Electronic Supplementary Information

Helicity-driven chiral self-sorting supramolecular polymerization with Ag⁺: right- and left-helical aggregates

Mirae Ok a,e, Ka Young Kim a,e, Heekyoung Choi a, Seonghan Kim b,c, Shim Sung Lee a, Jaeheung Cho b, Sung Ho Jung d and Jong Hwa Jung a

a Department of Chemistry and Research Institute of Natural Sciences Gyeongsang National University, Jinju 52828, Korea
b Department of Chemistry, Ulsan National Institute of Science and Technology, Ulsan 44919, Korea
c Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and Technology, Daegu 42988, Korea
d Department of Liberal Arts, Gyeongsang National University, Jinju 52828, Korea

e These authors are contributed equally.
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1. Methods

1.1 General characterization: The $^1$H 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 (JASCO J-815) was used to obtain the absorption spectra. IR spectra were observed over the range 500-4000 cm$^{-1}$, with a Thermo scientific Nicolet iS 10 instrument. Powder X-ray pattern (PXRD) was recorded on a Rigaku model NANPIX X-ray diffractometer with a Cu K$_\alpha$ radiation source.

1.2 AFM observation: Atomic force microscope (AFM) imaging was performed by using XE-100 and a PPP-NCHR 10 M cantilever (Park systems). The AFM samples were prepared by spin-coating (2000 rpm) onto freshly cleaved Muscovite Mica, and images were recorded with the AFM operating in noncontact mode in air at RT with resolution of 1024 × 1024 pixels, using moderate scan rates (0.3 Hz). AFM images were recorded for fibers obtained from different ratio of right- and left-handed helix at diverse Ag$^+$ equivalents. In each image, 50~100 fibers were selected from different regions of the mica and analyzed using XEI software developed by Park systems.

1.3 Circular dichroism (CD) and UV-vis studies: The CD and UV-vis spectra were recorded on a Jasco J-815 CD spectrophotometer. The 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 0.5 s. To elucidate the supramolecular polymerization process, we first prepared the sample by dissolving $R$-$L_1^1$ (7.2 mM) with or without AgNO$_3$ in H$_2$O/DMSO (1:1 v/v). After adding the sample to the CD and UV cells, it was heated to 90 °C (1 °C/min) to form the monomeric species in CD and UV-vis spectroscopy. Then the sample was cooled to 20 °C (5 °C/min) in UV-vis spectroscopy. The time-dependent CD and UV-vis spectral changes were measured at 20 °C.

1.4 Calculation of thermodynamic parameter: The thermodynamic parameters governing the supramolecular aggregation of $R$-$L_1^1$ 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 ($\Delta H_e$) and the entropy ($\Delta S_e$),
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 ($\alpha_{agg}$) of $R-L^1$ (7.0 mM) without and with AgNO$_3$ (1.2 equiv.) at 326 nm against temperature with heating experiments. An elongation binding constant ($K_e$) for aggregation at 293 K was estimated according to equation 1, from which the enthalpy change ($\Delta H$), and the entropy change ($\Delta S$) were determined:

$$K_e = e^\frac{-(\Delta H_e - T\Delta S)}{RT}$$

(equation 1)

1.5 Preparation of silver complexes: Different concentrations (0~2.0 equiv.) of aqueous Ag$^+$ solution were added to $R-L^1$ or $S-L^1$ (6.4 mM) solution in DMSO/H$_2$O (1:1 v/v). Time- and temperature-dependent CD and UV-vis spectra were measured.

1.6 Calculation of stability constants: The UV-vis titration with AgNO$_3$ for $R-L^1$ (50 µM) was performed in DMSO/H$_2$O (1:1 v/v). The titration was performed with 0-3.0 equiv. of AgNO$_3$ at 25 °C. Titration data were fitted into a desired binding model with HyperSpec to calculate stability constants for 1:1 and 2:1 (Ag$^+$: ligand) complexes, respectively.\(^5\-7\)

1.7 Theoretical calculations: We performed density functional theory (DFT) calculations to optimize the Ag$^+$ complex systems using the Gaussian 09 package.\(^8\) The unrestricted B3LYP functional was employed for all optimizations and frequency calculations with Def2-SVP level of theory for all atoms.\(^9\-11\) All calculations were performed in the gas phase. All the optimized structures were confirmed by vibrational frequency analysis with no imaginary frequency. The Cartesian coordinates are shown in Tables S2-S4.

