Electronic Supplementary Information (ESI)

A Single Gold Nanorod as a Plasmon Resonance Energy Transfer Based Nanosenor for High-Sensitivity Cu(II) Detection

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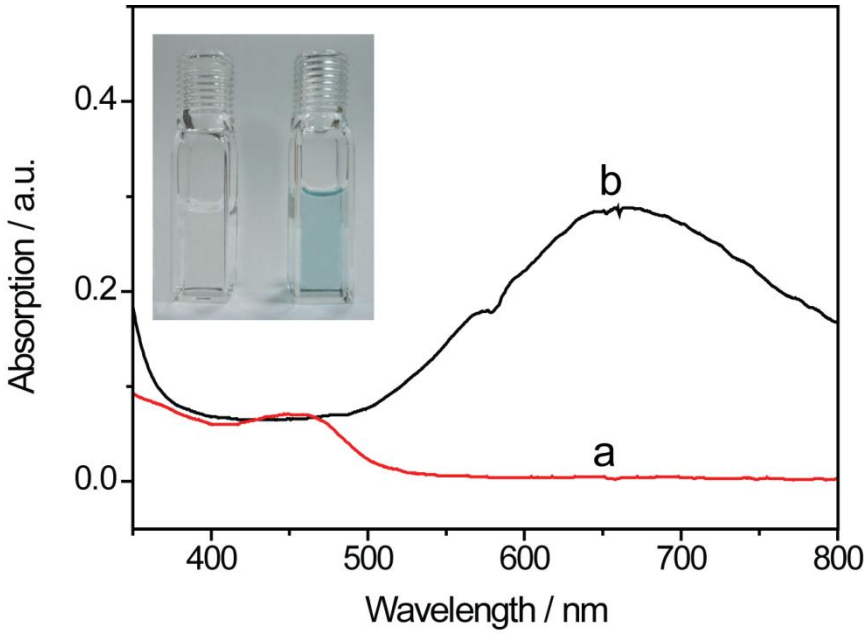


Figure S1. Absorption of TDPA before (a) and after (b) the complexation of Cu^{2+}. The inset is the image of TDPA before (transparent colour) and after (blue colour) the addition of Cu^{2+}.

