

# A zinc<sup>2+</sup>-dpbt framework: a luminescence sensing of Cu<sup>2+</sup>, Ag<sup>+</sup> MnO<sub>4</sub><sup>-</sup> and Cr(VI) (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup>) ions †

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## Real environmental samples preparation

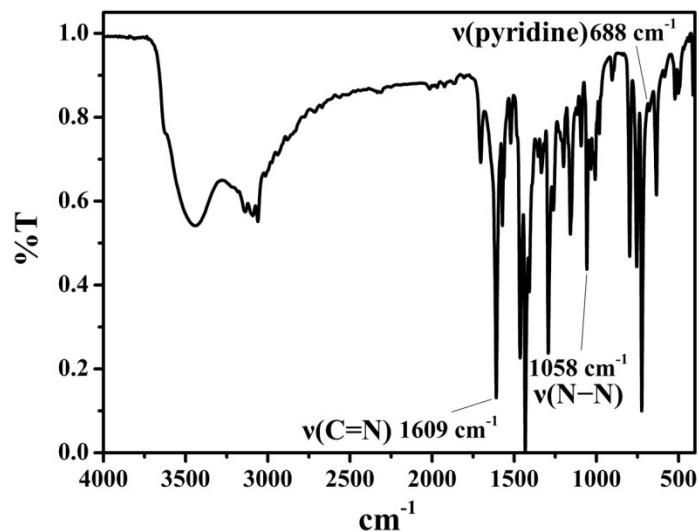
The reproducibility of **1** for sensing Cu<sup>2+</sup> and Ag<sup>+</sup> was also measured. After the first quenching experiment, the test material of **1** was recollected by centrifugation and washed several times with deionized water. The regenerated **1** was used again in the detection experiments and the fluorescence emission intensities were measured.

**Table S1** Selected Bond Lengths (Å) and Angles (°) for **1**

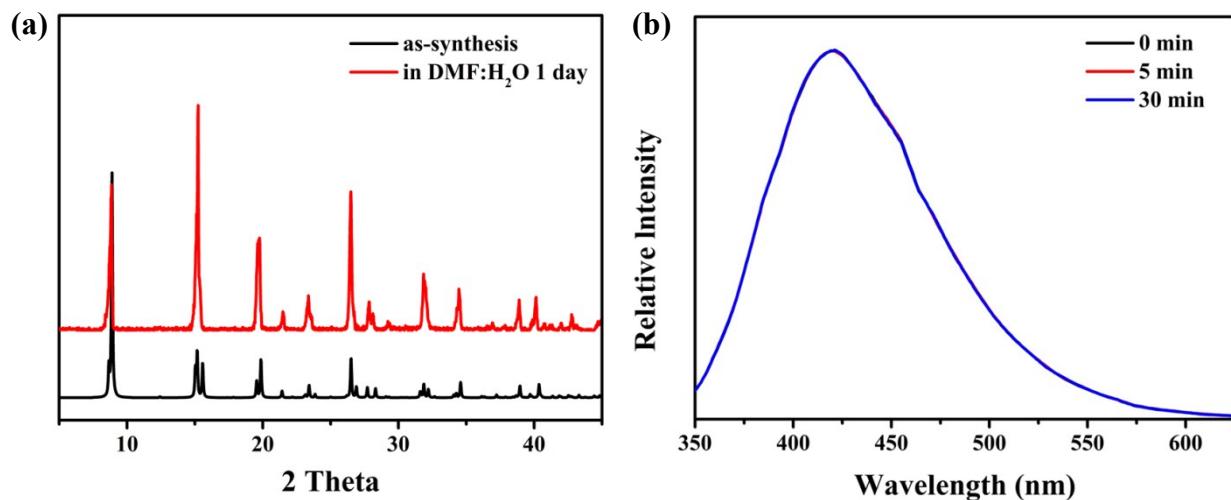
Symmetry codes: (A) -x+1/3, -y+2/3, -z+5/3; (B) y-1/3, -x+y+1/3, -z+4/3; (C) x-y+2/3, x+1/3, -z+4/3.			
Zn1—Cl1	2.3144 (8)	Zn1B—Cl1	2.5059 (8)
Zn1—N1	2.291 (2)	Zn1—N2	2.015 (2)
Zn1C—N4	2.023 (2)	Zn1—Cl1C	2.5058 (8)
Zn1—N4B	2.023 (2)		
Cl1—Zn1—Cl1C	102.23 (4)	N1—Zn1—Cl1	98.95 (7)
N1—Zn1—Cl1C	156.51 (6)	N2—Zn1—Cl1	112.93 (7)
N2—Zn1—Cl1C	87.83 (6)	N2—Zn1—N1	74.54 (8)
N2—Zn1—N4B	148.99 (9)	N4B—Zn1—Cl1	96.84 (6)
N4B—Zn1—Cl1C	94.38 (7)	N4B—Zn1—N1	93.08 (9)

