Ion-selective gold-thiol film on integrated screen-printed electrodes for analysis of Cu(II) ions

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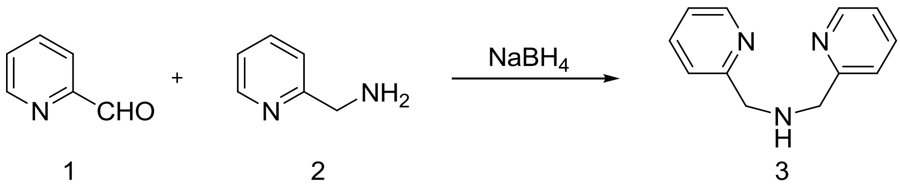
This supporting material contains the synthesis procedure of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol, supplementary data on the optimization of some experimental conditions and characterization of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol.

Contents:

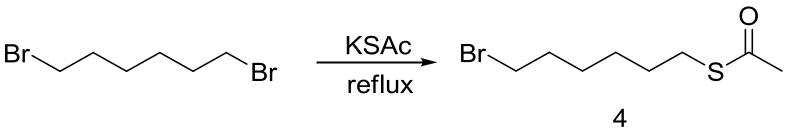
Section I. Synthesis procedure of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol

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



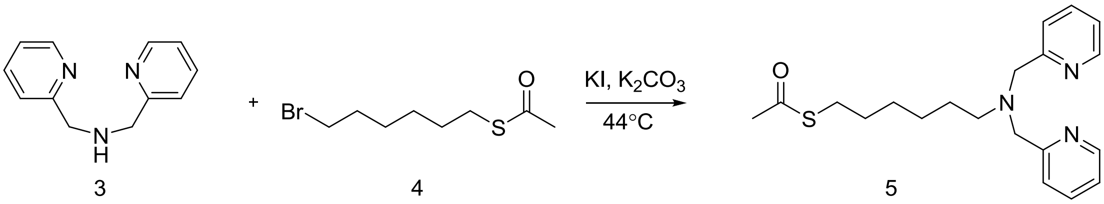
2-pyridinecarbaldehyde (2.51 g, 23.5 mmol) was dissolved in 50 mL methanol, and pyridin-2-ylmethanamine (2.54 g, 23.5 mmol) was added dropwise under ice-bath condition. The mixture was stirred for 1 h at room temperature. After that, $NaBH_4$ (0.89 g, 23.5 mmol) was added in portions at 0°C. The solution was stirred overnight, quenched with the addition of HCl, cooled with an ice-bath and then pH adjusted to 4. After removing 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 and 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)



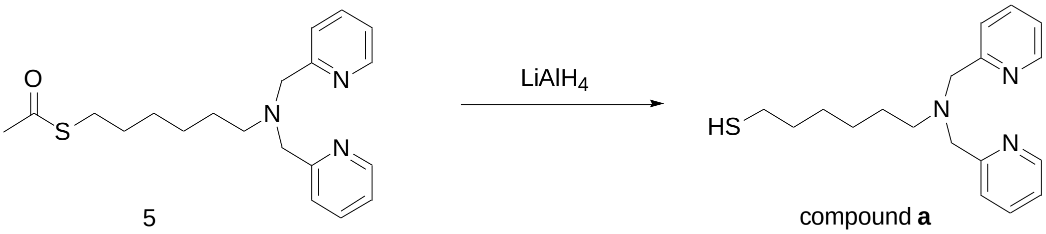
A solution of 1, 2-dibromohexthane (6.0 g, 24.8 mmol) and potassium thioacetate (1.4 g, 12.4 mmol,) in anhydrous THF (50 mL) was refluxed for 12 hours under argon. After cooling to room temperature, the KBr was removed by vacuum filtration. The solvent in the filtrate was removed under reduced pressure using a rotary evaporator. The residue was purified with column chromatography to give product **4** (1.9 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)



To a solution containing **4** (0.238g, 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 °C, then filtered. The solvent was removed under vacuum and the residue was purified with column chromatography to give product **6** (0.239g, 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 (compound a)



To a solution of $LiAlH_4$ (0.172 g, 4.0 mmol) in dry THF (5mL) was added dropwise at 0°C a solution of **5** (0.357 g, 1.0 mmol) in dry THF (5mL) 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 (0.2 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.

