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Supporting Information

Metallosupramolecular polymers formed with silver(I) ion in aqueous solution

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Methods

General characterization. The ^1H and ^{13}C NMR spectra were taken on a Bruker DRX 300, and Bruker DRX 500. Mass spectroscopy samples were analyzed on a JEOL JMS-700 mass spectrometer. The high resolution mass spectra (HR MS) were measured by electrospray ionization (ESI) with a micro TOF Focus spectrometer from SYNAPT G2 (Waters, U.K.). A UV-visible spectrophotometer (Thermo scientific Evolution 600) was used to obtain the absorption spectra. IR spectra were observed over the range $500\text{-}4000\text{ cm}^{-1}$, with a Thermo scientific Nicolet iS 10 instrument.

Preparation of silver complexes. Different concentrations (0, 0.5 and 1.0 equiv.) of Ag^+ solution (water) were added to the ligand **L** (10.9 mM) solution in a mixture of DMSO and H_2O (1:1 v/v).

SEM observation. FE-SEM images were observed using a JEOL (JSM-7900F). The images of samples using an accelerating voltage 5 kV and an emission current of $8\mu\text{A}$. Samples were prepared by dropping dilute solution of supramolecular nanostructure formed in a mixture of DMSO and H_2O (1:1 v/v) on glasses following by spinning, drying and coating them with a thin layer of Pt to increase the contrast.

Circular dichroism studies. The CD and UV-vis spectra were recorded on a Jasco J-815 CD spectrophotometer. CD and UV-vis spectra were determined over the range of 200-500 nm using a quartz cell with 0.1 mm path length. Scans were taken at rate of 200 nm/min with a sampling interval of 0.5 nm and response time of 0.5s. The scans were acquired for the supramolecular nanostructure directly at 25 °C.

Calculation of thermodynamic parameter. The thermodynamic parameters governing the supramolecular aggregation of **L** were obtained by the global fitting of the melting curves. This global fitting is performed by using the equilibrium (EQ) model reported by ten Eikelder and coworkers.¹ The values for the elongation enthalpy (ΔH_e) and the entropy (ΔS_e), and elongation binding constant (K_e) used in the cooperative supramolecular polymerization models were determined by the global fitting of the heating curves,²⁻⁴ which were obtained by plotting the degree of aggregation (α_{agg}) of **L** (13 mM) without and with AgNO_3 (0.5 and 1.0 equiv.) at 345 nm against temperature with heating experiments. An elongation binding constant (K_e) for aggregation at 293 K was estimated according to eq. 1, from which the enthalpy change (ΔH), and the entropy change (ΔS) were determined:

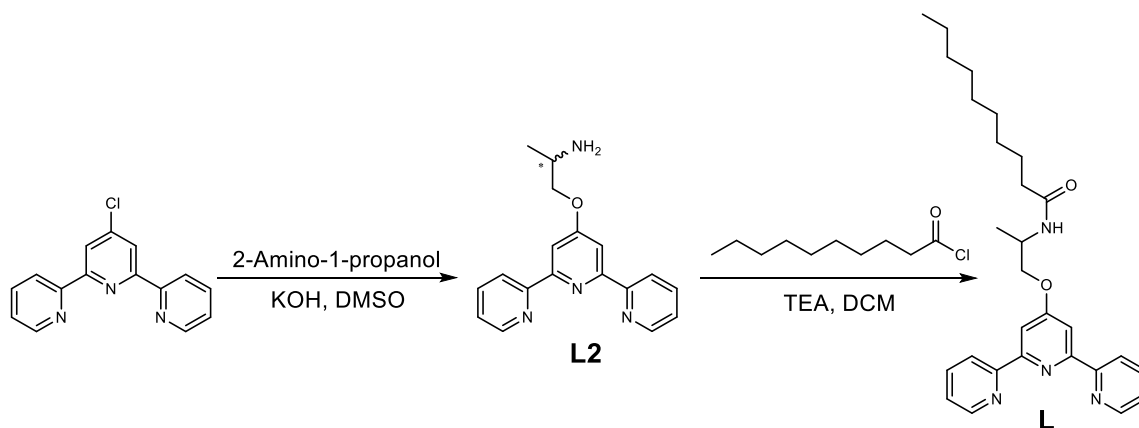
$$K_e = e^{-(\Delta H_e - T\Delta S_e)/RT} \quad (\text{eq. 1})$$

Material synthesis

L was synthesized according to the procedure shown in Scheme S1. All chemical reagents were purchased commercially without further purification, unless otherwise noted.

