

## **Robust fluorescent calcium coordination polymers as Cu<sup>2+</sup> sensors with high sensitivity and fast response**

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### Supporting Information

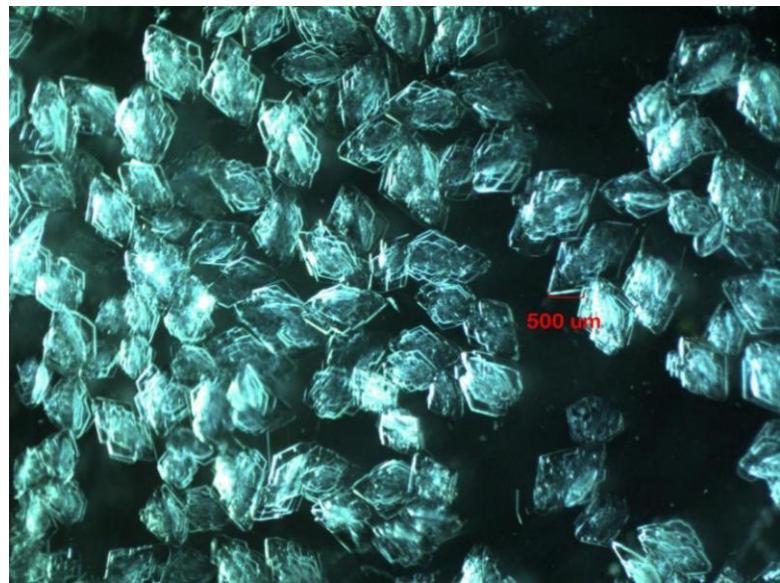


Figure S1. The crystal images of **1**.

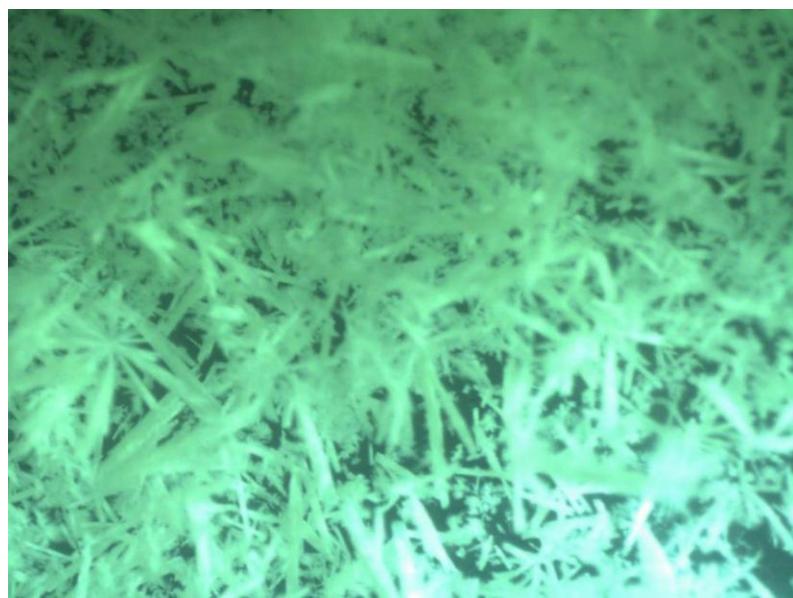
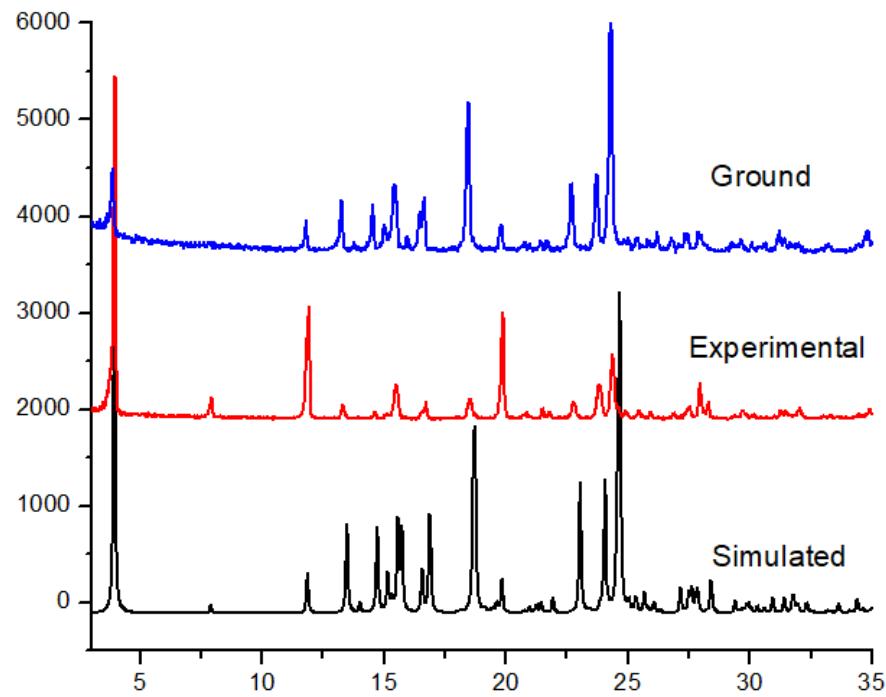
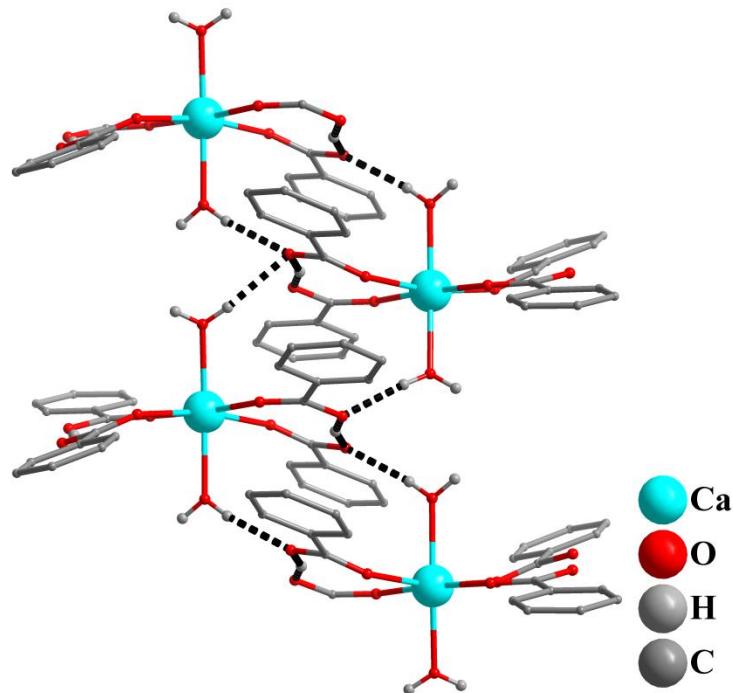


Figure S2. The crystal images of **2**.



