

Electronic Supplementary Information (ESI)

A ratiometric luminescent sensing of Ag⁺ ion via *in situ* formation of coordination polymers

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CONTENT

1. Chemicals and apparatus.....	S2
2. Synthesis of <i>N</i> -(2-(naphthalen-1-yl)-acetyl)- <i>L</i> -cysteine (NCys).....	S2
3. Figures S1-S11.....	S4-S11
4. Table S1.....	S11
5. NMR spectra of NCys.....	S12

Chemicals and apparatus. 2-(1-Naphthalene)acetic acid (NAA, 99 %) and *L*-cystine (98.5-101.5 %) were purchased from BBI (Bio Basic Inc.). Chemicals used for syntheses were as received from commercially available sources of AR grade. Solvents used for spectral investigations were further purified by redistillations so that no fluorescent impurity could be detected at the employed excitation wavelength.

¹H NMR and ¹³C NMR spectra were measured on Bruker Avance 400 NMR spectrometer at room temperature. Infrared spectra were recorded as Nujol mulls in KBr plates on Nicolet 360 FT-IR spectrometer. UV-visible absorption, circular dichroism (CD) and photoluminescent spectra were recorded on Evolution 300 UV-visible spectrophotometer, JASCO J-810 spectropolarimeter and Hitachi F-4500 fluorescence spectrophotometer, respectively. Elemental analyses for the synthesized product were carried out on EA-MA1110 elemental analyzer (Carlo Erba, Milan, Italy). High Resolution Mass Spectrum (HRMS) was recorded on Agilent 6520 Series Accurate-Mass Quadrupole Time-of-Flight LC/MS. pH was measured on Mettler Toledo 320 pH Meter.

Synthesis of *N*-(2-(naphthalen-1-yl)-acetyl)-*L*-cysteine (NCys). NCys was synthesized following a reported procedure.¹ A drop of *N,N*-dimethylformamide (DMF) and oxalyl chloride (0.5 mL, 5.33 mmol) were added to a stirred solution of 2-(1-naphthalene)acetic acid (0.5 g, 2.68 mmol) in CH₂Cl₂ (2.5 mL) at 0 °C. After stirred for 2 h at room temperature, the reaction mixture was concentrated in vacuo to give (2-naphthalen-1-yl)acetyl chloride. The resulting acid chloride was dissolved in tetrahydrofuran (THF, 2.0 mL) that was then added dropwise to solution of *L*-cystine (0.5 g, 2.08 mmol) in water (10 mL) containing NaOH (0.4 g, 10 mmol) at 0 °C. At the end of the reaction, pH of the solution was adjusted to 9 by HCl (1M) and white precipitates formed were filtered and washed with saturated NaHCO₃ solution. The precipitates were dispersed in ethanol/water (10 mL/6 mL) that was reduced by NaBH₄ (1 g, 26.31 mmol). The reduction reaction was conducted at 70 °C for 1 h and the resultant solution was then acidified to pH 2 by HCl (1M). The product was purified by flash column chromatography (SiO₂, MeOH/CH₂Cl₂, 1.5/10) to afford

NCys (0.26 g, 0.90 mmol, 34 %) as a white solid. ^1H NMR (400 MHz, CD_3OD): δ (ppm) 2.85-2.90 (m, 1H, H_β), 2.94-2.98 (m, 1H, H_β), 4.10 (s, 1H, ArCH_2), 4.63 (m, 1H, H_α), 7.42-7.55 (m, 4H, ArH), 7.80 (d, $J = 8$ Hz, 1H, ArH), 7.87 (d, $J = 8.8$ Hz, 1H, ArH), 8.06 (d, $J = 8.4$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 26.7, 41.2, 56.0, 125.1, 126.6, 126.9, 127.4, 129.0, 129.2, 129.7, 132.8, 133.7, 135.4, 173.0, 174.0; HRMS (ESI $^-$) ($\text{M}-\text{H}$) $^-$: calcd for $[\text{C}_{15}\text{H}_{14}\text{NO}_3\text{S}]^-$: 288.0694, found: 288.0699; Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$: C, 62.26; H, 5.23; N, 4.84. found: C, 62.30; H, 5.18; N, 4.79; IR, ν_{max} (KBr disk): 3372 (s, OH), 2531 (m, SH), 1737 (s, C=O), 1607 (s, C=O), 1202 (s, C-O) cm^{-1} .