Synthesis of Compound L2. (*R*)-(-)-2-amino-1-propanol (0.28 g, 3.7 mmol) was put into a stirred suspension of powdered KOH (1.05 g, 18.7 mmol) in dry DMSO (20 mL) at 60 °C. After 30 min, 4'-chloro-2,2':6',2''-terpyridine (1.00 g, 3.7 mmol) was put into the mixture. The mixture was then stirred for 4 h at 70 °C and poured into 600 mL of distilled water thereafter. CH₂Cl₂ (3 × 200 mL) was used to extract the aqueous phase. Residual water in dichloromethane was dried over Na₂SO₄ and CH₂Cl₂ was removed in vacuum, and the desired product was purified by recrystallization with ethyl acetate to give 0.72 g (72%) of **L2**. Mp = 118.3 °C; IR (KBr pellet): 3375, 2964, 2926, 2846, 1577, 1565, 1473, 1439, 1403, 1353, 1204, 799 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.70 (tdd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.62 (dt, *J* = 8.0, 1.1 Hz, 2H), 8.02 (s, 2H), 7.84 (td, *J* = 7.7, 1.8 Hz, 2H), 7.33 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 2H), 4.14 (dd, *J* = 9.0, 4.1 Hz, 1H), 3.94 (dd, *J* = 9.1, 7.6 Hz, 1H), 3.41 (dddd, *J* = 10.6, 7.6, 6.6, 4.2 Hz, 1H), 1.21 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆): δ 167.2, 157.1, 155.3, 149.7, 137.9, 125.0, 121.3, 107.3, 75.1, 46.2, 20.43; HR-Mass (*m/z*) calculated for C₁₈H₁₈N₄O [M]⁺: 306.3690, Found [M]⁺: 306.3690.

Synthesis of Compound L. In a two neck flask, **L2** (0.50 g, 1.64 mmol) and TEA (0.1 mL, 0.72 mmol) were poured into dry CH₂Cl₂ (10 mL). After cooling the solution in an ice bath and magnetically stirring the solution, decanoyl chloride (0.13 mL, 0.78 mmol) was added dropwise for reactions. The reactant was stirred for 3 h at room temperature. The crude product was purified by silica gel column chromatography (DCM / MeOH 97 : 3 v/v as the eluent) to give a white crystalline solid **L** in 47.44% yield (0.217 g). Mp = 235 °C; IR (ATR): 3297, 2917, 2849, 1637, 1583, 1534, 1468, 1443, 1405, 1359, 1197, 1034, 868, 792, 741, 622 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.72 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.65 (dt, *J* = 8.0, 1.1 Hz, 2H), 8.07 (s, *J* = 7.5 Hz, 2H), 7.89 (td, *J* = 7.7, 1.8 Hz, 2H), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H), 5.78 (s, 1H), 4.52 (m, 1H), 4.29 (dt, *J* = 9.9, 4.6 Hz, 2H), 2.20 (m, 2H), 1.64 (m, 2H), 1.32 (m, 12H), 0.87 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 172.68, 167.03, 155.73, 149.00, 136.99, 124.02, 121.44, 107.39, 70.88, 44.27, 36.95, 31.84, 29.44, 29.36, 29.28, 25.77, 22.66, 17.65, 14.11; HR-Mass (*m/z*) calculated for C₂₈H₃₆N₄O₂ [M]⁺ : 460.2838, Found [M]⁺: 460.2838.



Scheme S1 Synthetic method of **L**.

Table S1. Thermodynamic parameters of **L** with AgNO_3 (A) 0 equiv., (B) 0.5 equiv. and (C) 1.0 equiv. in a mixture of DMSO/ H_2O (1:1 v/v) after 72 h.

AgNO_3 (equiv.)	ΔG (kJ mol^{-1})	ΔH_e (kJ mol^{-1})	ΔS ($\text{J K}^{-1} \text{mol}^{-1}$)	K_e (L mol^{-1})	T_e (K)
0	-17.09	-174.98	-529.82	9.9×10^2	320.03
0.5	-14.52	-120.38	-355.22	4.5×10^2	307.61
1	-14.04	-145.63	-441.58	2.9×10^2	304.86

^aGibbs free energy. ^bElongation enthalpy. ^cEntropy. ^dElongation binding constant. ^eElongation Temperature.

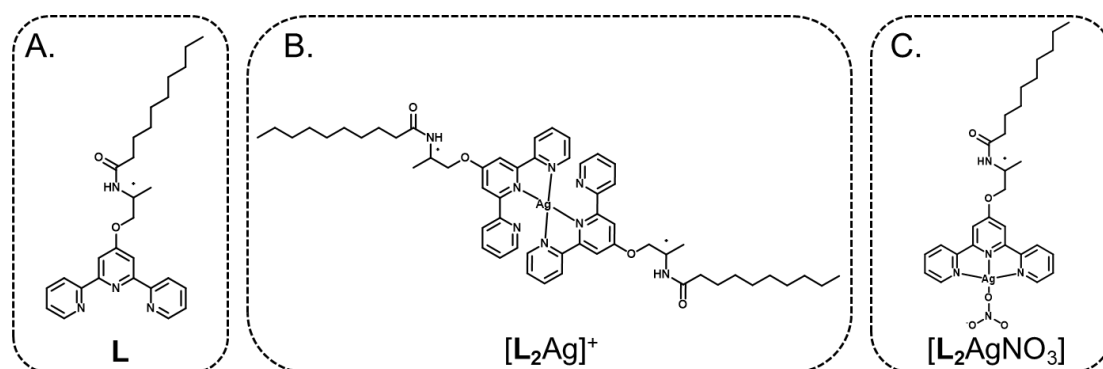


Fig. S1 (A) Chemical structures of (A) ligand **L**. Proposed structures for complexes (B) $[\text{L}_2\text{Ag}]^+$ and (C) $[\text{L}_2\text{AgNO}_3]$.