**Figure S3.** The PXRD pattern of **1** before grinding, after grinding and simulated from the single crystal X-ray data.

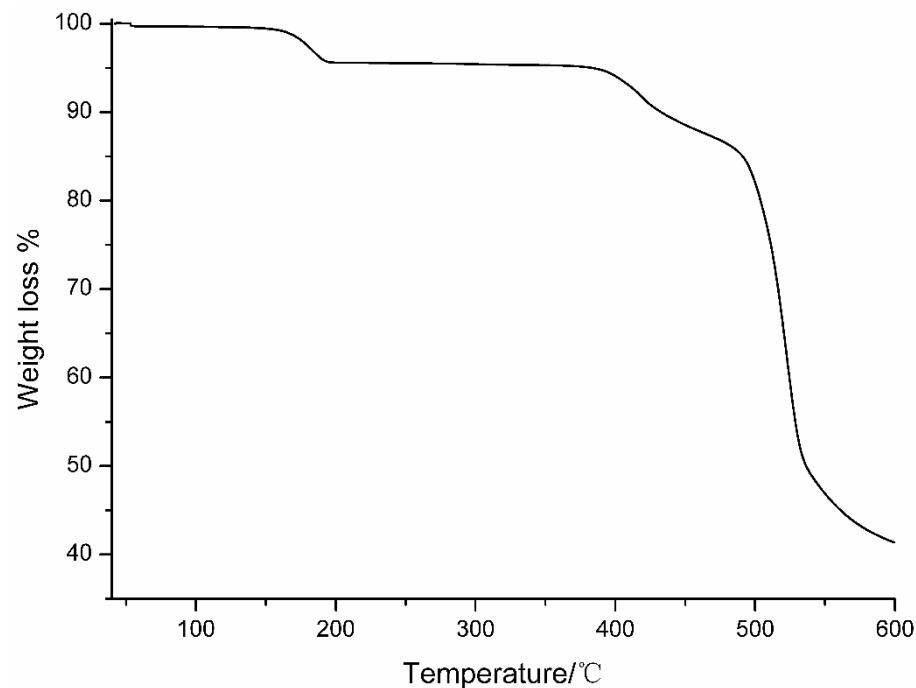


**Figure S4.** The H-bond interactions between the free  $\text{COO}^-$  and the terminal water molecules on the calcium PBU of framework **1**.

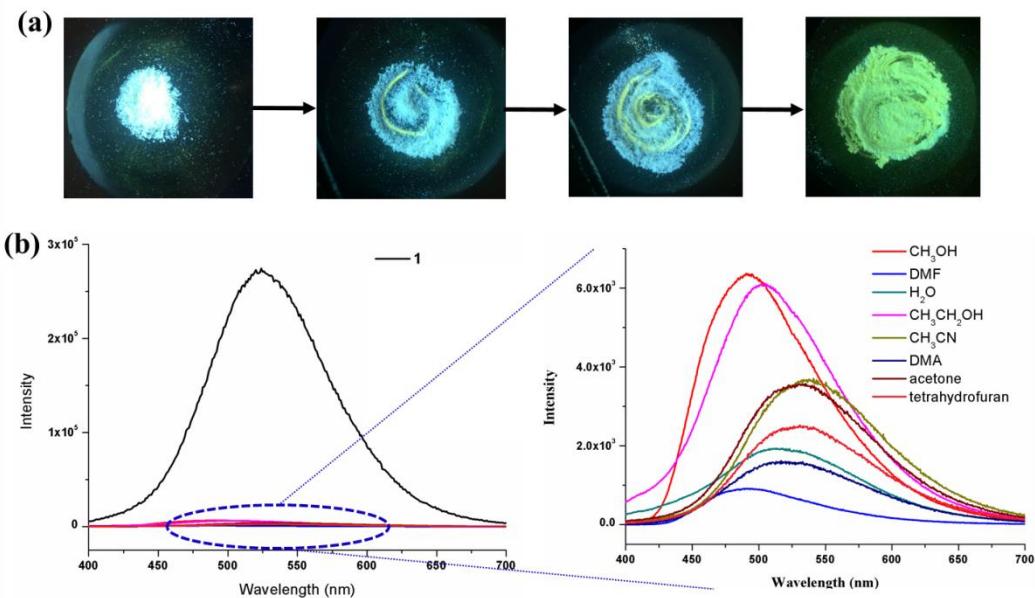
**Table S1.** H-bonds information for **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(4)#3	0.917(16)	1.544(17)	2.4282(15)	161(2)
O(5)-H(5A)...O(2)#5	0.827(19)	2.16(2)	2.957(3)	163(4)
O(5)-H(5B)...O(4)#6	0.832(19)	1.92(2)	2.748(3)	173(4)
O(6)-H(6)...O(2)#7	0.836(16)	2.032(17)	2.8605(15)	171(3)

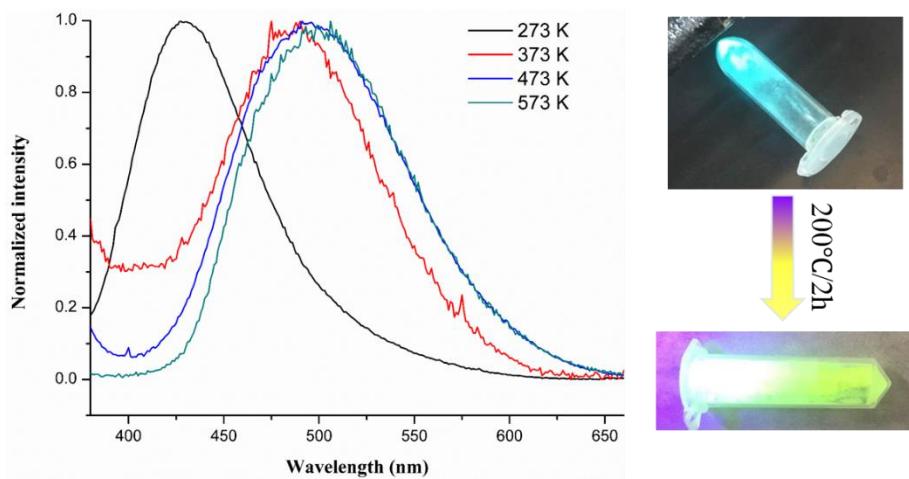
Symmetry transformations used to generate equivalent atoms: #3  $x+1/2, -y+1/2, z+1/2$ ; #5  $x, -y, z-1/2$ ; #6  $-x+1/2, y-1/2, -z+1/2$ ; #7  $x, -y+1, z-1/2$ .