2. Synthesis and characterization

2.1 Synthesis of $R-L^2$ and $S-L^2$

($R$ or $S$)-(−)-2-amino-1-propanol (0.28 g, 3.7 mmol) was added to 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 added to the mixture. The mixture was then stirred for 4 h at 70 °C and poured into 600 mL of distilled water thereafter. CH$_2$Cl$_2$ (3 × 200 mL) was used to extract the aqueous phase. Residual water in dichloromethane was dried over Na$_2$SO$_4$ and CH$_2$Cl$_2$ was removed in vacuum, and the desired product was purified by recrystallization with ethyl acetate to give 0.72 g (72%) of $R-L^2$ and $S-L^2$. Mp = 118.3 °C; IR (KBr pellet):
3375, 2964, 2926, 2846, 1577, 1473, 1439, 1403, 1353, 1204, 799 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 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); \(^1\)H NMR (300 MHz, CDCl\(_3\)): 

2.2 Synthesis of \(R\)-L\(^1\)

\(R\)-L\(^1\) and \(S\)-L\(^1\) was prepared according to a literature procedure.\(^1\) In a two neck flask, \(R\)-L\(^2\) (0.50 g, 1.64 mmol) and TEA (0.1 mL, 0.72 mmol) were added to dry CH\(_2\)Cl\(_2\) (10 mL). After cooling the solution in an ice bath, sebacoyl chloride (0.16 mL, 0.75 mmol) was added dropwise. The reactant was stirred for 3 h at room temperature. The crude product was recrystallized from CH\(_2\)Cl\(_2\) to give a white crystalline solid \(R\)-L\(^1\) in 49.7% yield (0.632 g). Mp = 198 °C; IR (KBr pellet): 3428, 3311, 2929, 2845, 1640, 1582, 1563, 1466, 1446, 1407, 1362, 1207, 1038, 785 cm\(^{-1}\); \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta\) 8.68 (m, 8H), 7.99 (m, 8H), 7.87 (d, \(J = 7.5\) Hz, 2H), 7.50 (ddd, \(J = 7.7, 4.8, 1.6\) Hz, 4H), 4.15 (m, 6H), 2.02 (t, \(J = 7.3\) Hz, 4H), 1.42 (d, \(J = 7.5\) Hz, 4H), 1.21 (s, 3H), 1.19 (s, 3H), 1.13 (s, 8H); \(^1\)C NMR (125 MHz, DMSO-d\(_6\)): \(\delta\) 172.3, 167.1, 157.2, 155.3, 149.7, 137.8, 125.0, 121.3, 107.2, 70.9, 44.1, 35.9, 29.2, 29.0, 25.7, 17.6; HR-Mass (m/z) calculated for C\(_{18}\)H\(_{18}\)N\(_4\)O \([\text{M}]^+\): 306.3690, Found [M]\(^+\): 306.3690.

2.3 Synthesis of \(S\)-L\(^1\)

The synthesis of \(S\)-L\(^1\) was performed as described in the synthesis of \(R\)-L\(^1\). 52.4% yield (0.632 g). Mp = 198 °C; IR (KBr pellet): 3426, 3310, 2928, 2845, 1642, 1581, 1561, 1466, 1445, 1405, 1362, 1206, 1037, 786 cm\(^{-1}\); \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta\) 8.70 (m, 8H), 7.95 (m, 8H), 7.86 (d, \(J = 7.4\) Hz, 2H), 7.46 (ddd, \(J = 7.7, 4.7, 1.6\) Hz, 4H), 4.17 (m, 6H), 2.12 (t, \(J = 7.2\) Hz, 4H), 1.40 (d, \(J = 7.6\) Hz, 4H), 1.19 (s, 3H), 1.17 (s, 3H), 1.11 (s, 8H); \(^1\)C NMR (125 MHz, DMSO-d\(_6\)): \(\delta\) 172.1, 167.0, 157.3, 155.0, 149.9, 137.6, 125.2, 121.5, 107.1, 70.8, 44.0, 35.7, 29.0, 28.8, 25.6, 17.5; HR-Mass (m/z) calculated for C\(_{46}\)H\(_{50}\)N\(_8\)O\(_4\) \([\text{M}]^+\): 778.3955, Found [M]\(^+\): 778.3953.
3. Supplementary scheme and figures

Scheme S1. Synthetic method of R-L\textsuperscript{1} or S-L\textsuperscript{1}.

Fig. S1 HR-ESI-MS spectra of R-L\textsuperscript{1} (6.4 mM) in the presence of different equiv. of AgNO\textsubscript{3}; (A) 0 equiv., (B) 0.1 equiv. and (C) 0.2 equiv. in DMSO/H\textsubscript{2}O (1:1 v/v) after 72 h aging.

