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Novel Photo- and Hydrochromic Europium Metal–Organic Framework with Highly Sensing Property for Anions

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Determination of the detection limit

Detection limit of **1'** for $Cr_2O_7^{2-}$ and CrO_4^{2-} anions was determined according to the following definitions:

$$S_b = \sqrt{\frac{\sum_{i=1}^{n} (x - \bar{x})^2}{n - 1}} \qquad (1)$$

$$S = \frac{\Delta I}{\Delta c} \qquad (2)$$

$$DL = \frac{3s_b}{S} \qquad (3)$$

Firstly, the standard deviation (sb) was calculated by measuring the fluorescence intensity of the hybrid film in pure water for more than 10 times and then got the average intensity. By fitting the data into equation 1, the value of standard deviation (S_b) was obtained. Secondly, a certain amount of analyte was added into the solvent and the resulting variation of the intensity (ΔI) was recorded. By fitting the data into equation 2, where ΔI is the variation of intensity, and Δc is the variation of quencher concentration, the value of precision S was calculated. Finally the detection limit, DL, was calculated according to Function 3.

Table S1 Crystal data and structure refinements for **1.**

compound	**1**
formula	$C_{36}EuO_{17}N_4H_{40}$
*f*w	1013.86
temp (K)	293(2) K
wavelength (Å)	0.71073
Crystal system	Triclinic
space group	*P*-1
a (Å)	9.7352(5)
b (Å)	14.1265(7)
c (Å)	14.9366(8)
V (Å³)	1810.23(16)
Z	2
F(000)	875
θ range (deg)	1.54 to 26.30
reflections collected/unique	11642 / 7338
R_{int}	0.0155
data / restraints /params	7338 / 0 / 412
GOF on F^2	1.069
R_1, wR_2 [a] $[I>2\sigma(I)]$	0.0402, 0.1100
R_1, wR_2 (all data)	0.0434, 0.1124

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

Table S2 Selected bond lengths [Å] and angles [°] for **1**.

Eu(1)-O(5)#1	2.3279(16)	Eu(1)-O(7)	2.4312(17)
Eu(1)-O(8)	2.3373(15)	Eu(1)-O(2)#2	2.4438(15)
Eu(1)-O(4)	2.4083(17)	Eu(1)-O(10)	2.4771(18)
Eu(1)-O(1)	2.4199(18)	Eu(1)-O(9)	2.5006(16)
O(5)-Eu(1)#3	2.3278(16)	O(1)-Eu(1)-O(2)#2	74.19(5)
O(5)#1-Eu(1)-O(4)	72.91(6)	O(5)#1-Eu(1)-O(8)	118.75(6)
O(8)-Eu(1)-O(4)	73.59(6)	O(7)-Eu(1)-O(2)#2	118.52(5)
O(5)#1-Eu(1)-O(1)	145.66(6)	O(5)#1-Eu(1)-O(10)	78.78(6)
O(8)-Eu(1)-O(1)	78.91(6)	O(8)-Eu(1)-O(10)	73.55(6)
O(4)-Eu(1)-O(1)	141.17(5)	O(4)-Eu(1)-O(10)	117.52(5)
O(5)#1-Eu(1)-O(7)	134.34(6)	O(1)-Eu(1)-O(10)	78.95(6)
O(4)-Eu(1)-O(7)	75.43(6)	O(7)-Eu(1)-O(10)	146.12(6)
O(8)-Eu(1)-O(7)	81.61(6)	O(2)#2-Eu(1)-O(10)	71.48(5)
O(1)-Eu(1)-O(7)	73.87(6)	O(5)#1-Eu(1)-O(9)	72.43(6)
O(5)#1-Eu(1)-O(2)#2	74.12(6)	O(8)-Eu(1)-O(9)	148.64(7)
O(8)-Eu(1)-O(2)#2	139.09(7)	O(4)-Eu(1)-O(9)	83.42(6)
O(4)-Eu(1)-O(2)#2	142.85(6)	O(1)-Eu(1)-O(9)	108.66(6)
O(7)-Eu(1)-O(9)	72.00(6)	O(2)#2-Eu(1)-O(9)	70.66(6)
O(10)-Eu(1)-O(9)	137.24(6)	C(37)-O(1)-Eu(1)	127.44(13)
C(37)-O(2)-Eu(1)#2	138.50(12)	C(39)-O(4)-Eu(1)	133.66(15)
C(38)-O(5)-Eu(1)#3	132.13(14)	C(40)#4-O(8)-Eu(1)	166.26(18)

Symmetry transformations used to generate equivalent atoms:

#1 x+1, y, z #2 -x+2, -y+1, -z+2

#3 x-1, y, z #4 -x+1, -y+1, -z+1

Table S3 Comparison among various MOF sensors for Cr(VI) detection.