Reference

- (1) B. M. R. Lienard, R. Hueting, P. Lassaux, M. Galleni, J. M. Frere, and C. J. Schofield, *J. Med. Chem.*, 2008, **51**, 684-688.

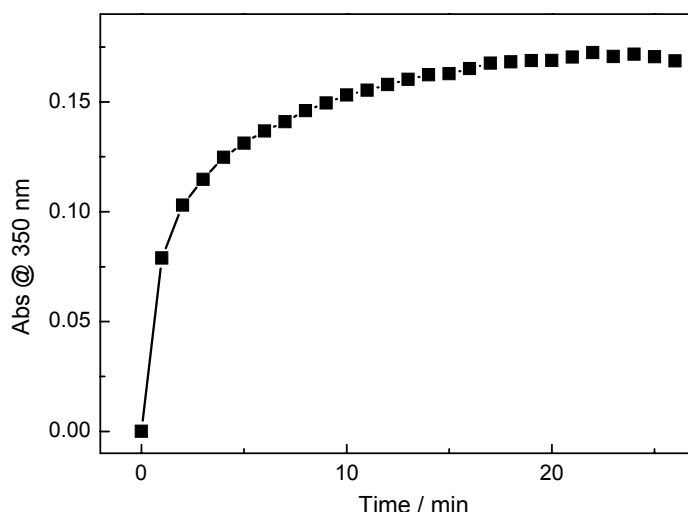


Fig. S1 Plots of absorbance at 350 nm against reaction time after NCys (25 μM) was mixed with 1 equivalent of Ag^+ in EtOH- H_2O solution (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0.

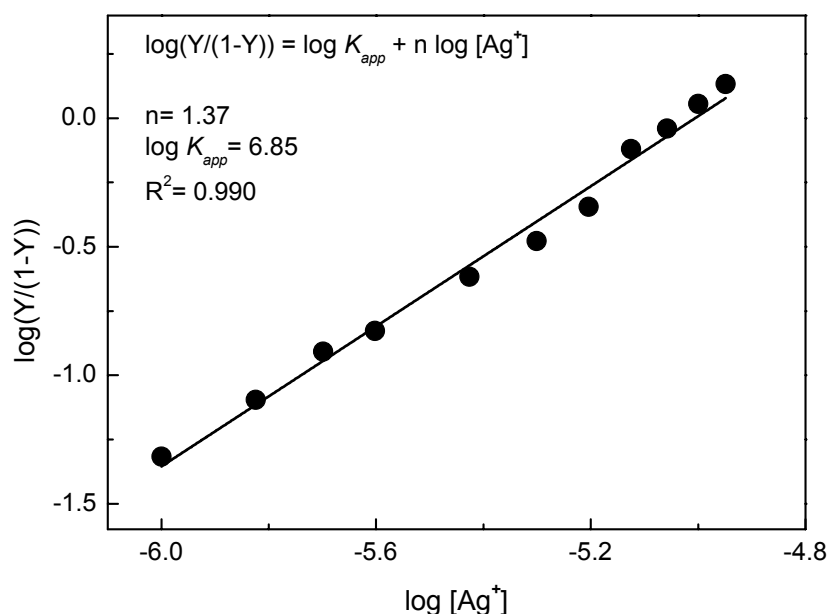


Fig. S2 Hill plot for the interaction of Ag^+ with NCys in EtOH- H_2O solution (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0 based on change in absorbance at 350 nm. $Y = (A - A_0) / (A_{\text{max}} - A_0)$, in which A_0 , A , and A_{max} are the absorbance at 350 nm in the absence of Ag^+ , in the presence of Ag^+ lower than 11.25 μM , and in the presence of 25 μM Ag^+ when maximum absorbance at 350 nm was observed, respectively. $[\text{NCys}] = 25 \mu\text{M}$.

