Electronic Supplementary Information (ESI)

Aggregated Coordination Polymers of Ag^+ with a Cysteine Derivative Ligand Containing an AIEgen

Jing-Jing Quan, Qian Wang, Zhao Li and Yun-Bao Jiang*

Department of Chemistry, College of Chemistry and Chemical Engineering, the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, and iChEM, Xiamen University, Xiamen 361005, China

E-mail: ybjiang@xmu.edu.cn

TABLE OF CONTENTS

S1. Experimental Section

S1.1 Materials and Reagents

All reagents of analytical grade were used without further purification. (4-Ethoxycarbonylphenyl) boronic acid, 1-(4-bromophenyl)-1,2,2-triphenylethylene, Tetrakis(triphenylphosphine)palladium, 1-(4-carboxyphenyl)-1,2,2-triphenylethene, triethylamine (NEt_3), 1-hydroxybenzotriazole (HOBT), and *N*, *N*′-dicyclohexylcarbodiimide (DCC) were purchased from Energy Chemical. K_2CO_3 (>98%), KOH (>99%), $AgNO_3$ (>99%) and Na_2SO_4 (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. L- and D-Cysteine ethyl ester hydrochloride (L-/D-CysOEt·HCl) were obtained from GL Biochem (Shanghai, China).

S1.2 Physical Measurements and Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend III NMR Spectrometer (600 or 850 MHz) using $Si(CH_3)_4$ as an internal standard. High-resolution mass spectrometry (HRMS) data were acquired on a Bruker Impact II spectrometer and Bruker autoflex maX MALDI-TOF MS, UV-Vis absorption spectra were collected on Varian Cary 300 UV spectrophotometer. CD spectrometry was conducted on JASCO J-810 Circular Dichroism Chiroptical Spectrometer. Emission spectra were obtained from a HITACHI F-4500 spectrofluorometer. Dynamic light scattering (DLS) data were collected on a Malvern Nano S90 Malvern Zetasizer Nano ZS. TEM images were taken on a JEM 1400 Transmission Electron Microscope with an accelerating voltage of 100 kV. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 microscope.

S2. Synthetic Details

S2.1 Synthesis

Synthesis of compound **TPE-Ph-COOH**. This was synthesized according to a modified procedure described in the literature for a related compound.[1,2] Briefly, 1-(4-

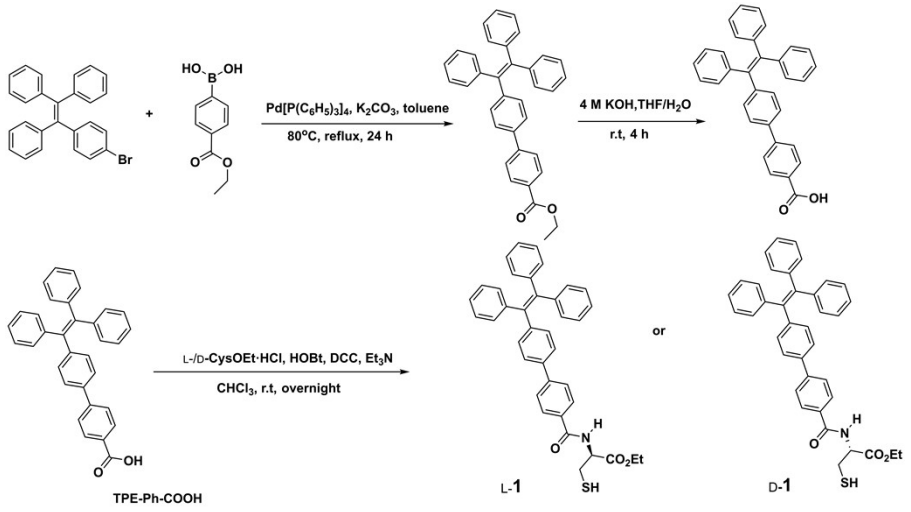
bromophenyl)-1,2,2-triphenylethylene (1.23 g, 3 mmol), (4-ethoxycarbonylphenyl)-boronic acid (0.63 g, 3 mmol), K_2CO_3 (0.84 g, 9 mmol), and dry toluene (25 mL) were added to a 100 mL 2-necked round flask. The mixture was bubbled with nitrogen for 30 min and equipped with a water condenser. Tetrakis(triphenylphosphine)palladium (0.03 g) was then added to the reaction mixture and stirred at 80 °C for 24 h under nitrogen. After the completion of reaction, monitored by TLC, the precipitates were removed and filtrate was collected. The obtained crude product was purified by silica gel column chromatography eluting with 3:1 (v/v) petroleum ether/dichloromethane to afford a bright yellow solid (0.94 g, 75%). The target molecule was obtained by hydrolyzing of the ethyl eater group. Then the ester was dissolved in THF (20 mL) and H_2O (20 mL) containing KOH (4.45 g) and the solution was refluxed for 4 h. After cooling, the solvent was evaporated and water (10 mL) and 5 N HCl solution were added to adjust solution pH to 3. The precipitate was filtered, washed with water, and dried to give the product **TPE-Ph-COOH** (96%, 1.03 g). **^{1}H NMR** (600 MHz, DMSO-*d*6, 298 K): δ (ppm) = 12.96 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.20 - 6.96 (m, 17H). **^{13}C NMR** (151 MHz, DMSO-*d*6, 298 K): δ (ppm) = 167.16 (s), 143.52 (s), 143.33 (s), 143.26 - 142.97 (m), 141.11 (s), 140.02 (s), 136.77 (s), 131.48 (s), 130.89 - 130.55 (m), 130.03 (s), 129.59 (s), 128.14 - 127.79 (m), 126.92 - 126.64 (m), 126.54 (s), 126.30 (s), 54.98 (s). **HRMS** (**ESI$^-$**): calcd. for $[M-H]^-$, 451.1704. Found: 451.1707.

Synthesis of compound L-**1** or D-**1**: 1.03 g **TPE-Ph-COOH** was dispersed in $CHCl_3$ under an ice bath, to which 2.5 mL triethylamine, 1-hydroxybenzotriazole (0.32 g, 2.4 mmol) and *N*, *N*′-dicyclohexylcarbodiimide (0.49 g, 2.4 mmol) were added and the mixture was stirred at 0°C for 40 min. A $CHCl_3$ solution (10 mL) of L- or D-cysteine ethyl ester hydrochloride (0.37 g, 2.0 mmol) was then added dropwise and the resultant solution was stirred at room temperature for 8 h. The solvent was removed by rotary evaporation, leading to an oily liquid. A saturated aqueous $NaHCO_3$ solution (30 mL) was added and the mixture was extracted with CH_2Cl_2

(DCM, 3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel, leading to a bright yellow solid.

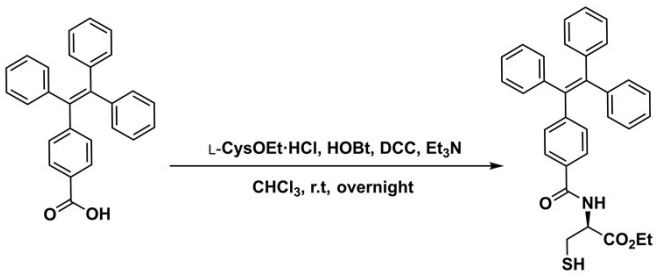
L-**1**: Yield: 979 mg (1.68 mmol, 74 %). **^{1}H NMR** (600 MHz, DMSO-*d*6, 298 K): δ (ppm) = 8.82 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.19 - 6.98 (m, 17H), 4.64 - 4.47 (m, 1H), 4.14 (ddd, *J* = 9.9, 7.5, 3.3 Hz, 2H), 3.05 - 2.96 (m, 1H), 2.95 - 2.86 (m, 1H), 2.68 (t, *J* = 8.5 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, DMSO-*d*6, 298 K): δ (ppm) = 170.41 (s), 166.22 (s), 143.29 - 142.94 (m), 142.27 (s), 140.96 (s), 139.98 (s), 136.80 (s), 132.31 (s), 131.39 (s), 130.88 - 130.49 (m), 128.15 (s), 128.07 - 127.72 (m), 126.89 - 126.36 (m), 126.19 (d, *J* = 8.4 Hz), 60.82 (s), 55.67 (s), 25.00 (s), 14.07 (s). **HRMS** (**ESI$^+$**): calcd. for $[M+H]^+$, 584.2254, $[M+Na]^+$, 606.2073. Found: 584.2255; 606.2077.

D-**1**: Yield: 913 mg (1.56 mmol, 69%). **^{1}H NMR** (600 MHz, DMSO-*d*6, 298 K): δ (ppm) = 8.83 (d, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.17 - 6.98 (m, 17H), 4.59 (dd, *J* = 12.8, 8.2 Hz, 1H), 4.14 (dd, *J* = 6.9, 4.6 Hz, 2H), 3.05 - 2.98 (m, 1H), 2.92 (dd, *J* = 22.3, 8.7 Hz, 1H), 2.68 (t, *J* = 8.5 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, DMSO-*d*6, 298 K): δ (ppm) = 170.41 (s), 166.23 (s), 143.09 (s), 142.28 (s), 140.96 (s), 139.98 (s), 136.81 (s), 132.32 (s), 131.40 (s), 130.89 - 130.50 (m), 128.16 (s), 128.07 - 127.66 (m), 126.89 - 126.35 (m), 126.19 (d, *J* = 8.7 Hz), 60.83 (s), 55.68 (s), 39.52 (s), 26.34 (s), 25.02 (s), 14.07 (s). **HRMS** (**ESI$^+$**): calcd. for $[M+H]^+$, 584.2254, $[M+Na]^+$, 606.2073. Found: 584.2256; 606.2080.



Scheme S1. Synthesis of compounds L-**1** and D-**1**.

Synthesis of compound L-**2**: 1-(4-carboxyphenyl)-1,2,2-triphenylethene (0.72 g, 2.00 mmol) and triethylamine (2.5 mL) were added into $CHCl_3$ suspension (20 mL). The reaction mixture was cooled down to 0 °C, then, 1-hydroxybenzotriazole (0.32 g, 2.4 mmol) and *N*, *N*′-dicyclohexylcarbodiimide (0.49 g, 2.4 mmol) were added. After the addition was complete, the mixture was stirred at 0°C for 40 min. Then, the mixture was added dropwise a $CHCl_3$ solution (10 mL) of L-cysteine ethyl ester hydrochloride (0.37 g, 2.00 mmol). After being stirred at room temperature for 8 h, the mixture was washed with diluted brine and saturated $NaHCO_3$, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and then purified by column chromatography on silica gel using dichloromethane- methanol (100:1, v/v) as eluent. A white solid was obtained after solvent removal under reduced pressure. Yield: 775 mg (1.52 mmol, 76%). **^{1}H NMR** (600 MHz, DMSO-*d*6, 298 K): δ (ppm) = 8.70 (d, *J* = 6.8 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.19 - 6.97 (m, 17H), 4.52 (d, *J* = 3.3 Hz, 1H), 4.19 - 4.07 (m, 2H), 3.02 - 2.83 (m, 2H), 2.66 (t, *J* = 8.1 Hz, 1H), 1.19 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR** (151 MHz, DMSO-*d*6, 298 K): δ (ppm) = 170.38 (s), 166.21 (s), 146.66 (s), 142.79 (d, *J* = 19.6 Hz), 141.54 (s), 139.76 (s), 131.44 (s), 130.62 (d, *J* = 9.7 Hz), 128.21 - 127.71 (m), 127.12 (s), 126.80 (d, *J* = 19.0 Hz), 60.81 (s), 55.65 (s), 39.52 (s), 24.94 (s), 14.06 (s). **HRMS** (**ESI$^+$**): calcd. for $[M+H]^+$, 508.1941, $[M+Na]^+$, 530.1760. Found: 508.1944; 530.1762.



Scheme S2. Synthesis of L-**2**.

S2.2 References

1. Q. Ye, F. Zheng, E. Zhang, H. K. Bisoyi, S. Zheng, D. Zhu, Q. Lu, H. Zhang and Q. Li, *Chem. Sci*, 2020, **11**, 9989.

2. G. Q. Yin, S. Kandapal, C. H. Liu, H. Wang, J. Huang, S. T. Jiang, T. Ji, Y. Yan, S. Khalife, R. Zhou, L. Ye, B. Xu, H. B. Yang, M. P. Nieh and X. Li, *Angew. Chem., Int. Ed.*, 2021, **60**, 1281.