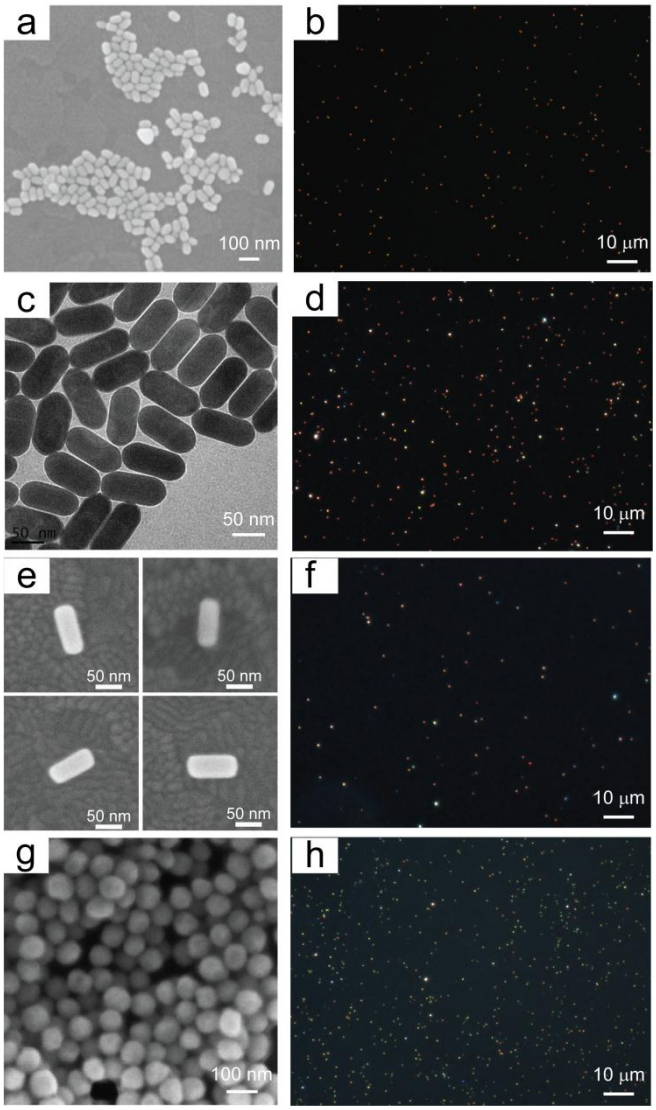


Figure S2. SEM images of 40 nm × 68 nm (a), 40 nm × 96 nm (e) gold nanorods, 80 nm nanospheres (g) and TEM image of 40 nm × 84 nm (c) nanorods, and dark-field images of 40 nm × 68 nm (b), 40 nm × 84 nm (d), 40 nm × 96 nm (f) gold nanorods and 80 nm nanospheres (h). Nanorods in SEM images (e) are samples for dark-filed observation for the low particle density.

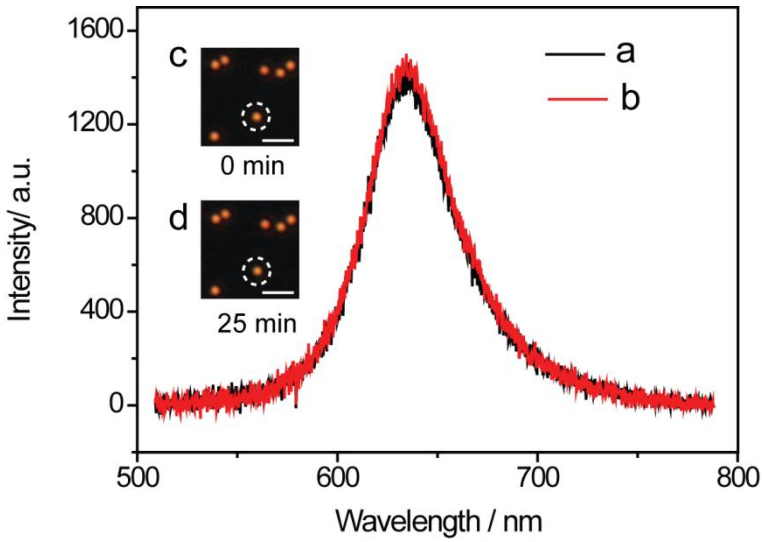
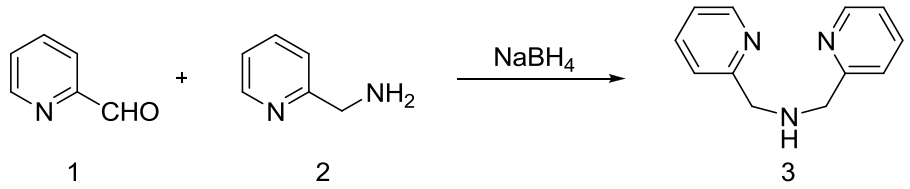


Figure S3. (a-b) Scattering spectra of single bare gold nanorod before (a) and after (b) the addition of 1mM Cu^{2+}. (c-d) Corresponding dark-field images of single bare gold nanorods before (c) and after (d) the addition of 1mM Cu^{2+}. The scale bars in c and d are 5μm.

Synthesis procedure of TDPA.