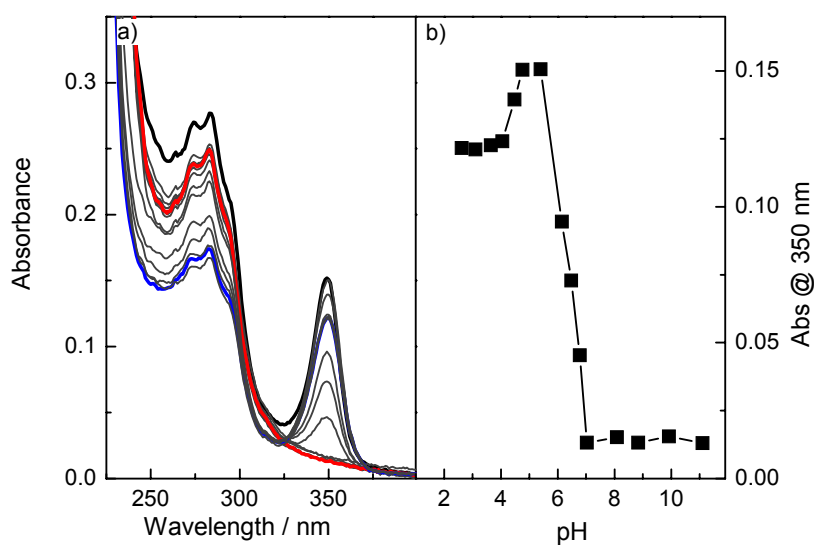


Fig. S3 (a) Absorption spectra of Ag(I)-NCys ($[\text{Ag}^+] = [\text{NCys}] = 25 \mu\text{M}$) coordination polymers in EtOH-H₂O (1:1, v/v) at different pH and (b) plot of absorbance at 350 nm as a function of pH.

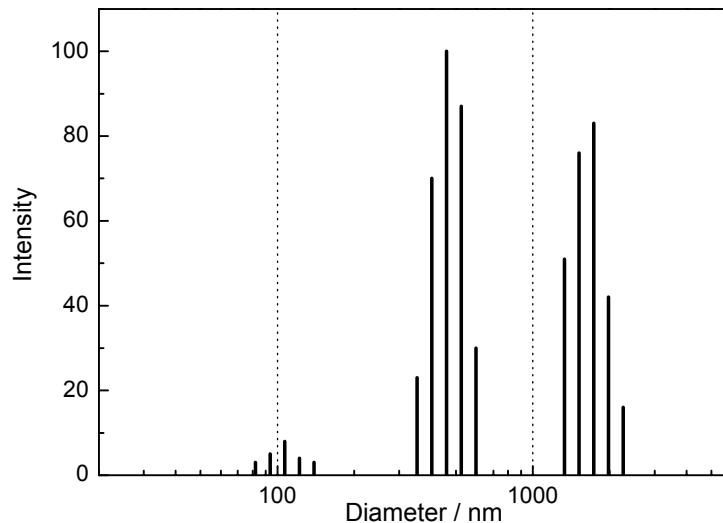


Fig. S4 Hydrodynamic diameter (D_h) of the Ag(I)-NCys polymers ($[\text{Ag}^+] = [\text{NCys}] = 25 \mu\text{M}$).

