Supporting Information

3D water-stable europium metal organic frameworks as a multi-responsive luminescent sensor for high-efficiency detection of $Cr_2O_7^{2-}$, MnO_4^-, Cr^{3+} ions and SDBS in aqueous solution

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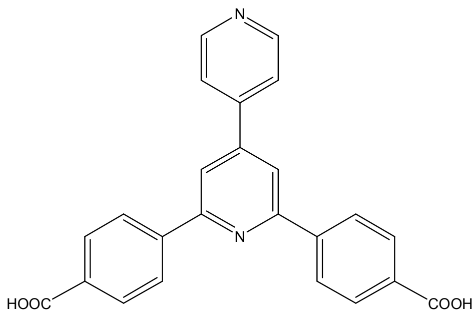

Scheme S1. Structure of bpydbH_2 ligand.

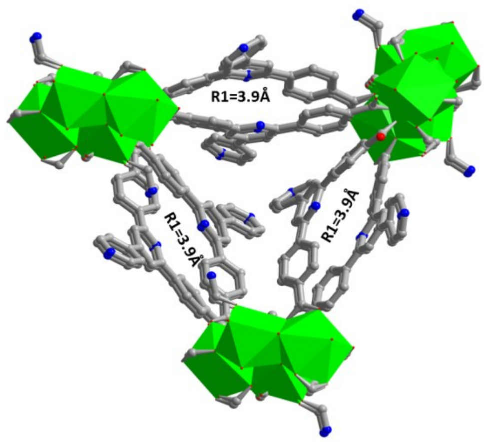

Fig. S1. The 3D framework of **1** contains two types irregular 1D channel along a direction and Eu^{3+} is represent as polyhedral.

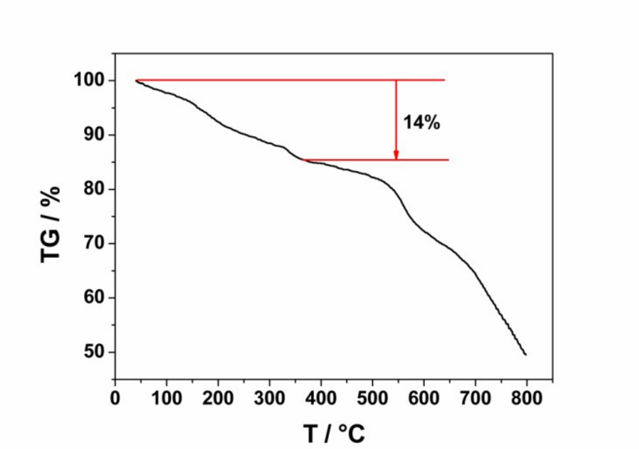

Fig. S2. TG curves for **1**.

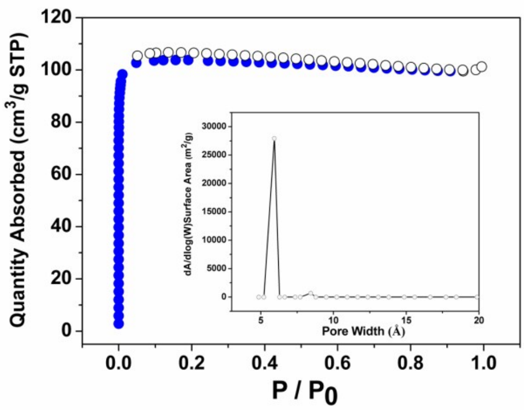

Fig. S3. The N_2 sorption isotherm of **1** at 77 K (solid symbol: adsorption, open symbol: desorption); (insert) The aperture distribution curve of **1**.