[Note] The peaks at m/z 801.3854 correspond to [R-L\textsuperscript{1}+Na]\textsuperscript{+}. 
Fig. S2 HR-ESI-MS spectra of R-L₁ (6.4 mM) in the presence of different equiv. of AgNO₃: (A) 0.3 equiv. and (B) 0.4 equiv. in DMSO/H₂O (1:1 v/v) after 72 h aging.
Fig. S3 HR-ESI-MS spectra of R-L¹ (6.4 mM) in the presence of different equiv. of AgNO₃; (A) 0.5 equiv. and (B) 0.6 equiv. in DMSO/H₂O (1:1 v/v) after 72 h aging.
Fig. S4 HR-ESI-MS spectra of R-L¹ (6.4 mM) in the presence of different equiv. of AgNO₃: (A) 0.8 equiv. and (B) 1.0 equiv. in DMSO/H₂O (1:1 v/v) after 72 h aging.
Fig. S5 HR-ESI-MS spectra of $R$-$L^1$ (6.4 mM) in the presence of different equiv. of AgNO$_3$; (A) 1.2 equiv. and (B) 1.4 equiv. in DMSO/H$_2$O (1:1 v/v) after 72 h aging.
Fig. S6 HR-ESI-MS spectra of R-L¹ (6.4 mM) in the presence of different equiv. of AgNO₃; (A) 1.6 equiv., and (B) 1.8 equiv. in DMSO/H₂O (1:1 v/v) after 72 h aging.
Fig. S7 HR-ESI-MS spectrum of [R-L′Ag₂NO₃]⁺.

Fig. S8 HR-ESI-MS spectrum of R-L¹ (6.4 mM) in the presence of AgNO₃ (2.0 equiv.) in DMSO/H₂O (1:1 v/v) after 72 h aging.
**Fig. S9** (A) AFM image of \( R-L^1 \) (6.4 mM) without \( \text{AgNO}_3 \) in DMSO/H\(_2\)O (1:1 v/v) after 72 h aging. Cross-sectional analysis (B) blue dots (for height) and (C) red dots (for pitch) in the image.

**Fig. S10** AFM images of \( R-L^1 \) (6.4 mM) in DMSO/H\(_2\)O (1:1 v/v) after 72 h aging. No shown all AFM images.
**Fig. S11** AFM images of $R$-$L^1$ (6.4 mM) with 0.2 equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber. No shown all AFM images.

**Fig. S12** AFM images of $R$-$L^1$ (6.4 mM) with 0.4 equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) after 72 h aging. No Shown all AFM images. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
Fig. S13 AFM images of \( R-\textbf{L}_1 \) (6.4 mM) with 0.6 equiv. of AgNO\(_3\) in DMSO/H\(_2\)O (1:1 v/v) after 72 h aging. No shown all AFM images. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
**Fig. S14** AFM images of $R$-$L^1$ (6.4 mM) with 0.8 equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) after 72 h aging. No shown all AFM images. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.

**Fig. S15** AFM images of $R$-$L^1$ (6.4 mM) with 1.0 equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) after 72 h aging. No shown all AFM images. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
**Fig. S16** AFM images of \( R\-L^1 \) (6.4 mM) with 1.2 equiv. of AgNO\(_3\) in DMSO/H\(_2\)O (1:1 v/v) after 72 h aging. No shown all AFM images. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.

**Fig. S17** Species distribution depending on [AgNO\(_3\)]/[\( R\-L^1 \)] ratios monitored by ESI-MS.
Fig. S18 AFM images of \( R\)-L\(^1 \) (6.4 mM) with 2.0 equiv. of AgNO\(_3\) in DMSO/H\(_2\)O (1:1 v/v) after 72 h aging.

Fig. S19 AFM image of \( S\)-L\(^1 \) (6.4 mM) without AgNO\(_3\) in DMSO/H\(_2\)O (1:1 v/v) after 72 h aging.

[Note] Since unaggregated species are visible in the AFM background, we did not include the background in the calculation of right- and left-handed fibers.
**Fig. S20** AFM image of S-L₁ (6.4 mM) with 0.2 equiv. of AgNO₃ in DMSO/H₂O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.

**Fig. S21** AFM image of S-L₁ (6.4 mM) with 0.4 equiv. of AgNO₃ in DMSO/H₂O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
Fig. S22 AFM image of S-L¹ (6.4 mM) with 0.6 equiv. of AgNO₃ in DMSO/H₂O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.

Fig. S23 AFM image of S-L¹ (6.4 mM) with 0.8 equiv. of AgNO₃ in DMSO/H₂O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
**Fig. S24** AFM image of S-L₁ (6.4 mM) with 1.0 equiv. of AgNO₃ in DMSO/H₂O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.