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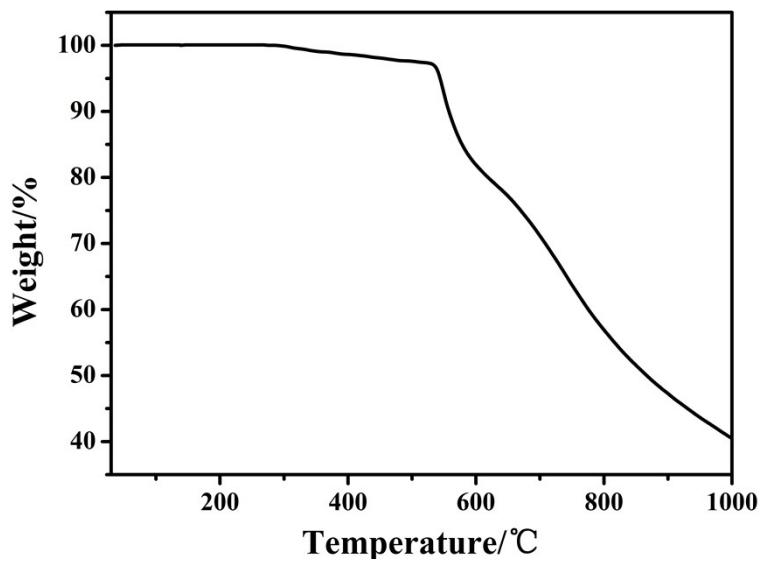
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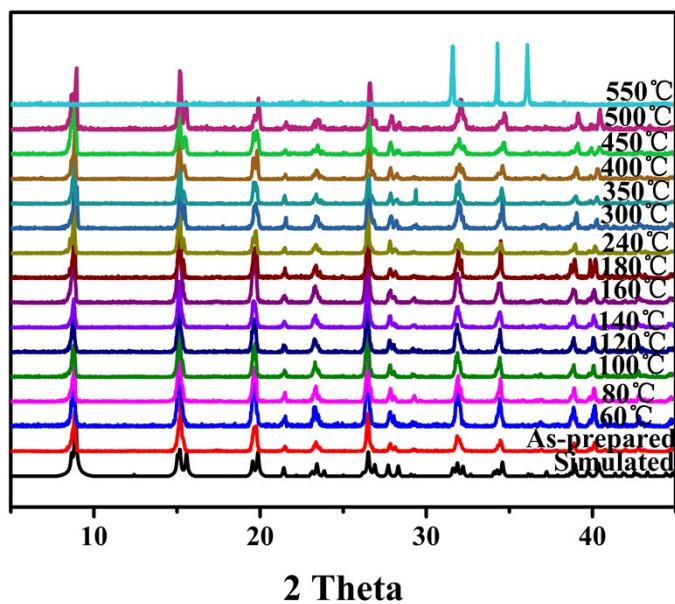
**Fig. S1** IR spectra of complex **1**.



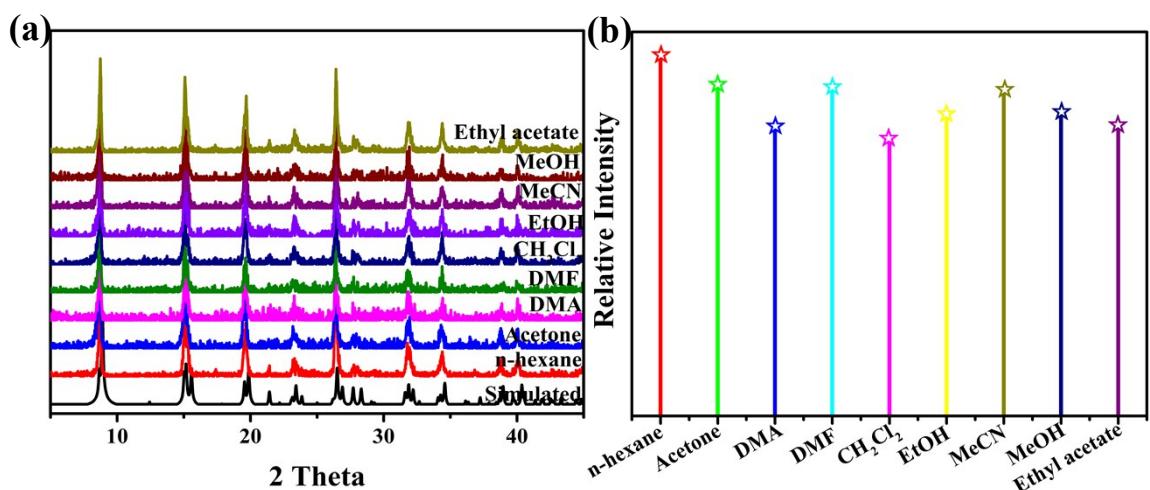
**Fig. S2** (a) Complex **1** was placed in DMF: H<sub>2</sub>O( V/V=1:1) solutions for 1day of PXRD patterns. (b) Fluorescence measurements of **1** immersed into the DMF: H<sub>2</sub>O( V/V=1:1) solutions as the suspensions for 0 min and after 30 min.



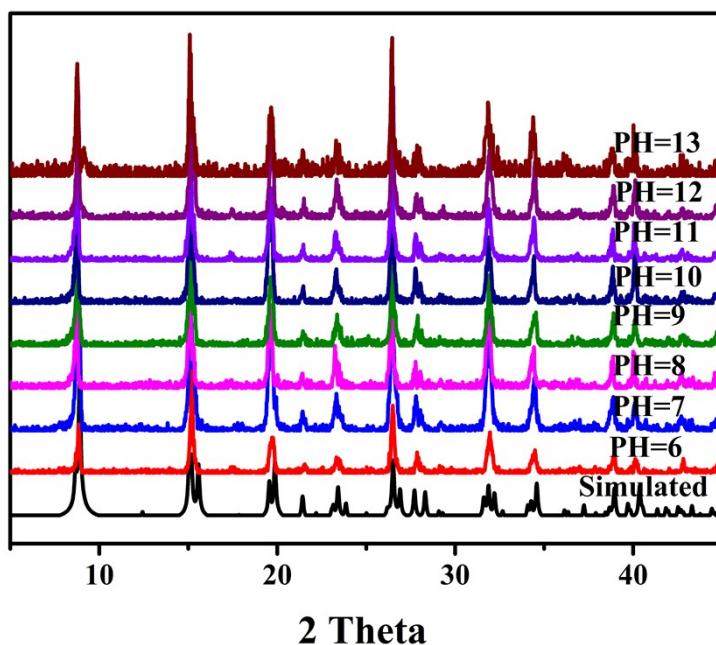
**Fig. S3** TGA curve of **1**.