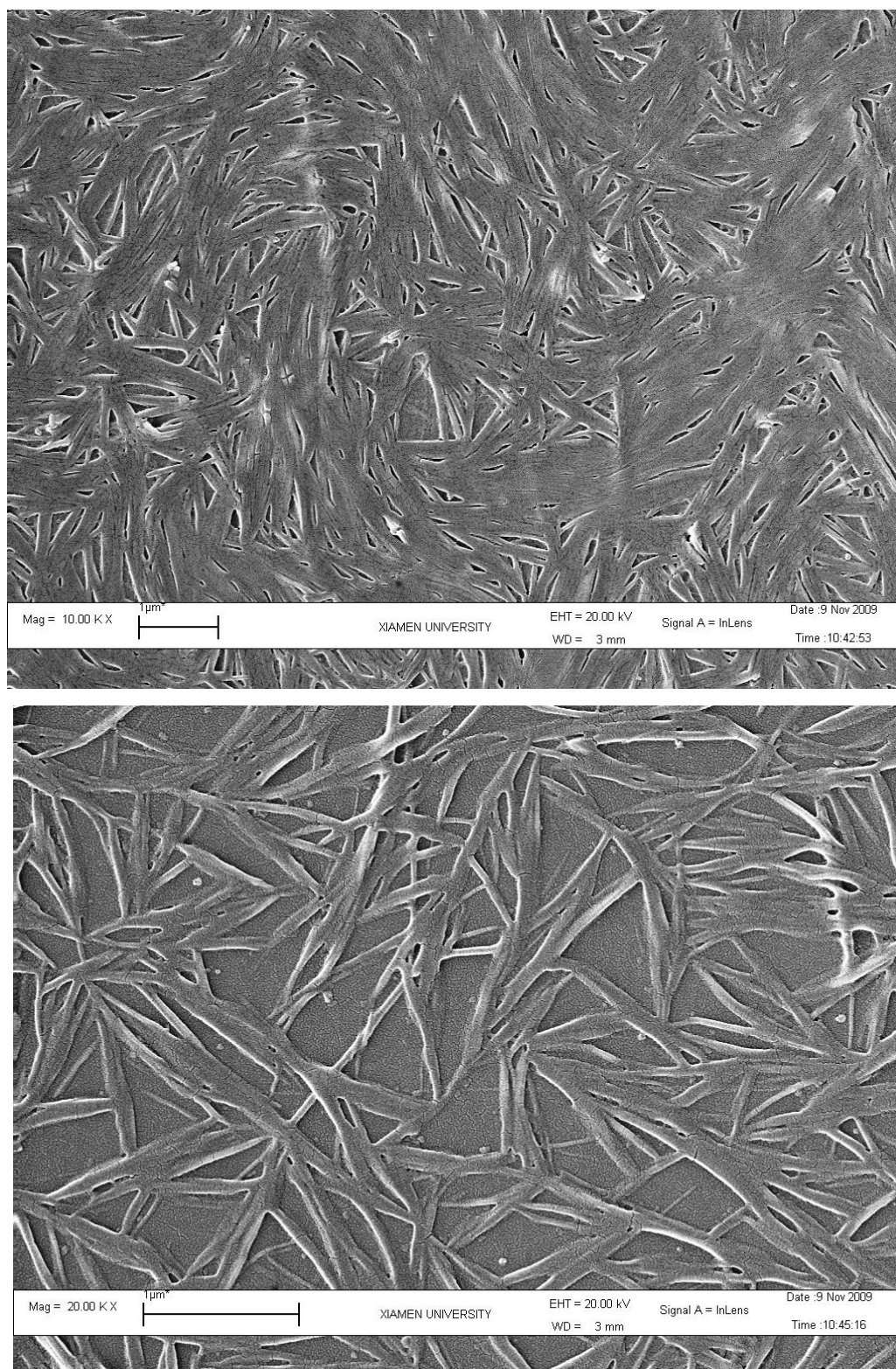


Fig. S5 SEM images of 25 μM NCys with 1 equivalent of Ag^+

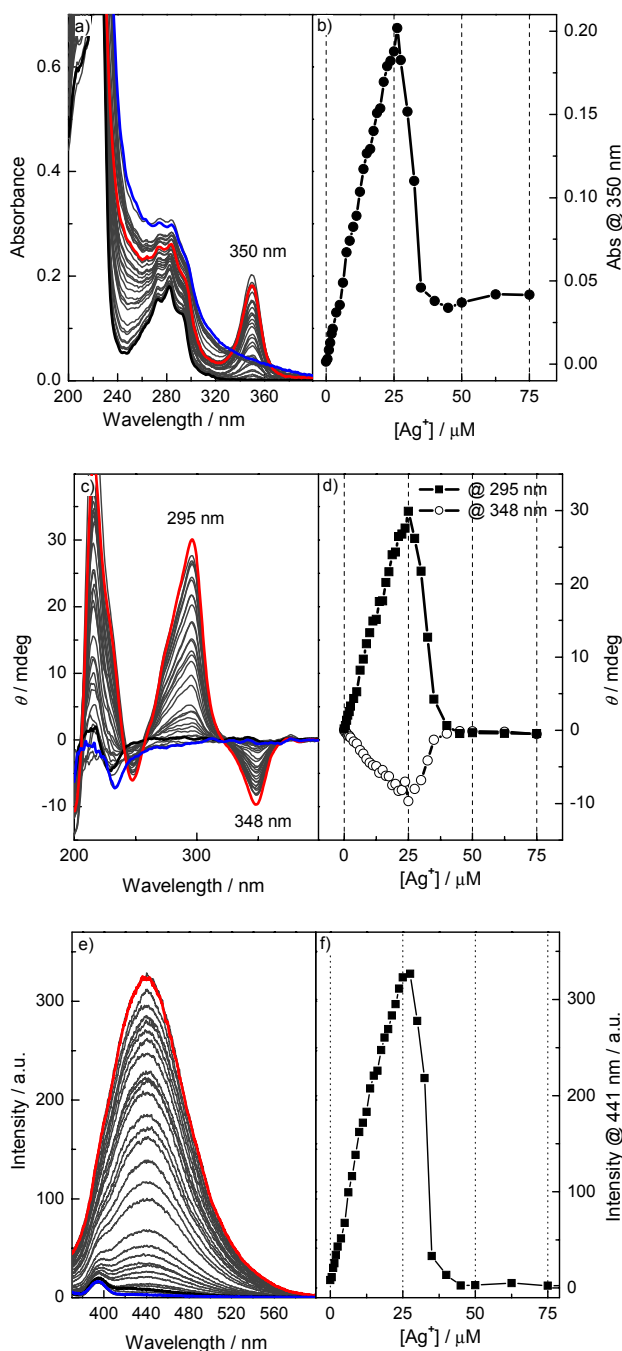


Fig. S6 Absorption (a), CD (c) and PL (e, $\lambda_{\text{ex}} = 350 \text{ nm}$) spectra of NCys (25 μM) in EtOH-H₂O solution (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0 in the presence of increasing concentration of Ag^+ ($[\text{Ag}^+]/\mu\text{M}$: —, 0; —, 25; —, 75), and plots of