

### Electronic Supplementary Information

#### An anthraquinone-based highly selective colorimetric and fluorometric sensor for sequential detection of Cu<sup>2+</sup> and S<sup>2-</sup> with intracellular application

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#### Supplementary figures

**Fig. S1** <sup>1</sup>H NMR spectrum of compound **L**.

**Fig. S2** <sup>13</sup>C NMR spectrum of compound **L**.

**Fig. S3** ESI-mass spectrum of compound **L**.

**Fig. S4** The absorption at 628nm of **L** as a function of time after adding Cu<sup>2+</sup>. [**L**] = 2×10<sup>-5</sup> M, [Cu<sup>2+</sup>]=1×10<sup>-4</sup> M.

**Fig. S5** Nanosecond fluorescence lifetime decay profiles of **L** upon the addition of Cu<sup>2+</sup> ion. THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl), [**L**]=8×10<sup>-6</sup> M, [Cu<sup>2+</sup>]= 8×10<sup>-6</sup> M.

**Fig. S6** (a) Effect of different metal ions on fluorescence spectra of **L** in THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl), [**L**]=8×10<sup>-6</sup> M, [M<sup>n+</sup>]= 1.6×10<sup>-5</sup> M; (b) metal-ion responses for **L** (8 μM) in the absence and presence of metal ions in THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl), [Cu<sup>2+</sup>]=1.6×10<sup>-5</sup> M, [M<sup>n+</sup>]= 1.6×10<sup>-5</sup> M; (c) The influence with higher concentration of K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> ions on fluorescence spectra of **L** and **L**+Cu<sup>2+</sup>, [**L**]=8.0×10<sup>-6</sup> M, [Cu<sup>2+</sup>]=1.6×10<sup>-5</sup> M, [M<sup>n+</sup>]= 1.0×10<sup>-2</sup> M; (d) The influence with higher concentration of K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> ions on UV-vis spectra of **L** and **L**+Cu<sup>2+</sup>, [**L**]=2.0×10<sup>-5</sup> M, [Cu<sup>2+</sup>]=4.0×10<sup>-5</sup> M, [M<sup>n+</sup>]= 1.0×10<sup>-2</sup> M.

**Fig. S7** (a) Effect of pH on fluorescence at 604 nm of **L** and **L**-Cu<sup>2+</sup> ensemble in THF/H<sub>2</sub>O (1:1, v/v), [**L**] = 8×10<sup>-6</sup> M, [Cu<sup>2+</sup>]=4×10<sup>-5</sup> M; (b)Effect of pH on absorbance at 628 nm of **L** and **L**-Cu<sup>2+</sup> ensemble in THF/H<sub>2</sub>O (1:1, v/v), [**L**] = 2×10<sup>-5</sup> M, [Cu<sup>2+</sup>]=1×10<sup>-4</sup> M.

**Fig. S8** The stability of **L** and **L**+Cu<sup>2+</sup> in THF:H<sub>2</sub>O=1:1 (v/v), pH=7.4 (tris-HCl).

**Fig. S9** (a) Job's plot from fluorescence emission for **L** and Cu<sup>2+</sup> complexation in THF:H<sub>2</sub>O=1:1 (v/v), pH=7.4 (tris-HCl). The total concentration of **L** and Cu<sup>2+</sup> is 2×10<sup>-5</sup> M; (b) Benesi-Hildebrand plot from fluorescence titration data of **L** with Cu<sup>2+</sup>.