**Fig. S4** PXRD patterns of **1** at different temperatures and the simulated one calculated from the single crystal structure analysis.

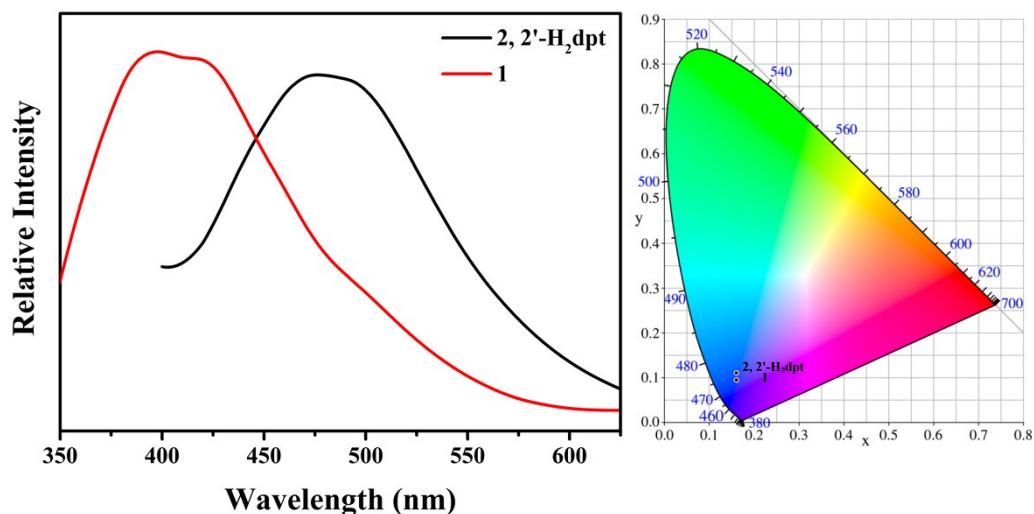


**Fig. S5** The PXRD patterns of **1** treated in different solvents.(a) Fluorescence measurements of **1** in various pure solvents. (b)