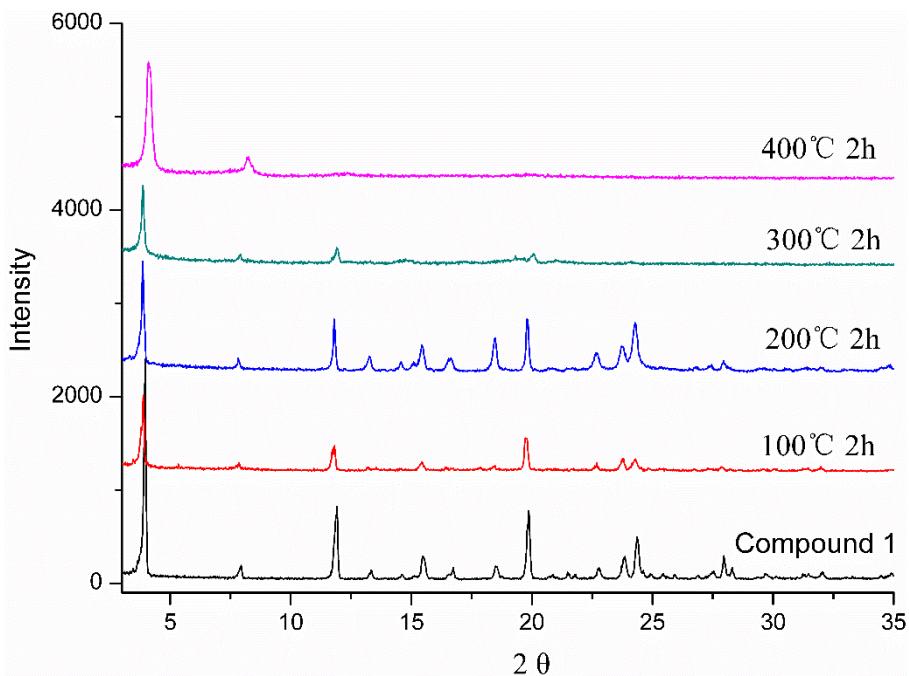
**Figure S5.** TGA curve for as-made **1** from 30°C to 600°C.



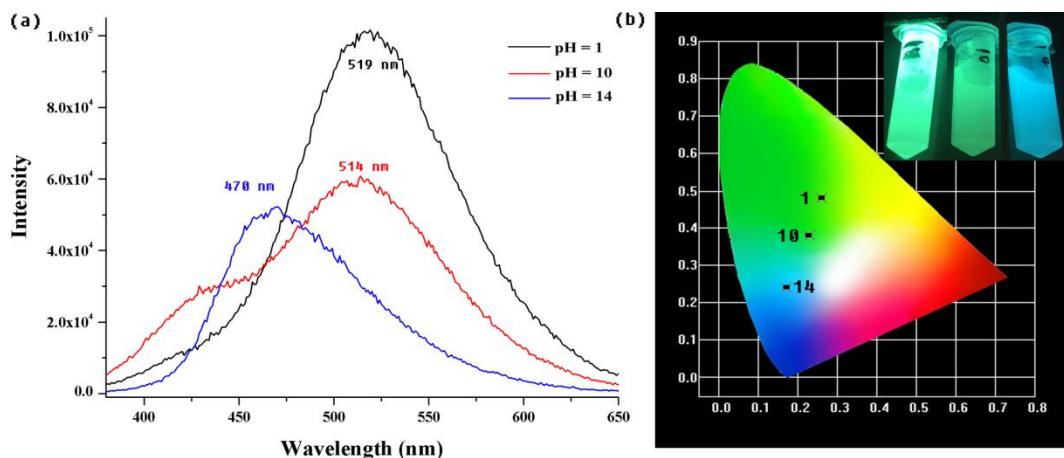
**Figure S6.** (a) Photographic images of the luminescent shifts in emission of **1** when ground through the use of a mortar and pestle. (b) The FL spectra for powdered sample **1** in the solid state (black curve, left side) and those dispersed in various solvents (curves in the outlined section on the left side and enlarged version on the right side).



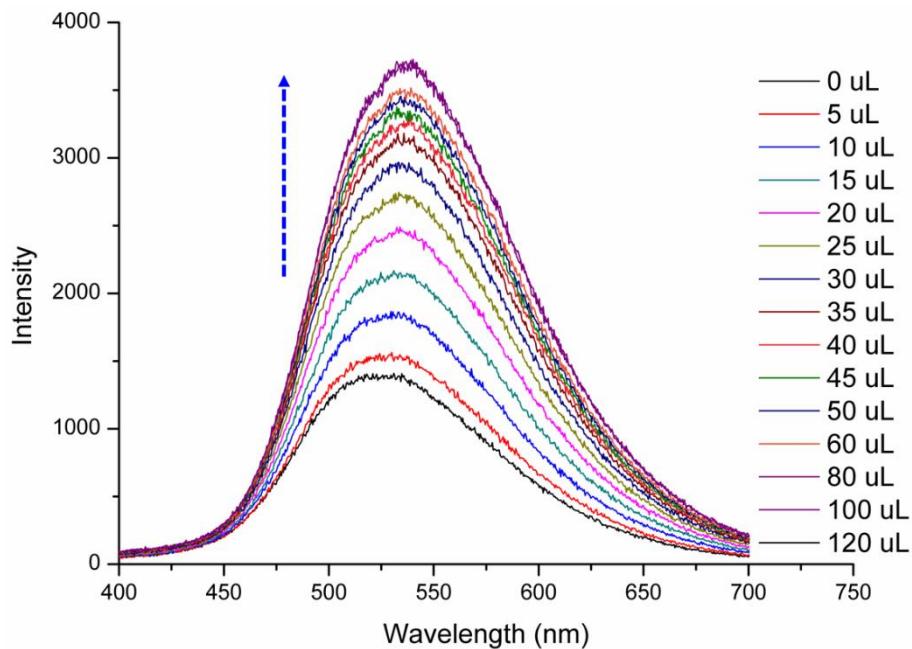
**Figure S7.** The FL spectra of as-made **1** after being held at different temperatures for 2 hours and photographs of the changes in emission under 365 nm excitation with a UV lamp.