Fluorescent Materials	analyte	Quenching Constant (K_{SV}, M^{-1})	Detection Limits (μM)	Ref.
$[Zn(2\text{-}NH_2bdc)\ (bibp)]_n$	$Cr_2O_7^{2-}$	6555070		13a
$[Eu_7(mtb)_5(H_2O)_{16}]\cdot NO_3\cdot 8DMA\cdot 18H_2O$	CrO_4^{2-}	3.3×10^4	0.011	13f
$\{[Tb_4(BPDC)_4(3\text{-}OH)_4(H_2O)_8]\cdot 11H_2O\}n$	$Cr_2O_7^{2-}$	1.13×10^4	0.1	13e
$\{[Tb_4Mn(BPDC)_3(3\text{-}OH)_4(HCOO)_{1.5}(H_2O)_4]\cdot 2.5OH\cdot 8H_2O\}n$	$Cr_2O_7^{2-}$	5×10^3	0.1	13e
$[Zn(btz)]_n$	$Cr_2O_7^{2-}$	4.23×10^3	2	13b
	CrO_4^{2-}	3.19×10^3	20	
$[Zn_2(ttz)H_2O]n$	$Cr_2O_7^{2-}$	2.19×10^3	20	13b
	CrO_4^{2-}	2.35×10^3	20	
$\{[Eu_2L_{1.5}(H_2O)_2EtOH]\cdot DMF\}n$	$Cr_2O_7^{2-}$	1.53×10^3	10	13g
NH_2–Zn-MOF	$Cr_2O_7^{2-}$	7.59×10^3	3.9	13c
	CrO_4^{2-}	4.45×10^3	4.8	
$\{[Cd(L)(BPDC)]\cdot 2H_2O\}_n$	$Cr_2O_7^{2-}$	6.4×10^3	37.6	13d
$\{[Cd(L)(SDBA)(H_2O)]\cdot 0.5H_2O\}n$	$Cr_2O_7^{2-}$	4.97×10^3	48.6	13d
$[Zn(IPA)(L)]_n$	$Cr_2O_7^{2-}$	1.37×10^3	12.02	13h
	CrO_4^{2-}	1.00×10^3	18.33	
$[Cd(IPA)(L)]_n$	$Cr_2O_7^{2-}$	2.91×10^3	2.26	13h
	CrO_4^{2-}	1.3×10^3	2.52	
$[Eu(ipbp)_2(H_2O)_3]\cdot Br\cdot 6H_2O$	$Cr_2O_7^{2-}$	8.98×10^3	5.16	this work
	CrO_4^{2-}	7.08×10^3	5.82	

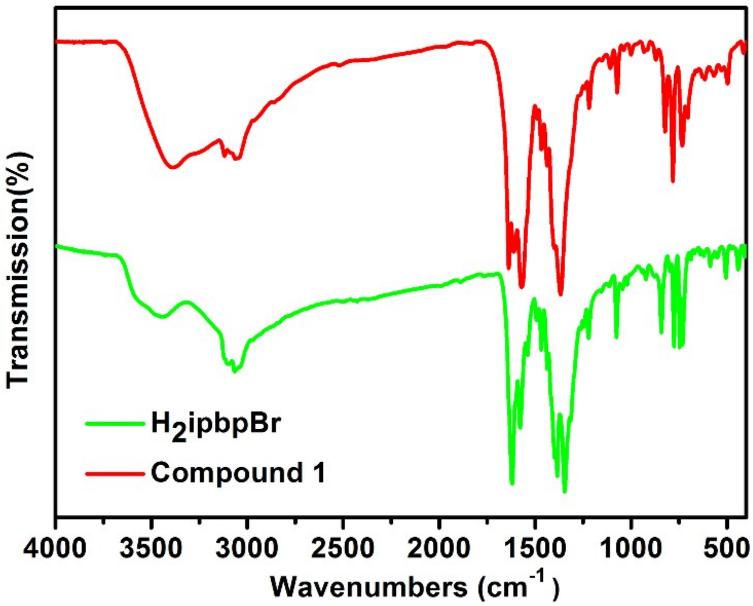


Fig. S1 IR spectra of H_2ipbpBr and **1**.