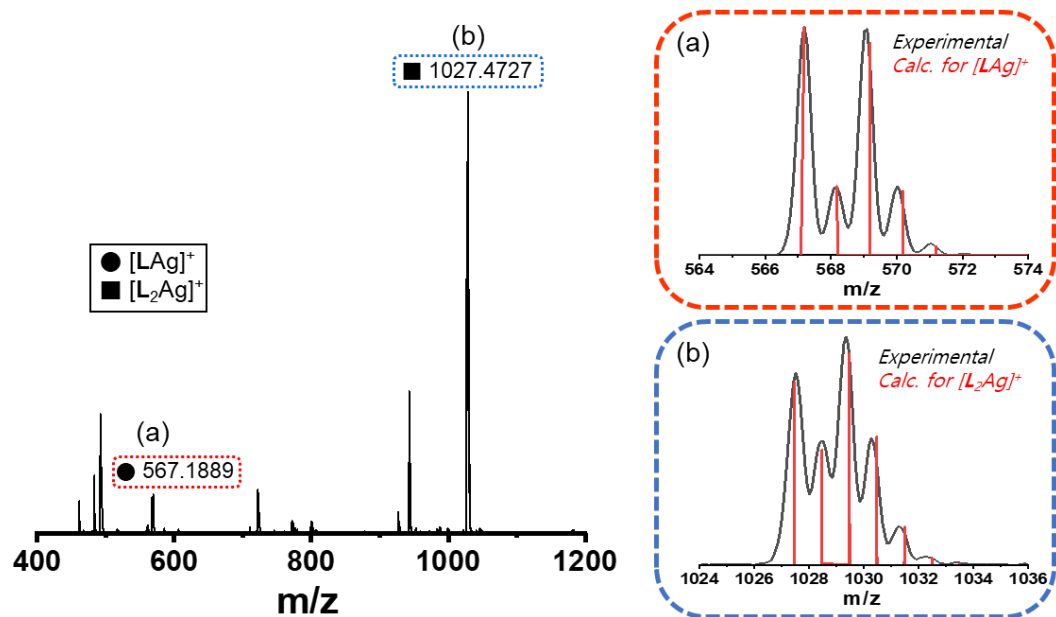


Fig. S2 HR-ESI-MS spectrum of **L** (10.9 mM) with AgNO₃ 0.5 equiv. in a mixed H₂O and DMSO (1:1 v/v) after 72 h.

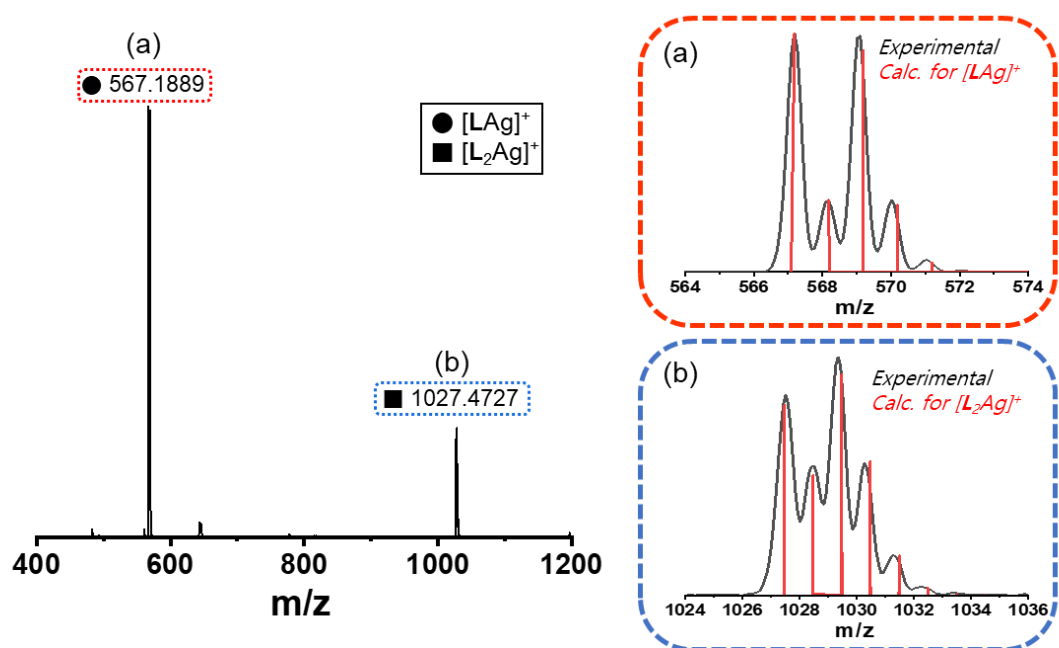


Fig. S3 HR-ESI-MS spectrum of **L** (10.9 mM) with AgNO₃ 1.0 equiv. in a mixed H₂O and DMSO (1:1 v/v) after 72 h.

