

Supporting Information

for

A fluorescent metal-organic framework constructed from semi-rigid ligand for the sensitive sensing of 2,4,6-trinitrophenol

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Experimental

Materials and General Methods. The reagents and solvents were commercially available and used as received. UV-Vis absorption spectra were measured using a *Jingke L6S* spectrometer. Elemental analyses (C, H, N) were carried out on an *Elementar Vario EL III analyzer*. Powder X-ray diffraction (PXRD) data were collected on a *Bruker D8 ADVANCE* diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å). Fourier transform infrared (FT-IR; Figure S7) spectra were recorded on *PerkinElmer Spectrum One* with KBr pellets in the range 4000-400 cm⁻¹. Thermogravimetric analysis (TGA; Figure S8) was performed under nitrogen atmosphere with a heating rate of 10 °C min⁻¹ using an *NETZSCH STA 449C* unit.

Synthesis of H₆bmipia. Dimethyl 5-amino-phthalate (209 mg, 1 mmol), dimethyl 5-bromomethyl phthalate (631.4 mg, 2.2 mmol) and sodium hydroxide (88 mg, 2.2 mmol) were added into a 250 mL round-bottom flask, and then 50 mL distilled water was added. The reaction was refluxing at 80 °C for 24 h before filtration. Then, the dry white filter cake was transferred to the round-bottom flask, followed, sodium hydroxide and 50 mL l distilled water were added into the flask, the reaction was also refluxing at 80 °C for 24 h. Then reaction mixture was poured into the beaker and hydrochloric acid was added, to adjust the pH to 1-2. The yellow solid product was obtained after filtration and drying (800 mg, 81.0 %). ¹H NMR (500 MHz, DMSO): δ 13.00 (s, 2H, -COOH), δ 12.60 (s, 4H, -COOH), δ 8.53(s, 2H, -COOH), δ 8.35(s, 4H, ArH), δ 7.78 (s, 2H, ArH), δ 4.58 (s, 4H, -CH₂).

Synthesis of $\{[\text{Cd}_3(\text{bmipia})_2] \cdot 10\text{DMF} \cdot 5\text{H}_2\text{O}\}_n$ (FCS-2). A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.046 g, 0.15 mmol), H_6bmipia (0.020 g, 0.05 mmol) and 10 mL DMF was sealed in a 25 mL Teflon-lined stainless steel autoclave. The reactants were heated at 150 °C for 72 hours, then cooled naturally to room temperature. Colorless block crystals were collected by filtration, washed with distilled water, and dried in air at ambient temperature. Yield: 36 % (based on Cd). Anal. Calcd for $\text{Cd}_3\text{C}_{82}\text{H}_{106}\text{N}_{12}\text{O}_{39}$ (2221.01): C 44.34, H 4.81, N 7.57; found: C 44.73, H 4.46, N 7.80. IR (KBr, cm^{-1} ; Figure S7): 3434 (s, br), 2362 (m), 1612 (s), 1567 (s), 1373 (s), 1245 (w), 1120 (w), 781 (m), 731 (m).

X-ray Crystallographic Study. Single crystal X-ray data of **FCS-2** was collected on *Bruker APEX-II* diffractometer. The structure was solved by direct methods and developed by difference Fourier techniques, both using the SHELXL software package.^{S1} All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms attached to carbon atoms were generated geometrically. Attempts to locate and model the highly disordered solvent molecules in the pores were unsuccessful. Therefore, the SQUEEZE routine of PLATON were used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities.^{S2} Crystallographic data and structure refinements for **FCS-2** are listed in Table S1.

Fluorescence Sensing Measurement. The photoluminescence excitation and emission spectra were recorded on a Hitachi F-4500 spectrophotometer. The fluorescence properties of **FCS-2** in solid state and in DMF suspensions were examined at room temperature. The suspensions were prepared by introducing 20 mg fine grinding sample of **FCS-2** immersed in DMF (20 mL), treated by ultrasonication for about 30 minutes, and then aged for half an hour to form stable emulsions. In typical fluorescence quenching experimental setup, 2 mL suspension of **FCS-2** in DMF was placed in a 1 cm quartz cuvette and the fluorescence response upon excitation at 362 nm was measured in situ after incremental addition of freshly prepared 2 mM analyte solution at room temperature.

References

- (S1) G. M. Sheldrick, SHELXS97. *Acta Crystallogr., Sect. A* **2008**, 64, 112.
- (S2) A. L. Spek, Single-crystal structure validation with the program PLATON, *J. Appl. Cryst.* **2003**, 36, 7-13.

Table S1. Crystallographic Data for FCS-2.

