

## Supporting information

### Two luminescent cuprous iodides with hitherto-unknown free imidazolate sites for efficiently sensing Fe<sup>3+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>

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#### General Remarks

All analytical grade chemicals were obtained commercially and used without further purification. Elemental analyses (C and H) were performed using a PE2400 II elemental analyzer. PXRD patterns were obtained using a Bruker D8 Advance XRD diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). IR spectra were obtained from a powdered sample pelletized with KBr on an ABB Bomen MB 102 series IR spectrophotometer in the range of 400–4000cm<sup>-1</sup>. The solid-state UV/Vis spectra were measured at room temperature using an Agilent Cary 5000 UV/Vis spectrophotometer. Photoluminescent spectrum and lifetime were performed on an Edinburgh FLS 980 analytical instrument equipped with 450 W xenon lamp and UF900H high-energy microsecond flash-lamp as the excitation source. The quantum yield (QY) is measured by the Edinburgh FLS1000 fluorescence, which is equipped with a 450W Xe lamp and a monochromator for wavelength discrimination, an integrating sphere for the sample chamber, and an R928P analyzer for signal detection. The XPS spectra were collected on an AEI (Kratos) ES 200 B X-ray photoelectron spectrometer with a base pressure of about  $\sim 10^{-8}$  Torr.

#### Crystal Structure Determinations

The intensity data of **1** and **2** were collected on a Bruker diffractometer-SMART-APEX II using a  $\omega$ -scan method with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages,<sup>S1</sup> respectively. The structures were solved

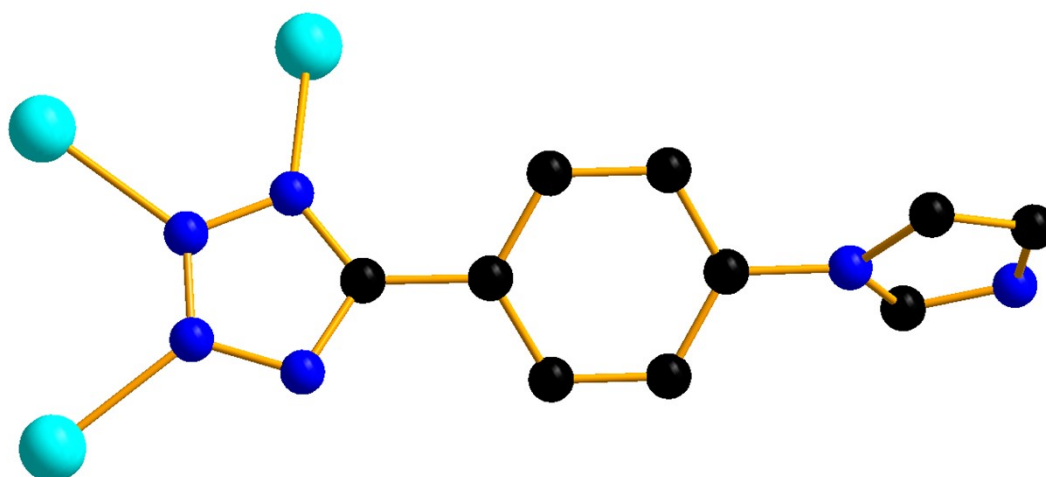
by direct methods using SHELXS-97 and refined by full-matrix least-squares on F<sup>2</sup> using the SHELXL-97 program.<sup>S2</sup> The non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized locations and refined as riding. Technical details of data collections and refinement are summarized in Table S1.

Table S1 Crystallographic data for **1** and **2**.

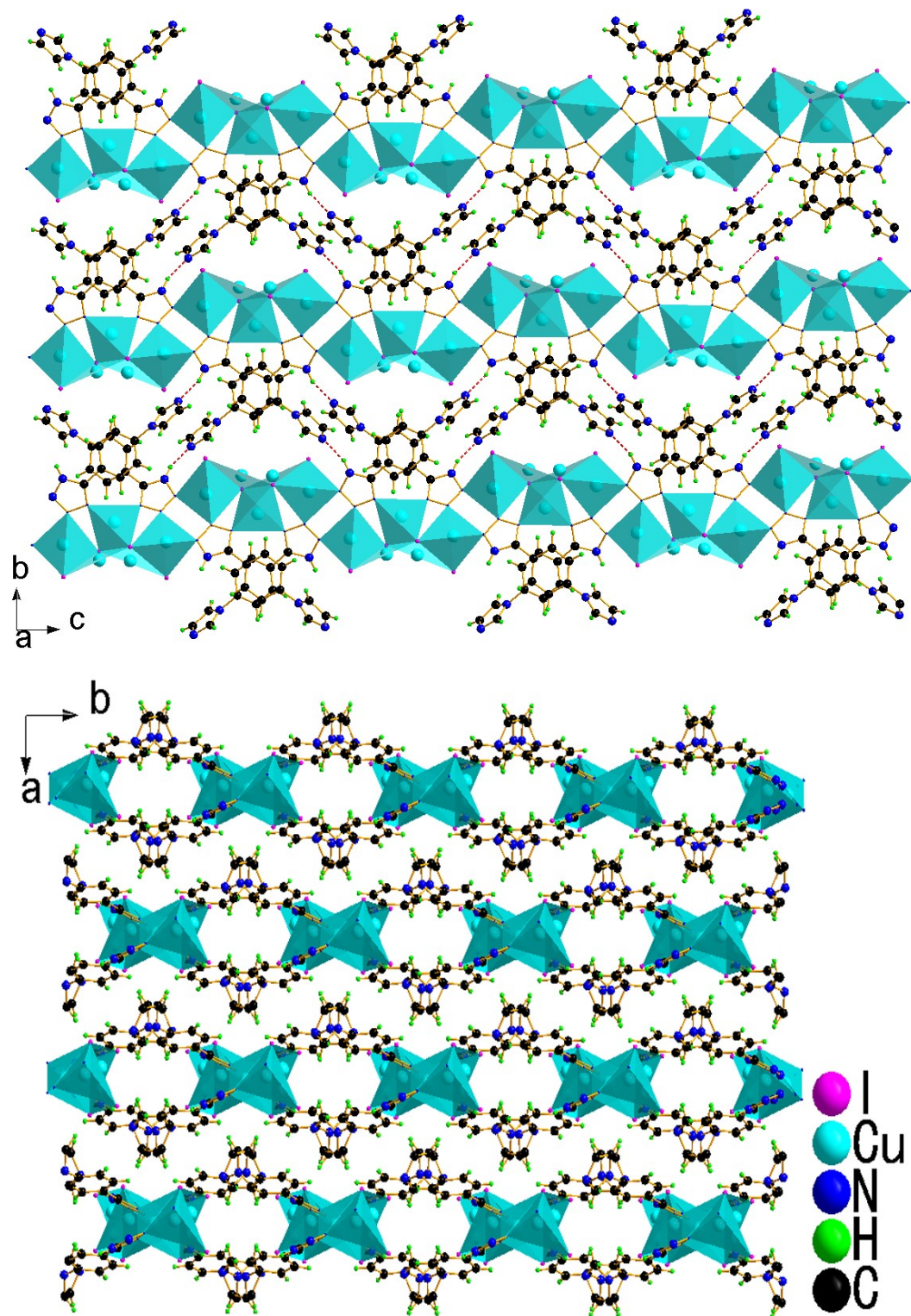
	<b>1</b>	<b>2</b>
Chemical formula	C <sub>20</sub> H <sub>16</sub> Cu <sub>4</sub> I <sub>4</sub> N <sub>12</sub>	C <sub>20</sub> H <sub>16</sub> Cu <sub>2</sub> I <sub>4</sub> N <sub>12</sub> Pb
Fw	1186.2	1266.35
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a (Å)	15.5655(11)	16.4277(8)
b (Å)	11.3560(9)	10.8605(6)
c (Å)	17.3817(11)	17.2943(8)
β (deg)	92.384(2)	98.6794(19)
V (Å <sup>3</sup> )	3069.8(4)	3050.2(3)
Z	8	4
T (K)	296(2)	296(2)
ρ <sub>calc</sub> (g.cm <sup>-3</sup> )	2.567	2.758
F(000)	2192	2288
θ range (deg)	3.191 ≤ θ ≤ 25.095	3.141 ≤ θ ≤ 27.483
Reflections collected	14079	10540
Unique reflections	2741	3446
Reflections (I>2σ(I))	2248	2764
R1, wR2 [I>2σ(I)] <sup>[a]</sup>	0.0345, 0.0749	0.0530, 0.1154
R1, wR2 (all data)	0.0495, 0.0832	0.0722, 0.1230
goodness-of-fit on F <sup>2</sup>	1.054	1.042

### Computational methods

The band structure and density of states (DOS) of **1** and **2** were theoretically calculated by using the computer code CASTEP.<sup>s3</sup> The total energy is calculated with the density functional theory (DFT) using the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA).<sup>s4</sup> The following orbital electrons are treated as valence electrons: H 1s<sup>1</sup>, N 2s<sup>2</sup> 2p<sup>3</sup>, C 2s<sup>2</sup> 2p<sup>2</sup>, Cu 3d<sup>10</sup> 4s<sup>1</sup>, I 5s<sup>2</sup> 5p<sup>5</sup> and 5d<sup>10</sup> 6s<sup>2</sup> 6p<sup>2</sup>. The number of plane waves included in the basis is determined by a cutoff energy of 270 eV, and the numerical integration of the Brillouin zone is performed using a Monkhorst–Pack k point sampling: 2 × 2 × 1. The Fermi level (E<sub>F</sub> = 0 eV) was selected as the reference of the energy.

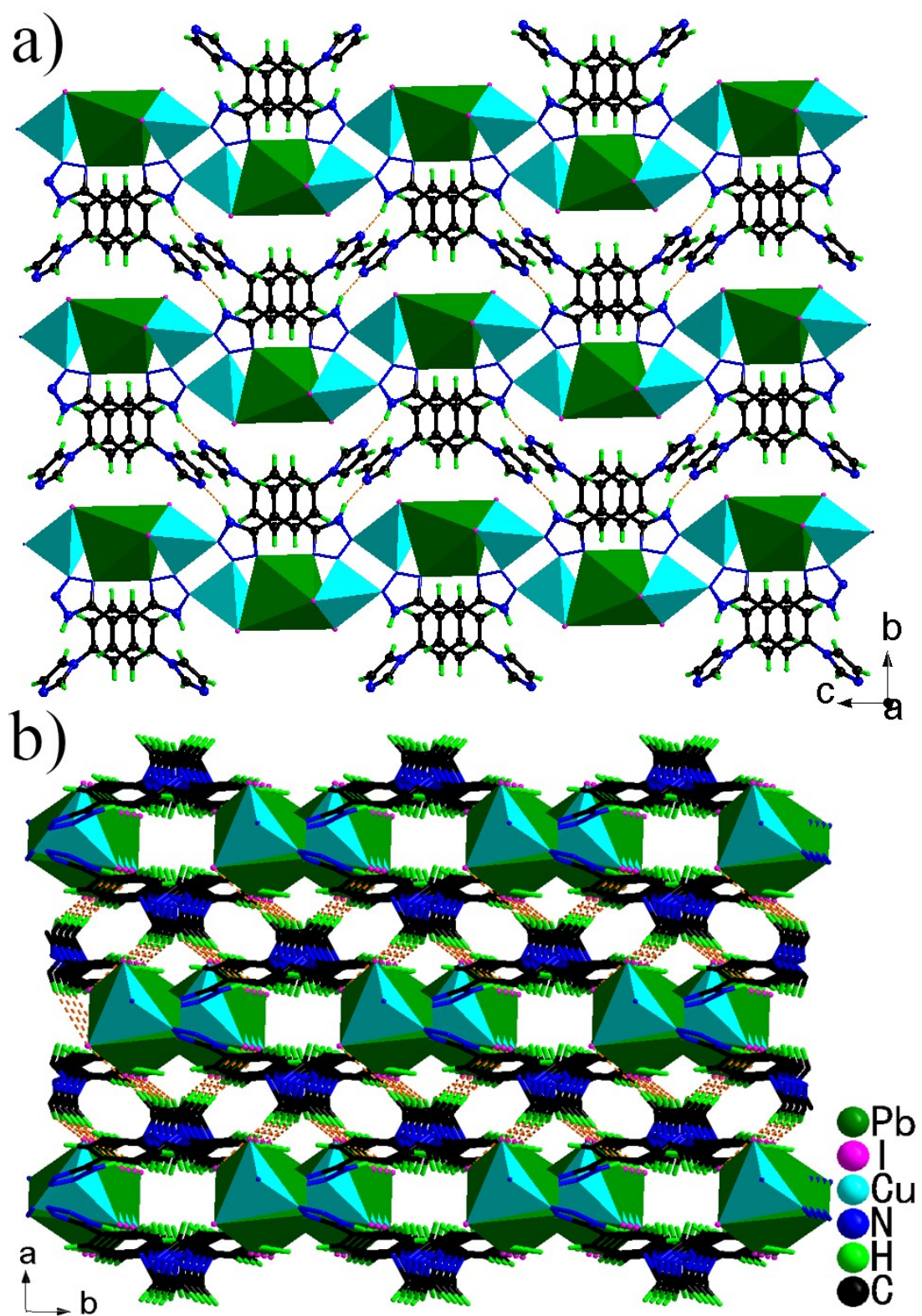


**Fig. S1** The coordination mode of HL ligand.



**Fig. S2** a) The layer constructed by the N–H···N H-bonds in **1**. b) the 3-D supramolecular structure.





**Fig. S3** a) The layer constructed by the N–H···N H-bonds in 2. b) the 3-D network structure.

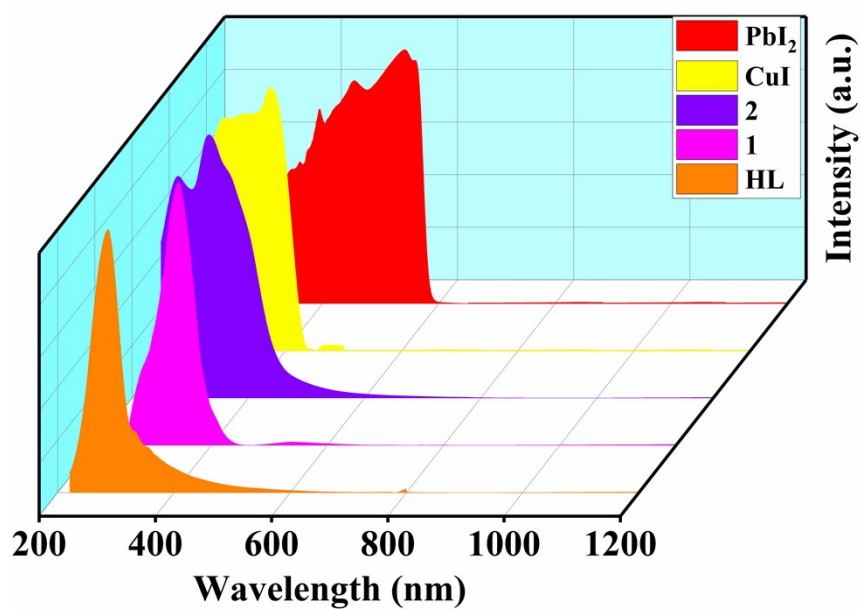


Fig. S4 The UV-vis spectra of 1, 2, HL, CuI and PbI<sub>2</sub> at room temperature.

