Two isostructural Ln³⁺-based heterometallic MOFs for the detection

of nitro-aromatic and $Cr_2O_7^{2-}$

Yuxiao Zhang, YitingYing, Meng Feng, Liang Wu, Dongmei Wang* and Chunxia Li*

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, P. R. China. E-mail: <u>dmwang@zjnu.edu.cn</u>, <u>cxli@zjnu.edu.cn</u>.

Calculation procedures of fluorescence quenching efficiency

The fluorescence quenching efficiency of In/Eu-CBDA and In/Tb-CBDA can be evaluated by the Stern-Volmer constant (Ksv), which is calculated by using the Stern-Volmer equation:

$$I_0/I = 1 + Ksv[M]$$

 $(I_0 =$ the initial luminescence intensity, I = the luminescence intensity after the addition of the analytes, [M] = the concentration of the analytes and K_{SV} = the Stern–Volmer constant).



Fig. S1 Powder XRD spectra of In/Tb-CBDA, In/Eu-CBDA and single crystal structures.



Fig. S2 PXRD patterns for In/Eu-CBDA samples (a) at different pH and (b) at variable temperatures.



Fig. S3 Sorption isotherm and pore size distribution of In/Eu-CBDA at 77 K.



Fig. S4 Isosteric heat of CO_2 (a), CH_4 (b), C_2H_6 (c), and C_3H_8 (d) for In/Eu-CBDA.



Fig. S5 Excitation and emission spectra of (a) CBDA (b) In/Eu-CBDA and (c) In/Tb-CBDA.



Fig. S6 (a) and (b) are the fluorescence spectra of 1,4-dinitrobenzene for In/Eu-CBDA and In/Tb-CBDA at different concentrations; (c) and (d) are the Stern-Volmer (SV) spectrum of 1,4-dinitrobenzene for In/Eu-CBDA and In/Tb-CBDA.



Fig. S7 (a) Fluorescence intensity spectrogram of In/Tb-CBDA in aqueous solution containing different competing ions and fluorescence intensity spectrum after adding $Cr_2O_7^{2-}$. UV-Vis absorption spectra of (b) In/Eu-CBDA and (c) In/Tb-CBDA in DMF solutions with different potassium anions.



Fig. S8 The reproducibility of the quenching ability of (a) In/Eu-CBDA and (b) In/Tb-CBDA on $Cr_2O_7^{2-}$.



Fig. S9 The powder XRD patterns for In/Eu-CBDA and In/Tb-CBDA after fluorescent detection.

Materials	Ksv (M ⁻¹)	Detection limit (ppb)	Solvent	Reference
In/Eu-CBDA	1.08×10^{4}	2.15×10 ⁸	DMF	This work
In/Tb-CBDA	1.72×10^{4}	8.72×10^{6}	water	This work
Zn-MOF-1	2.07×10^{4}	3.53×10^{6}	water	[1]
[Zn ₂ (TPOM)(NH ₂ -BDC) ₂]·4H ₂ O	7.59×10 ³	3.90×10 ⁶	DMF	[2]
$[Cd(L)(TPOM)_{0.75}]$ ·xS	1.35×10^{4}		water	[3]
$[Zn(L)(BBI) \cdot (H_2O)_2]$	1.17×10^{4}		water	[3]
[Eu(Hpzbc) ₂ (NO ₃)]·H ₂ O		2.20×10^{7}	ethanol	[4]
$[Zn_2(TPOM)(NDC)_2]$ ·3.5H ₂ O	9.21×10 ³	2.35×10^{6}	water	[5]
534-MOF-Tb	1.37×10^{4}	1.40×10^{8}	water	[6]
Eu ³⁺ @MIL-121	4.34×10 ³	5.40×10^{4}	water	[7]
$[Zn_7(TPPE)_2(SO_4^{2-})_7](DMF \cdot H_2O)$	1.09×10^{4}	26.98	water	[8]
[Tb(TATAB)(H ₂ O) ₂]·NMP	1.11×10^{4}		water	[9]
$[Zn_3(tza)_2(\mu_2-OH)_2(H_2O)_2]H_2O$	5.02×10 ³	1.00×10^{6}	water	[10]
[Zn(btz)]n	3.19×10 ³	5.20×10^{2}	water	[11]
$[Zn_2(ttz)H_2O]_n$	2.19×10 ³	1.04×10^{3}	water	[11]
$[Eu(ipbp)_2(H_2O)_3]Br \cdot 6H_2O$	8.98×10 ³	5.16×10 ⁹	water	[12]
$[Eu_7(mtb)_5(H_2O)_{16}] \cdot NO_3 \cdot 8DMA \cdot 18H_2O$	3.34×10^{4}	0.56	water	[13]
[Zn ₃ (bpanth)(oba) ₃]·2DMF	9.40×10 ⁴	7.00×10^{2}	water	[14]
Zr ₆ O ₄ (OH) ₇ (H2O) ₃ (BTBA) ₃	1.57×10^{4}	1.50×10^{6}	water	[15]

