

## Supplementary Material

### **A unique bifunctional probe for detecting silicate anion and cupric cation: the modified silica nanoparticles and coordination**

Mingdi Yang,<sup>‡ab</sup> Tingting Yu,<sup>‡a</sup> Hongping Zhou,<sup>\*a</sup> Mingzai Wu,<sup>\*a</sup> Xiaojiao Zhu,<sup>a</sup> Xuanjun Zhang,<sup>c</sup> Kong Lin,<sup>a</sup> Weiju Zhu,<sup>a</sup> Zhichao Wu,<sup>a</sup> Yupeng Tian<sup>a</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, School of Physics and Materials Science, Anhui University and Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Hefei, 230601, P. R. China.

<sup>b</sup> School of Materials and Chemical Engineering, Anhui Jianzhu University, Hefei 230601, P. R. China.

<sup>c</sup> Faculty of Health Sciences, University of Macau, Macau, P. R. China.

<sup>‡</sup> These authors contributed equally to this work and should be considered co-first authors.

<sup>\*</sup> Corresponding author.

*E-mail addresses:* zhpzhp@263.net; mingzaiwu@gmail.com

## Contents

- 1. Instruments, synthesis procedures and chemical characterizations.**
- 2. Influence of cations on the fluorescence spectra of L with SiO<sub>3</sub><sup>2-</sup>.**
- 3. Fluorescence titration experiments of L with SiO<sub>3</sub><sup>2-</sup>.**
- 4. TEM images and elemental analysis of NPs.**
- 5. Chemical modification of silica surface in L and SiO<sub>3</sub><sup>2-</sup>-mixture.**
- 6. Detection limits and binding constant analyses of L with Cu<sup>2+</sup>.**
- 7. The cytotoxicity of L on HeLa cells by MTT assay.**

## **Instruments**

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE-400 MHz and 100 MHz instrument with dimethyl sulfoxide- $d_6$  as solvent and tetramethylsilane (TMS,  $\delta = 0$  ppm) as internal standard. FT-IR spectra were taken by a Nicolet FT-IR NEXUS 870 spectrometer (KBr discs) in the 4000-400  $\text{cm}^{-1}$  region. Mass spectra were recorded on an auto flex speed MALDI-TOF mass spectrometer. UV-vis and photoluminescence spectra were recorded using a UV-265 spectrophotometer and a Hitachi F-7000 fluorescence spectrophotometer, respectively. SEM images were obtained using a Hitachi S-4800 scanning electron microscope. HRTEM images were obtained using a JEM-2100F electron microscope. DLS measurements were conducted on a Delsa PNA54412AB Nano Submicron Grain Particle Size Analyzer. Powder X-ray diffraction experiments were operated on a Bruker D8 Advance powder X-ray diffractometer with Cu  $K\alpha$  radiation and a Lyne Eye detector, and fluorescence microscopy was visualized using Olympus confocal laser scanning microscope (model FV1000, Tokyo, Japan).

## **General synthesis of probe L**

Intermediate **M** was prepared according to previous methods, then reacted with 4-(diethylamino)salicylaldehyde to afford probe **L**. The detailed steps is as follows: a 0.20 g (0.529 mmol) **M** and 20 mL ethanol were added into a round-bottom flask equipped with a magnetic stirrer at room temperature, and 0.153 g (0.794 mmol) of 4-(diethylamino)salicylaldehyde was added dropwise. The reaction mixture was monitored by thin-layer chromatography (TLC). After the completion of the reaction,

the reaction mixture was filtered and recrystallized with ethanol to produce 0.24 g solid. Yield: 82.1%.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ),  $\delta$  (ppm): 14.20 (s, 1H), 9.68 (s, 1H), 8.67 (s, 1H), 7.51 ( $J = 8$ , d, 2H), 7.34-7.32 (t, 5H), 7.26 ( $J = 8$ , d, 1H), 7.03-7.08 (m, 10H), 6.95 ( $J = 8$ , d, 2H), 6.28 ( $J = 12$ , d, 1H), 5.98 (s, 1H), 3.41-3.3 (m, 4H), 1.14-1.11 ( $J = 4$ , t, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ),  $\delta$  (ppm): 165.79, 157.69, 151.63, 150.05, 146.94, 146.23, 135.37, 133.84, 131.43, 129.37, 127.57, 126.992, 126.67, 124.06, 123.20, 123.03, 118.58, 118.15, 113.60, 108.95, 103.73, 97.21, 43.49, 12.47. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3426.01 (w), 2970.90 (m), 1592.71 (s), 1491.99 (s), 1416.27 (m), 1339.79 (s), 1276.94 (s), 1233.02 (s), 1137.60 (s), 1074.75 (s), 967.22 (s), 815.77 (s), 752.16 (s), 695.37 (s). MS (ESI): calcd for  $[\text{M}+\text{H}]^+$ : 554.2729; found, 554.2810.

