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Supporting Information

Extremely stable europium-organic framework for luminescent sensing $Cr_2O_7^{2-}$ and Fe^{3+} in aqueous system

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EXPERIMENT SECTION

Instruments

The purity of the bulk samples were determined by Bruker D8 Advance powder X-ray diffractometer. Thermal stability were performed on TA Q50 apparatus in the temperature range of 30-800 °C under nitrogen atmosphere. Elemental analyses (C, H and N) were performed on an Elementar Vario MICRO elemental analyzer. The infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer as KBr pellets in the range of 400-4000 cm^{-1}. The UV-Vis absorption spectra were recorded on a Thermo Scientific NanoDrop 2000c spectrometer. The solid state emission and excitation spectra were tested on a Horiba Jobin-Yvon Fluorolog-3 spectrophotometer. Luminescent behavior in aqueous solution were recorded on Agilent Cary Eclipse.

Structure determination

Data collection for Ln-MOFs were performed on Bruker APEXII diffractometer equipped with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) by using the ω-scan and φ-scan mode at room temperature. The structures were solved by direct methods followed by successive difference Fourier methods, and refined on F^2 by full-matrix least-squares using SHELXTL-2018 program package. All non-hydrogen atoms were refined anisotropically. Ligand 1,3-bdc^{2-} that generated by the operation of inversion center was disordered, and hydrogen atoms on it were not determined. The other hydrogen atoms of organic ligands were generated theoretically. The number of lattice water molecules was determined according to the results of the thermogravimetry and elemental analysis. The molecular formulas for all Ln-MOFs contain the lattice water molecules that were not determined according to difference Fourier peaks. Crystallographic data of Ln-MOFs were listed in Table S1.

Syntheses

H_2LCl_2 was synthesized according to the method reported.[1] Other reagents in analytical grade were commercially purchased from Aladdin and Sinopharm and used without further purification.

[$Eu_2L(1,3\text{-}bdc)_3$]·$5H_2O$: 0.01 mmol (42 mg) H_2LCl_2, 0.02 mmol (32 mg) 1,3-H_2bdc, 0.01 mmol (35 mg) Eu_2O_3 were added to the 20 mL Telfon-lined stainless steel container, following with 6 mL deionized H_2O. Then the mixture was heated at 140 °C for 96 hours. After cooling to room temperature, colorless crystals were obtained with further filtration. Anal. Calcd. for $C_{44}H_{38}Eu_2N_2O_{21}$ (%): C, 42.80; H, 3.10; N, 2.27. Found (%): C, 42.73; H, 3.16; N, 2.20. IR (KBr, cm^{-1}): 3423 (s), 3034 (w), 1652(s), 1607(s), 1450 (s), 1397 (s), 1181 (w), 1133 (w), 1078 (w), 917 (w), 844 (m), 784 (w).

[$Sm_2L(1,3\text{-}bdc)_3$]·$5H_2O$: The synthesized procedure was same with Eu-MOF except lanthanide salt. 0.01 mmol (35 mg) Sm_2O_3 was used instead of Eu_2O_3. Anal. Calcd. for $C_{44}H_{38}Sm_2N_2O_{21}$ (%): C, 42.29; H, 3.23; N, 2.24. Found (%): C, 42.25; H, 3.08; N, 2.38. IR (KBr, cm^{-1}): 3431 (s), 3034 (w), 1651 (s), 1607 (s), 1547 (s), 1480 (s), 1449 (s), 1398 (s), 1181 (w), 1133 (w), 1078 (w), 917 (w), 844 (w), 743 (w).

[$Dy_2L(1,3\text{-}bdc)_2$]·$5H_2O$: The method was same with Eu-MOF but using 0.01 mmol (37 mg) Dy_2O_3 instead of Eu_2O_3. Anal. Calcd. for $C_{44}H_{38}Dy_2N_2O_{21}$ (%): C, 41.49; H, 3.17; N, 2.20. Found (%): C, 42.17; H, 3.16; N, 2.29. IR (KBr, cm^{-1}): 3435 (s), 3034 (w), 1659 (s), 1608 (s), 1551 (s), 1454 (s), 1401 (s), 1183 (w), 1160 (w), 1133 (w), 1079 (w), 1044 (w), 1021 (w), 920 (w), 847 (m), 744 (s).

Table S1 Crystallographic data for Ln-MOFs.

Compounds	**Eu-MOF**	**Sm-MOF**	**Dy-MOF**
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P* -1	*P* -1	*P* -1
a (Å)	10.0810(8)	10.0830(7)	10.0735(12)
b (Å)	11.4845(9)	11.4747(8)	11.4617(14)
c (Å)	12.2758(10)	12.2880(9)	12.2530(14)
α (°)	117.1100(10)	117.1020(10)	117.1650(10)
β (°)	99.5530(10)	99.4780(10)	99.5150(10)
γ (°)	104.7060(10)	104.6280(10)	104.7310(10)
V (Å^3)	1156.32(16)	1158.21(14)	1150.4(2)
Z	2	2	2
T (K)	296(2)	296(2)	296(2)
Measured reflections	6863	8236	6933
Independent reflections	5032	5102	5051
R_{int}	0.0144	0.0164	0.0144
D_c (g cm^{-3})	1.661	1.654	1.700
F(000)	564	562	562
S	1.082	1.169	1.048
R_1 (I >2σ(I))[a]	0.0355	0.0347	0.0399
wR_2 (I >2σ(I))[b]	0.0989	0.0949	0.1083

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Comparison of sensing ability in terms of quenching coefficient (*K*sv) and detection limitation (DL) of Eu-MOFs towards $Cr_2O_7^{2-}$ and Fe^{3+}.

Compounds	Medium	Analytes	Quenching coefficient (*K*sv, M^{-1})	Detection limitation (DL, M)	Refs
$[Eu_2L(1,3\text{-bdc})_3]\cdot 5H_2O$	H_2O	$Cr_2O_7^{2-}$	1.55×10^4	[a] 9.2×10^{-6}	This work
		Fe^{3+}	1.25×10^4	[a] 2.3×10^{-3}	
$[Eu(HL)(H_2O)_2(NO_3)]\cdot NO_3$	H_2O	$Cr_2O_7^{2-}$	7.52×10^4	[a] 1.7×10^{-5}	S1
		Fe^{3+}	4.03×10^4	[a] 4.3×10^{-5}	
[EuL(Himdc)(ina)(H_2O)]	H_2O	$Cr_2O_7^{2-}$	2.46×10^3	[b] 10^{-5}	S2
		Fe^{3+}	1.30×10^4	[b] 10^{-5}	
$[Eu(HL)(H_2O)_3]$	H_2O	$Cr_2O_7^{2-}$	5.50×10^3	[a] 5.1×10^{-4}	S3
		Fe^{3+}	5.30×10^3	[a] 1.2×10^{-3}	
$[Eu(L)_2(NO_3)]$	CH_3CN	$Cr_2O_7^{2-}$	1.06×10^4	[b] 10^{-6}	S4
		Fe^{3+}	1.39×10^4	[b] 10^{-7}	
$[Eu(ppda)(bdc)_{0.5}(C_2H_5OH)(H_2O)]$	DMF	$Cr_2O_7^{2-}$	4.03×10^3	[b] 10^{-5}	S5
		Fe^{3+}	2.10×10^4	[b] 10^{-5}	
$[Eu_2(L)_{1.5}(H_2O)_2(EtOH)]\cdot$	DMF	$Cr_2O_7^{2-}$	1.53×10^3	[b] 10^{-5}	S6

DMF		Fe^{3+}	2.94×10^3	[b] 10^{-5}	
$[Eu_3(L)_2(OH)(DMF)_{0.22}(H_2O)_{5.78}]$	DMF	$Cr_2O_7^{2-}$	6.63×10^3	—	S7
		Fe^{3+}	—	[a] 1.8×10^{-5}	
$[Eu(Hpzbc)_2(NO_3)]\cdot H_2O$	EtOH	$Cr_2O_7^{2-}$	—	[a] 2.2×10^{-5}	S8
		Fe^{3+}	2.6×10^3	[a] 2.6×10^{-5}	
Eu-BDC-NH_2	DMF	$Cr_2O_7^{2-}$	7.32×10^3	—	S9
		Fe^{3+}	4.93×10^3	—	
Eu-BDC-F	DMF	$Cr_2O_7^{2-}$	9.69×10^3	—	
		Fe^{3+}	7.52×10^3	—	
Eu-1,4-NDC	DMF	$Cr_2O_7^{2-}$	1.12×10^4	—	
		Fe^{3+}	9.34×10^3	—	

[a] Detection limitation calculated by $3\delta/k$; [b] Detection limitation according to the experiment data which is usually much lower than the calculated value since the error exits in calculation.

$[Eu_2L(1,3\text{-bdc})_3]\cdot 5H_2O$, H_2LCl_2: 4-Bis(4-carboxylatopyridinium-1-methylene)benzene dichloride

$[Eu(HL)(H_2O)_2(NO_3)]\cdot NO_3$, H_2L: 4-(3,5-dicarboxylphenyl)-2-methylpyridine

$[EuL(H_2O)_2]\cdot NMP\cdot H_2O$, H_3L: 4,4′,4″-striazine-1,3,5-triyltri-m-aminobenzoate

[EuL(Himdc)(ina)(H_2O)], H_3imdc: imidazole-4,5-dicarboxylic acid; Hina: isonicotinic acid

$[Eu(HL)(H_2O)_3]$, H_4L:1-(3,5-dicarboxylatobenzyl)-3,5-pyrazole dicarboxylic acid

$[Eu(L)_2(NO_3)]$, H_2L: 3-bis(3-carboxyphenyl)imidazolium

$[Eu(ppda)(bdc)_{0.5}(C_2H_5OH)(H_2O)]$, H_2ppda: 4-(pyridin-3-yloxy)-phthalic acid

$[Eu_2(L)_{1.5}(H_2O)_2(EtOH)]\cdot DMF$, H_4L: 5,5'-(carbonylbis(azanediyl))diisophthalic acid

$[Eu_3(L)_2(OH)(DMF)_{0.22}(H_2O)_{5.78}]$, H_4L: 3,5-bis(isophthalic acid)-1H-1,2,4-triazole

$[Eu(Hpzbc)_2(NO_3)]\cdot H_2O$, H2pzbc: 3-(1H-pyrazol-3-yl) benzoic acid

References

S1. W. Gao, F. Liu, B.-Y. Zhang, X. M. Zhang, J.-P. Liu, E. Q. Gao and Q. Y. Gao, *Dalton Trans.,* 2017, **46**, 13878.

S2. L. H. Liu, X. T. Qiu, Y. J. Wang, Q. Shi, Y. Q. Sun and Y. P. Chen, *Dalton Trans.,* 2017, **46**, 12106.

S3. W. Q. Tong, T. T. Liu, G. P. Li, J. Y. Liang, L. Hou and Y. Y. Wang, *New J. Chem.,* 2018, **42**, 9221.

S4. Y. Yang, F. Qiu, C. Xu, Y. Feng, G. Zhang and W. Liu, *Dalton Trans.,* 2018, **47**, 7480.

S5. X. Zhang, Z. Zhan, X. Liang, C. Chen, X. Liu, Y. Jia and M. Hu, *Dalton Trans.,*

2018, **47**, 3272.

S6. W. Liu, X. Huang, C. Xu, C. Chen, L. Yang, W. Dou, W. Chen, H. Yang and W. Liu, *Chem. Eur. J.,* 2016, **22**, 18769.

S7. J. Q. Liu, G. P. Li, W. C. Liu, Q. L. Li, B. H. Li, R. W. Gable, L. Hou and S. R. Batten, *Chempluschem,* 2016, **81**, 1299.

S8. G. P. Li, G. Liu, Y. Z. Li, L. Hou, Y. Y. Wang and Z. Zhu, *Inorg. Chem.,* 2016, **55**, 3952.

S9. P. Yi, H. Huang, Y. Peng, D. Liu and C. Zhong, *RSC Adv.,* 2016, **6**, 111934.

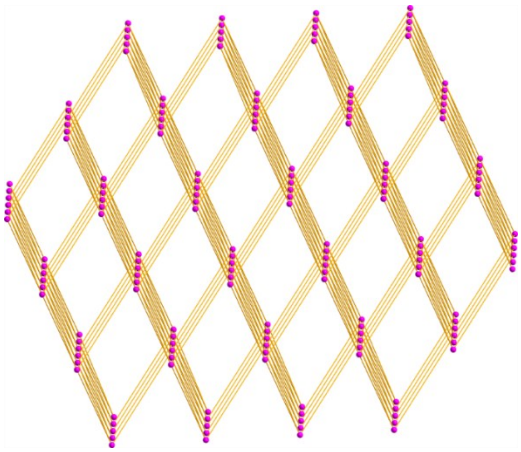

Figure S1. The topology architecture simplified by means of six-connected nodes (Eu^{3+} paddlewheel dinuclear) and two-connected linkers (ligands L and 1,3-bdc^{2-}).

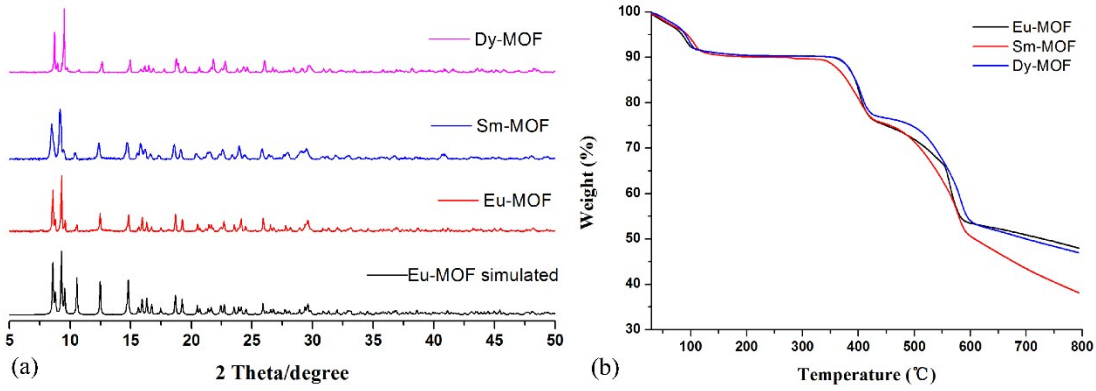

Figure S2. (a) The PXRD patterns of Ln-MOFs; (b) The TGA diagrams of Ln-MOFs.

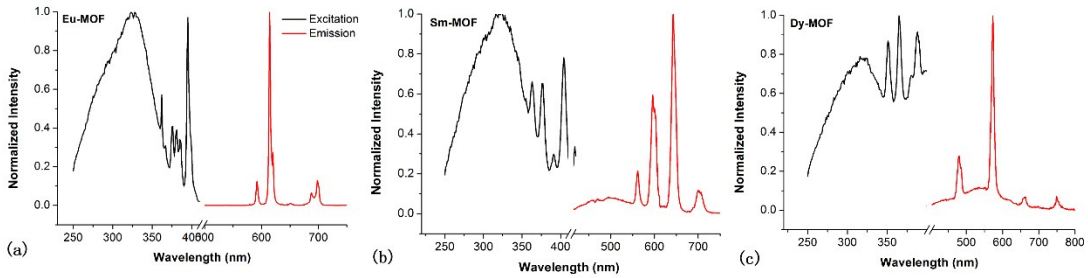

Figure S3. Solid luminescent spectra of Ln-MOFs excited based on ligand absorption.

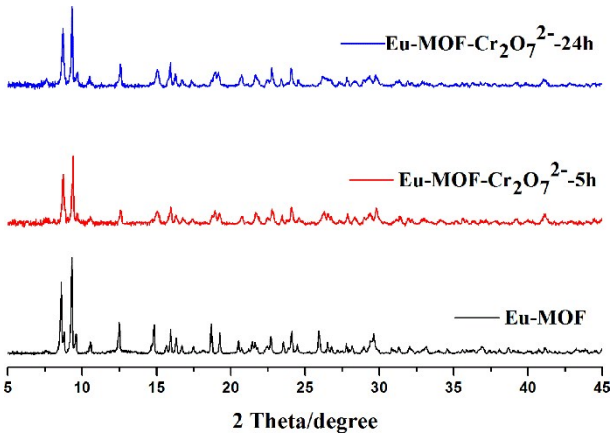

Figure S4. The PXRD patterns of Eu-MOF before and after immersing in $Cr_2O_7^{2-}$ aqueous solution for 5 hours and 24 hours.

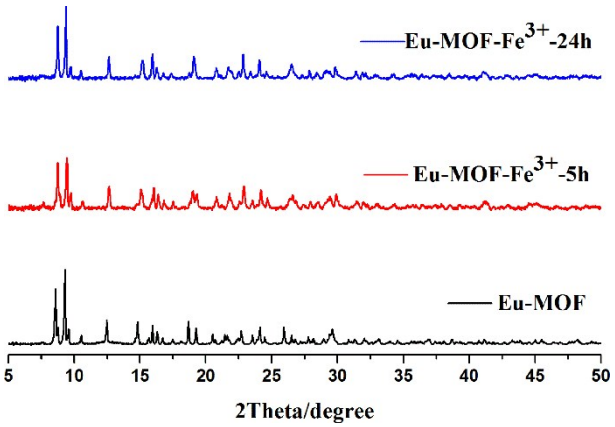

Figure S5. The PXRD patterns of Eu-MOF before and after immersing in Fe^{3+} aqueous solution for 5 hours and 24 hours.

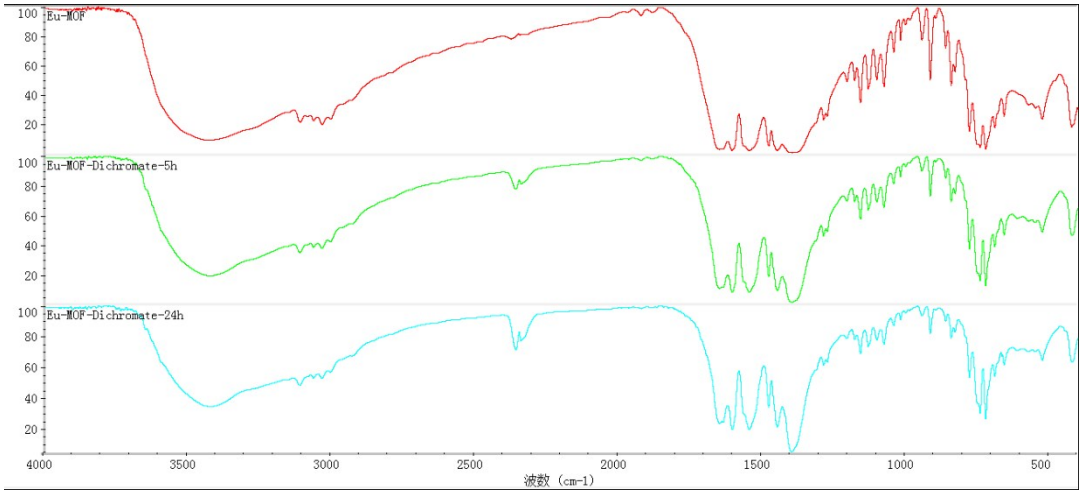

Figure S6. The IR diagrams of Eu-MOF before and after immersing in $Cr_2O_7^{2}$ aqueous solution for 5 hours and 24 hours.