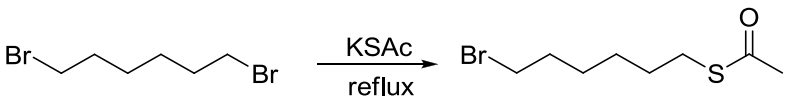
Synthesis of bis(2-pyridylmethyl)amine (DPA) 3



1 2 3

2-pyridinecarbaldehyde (2.51 g, 23.5 mmol) was dissolved in 50 mL methanol, and pyridin-2-ylmethanamine (2.54 g, 23.5 mmol) was added dropwise under ice-bath condition. The mixture was stirred for 1 h at room temperature. After that, $NaBH_4$ (0.89 g, 23.5 mmol) was added in portions at 0 ℃. The solution was stirred overnight, quenched with the addition of HCl, cooled with an ice-bath and then adjusted pH to 4. After remove the solvent, 25 mL H_2O was added to the residue. The solvent was extracted with CH_2Cl_2 until the organic phase became colorless. The aqueous phase was separated, its Ph was adjusted to 10 using Na_2CO_3 and the product was extracted with CH_2Cl_2. The solvent was dried with anhydrous Na_2SO_4, removed under vacuum. The product was obtained without further purification (4.10 g, 85%). ^{1}H NMR δ = (400 MHz, $CDCl_3$) 8.61 – 8.51 (2 H, m), 7.63 (2 H, td, *J* = 7.6, 1.9), 7.39 – 7.27 (2 H, m), 7.18 – 7.09 (2 H, m), 3.98 (4 H, d, *J* = 1.8), 2.78 (1 H, s).

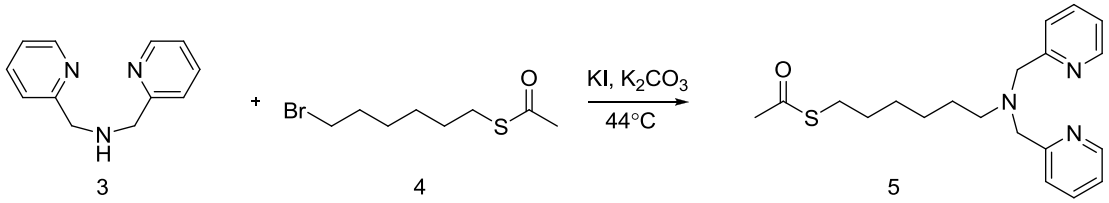
Synthesis of 6-bromohexyl ethanethioate 4



4

A solution of 1, 2-dibromohexthane (6.00 g, 24.8 mmol) and potassium thioacetate (1.40 g, 12.4 mmol,) in anhydrous THF (50 mL) was refluxed for 12 hours under argon. After cooling to room temperature, the KBr was removed by vacuum filtration. The solvent in the filtrate was removed under reduced pressure in a rotary evaporator. The residue was purified with column chromatography to give product **4** (1.90 g, 65%). 1H NMR ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.40 (t, *J* = 6.8, 2H), 2.87 (t, *J* = 7.3, 2H), 2.33 (s, 3H), 1.93 – 1.79 (m, 2H), 1.59 (m, 2H), 1.52 – 1.31 (m, 4H).

Synthesis of 6-(bis(pyridin-2-ylmethyl)amino)hexyl ethanethioate (5)

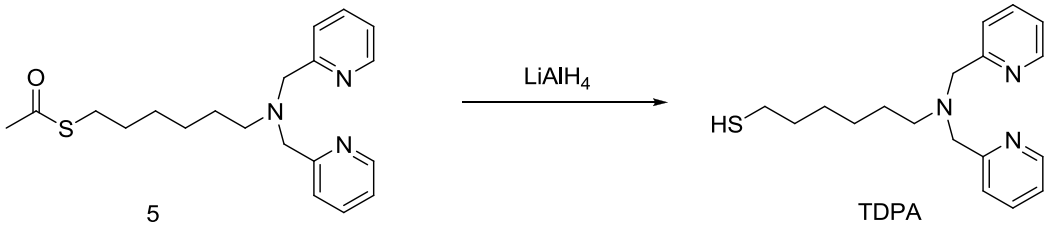


3 4 5

To a solution containing **4** (0.24g, 1.0 mmol), K_2CO_3 (0.276 g, 2.0 mmol) and KI (0.033g, 0.2 mmol) in 15 mL acetone was added dropwise a solution of DPA **3** (0.298g, 1.5 mmol) in 5 mL