**Fig. S1**  $^1\text{H}$  NMR spectrum of **L**

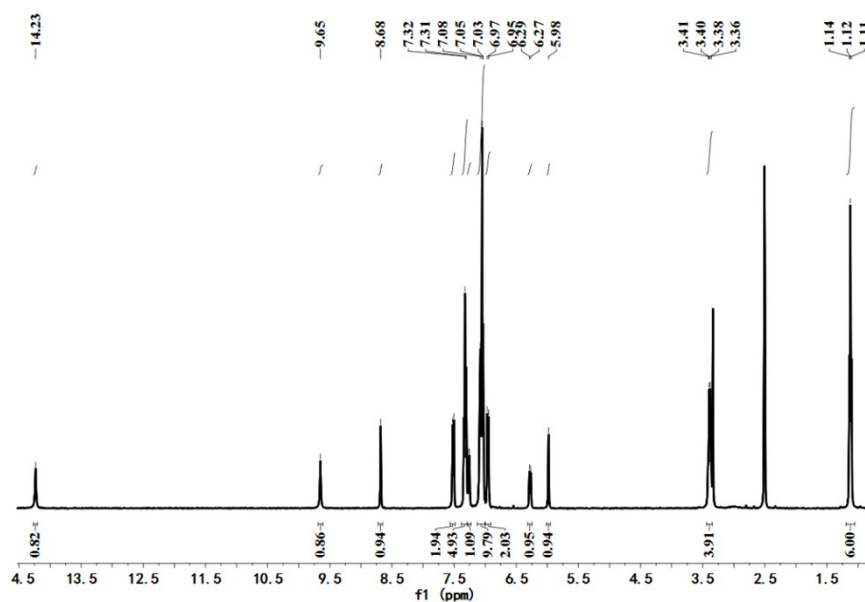


Fig. S2  $^{13}\text{C}$  NMR spectrum of L