absorbance (b), θ (d) and PL intensity (f) against Ag^+ concentration. Note that the absorbance, θ and emission intensity decrease in the presence of excess Ag^+ , which could be due to that the coordination polymers are destroyed. The SEM images do show the ordered nano-scale structures were lost at high Ag^+ concentration (Fig. S7).

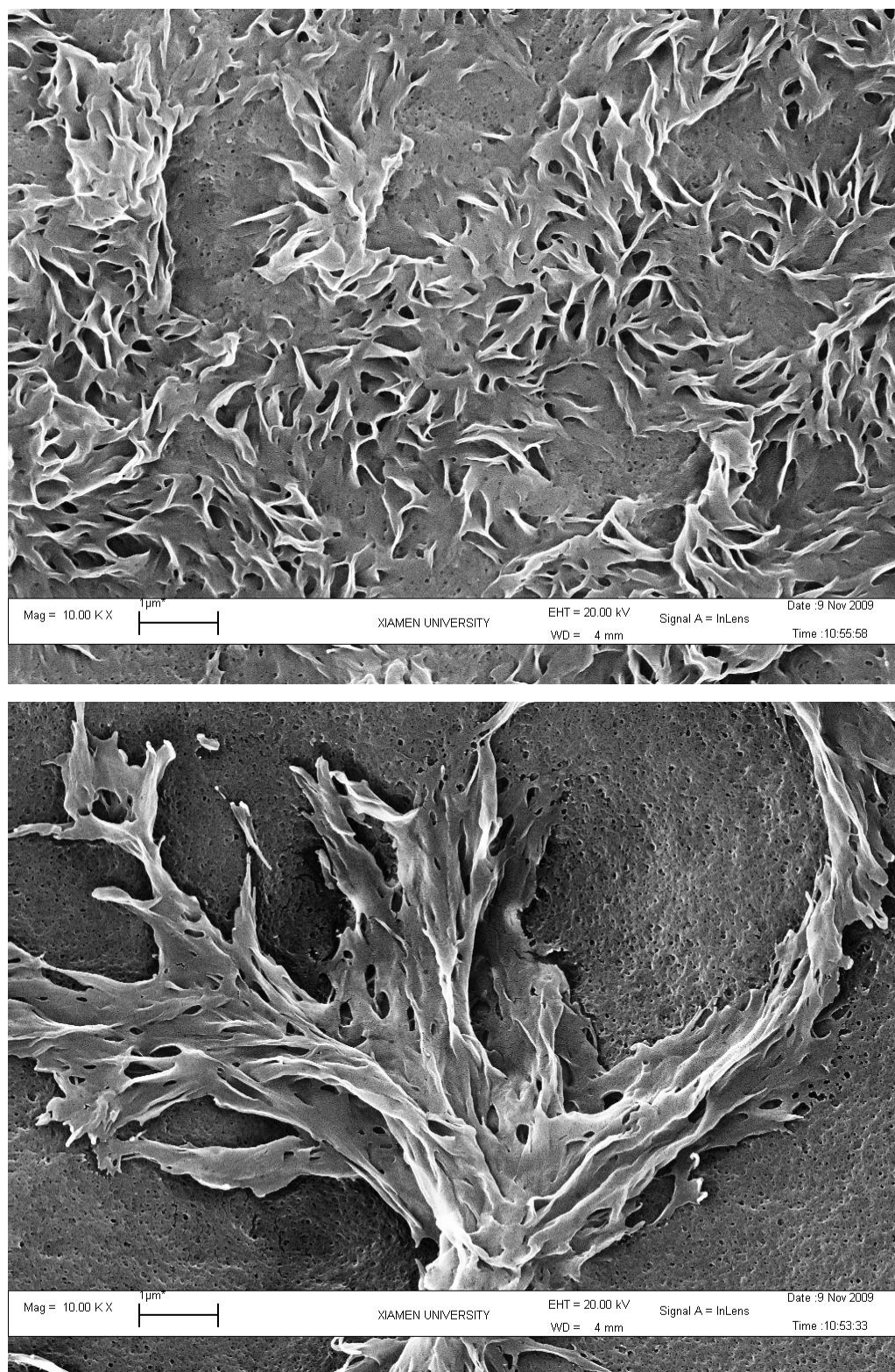


Fig. S7 SEM images of 25 μM NCys with 5 equivalents of Ag^+ .