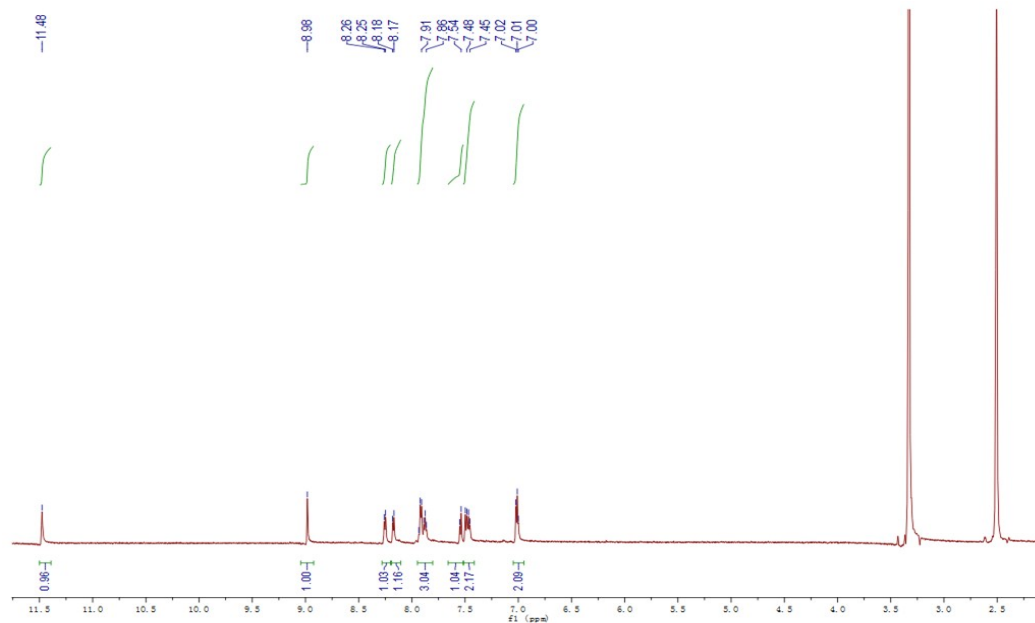
**Fig. S10** (a) Anion fluorescence responses for **L**-Cu<sup>2+</sup> in the absence and presence of anions in THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl), [**L**]=[Cu<sup>2+</sup>]=8×10<sup>-6</sup> M, [anion]= 6.4×10<sup>-5</sup> M; (b) Anion UV-vis responses for **L**-Cu<sup>2+</sup> in the absence and presence of anions (top) and their corresponding colorimetric responses (bottom). THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl) [**L**]=[Cu<sup>2+</sup>]=2×10<sup>-5</sup> M, [anion]= 1.6×10<sup>-4</sup> M.

**Fig. S11** The kinetic study of the response of **L**-Cu<sup>2+</sup> to S<sup>2-</sup> (6 equiv) under pseudo-first-order conditions. [**L**] = [Cu<sup>2+</sup>] = 2×10<sup>-5</sup> M, [S<sup>2-</sup>]=1.2×10<sup>-4</sup> M.

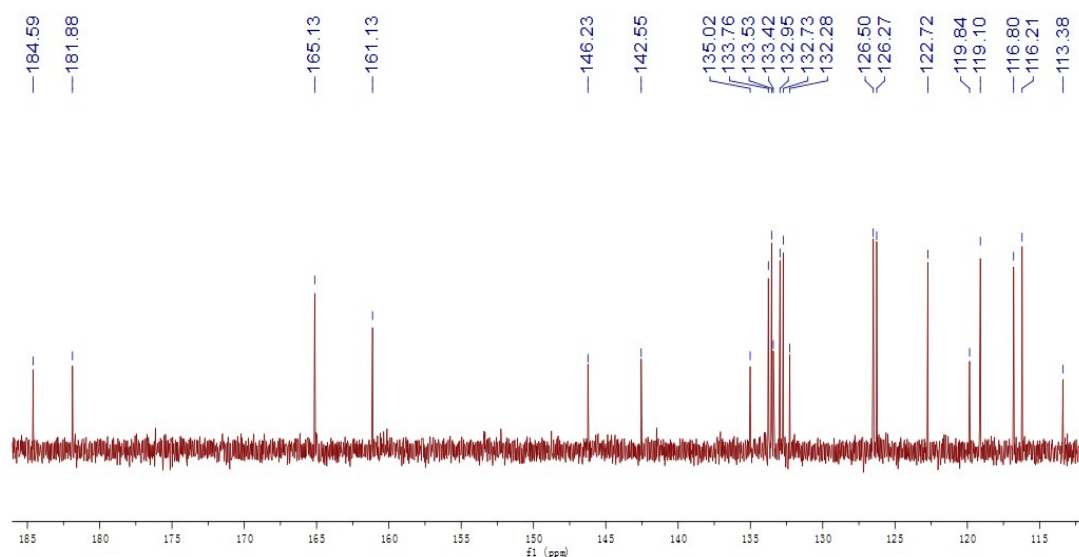
**Fig. S12** Absorbance changes of **L** at 628nm upon alternate addition of Cu<sup>2+</sup> and S<sup>2-</sup>. THF:H<sub>2</sub>O=1:1 (v/v), pH=7.4 (tris-HCl), [**L**] =2×10<sup>-5</sup> M.