S3. Additional Data

S3.1 Experimental Data

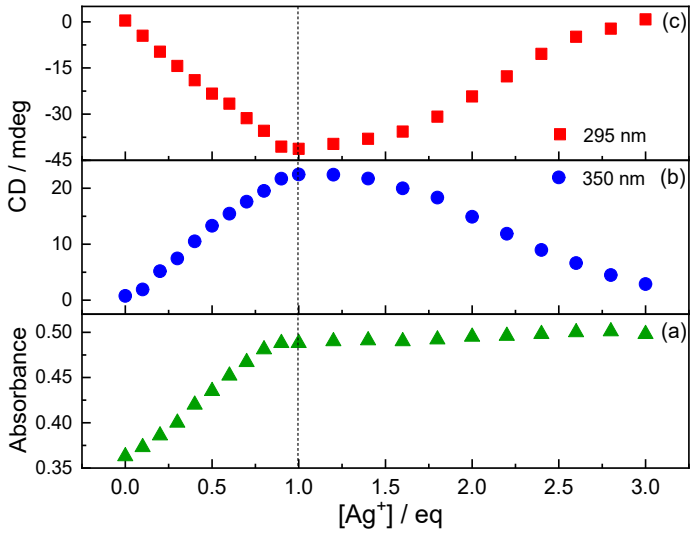


Fig. S1 Plots of absorbance at 350 nm (a) and CD signals at 350 nm (b) and 295 nm (c) of D-**1** in THF in the presence of Ag^+ of increasing concentration. [D-**1**] = 25 μM, [Ag^+] = 0 - 75 μM.

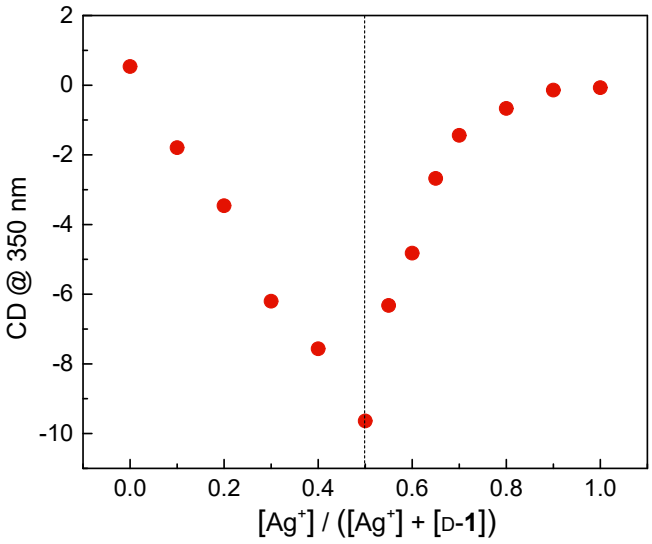


Fig. S2 Job's plot establishing 1:1 stoichiometry of the binding of D-**1** with Ag^+ using CD signal at 350 nm.

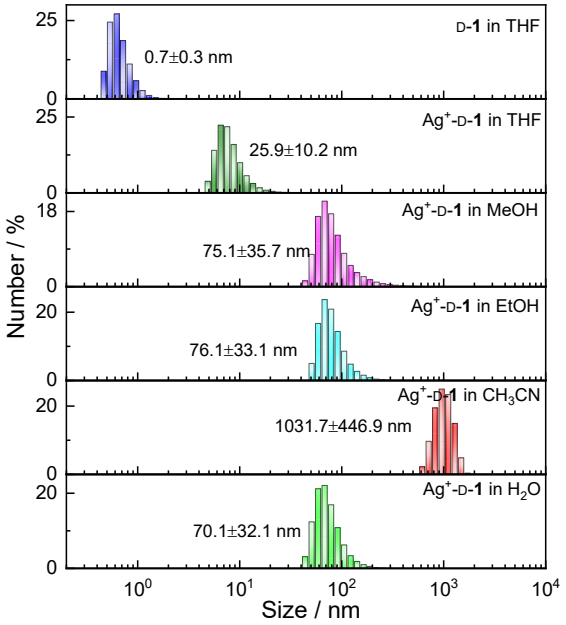


Fig. S3 Dynamic light scattering analyses of size distributions of Ag^+-D-**1** coordination polymer in different solvents. [D-**1**] = [Ag^+] = 25 μM.

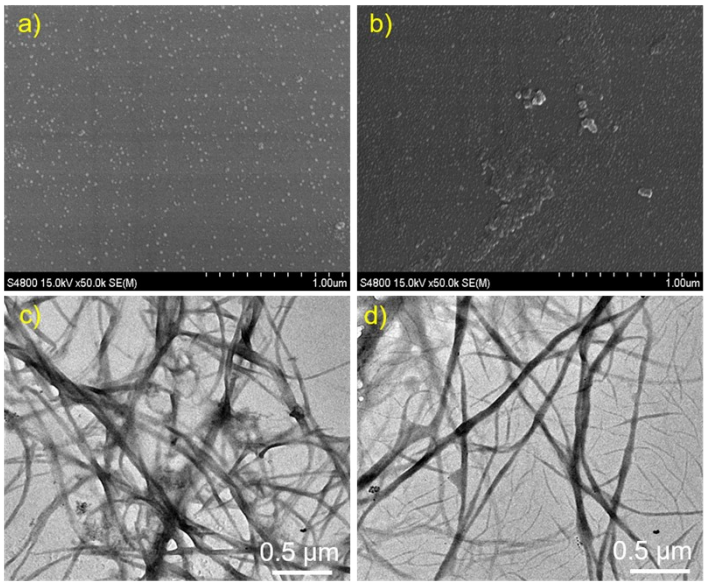


Fig. S4 SEM (a, b) and TEM (c, d) images of supramolecular structures formed in THF solution of L-**1** (a), D-**1** (b), Ag^+-L-**1** (c) and Ag^+-D-**1** (d).

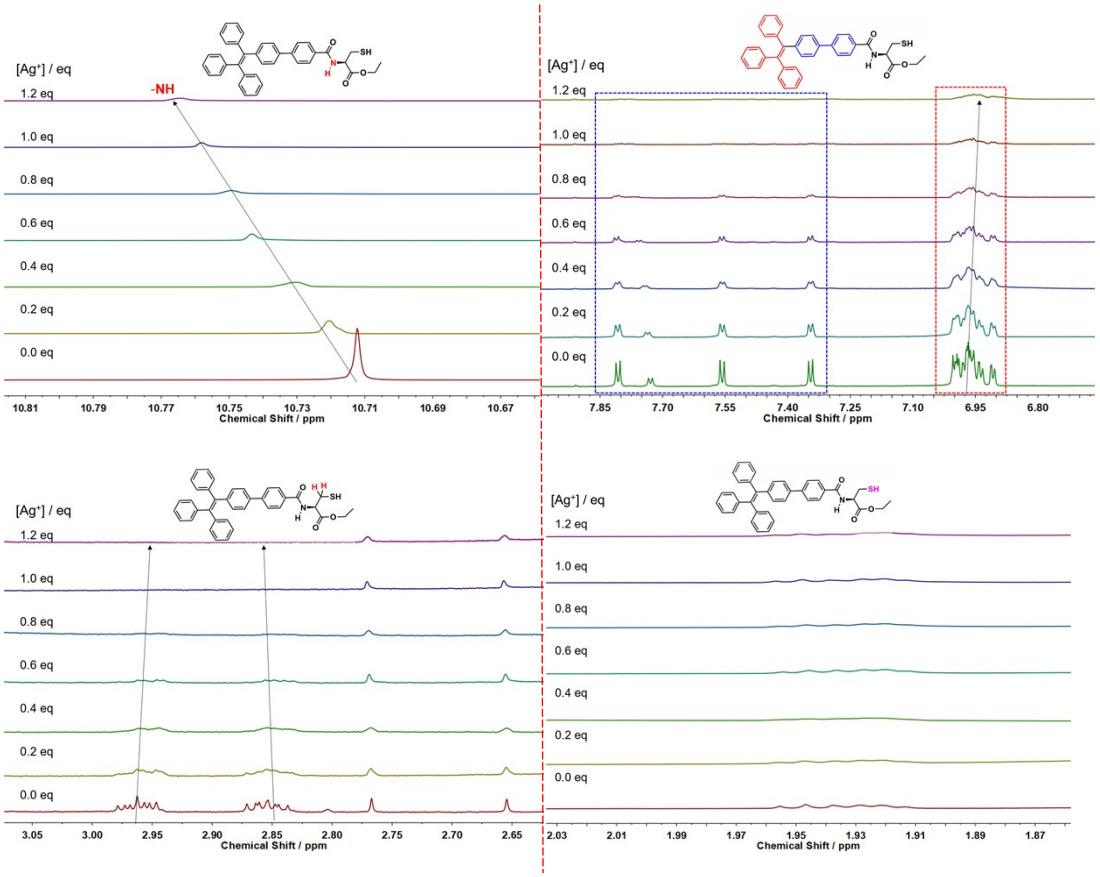


Fig. S5 Partial ^{1}H NMR spectra of L-**1** in THF-d_8 in the presence of Ag^+. [L-**1**] = 25 μM, [Ag^+] = 0 - 30 μM.

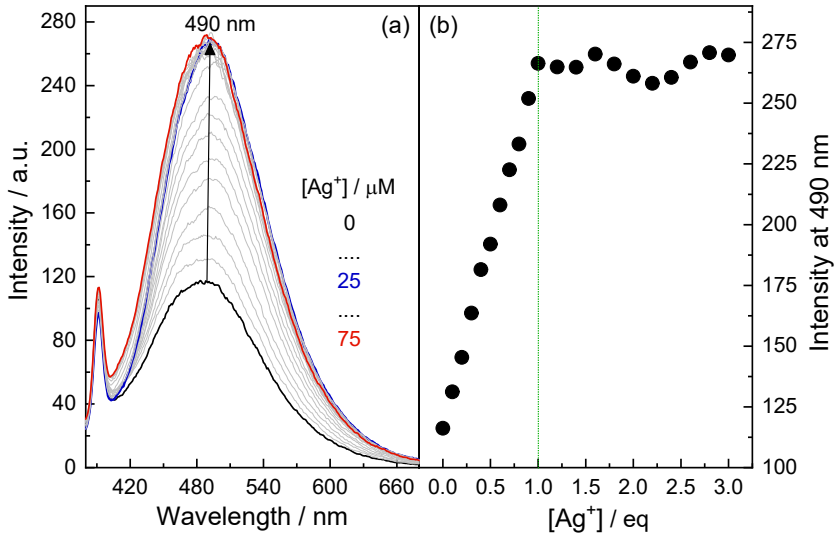


Fig. S6 (a) Fluorescence spectra of D-**1** in THF upon titration by Ag^+ and (b) plots of fluorescence intensity at 490 nm versus concentration of Ag^+. λex = 350 nm, [D-**1**] = 25 μM, [Ag^+] = 0 - 75 μM.

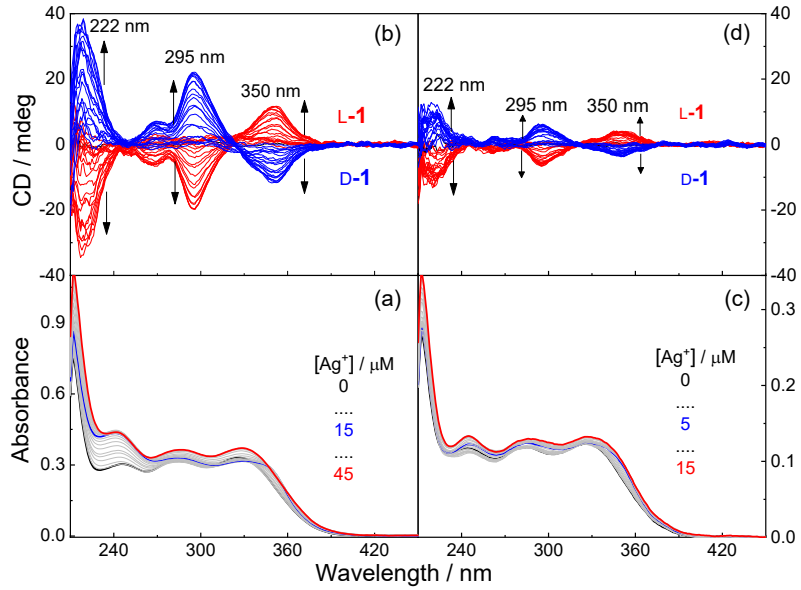


Fig. S7 Absorption (a, c) and CD (b, d) spectra of L-/D-**1** in THF in the presence of Ag^+ of increasing concentration. [L-**1**] = [D-**1**] = 15 μM (a, b), 5 μM (c, d).