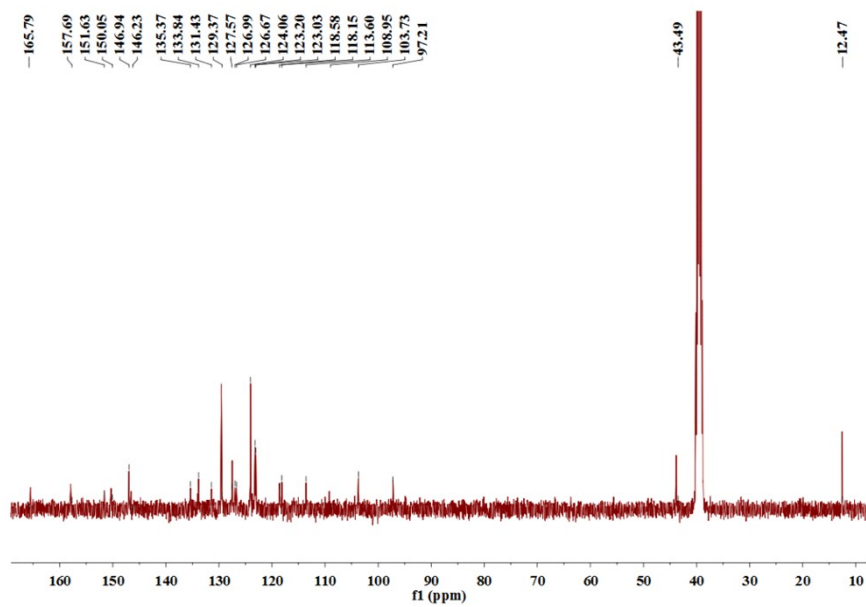
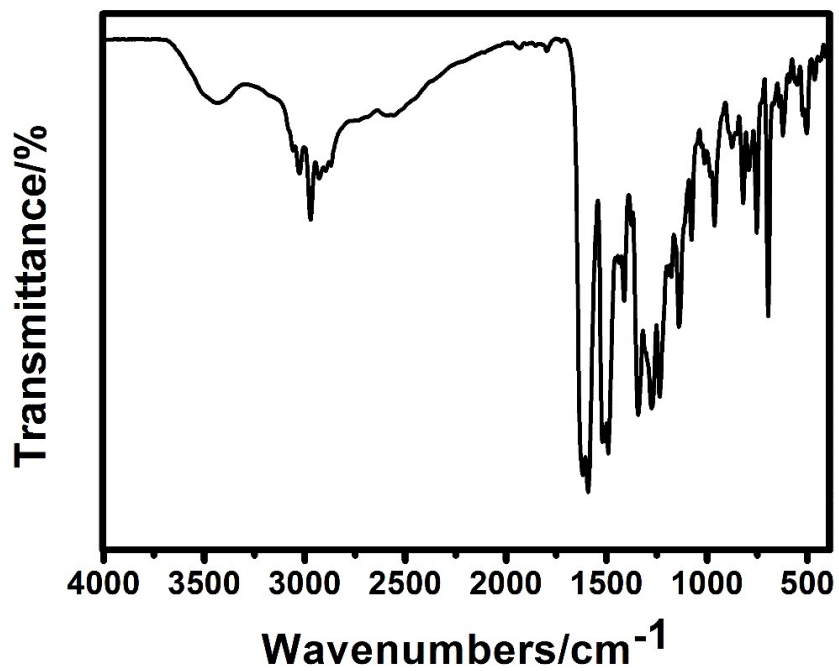
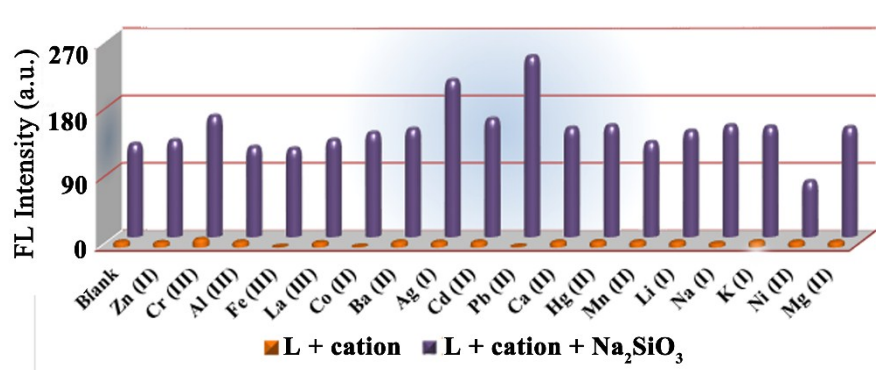
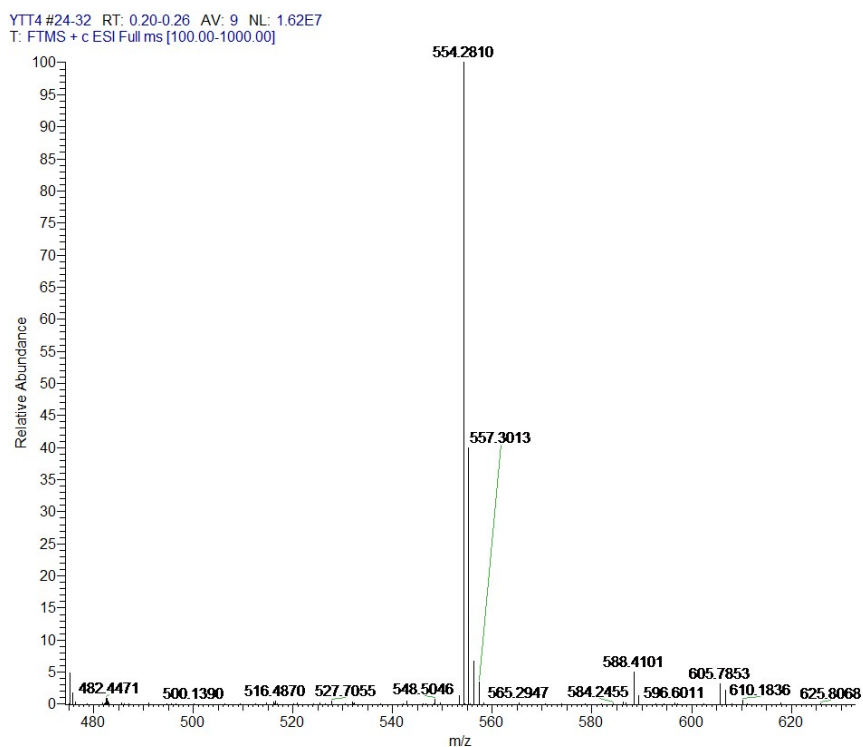