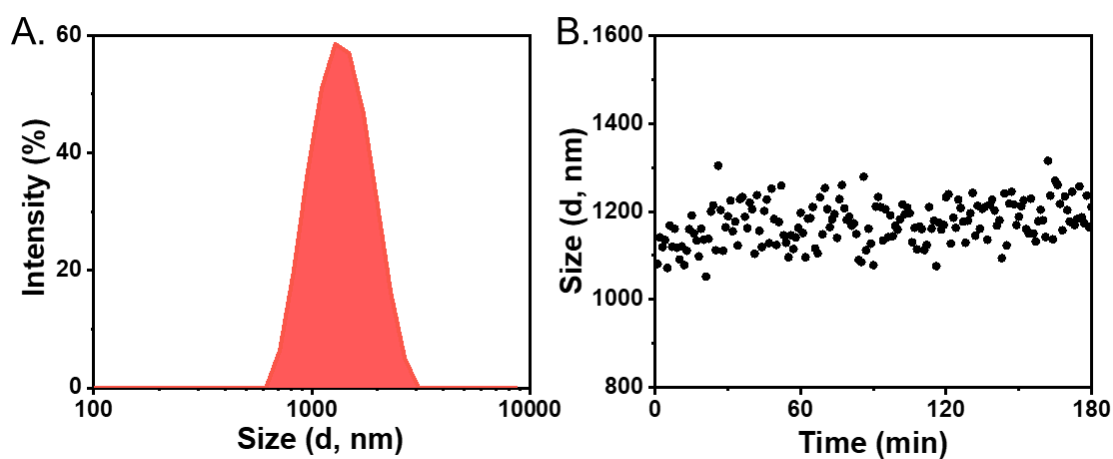


Fig. S4 (A) DLS spectrum of of **L** (10.9 mM) with AgNO_3 1.0 equiv. in a mixed H_2O and DMSO (1:1 v/v) after 72 h. (B) Plot of DLS spectra change of of **L** (10.9 mM) with AgNO_3 1 equiv. in a mixture of H_2O and DMSO (1:1 v/v).

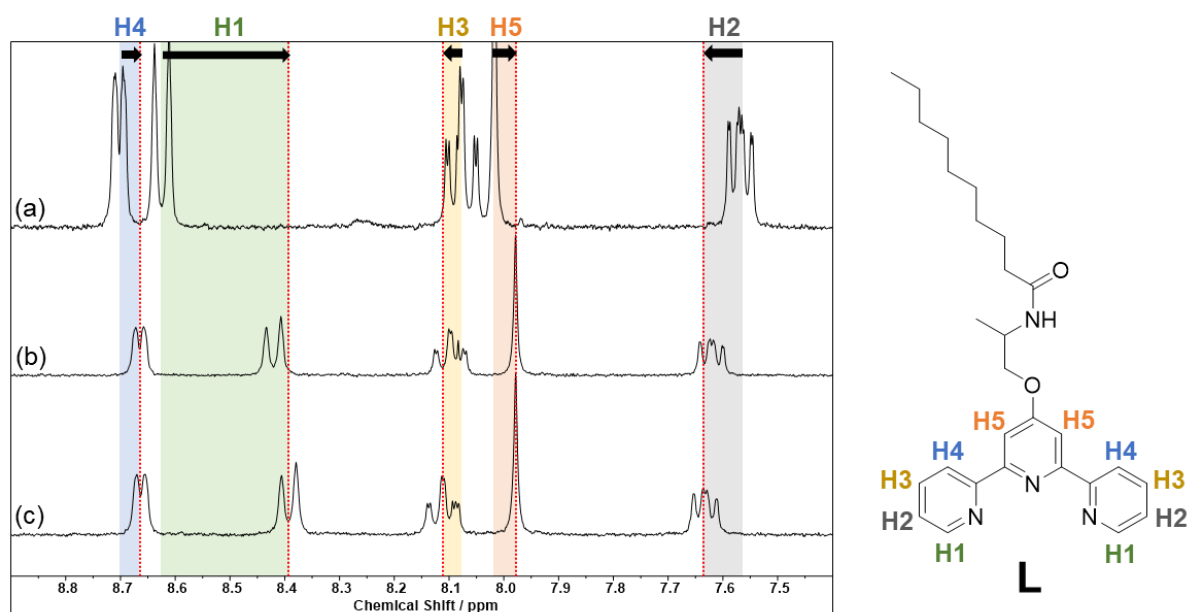


Fig. S5 ^1H NMR spectra of **L** with AgNO_3 (A) 0 equiv., (B) 0.5 equiv. and (C) 1.0 equiv. in a mixture of D_2O and DMSO-d_6 (1:1 v/v).