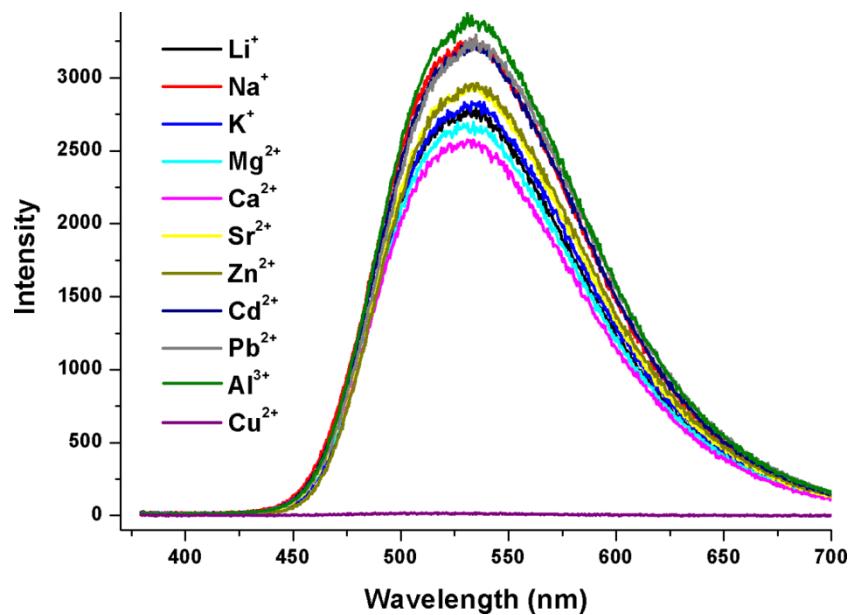
**Figure S8.** The PXRD patterns of **1** after heating under different temperatures for 2 hours.



**Figure S9.** (a) The FL spectra of **1** dispersed in different pH solutions. (b) CIE coordinates calculated from the FL spectra. Inset are photographs showing changes of emission color of sample **1** under excitation with a 365 nm UV lamp.



**Figure S10.** The FL spectra of **1** after addition of pH 1 solution into the emulsion of **1** within 10 seconds.

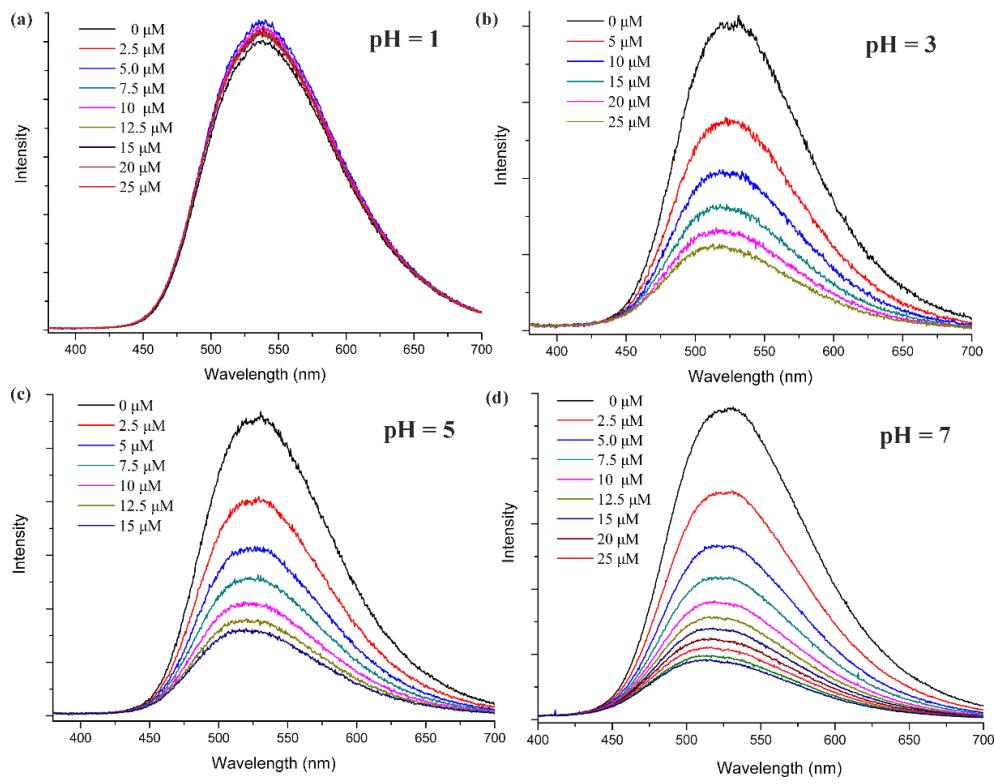


**Figure S11.** The FL spectra of **1** dispersed at different  $10^{-4}$  M metal ions solutions within 10 seconds.

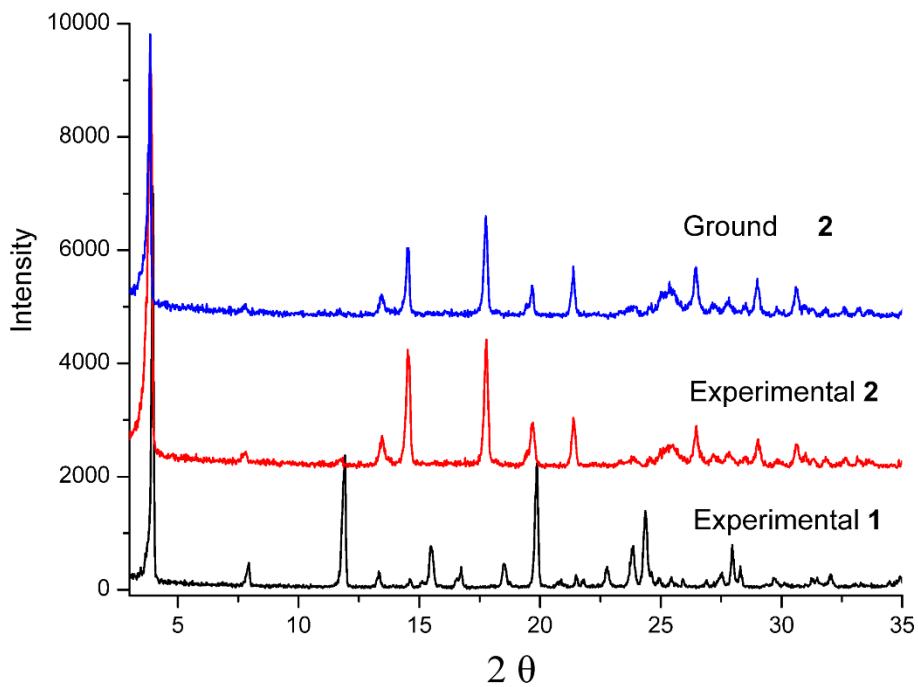
**Table S2.** Summary of reported CP-based FL sensors for Cu<sup>2+</sup> in water.

