Electronic Supporting Information

A stable luminescent anionic porous metal-organic framework for moderate adsorption of CO$_2$ and selective detection of nitro explosives

En-Long Zhou, Peng Huang, Chao Qin,* Kui-Zhan Shao, Zhong-Min Su*
Experimental Section

Materials and Instrumentation: All chemicals were obtained commercially and used without additional purification. Single-crystal diffractometry was conducted on a Bruker Smart Apex CCD II area-detector diffractometer with graphite-monochromated Mo $K_{\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer and the rare earth metal contents were determined with a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 4000-400 cm$^{-1}$ on Mattson Alpha-Centauri spectrometer using KBr pellets. Thermal gravimetric (TG) analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N$_2$ with a heating rate of 10 °C/min. Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX-3 instrument with Cu $K\alpha$ radiation in the angular range $2\theta = 3°-50°$ at 293 K. Gas adsorption measurement was measured with Quantachrome Autosorb-iQ. UV-vis absorption spectra were recorded on Hitachi U3030 spectrometer. The emission spectra were recorded using the F-4500 FL spectrophotometer.

Synthesis of [(CH$_3$)$_2$NH$_2$]$_3$[Zn$_4$Na(BPTC)$_3$]$\cdot$4CH$_3$OH$\cdot$2DMF (1): A mixture of sodium biphenyl-3,3',5,5'-tetracarboxylate (Na$_4$BPTC, 42mg, 0.1 mmol) and ZnCl$_2$ (27 mg, 0.2 mmol) were dissolved in 3 mL N,N-dimethylformamide (DMF) and 3 mL methanol(MeOH) and stired
for 10 minutes. Then the mixture was transferred into and sealed in a Teflon reactor (18 mL) and heated at 100 °C for 72 h. Colorless block crystals of the product were formed and collected by filtration and washed with DMF several times after the mixture was cooled to room temperature. Yield: 40 mg (~93.8% based on H₄BPTC). Elemental analysis for C₆₄H₇₂O₃₀N₅NaZn₄ (%): calcd. H: 4.33 C: 45.86 N: 4.18%. found: 4.12 C: 46.02 N: 4.27%.

**X-ray Crystallography:** Single-crystal diffractometry was conducted on a Bruker Smart Apex CCD II area-detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography. Empirical absorption corrections were applied. The structures were solved by using the direct method and refined through the full-matrix least-squares method on F² using SHELXS-97. The total interstitial solvent molecule contents were determined by TGA.

Crystal data of 1: Monoclinic, a = 12.285(5) Å, b = 31.023(5) Å, c = 22.686 Å, V = 8623(4) Å³, T = 298(2) K, space group C2/c, Z = 4, 18663 reflections measured, 5944 independent reflections (R_int = 0.0530). The final R₁ values were 0.0938 (I > 2σ(I)). The final wR(F²) values were 0.1312 (I > 2σ(I)). The goodness of fit on F² was 0.8650.
**Small solvent molecule sensing experiments:** The activated and fine grinding sample of 1a (3 mg) was immersed in different pure organic solvents (3 mL). Then the sample was treated by ultrasonication for 3 h and then aged for 2 days to form a stable emulsion before the fluorescence study.

**Aromatic compounds sensing experiments:** The activated and fine grinding sample of 1a (2 mg) was immersed in DMF (3 mL), treated by ultrasonication for 30 min. Then equal volume (80 μL) of aromatic molecules was added into the above samples. Finally, stable emulsion was formed by ultrasonication for additional 3 h and then aged for 2 days before the fluorescence study. The aromatic compounds are benzene (Bz), toluene (TO), nitrobenzene (NB), chlorobenzene (CB), o-xylene (OX), p-xylene (PX), m-xylene (MX) and styrene (ST).

**Nitro compounds sensing experiments:** In typical experimental setup, 2 mg of 1a is weighed and dispersed in 2 mL DMF, treated by ultrasonication for 3 h and aged for 2 days to form stable emulsion. The fluorescence of emulsion upon excitation at 295 nm was measured in-situ after incremental addition of freshly prepared analyte solutions (1mM).

**Gas adsorption experiments:** The N₂ and CO₂ sorption measurements were performed on an automatic volumetric adsorption equipment (Quantachrome Autosorb-iQ). Before gas adsorption measurements, the sample was immersed in dichloromethane for 24 h, and the extract was
decanted. Fresh dichloromethane was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the methonal solvates. After the removal of dichloromethane by decanting, the sample was activated by drying under a dynamic vacuum at 373 K overnight. Before the measurement, the sample was dried again by using the ‘outgas’ function of the surface area analyzer for 12 h at 373 K.
Fig. S1 PXRD patterns of the simulated one and as synthesized sample.

Fig. S2 The IR spectroscopy of compound 1.
**Fig S3.** The two type of coordination codes of BPTC ligand in compound 1.

**Figure S4.** The small 1D hexagonal channel in the 2D sheet viewed along the crystallographic c axis.

**Figure S5.** The 3D structure viewed along the a axis.
Figure S6. The natural tiling of compound 1.

Figure S7. The TG curve of compound 1.
Figure S8. The XRD patterns of compound 1 in the solution of different pH.