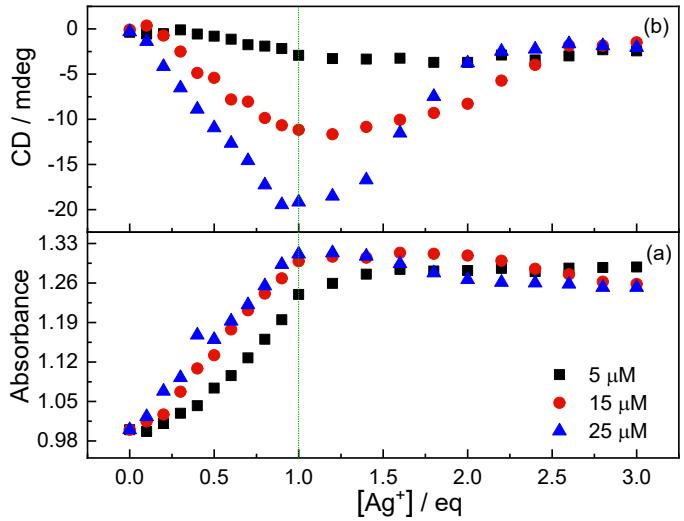


Fig. S8 Plots of enhancement in absorbance (a) and CD signal (b) of D-**1** at 350 nm in THF against concentration of Ag^+. [D-**1**] = 5 μM, 15 μM, 25 μM, [Ag^+] = 0 - 75 μM.

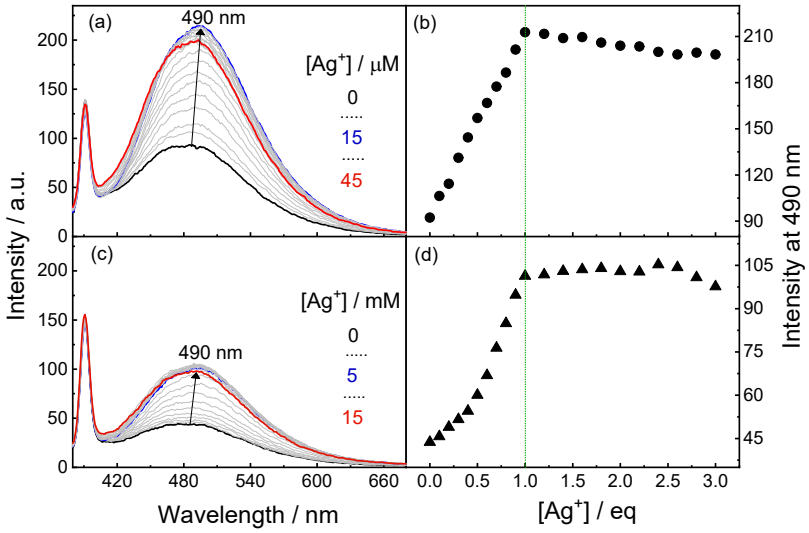


Fig. S9 Fluorescence spectra of D-**1** (a, c) in THF in the presence of Ag^+ and plots of fluorescence intensity at 490 nm (b, d) versus concentration of Ag^+. λex = 350 nm; [D-**1**] = 15 μM (a, b), 5 μM (c, d).

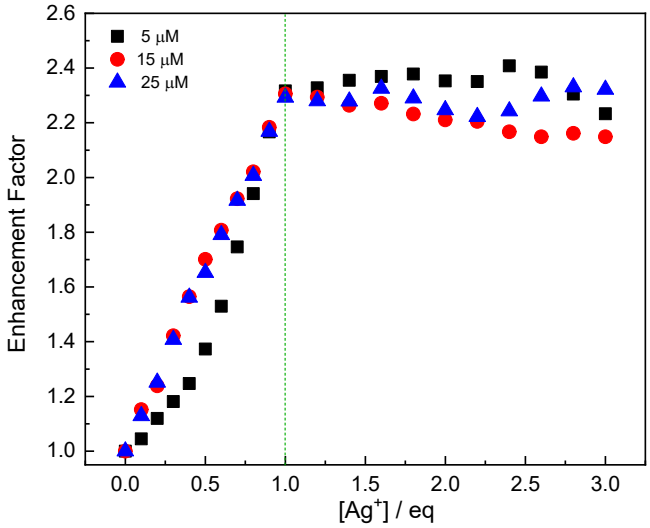


Fig. S10 Enhancement of fluorescence intensity at 490 nm of D-**1** in THF by Ag^+ of increasing concentration. [D-**1**] = 5 μM, 15 μM, 25 μM, [Ag^+] = 0 - 75 μM.

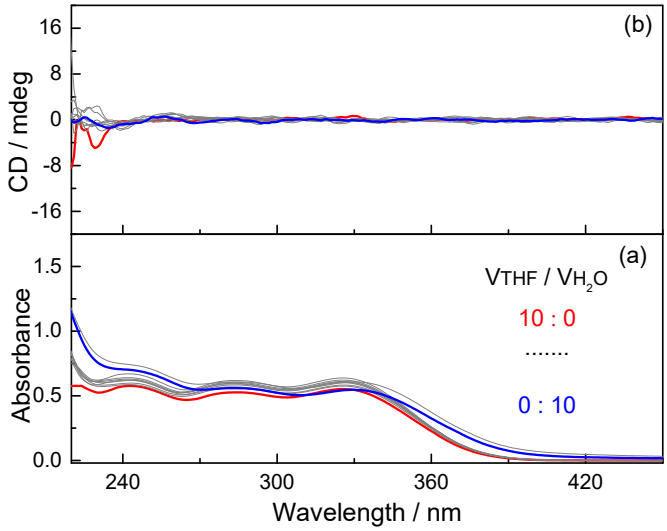


Fig. S11 Absorption (a) and CD (b) spectra of D-**1** in THF containing varying content of water. [D-**1**] = 25 μM.

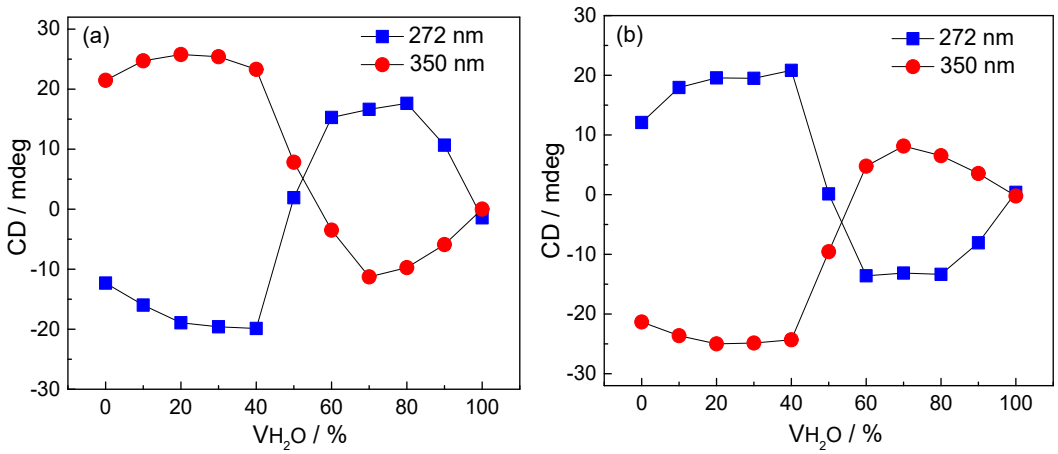


Fig. S12 CD signals at 272 nm and 350 nm of Ag$^+$-L-**1** (a) and Ag$^+$-D-**1** (b) in THF containing increasing water content. [Ag$^+$-L-**1**] = [Ag$^+$-D-**1**] = 25 μM.

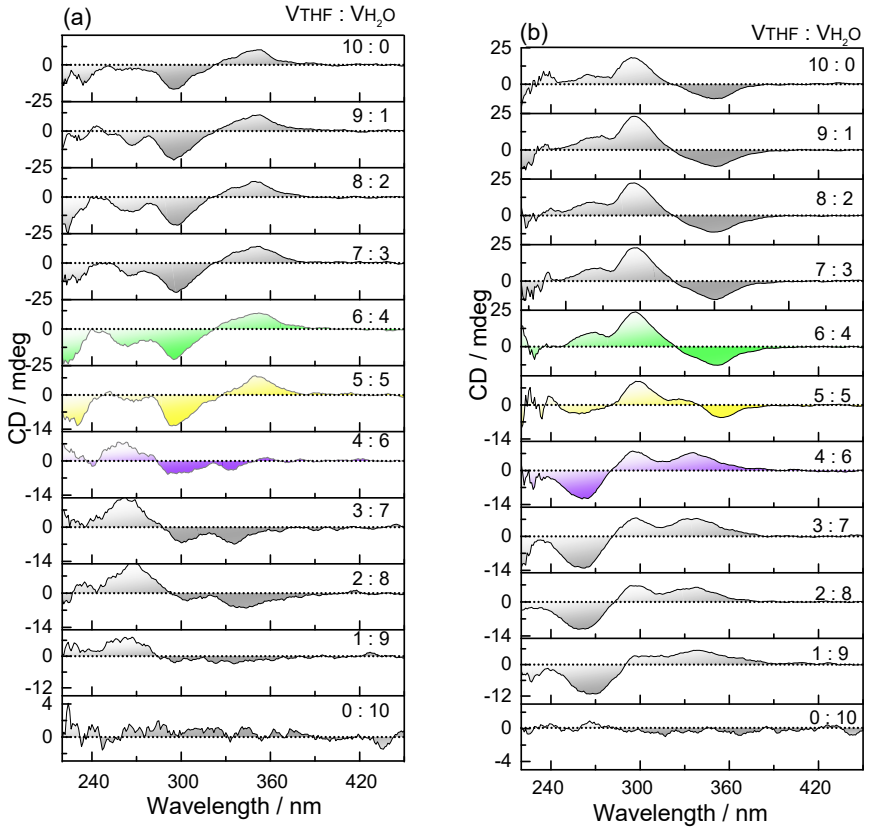


Fig. S13 Traces of CD spectra of Ag$^+$-L-**1** (a) and Ag$^+$-D-**1** (b) coordination polymers in THF containing increasing fraction by volume water. [Ag$^+$-L-**1**] = [Ag$^+$-D-**1**] = 15 μM.

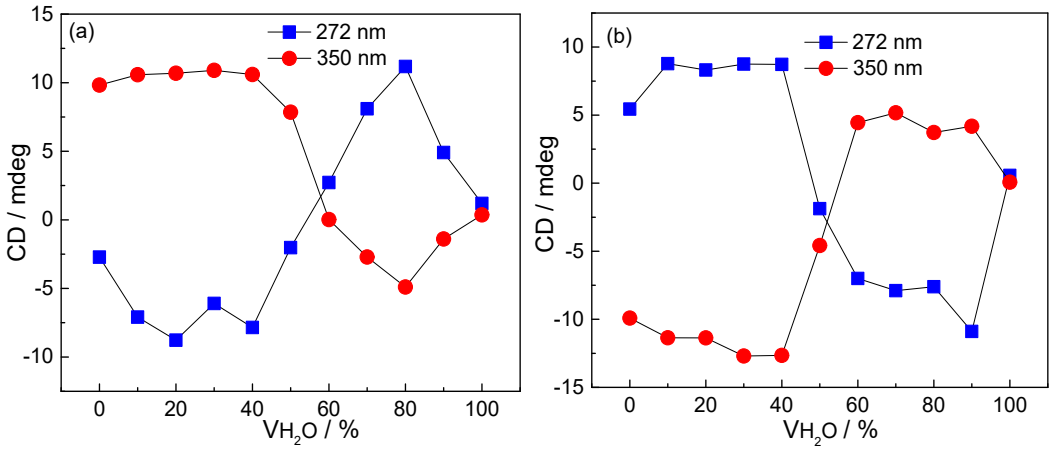


Fig. S14 CD signals at 272 nm and 350 nm of Ag^{+}-L-**1** (a) and Ag^{+}-D-**1** (b) coordination polymers in THF containing increasing fraction by volume water. [Ag^{+}-L-**1**] = [Ag^{+}-D-**1**] = 15 μM.