acetone. The mixture was stirred for 18h at 44 ℃, then filtrated. The solvent was removed under vacuum, the residue was purified with column chromatography to give product **5** (0.24g, 67%). ^{1}H NMR δ_{H} (400 MHz, $CDCl_3$) 8.55 – 8.49 (2 H, m), 7.66 (2 H, td, *J* = 7.7, 1.8), 7.53 (2 H, d, *J* = 7.8), 7.17 – 7.11 (2 H, m), 3.80 (4 H, s), 2.86 – 2.78 (2 H, m), 2.53 (2 H, dd, *J* = 13.4, 6.1), 2.31 (3H, s), 1.51 (4 H, dt, *J* = 11.3, 5.3), 1.34 – 1.22 (4 H, m).

Synthesis of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol (TDPA)



5 TDPA

To a solution of $LiAlH_4$ (0.17 g, 4.0 mmol) in dry THF (5 mL) was added dropwise at 0 ℃ a solution of **5** (0.357 g, 1.0 mmol) in dry THF (5 mL) over 15 min. The mixture was stirred for 4 h, and then poured into ice water (50 mL). The white precipitation was filtered. The water phase was extracted with CH_2Cl_2 (30 mL × 3). The organic phase was collected and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified with column chromatography to give product (0.19 g, 63%). ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.44 (2 H, d, *J* 4.2), 7.58 (2 H, td, *J* = 7.7, 1.7), 7.46 (2 H, d, *J* = 7.8), 7.07 (2 H, dd, *J* = 6.5, 5.3), 3.75 (4 H, s), 2.58 – 2.44 (4 H, m), 1.60 – 1.41 (4 H, m), 1.30 – 1.13 (4 H, m). ^{13}C NMR δ (101 MHz, $CDCl_3$) 159.86, 148.95, 136.39, 122.86, 121.91, 60.44, 54.34, 38.94, 29.69, 29.13, 28.77, 28.32, 26.90. HRMS (EI+) calculated 315.1769, found 315.1766.

^{1}H NMR, ^{13}C NMR and MS characterization of intermediates and target compounds

