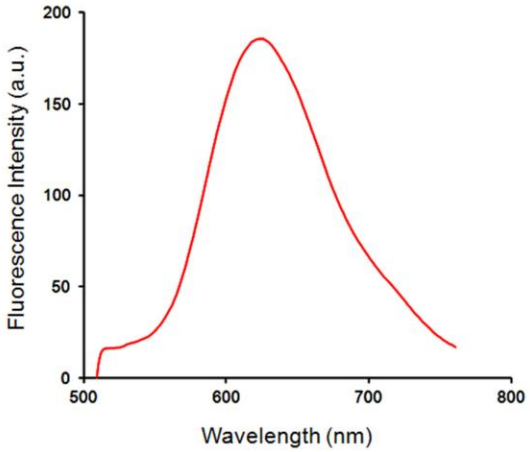


Fig. S4. Fluorescence spectra of **1** in the solid state. λ_{ex} = 398 nm

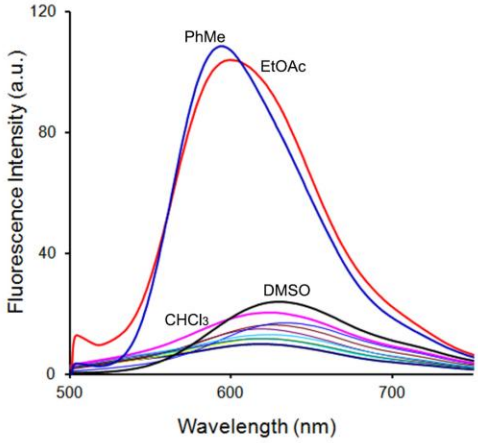


Fig. S5. Fluorescence spectra of **1** (0.1 mM) in different solvents at 298K. λ_{ex} = 398 nm.

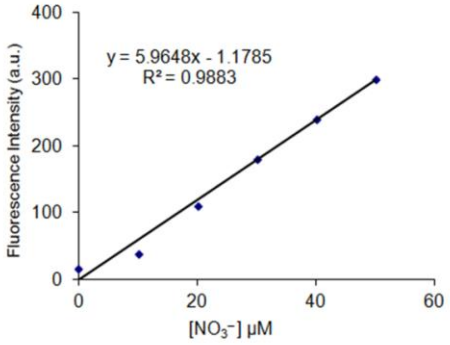


Fig. S6. Plot of fluorescence intensity change 581 nm) of **1** with varied concentrations of NO_3^- at 298K, the limit of detection of NO_3^- was calculated to be 4.75 $\times 10^{-7}$ M by the formula (3σ/K).

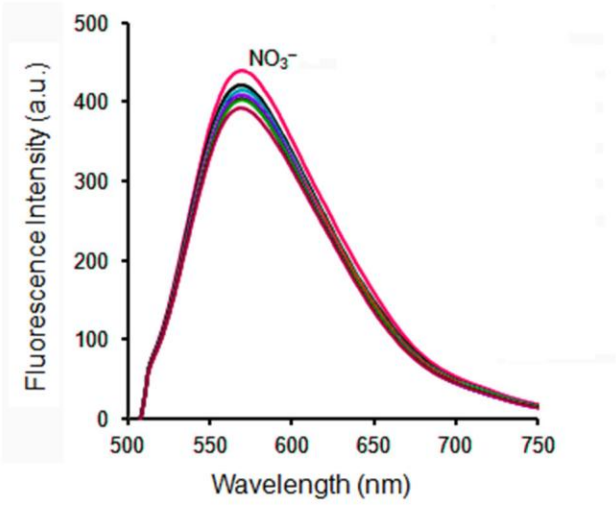


Fig. S7. Fluorescence responses of **1** (10 μM) in 10 mM HEPES buffer (pH 7.4) to various tested anions (F^-, Cl^-, Br^-, NO_3^-, $H_2PO_4^-$, SO_4^{2-}, HSO_4^-, BF_4^-, CH_3COO^-, ClO_4^-, S^{2-}, NO_2^-, PF_6^-, $C_2O_4^{2-}$, and citrate, each of 100 μM) in the presence of 100 μM NO_3^-.λ_{ex} = 398 nm.