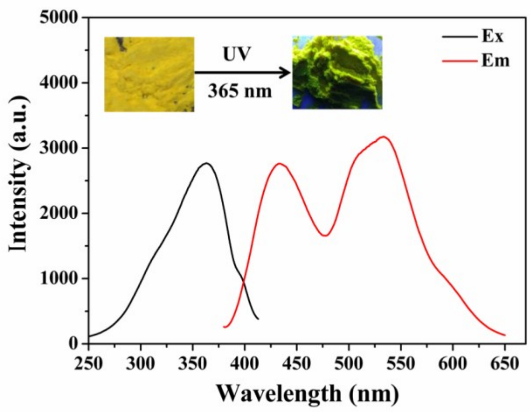

Fig. S4. The excitation and emission spectra of free bpydbH_2 ligand; (inset) image of ligand under irradiation of 365 nm UV light.

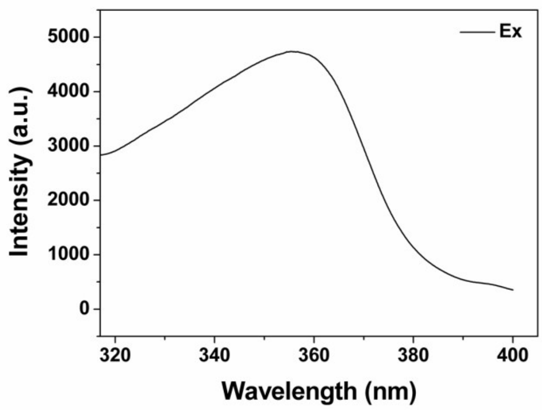

Fig. S5. The excitation spectrum of **1**(λ_{em} = 617 nm).

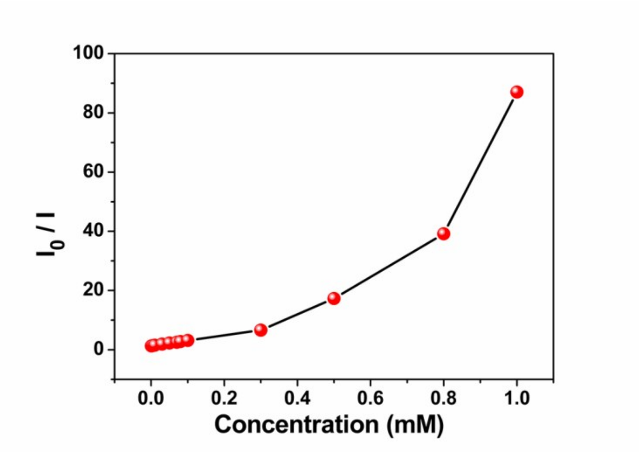

Fig. S6. The I_0/I versus the concentration of $Cr_2O_7^{2-}$ ion for **1** (from 0 to 1 mM).

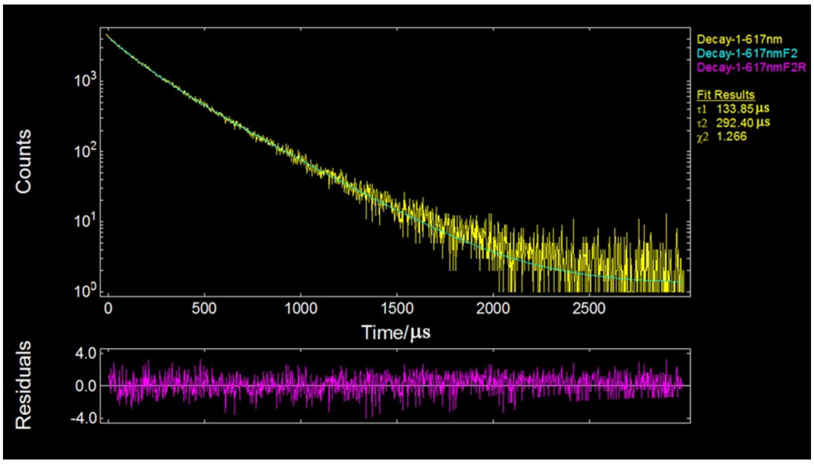

Fig. S7. Luminescence decay of **1** measured at the excitation/emission maxima, which can be fitted with two-exponential decay $I(t) = A + B_1e^{-t/\tau_1} + B_2e^{-t/\tau_2}$, where A is a constant, and B_1 and B_2 are pre-exponential factors; τ_1 and τ_2 are fitted time constants of the decay. The fluorescence lifetime was calculated according to $\tau = (B_1\tau_1^2+B_2\tau_2^2)/(B_1\tau_1+B_2\tau_2)$.