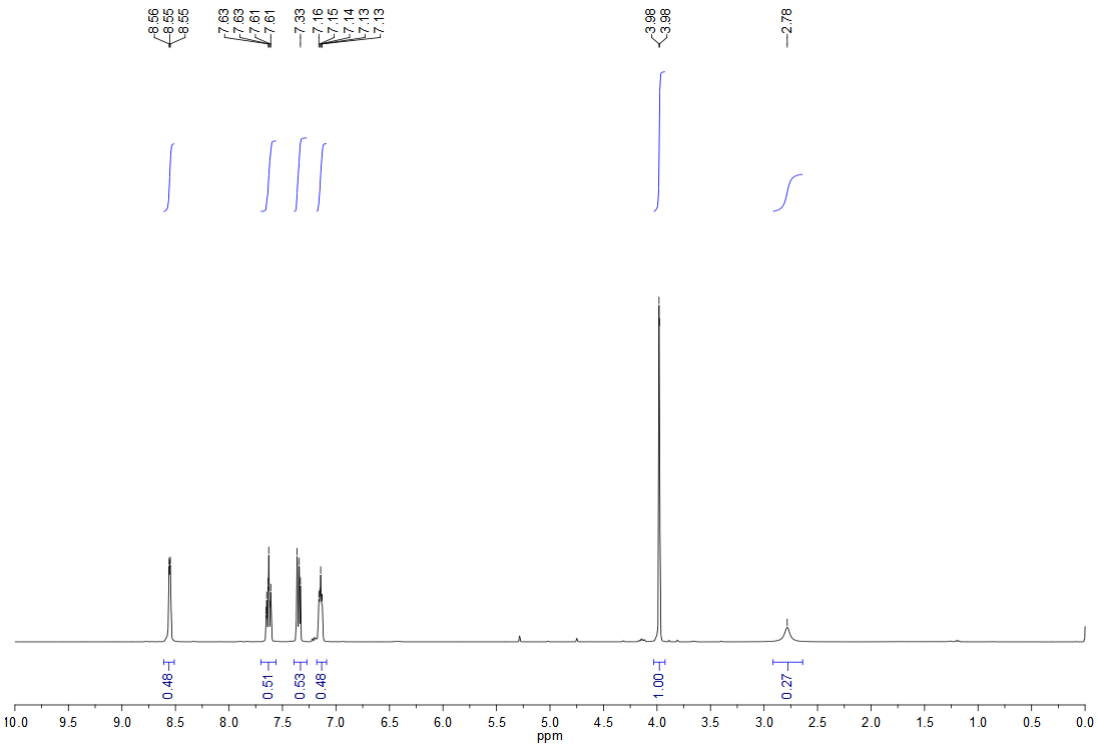


Figure S4. ^{1}H NMR of bis(2-pyridylmethyl)amine.

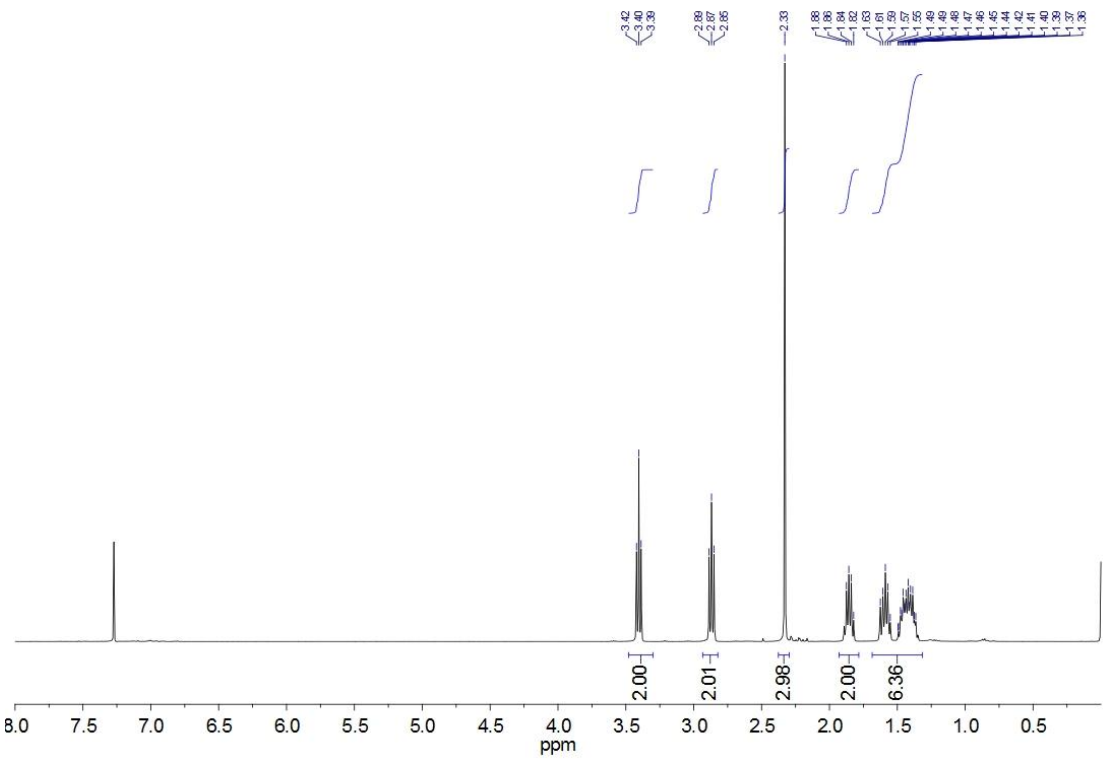


Figure S5. [1]H NMR spectrum of 6-bromohexyl ethanethioate.