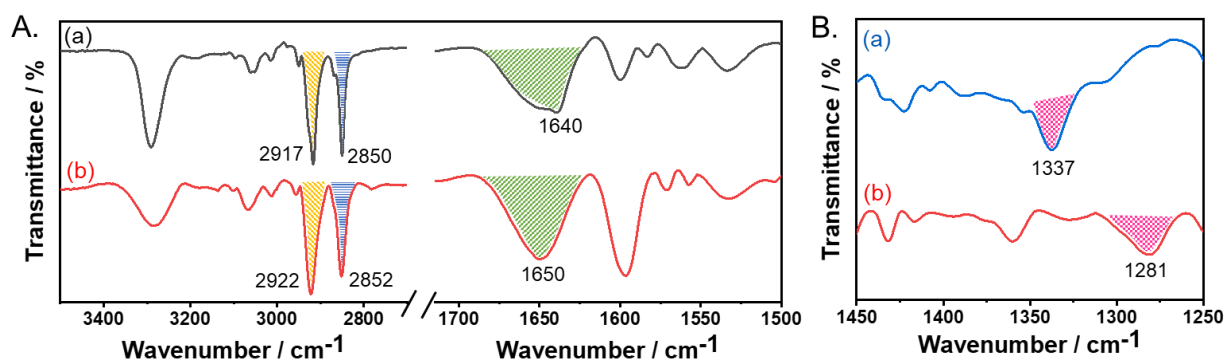


Fig. S6 (A) FT-IR spectra of **L** with AgNO_3 (a) 0.5 equiv. (black line) and (b) 1.0 equiv. (red line). (B) FT-IR spectra of (a) AgNO_3 (blue line) and (b) 1.0 equiv. (red line).

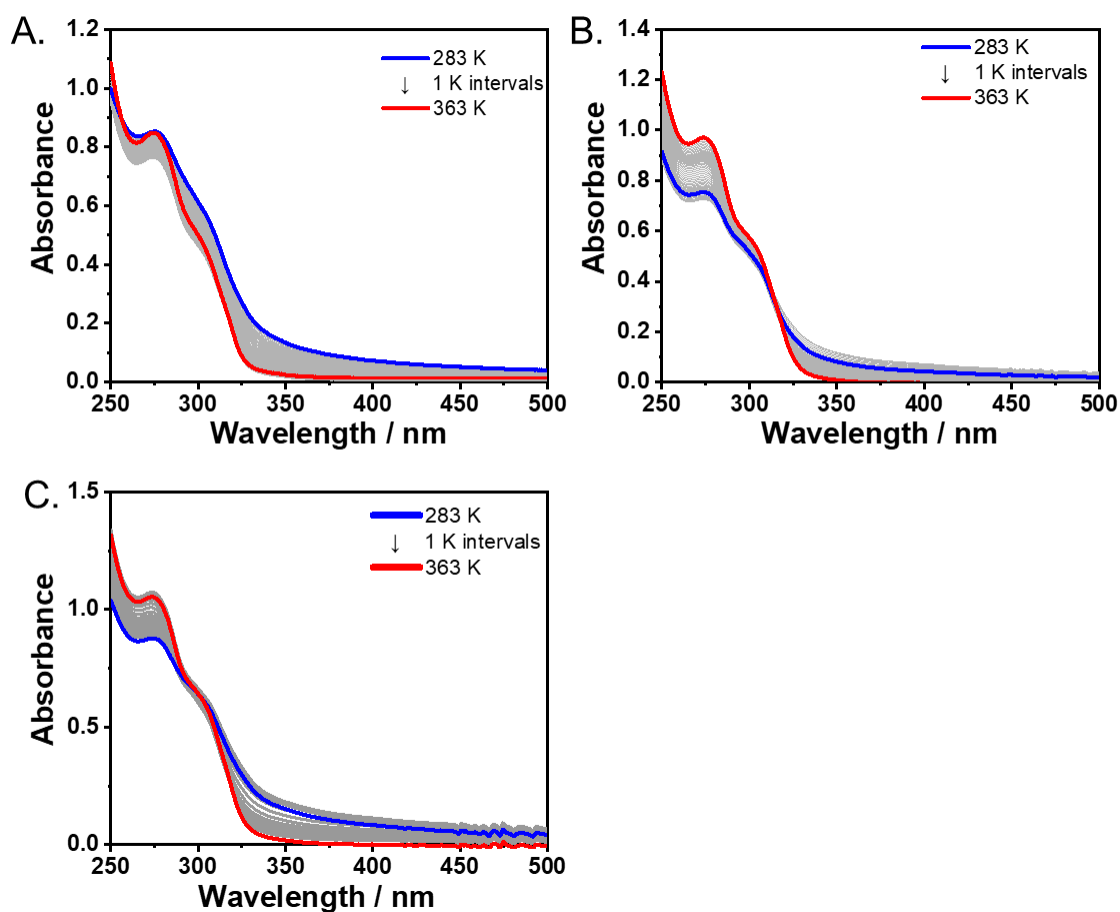


Fig. S7 Temperature-dependent UV spectra of different concentrations of **L** with AgNO_3 (A) 0 equiv., (B) 0.5 equiv. and (C) 1.0 equiv. in a mixture of DMSO/ H_2O (1:1 v/v) after 72 h.