Fig S9. The PXRD patterns of compound 1 immersed in water at 80 °C
Fig S10. The XRD patterns of simulated, as synthesized and desolvated 1 (1a).

Fig S11. The TG curve of desolvated compound 1 (1a).
### Table S1. The relevant data of CO$_2$ adsorption capacities for MOFs at 273 K

<table>
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<tr>
<th>Compound</th>
<th>Surface area (m$^2$/g)</th>
<th>Langmuir</th>
<th>BET</th>
<th>Capacity (wt%)</th>
<th>Pressure (bar)</th>
<th>Ref</th>
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<td>Co$<em>6$(int)$</em>{18}$(μ$_2$-OH)$_4$(H$_2$O)$_2$</td>
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### Table 2. The relevant data of CO$_2$ adsorption capacities for MOFs at 298 K

<table>
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<tr>
<th>Compound</th>
<th>Surface area (m$^2$/g)</th>
<th>Langmuir</th>
<th>BET</th>
<th>Capacity (wt%)</th>
<th>Pressure (bar)</th>
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<td>Compound 1</td>
<td>1002</td>
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<td>9.4</td>
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SIFSIX-2-Cu-i  |  821  |  735  |  23.8  |  1  | Nature, 2013, 495, 80
MAF-35          |  1043 |  974  |  19.6  |  1  | Chem, Commun. 2013, 49, 11728
Mg₂(dobpdc)     |       |       |  16.5  |  1  | J. Am. Chem. Soc. 2012, 134, 7056
Cu-BTTr       |  1900 |  1770 |  14.3  |  1  | J. Am. Chem. Soc., 2009, 131, 8784
NTU-111        |  2450 |       |  13.3  |  1  | Chem. Commun. 2014, 50, 4683-4685
Co₉(int)₁₈(μ₂-OH)₂(H₂O)₂ |  835 |  600  |  11.5  |  1  | CrystEngComm, 2014, 16, 4088-4090.
IFMC-69         |  664  |  581  |  7.3   |  1  | Chem. Sci., 2014, 5, 1368-1374
ROD-6           |  535  |  345  |  7.73  |  1  | Chem. Commun. 2014, 50, 4047-4049
ZIF-301         |  825  |  680  |  6.4   |  1  | Angew. Chem. Int. Ed. 2014, 53, 10645

Fig S12. The CO₂ isosteric adsorption enthalpies calculated by Clausius–Clapeyron.
equation between isotherms at 273 and 298 K.

Fig S13. The excitation and emission spectra of BPTC.

Fig S14. The excitation and emission spectra of compound 1.
Fig S15. The PL spectra of 1a that were immersed in different small solvents.

Fig S16. The PL spectra of 1a upon incremental addition of acetone to 1a dispersed in DMF.
Fig S17. The PL spectra of 1a that were immersed in different aromatic compounds.

Fig S18. The emission spectra of compound 1a immersed in DMF.
**Fig S19.** Quenching percentage upon addition of different 10 µL nitro explosives (1mM)

**Fig. S20** Emission spectra of compound 1a dispersed in DMF upon incremental addition of 1,3-DNB solution (1mM) in DMF.
**Fig. S21** Emission spectra of compound 1a dispersed in DMF upon incremental addition of NB solution (1mM) in DMF.

**Fig. S22** Emission spectra of compound 1a dispersed in DMF upon incremental addition of TNP solution (1mM) in DMF.
Fig. S23 Emission spectra of compound 1a dispersed in DMF upon incremental addition of \textit{m}-MNT solution (1mM) in DMF.

Fig. S24 Emission spectra of compound 1a dispersed in DMF upon incremental addition of \textit{o}-MNT solution (1mM) in DMF.
**Fig. S25** Emission spectra of compound 1a dispersed in water upon incremental addition of 1,3-DNB solution (1mM) in DMF.

**Fig. S26** Emission spectra of compound 1a dispersed in water upon incremental addition of NB solution (1mM) in DMF.
**Fig. S27** Emission spectra of compound 1a dispersed in water upon incremental addition of TNP solution (1mM) in DMF.

**Fig. S28** Emission spectra of compound 1a dispersed in water upon incremental addition of *m*-MNT solution (1mM) in DMF.
Fig. S29 Emission spectra of compound 1a dispersed in water upon incremental addition of o-MNT solution (1mM) in DMF.

Fig. S30 Corresponding Stern-Volmer plots of I₀/I-1 versus analyte concentrations in DMF.
Fig. S31 Emission spectrum of 1a in water upon addition of DMF solution of DNB followed by TNP (1mM, DNB and TNP 40 µL addition each time).

Fig. S32 Emission spectrum of 1a in water upon addition of DMF solution of NB followed by TNP (1mM, NB and TNP 40 µL addition each time).
Fig. S33 Shapes of HOMO and LUMO of the molecular orbitals considered and the relative energy level investigated by the B3LYP/6-31G** method.

Table S3: HOMO and LUMO energies calculated for explosive analytes (at B3LYP/6-31G* level of theory).

<table>
<thead>
<tr>
<th>Analytes</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Band gap (eV)</th>
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<tr>
<td>NB</td>
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<td>TNP</td>
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Fig. S34 Spectral overlap between the absorption spectra of analytes and the emission spectrum of 1a in DMF.