**Fig. S13** Photographs of test strips of **L-Cu<sup>2+</sup>** at various concentrations of **S<sup>2-</sup>**: (from left to right, 0 mol/L,  $0.8 \times 10^{-3}$  mol/L,  $1.6 \times 10^{-3}$  mol/L,  $2.4 \times 10^{-3}$  mol/L,  $3.2 \times 10^{-3}$  mol/L)

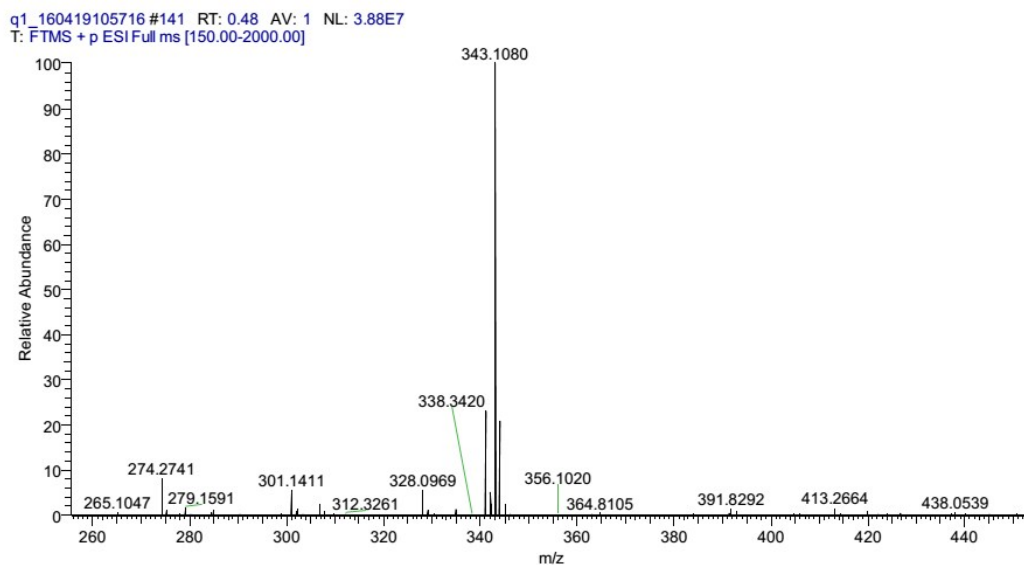
**Fig. S14** Cell cytotoxic effect of **L**, **Cu<sup>2+</sup>**, **S<sup>2-</sup>**, **CuS** on SMMC-7721 cells.