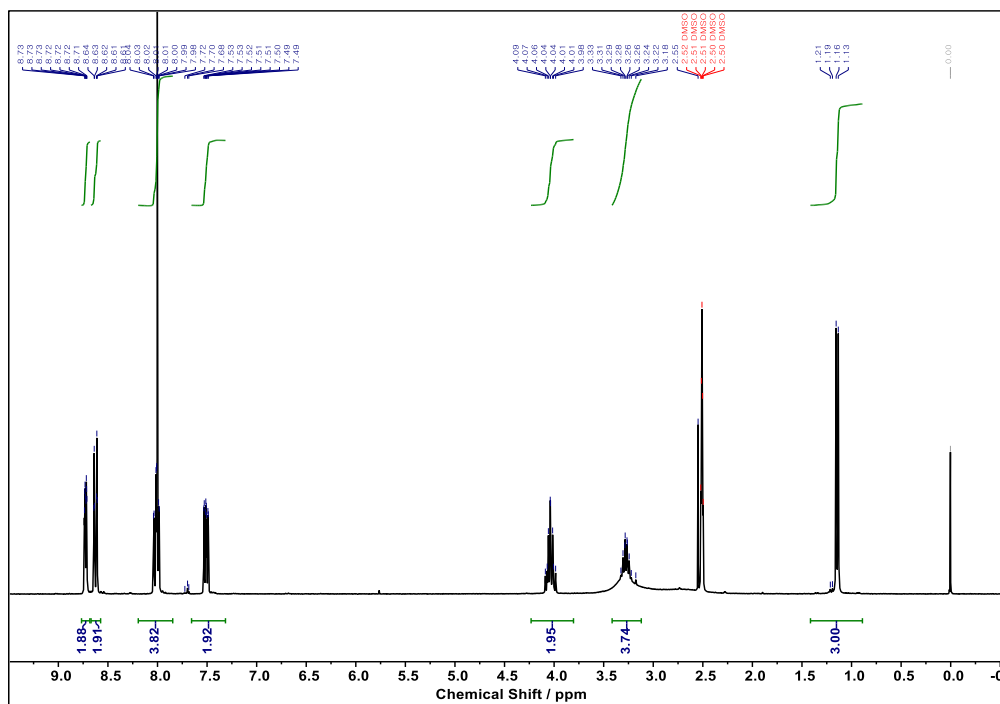


Fig. S8 ^1H NMR spectrum (300 MHz) of **L2** in CDCl_3 at 25 $^\circ\text{C}$.

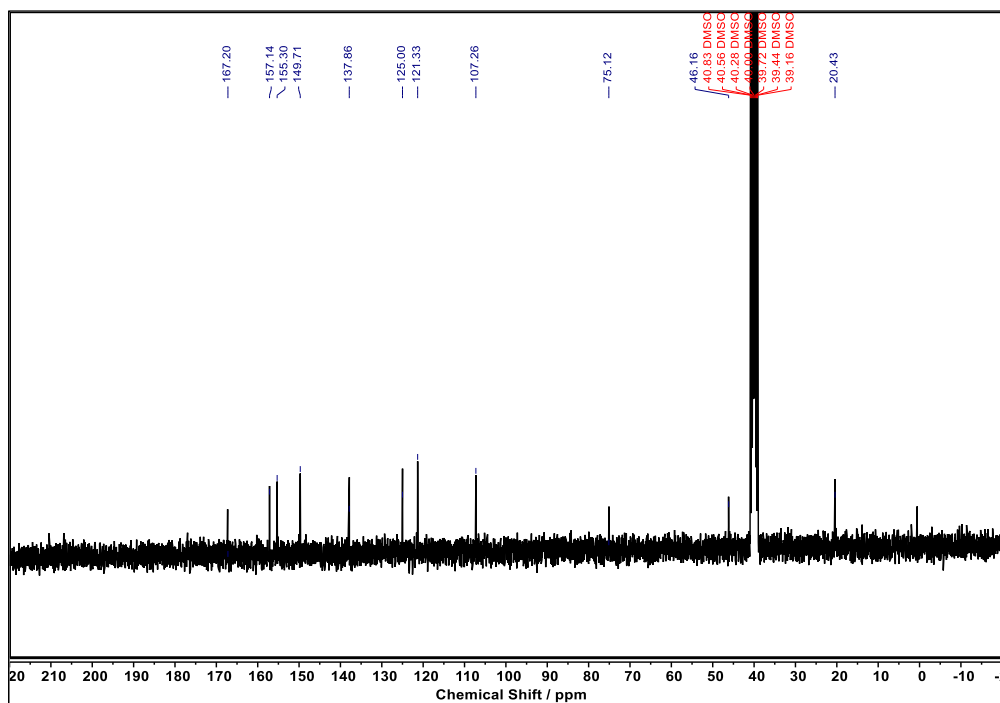


Fig. S9 ^{13}C NMR spectrum (125 MHz) of **L2** in $\text{DMSO}-d_6$ at 25 $^\circ\text{C}$.