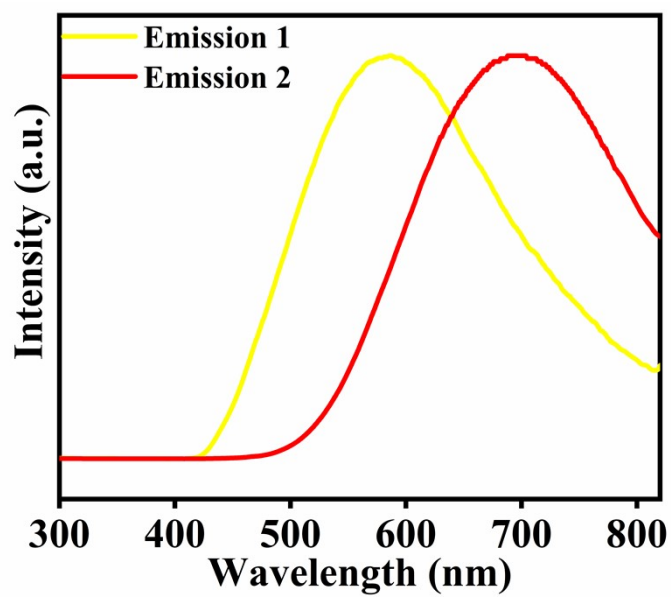
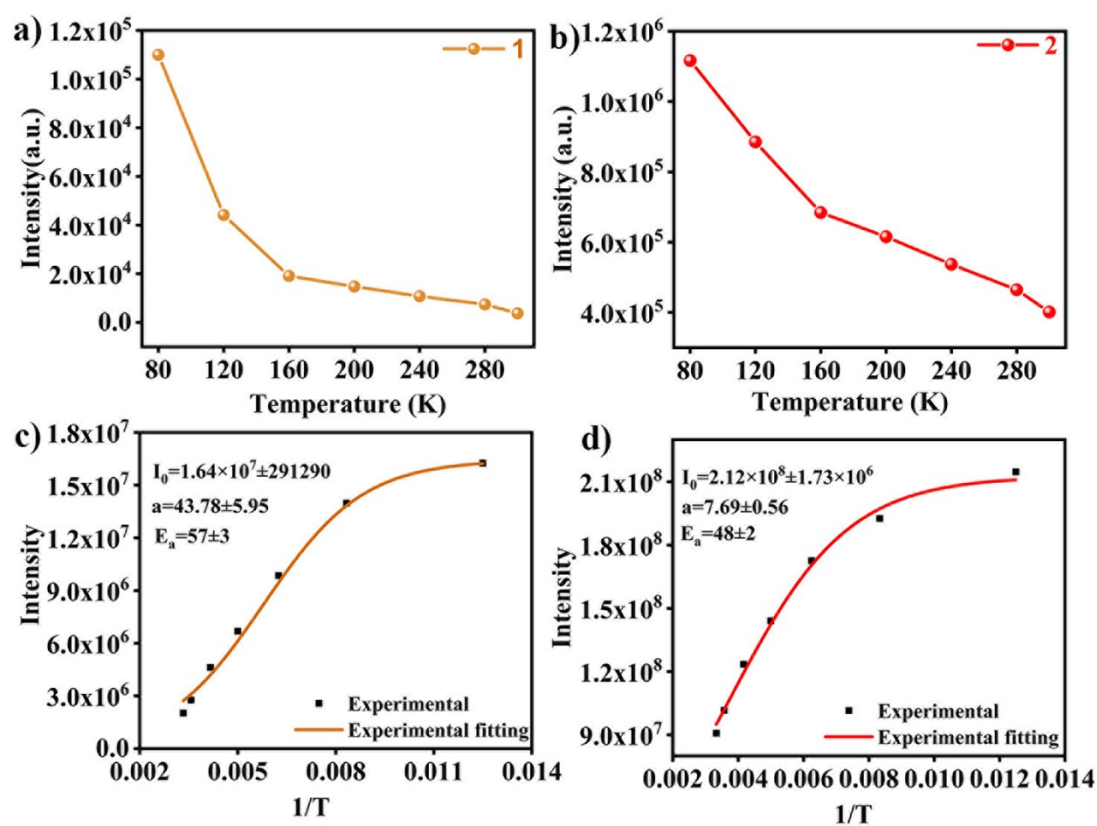
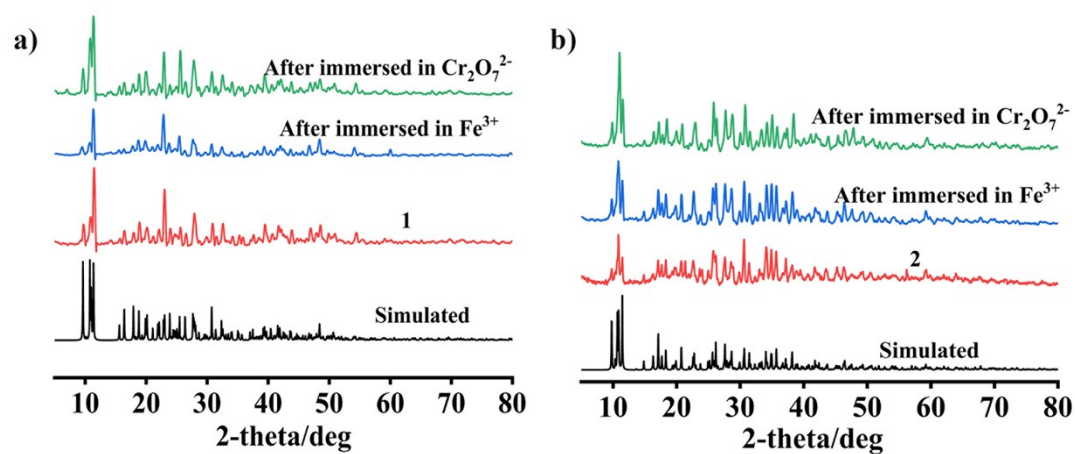