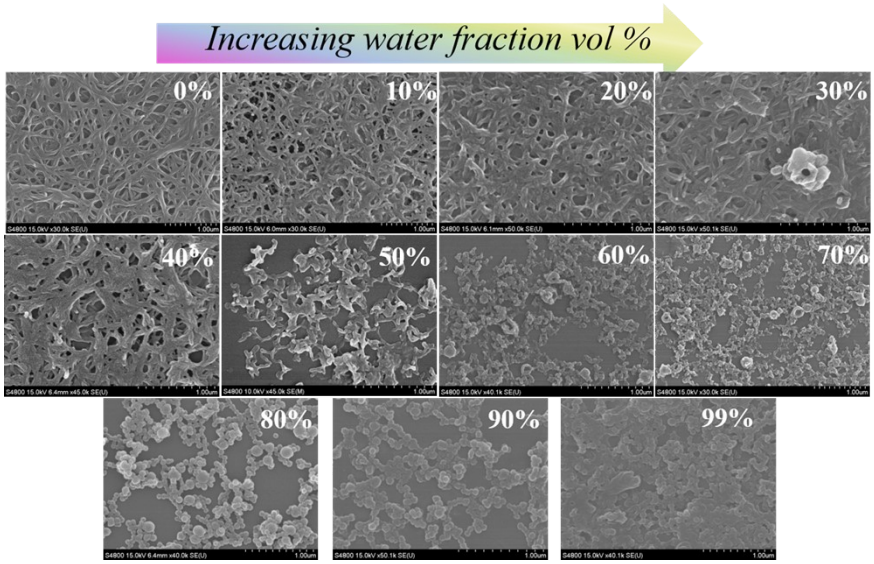


Fig. S15 SEM images of Ag^{+}-D-**1** coordination polymers formed in H_2O/THF of increasing water volume fraction. [Ag^{+}-D-**1**] = 25 μM.

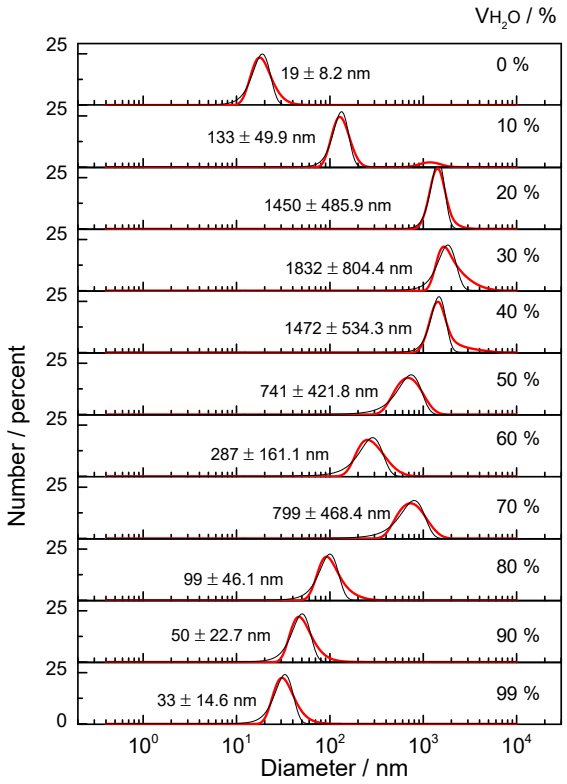


Fig. S16 DLS size distribution of Ag^{+}-D-**1** coordination polymers in H_2O/THF mixture of increasing water volume fraction. [Ag^{+}-D-**1**] = 25 μM.

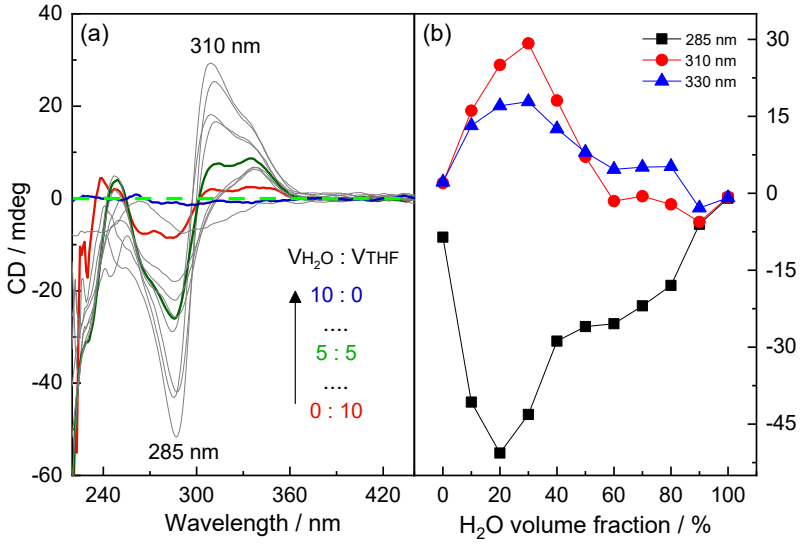


Fig. S17 (a) CD spectra and (b) plots of CD signals of Ag^{+}-L-**2** coordination polymers in H_2O/THF of varying water volume fraction. [Ag^{+}-L-**2**] = 25 μM.

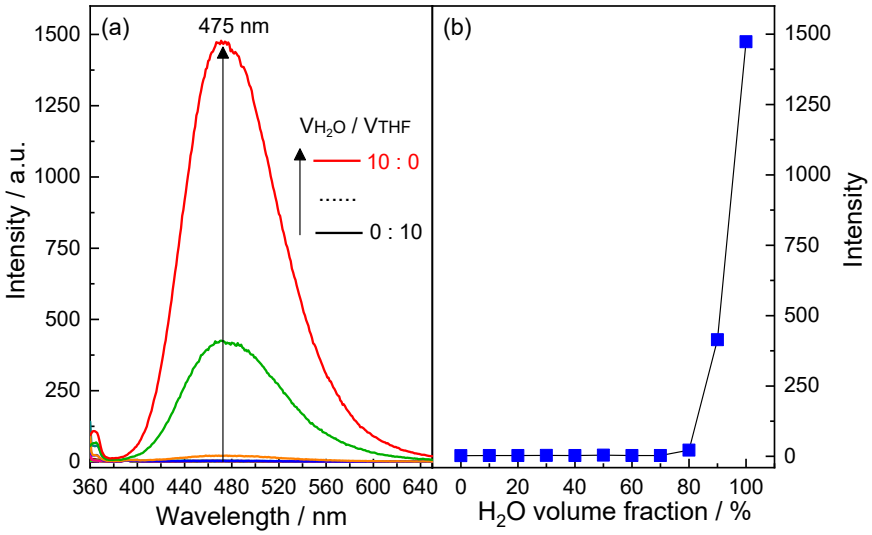


Fig. S18 (a) Fluorescence spectra of L-**2** in H_2O/THF binary solvent of varying volume ratio and (b) plots of fluorescence intensity at 475 nm of L-**2** versus water volume fraction. λex = 350 nm, [L-**2**] = 25 μM.

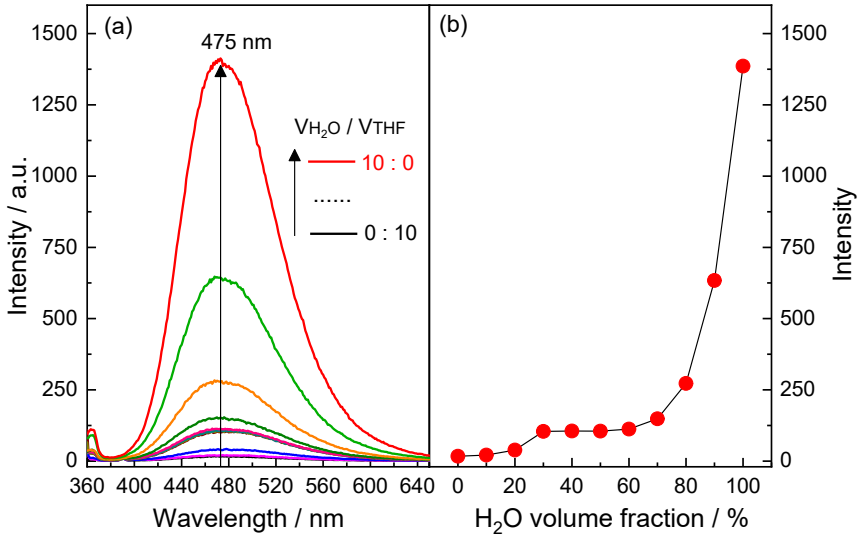


Fig. S19 (a) Fluorescence spectra of Ag^+-L-**2** coordination polymers in H_2O/THF binary solvent of varying volume ratio and (b) plots of fluorescence intensity at 475 nm of Ag^+-L-**2** versus water volume fraction. λex = 350 nm, [Ag^+-L-**2**] = 25 μM.

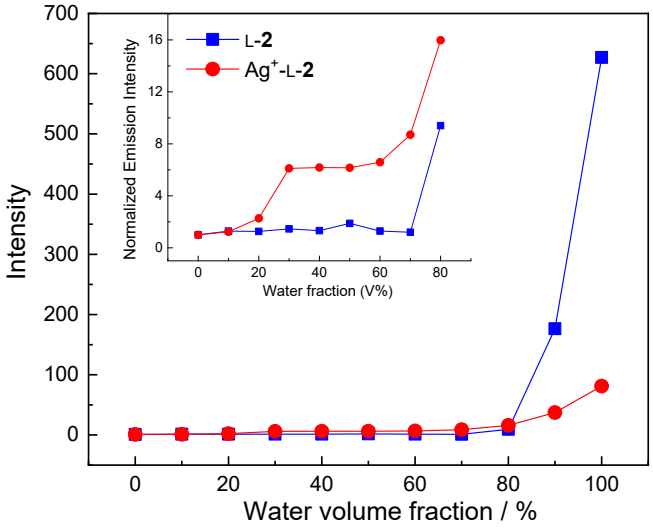


Fig. S20 Fluorescence intensity of L-**2** (blue square) and Ag^{+}-L-**2** coordination polymer (red dot) at 475 nm in THF containing water of varying volume fraction. Inset shows fluorescence intensity enhancement factor as a function of water volume fraction in H_2O/THF. λex = 350 nm, [L-**2**] = [Ag^{+}-L-**2**] = 25 μM.

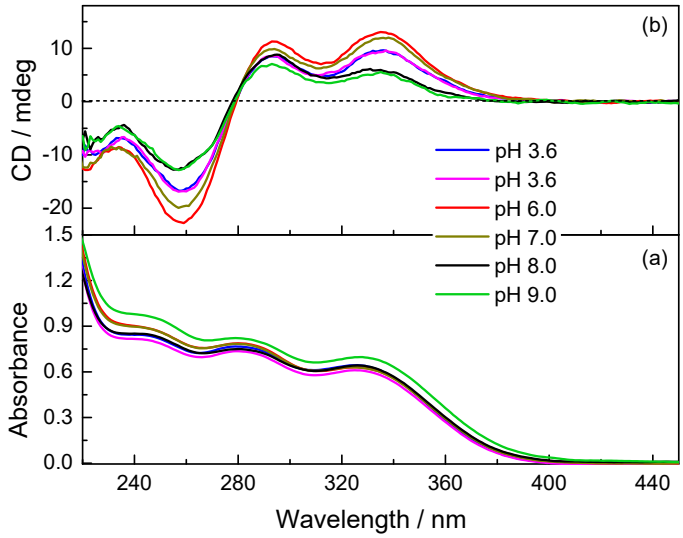


Fig. S21 Absorption (a) and CD spectra (b) of Ag^{+}-D-**1** coordination polymers in 3:7 (v/v) THF/H_2O binary mixtures of varying pH. [Ag^{+}-D-**1**] = 25 μM.