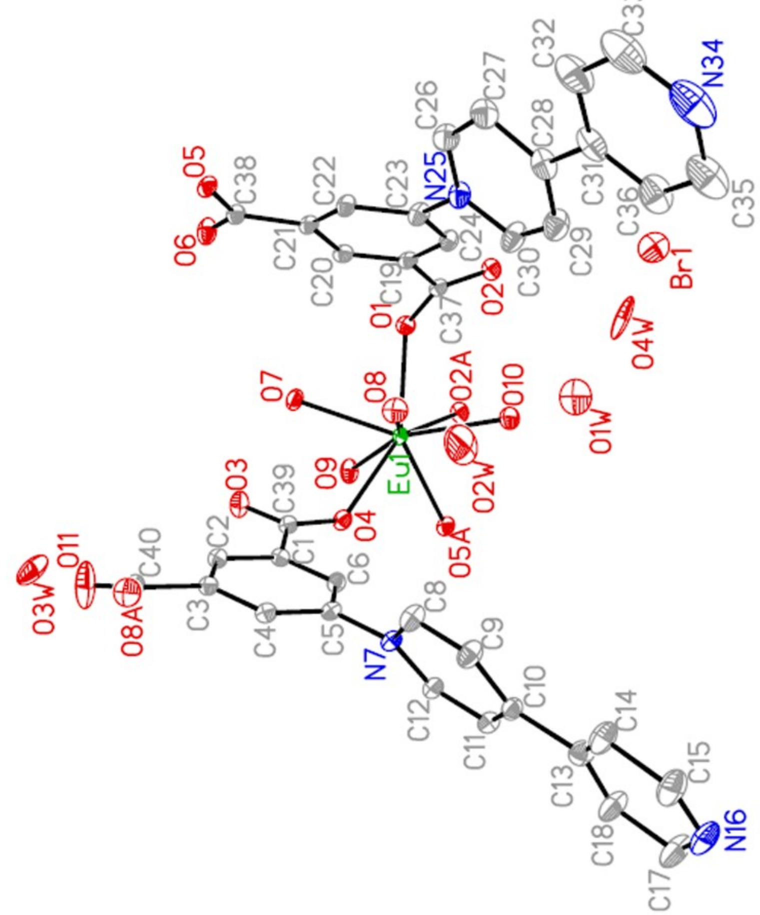


Fig. S2 The asymmetric unit of **1** showing ellipsoid at the 30% probability level. The hydrogen atoms are omitted for clarity, and some guest water molecules could not be precisely located by using single crystal X-ray crystallography due to its highly disorder.