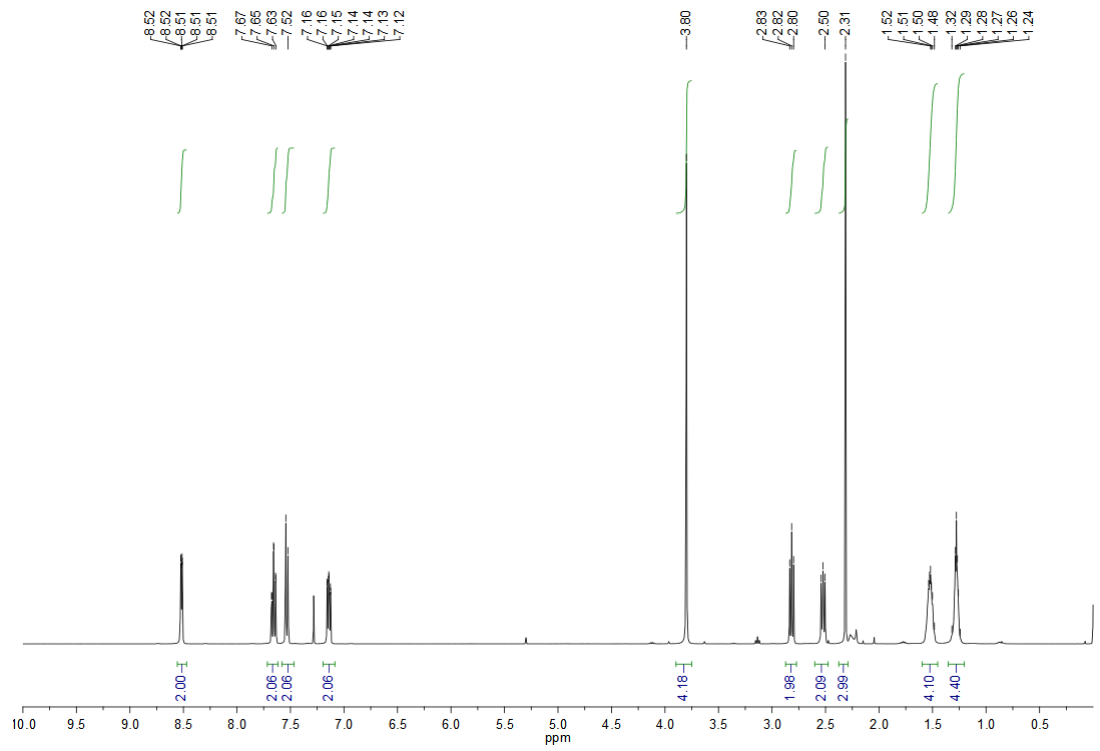


Figure S6. 1H NMR of 6-(bis(pyridin-2-ylmethyl)amino)hexyl ethanethioate.