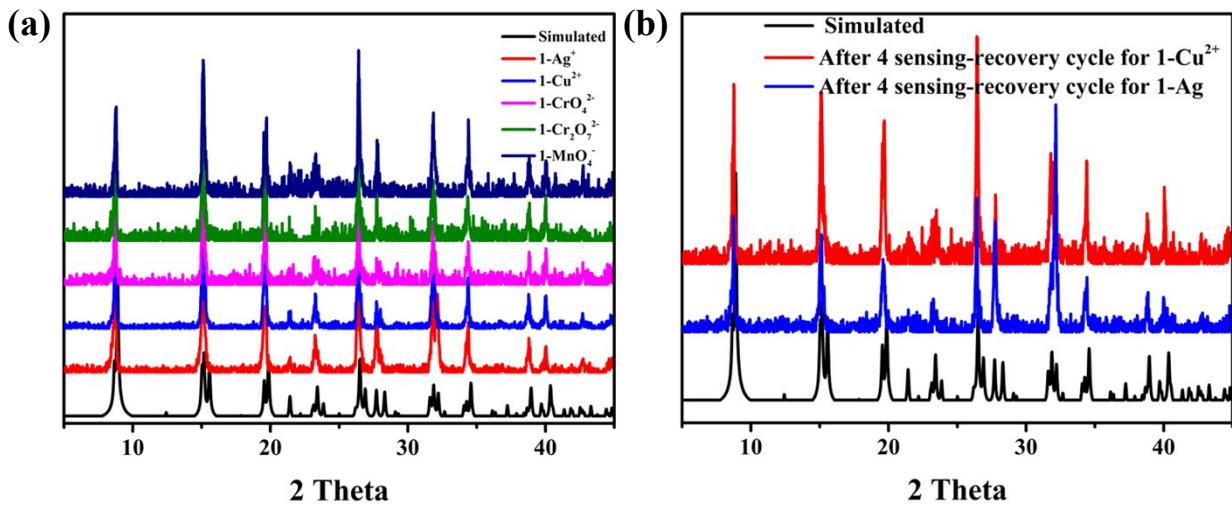


**2 Theta**

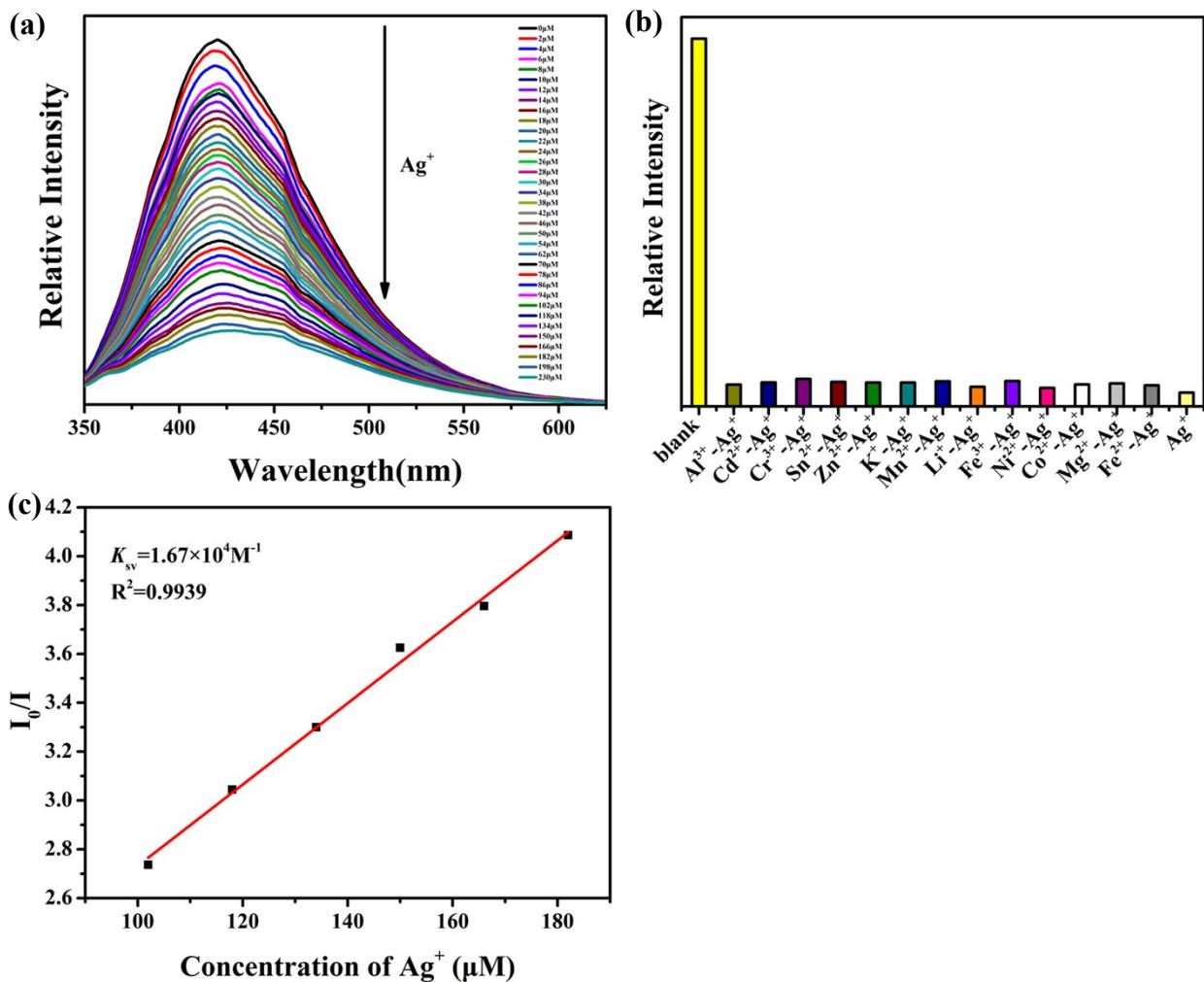
**Fig. S6.** PXRD patterns of **1** in different pH values in the range of 6-13.



**Fig. S7** The solid luminescent emissions of ligand 2,2'-H<sub>2</sub>dbpt and **1**.



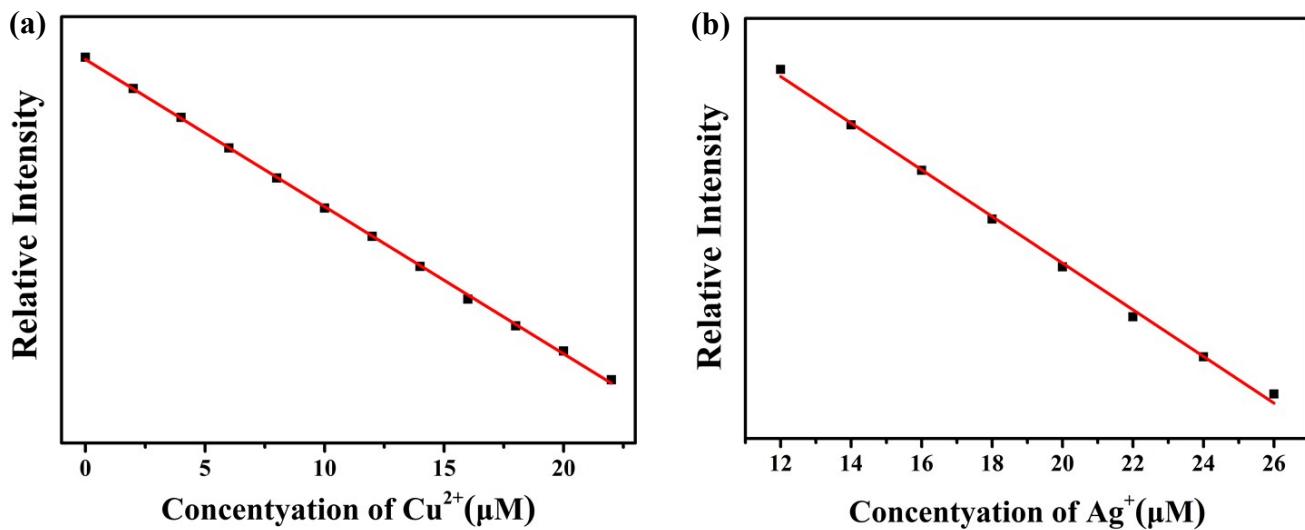
**Fig. S8** (a) Powder X-ray diffraction patterns of the activated framework, and diffraction patterns obtained after the introduction of various metal ions: 1-Cu<sup>2+</sup>, 1-Ag<sup>+</sup>, 1-MnO<sub>4</sub><sup>-</sup>, 1-Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and 1-CrO<sub>4</sub><sup>2-</sup>. (b) PXRD curves of 1 after four sensing recovery cycles for Ag<sup>+</sup> and Cu<sup>2+</sup> ions showing that structural integrity of the framework is maintained.