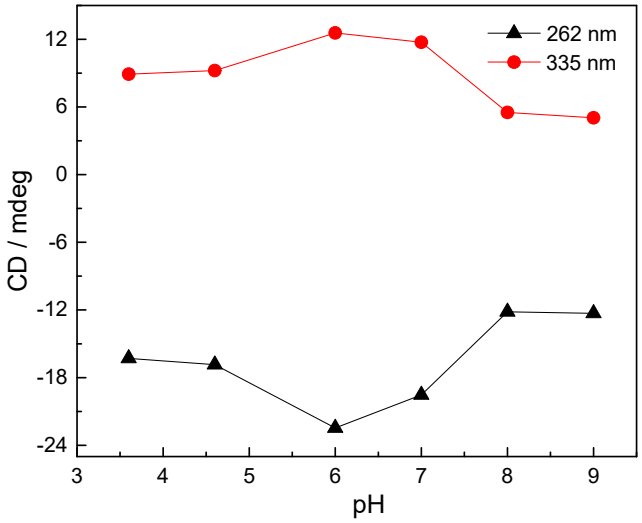


Fig. S22 Plots of CD signals of Ag^{+}-D-**1** coordination polymers in 3:7 (v/v) THF/H_2O binary mixture against pH. [Ag^{+}-D-**1**] = 25 μM.

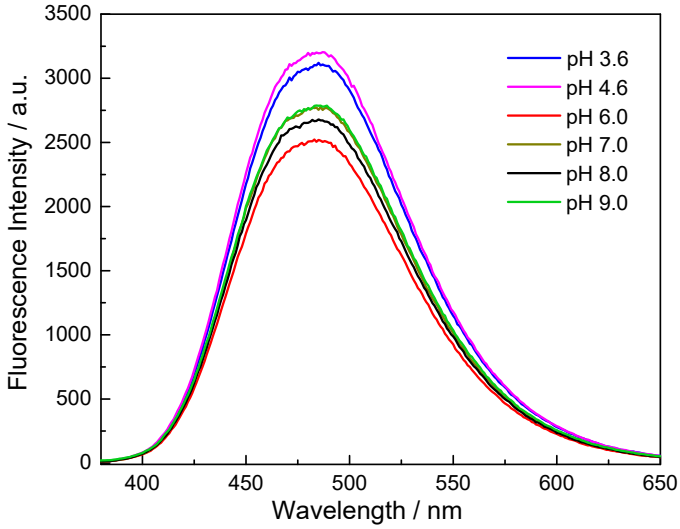


Fig. S23 pH-dependent emission spectra of Ag^{+}-D-**1** coordination polymers in 3:7 (v/v) THF/H_2O binary mixtures of varying pH. Excitation wavelength is 350 nm; [Ag^{+}-D-**1**] = 25 μM.

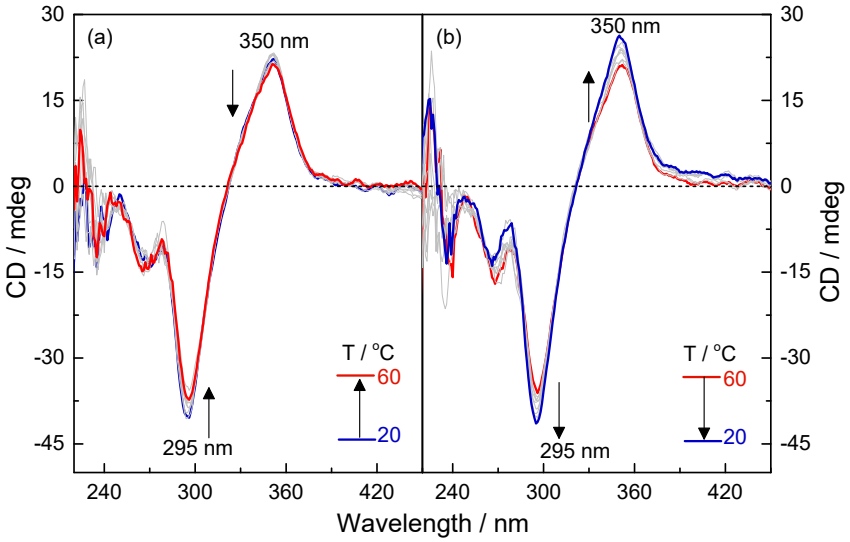


Fig. S24 Temperature-dependent CD spectra of Ag^{+}-L-**1** coordination polymers in THF upon heating (a) and later cooling (b). [Ag^{+}] = [L-**1**] = 25 μM.

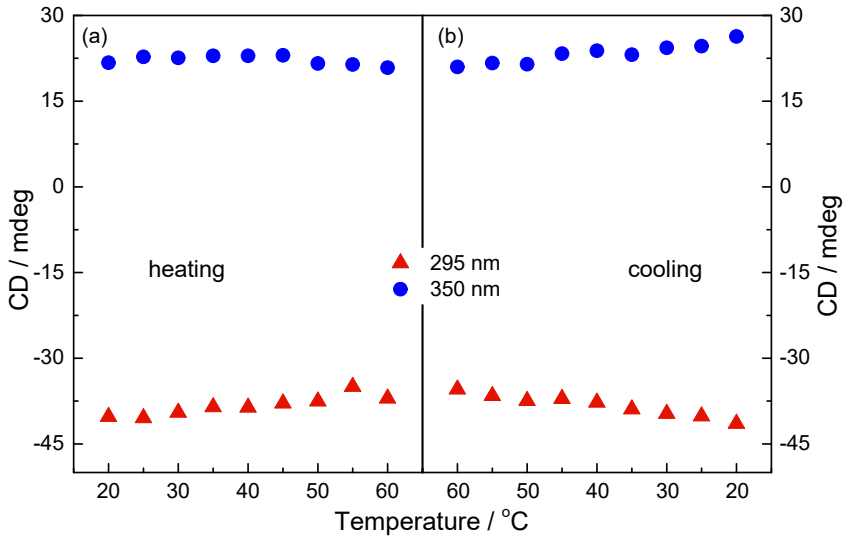


Fig. S25 Plots of CD signals at 295 nm and 350 nm of Ag^{+}-L-**1** coordination polymers in THF against temperature. [Ag^{+}] = [L-**1**] = 25 μM.

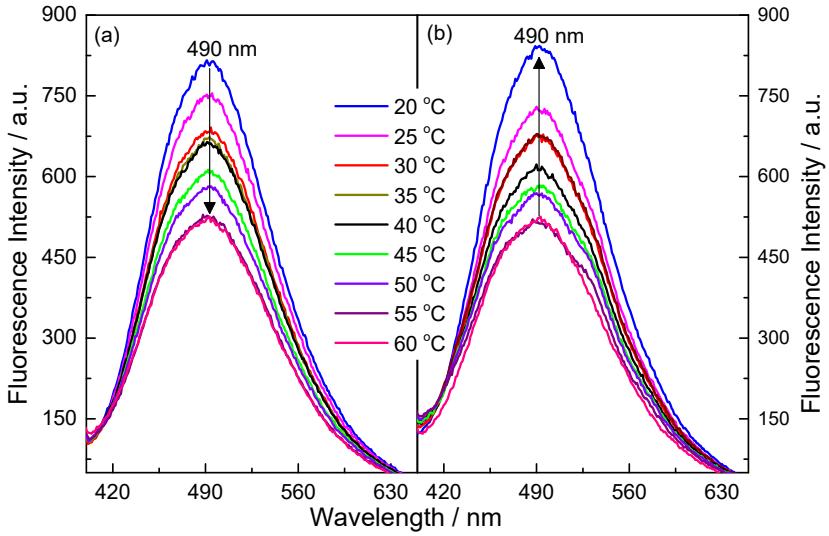


Fig. S26 Temperature-dependent fluorescence spectra of Ag^{+}-L-**1** coordination polymers in THF upon heating (a) and later cooling (b). λex = 350 nm, [Ag^{+}] = [L-**1**] = 25 μM.

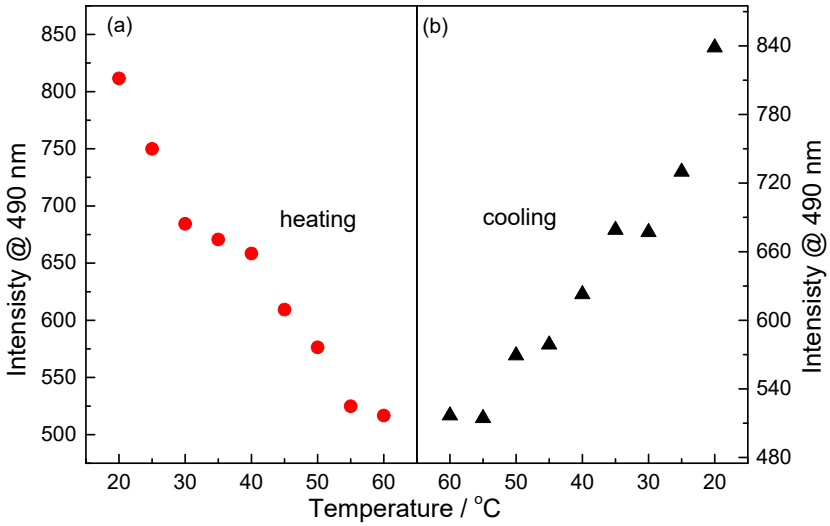


Fig. S27 Plots of emission intensity at 490 nm of Ag^{+}-L-**1** coordination polymers in THF against temperature. λex = 350 nm, [Ag^{+}] = [L-**1**] = 25 μM.

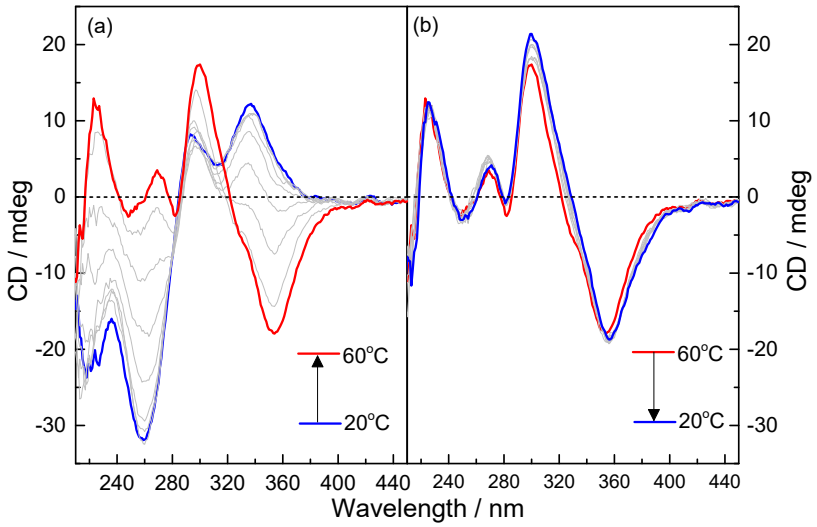


Fig. S28 Temperature-dependent CD spectra of Ag^+-D-**1** coordination polymers in 3:7 (v/v) THF/H_2O upon heating (a) and later cooling (b). [Ag^+] = [D-**1**] = 25 μM.

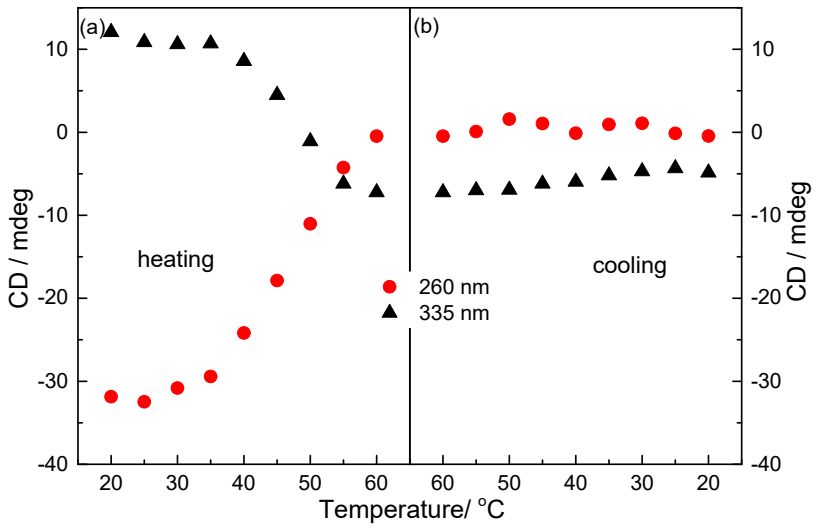


Fig. S29 Plots of CD signals at 260 nm and 335 nm of Ag^+-D-**1** coordination polymers in 3:7 (v/v) THF/H_2O against temperature. [Ag^+] = [D-**1**] = 25 μM.