**Fig. S25** AFM image of S-L₁ (6.4 mM) with 1.2 equiv. of AgNO₃ in DMSO/H₂O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
Fig. S26 AFM images of a mixture of $R\cdot L^1$ (6.4 mM) and $S\cdot L^1$ (6.4 mM) without AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
Fig. S27 AFM image of a mixture of $R$-$L^1$ (6.4 mM) and $S$-$L^1$ (6.4 mM) with 0.6 equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
**Fig. S28** LD spectra of \( R\)-L\(^1 \) (6.4 mM) with AgNO\(_3\) (0, 1.2, and 2.0 equiv.) in DMSO/H\(_2\)O (1:1 v/v) after 72 h aging.

**Fig. S29** CD spectra of \( S\)-L\(^1 \) (8 mM) upon stepwise addition of AgNO\(_3\) (0-2.0 equiv.) in DMSO/H\(_2\)O (1:1 v/v). The negative signal observed at ~297 nm (blue line) originates from free \( S\)-L\(^1 \), while the positive signal at ~307 nm (red line) originates from [S-L\(^1\)Ag]\(^+\).
Fig. S30 Time-dependent (0-1000 min) UV-vis spectra of R-L₁ (7.2 mM) in the presence of different equiv. of AgNO₃ in DMSO/H₂O (1:1 v/v) (cell path length: 0.2 mm): (a) 0 equiv. and (b) 0.4 equiv.

[Note] To elucidate the supramolecular polymerization process, we first prepared the sample by dissolving R-L₁ (7.2 mM) in H₂O/DMSO (1:1 v/v). After adding the sample to the UV cell, it was heated to 90 °C (1 °C/min) to form the monomeric species in UV-vis spectroscopy. Then the sample was cooled to 20 °C (5 °C/min) in UV-vis spectroscopy. The time-dependent UV-vis spectral changes were measured at 20 °C.
Fig. S31 Time-dependent (0-1000 min) UV-vis spectra of R-L\textsuperscript{1} (7.2 mM) in the presence of different equiv. of AgNO\textsubscript{3} in DMSO/H\textsubscript{2}O (1:1 v/v) (cell path length: 0.2 mm): (a) 0.6 equiv. and (b) 0.8 equiv.
Fig. S32 Time-dependent (0-1000 nm) UV-vis spectra of $R$-$L^1$ (7.2 mM) in the presence of different equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) (cell path length: 0.2 mm): (a) 1.2 equiv. and (b) 1.4 equiv.
Fig. S33 Fitting of UV–vis titration data to determine the association constant for the formation of $[R-L^1Ag]^+$ and $[R-L^1(AgNO_3)_2]$ with HyperSpec softwareS1 by employing the 1:1 and 2:1 (Metal : L) binding model$^{5-7}$: (a) UV–vis titration of $R-L^1$ (0.05 mM) with Ag$^+$ (0-3.0 equiv.) in DMSO : H$_2$O (1:1 v/v) and (b) HyperSpec output (circle: experimental points, solid line: theoretical fit).

Fig. S34 Time-dependent AFM images of $R-L^1$ (6.4 mM) in the presence of 1.2 equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v). Aging times: (A) 1 h, (B) 3 h, (C) 1 day, and (D) 3 days.
Fig. S35 ESI-MS spectrum of $R$-$L^1$ (6.4 mM) with 1.2 equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v) after 1 h aging.
Fig. S36 Time-dependent (0-760 min) CD spectral changes of R-L¹ (8 mM) in the presence of AgNO₃ (0-1.4 equiv.) in DMSO/H₂O (1:1 v/v) at 20 °C (cell path length: 0.1 mm): (A) 0 equiv., (B) 0.4 equiv., (C) 0.8 equiv., (D) 1.2 equiv., and (E) 1.4 equiv.

[Note] To elucidate the supramolecular polymerization process, we first prepared the sample by dissolving R-L¹ (7.7 mM) in H₂O/DMSO (1:1 v/v). After adding the sample to the CD cell, it was heated to 90 °C (1 °C/min) to form the monomeric species in circular dichroism (CD) spectroscopy. Then the sample was cooled to 20 °C (5 °C/min) in CD spectroscopy. The time-dependent CD spectral changes were measured at 20 °C.
**Fig. S37** AFM images of a mixed sample of aggregate I (7.2 mM, 50 μL) and aggregate III (7.2 mM, 21.5 μL) (Ag⁺ : R-L1 molar ratio = 0.6) after 72 h aging. The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
Fig. S38 AFM images of (A) aggregate I and (B) aggregate III. AFM image of a mixed sample of aggregate I (7.2 mM, 50 μL) and aggregate III (7.2 mM, 50 μL) after aging for (C) 10 min, (D) 1 h, and (E) 1 day. The molar ratio of Ag$^+$ to R-L$^1$ in the mixed sample is 1.0 equiv. (F) Time-dependent CD spectra of the mixed sample of aggregate I (7.2 mM, 50 μL) and aggregate III (7.2 mM, 50 μL) in DMSO/H$_2$O (1:1 v/v). The blue arrows indicate right-handed helical fiber. The pink arrows indicate left-handed helical fiber.
Fig. S39 Plot of CD spectral changes (at 323.5 nm) of R-L₁ vs temperature in the presence of different equiv. of AgNO₃: (a) 0.6 equiv. of AgNO₃ and (c) 1.2 equiv. of AgNO₃. (b) Aggregate I (7.2 mM, 50 μL) + aggregate III (7.2 mM, 21.5 μL), consisting 0.6 equiv. of AgNO₃. (d) Aggregate I (7.2 mM, 50 μL) + aggregate III (7.2 mM, 75 μL), consisting 1.2 equiv. of AgNO₃.