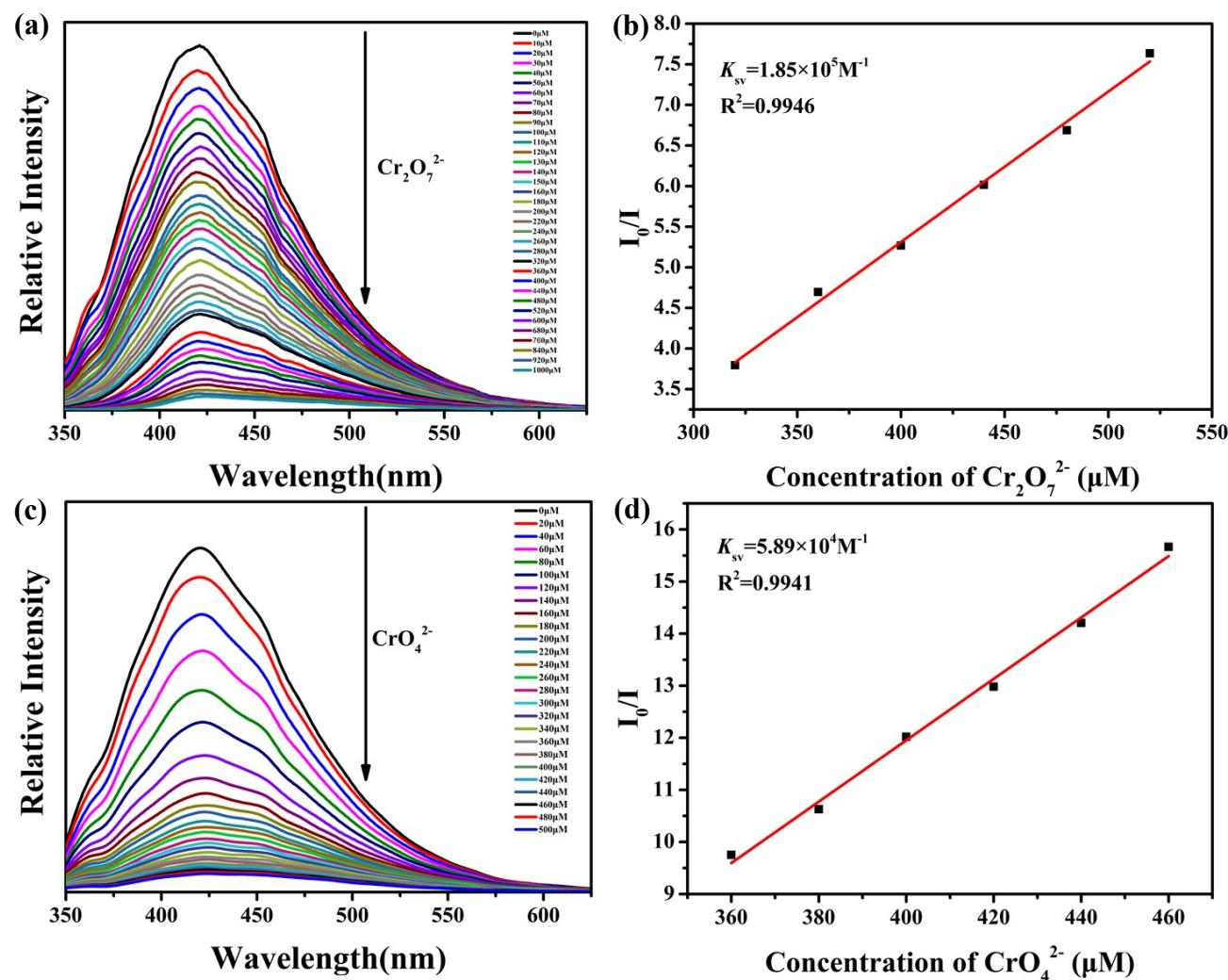
**S9** (a) Emission spectra of 1 dispersed in DMF: H<sub>2</sub>O (V/V=1:1) solution with different

**Fig.**

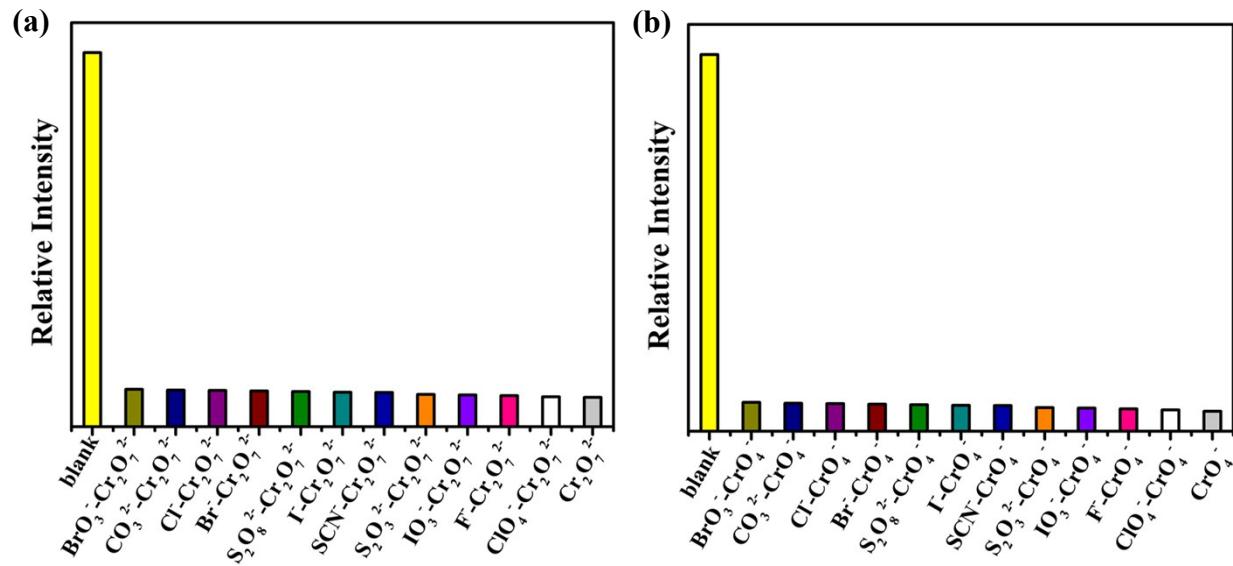
concentrations of  $\text{Ag}^+$ . (b) Emission spectra of **1** dispersed in DMF:  $\text{H}_2\text{O}$  (V/V=1:1) solution with different concentrations of  $\text{Ag}^+$ . (c) The Stern–Volmer plot of  $I_0/I$  versus  $\text{Ag}^+$  concentration.