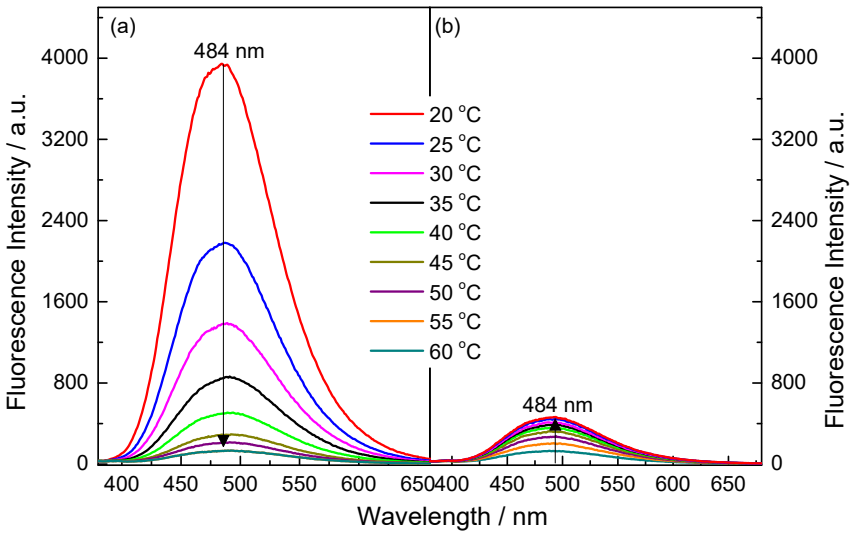


Fig. S30 Temperature-dependent fluorescence spectra of Ag^+-L-**1** coordination polymers in 3:7 (v/v) THF/H_2O upon heating (a) and later cooling (b). λex = 350 nm, [Ag^+] = [L-**1**] = 25 μM.

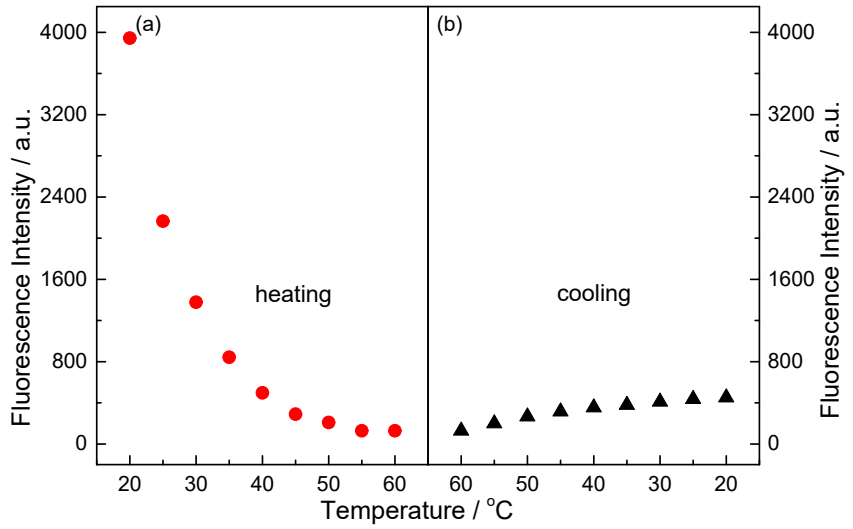


Fig. S31 Plots of emission intensity at 484 nm of Ag^+-L-**1** coordination polymers in 3:7 (v/v) THF/H_2O against temperature. λex = 350 nm, [Ag^+] = [L-**1**] = 25 μM.

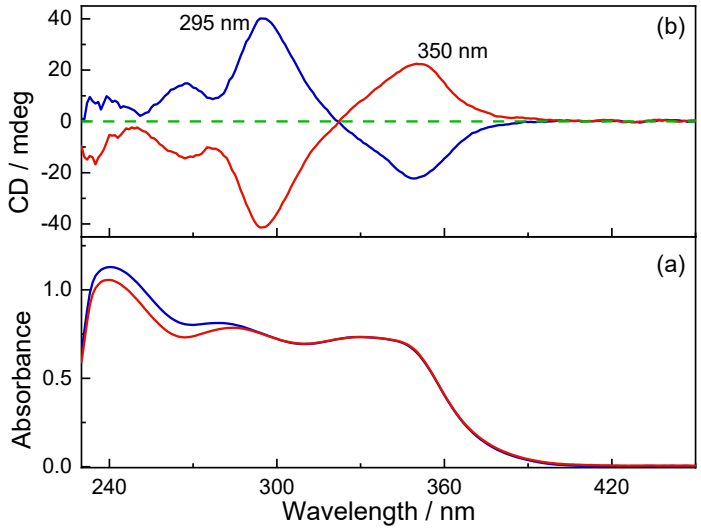


Fig. S32 Absorption (a) and CD (b) spectra of Ag^+-L-**1** (red) and Ag^+-D-**1** (blue) coordination polymers in THF. [Ag^+] = [L-/D-**1**] = 25 μM.

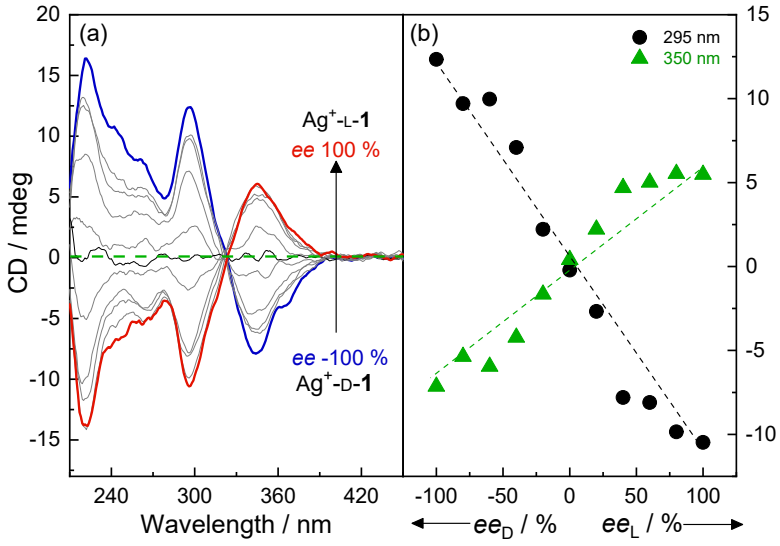


Fig. S33 (a) CD spectra of Ag^+-**1** coordination polymers in CH_3CN of varying *ee* of **1** and (b) plots of CD signals at 295 nm and 350 nm versus *ee*. [Ag^+] = 25 μM, [L-**1**] + [D-**1**] = 25 μM.

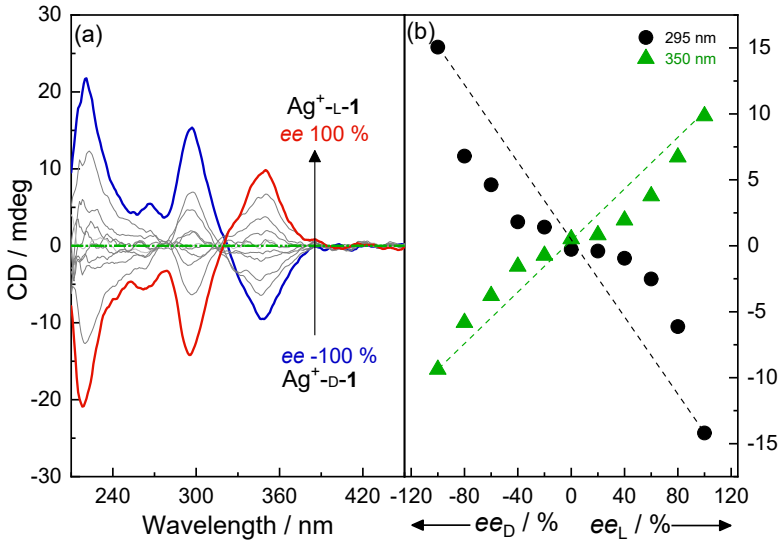


Fig. S34 (a) CD spectra of Ag^+-**1** coordination polymers in CH_3OH of varying *ee* of **1** and (b) plots of CD signals at 295 nm and 350 nm versus *ee*. [Ag^+] = 25 μM, [L-**1**] + [D-**1**] = 25 μM.

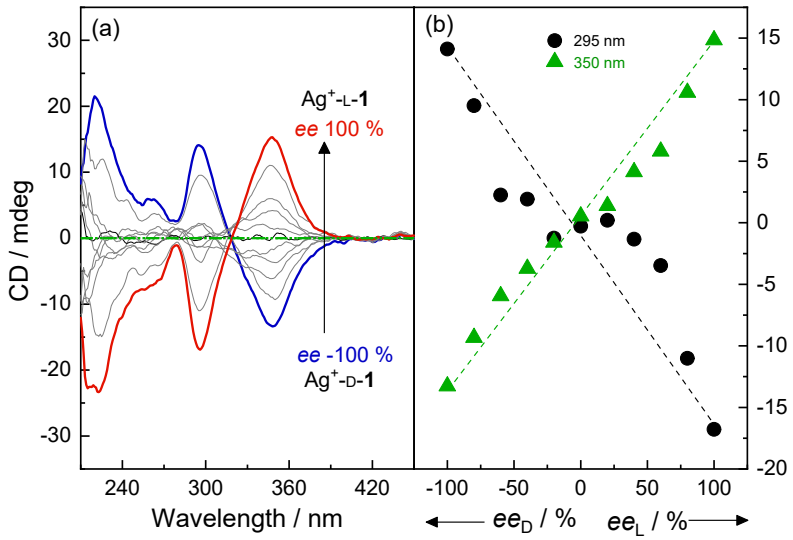


Fig. S35 (a) CD spectra of Ag^+-**1** coordination polymers in C_2H_5OH of varying *ee* of **1** and (b) plots of CD signals at 295 nm and 350 nm versus *ee*. [Ag^+] = 25 μM, [L-**1**] + [D-**1**] = 25 μM.

S3.2 ^{1}H NMR and ^{13}C NMR Spectra and HRMS of New Compounds

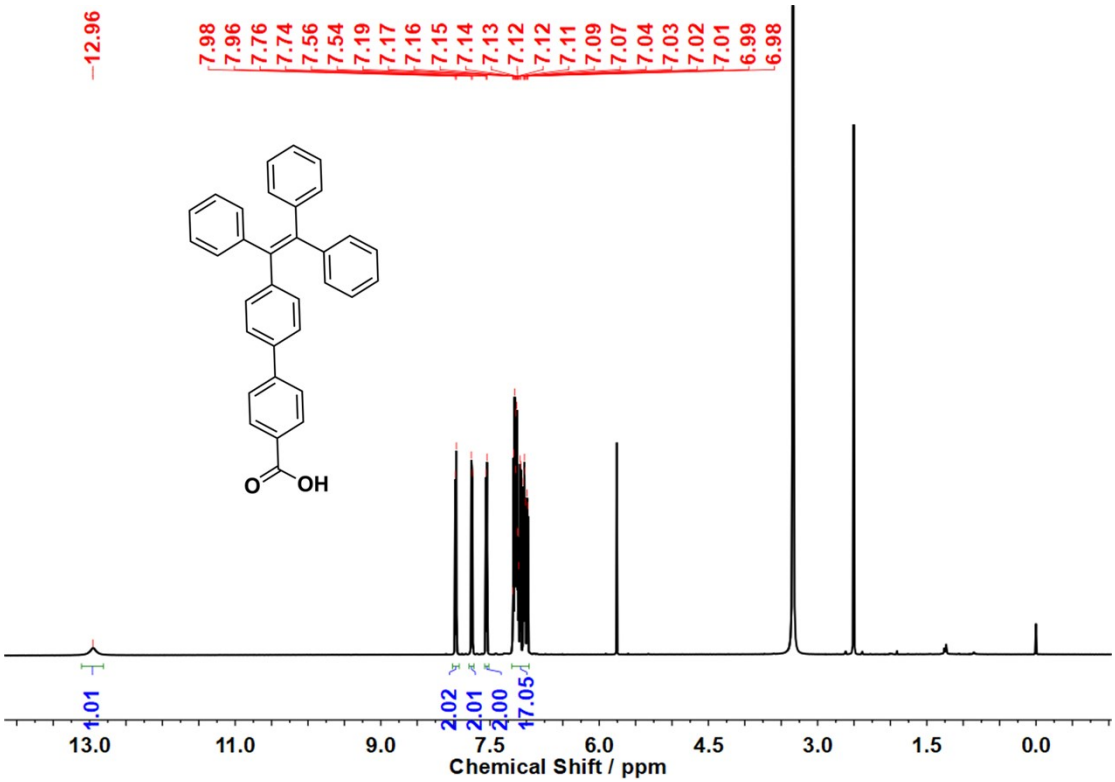


Fig. S36 ^{1}H NMR (600 MHz, DMSO-*d*6) spectrum of **TPE-Ph-COOH**.