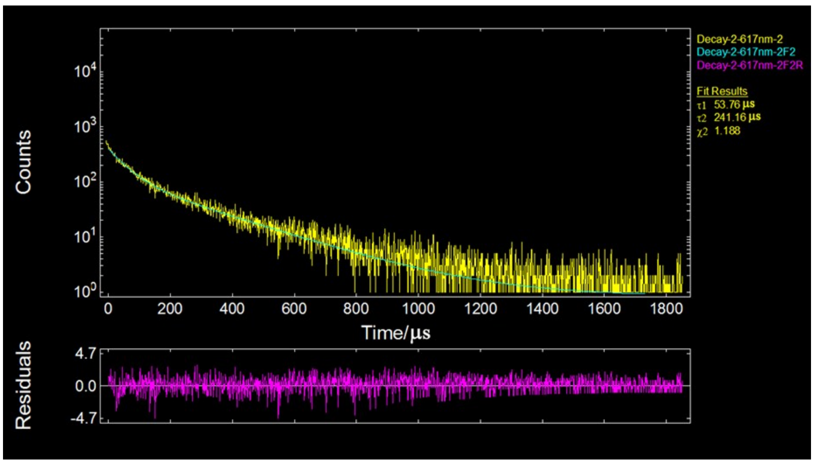

Fig. S8. Fit result of the time-resolved fluorescence decay traces of **1**@$Cr_2O_7^{2-}$.

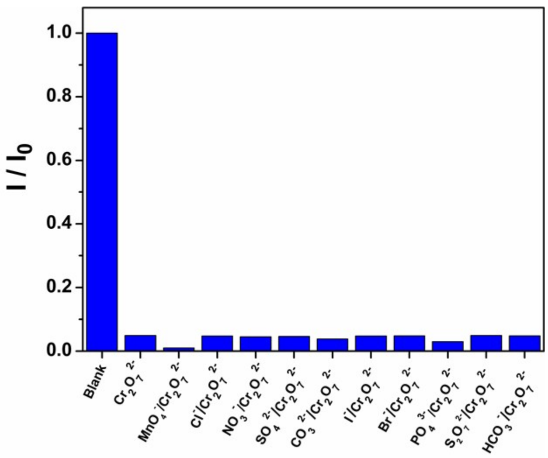

Fig. S9. Comparision of the luminescence intensity of **1** in the presence of mixed anions in 10^{-3} M.

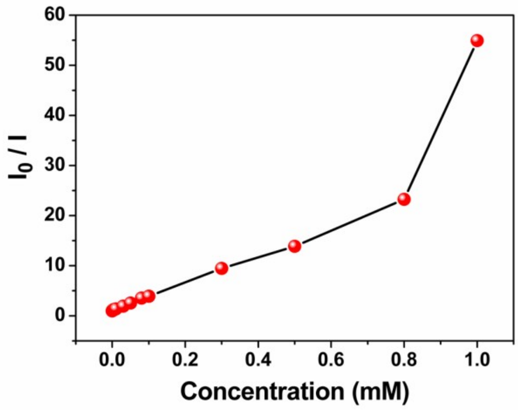

Fig. S10. The I_0/I versus the concentration of MnO_4^- ion for **1** (from 0 to 1 mM).