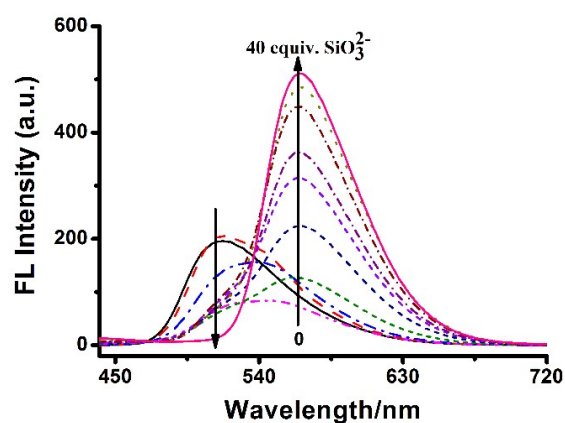
Fig. S3 IR spectrum of L



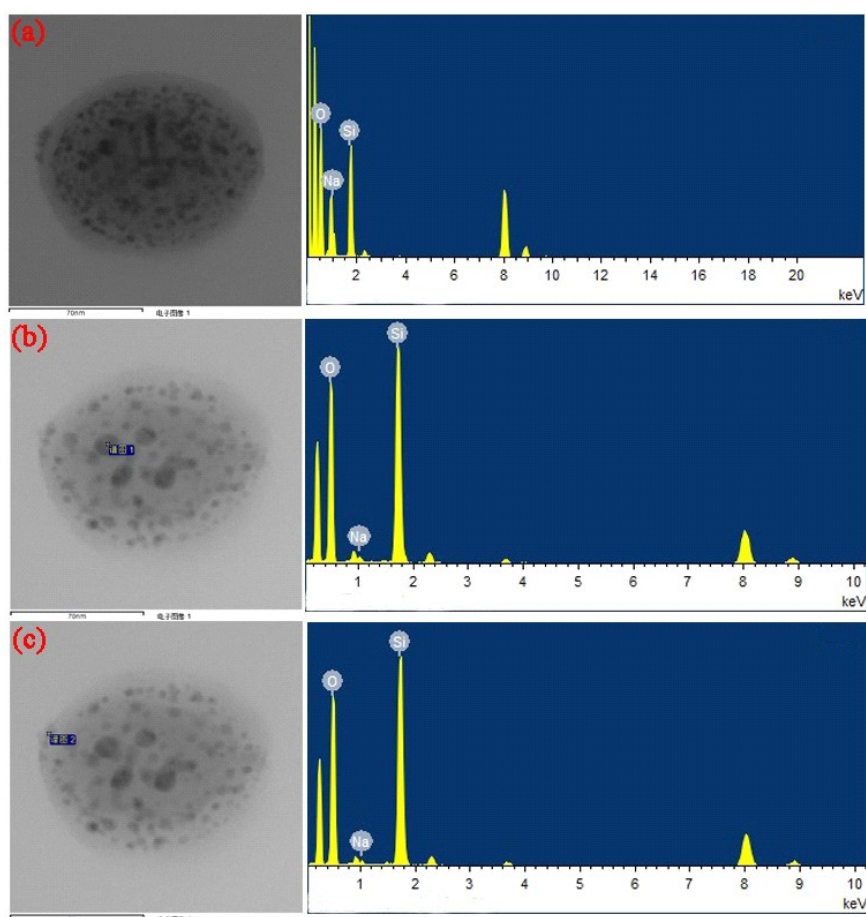
**Fig. S4** MS spectrum of L



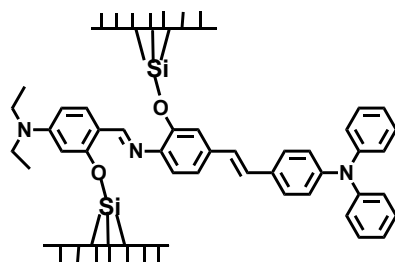
**Fig. S5** The fluorescence response (583 nm) of probe L (10 μM) upon addition of various cations (1 equiv.) in and without the presence of SiO<sub>3</sub><sup>2-</sup> (20 equiv.).