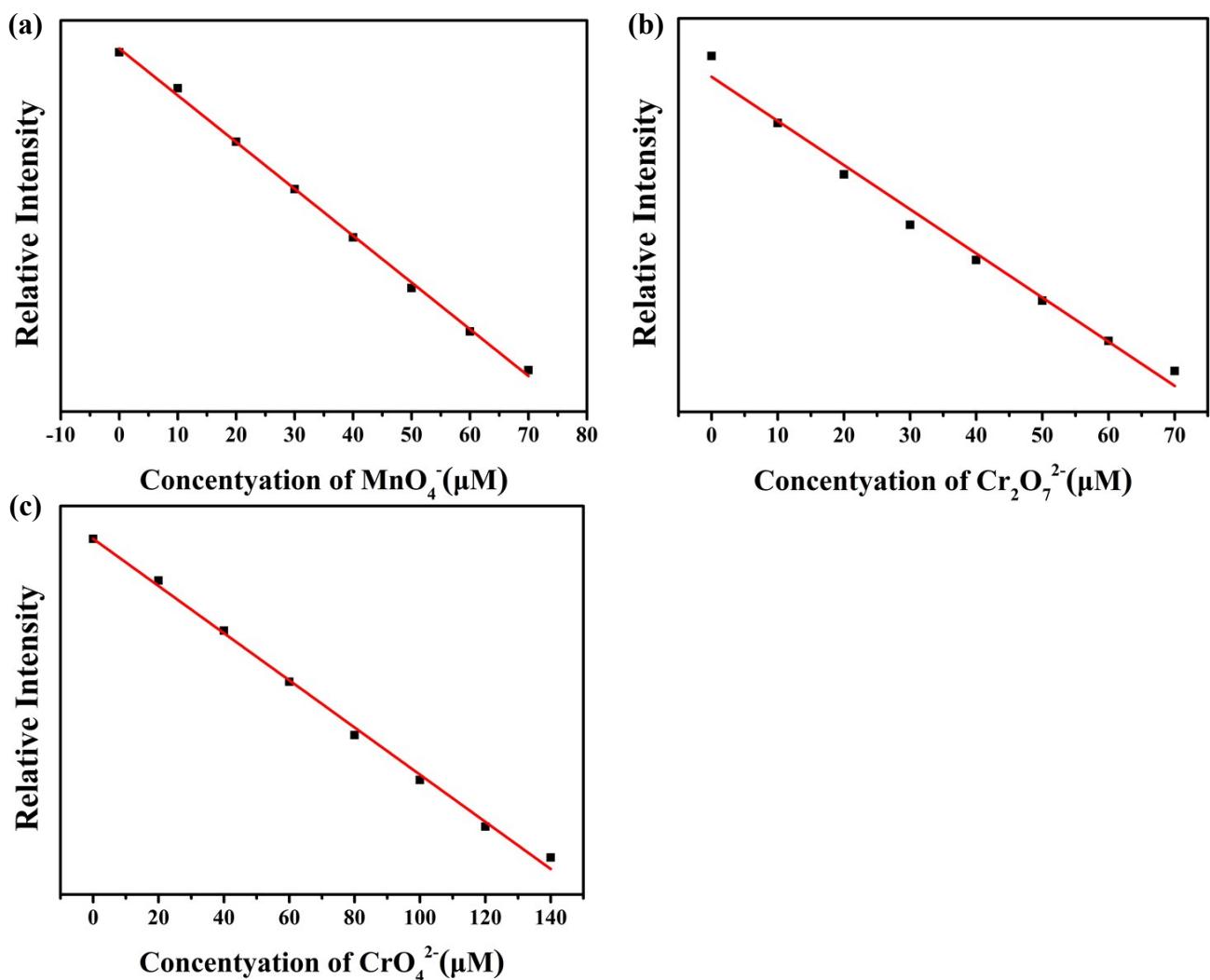
**Fig. S10** Linear region of fluorescence intensity of **1** in DMF:  $\text{H}_2\text{O}$  (V/V=1:1) solution upon addition of  $\text{Cu}^{2+}$  (a) and  $\text{Ag}^+$  (b).



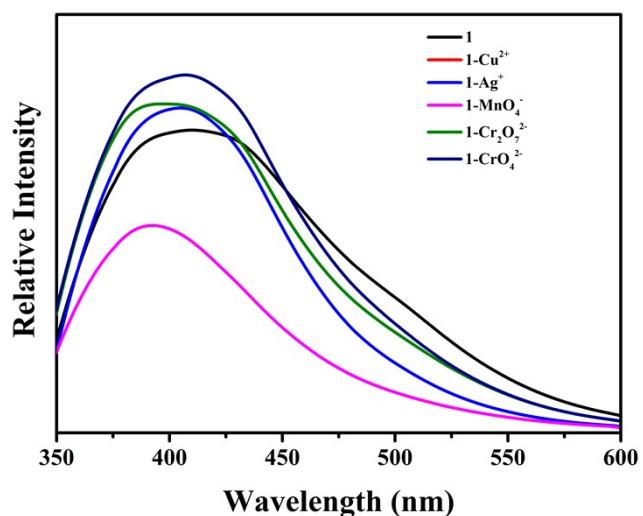
**Fig. S11** (a) Emission spectra of **1** dispersed in DMF: H<sub>2</sub>O (V/V=1:1) solution with different concentrations of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. (b) The Stern–Volmer plot of I<sub>0</sub>/I versus Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> concentration. (c) Emission spectra of **1** dispersed in DMF: H<sub>2</sub>O (V/V=1:1) solution with different concentrations of CrO<sub>4</sub><sup>2-</sup>. (d) The Stern–Volmer plot of I<sub>0</sub>/I versus CrO<sub>4</sub><sup>2-</sup> concentration.