Section II. Optimization of experimental conditions

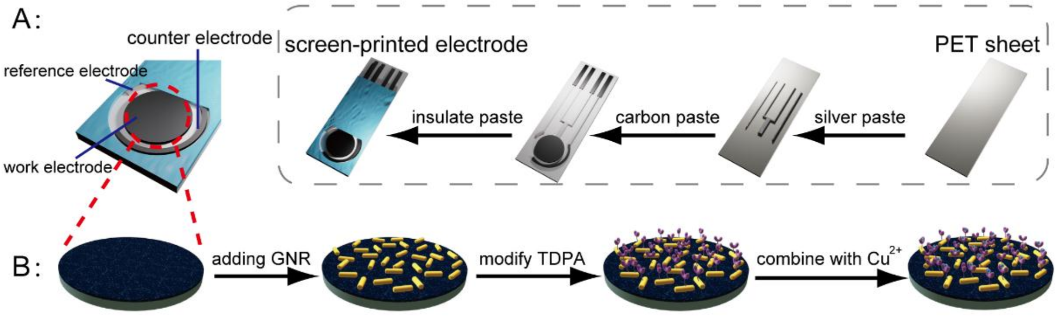


Fig. S1 The procedure for preparing (A) screen-printed electrodes (SPEs) and (B) modified ion-selective electrodes (ISEs) for Cu(II) ions detection.

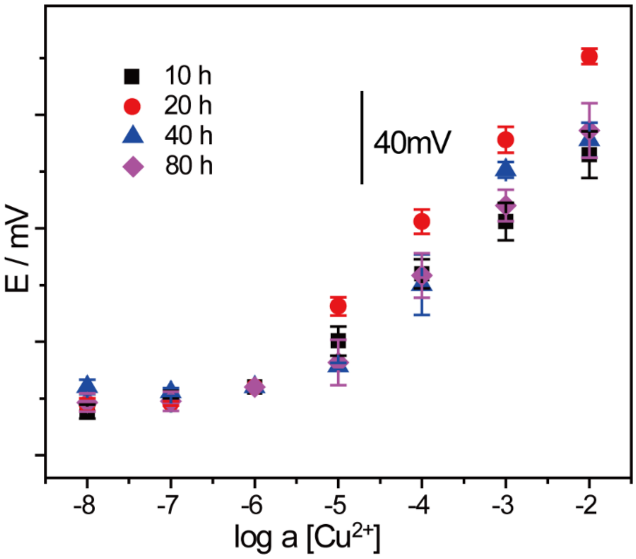


Fig. S2 The effect of the self-assembly time on the potentiometric response to different concentration of Cu(II) ions.

Table S1 The calculated values for R_s, R_{ct}, C_{dl}, CPE and Z_w in the equivalent circuit models of the impedance data.

	Bare SPE	GNR/SPE	comp. **a**/GNR/SPE	comp. **a**-Cu/GNR/SPE
R_s	258.0	148.7	855.5	636.9
C_{dl}	2.8×10^{-7}	5.9×10^{-7}	-	-
R_{ct}	1083.0	303.5	2909	1009
Z_w	0.2	0.0014	0.00076	0.0013
CPE	-	-	1.9×10^{-6}	4.25×10^{-6}
n	-	-	0.79	0.74

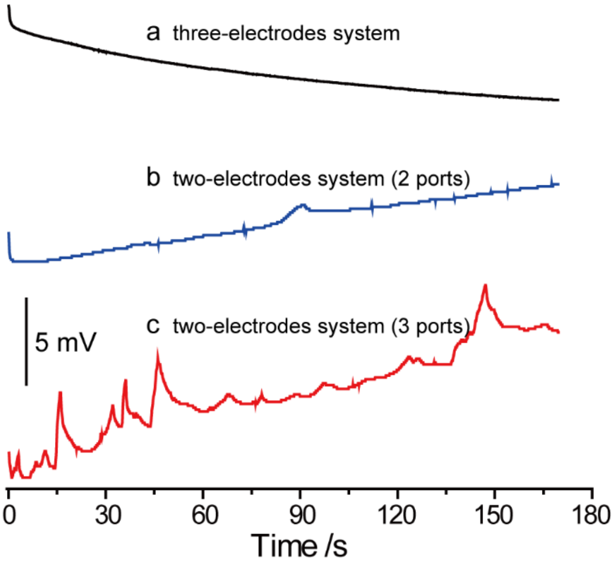


Fig. S3 The open-circuit potential recorded when SPEs immersed in blank solution under (a) three-electrodes system; (b) two-electrodes system with 2 ports connected (working electrode port and reference electrode port) and (c) two-electrodes system with 3 ports connected (auxiliary electrode and reference electrode ports are connected to Ag/AgCl reference electrode).