**Fig. S6** Fluorescence titration curves of probe **L** in acetonitrile solution (20  $\mu\text{M}$ ) upon addition of  $\text{SiO}_3^{2-}$  from 0 equiv. to 40 equiv.



**Fig. S7** TEM images and elemental analysis (by EDS) of the nanoparticle. (a) Elemental analysis of the whole particle; (b, c) elemental analysis of the extremely small particles in different location.



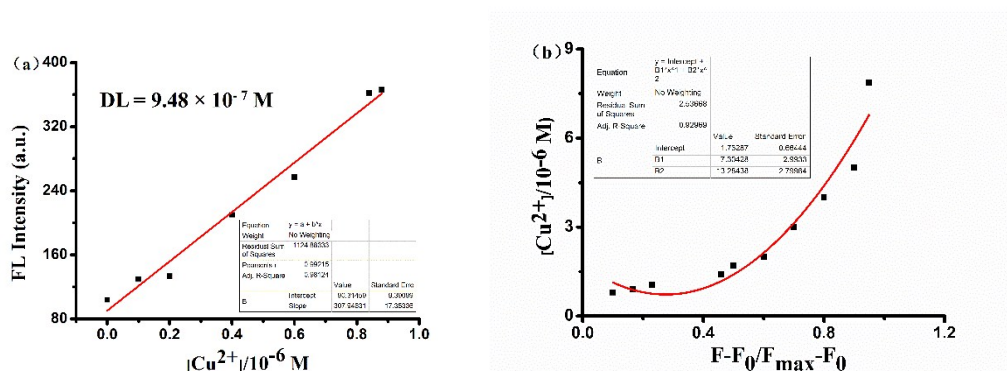
**Scheme S2** Chemical modification of silica surface in **L** and  $\text{SiO}_3^{2-}$ -mixture.

## Calculation method of association constant

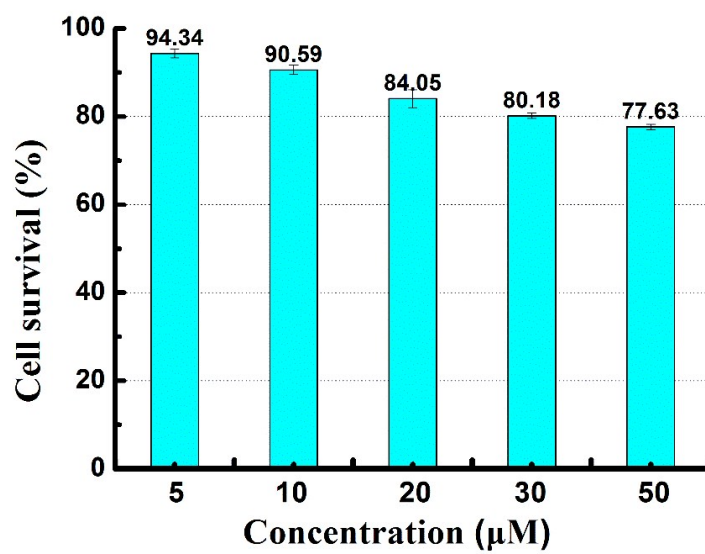
Assuming a 2:1 complex formation, the association constant was calculated on the basis of the titration curves of the sensor **L** with  $\text{Cu}^{2+}$ . Association constants were determined by a linear least square fitting of data with the following equation as a referenced method.

$$[\text{Cu}^{2+}] = 1/2K_a[\text{L}]_0 \cdot x/(1-x^2) + [\text{L}]_0/2 \cdot x$$

Where  $K_a$  is complex association constant;  $[\text{Cu}^{2+}]$  is the concentration of  $\text{Cu}^{2+}$ ;  $[\text{L}]_0$  is the initial concentration of sample;  $x = (F - F_0)/(F_{\text{max}} - F_0)$ ;  $F$ ,  $F_0$  and  $F_{\text{max}}$  is the fluorescence intensity at 463 nm, free ligand and the fluorescence intensity at 463 nm upon the addition of  $\text{Cu}^{2+}$ .



**Fig. S8** (a) Normalized response of fluorescence signal of **L** in the presence of different concentrations of  $\text{Cu}^{2+}$ ; (b) FL intensity ratio  $(F - F_0 / F_{\text{max}} - F_0)$  as the concentration of  $\text{Cu}^{2+}$ .



**Fig. S9** MTT assay of HeLa cells treated with probe L at different concentrations for 24 h.