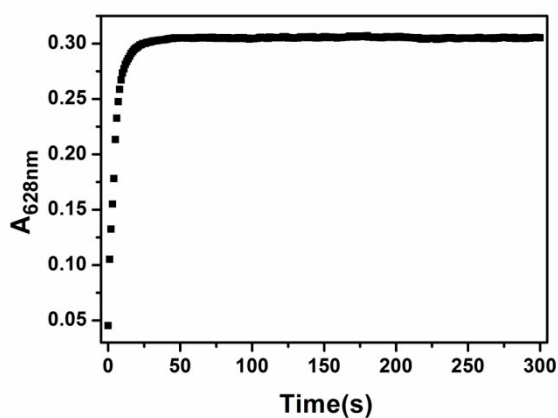
**Fig. S1** <sup>1</sup>H NMR spectrum of compound **L**.



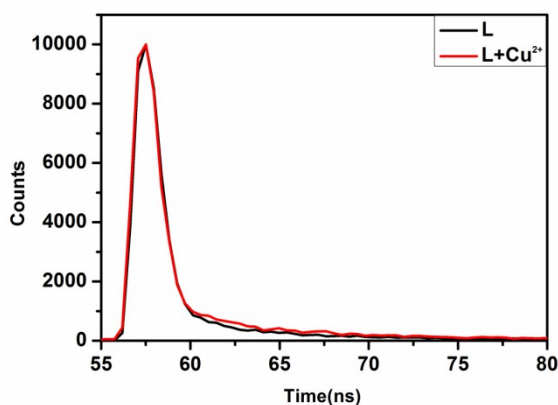
**Fig. S2** <sup>13</sup>C NMR spectrum of compound **L**.



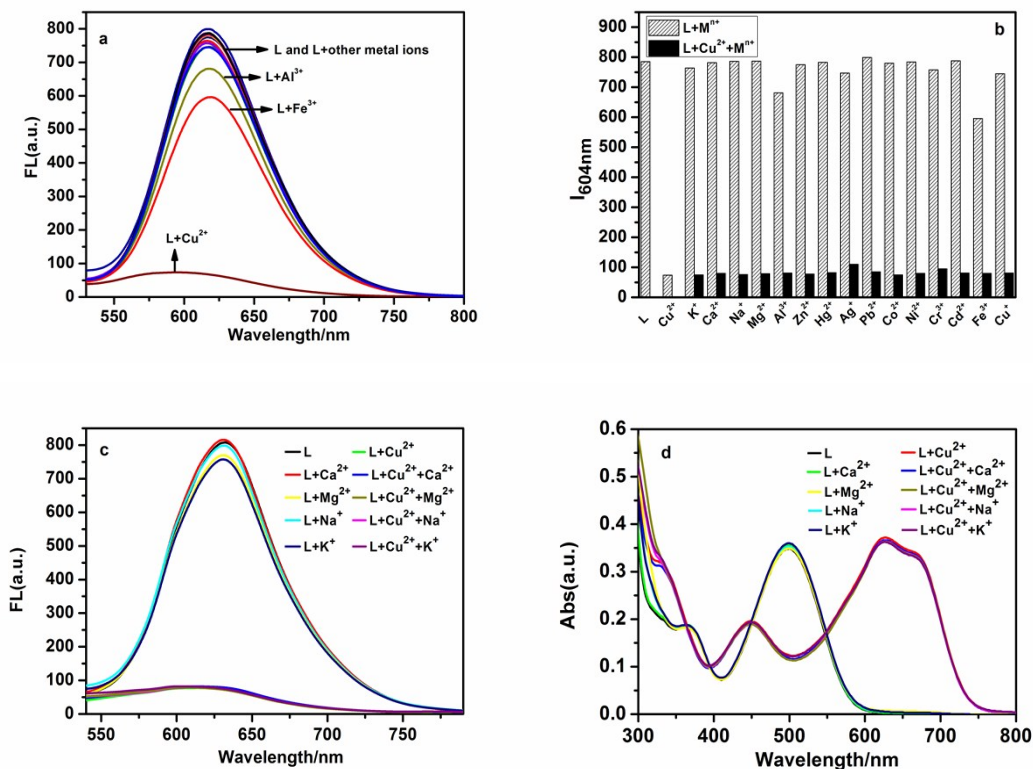
**Fig. S3** ESI-mass spectrum of compound **L**.