Name of CP	<i>K</i> <sub>sv</sub>	LOD	Solvents	Response time	Ref.
<b>1</b>	<b><math>1.56 \times 10^5 \text{ M}^{-1}</math></b>	<b>0.79 μM (0.064 ppm)</b>	<b>H<sub>2</sub>O</b>	<b>within 10 s</b>	<b>This work</b>
<b>2</b>	<b><math>4.39 \times 10^5 \text{ M}^{-1}</math></b>	<b>0.13 μM (8.32 ppb)</b>	<b>H<sub>2</sub>O</b>		
Eu <sup>3+</sup> @MOF-253	—	0.66 μM	H <sub>2</sub> O	—	1
[Cd <sub>2</sub> (L)(OH)(H <sub>2</sub> O) <sub>2</sub> ]	$3.09 \times 10^4 \text{ M}^{-1}$	0.666 ppm	H <sub>2</sub> O	—	2
[Cd (Ligand)]·2DMF	$4.1 \times 10^3 \text{ M}^{-1}$	3 ppm	DMF	—	3
Eu <sub>2</sub> (TBrTA) <sub>3</sub> (H <sub>2</sub> O) <sub>8</sub> ·2H <sub>2</sub> O	4612.0 M <sup>-1</sup>	75.2 μM (4.78 ppm)	ethanol	—	4
[Eu <sub>2</sub> (MTBC)(OH) <sub>2</sub> (DMF) <sub>3</sub> (H <sub>2</sub> O) <sub>4</sub> ]·2DMF·7H <sub>2</sub> O	2251.4 M <sup>-1</sup>	17.2 μg/L	DMF and H <sub>2</sub> O	3 min	5
UiO-66(OH) <sub>2</sub> @PCN224	$4.03 \times 10^5 \text{ M}^{-1}$	0.068 nM	H <sub>2</sub> O	40 s	6
[Zn <sub>2</sub> Na(L)(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ][OAc]·2H <sub>2</sub> O	$7.75 \times 10^4 \text{ M}^{-1}$	0.65 μM	H <sub>2</sub> O	60 s	7
Ce(1,5-NDS) <sub>1.5</sub> (H <sub>2</sub> O) <sub>5</sub>	7668 M <sup>-1</sup>	3.0 μM	H <sub>2</sub> O	5 min	8
[Zn(btca)(py) <sub>2</sub> ]	$2.92 \times 10^4 \text{ M}^{-1}$	3 ppm	H <sub>2</sub> O	—	9
Cd(INA)(pytpy)(OH)·2H <sub>2</sub> O	$1.3 \times 10^5 \text{ M}^{-1}$	3.98 μM	H <sub>2</sub> O	—	10
MOF-525	$4.5 \times 10^5 \text{ M}^{-1}$	67 nM	DMF	40 s	11
Cd-MOF-74	1806 M <sup>-1</sup>	78.7 μM	H <sub>2</sub> O	—	12
Nd <sub>2</sub> (NH <sub>2</sub> -BDC) <sub>3</sub> (DMF) <sub>4</sub>	none	24.95 μM	DMF	—	13
[Tb <sub>2</sub> (DCSAL) <sub>3</sub> (H <sub>2</sub> O) <sub>11</sub> ]·3DCSAL·4H <sub>2</sub> O	$4.8 \times 10^4 \text{ M}^{-1}$	0.17 μM	acetonitrile	—	14
MIL-53-L	$6.15 \times 10^3 \text{ M}^{-1}$	10 μM	H <sub>2</sub> O	—	15
PCN-222-Pd(II)	none	50 nM	Organic solvents	5 min	16
H <sub>2</sub> [Dy <sub>2</sub> (PABA) <sub>4</sub> (bpy) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·(bpy) <sub>2</sub> (EtOH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	none	10 <sup>-5</sup> M	H <sub>2</sub> O	2 min	17

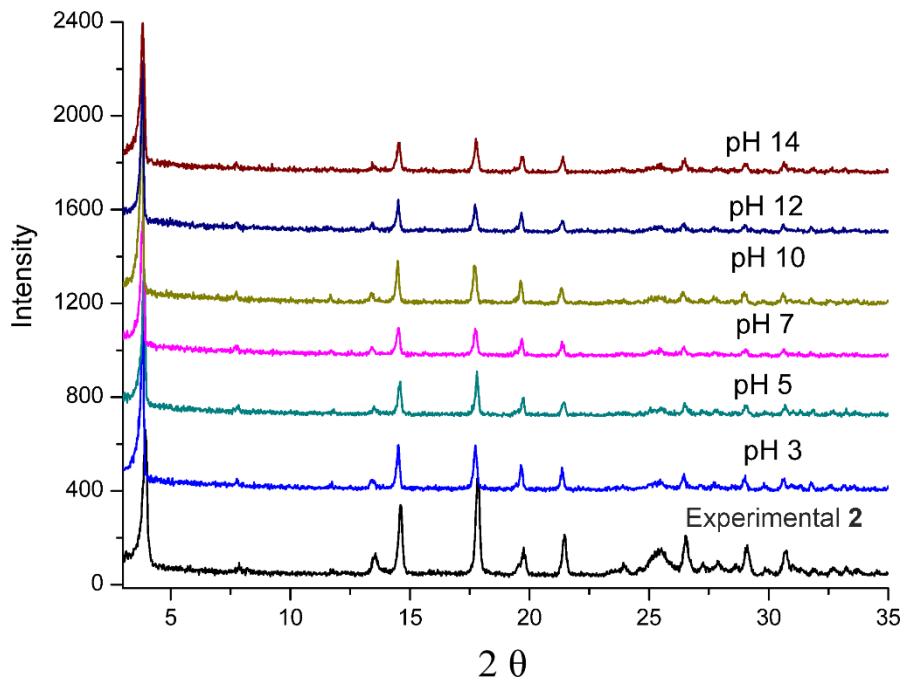
$\text{SiO}_2@\text{ZIF-8}$	$1.83 \times 10^6 \text{ M}^{-1}$	3.8 nM	HEPES buffer	within minutes	18
InPCF-1	$1840 \text{ M}^{-1}$	$10^{-5} \text{ M}$	DMF	—	19
$[\text{Eu}(\text{pdc})_{1.5}(\text{DMF})] \cdot (\text{DMF}) \cdot 0.5(\text{H}_2\text{O})_{0.5}$	$2146 \text{ M}^{-1}$	$10 \mu\text{M}$	DMF	30 min	20
$[\text{Eu}(\text{HL})(\text{L})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	$1163 \text{ M}^{-1}$	$10 \mu\text{M}$	$\text{H}_2\text{O}$	—	21
$[\text{Eu}_2\text{K}_2(\text{dcppa})_2(\text{H}_2\text{O})_6] \cdot \text{mH}_2\text{O}$	$5.2 \times 10^4 \text{ M}^{-1}$	$10^{-6} \text{ M}$	ethanol	8 min	22
$[\text{Cd}(2\text{-aip})(\text{bpy})] \cdot 2\text{DMF}$	none	10 mM	DMF	within 10 s	23
ZnMGO	$3.07 \times 10^4 \text{ M}^{-1}$	$1.0 \mu\text{M}$	$\text{H}_2\text{O}$	10 min	24
$[\text{Mg}_3(\text{ndc})_{2.5}(\text{HCO}_2)_2(\text{H}_2\text{O})][\text{NH}_2\text{Me}_2 \cdot 2\text{H}_2\text{O} \cdot \text{DMF}]$	$1.986 \times 10^3 \text{ M}^{-1}$	$10 \mu\text{M}$	$\text{H}_2\text{O}$	7 days	25
$\text{Eu}_3(\text{hcoo})_2(\text{R-COO})_8$	$2350 \text{ M}^{-1}$	$10 \mu\text{M}$	DMF	—	26
Cd(H <sub>2</sub> ttac)bpp	none	$0.63 \mu\text{M}$	DMF	—	27
$\text{Eu}(\text{FBPT})(\text{H}_2\text{O})(\text{DMF})$	none	$10 \mu\text{M}$	DMF	—	28