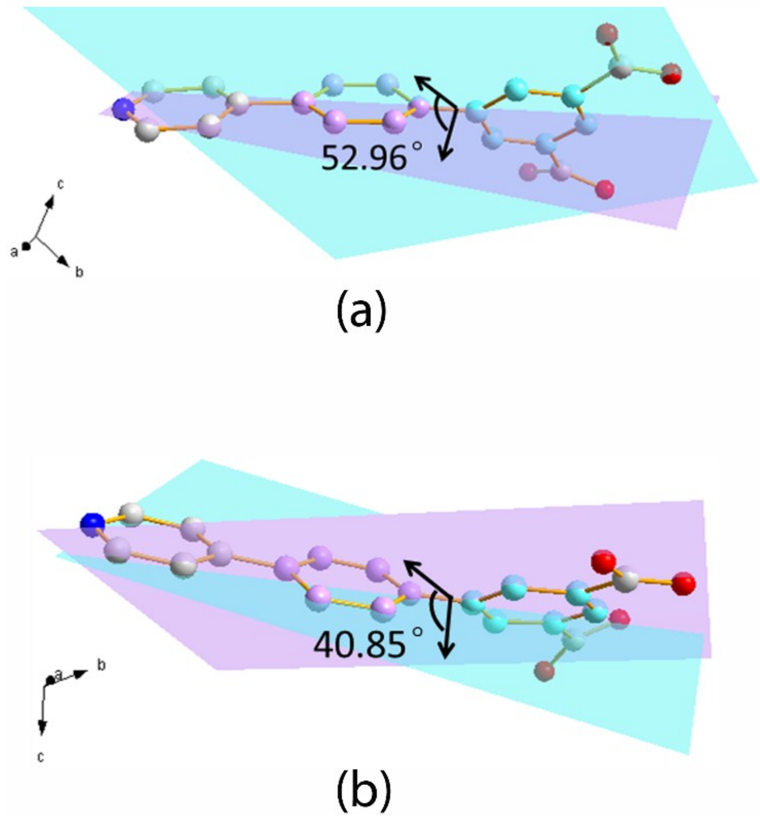


Fig. S3 The dihedral angles of ipbp^{2-} ligand in compound **1** for (a) mode I and (b) mode II.

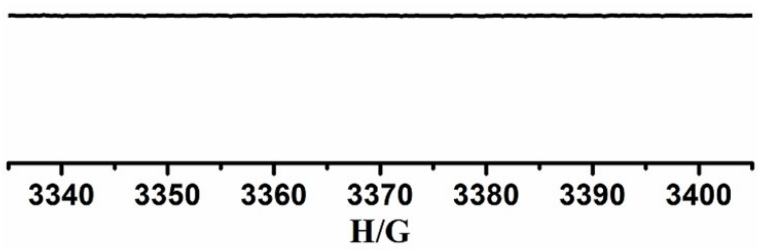


Fig. S4 EPR signal of paled sample of compound **1.**

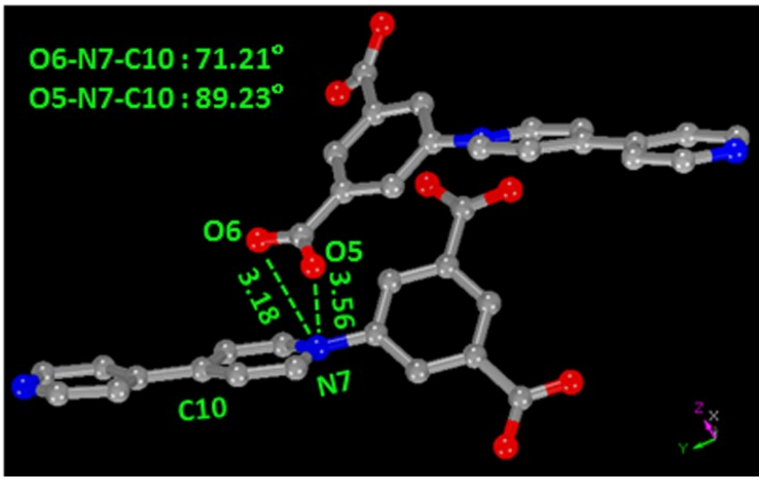


Fig. S5 The orientations and distances of carboxylate oxygen atoms and pyridinium nitrogen atoms between adjacent ribbons of rings in compound **1**.

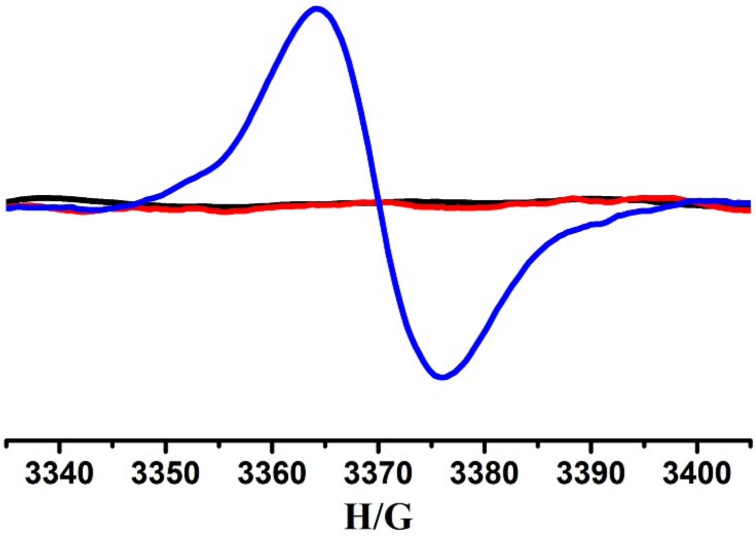


Fig. S6 EPR signals of **1** after heated in moisture (dark)**, 1-D** after kept in moisture (red) and in desiccator (blue).