[Note] Temperature-dependent CD spectral changes were observed by heating with 1 °C/min.

Fig. S40 (A) Time-dependent CD spectra of aggregate I upon addition of AgNO₃ (1.2 equiv.) in DMSO/H₂O (1:1 v/v). (B) Plot of CD spectral changes (at 323.5 nm) of aggregate I upon addition of AgNO₃ (1.2 equiv.) vs time.
Fig. S41 (A) FT-IR spectra of sol state (brown line) of $R$-$L^1$ and aggregate I (blue line). (B) FT-IR spectra of (a) AgNO$_3$ (black line), (b) aggregate I (blue line), (c) aggregate II (purple line), and (d) aggregate III (pink line).
Fig. S42 Temperature-dependent $^1$H NMR spectra of aggregate I in DMSO-$d_6$/D$_2$O (1:1 v/v); (a) 368 K, (b) 363 K, (c) 353 K, (d) 343 K, (e) 333 K, (f) 323 K, (g) 313 K, and (h) 303 K.

Fig. S43 Temperature-dependent $^1$H NMR spectra of aggregate II in DMSO-$d_6$/D$_2$O (1:1 v/v); (a) 343 K, (b) 333 K, (c) 323 K, (d) 313 K, and (e) 303 K.
**Fig. S44** WAXD patterns of $R$-$L^1$ (6.4 mM) in the presence of different equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v): (A) 0.5 equiv., (B) 0.8 equiv., and (C) 1.2 equiv.

**Fig. S45** WAXD patterns of $R$-$L^1$ (6.4 mM) in the presence of different equiv. of AgNO$_3$ in DMSO/H$_2$O (1:1 v/v): (A) 0 equiv., (B) 2.0 equiv.
Fig. S46 DFT-optimized structures of (A) R-L\textsuperscript{1}, (B) [R-L\textsuperscript{1}(AgNO\textsubscript{3})\textsubscript{2}], and (C) partial [R-L\textsuperscript{1}Ag]\textsuperscript{+}. Note for the structure (C): Since NO\textsubscript{3}\textsuperscript{-} remains uncoordinated in the FT-IR study, its coordination was ignored in the DFT calculation.

Fig. S47 Temperature-dependent absorption changes of (A) aggregate I and (B) aggregate II through heating (red points) and cooling (blue points).

[Note] In our repeated measurements of the cooling and heating curves for aggregate I (based on R-L\textsuperscript{1}), no evidences of the hysteresis were found (Fig. S47A). During the heating and cooling, the \(T_c\) values are 327.2 and 325.7 K, respectively. While the \(T_m\) values are 317.5 and 316.9 K, respectively.
Fig. S48 Temperature-dependent UV spectra of different concentrations of R-L₁ with AgNO₃ (A) aggregate I, (B) aggregate II, and (C) aggregate III in DMSO/H₂O (1:1 v/v). The melting curves of aggregate II and aggregate III were measured by varying the aging time of the same sample (1.2 equiv. of AgNO₃). Aggregates I and II were measured after aging for 3 days, and aggregate III was measured after aging for 1 h.
Fig. S49 (A) Time-dependent UV-vis spectral changes of different [R-L1] in the presence 0.6 equiv. of AgNO3 in DMSO/H2O (1:1 v/v): (a) 6.4 mM, (b) 6.8 mM, (c) 7.2 mM, and (d) 8.5 mM. (B: raw spectral data for the plots in A) Time-dependent UV-vis spectra of different [R-L1] in the presence 0.6 equiv. of AgNO3: (a) 6.4 mM, (b) 6.8 mM, (c) 7.2 mM, and (d) 8.5 mM in DMSO/H2O (1:1 v/v) at 20 °C (cell path length: 0.1 mm).
**Table S1.** Photochemical, helical, and morphology properties of supramolecular polymers based on R-L1 without and with AgNO3.