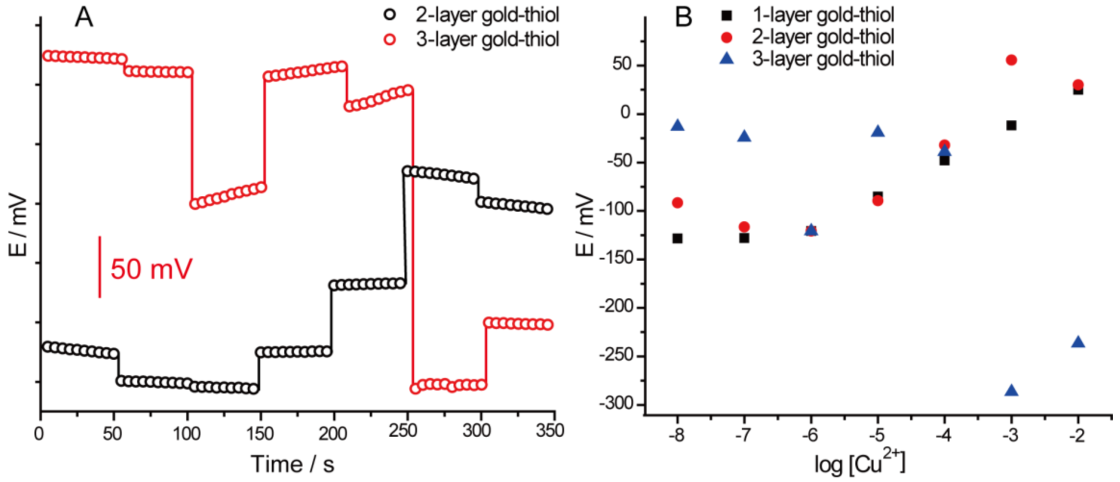


Fig. S4 (A) The open-circuit potential responses of 2-layer gold-thiol modified SPE (black) and 3-layer gold-thiol modified SPE (red) against time recorded in $CuSO_4$ solution over the range from 1.0×10^{-8} to 1.0×10^{-2} M and (B) the corresponding potential responses against the concentration of Cu(II) ions of 2-layer gold-thiol modified SPE (circle) and 3-layer gold-thiol modified SPE (triangle) compared to the 1-layer gold-thiol modified SPE (square). For comparison, experimental lines were shifted to give the same value at 1.0×10^{-6} M $CuSO_4$.

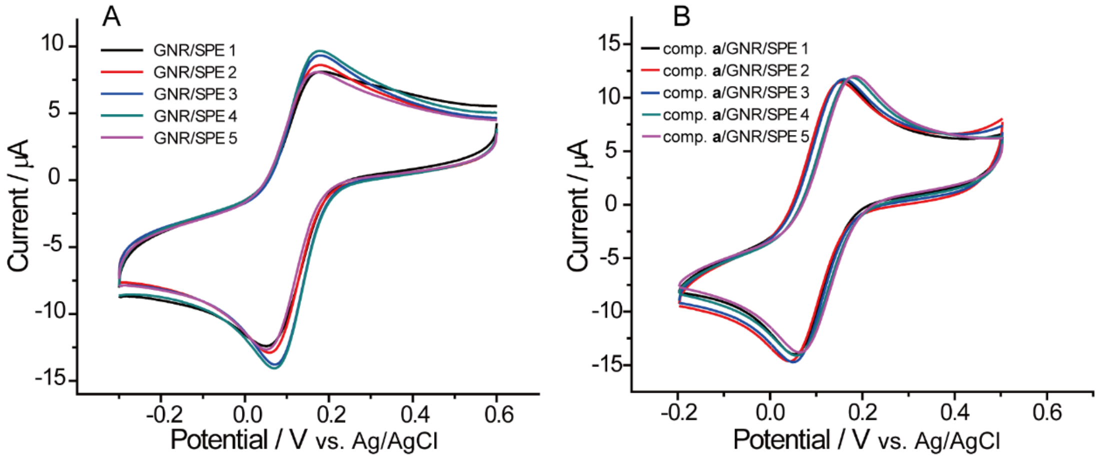


Fig. S5 CVs of (A) different GNR/SPEs and (B) compound **a**/GNR/SPEs in the presence of 1.0 mM $K_3Fe(CN)_6$ redox label solution that included 0.5 M KNO_3.