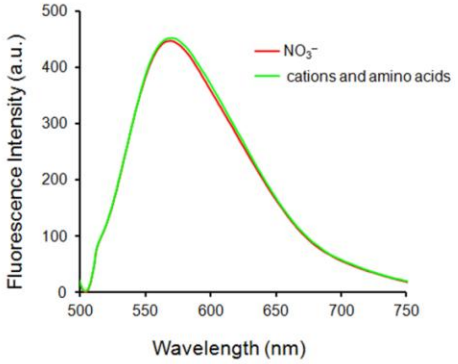


Fig. S8. Fluorescence responses of **1** (10 μM) in 10 mM HEPES buffer (pH 7.4) to various tested cations (mixture of NaCl, KCl, $Zn(NO_3)_2$, $Cu(NO_3)_2$, and amino acids including cysteine, glutamic acid, lysine, glutamine, tryptophan, methionine, valine, leucine, alanine, glycine, each of 100 μM) in the presence of 100 μM NO_3^-.λ_{ex} = 398 nm.

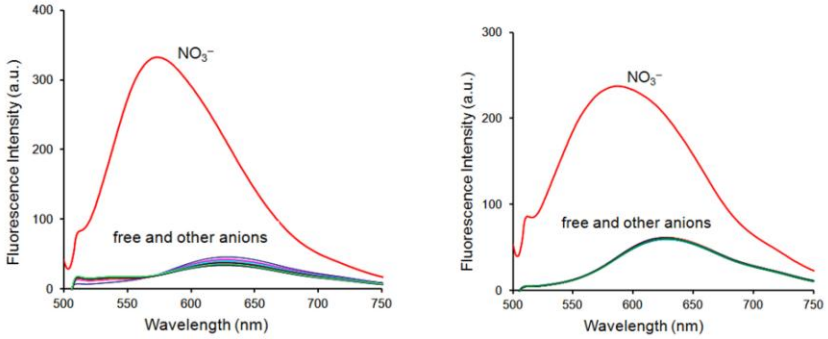
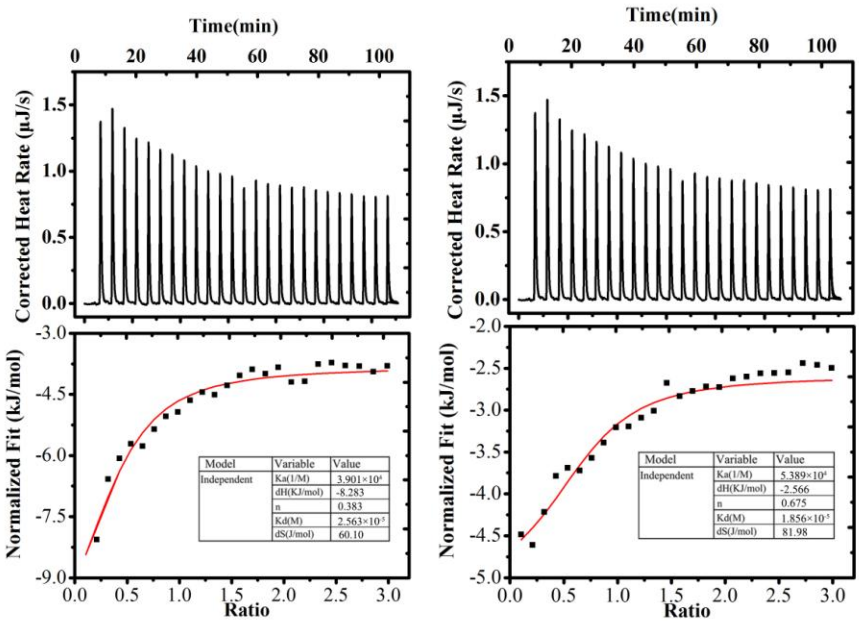


Fig. S9. Fluorescence response of **1** (10 μM) for anions (F^-, Cl^-, Br^-, NO_3^-, $H_2PO_4^-$, SO_4^{2-}, HSO_4^-, BF_4^-, CH_3COO^-, ClO_4^-, S^{2-}, NO_2^-, PF_6^-, $C_2O_4^{2-}$, and citrate, each of 100 μM) in aqueous solution at different pH values: (a) pH 3.0; (b) pH 10.0. λ_{ex} = 398 nm.