| UV-vis absorption | \([R-L1]_n\) | \([R-L1\text{Ag}^+]_n\) | \([R-L1(\text{AgNO}_3)_2]_n\) |
|-------------------|-----------------|-----------------|-----------------|
| ILCT              | 280 nm          | 285 nm          | 285 nm          |
| MLCT              | *No MLCT*       | 318 nm, 326 nm  | 318 nm, 326 nm  |
| CD                | Positive(P-type)| Negative(M-type)| Negative(M-type)|
| Morphology        | Right-handed helix | Left-handed helix | Spherical structure |
| Pitch Angle       | *ca. 28±3°*     | *ca. 30±3°*     |                 |
| Length            | *ca. 55±7 nm*   | *ca. 75±5 nm*   |                 |
| Height            | *ca. 8 nm*      | *ca. 5 nm*      | *ca. 7.5 nm*    |

**Table S2.** Cartesian coordinates of an optimized structure for R-L1.

| atom | x     | y     | z     | atom | x     | y     | z     |
|------|-------|-------|-------|------|-------|-------|-------|
| O    | 20.34365 | -6.24608 | -2.00909 | C    | 1.82848  | 0.18669 | 1.81205 |
| O    | 16.88319 | -3.24205 | -3.47785 | C    | 2.18332  | 1.46574 | 2.24218 |
| O    | 5.37778  | -5.06214 | -1.13148 | C    | 1.81736  | 2.43657 | 2.35309 |
| O    | 1.13451  | -4.27374 | -1.0479  | C    | -0.12463 | 2.07062 | 2.02935 |
| N    | 23.26064 | -10.4009 | 1.05595  | H    | 24.12196 | -4.10394 | 0.13602 |
| N    | 23.56973 | -5.77757 | 3.02392  | H    | 25.47902 | -2.67092 | 1.67436 |
| N    | 22.71489 | -7.64564 | 1.09797  | H    | 19.15803 | -3.6598  | -3.72442 |
| N    | 17.96563 | -5.21253 | -3.14253 | H    | 19.88235 | -4.28622 | -1.49065 |
| N    | 4.21376  | -4.60544 | -3.02156 | H    | 21.25165 | -4.47956 | -2.63137 |
| N    | -3.80583 | -2.66107 | 1.81472  | H    | 20.7719  | -5.01773 | -5.09962 |
| N    | -1.12425 | -1.88857 | 1.49042  | H    | 19.92074 | -6.5101  | -4.6324  |
| N    | -0.47187 | 0.85201  | 1.62226  | H    | 19.08667 | -5.27804 | -5.62215 |
| C    | 20.94845 | -10.7713 | 0.52017  | H    | 17.89463 | -6.16864 | -2.81395 |
| C    | 21.07487 | -12.1268 | 0.82529  | H    | 4.25495  | -4.2617  | -3.97384 |
| C    | 22.31569 | -12.6073 | 1.24543  | H    | 19.98504 | -10.361  | 0.21144 |
| C    | 23.37382 | -11.6958 | 1.34215  | H    | 20.21353 | -12.7952 | 0.7442   |
| C    | 24.29709 | -5.01334 | 3.83548  | H    | 22.4646  | -13.6599 | 1.49715  |
| C    | 25.00267 | -3.88141 | 3.41019  | H    | 24.3643  | -12.037  | 1.66815  |
| C    | 24.93682 | -3.53861 | 2.05937  | H    | 24.32421 | -5.31286 | 4.89056  |
| C    | 24.17316 | -4.33206 | 1.2025   | H    | 25.58753 | -3.29241 | 4.1204   |
| C    | 23.50013 | -5.45068 | 1.72657  | H    | 20.615   | -8.69953 | -1.3483  |
| C    | 22.07255 | -9.93514 | 0.64809  | H    | 21.88288 | -4.70055 | -0.33785 |
| C    | 21.98778 | -8.47208 | 0.33498  | H    | 15.581   | -4.9599  | -1.51368 |
| C    | 22.67405 | -6.33847 | 0.84489  | H    | 15.62528 | -6.17039 | -2.79773 |
| C    | 21.89925 | -5.77909 | -0.19045 | H    | 14.29999 | -4.63596 | -4.29306 |
| C    | 21.18443 | -8.01632 | -0.71715 | H    | 14.35478 | -3.38244 | -3.06216 |
| atom | x     | y     | z     | atom | x     | y     | z     |
|------|-------|-------|-------|------|-------|-------|-------|
| Ag   | -1.82356 | -1.66345 | 3.23628 | C    | -1.01212 | -3.29874 | 0.48541 |
| Ag   | 22.86432  | -6.93279  | 3.31484  | C    | 1.00908  | -3.19914  | -0.8307 |
| O    | 23.66205  | -6.22014  | 5.32723  | C    | 1.60942  | -2.48651  | 0.21666 |
| O    | 24.78481  | -7.25705  | 6.86734  | C    | 0.84781  | -2.22313  | 1.3673 |
| O    | 24.24329  | -8.29714  | 5.03959  | C    | 1.41884  | -1.46418  | 2.52765 |
| O    | -4.14505  | -0.81871  | 4.02301  | C    | 2.8001  | -1.39567  | 2.77173 |
| O    | -4.32043  | -0.31223  | 6.12736  | C    | 3.25661  | -0.67205  | 3.87465 |
| O    | -2.42121  | -1.00313  | 5.33743  | C    | 2.32865  | -0.0449  | 4.70736 |
| O    | 20.0495  | -7.09945  | 2.58035  | C    | 0.97074  | -0.17474  | 4.39951 |
| O    | 17.18979  | -5.05571  | -5.78945  | H    | 21.30362  | -3.09877  | -0.2439 |
| O    | 5.6253  | -4.90053  | -2.50909  | H    | 22.43026  | -1.15751  | 0.8373 |
| O    | 1.61313  | -3.50397  | -1.99266  | H    | 19.41316  | -5.59775  | -5.47641 |
| N    | 24.2482  | -7.27334  | 5.77304  | H    | 19.5613  | -5.14423  | -3.09624 |
| N    | -3.65974  | -0.70043  | 5.17906  | H    | 21.14635  | -5.73041  | -3.69961 |
| N    | 21.87497  | -9.09177  | 2.76091  | H    | 21.20617  | -7.35789  | -5.69711 |
| N    | 23.0669  | -4.75383  | 2.11528  | H    | 20.17326  | -8.52404  | -4.83692 |