Fig. S5 Emission spectra of 1 and 2 at room temperature



**Fig. S6** Temperature dependent luminescent intensity of 1 (a) and 2 (b). The theoretical fitting data from Arrhenius-type model for 1 (c) and 2 (d).



**Fig. S7** Simulated, experimental and after immersed XRD patterns of 1 (a) and 2 (b).

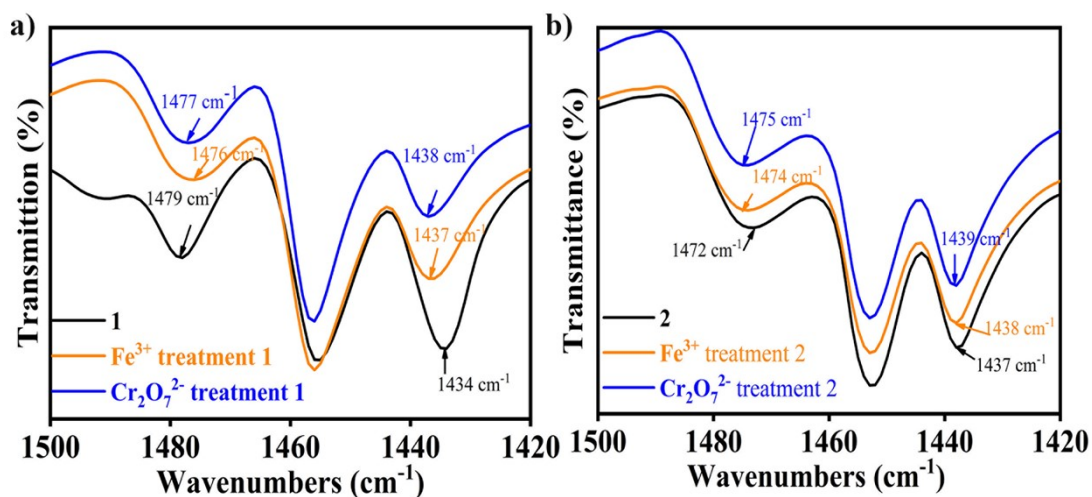


Fig. S8 IR of 1-2 and 1-2 treated with  $\text{Fe}^{3+}$   $\text{Cr}_2\text{O}_7^{2-}$ .