Section III. Characterization of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol

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

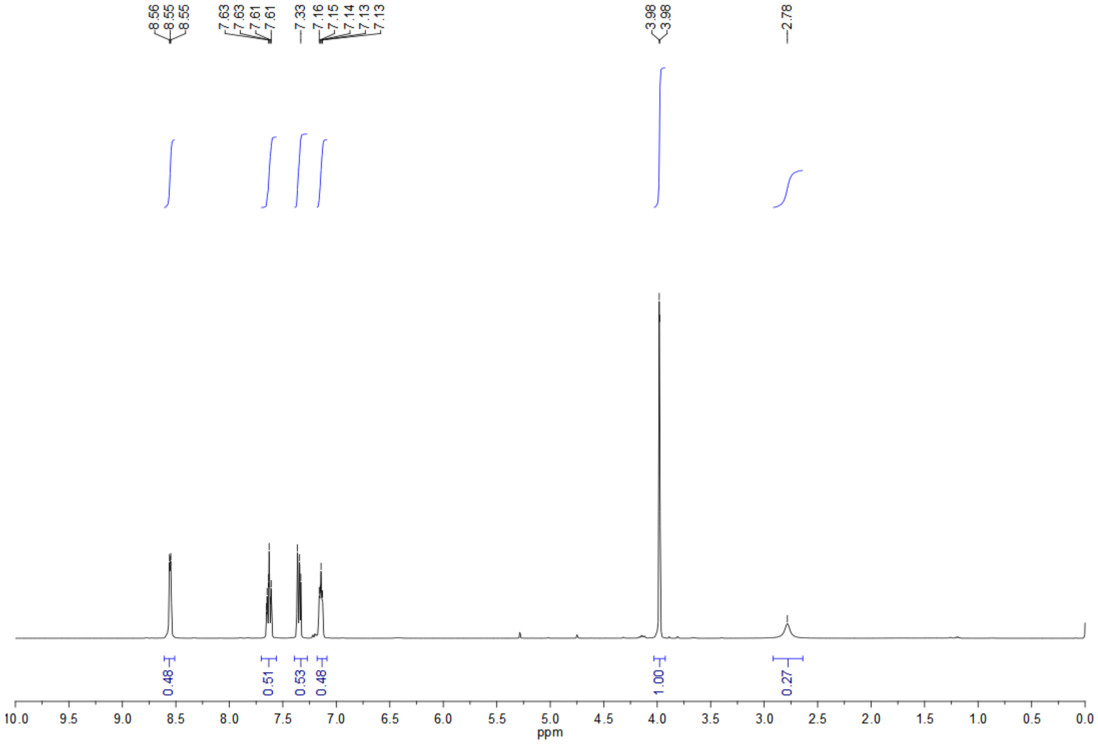


Fig. S6 ^{1}H NMR of bis(2-pyridylmethyl)amine.