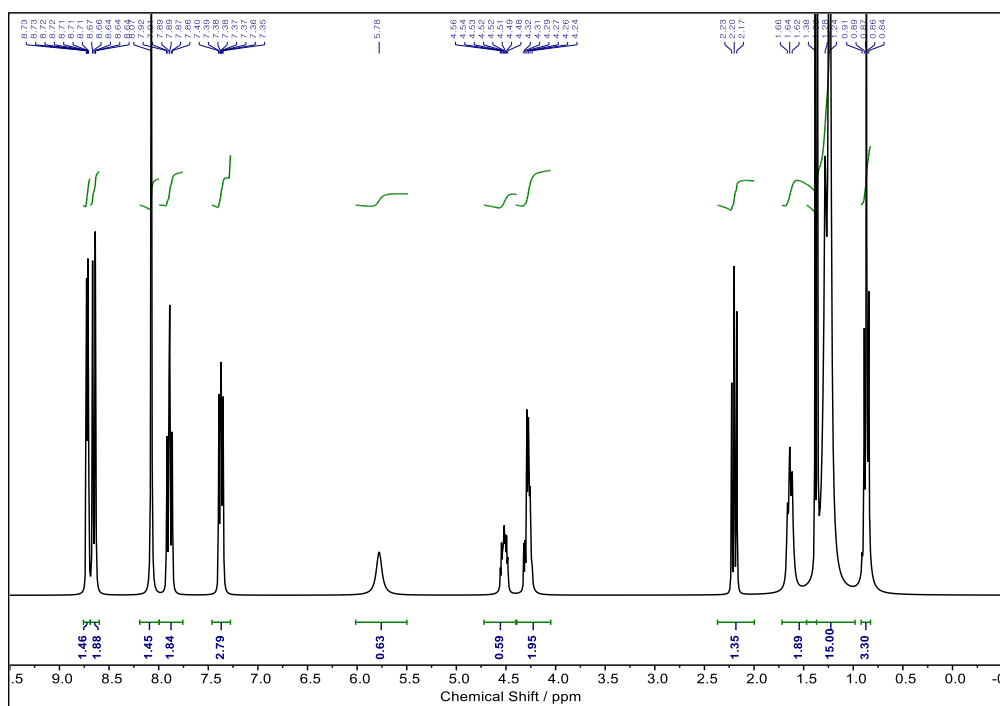


Fig. S10 ^1H NMR spectrum (300 MHz) of **L** in CDCl_3 at 25 $^\circ\text{C}$.

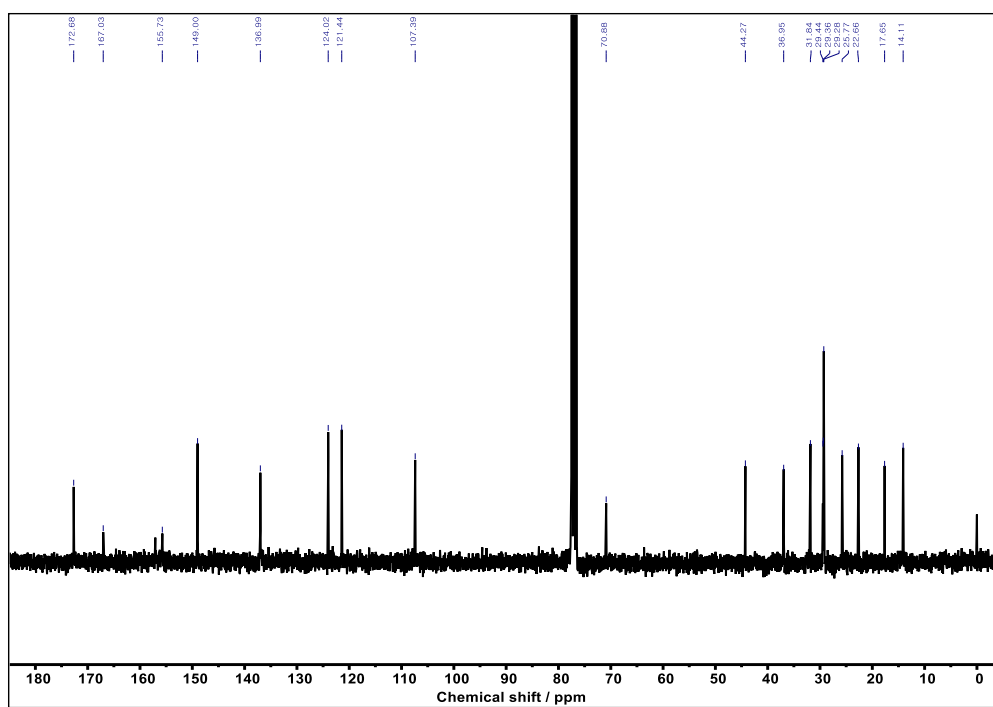


Fig. S11 ^{13}C NMR spectrum (75 MHz) of **L** in CDCl_3 at 25 $^\circ\text{C}$.