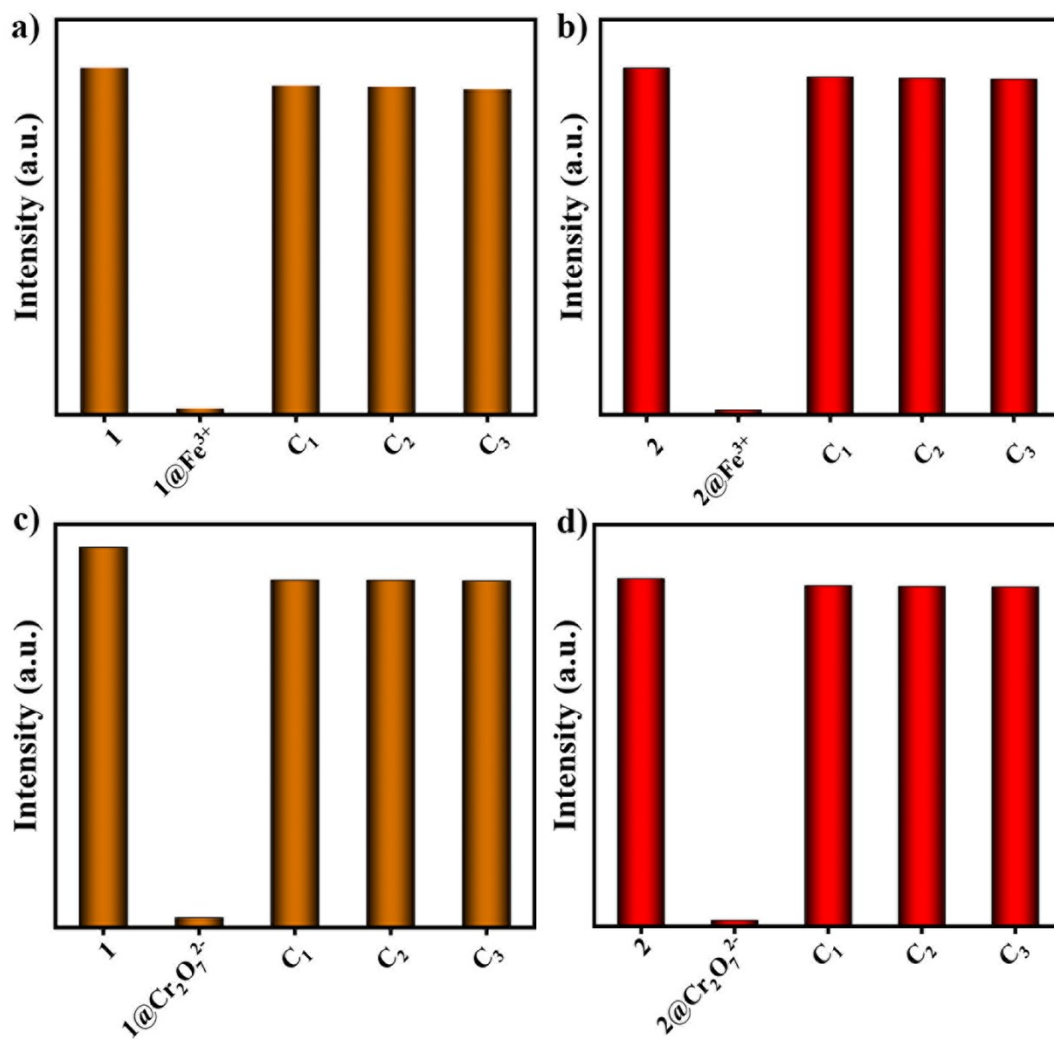
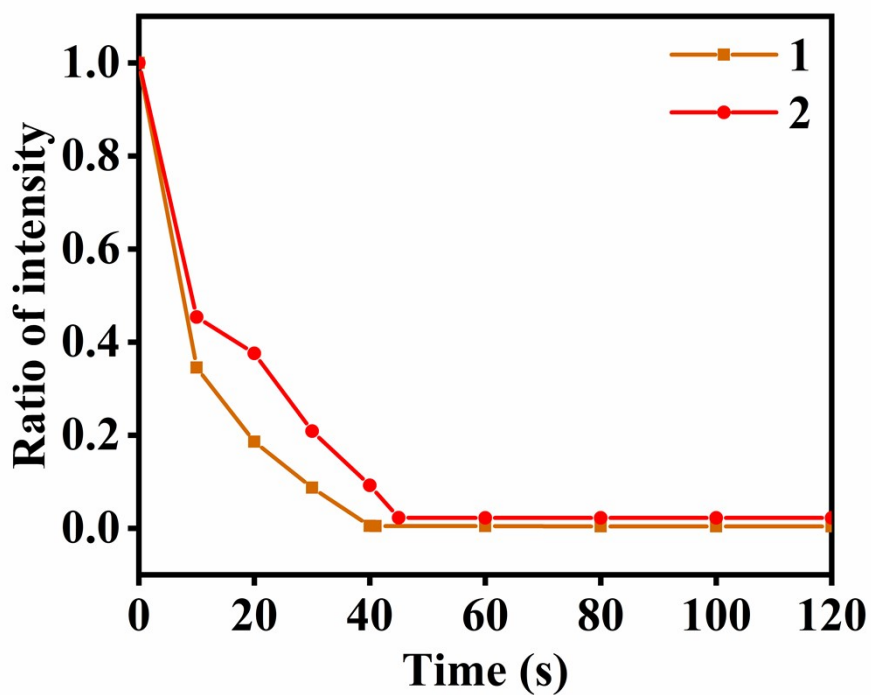
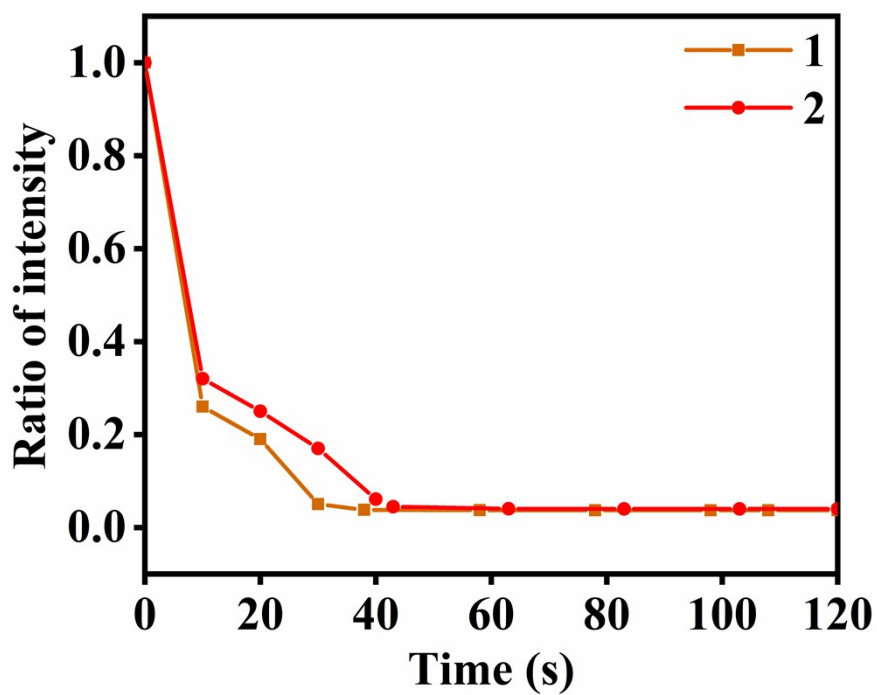


Fig. S9 Luminescent intensity of 1 and 2 after three recycles (C1, C2, C3) in  $\text{Fe}^{3+}$  (a), (b) and  $\text{Cr}_2\text{O}_7^{2-}$  (c), (d) solutions (0.01 mol/L).





**Fig. S10** Luminescent intensity of 1 and 2 at different reaction times in  $\text{Fe}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  solutions

## References

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