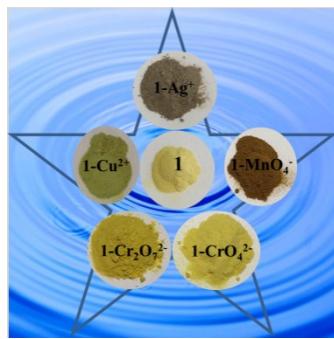
**Fig. S12** (a) Luminescence intensity of the **1** dispersed in a mixture of other anions with Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (a) and CrO<sub>4</sub><sup>2-</sup> (b).



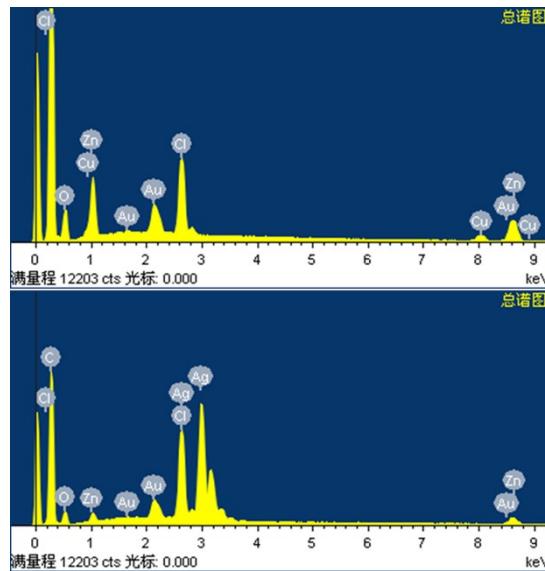
**Fig. S13** Linear region of fluorescence intensity of **1** in DMF:  $\text{H}_2\text{O}$  (V/V=1:1) solution upon addition of  $\text{MnO}_4^-$  (a),  $\text{Cr}_2\text{O}_7^{2-}$  (b) and  $\text{CrO}_4^{2-}$  (c).



**Fig. S14** Emission spectra of **1**, **1-Cu<sup>2+</sup>**, **1-Ag<sup>+</sup>**, **1-MnO<sub>4</sub><sup>-</sup>**, **1-Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>** and **1-CrO<sub>4</sub><sup>2-</sup>** in solid state at room temperature.



**Fig. S15** The photographs of **1-M<sup>n+</sup>** ( $M = Cu^{2+}$ ,  $Ag^+$ ,  $MnO_4^-$  and  $Cr(VI)$ ( $Cr_2O_7^{2-}$  and  $CrO_4^{2-}$ ), respectively) as solid.



**Fig. S16** EDS spectrum of **1-Cu<sup>2+</sup>** and **1-Ag<sup>+</sup>**.

**Table S2** ICP-MS analysis results for  $Cu^{2+}$  and  $Ag^+$  included **1**.

Complex	Zn <sup>2+</sup> Content (%)	Cu <sup>2+</sup> Content (%)	Ag <sup>+</sup> Content (%)
<b>1-Cu<sup>2+</sup></b>	35.68	6.31	
<b>1-Ag<sup>+</sup></b>	27.47		37.84

**Table S3.**  $K_{sv}$  and LOD of MOF-based luminescent sensors for  $Cu^{2+}$ ,  $Ag^+$ ,  $MnO_4^-$ ,  $Cr_2O_7^{2-}$  and  $CrO_4^{2-}$ .

MOF-based fluorescent materials	Analyte	Detection limits	Quenching constant ( $M^{-1}$ )	Recyclability	Solvent	Ref
Cd <sub>2</sub> (L <sub>3</sub> )(DMF) <sub>2</sub> (Cd-MOF-74)	Cu <sup>2+</sup>	78.7 $\mu$ M	1806	NO	Water	1
[Cd(L) <sub>2</sub> ]·(DMF) <sub>0.92</sub>	Cu <sup>2+</sup>	3.9ppm	4.4×10 <sup>3</sup>	YES	DMF	2
{[Eu <sub>2</sub> K <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sub>n</sub> ·5H <sub>2</sub> O}	Cu <sup>2+</sup>	10 <sup>-6</sup> M	5.2×10 <sup>4</sup>	NO	Ethanol	3
Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (L <sub>2</sub> -H <sub>2</sub> ) <sub>3</sub>	Cu <sup>2+</sup>	67nM	4.5×10 <sup>5</sup>		Water	4
{Zn <sub>5</sub> (L) <sub>2</sub> (DMF) <sub>2</sub> (μ <sub>3</sub> -H <sub>2</sub> O)}·2DMF}	Cu <sup>2+</sup>	1.01ppm	1.10×10 <sup>3</sup>	NO	DMF	5