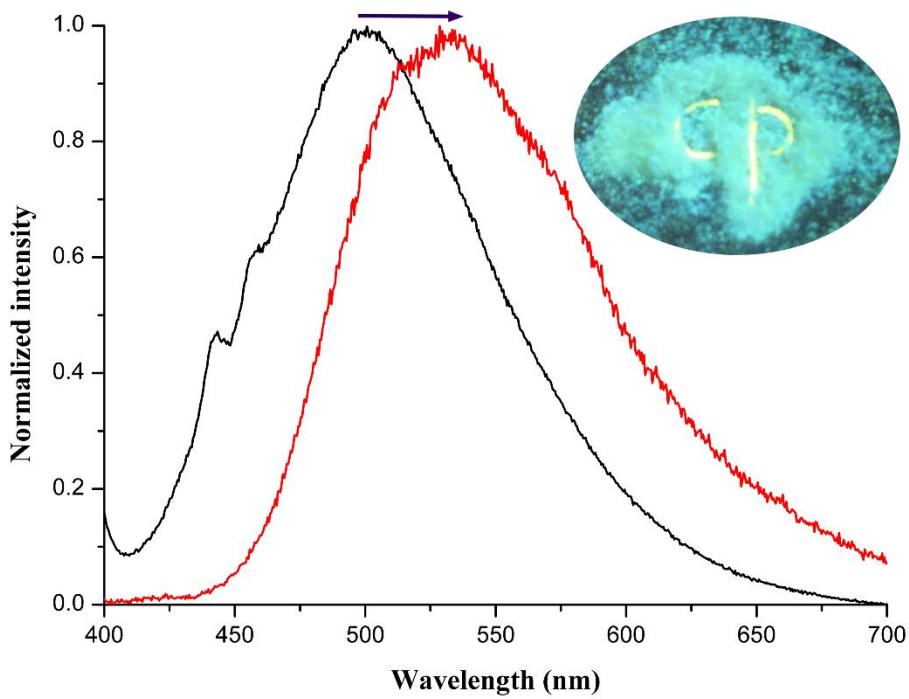
**Figure S12.** FL intensity of **1** dispersed in different pH conditions upon addition of  $10^{-3}$  M Cu<sup>2+</sup> ions within 10 seconds.



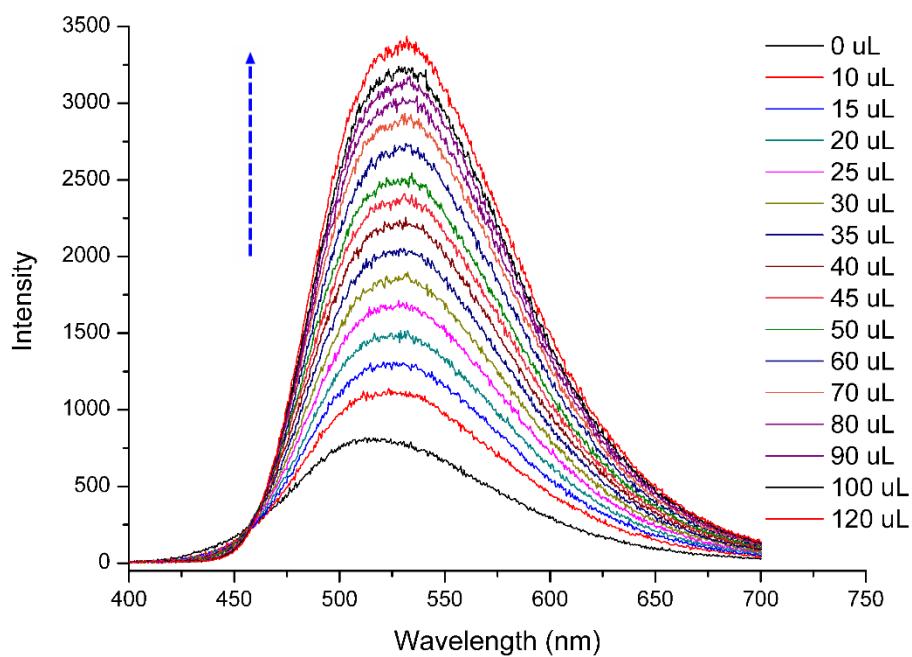
**Figure S13.** The PXRD patterns of **2** before and after grinding. Experimental PXRD pattern of **1** was presented for comparison.



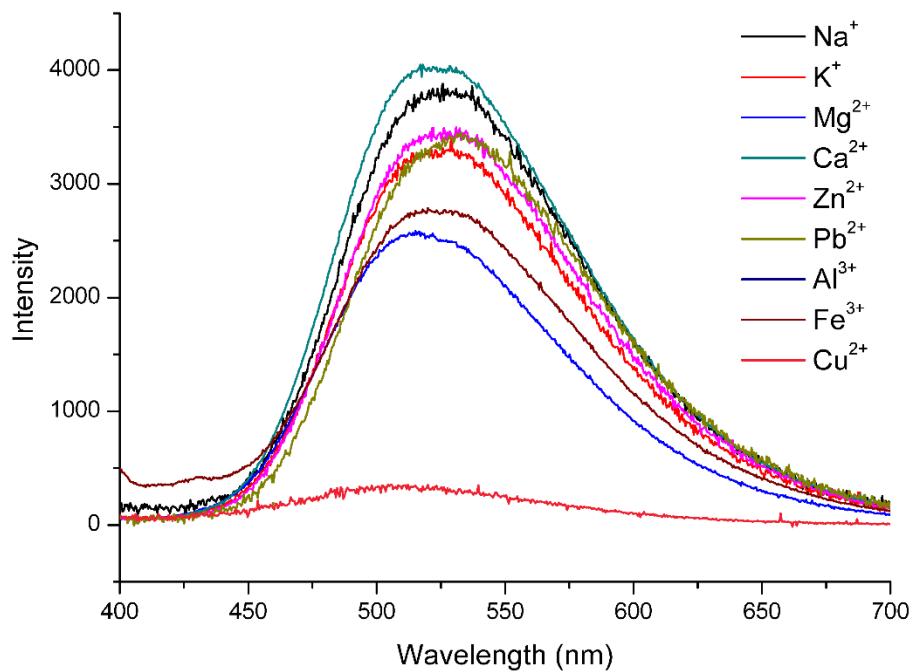
**Figure S14.** The PXRD pattern of **2** after exposure to different pH conditions for 24 hours.



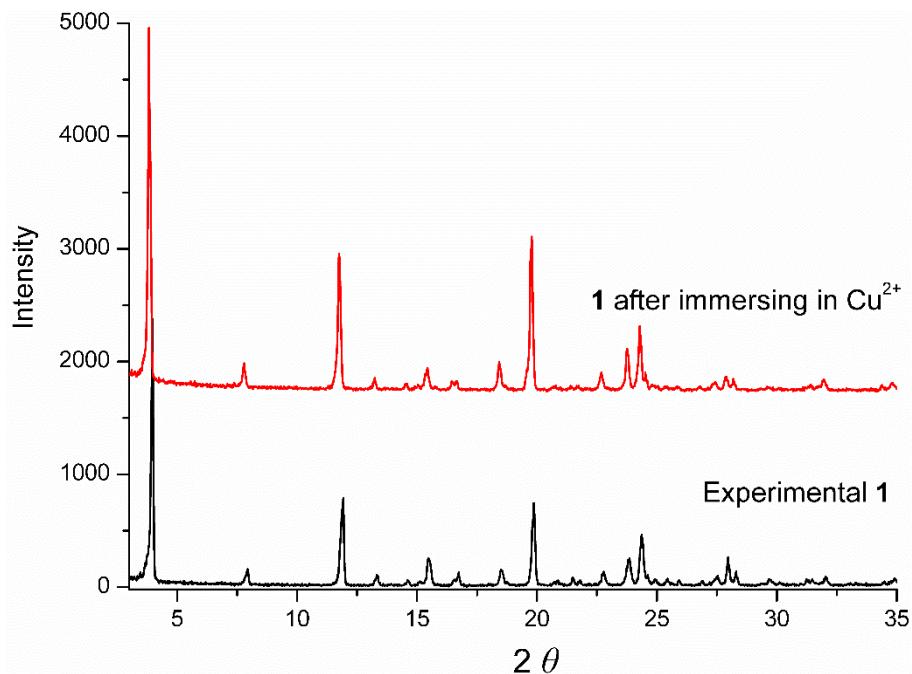
**Figure S15.** The solid state FL spectra of **2** before (black) and after (red) grinding. Inset is a photograph showing color change under pressure at room temperature under a 365 nm UV lamp.



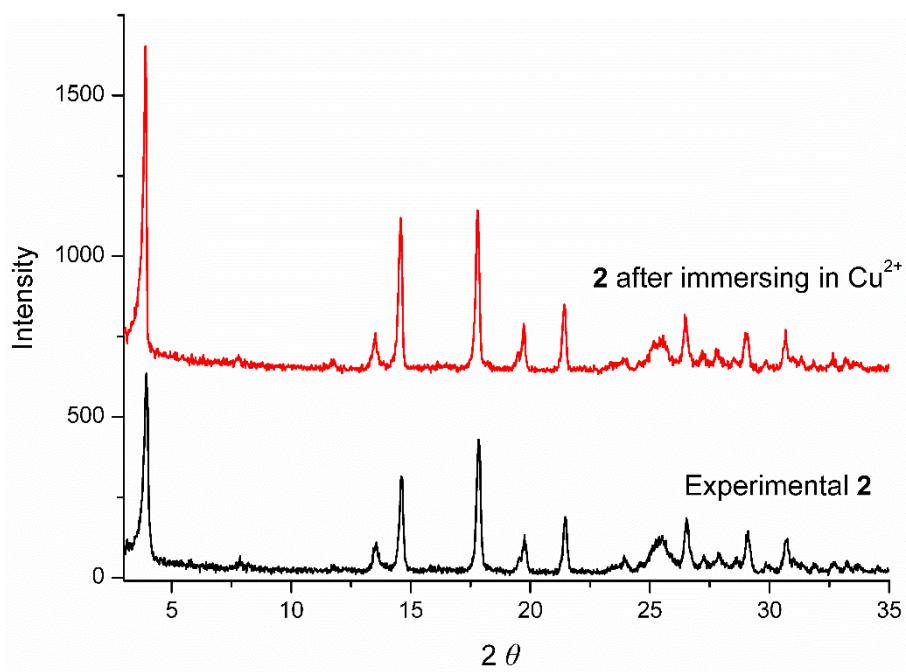
**Figure S16.** The FL spectra of **2** after addition of pH 1 solution within 10 seconds.



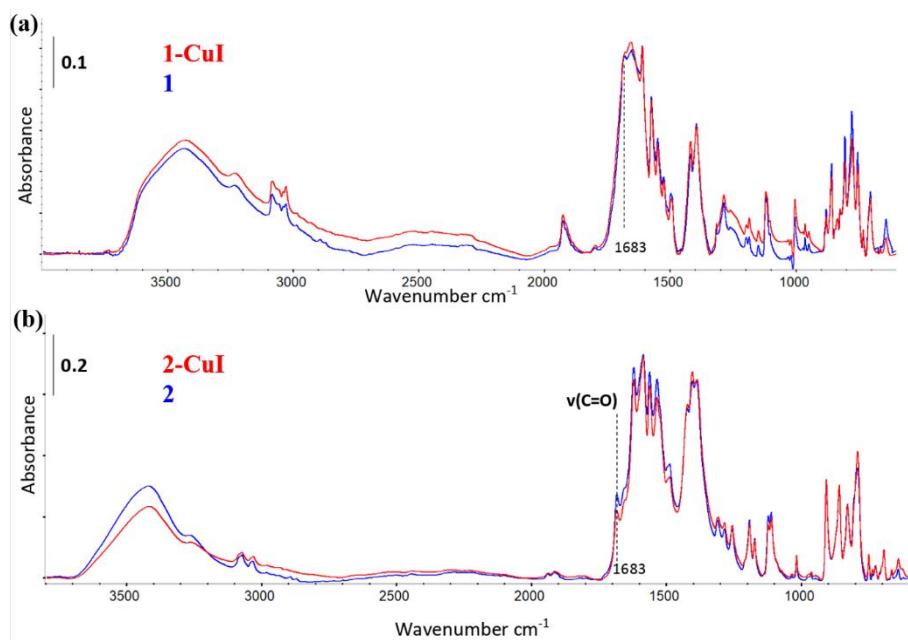
**Figure S17.** The FL spectra of **2** dispersed in different metal ions solutions within 10 seconds.



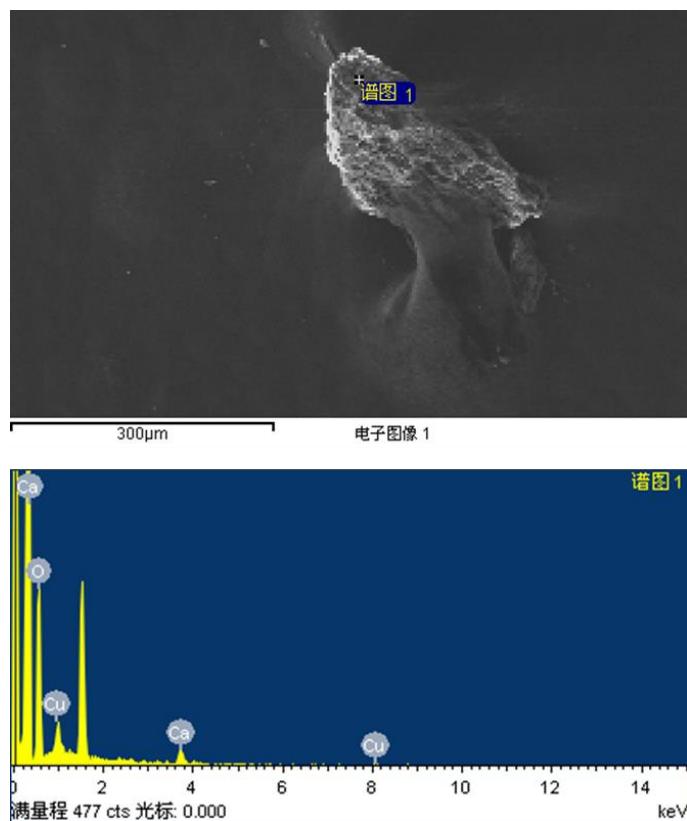
**Figure S18.** The PXRD patterns of **1** before and after exposure to  $10^{-2}$  M Cu<sup>2+</sup> solution for 24 hours.



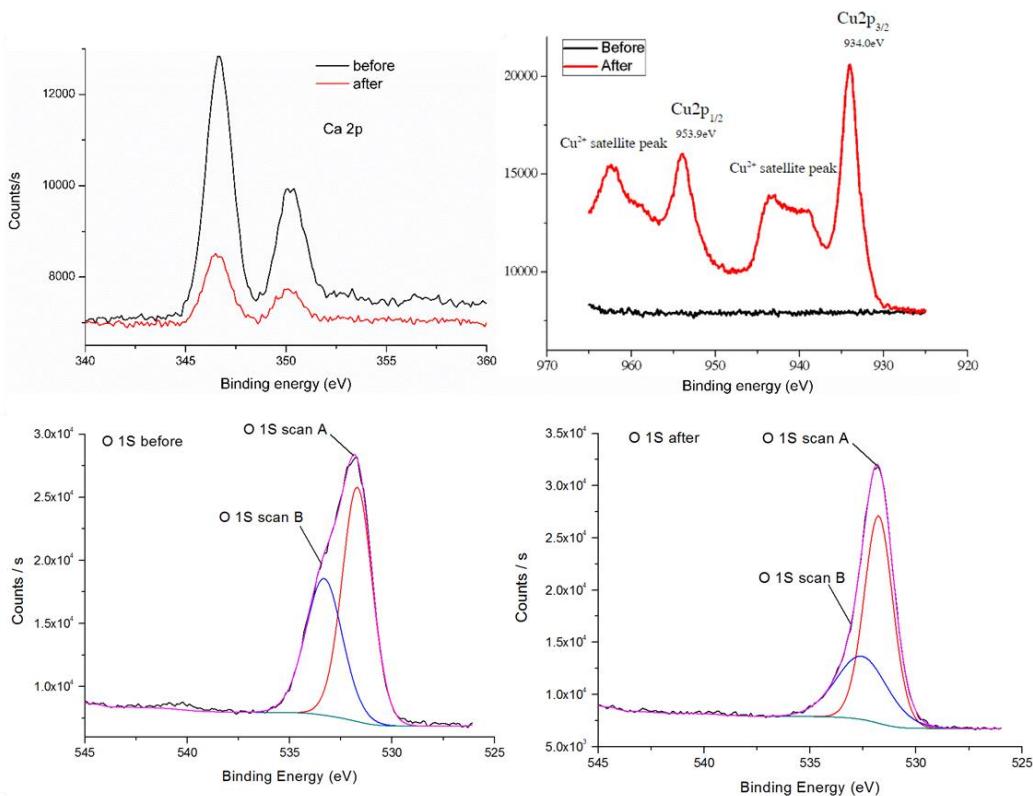
**Figure S19.** The PXRD patterns of **2** before and after exposure to a  $10^{-2}$  M Cu<sup>2+</sup> solution for 24 hours.



**Figure S20.** IR spectra of the title compounds before and after immersing into  $10^{-3}$  (**1**) or  $10^{-4}$  M (**2**)  $\text{Cu}^{2+}$ .



**Figure S21.** The EDS results after exposing **1** to  $10^{-3}$  M  $\text{Cu}^{2+}$  solution for 24 hours.



**Figure S22.** The XPS spectra of **1** before and after exposure to  $10^{-3}$  M  $\text{Cu}^{2+}$  for 24 hours.

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