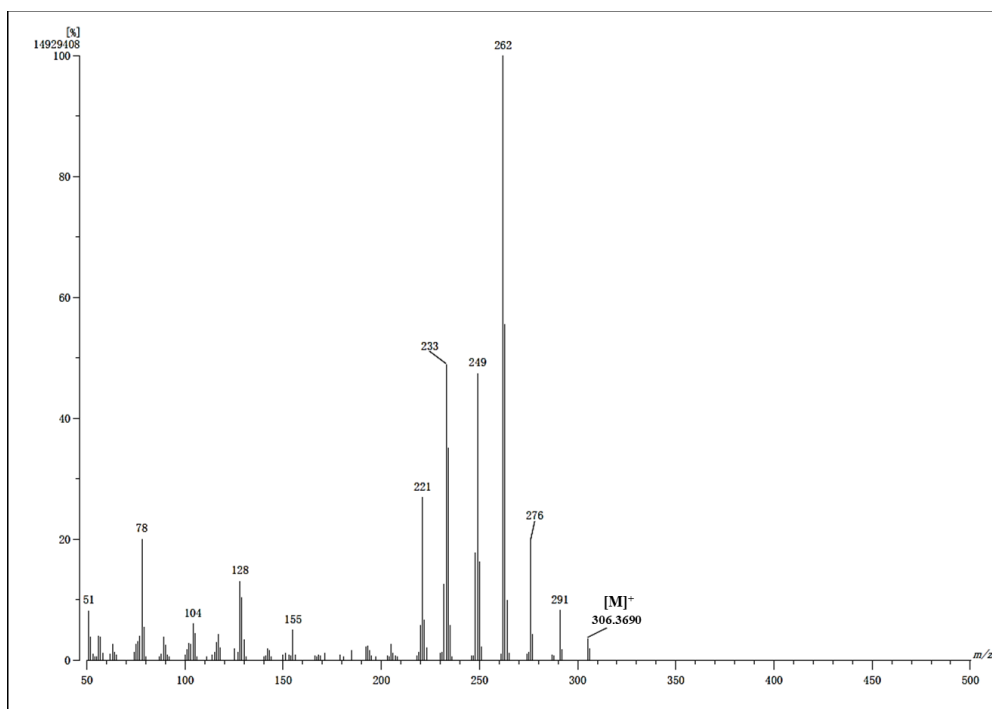


Fig. S12 HR EI-MS spectrum of **L2** in MeOH.

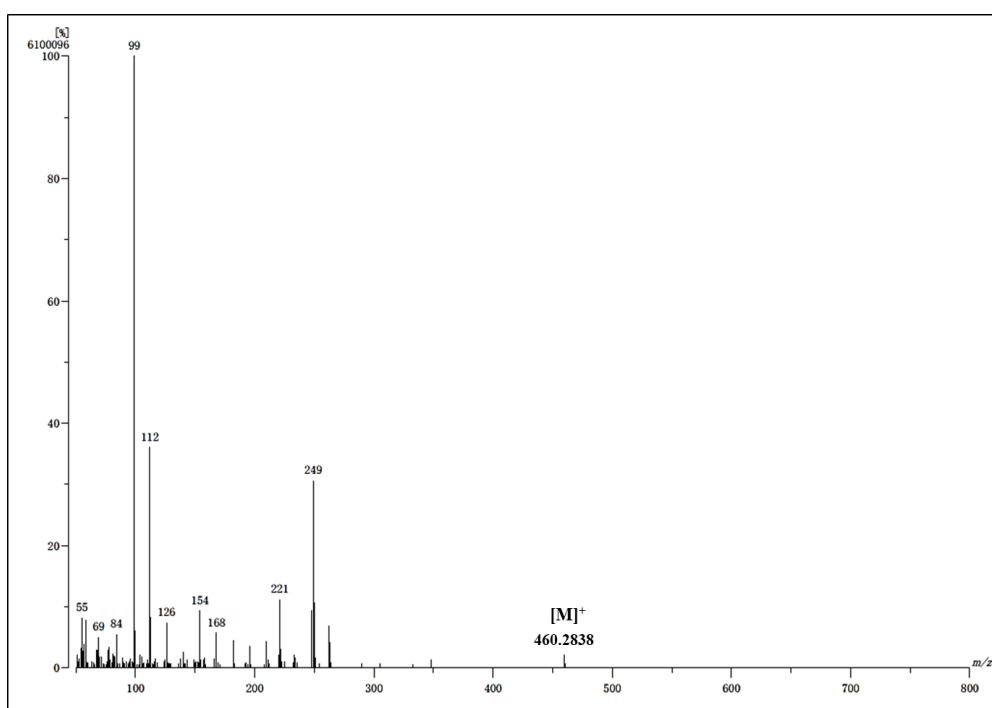


Fig. S13 HR EI-MS spectrum of **L** in MeOH.

References

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