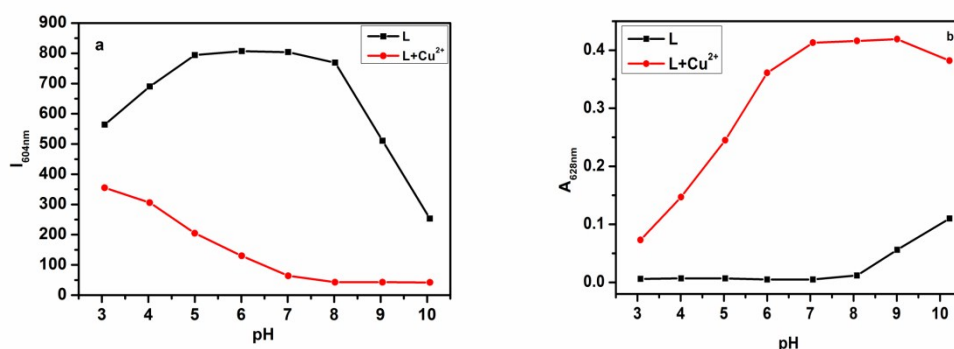
**Fig. S4** The absorption at 628nm of **L** as a function of time after adding  $\text{Cu}^{2+}$ .  $[\text{L}] = 2 \times 10^{-5} \text{ M}$ ,  $[\text{Cu}^{2+}] = 1 \times 10^{-4} \text{ M}$ .



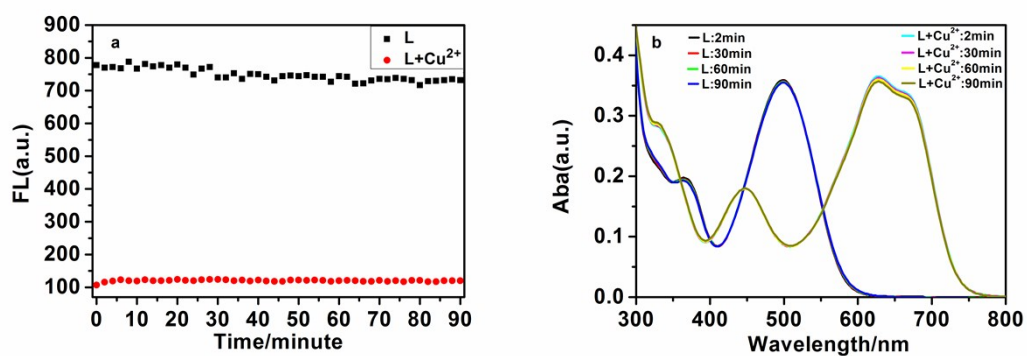
**Fig. S5** Nanosecond fluorescence lifetime decay profiles of **L** upon the addition of  $\text{Cu}^{2+}$  ion. THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl),  $[\text{L}] = 8 \times 10^{-6} \text{ M}$ ,  $[\text{Cu}^{2+}] = 8 \times 10^{-6} \text{ M}$ .