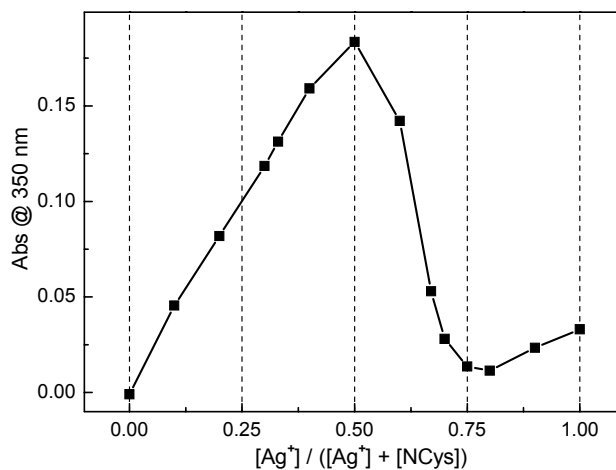
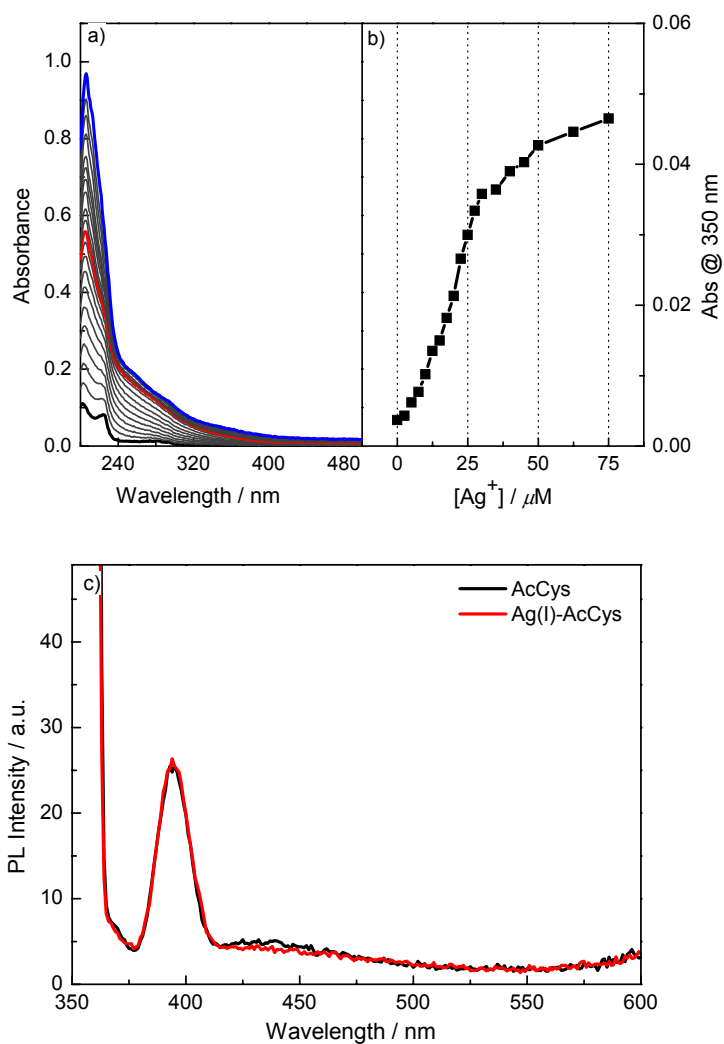


Fig. S8 Job plot for Ag(I)-NCys polymers in EtOH-H₂O (1:1, v/v) with 5 mM NaAc-HAc of pH 5.0. Total concentration of Ag⁺ and NCys was 50 μ M.