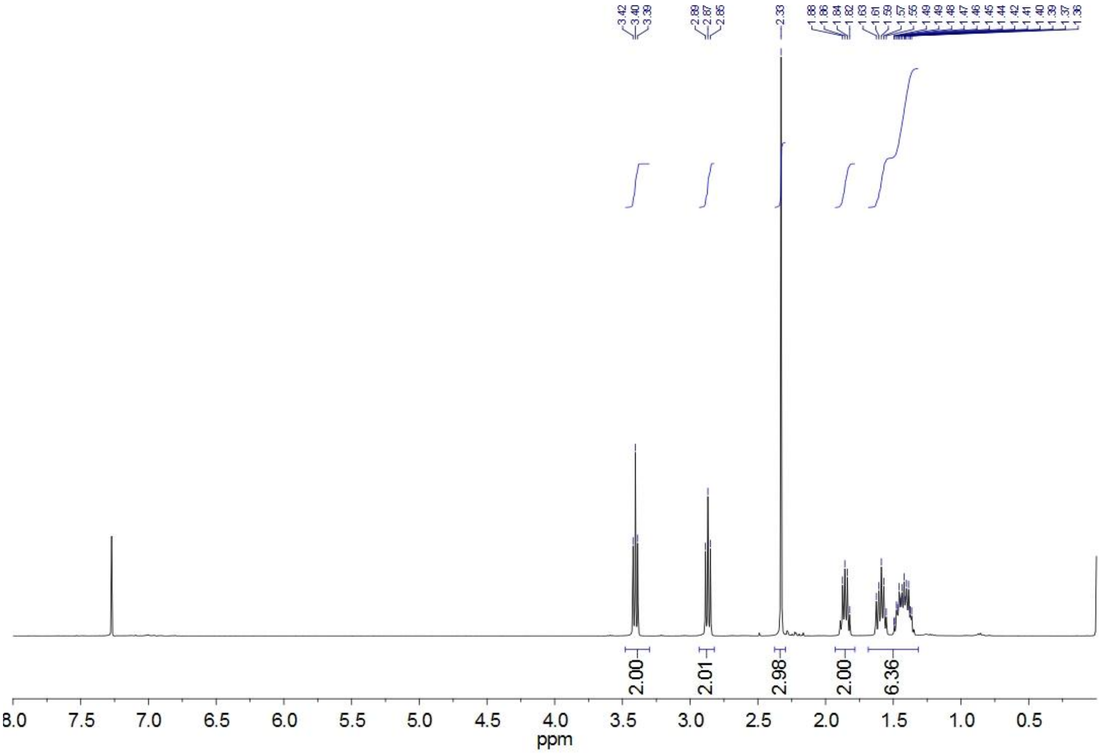


Fig. S7 ^{1}H NMR spectrum of 6-bromohexyl ethanethioate.

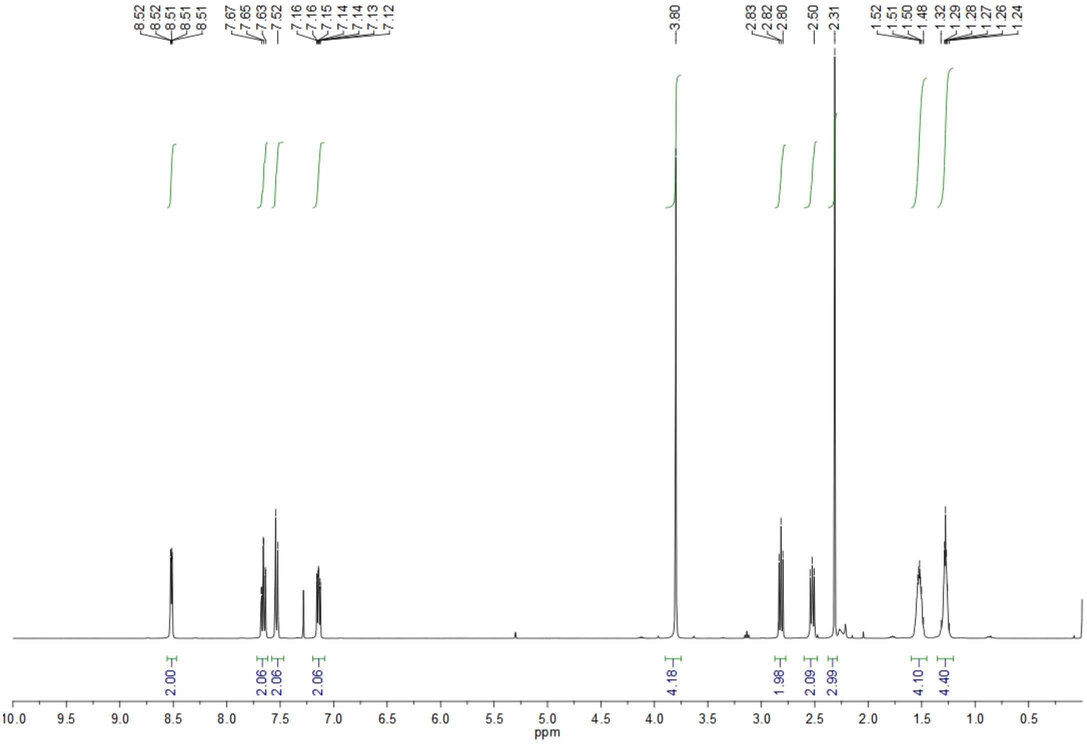


Fig. S8 1H NMR of 6-(bis(pyridin-2-ylmethyl)amino)hexyl ethanethioate.

