Electronic Supplementary Information

Fluorescence enhancement through the formation of a single-layer two-dimensional supramolecular organic framework and its application in highly selective recognition of picric acid

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Section 1: Materials and General Methods

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Compound 3 were synthesized according to the literature.\textsuperscript{1} \textsuperscript{1}H and \textsuperscript{13}C NMR, NOESY, DOSY and COSY NMR spectra were recorded on a Bruker Avance DMX 400 or a 500 MHz Agilent spectrometer at 25°C. UV-Vis absorption spectra were recorded with a Unico 4802 UV-vis double beam spectrophotometer at 25 °C. Fluorescence emission spectra were recorded with a F-4600 FL spectrophotometer at 25 °C. Dynamic light scattering (DLS) experiments were performed on a Zetasizer Nano ZS90 light-scattering instrument (Malvern, UK) at 25 °C. Synchrotron radiation SAXS experiments were performed on the BL16B beamline of Shanghai Synchrotron Radiation Facility, using a fixed wavelength of 0.124 nm, a sample to detector distance of 2.01 m and an exposure time of 3,600 s.

Section 2. Synthesis and Characterizations

\textbf{Compound 2:} Compounds 3 (6.1 g, 33 mmol) and 4 (10 g, 49.5 mmol) were dissolved in anhydrous CH\textsubscript{3}CN (150 mL) and refluxed for 24 hours. The resulting mixture was cooled to room temperature and filtered. The filter cake was washed with acetone (100 ml \times 3) and dried to give compound 2 as a yellow solid (10 g, 78%). \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}OD): \(\delta\) 9.27 (d, \(J = 2.5\) Hz, 1 H), 9.09 (d, \(J = 7.3\) Hz, 2 H), 8.91 (dd, \(J_1 = 8.7\) Hz, \(J_2 = 2.5\) Hz, 1 H), 8.61 (d, \(J = 7.2\) Hz, 2 H), 8.32 (d, \(J = 8.6\) Hz, 1 H), 8.22 (d, \(J = 9.0\) Hz, 2 H), 7.25 (d, \(J = 8.9\) Hz, 2 H), 3.97 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}OD): \(\delta\) 164.70, 158.43, 149.59, 144.78, 143.48, 138.66, 131.32, 130.54, 129.64, 124.97, 122.71, 121.77, 115.34, 54.99. MS (ESI): \textit{m/z} 352.2 [M-Cl]\textsuperscript{+}. HRMS (ESI) Calcd. for C\textsubscript{18}H\textsubscript{14}N\textsubscript{3}O\textsubscript{5} [M-Cl]\textsuperscript{+}: 352.0928. Found: 352.0930.
Compound 1: Compounds 2 (0.8 g, 2.1 mmol) and 5 (0.1 g, 0.34 mmol) were dissolved in anhydrous ethanol (10 mL) and sealed in a schlenk tube under argon atmosphere. The mixture was refluxed for 4 days. After being cooled to room temperature, the solvent was evaporated and the resulting residue was purified by flash column chromatography (acetone, acetone/methanol = 1:1, then to methanol/H₂O/ NH₄Cl (saturated aq.) = 6:3:1 gradually). An orange solid was obtained and it was further dissolved in a small amount of water and then filtered (so as to remove excess NH₄Cl). The filter cake was dried to afford compound 1 as a red solid (32 mg, 10.3%). ¹H NMR (400 MHz, CD₃OD): δ 9.00 (d, J = 8.0 Hz, 6 H), 8.46 (d, J = 8.0 Hz, 6 H), 8.10 (d, J = 8.1 Hz, 6 H), 7.79 (d, J = 8.0 Hz, 6 H), 7.55 (d, J = 8.1 Hz, 6 H), 7.25 (d, J = 8.0 Hz, 6H), 3.95 (s, 9 H). ¹³C NMR (125 MHz, CD₃OD): δ 164.15, 156.43, 148.76, 143.54, 138.35, 130.04, 125.67, 125.28, 124.39, 123.19, 115.21, 54.91. MS (ESI): m/z 266.1 [M-3Cl]³⁺. HRMS (ESI) Calcd. for C₅₁H₄₅N₄O₃ [M-3Cl]³⁺: 265.7825. Found: 265.7826.

Reference
Figure S1 Job’s plot obtained by recording the absorbance at 414 nm for the solution of 1 and CB[8] in a binary solvent of H₂O/CH₃OH (17:3) at 25 °C, ([1] + [CB[8]] = 2.0 × 10⁻⁵ M), confirming the 2:3 stoichiometry of their complex.

Figure S2 2D ¹H NMR NOESY spectrum (400 MHz) of (1 + CB[8]) (2:3, [1] = 0.5 mM) in a binary solvent of D₂O/CD₃OD (17:3, v/v) at 25 °C.
**Figure S3** The plot of $D_h$ vs. the concentration of (1 + CB[8]) (2:3) in a binary solvent of H$_2$O/CH$_3$OH (17:3, v/v) at 25 °C.

**Figure S4** DOSY-NMR spectrum (500 MHz) of 1 (1.0 mM) in D$_2$O/CD$_3$OD (17:3, v/v). The ordinate represents the log value of the diffusion constant.

**Figure S5** DOSY-NMR spectrum (500 MHz) of (1 + CB[8]) (2:3, [1] =1.0 mM) in D$_2$O/CD$_3$OD (17:3, v/v). The ordinate represents the log value of the diffusion constant.
**Figure S6** Fluorescence titration spectra of 1 (0.3 μM) with CB[7] in water at 25 °C. λ<sub>ex</sub> = 414 nm.

**Figure S7** Fluorescence spectra of the 2D SOF in the presence of different nitroaromatics in water at 25 °C. λ<sub>ex</sub> = 414 nm.

**Figure S8** (I<sub>max</sub> -I)/(I<sub>max</sub> -I<sub>min</sub>) vs lg[PA] plot for the fluorescence titration. The intercept at X-axis shows the lowest concentration of PA which can be detected.
Figure S9 $^1$H NMR (500MHz, CD$_3$OD) and $^{13}$C NMR (125 MHz, CD$_3$OD) spectra of compound 2.
Figure S10 $^1$H NMR (400MHz, CD$_3$OD) and $^{13}$C NMR (125MHz, CD$_3$OD) spectra of compound 1.
Figure S11 2D $^1$H NMR COSY spectrum (500 MHz, CD$_3$OD) of 1 at 25 °C.