Electronic Supplementary Information (ESI)

A Luminescent Metal-Organic Framework for Highly Selective

Sensing of Nitrobenzene and Aniline

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Contents Experimental details for the anti-interference ability of gea-MOF-1......2 Fig. S2 Excitation (at 284 nm) and emission (at 385 nm) spectra of H₃BTB in the solid state at room Fig. S3 Excitation (at 290 nm) and emission (at 373 nm) spectra of gea-MOF-1 in the solid state at Fig. S4 Emission spectra of gea-MOF-1 (5 mg) at room temperature in different solvents (5 mL) (λ_{ex} = Fig.S5 The fluorescence intensity of gea-MOF-1 in different concentration of nitroaromatic compounds (a) 2,4-dinitrophenol (DNP), (b) p-nitrophenol (PNP), (c) 4-nitrotoluene (4-NP), (d) o-Fig.S6 Emission spectra of methanol suspension of gea-MOF-1 upon addition of different nitroaromatic compounds (a) 2,4-dinitrophenol (DNP), (b) p-nitrophenol (PNP), (c) 4nitrotoluene (4-NP), (d) o-nitrophenol (ONP) followed by NB (λ_{ex} = 290 nm) Fig. S7 Fluorescence intensity ratio histograms of gea-MOF-1 dispersed in methanol with the addition Fig. S8 Reproducibility of the quenching ability of gea-MOF-1 dispersed in methanol to NB ($\lambda_{ex} = 290$) nm)......7 Fig. S9 Fluorescence intensity ratio histograms of gea-MOF-1 dispersed in methanol with the addition of different organic amines (pink) and subsequent addition of AN (blue) (λ_{ex} = 290 nm)......7 Fig. S10 Reproducibility of the quenching ability of gea-MOF-1 dispersed in methanol to AN (λ_{ex} = Fig. S12 The UV-vis absorption spectra of NB, DNP, PNP, 4-NP, ONP, AN in methanol.....8 Materials and general methods

All solvents and starting materiels for synthesis were purchased commercially and were used as received. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 advanced automated diffractometer with Cu-K radiation. Luminescencespectra for the solid samples and liquid

samples were investigated with a HitachiF-4500 fluorescence spectrophotometer and Varian Cary Eclipse Fluorescence spectrophotometer, respectively. All UV/Vis spectra were measured on a SP-752(PC) UV-Vis spectrophotometer (Shanghai Spectrum Instrument Co., Ltd).

Synthesis of gea-MOF-1

The crystal of **gea-MOF-1** was synthesized according to references. A solution of $Y(NO_3)_3 \cdot 6H_2O$ (8.6 mg, 0.0225mmol), H₃BTB (6.6 mg, 0.015 mmol), 2-fluorobenzoic acid (95.2 mg, 0.675 mmol), DMF (2 mL) and H₂O (0.5 mL) was prepared in a 20 ml scintillation vial and subsequently heated to 378 K for 36 hours in a preheated oven.

Experimental details for the anti-interference ability of gea-MOF-1

The powder sample of gea-MOF-1 (36 mg) was immersed in methanol (100 mL). Treated by ultrasonication and then aged to generate stable suspensions before the fluorescence study. Some aromatic compounds with the same concentrations of 60 ppm were added to the methanol suspension of gea-MOF-1, and the corresponding emission spectra were monitored. With the subsequent addition of 60 ppm nitrobenzene into the parallel tests, and the corresponding emission spectra were monitored.

MOF	Quantity(mg)/solvent (mL)	NB concentration	Quenching efficiency	Ref.
$[Tb(L_1)_{2/3}(L_2)_{1/2}(H_2O)_2]^{\cdot}2H_2O$	3 mg/5 mL	1000 ppm	60%ª	[1]
$\{[(UO_2)_2(H_2TTHA)(H_2O)]\cdot 4,4'\text{-bipy}\cdot 2H_2O\}_n$	2 mg/3 mL	1000 ppm	90% ^b	[2]
$Mg_4(L)(DMF)_4(H_2O)_4(DMF)_{0.5}$	5 mg/3 mL	1500 ppm	100%	[3]
$[Eu(L)_{1.5}(DEF)]_n$	3 mg/5 mL	970 ppm	100%	[4]
[Cd ₃ (NTB) ₂ (DMA) ₃]·2DMA	°/3 mL	600 ppm	79%	[5]
$[Zn_2(trz)_2(bpdc)] \cdot DMA$	3 mg/3 mL	500 ppm	89%	[6]
Tb ³⁺ @NENU-522	3 mg/3 mL	2000 ppm	100%	[7]
[Cd(ppvppa)(1,4-NDC)] _n	2 mg/2 mL	800 ppm	94%	[8]
$Cd_{2.5}Na(NTB)_2(DMF)_4]\cdot 3DMF$	0.3 mg/3 mL	500 ppm	83%	[9]
$[Zn_3(HL)_2(fma)_2]\cdot DMA\cdot H_2O$	0.3 mg/3 mL	300 ppm	92%	[10]
$[Tb(mtpc)_{1.5}(DMA)(H_2O)]\cdot 2H_2O$	0.4 mg/5 mL	150ppm	87.9%	[11]
$(DMA)_2[Y_9(\mu_3\text{-}OH)_8(\mu_2\text{-}OH)_3BTB_6]_n\cdot(solv)_x$	1.8 mg/5 mL	60 ppm	93.1%	This work

Table S1 Summary of the quenching efficiency of luminescent MOF sensors for NB^a

^a The values were estimated from the literature^[1]. ^b The values were estimated from the literature^[2].