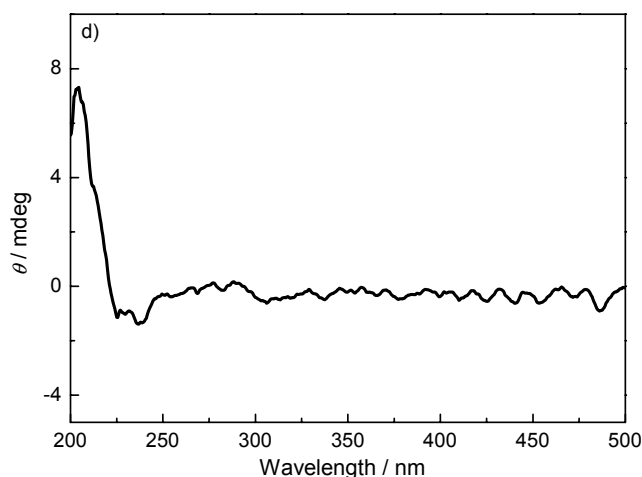


Fig. S9 (a) Absorption spectra of AcCys ($25\ \mu\text{M}$) in EtOH- H_2O solution (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0 in the presence of increasing concentration of Ag^+ , (b) plots of absorbance at 350 nm against Ag^+ concentration, and (c) PL and (d) CD spectra of Ag(I)-AcCys mixture in EtOH- H_2O solution (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0.

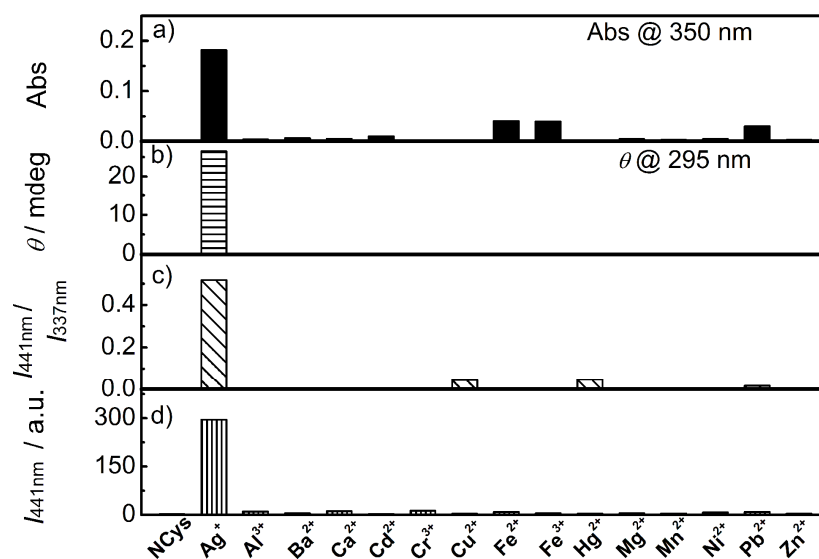


Fig. S10 Spectral response of NCys ($25\ \mu\text{M}$) toward 1 equivalent of metal ion in EtOH- H_2O (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0. Excitation wavelengths were 283 nm (c) and 350 nm (d), respectively.