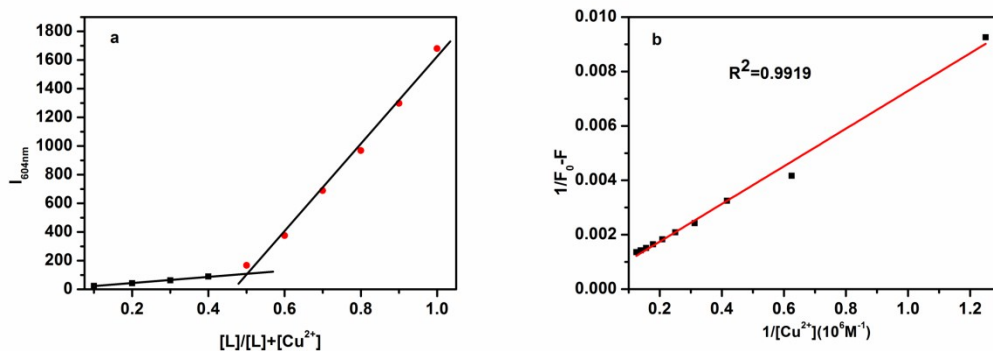
**Fig. S6** (a) Effect of different metal ions on fluorescence spectra of **L** in THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl), [**L**]= $8.0 \times 10^{-6}$  M, [ $M^{n+}$ ]=  $1.6 \times 10^{-5}$  M; (b) metal-ion responses for **L** (8  $\mu$ M) in the absence and presence of metal ions in THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl), [ $Cu^{2+}$ ]= $1.6 \times 10^{-5}$  M, [ $M^{n+}$ ]=  $1.6 \times 10^{-5}$  M; (c) The influence with higher concentration of K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> ions on fluorescence spectra of **L** and **L**+Cu<sup>2+</sup>, [**L**]= $8.0 \times 10^{-6}$  M, [ $Cu^{2+}$ ]= $1.6 \times 10^{-5}$  M, [ $M^{n+}$ ]=  $1.0 \times 10^{-2}$  M; (d) The influence with higher concentration of K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> ions on UV-vis spectra of **L** and **L**+Cu<sup>2+</sup>, [**L**]= $2.0 \times 10^{-5}$  M, [ $Cu^{2+}$ ]= $4.0 \times 10^{-5}$  M, [ $M^{n+}$ ]=  $1.0 \times 10^{-2}$  M.



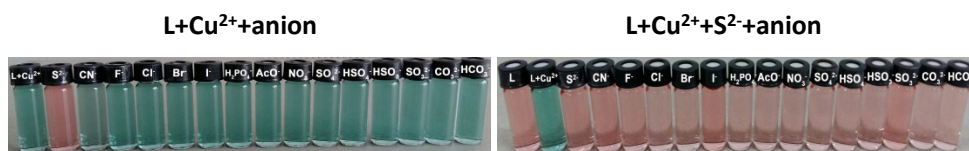
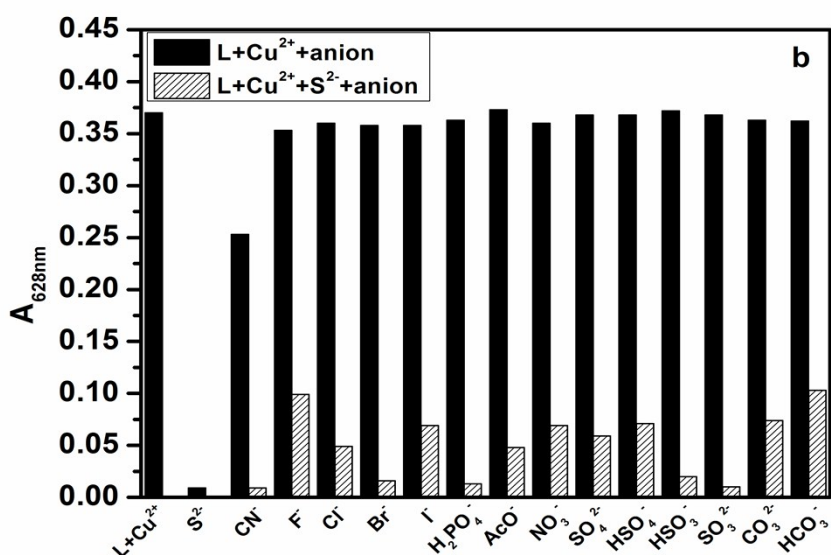
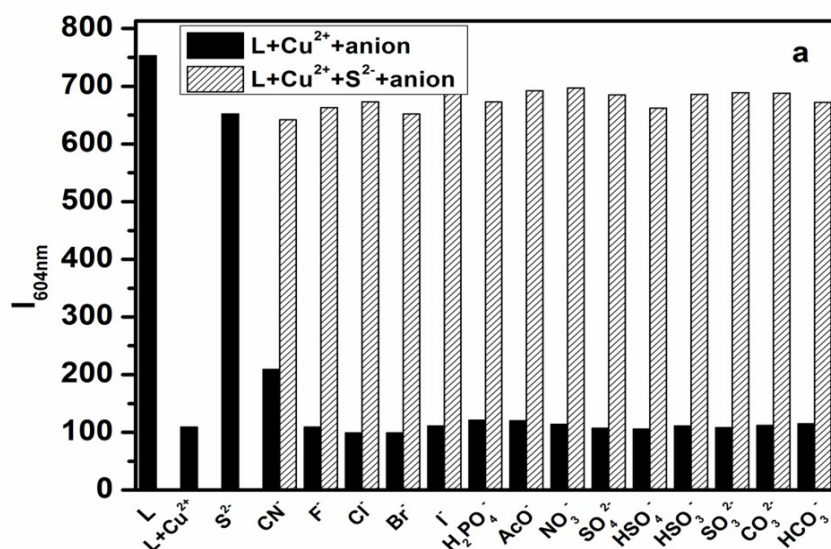
**Fig. S7** (a) Effect of pH on fluorescence at 604 nm of **L** and **L**-Cu<sup>2+</sup> ensemble in THF/H<sub>2</sub>O (1:1, v/v), [**L**] =  $8 \times 10^{-6}$  M, [ $Cu^{2+}$ ]= $4 \times 10^{-5}$  M; (b) Effect of pH on absorbance at 628 nm of **L** and **L**-Cu<sup>2+</sup> ensemble in THF/H<sub>2</sub>O (1:1, v/v), [**L**] =  $2 \times 10^{-5}$  M, [ $Cu^{2+}$ ]= $1 \times 10^{-4}$  M.