	$\text{Ag}^+$	0.64 ppm	$2.24 \times 10^3$	NO	DMF	
$\text{EuC}_{12}\text{H}_{10}\text{Br}_6\text{O}_{11}$	$\text{Cu}^{2+}$	$7.52 \times 10^{-5}\text{M}$	4612.0	YES	Ethanol	6
$[\text{Cd(L)(TPOM)}_{0.75}] \cdot x\text{S}$	$\text{Cu}^{2+}$		17890	YES	Water	7
$[\text{Zn(L)(BBI)} \cdot (\text{H}_2\text{O})_2]$	$\text{Cr}_2\text{O}_7^{2-}$		11680			
$[\text{Cd(L)(TPOM)}_{0.75}] \cdot x\text{S}$	$\text{Cr}_2\text{O}_7^{2-}$		13450			
$[\text{Eu}_6\text{Zn}_6(\text{L}_2)_2(\text{L}_3)_2\text{O}_2(\text{OAc})_{18}]$	$\text{Ag}^+$	7.59 $\mu\text{M}$	32520	NO	DMF	8
$[\text{Eu}_6\text{Zn}_6(\text{L}_2)_2(\text{L}_3)_2\text{O}_2(\text{OAc})_{18}]$	$\text{Ag}^+$	2.26 $\mu\text{M}$	32520	NO	DMF	9
$\{\text{Co}_2(\text{C}_{17}\text{H}_8\text{O}_8)(\text{C}_{14}\text{H}_{14-}\text{N}_4)_2\} \cdot 3\text{H}_2\text{O}\}_n$	$\text{Ag}^+$	23nM	$3.4 \times 10^5$	NO	Water	10
$\{\text{Tb}_2(\text{L})_2(\text{H}_2\text{O})_2\}_n \cdot (5\text{H}_2\text{O}) \cdot (6\text{DMAC})\}_n$	$\text{MnO}_4^-$	$4.48 \times 10^{-5}\text{ mM}$	1200	YES	Water	11
$\{\text{Eu}_2(\text{L})_2(\text{H}_2\text{O})_2\}_n \cdot (5\text{H}_2\text{O}) \cdot (6\text{DMAC})\}_n$	$\text{Cr}_2\text{O}_7^{2-}$	$8.94 \times 10^{-5}\text{ M}$	1052			
$[\text{Cd(L)}_2(\text{H}_2\text{O})_2]_n$	$\text{MnO}_4^-$	$1.73 \times 10^{-4}\text{ M}$	$2.2 \times 10^4$	NO	Water	12
	$\text{Cr}_2\text{O}_7^{2-}$	$1.75 \times 10^{-4}\text{ M}$	$1.1 \times 10^4$			
	$\text{CrO}_4^{2-}$	$3.41 \times 10^{-5}\text{ M}$	$5.1 \times 10^4$	NO		
$\{\text{Eu}(\text{L})(\text{H}_2\text{O})_2\} \cdot 5\text{H}_2\text{O}\}_n$	$\text{MnO}_4^-$		$0.51 \times 10^3$	NO	Water	13
	$\text{Cr}_2\text{O}_7^{2-}$		$1.36 \times 10^3$			
	$\text{CrO}_4^{2-}$		$1.74 \times 10^3$			
$[\text{Cd}_3(\text{bpe})_2(\text{ceba})_2(\text{fa})_2(\text{H}_2\text{O})_2]_n$	$\text{Cr}_2\text{O}_7^{2-}$		9510	NO	Water	14
$[\text{Eu}_2(\text{tpbpc})_4 \cdot \text{CO}_3 \cdot 4\text{H}_2\text{O}] \cdot \text{DMF}$	$\text{Cr}_2\text{O}_7^{2-}$	1.07ppm	$1.04 \times 10^4$	YES	Water	15
	$\text{CrO}_4^{2-}$	0.33ppm	$4.85 \times 10^3$	YES		
$\{\text{Zn(btz)}\}_n$	$\text{Cr}_2\text{O}_7^{2-}$	$2 \times 10^{-6}\text{ M}$	$4.23 \times 10^3$	YES	Water	16
$\{\text{Zn(btz)}\}_n$	$\text{CrO}_4^{2-}$	$10^{-5}\text{ M}$	$3.19 \times 10^3$			
$\{\text{Zn}_2(\text{ttz})\text{H}_2\text{O}\}_n$	$\text{Cr}_2\text{O}_7^{2-}$	$2 \times 10^{-5}\text{ M}$	$2.19 \times 10^3$			
$\{\text{Zn}_2(\text{ttz})\text{H}_2\text{O}\}_n$	$\text{CrO}_4^{2-}$	$2 \times 10^{-5}\text{ M}$	$2.35 \times 10^3$			
$\{\text{Zn}_3(\text{L})(\text{OH})(\text{H}_2\text{O})_5\} \cdot \text{NMP} \cdot 2\text{H}_2\text{O}\}_n$	$\text{MnO}_4^-$	$3.38 \times 10^{-4}\text{ M}$	$1.1 \times 10^4$	YES	Water	17
	$\text{Cr}_2\text{O}_7^{2-}$		$6.05 \times 10^{-5}\text{ M}$			
$\{\text{Zn}_3(\text{L})(\text{OH})(\text{H}_2\text{O})_5\} \cdot \text{NMP} \cdot 2\text{H}_2\text{O}\}_n$	$\text{CrO}_4^{2-}$	$4.29 \times 10^{-4}\text{ M}$	$1.3 \times 10^4$			
$\{\text{Zn}_6\text{Cl}_6(2,2'\text{-dbpt})_3\} \cdot 2\text{H}_2\text{O}\}_n$	$\text{Cu}^{2+}$	0.73 $\mu\text{M}$	$5.96 \times 10^4$	NO	Water	Thiwo rk
	$\text{Ag}^+$	6.40 $\mu\text{M}$	$1.67 \times 10^4$			
	$\text{MnO}_4^-$	6.14 $\mu\text{M}$	$2 \times 10^5$			
	$\text{Cr}_2\text{O}_7^{2-}$	13.64 $\mu\text{M}$	$1.85 \times 10^5$			
	$\text{CrO}_4^{2-}$	12.33 $\mu\text{M}$	$5.89 \times 10^4$			

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