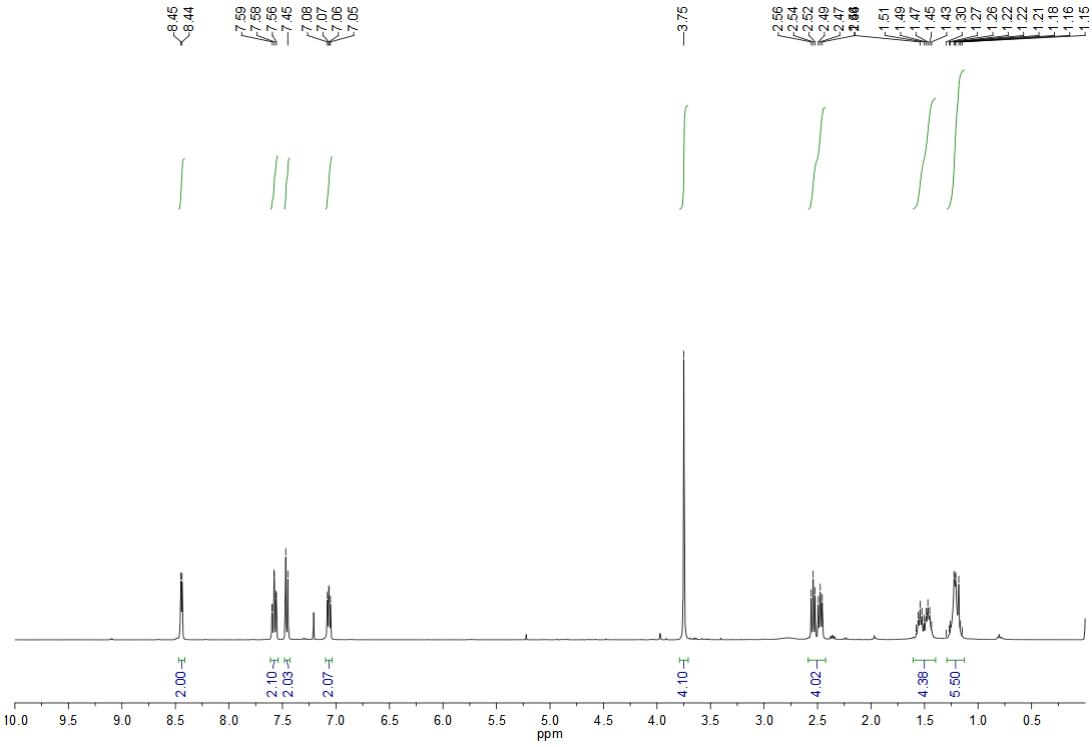


Figure S7. ^{1}H NMR of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol.

