## *In situ* synthesizing red emissive copper nanoclusters in supramolecular hydrogels

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## **Electronic Supplementary Information (ESI)**

## **Chemicals and characterizations**

All chemicals at AR grade were purchased from Sangon (Shanghai) and Guoyao group (China). Field emission scanning electron microscopy (FESEM) experiments were carried out on HITACHI S–4800 working at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) experiments were performed on HITACHI H-7650 system. High resolution transmission electron microscopy (HRTEM) experiments were carried out on Tecnai F30 (300 KV). For FESEM characterization, samples were prepared by freeze-drying the original hydrogels under vacuum at –80 °C. PL spectra were taken on a Hitachi F–4600 fluorescence spectrophotometer using excitation and emission slits of 5 nm. PL decay curves were measured on an Edinburgh FLS-920-TCSPC system. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Quantum 2000 scanning ESCA microprobe with a minimum X-ray beam size of less than 10  $\mu$ m. Electron paramagnetic resonance (EPR) was measured using a Bruker EMX-10/12 spectrometer. Mass spectrum was measured by a Bruker UltrafleXtreme MALDI TOF/TOF instrument.



**Fig. S1** Photographs of the SDOC- $Cu^{2+}$  (a, 100 mM SDOC and 50 mM  $Cu^{2+}$ ) and SLC- $Cu^{2+}$  (b, 20 mM SLC and 10 mM  $Cu^{2+}$ ) supramolecular hydrogels, respectively.



**Fig. S2** FESEM images of SDOC- $Cu^{2+}$  (a) and SLC- $Cu^{2+}$  (b) supramolecular hydrogels (80 mM SDOC or SLC and 40 mM  $Cu^{2+}$ ), respectively.



**Fig. S3** Photographs of time-dependent change of emission of the SC-Cu<sup>2+</sup> hydrogel in the dark before (blank) and after introducing Cys solution (0–3 h) under a 365 nm hand-held UV lamp, 100  $\mu$ L SC-Cu<sup>2+</sup> supramolecular hydrogel (40 mM Cu<sup>2+</sup> and 80 mM SC), 300  $\mu$ L 200 mM Cys solution was introduced.



**Fig. S4** The effect of the molar ratio of Cys to  $Cu^{2+}$  on the photoluminescence of the resulting Cys-Cu<sup>2+</sup> solution system,  $Cu^{2+}$  concentration was fixed to 40 mM. 20 mM acetate buffer (pH = 3).



Fig. S5 pH effect on the photoluminescence of the resulting Cys-Cu<sup>2+</sup> solution system,  $[Cu^{2+}] = 40 \text{ mM}$  and [Cys] = 600 mM.



**Fig. S6** The effect of the molar ratio of GSH to  $Cu^{2+}$  on the photoluminescence of the resulting GSH- $Cu^{2+}$  solution system,  $Cu^{2+}$  concentration was fixed to 40 mM. 20 mM acetate buffer (pH = 3).

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Fig. S7 MALDI-TOF MS spectrum of Cu-Cys solution.



Fig. S8 EPR spectra of  $Cu(NO_3)_2$  (1) and Cu-Cys (2) solution.



Fig. S9 High-resolution *Cu2p* XPS spectra of Cu(NO<sub>3</sub>)<sub>2</sub> and Cu-Cys dried samples.



Fig. S10 Auger line from XPS spectra of  $Cu(NO_3)_2$  and Cu-Cys dried samples.

	Cu-Cys	Cu(NO <sub>3</sub> ) <sub>2</sub>
<i>Emnn</i> , eV	569.98	571.45
$(E_B)p, eV$	931.64	932.04
<i>α</i> ', eV	1848.26	1847.19

**Table S1:** *Emnn*,  $(E_B)_P$  (Cu(2p3/2)), and  $\alpha$ ' obtained from Fig. S9 and S10<sup>*a*</sup>

a. The modified Auger parameter ( $\alpha$ ') can be obtained from following equations,

 $\alpha' = (E_B)_P + (E_K)_A \tag{1}$ 

 $(E_K)_A = 1486.6 - E_{mnn}$  (2)

in which  $\alpha$ ' is modified Auger parameter;  $(E_B)_P$  and  $(E_K)_A$  are binding energy and kinetic energy, respectively; A and P in the subscript represent Auger and XPS peak, respectively;

*Emnn* is binding energy of the sharpest Auger line.

Thus,  $\alpha' = 1.07$  eV, indicated that the chemical state of Cu in the Cu-Cys system should be +1 or 0 rather than +2.

Table S2: The reported binding energy of Cu(	2p3/2)
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	Binding energy [eV] / Cu(2p3/2)	References
$Cu^0$	932.0	S1a
	932.6	S1c
	932.7-932.8	S1d
$Cu_2O$	932.6	S1c
	932.5-932.8	S1d

**References:** 

S1: (a) B. K. Park, S. Jeong, D. Kim, J. Moon, S. Lim and J. S. Kim, J. Colloid and Interface Science, 2007, 311, 417–424; (b) M. A. Vesaghi, A. Shafiekhani, A. Baghizadeh and M. Lameii, Applied Surface Science, 2008, 255, 2730–2734; (c) P. E. Laibinis and G. M. Whitesides, J. Am. Chem. Soc., 1992, 114, 9022–9028; (d) A. Galtayries and J.-P. Bonnelle, Surf. Interface Anal., 1995, 23, 171–179.



Fig. S11 PL decay curve of Cu-Cys system.



**Fig. S12** Photographs of the resulting hydrogels of SC-Cu<sup>2+</sup>, SDOC-Cu<sup>2+</sup>, and SLC-Cu<sup>2+</sup> after adding Cys.



**Fig. S13** The effect of the molar ratio of Cys to  $Cu^{2+}$  on the photoluminescence of the resulting SC-Cu<sup>2+</sup> hydrogels after adding Cys under 20 mM acetate buffer (pH = 3), Cu<sup>2+</sup> concentration was fixed to 40 mM and the molar ratio of SC to Cu<sup>2+</sup> is 2:1.