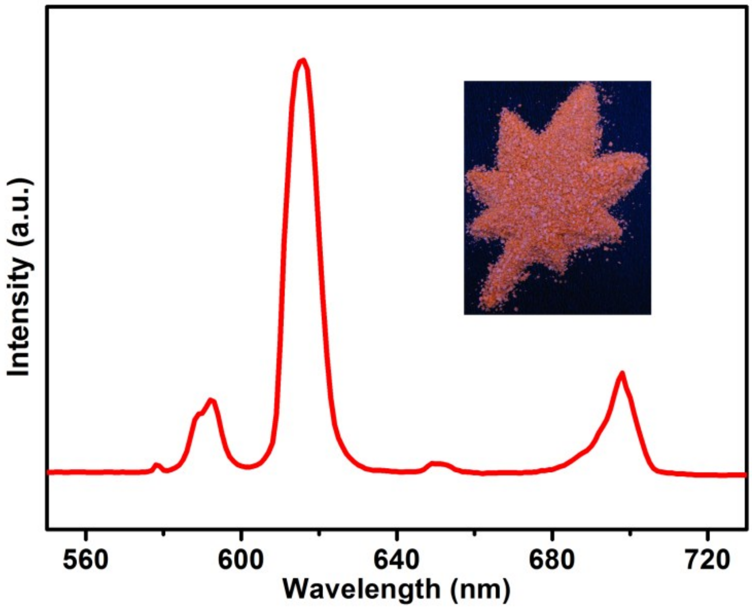
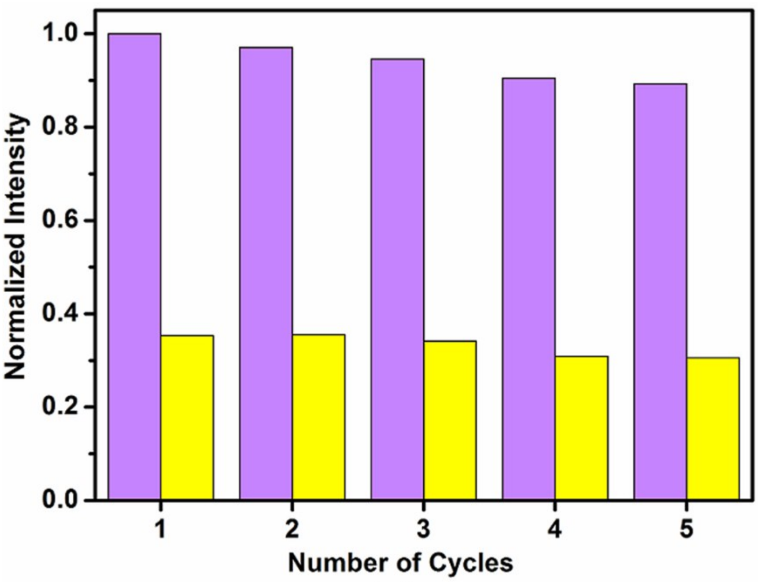
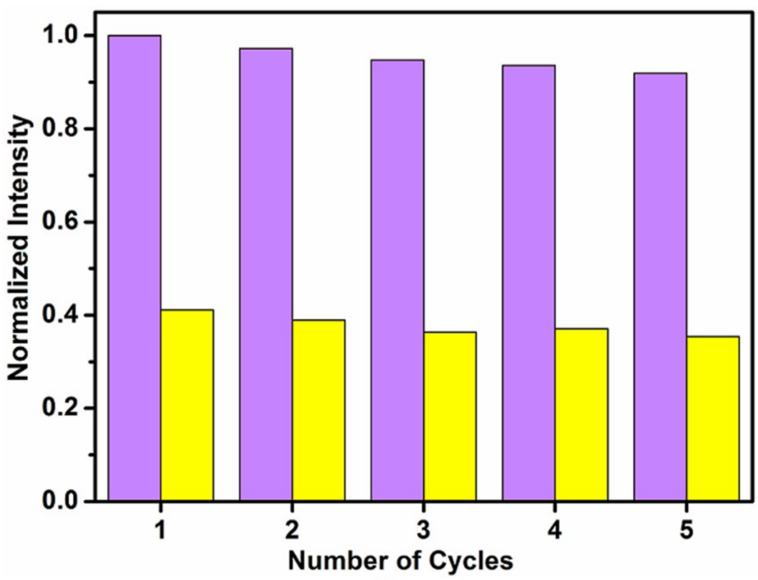