Compound	FCS-2
Empirical formula	Cd ₃ C ₈₂ H ₁₀₆ N ₁₂ O ₃₉
Formula mass	2221.01
Crystal system	monoclinic
Space group	C2/c
a (Å)	35.699(4)
b (Å)	16.305(2)
c (Å)	36.670(4)
α (°)	90
β (°)	102.959(4)
γ (°)	90
V (Å³)	20801(4)
Z	8
D_{calc} (g·cm⁻³)	1.418
Reflections collected	63882 / 7891
Data	6470 / 517
[I>2σ(I)]/parameters	
Goodness-of-fit on F²	1.041
R₁ indices (I > 2σ(I))	0.0734
wR₂ indices (all data)	0.2074

^a $R = \sum||F_o| - |F_c|| / \sum|F_o|$. ^b $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

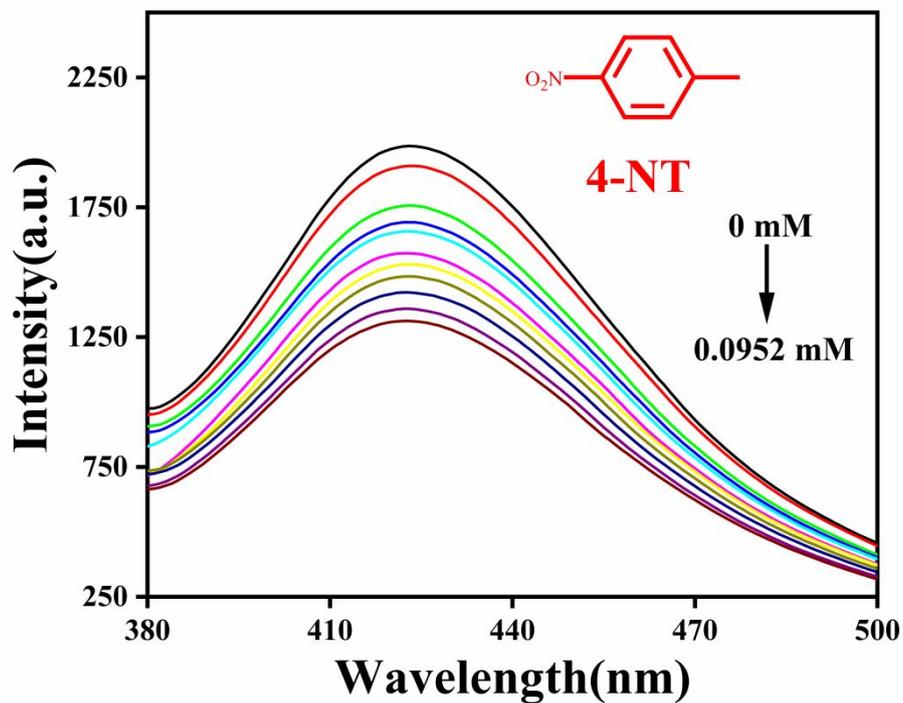


Figure S1. The fluorescence titration of FCS-2 upon incremental addition of 4-NT solution.