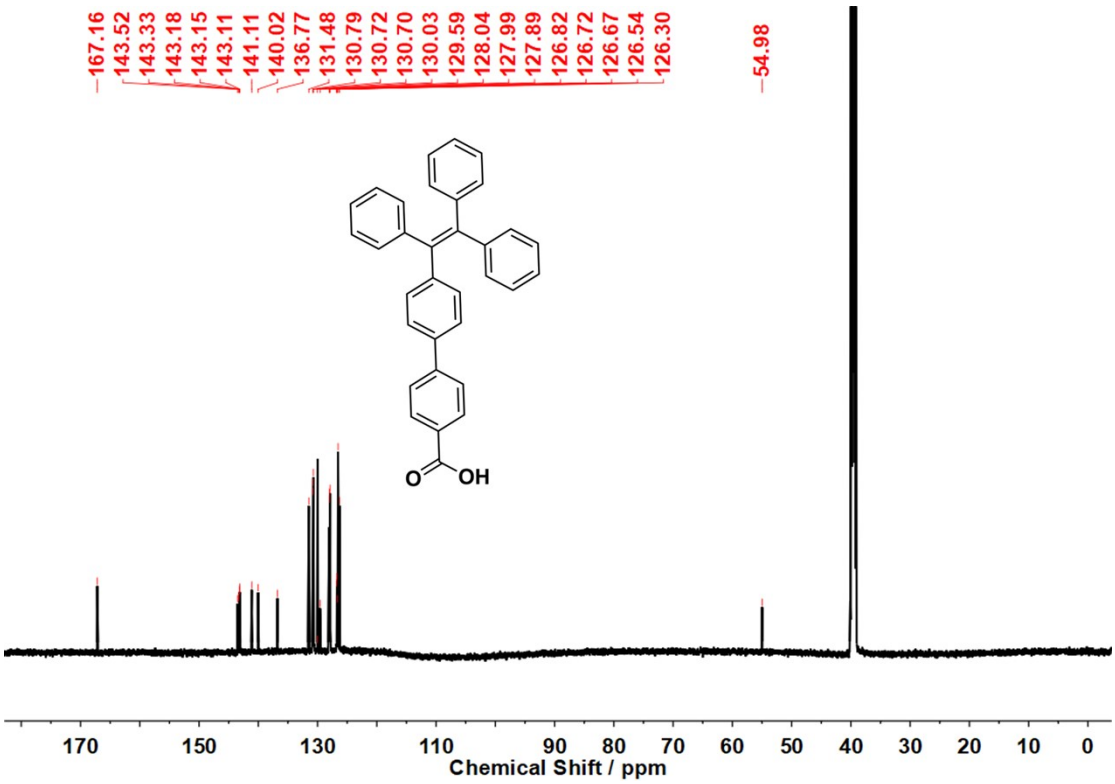


Fig. S37 ^{13}C NMR (151 MHz, DMSO-*d*6) spectrum of **TPE-Ph-COOH**.

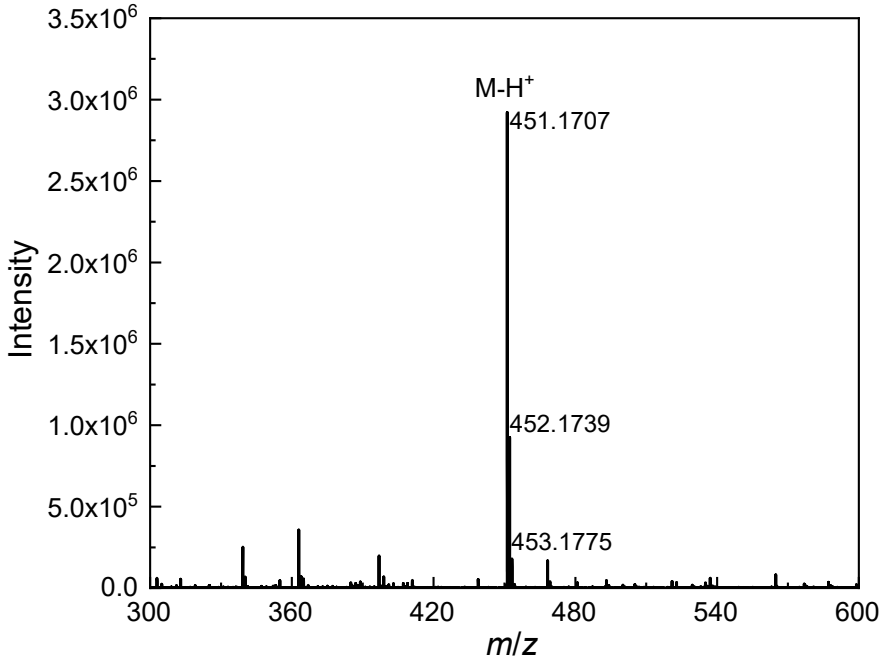


Fig. S38 HRMS of **TPE-Ph-COOH**.

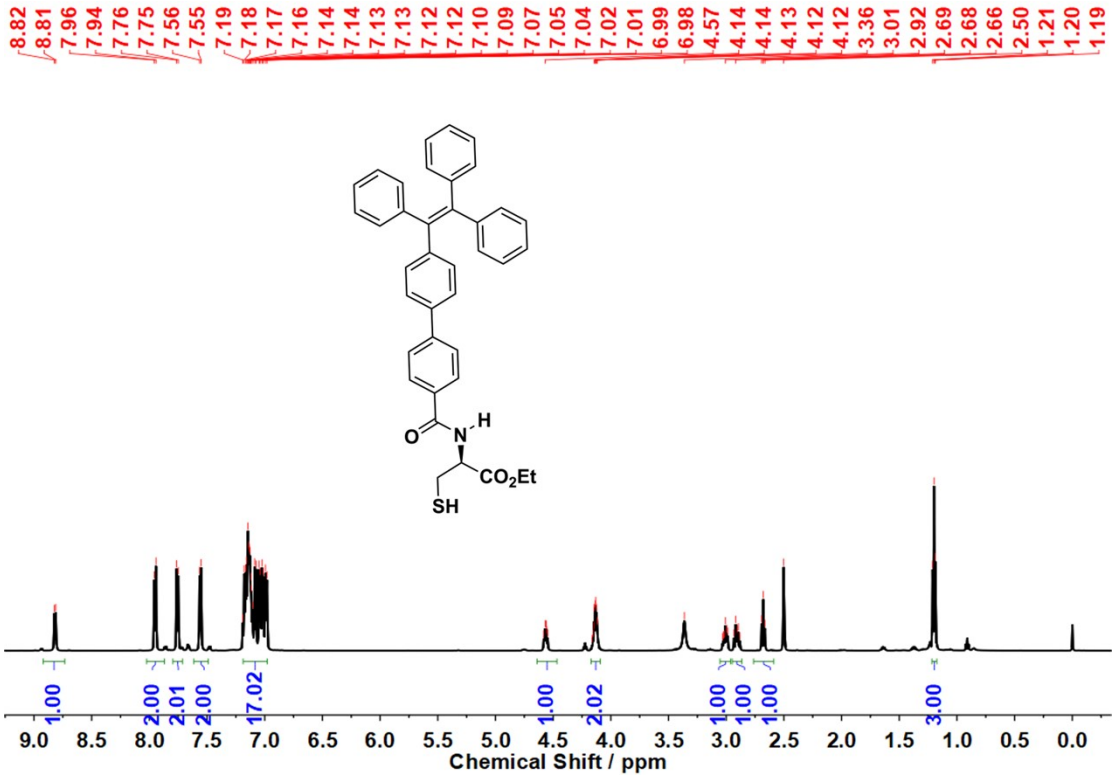


Fig. S39 ^{1}H NMR (600 MHz, DMSO-*d*$_6$) spectrum of L-**1**.

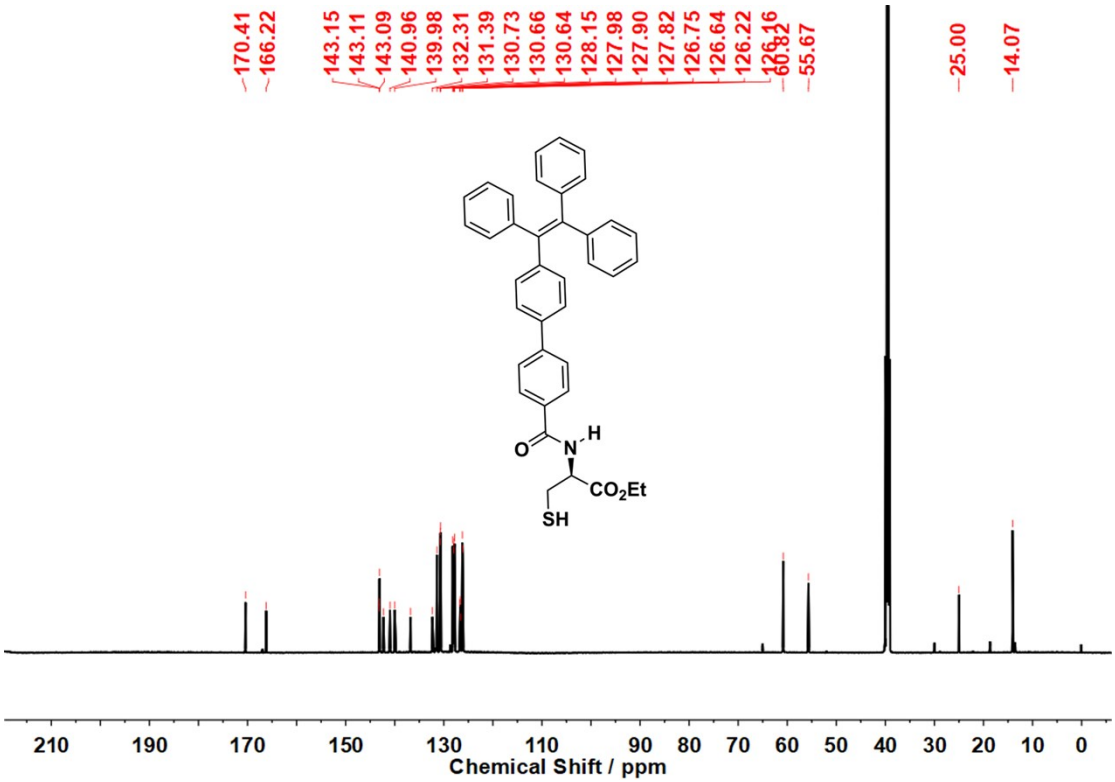


Fig. S40 ^{13}C NMR (151 MHz, DMSO-*d*6) spectrum of L-**1**.