Table S3. Cartesian coordinates of an optimized structure for [R-L\(^{1}\)(AgNO\(_{3}\))]\(_{2}\).
Table S4. Cartesian coordinates of an optimized Structure for Partial \([R\cdot L_1\cdot Ag]^+\).

| atom | x      | y      | z      | atom | x      | y      | z      |
|------|--------|--------|--------|------|--------|--------|--------|
| Ag   | 3.1521 | -1.2514| 0.8467 | C    | 10.4529| 1.6876 | -0.0604|
| Ag   | 3.5853 | 1.47762| 1.45262| C    | 11.4602| 2.55669| 0.71412|
|   | 1.31004 | -0.8902 | 12.45217 | 3.20841 | -0.25491 |
|---|---------|---------|-----------|---------|-----------|
| O | -3.38266 |         |           |         |           |
| O | -2.9963  | -0.93771| 1.73704   | 10.41521| 3.54984   |
| O | 9.70799  | 0.79438 | 0.78368   | 11.06207| 2.51053   |
| O | 9.59967  | 4.3631  | 3.25108   | 10.64339| 2.65922   |
| N | 2.29449  | -3.44141| 0.48382   | 8.29636 | 3.16137   |
| N | -4.9286  | -0.27001| -0.34558  | 8.3027  | -1.05934  |
| N | 0.89195  | -1.0259 | 0.3258    | -1.59251| -3.02439  |
| N | 2.10177  | 1.64182 | -0.29999  | -1.59432| 1.21538   |
| N | 4.46445  | 3.6604  | 1.76068   | 3.0187  | -2.77934  |
| N | 5.8083   | 1.21141 | 2.10738   | 4.06318 | -4.50345  |
| N | 4.57955  | -1.51131| 2.65756   | 6.55903 | -3.06399  |
| N | 10.78145 | 3.56743 | 1.51174   | 7.56845 | -1.27439  |
| C | 0.94692  | -5.83956| 0.09141   | 4.1924  | -3.80793  |
| C | 2.34199  | -5.80556| 0.07322   | 3.65989 | 2.83781   |
| C | 2.9715   | -4.57696| 0.27514   | 2.30781 | 4.02725   |
| C | 0.24165  | -4.65514| 0.30713   | -0.16032| 3.48222   |
| C | 0.94922  | -3.45871| 0.50403   | -5.56936| -0.95232  |
| C | -3.25919 | 0.49714 | -3.62149  | -0.84803| -4.66144  |
| C | -4.38539 | 0.04747 | -2.69756  | -2.30499| 0.01372   |
| C | -4.17125 | 0.43147 | -1.23578  | -3.49089| 0.24079   |
| C | -6.02366 | 1.28859 | 1.26452   | -3.11675| 1.58568   |
| C | -5.13786 | 0.04993 | 1.0702    | -4.5477 | -1.04164  |
| C | -3.8379  | 0.21835 | 1.86659   | -5.33849| 0.51307   |
| C | -1.09086 | 0.25512 | 0.79819   | -5.656  | -0.82841  |
| C | -1.75931 | -0.8939 | 1.25344   | -5.54552| 2.18163   |
| C | -1.07324 | -2.12096| 1.16767   | -6.99531| 1.14528   |
| C | 0.2368   | -2.15231| 0.69402   | -6.21654| 1.47507   |
| C | 0.21498  | 0.13724 | 0.31758   | -4.09296| 0.29712   |
| C | 2.60255  | 2.59367 | -1.1138   | -3.31971| 1.13024   |
| C | 1.84126  | 3.27129 | -2.06153  | 0.40969 | -6.77677  |
| C | 0.80245  | 1.30128 | -0.42567  | 2.93374 | -6.70655  |
| C | -0.03945 | 1.96871 | -1.33486  | -1.09502| 1.69388   |
| C | 0.4841   | 2.9652  | -2.1571   | 2.721   | 4.78272   |
| C | 6.48559  | 2.31074 | 1.71296   | 3.88081 | 6.91949   |