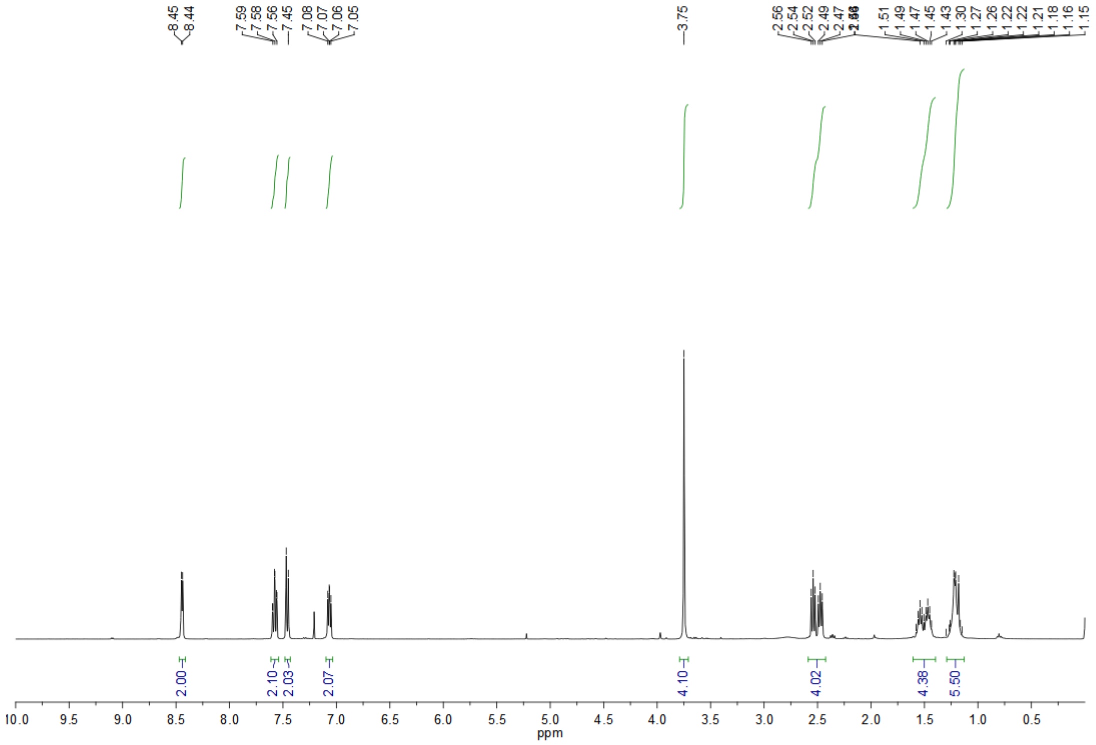


Fig. S9 ^{1}H NMR of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol.