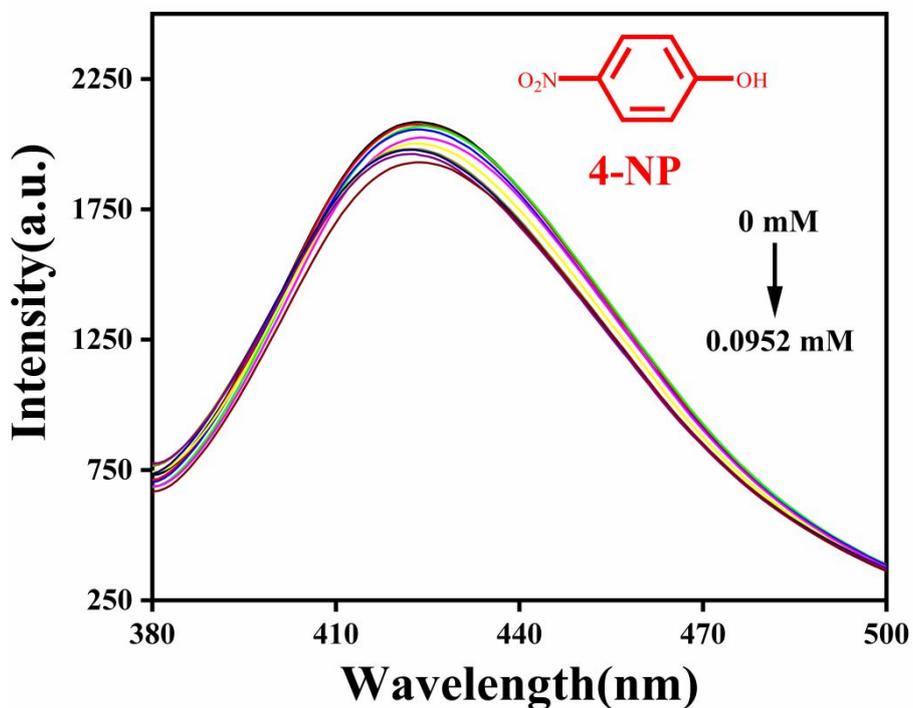


Figure S2. The fluorescence titration of FCS-2 upon incremental addition of 4-NP solution.

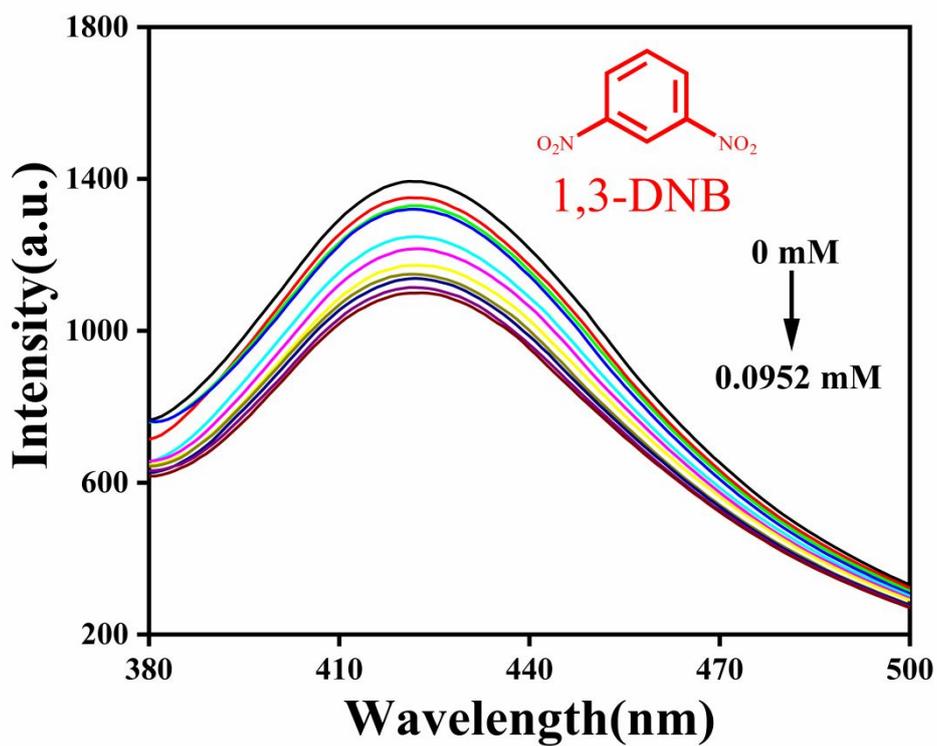


Figure S3. The fluorescence titration of FCS-2 upon incremental addition of 1,3-DNB solution.

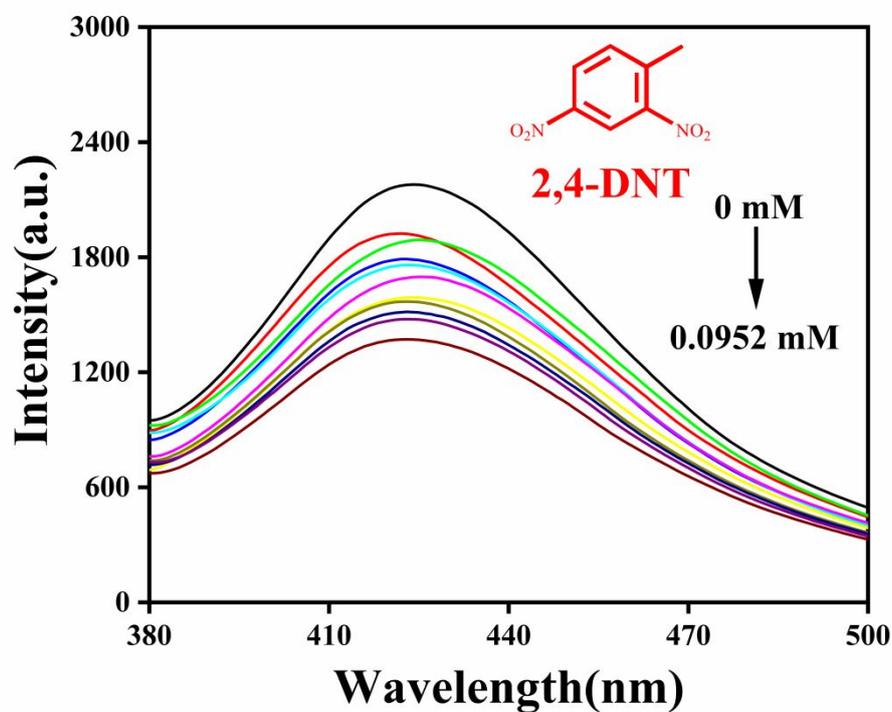


Figure S4. The fluorescence titration of FCS-2 upon incremental addition of 2,4-DNT solution.

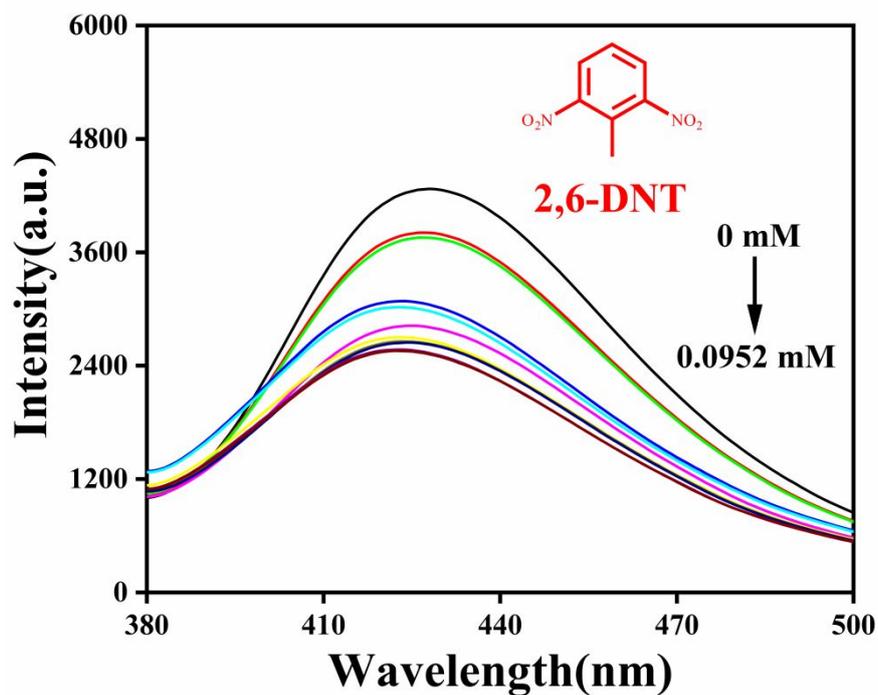


Figure S5. The fluorescence titration of FCS-2 upon incremental addition of 2,6-DNT solution.

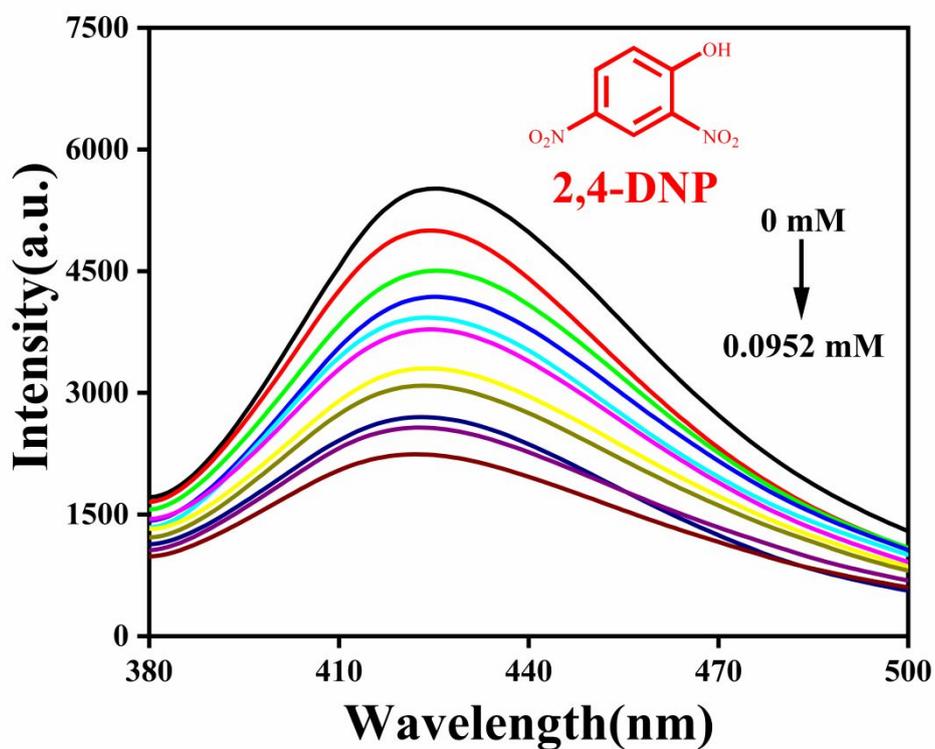


Figure S6. The fluorescence titration of FCS-2 upon incremental addition of 2,4-DNP solution.

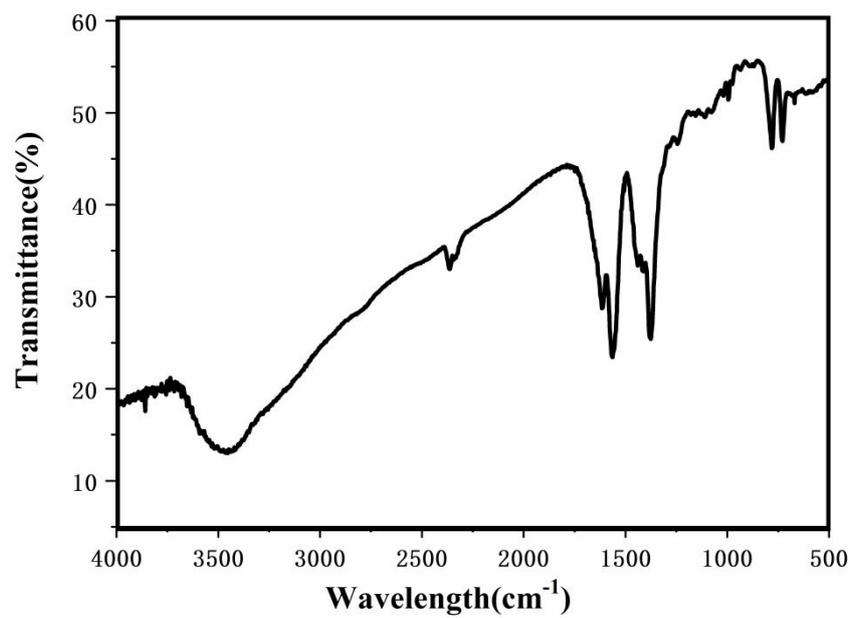


Figure S7. FT-IR spectrum for compound **FCS-2**.

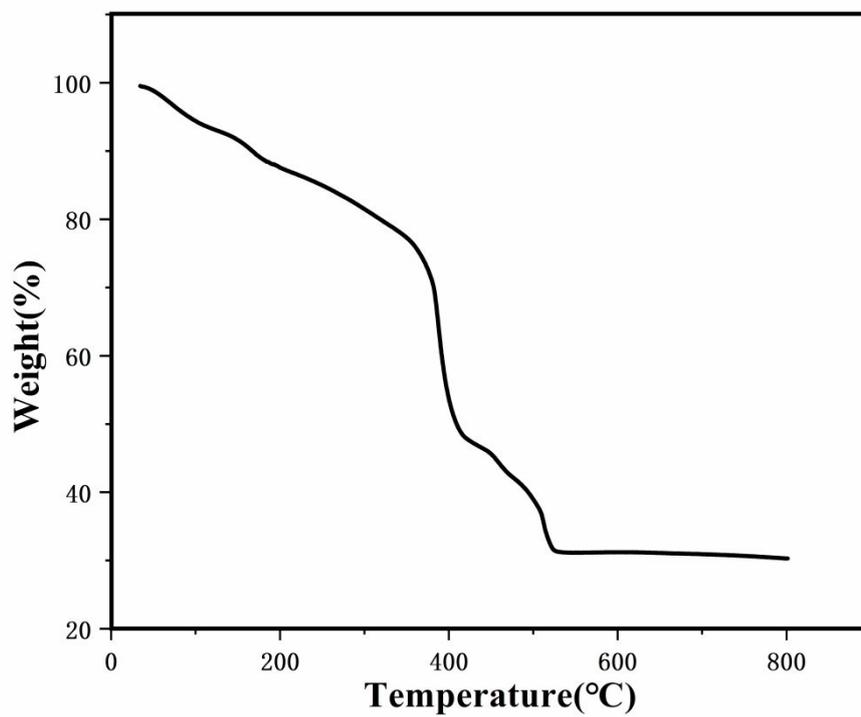


Figure S8. TGA curve for compound **FCS-2**.