^c The quantity of MOF is missed in literature ^[5].



Fig. S1 PXRD patterns of gea-MOF-1



Fig. S2 Excitation (at 284 nm) and emission (at 385 nm) spectra of H_3BTB in the solid state at room temperature.



Fig. S3 Excitation (at 290 nm) and emission (at 373 nm) spectra of gea-MOF-1 in the solid state at room temperature.



Fig. S4 Emission spectra of **gea-MOF-1** (5 mg) at room temperature in different solvents (5 mL) ($\lambda_{ex} = 290 \text{ nm}$)



Fig.S5 The luminescent intensity of **gea-MOF-1** in different concentration of nitroaromatic compounds (a) 2,4-dinitrophenol (DNP), (b) p-nitrophenol (PNP), (c) 4-nitrotoluene (4-NP), (d) o-nitrophenol (ONP) (λ_{ex} = 290 nm)



Fig.S6 Emission spectra of methanol suspension of **gea-MOF-1** upon addition of different nitroaromatic compounds (a) 2,4-dinitrophenol (DNP), (b) p-nitrophenol (PNP), (c) 4-nitrotoluene (4-NP), (d) o-nitrophenol (ONP) followed by NB (λ_{ex} = 290 nm)



Fig. S7 Fluorescence intensity ratio histograms of **gea-MOF-1** dispersed in methanol with the addition of different aromatic compounds (pink) and subsequent addition of NB (blue) (λ_{ex} = 290 nm)



Fig. S8 Reproducibility of the quenching ability of **gea-MOF-1** dispersed in methanol to NB (λ_{ex} = 290 nm).



Fig. S9 Fluorescence intensity ratio histograms of **gea-MOF-1** dispersed in methanol with the addition of different organic amines (pink) and subsequent addition of AN(blue) (λ_{ex} = 290 nm)



Fig. S10 Reproducibility of the quenching ability of **gea-MOF-1** dispersed in methanol to AN (λ_{ex} = 290 nm)



Fig. S11 The PXRD patterns of gea-MOF-1: the samples after 5 quenching cycles



Fig. S12 The UV-vis absorption spectra of NB, DNP, PNP, 4-NP, ONP, AN in methanol

Reference:

[1] J. Z. Wang, W. Sun, S. Y. Chang, H. T. Liu, G. N. Zhang, Y. Q. Wang and Z. L. Liu, RSC *Adv.*, 2015, **5**, 48574-48579; [2] J. Song, X. Gao, Z. N. Wang, C. R. Li, Q. Xu, F. Y. Bai, Z. F. Shi and Y. H. Xing, *Inorg. Chem.*, 2015, **54**, 9046-9059;

[3] S. L. Xie, H. F. Wang, Z. H. Liu, R. Dai and L. Z. Huang, RSC Adv., 2015, 5, 7160-7172;

[4] S. N. Zhao, X. Z. Song, M. Zhu, X. Meng, L. L. Wu, S. Y. Song, C. Wang and H. J. Zhang, RSC Adv., 2015, 5, 93-98;

[5] X. L. Hu, F. H. Liu, C. Qin, K. Z. Shao and Z. M. Su, Dalton Trans., 2015, 44, 7822-7827;

[6] F. H. Liu, C. Qin, Y. Ding, H. Wu, K. Z. Shao and Z. M. Su, Dalton Trans., 2015, 44, 1754-1760;

[7] W. Xie, S. R. Zhang, D. Y. Du, J. S. Qin, S. J. Bao, J. Li, Z. M. Su, W. W. He, Q. Fu and Y. Q. Lan, Inorg. Chem., 2015, 54, 3290-3296;

[8] M. M. Chen, X. Zhou, H. X. Li, X. X. Yang and J. P. Lang, Cryst. Growth Des., 2015, 15, 2753-2760;

[9] X. L. Hu, C. Qin, X. L. Wang, K. Z. Shao and Z. M. Su, New J. Chem., 2015, 39, 7858-7862;

[10] X. L. Hu, C. Qin, L. Zhao, F. H. Liu, K. Z. Shao and Z. M. Su, RSC Adv., 2015, 5, 49606-49613;

[11] X. M. Cao, N. Wei, L. Liu, L. Li and Z. B. Han, RSC Adv., 2016, 6, 19459-19462