Table S1 Comparison of detection ability on representative MOFs towards $Cr_2O_7^2$.

- (1) X.-Y. Guo, F. Zhao, J.-J. Liu, Z.-L. Liu and Y.-Q. Wang, J. Mater. Chem. A, 2017, 5, 20035-20043.
- (2) R. Lv, J. Wang, Y. Zhang, H. Li, L. Yang, S. Liao, W. Gu and X. Liu, J. Mater. Chem. A, 2016, 4, 15494-15500.
- (3) Y. Zhao, X. Xu, L. Qiu, X. Kang, L. Wen and B. Zhang, *ACS Appl Mater*. *Interfaces*, 2017, **9**, 15164-15175.
- (4) G.-P. Li, G. Liu, Y.-Z. Li, L. Hou, Y.-Y. Wang and Z. Zhu, *Inorg. Chem.*, 2016, 55, 3952-3959.
- (5) R. Lv, H. Li, J. Su, X. Fu, B. Yang, W. Gu and X. Liu, *Inorg. Chem.*, 2017, 56, 12348-12356.
- (6) M. Chen, W.-M. Xu, J.-Y. Tian, H. Cui, J.-X. Zhang, C.-S. Liu and M. Du, J. Mater. Chem. C, 2017, 5, 2015-2021.
- (7) J.-N. Hao and B. Yan, New J. Chem., 2016, 40, 4654-4661.
- (8) X.-X. Wu, H.-R. Fu, M.-L. Han, Z. Zhou and L.-F. Ma, Cryst. Growth Des., 2017, 17, 6041-6048.
- (9) G.-X. Wen, M.-L. Han, X.-Q. Wu, Y.-P. Wu, W.-W. Dong, J. Zhao, D.-S. Li and L.-F. Ma, *Dalton Trans.*, 2016, 45, 15492-15499.

- (10) T.-Q. Song, J. Dong, H.-L. Gao, J.-Z. Cui and B. Zhao, *Dalton Trans.*, 2017, **46**, 13862-13868.
- (11) C.-S. Cao, H.-C. Hu, H. Xu, W.-Z. Qiao and B. Zhao, *CrystEngComm*, 2016, **18**, 4445-4451.
- (12) C. Zhang, L. Sun, Y. Yan, H. Shi, B. Wang, Z. Liang and J. Li, *J. Mater. Chem. C*, 2017, **5**, 8999-9004.
- (13) W. Liu, Y. Wang, Z. Bai, Y. Li, Y. Wang, L. Chen, L. Xu, J. Diwu, Z. Chai and S. Wang, ACS Appl Mater. Interfaces, 2017, 9, 16448-16457.
- (14) Z.-Q. Yao, G.-Y. Li, J. Xu, T.-L. Hu and X.-H. Bu, Chem. Eur. J., 2018, 24, 3192-3198.
- (15) T. He, Y.-Z. Zhang, X.-J. Kong, J. Yu, X.-L. Lv, Y. Wu, Z.-J. Guo and J.-R. Li, *ACS Appl Mater. Interfaces*, 2018, **10**, 16650-16659.