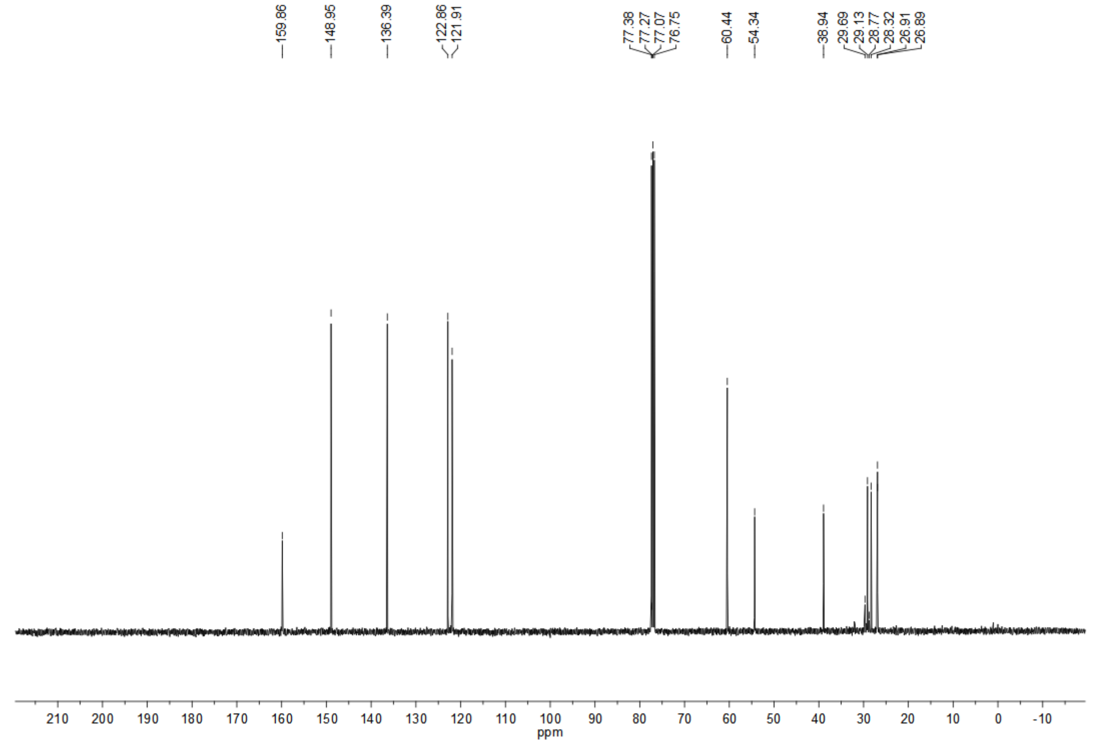


Fig. S10 ^{13}C NMR of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol.

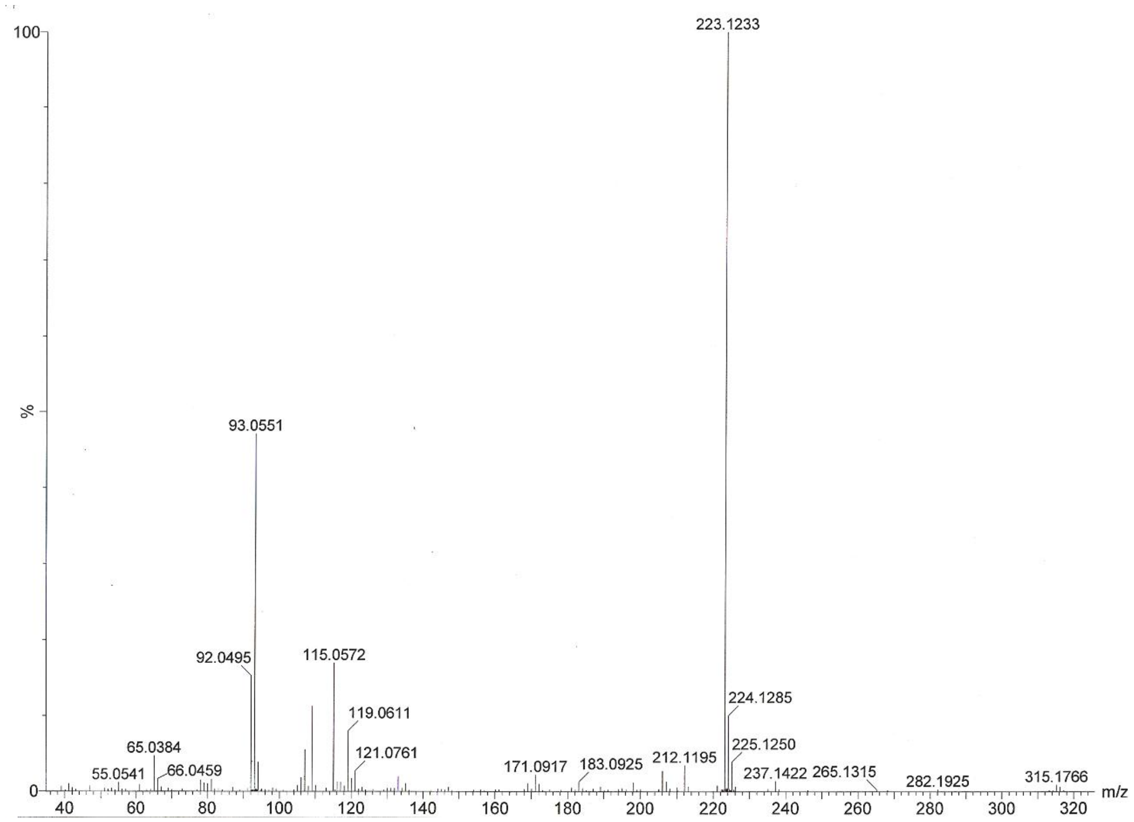


Fig. S11 HRMS (EI+) of 6-(bis(pyridin-2-ylmethyl)amino)hexane-1-thiol.