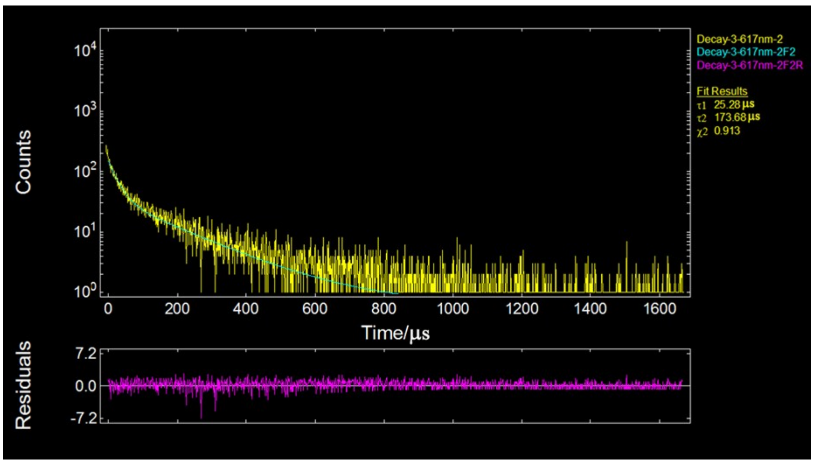

Fig. S11. Fit result of the time-resolved fluorescence decay traces of **1**@MnO_4^-.

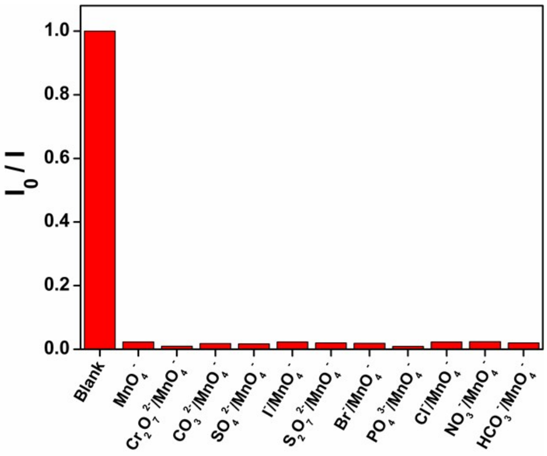

Fig. S12. Comparision of the luminescence intensity of **1** in the presence of mixed anions in 10^{-3} M.

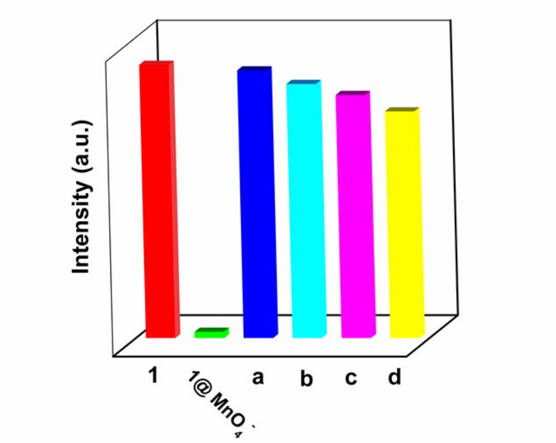

Fig. S13. Luminescent intensity at 617 nm of **1** after four recycles (a, b, c, d) in MnO_4^- solutions (10^{-3} M).

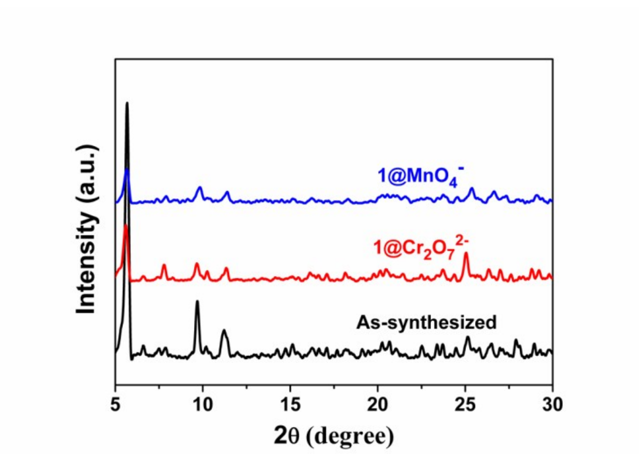

Fig. S14. The PXRD patterns of **1** after soaking in $Cr_2O_7^{2-}$ or MnO_4^- ions aqueous solution.

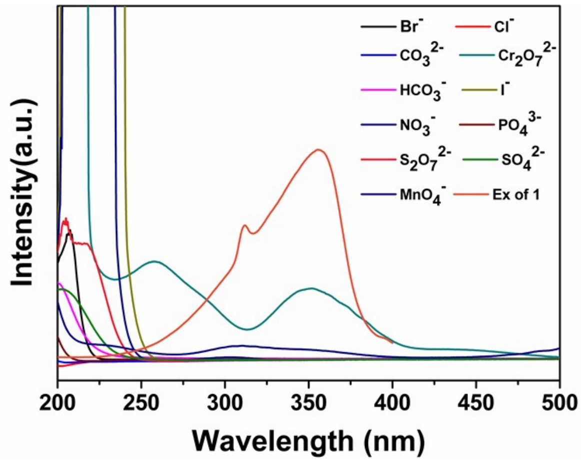

Fig. S15. UV-vis spectra of different anions and excitation spectra of **1** in aqueous solution.

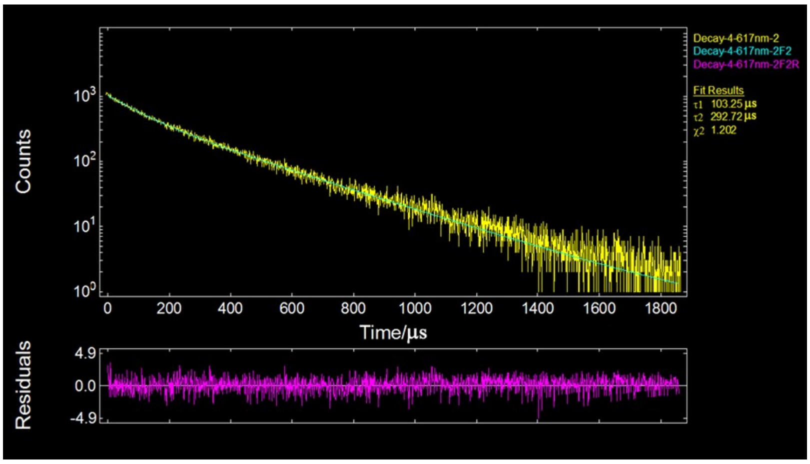

Fig. S16. Fit result of the time-resolved fluorescence decay traces of **1**@Cr^{3+}.

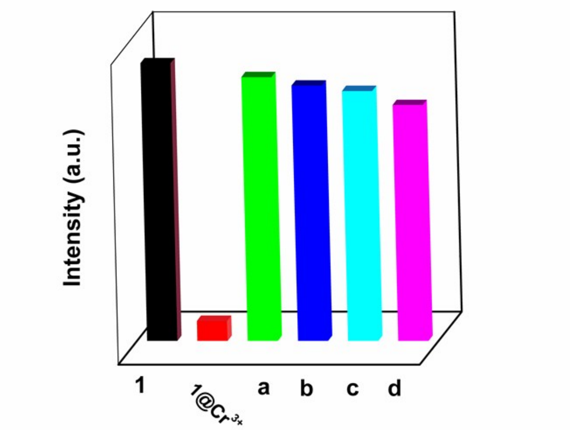

Fig. S17. Luminescent intensity at 617 nm of **1** after four recycles in Cr^{3+} solutions (10^{-2} M).

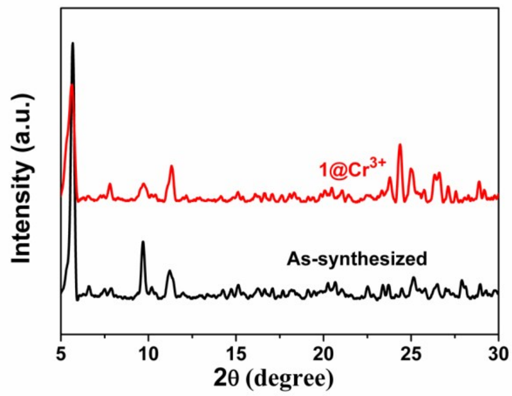

Fig. S18. The PXRD patterns of **1** after soaking in Cr^{3+} ions aqueous solution.

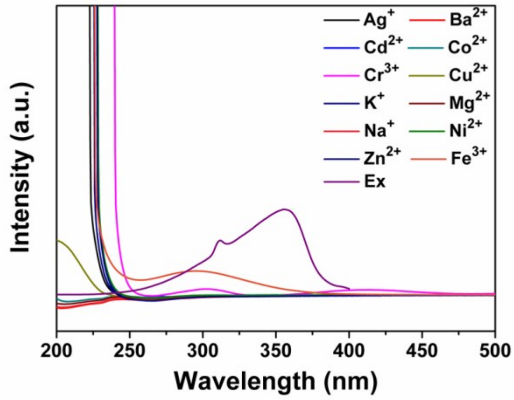

Fig. S19. UV-vis spectra of different metal ions and excitation spectra of **1** in aqueous solution.

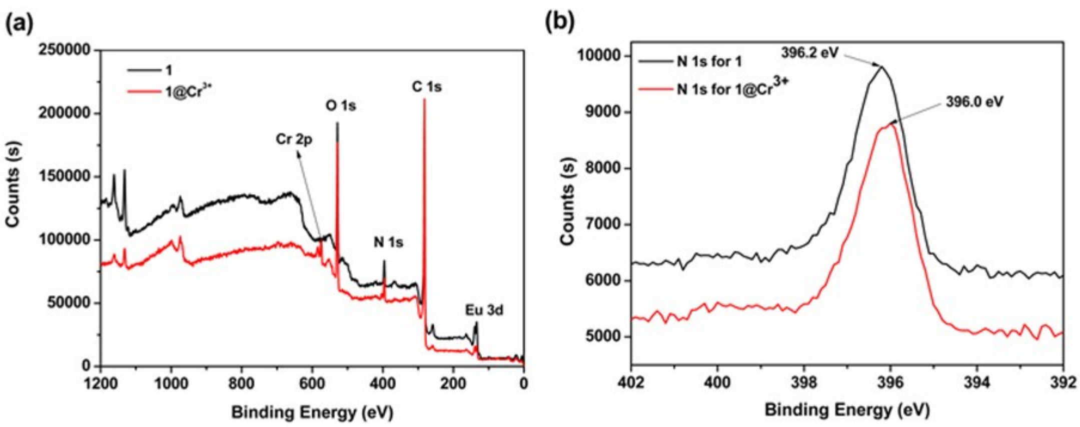

Fig. S20. (a) XPS for **1** and **1**@Cr^{3+}; (b) N 1s XPS for **1** and **1**@Cr^{3+}.

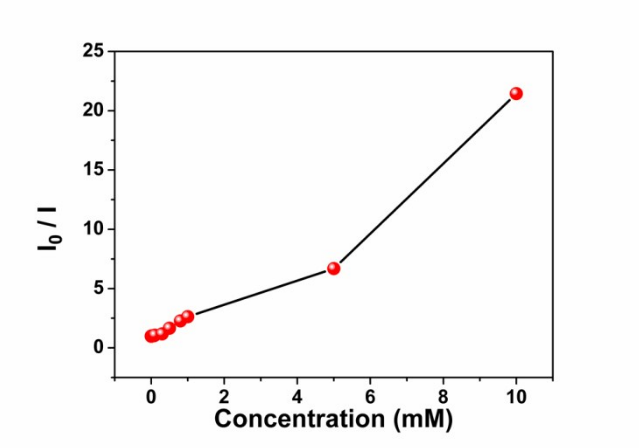

Fig. S21. The I_0/I versus the concentration of SDBS for **1** (from 0 to 10 mM).

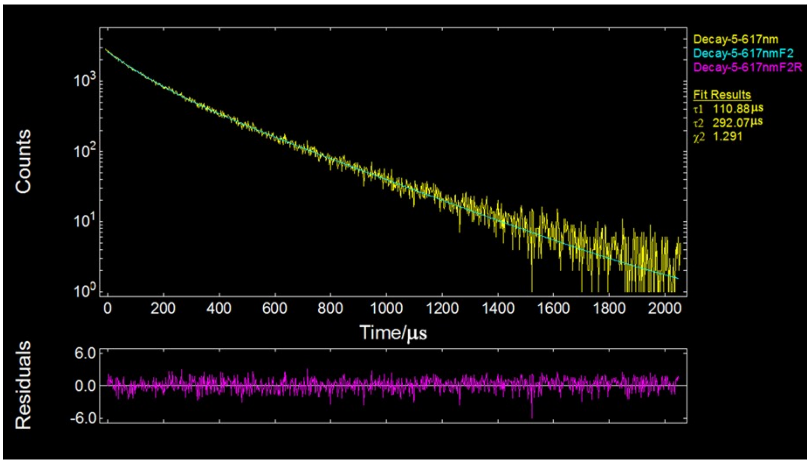

Fig. S22. Fit result of the time-resolved fluorescence decay traces of **1**@SDBS.

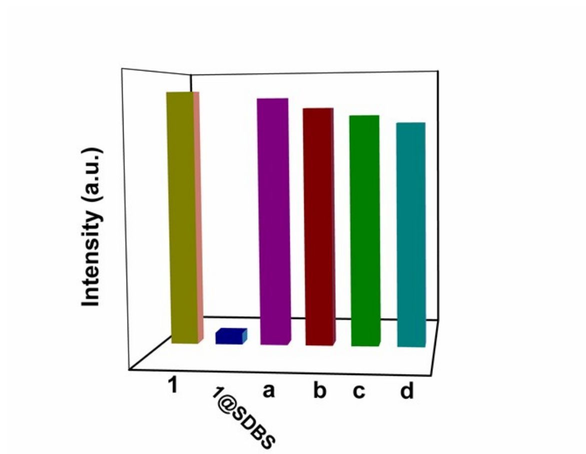

Fig. S23. Luminescent intensity at 617 nm of **1** after four recycles in SDBS solutions (10^{-2} M).

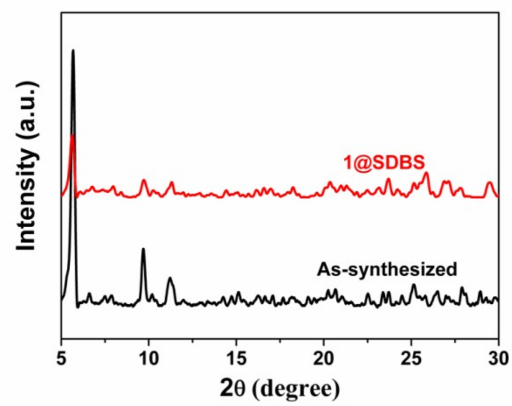

Fig. S24. The PXRD patterns of **1** after soaking in SDBS aqueous solution.

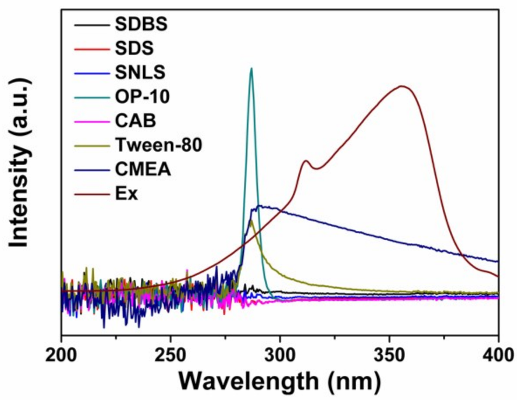

Fig. S25. UV-vis spectra of different surfactant and excitation spectra of **1** in aqueous solution.

Table S1 Performance comparison between various Ln-MOFs fluorescent sensors for $Cr_2O_7^{2-}$ and Cr^{3+} ions.

Ln-MOF-based Fluorescent Materials	Analyte	Quenching Constant K_{sv} (M^{-1})	Detection Limits	Slovent	Ref
$\{[Eu_3(bpydb)_3(HCOO)(OH)_2(DMF)]\cdot 3DMF\cdot 2H_2O\}n$	$Cr_2O_7^{2-}/Cr^{3+}$	$1.33\times10^4/2.24\times10^3$	0.5uM/1uM	water	This work
$\{[Eu_2L_{1.5}(H_2O)_2EtOH]\cdot DMF\}_n$	$Cr_2O_7^{2-}$	1.53×10^3	10uM	DMF	[1]
$[Eu(Hpzbc)_2(NO_3)]\cdot H_2O$	$Cr_2O_7^{2-}$	—	22uM	ethanol	[2]
$[Eu_2(tpbpc)_4\cdot CO_3\cdot 4H_2O]\cdot DMF\cdot Solvent$	$Cr_2O_7^{2-}/Cr^{3+}$	$1.04\times10^4/5.14\times10^2$	4.9uM/70uM	water	[3]
$[Eu(L)(HCOO)(H_2O)]_n$	$Cr_2O_7^{2-}/Cr^{3+}$	$2.76\times10^3/1.36\times10^3$	10uM/15uM	water	[4]
$[Tb(L)(HCOO)(H_2O)]_n$	$Cr_2O_7^{2-}/Cr^{3+}$	$2.13\times10^3/1.00\times10^3$	2.1uM/1.9uM	water	[4]
$[(CH_3)_2NH_2]_2[Eu_6(\mu_3\text{-}OH)_8(BDC\text{-}NH_2)_6(H_2O)_6]$	$Cr_2O_7^{2-}$	7.32×10^3	—	DMF	[5]
$[(CH_3)_2NH_2]_2[Eu_6(\mu_3\text{-}OH)_8(BDC\text{-}F)_6(H_2O)_6]$	$Cr_2O_7^{2-}$	9.69×10^3	—	DMF	[5]
$[(CH_3)_2NH_2]_2[Eu_6(\mu_3\text{-}OH)_8(1,4\text{-}NDC)_6(H_2O)_6]$	$Cr_2O_7^{2-}$	1.12×10^4	—	DMF	[5]
$[Eu(ipbp)_2(H_2O)_3]\cdot Br\cdot 6H_2O$	$Cr_2O_7^{2-}$	8.98×10^3	5.16uM	DMF/ H_2O	[6]
$\{[Tb(TATAB)(H_2O)_2]\cdot NMP\cdot H_2O\}_n$	$Cr_2O_7^{2-}$	1.11×10^4	—	water	[7]

L=5,5-((carbonyl bis(azanediyl)) diisophthalic acid [1];

H_2pzbc=3-(1H-Pyrazol-3-yl) benzoic acid [2];

Htpbpc=4’-[4,2’;6’,4’]-terpyridin-4’-yl-biphenyl-4-carboxylicacid[3]; H_2L=5-((2’-cyano-[1,1’-biphenyl]-4-yl)methoxy) isophthalic acid [4]; H_2ipbpBr=1-(3,5-dicarboxyphenyl)-4,4’-bipyridinium bromide[6]; H_3TATAB=4,4′,4″-*s*-triazine-1,3,5-triyltri-*m*-aminobenzoic acid [7].

References

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