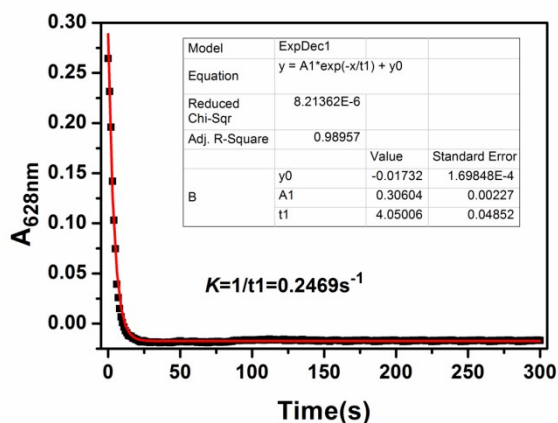
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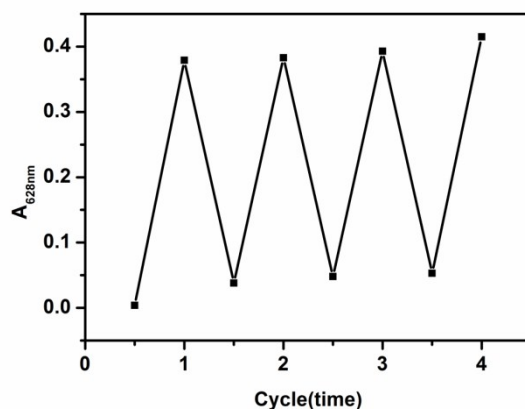
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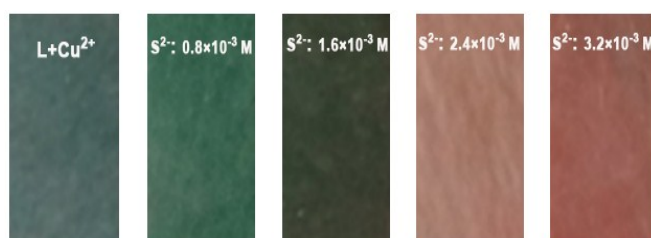
**Fig. S10**(a) Anion fluorescence responses for  $L-Cu^{2+}$  in the absence and presence of anions in THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl),  $[L]=[Cu^{2+}]=8\times 10^{-6}$  M,  $[anion]=6.4\times 10^{-5}$  M; (b) Anion UV-vis responses for  $L-Cu^{2+}$  in the absence and presence of anions (top) and their corresponding colorimetric responses (bottom). THF:H<sub>2</sub>O=1:1(v/v), pH=7.4 (tris-HCl)  $[L]=[Cu^{2+}]=2\times 10^{-5}$  M,  $[anion]=1.6\times 10^{-4}$  M.



