## **Electronic Supporting Information**

## for

Optically Active Red-emitting Cu Nanoclusters Originating from Complexation and Redox Reaction between Copper (II) and D/L-Penicillamine

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**Figure S1** The absorption (a) and CD (b) spectra of D-, L- and *Rac*-Pen, inset shows the photographs of D-, L- and *Rac*-Pen solution under daylight.



Figure S2 The FT-IR spectra of D-Pen-CuNCs, D-Pen-Cu Complex, and D-Pen.



**Figure S3** (a) The XPS of Cu 2p electrons for D-Pen-CuNCs and D-Pen-Cu Complex; (b) the corresponding AES spectrum in the Cu LMM region of D-Pen-CuNCs and D-Pen-Cu Complex.



**Figure S4** (a) PL spectra of the resultant D-Pen-CuNCs with the increasing ratio of D-Pen to copper (II); (b) Plots of PL intensity of D-Pen-CuNCs at 625 nm *versus* the ration of D-Pen to copper (II); (c) PL spectra of the resultant D-Pen-CuNCs with the prolonging reaction time at a fixed concentration of D-Pen and copper (II); (d) Plots of PL intensity of D-Pen-CuNCs at 625 nm *versus* the reaction time.



**Figure S5** Comparison of PL spectra between the resultant complexes with the different ratios of D-Pen to excessive copper (II) and the resultant D-Pen-CuNCs with a fixed 5:1 ratio of D-Pen to copper (II). The inset displays the photographs of the corresponding complexes (1-5) and CuNCs (6) under the irradiation of visible and 365 nm UV light.



**Figure S6** Comparison of PL spectra between D-Pen-CuNCs and D-Pen-Cu Complex. The insets display the photographs of the corresponding CuNCs and Cu complex solution under the irradiation of visible and 365 nm UV light.



**Figure S7** The PL spectra of the aggregated and dispersed D-Pen-CuNCs (a) and L-Pen-CuNCs (b); the inset displays the photographs of the corresponding aggregated and dispersed CuNCs under the irradiation of visible and UV light.



**Figure S8** TEM images of the aggregated L-Pen-CuNCs on the reaction condition (a) and the dispersed species by adjusting pH to alkaline environment (b).



Figure S9 Cellular toxicity of D-Pen- and L-Pen-CuNCs on Hep-2 cell viability.

	$CuCl_2$ ( $\lambda ex 372 \text{ nm}$ )	Cu(NO <sub>3</sub> ) <sub>2</sub> (λex 345 nm)	CuSO <sub>4</sub> (\lambda ex 372 nm)
а	18.6%	21.4%	12.5%
b	42.8%	50.6%	42.3%

**Table S1** The absolute PL QYs of *D*-Pen-CuNCs

*a* Concentration: Cu (II) precursors, 1.0 mM; *D*-Pen, 10 mM; *b* Cu (II) precursors, 3.0 mM; *D*-Pen, 15 mM. The mixture was reacted for 2 h. The isolation and purification of the resultant CuNCs were performed through repeated centrifugation and washing steps, and then the products were used for the measurements of the PL QYs.