(a) (b)

Fig. S10. (a) Microcalorimetric titration of **1** with $NaNO_3$ in aqueous solution (pH 7.4) at 298.15 K. Nano ITC data for 24 sequential injections (each of 4 μL) of $NaNO_3$ solution (1.0 mM) into **1** solution (0.01 mM). (b) Microcalorimetric titration of **1** with $NaNO_3$ in aqueous solution (pH 3.0) at 298.15 K. Nano ITC data for 25 sequential injections (each of 3 μL) of $NaNO_3$ solution (1.0 mM) into **1** solution (0.01 mM).

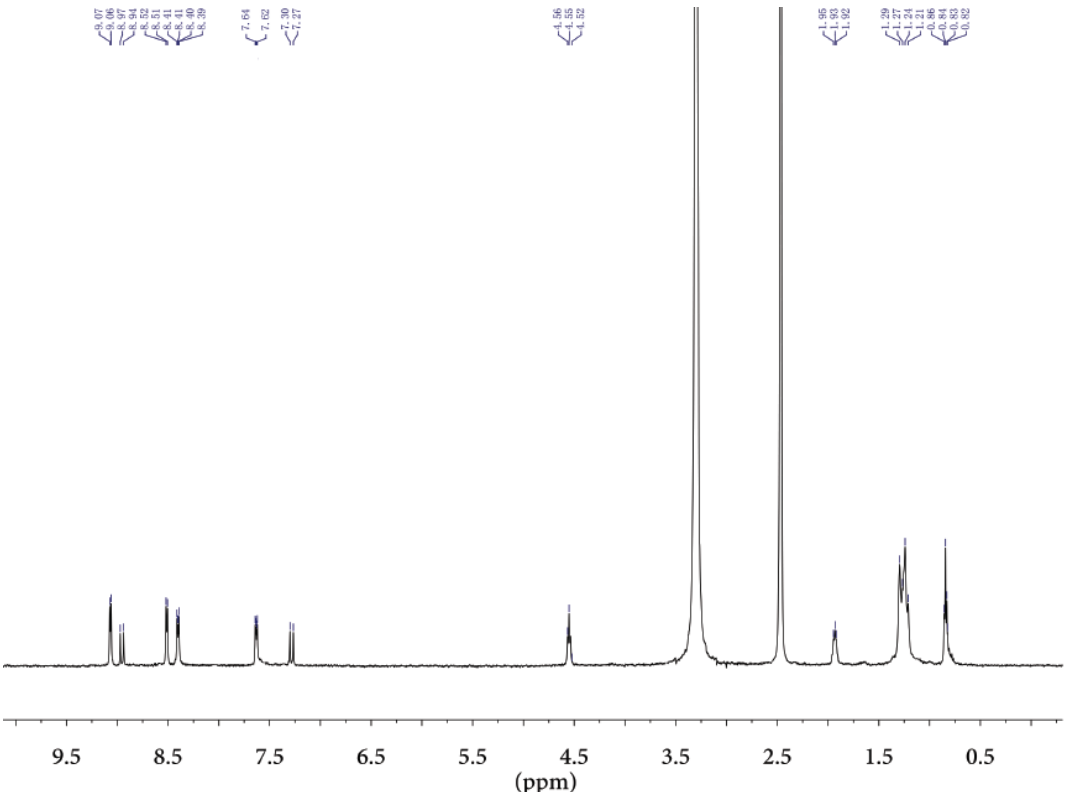


Fig. S11. ^{1}H NMR spectra of **1** in DMSO-$_{d6}$.