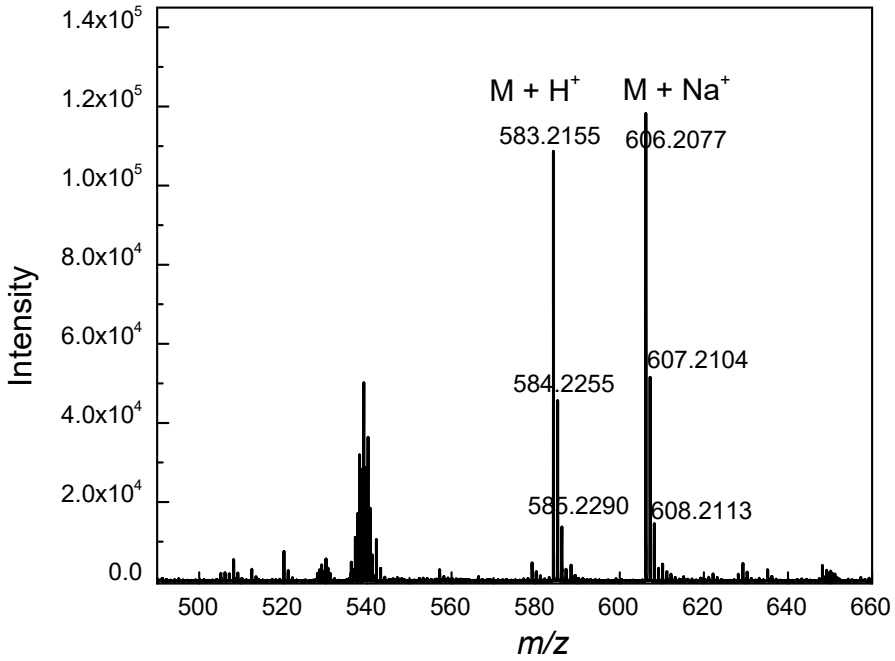


Fig. S41 HRMS of L-**1**.

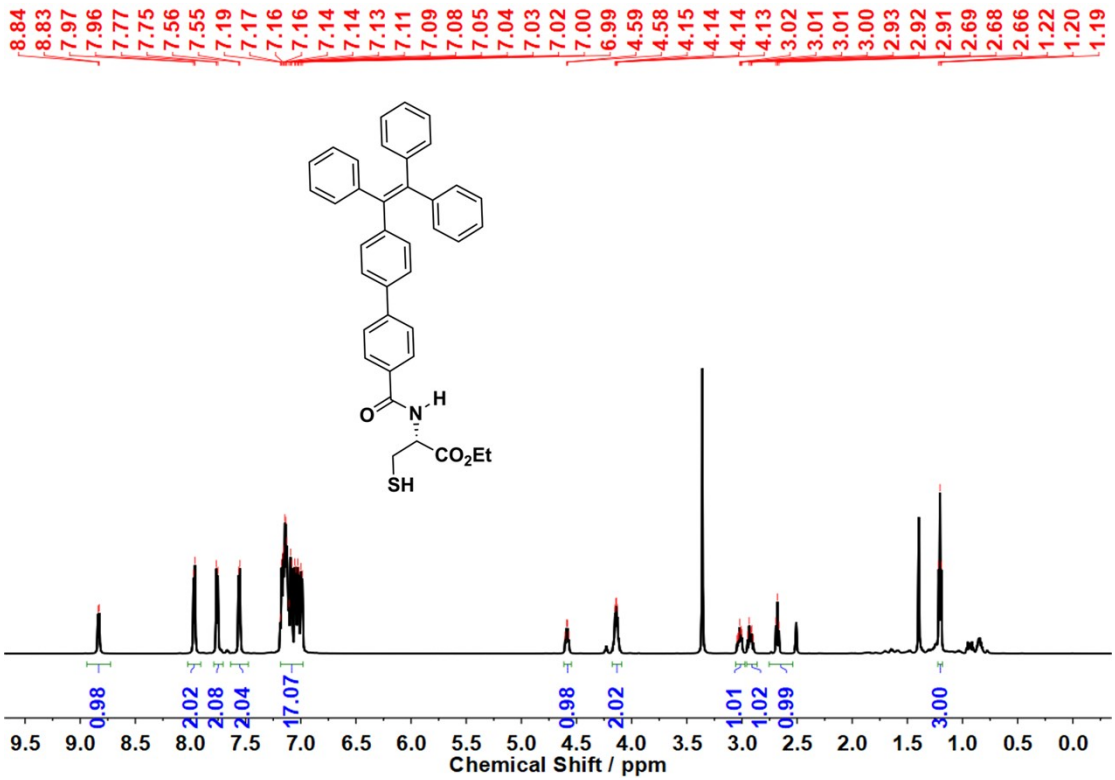


Fig. S42 ^{1}H NMR (600 MHz, DMSO-*d*$_6$) spectrum of D-**1**.

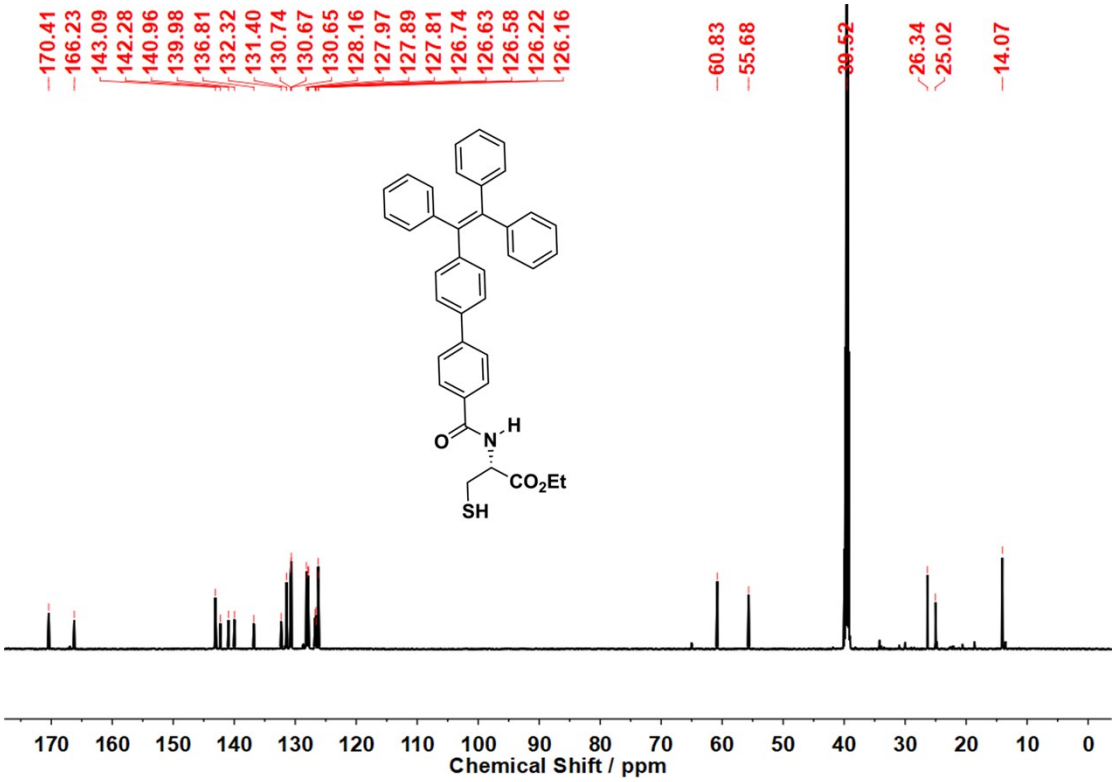


Fig. S43 ^{13}C NMR (151 MHz, DMSO-*d*$_6$) spectrum of D-**1**.

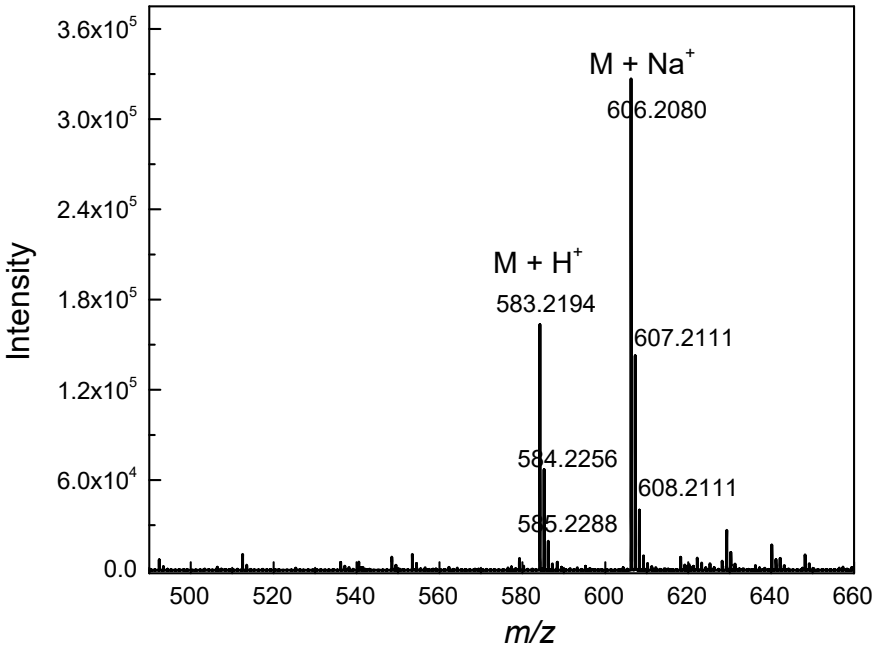


Fig. S44 HRMS of D-**1**.

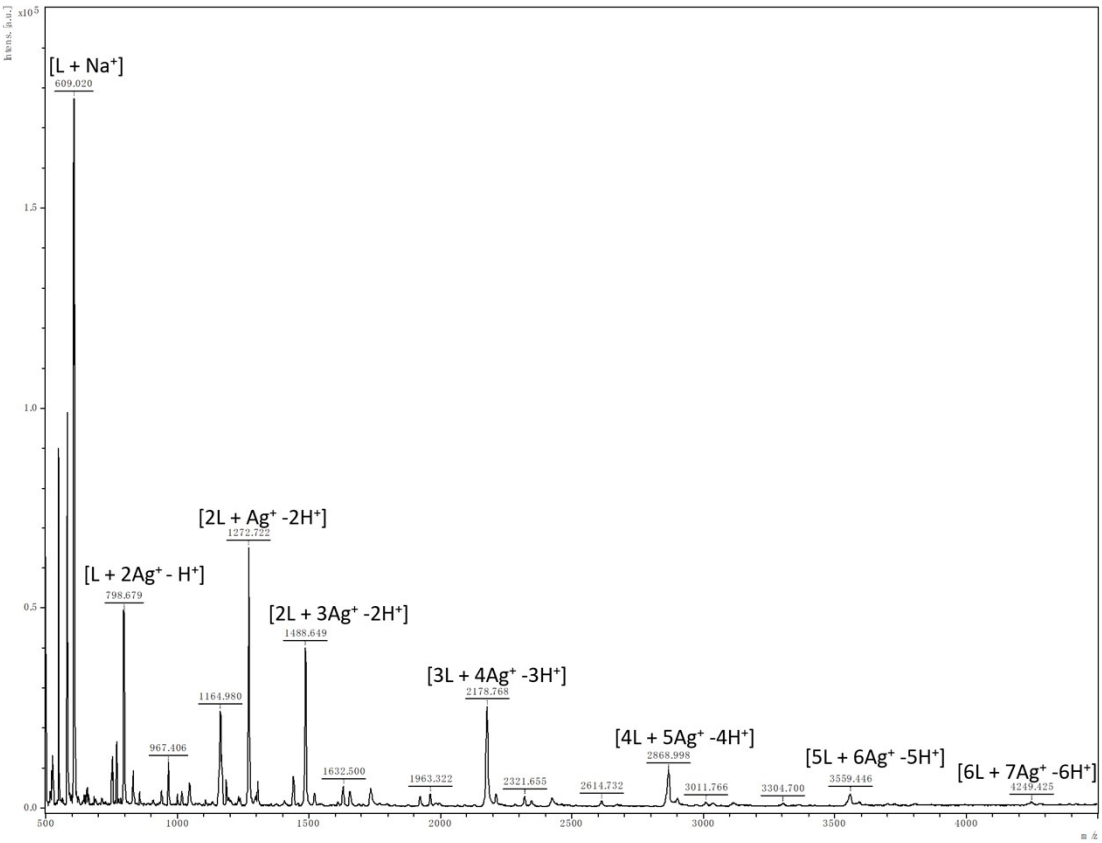


Fig. S45 MALDI-TOF MS of Ag^{+}-L-**1** coordination polymer.