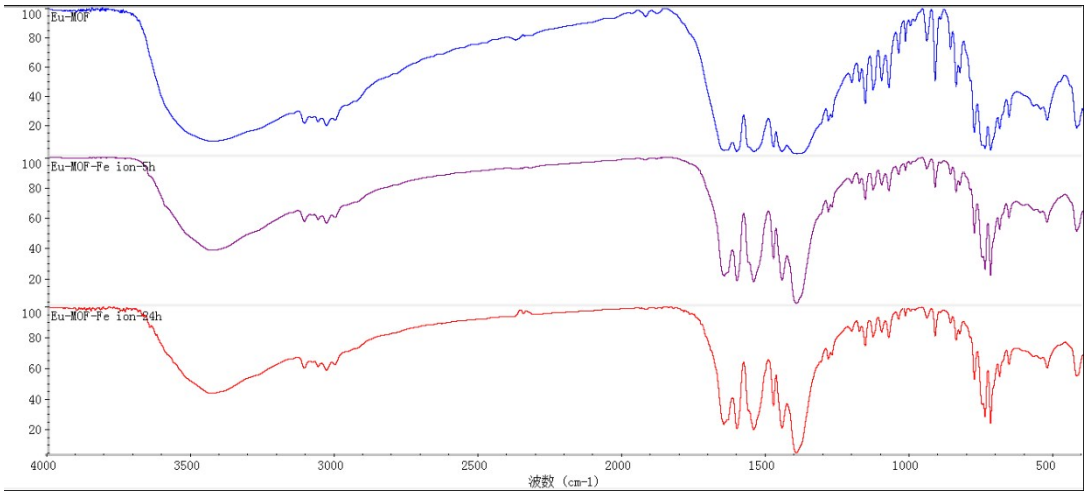

Figure S7. The IR diagrams of Eu-MOF before and after immersing in Fe^{3+} aqueous solution for 5 hours and 24 hours.

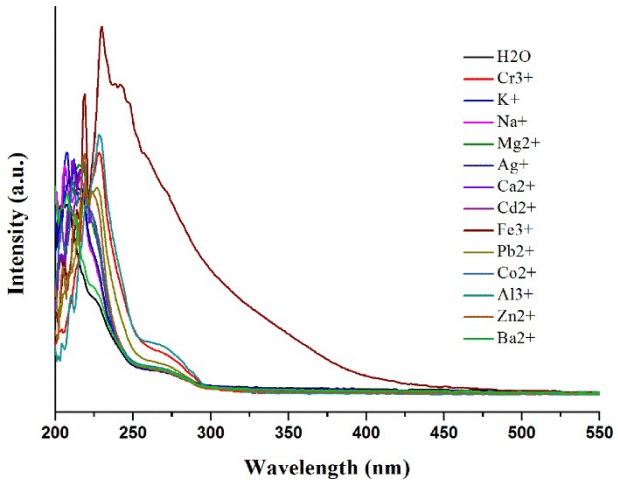

Figure S8. The UV-vis absorption spectra of different cations (0.15mM) in water solution.

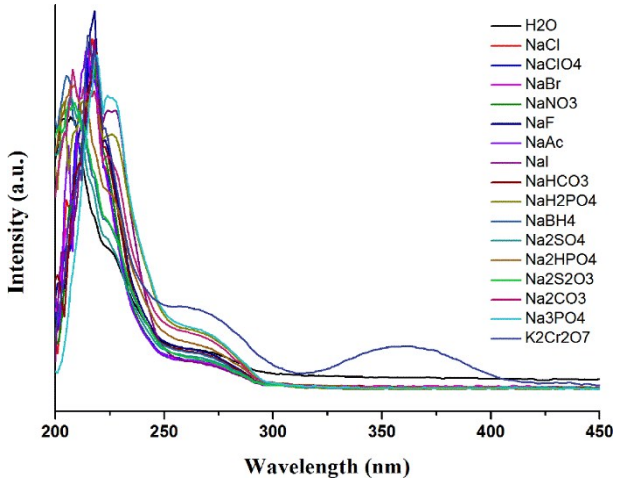

Figure S9. The UV-vis absorption spectra of different anions (0.15mM) in water solution.

References

[1] J. K. Sun, P. Wang, C. Chen, X. J. Zhou, L. M. Wu, Y. F. Zhang, J. Zhang, Dalton Trans. 41 (2012) 13441.