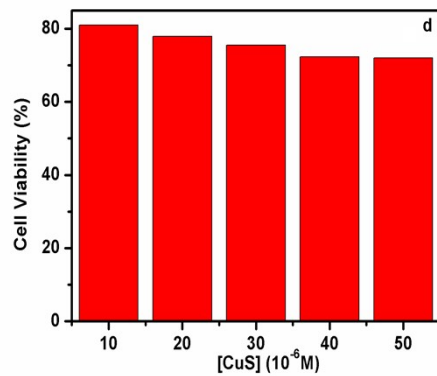
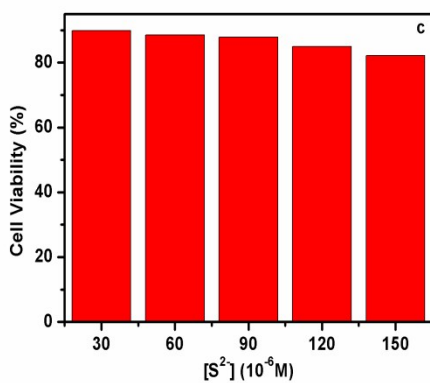
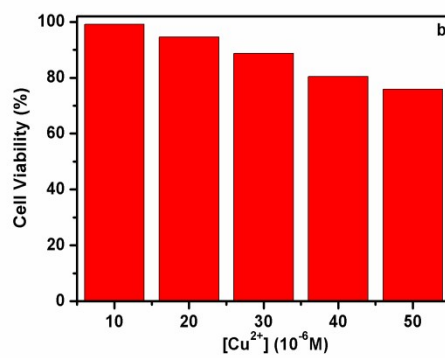
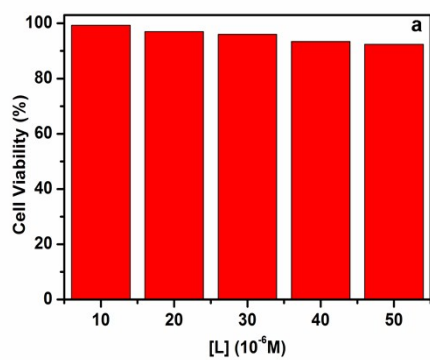
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**Fig. S12** Absorbance changes of **L** at 628nm upon alternate addition of **Cu<sup>2+</sup>** and **S<sup>2-</sup>**. THF:H<sub>2</sub>O=1:1 (v/v), pH=7.4 (tris-HCl),  $[L] = 2 \times 10^{-5} M$ .



**Fig. S13** Photographs of test strips of **L-Cu<sup>2+</sup>** at various concentrations of **S<sup>2-</sup>**: (from left to right, 0 mol/L,  $0.8 \times 10^{-3} \text{ mol/L}$ ,  $1.6 \times 10^{-3} \text{ mol/L}$ ,  $2.4 \times 10^{-3} \text{ mol/L}$ ,  $3.2 \times 10^{-3} \text{ mol/L}$ )



**Fig. S14** Cell cytotoxic effect of L,  $\text{Cu}^{2+}$ ,  $\text{S}^{2-}$ , CuS on SMMC-7721 cells.