Fig. S7 Solid-state fluorescent emission spectrum of **1** (the inserted photograph is the sample of **1** under 365 UV light).



(a)



(b)

Fig. **S8** The quenching and recovery test of micrometer-sized **1′** (2.5 mg) dispersed in DMF/H_2O (1.72 ml/0.28 ml) in the presence of (a) $Cr_2O_7^{2-}$ and (b) CrO_4^{2-} . The violet bars represent the original fluorescence intensity and yellow bars represent the intensity in the presence of 0.33 mM analyte.

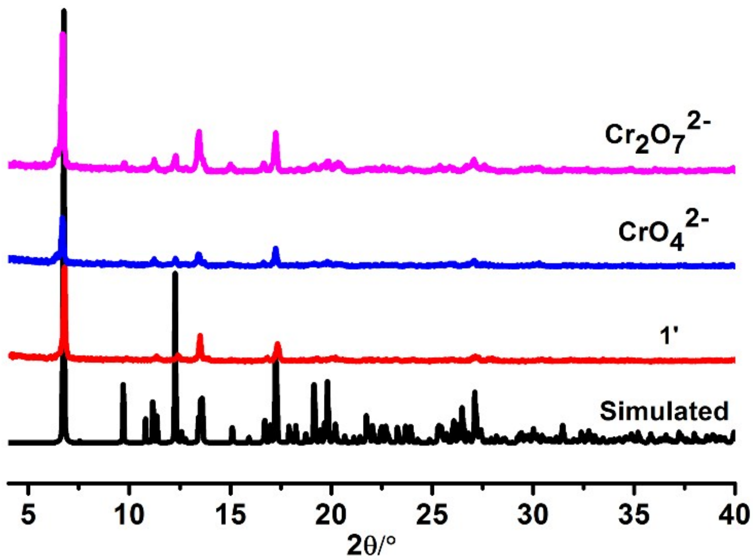


Fig. S9 Powder XRD patterns of simulated of **1**, experimental of **1'** and **1'** after repeated for five times of sensing $Cr_2O_7^{2-}$ and CrO_4^{2-} anions.

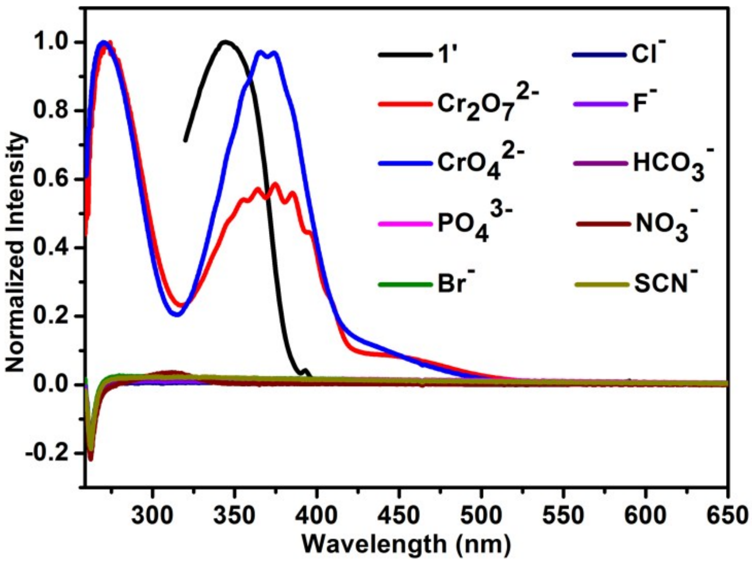


Fig. S10 Spectral overlap between the absorption spectra of anions and the excitation spectrum of **1'** in DMF/H_2O.