| C | 6.46983  | 0.03839 | 2.17957   | 6.38799 | 6.88216   |
| C | 7.78372  | -0.10154| 1.73901   | 7.61303 | 4.73536   |
| C | 7.79772  | 2.2502  | 1.23089   | 9.76849 | 2.31409   |
| C | 8.46354  | 1.01405 | 1.21032   | 10.99459| 1.02389   |
| C | 3.80808  | 4.81186 | 1.94336   | 13.00602| 2.45147   |
| C | 5.80415  | 3.63359 | 1.88798   | 11.93636| 3.86803   |
| C | 6.53431  | 4.78058 | 2.23505   | 13.178  | 3.81757   |
| C | 4.45648  | 6.00333 | 2.27394   | 12.01335| 1.89266   |
| C | 5.84277  | 5.97943 | 2.42913   | 10.40543| 4.36691   |
| C | 4.0325   | -2.4616 | 3.44206   | 12.15812| 2.59537   |
| C | 5.82943  | -1.08954| 2.93326   | 10.80908| 1.50468   |
| C | 6.56512  | -1.64585| 3.99385   | 9.55336 | 2.56393   |
| C | 4.69421  | -3.04651| 4.51819   | 11.12886| 1.89061   |
| C | 5.99718  | -2.63473| 4.79462   | 10.92384| 3.64688   |
Table S5. Thermodynamic parameters for aggregate I, aggregate II, and aggregate III (*R-L*: 7 mM) in mixed DMSO and H$_2$O (1:1 v/v).

| Aggregate  | $\Delta G$ (kJ mol$^{-1}$) | $\Delta H_e$ (kJ mol$^{-1}$) | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) | $K_e$ (L mol$^{-1}$) | $T_e$ (K) |
|------------|----------------------------|----------------------------|---------------------------------|---------------------|------------|
| Aggregate I | -22.25                     | -89.6                      | -226                            | $1.4 \times 10^4$   | 335.70     |
| Aggregate II | -20.33                     | -155.22                    | -453                            | $1.0 \times 10^4$   | 314.28     |
| Aggregate III | -17.48                     | -171.81                    | -518                            | $3.7 \times 10^3$   | 307.28     |

*a*Gibbs free energy. *b*Elongation enthalpy. *c*Entropy. *d*Elongation binding constant. *e*Elongation Temperature. The melting curves of aggregate II and aggregate III were measured by varying the aging time of the same sample (AgNO$_3$ 1.2 equiv.). Aggregates I and II were measured after aging for 3 days, and aggregate III was measured after aging for 1 hour.
4. Analytical data

4.1 $^1$H-NMR and $^{13}$C-NMR spectroscopy

![Fig. S51 $^1$H NMR spectrum (300 MHz) of $R$-L$_2^2$ in CDCl$_3$ at 25 °C.](image1)

![Fig. S52 $^{13}$C NMR spectrum (75 MHz) of $R$-L$_2^2$ in DMSO-$d_6$ at 25 °C.](image2)
Fig. S53 $^1$H NMR spectrum (300 MHz) of $R$-$L^1$ in DMSO-$d_6$ at 25 °C.

Fig. S54 $^{13}$C NMR spectrum (75 MHz) of $R$-$L^1$ in DMSO-$d_6$ at 25 °C.
4.2 HR mass spectrometry

Fig. S55 HR EI-MS spectrum of R-L₂ in DCM.

Fig. S56 HR FAB-MS spectrum of R-L₁ in DCM.
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