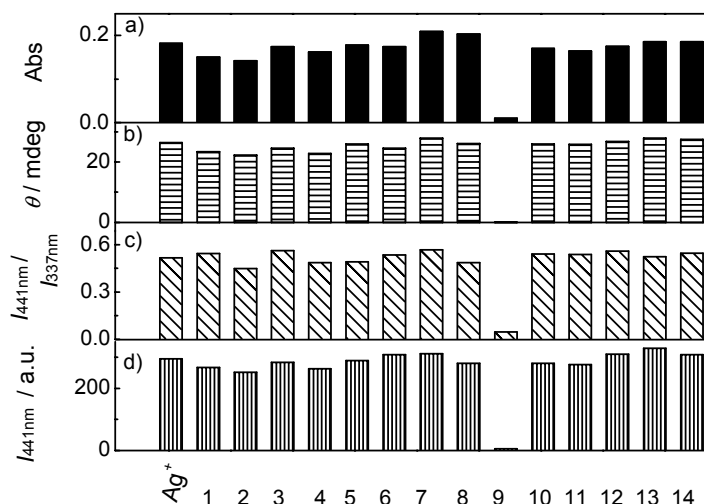


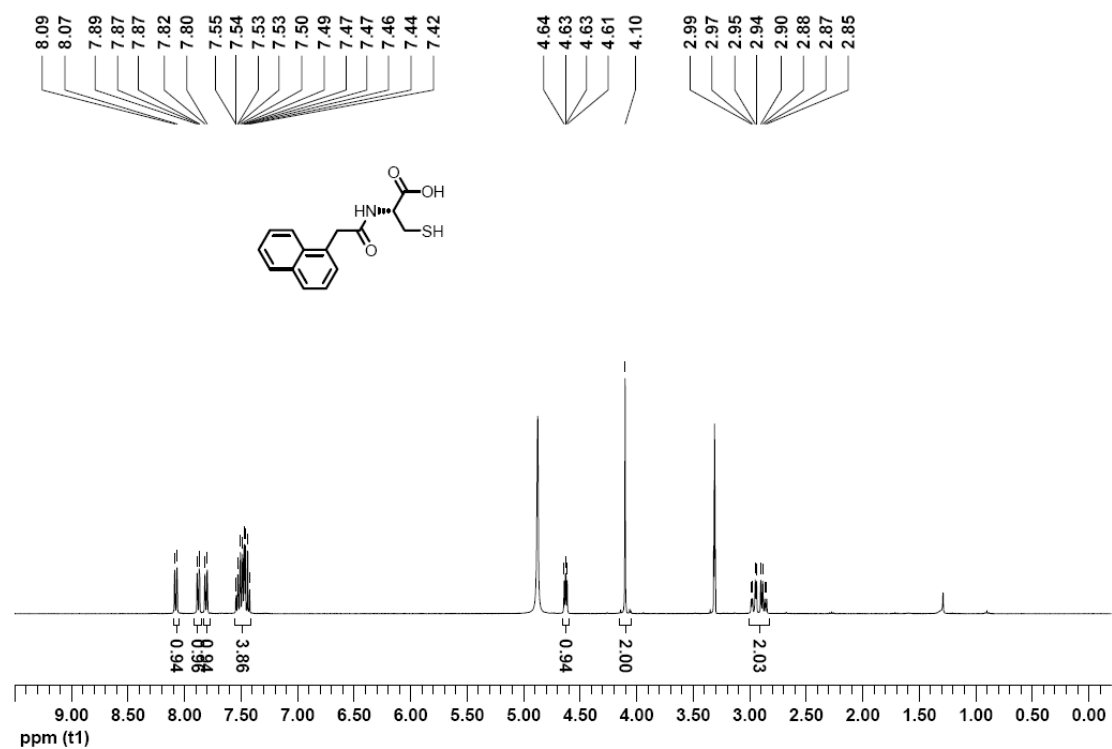
Fig. S11 Spectral response of 25 μM NCys toward 1 equivalent of Ag^+ and 1 equivalent of other metal ion (1, Al^{3+} ; 2, Ba^{2+} ; 3, Ca^{2+} ; 4, Cd^{2+} ; 5, Cr^{3+} ; 6, Cu^{2+} ; 7, Fe^{2+} ; 8, Fe^{3+} ; 9, Hg^{2+} ; 10, Mg^{2+} ; 11, Mn^{2+} ; 12, Ni^{2+} ; 13, Pb^{2+} ; 14, Zn^{2+}) in EtOH- H_2O solution (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0 and 1 mM EDTA. (a) absorbance at 350 nm, (b) θ at 295.5 nm, (c) ratio of PL intensity at 441 nm to that at 337 nm ($\lambda_{\text{ex}} = 283$ nm), and (d) PL intensity at 441 nm ($\lambda_{\text{ex}} = 350$ nm).

Table S1 Constants in Hill equation obtained by fitting absorbance at 350 nm, θ at 295 nm or PL intensity at 441 nm as a function of Ag^+ concentration^a

	n	$\log K_{\text{app}}$	R^2
Abs @ 350 nm	1.37	6.85	0.990
θ @ 295 nm	1.40	7.02	0.990
I @ 441 nm ^b	1.45	7.18	0.983

^a Hill equation is $\log[Y/(1-Y)] = n \log[\text{Ag}^+] + \log K_{\text{app}}$, in which Y, n, $[\text{Ag}^+]$ and K_{app} represent fraction of ligand binding sites filled, Hill coefficient, Ag^+ concentration and apparent association constant, respectively. For details of Hill plot see, Y.-B. Ran, A.-F. Li, J.-S. Zhao, J.-S. Shen, Y.-B. Jiang, *Chem. Commun.*, 2010, **46**, 4938-4940. ^b Excitation wavelength was 350 nm.

^1H NMR (400 MHz, CD_3OD)



^{13}C NMR (100 MHz, CD_3OD)