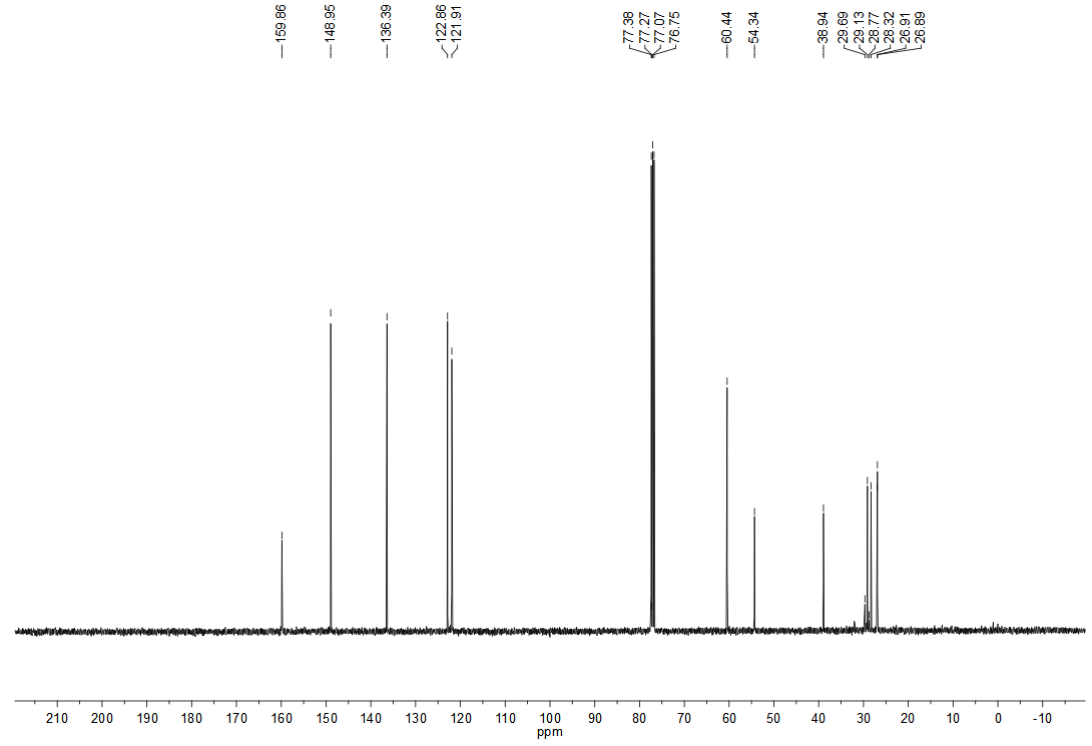


Figure S8. ^{13}C NMR of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol.

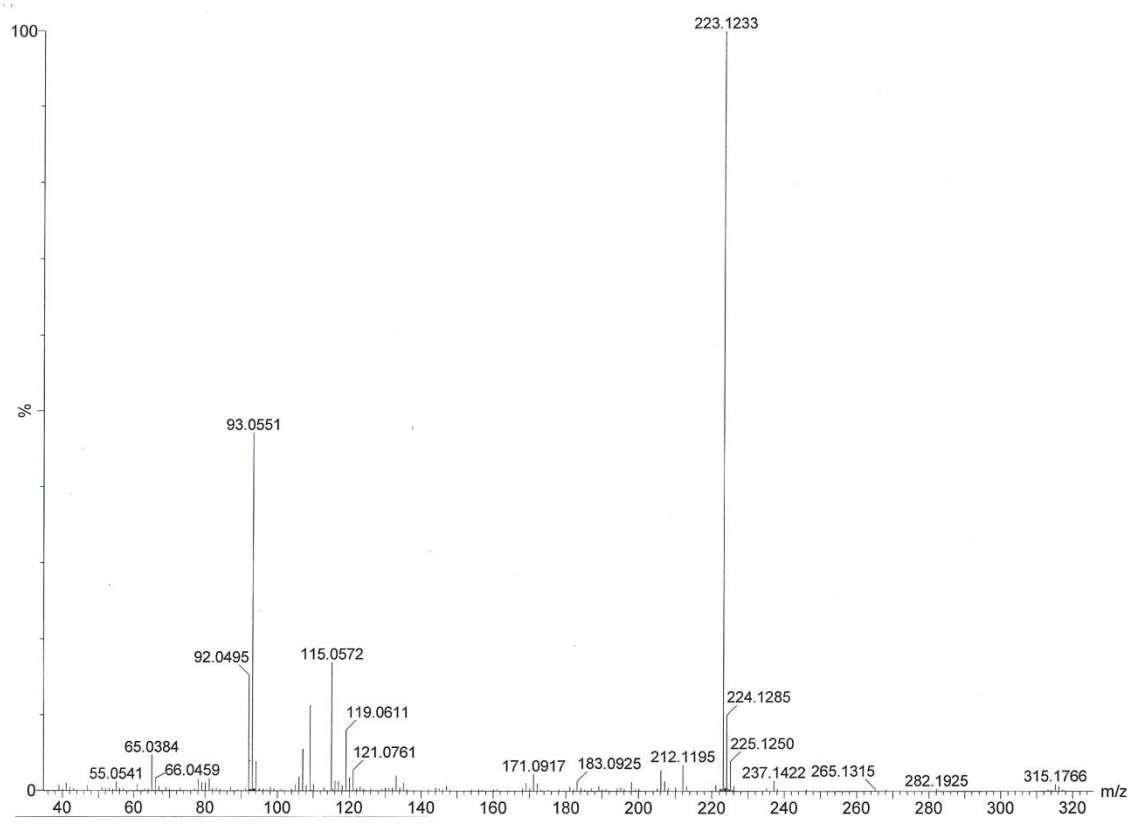


Figure S9. HRMS (EI+) of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol.