Electronic supplementary information for:

**Table of Contents:**

**Experimental Section**

**Supporting References**

**Supporting Data**

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**Helix-helix inversion of an optically-inactive π-conjugated foldamer triggered by concentration changes of a single enantiomeric guest leading to a change in the helical stability**

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Experimental Section

1. Materials and Instruments

Materials. All starting materials and dehydrated solvents were purchased from Aldrich Co. (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan) and Tokyo Kasei Kogyo (TCI) (Tokyo, Japan) unless otherwise noted. 4,5-Diiodophthalic acid,41 4S2 and 10S3 were synthesized according to the reported methods. Polytetrafluoroethylene (PTFE) membrane filters (0.02, 0.10, 0.20 and 0.45 µm pore size) were purchased from Advantec Co., Ltd. (Tokyo, Japan).

Instruments. The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The NMR spectra were obtained using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for 1H and 125 MHz for 13C. Chemical shifts are reported in parts per million (δ) downfield from tetramethysilane (TMS) as the internal standard in CDCl3, and from residual undeuterated solvent as the internal standard in DMSO-d6. The recycling preparative HPLC was performed with an LC-928R liquid chromatograph (Japan Analytical Industry, Tokyo, Japan) equipped with two size exclusion chromatography (SEC) columns (2 × JALGEL-2H (1 × 60 cm)) in series and a UV-visible detector (254 nm, JAI UV-310), and CHCl3 was used as the eluent. The SEC measurements were performed with a JASCO PU-1580 liquid chromatograph equipped with a UV-visible detector (254 nm, JASCO UV-1570) and a column oven (JASCO CO-1565). The number-average molecular weight (Mn) and its distribution (Mw/Mn) were determined at 40 ˚C using a Tosoh TSKgel Multipore HXL-M (0.78 (i.d.) × 30 cm) SEC column (Tosoh, Tokyo, Japan), and tetrahydrofuran (THF) with 0.5 wt% tetra-n-butylammonium bromide (TBAB) was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). The electron spray ionization mass spectra (ESI-MS) were recorded using a JEOL JMS-T100CS spectrometer (Akishima, Japan). The elemental analyses were performed by the laboratory of elemental analyses in the Department of Agriculture, Nagoya University. The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured in a 1-cm quartz cell on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The temperature was controlled by a JASCO PTC-423L apparatus. The fluorescence spectra were measured in a 1-cm quartz cell on a JASCO FP-6500 spectrofluorometer. The concentrations of the polymers were calculated based on the monomer units.
2. Synthetic Procedures

Abbreviations of chemicals:
EDC·HCl: 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride,
HOBt: 1-hydroxybenzotriazole monohydrate,
\(^3\)Pr\(_2\)NH: diisopropylamine,
NEt\(_3\): triethylamine,
TBAF: tetra-\(n\)-butylammonium fluoride,
Tg: 2-(2-(2-methoxyethoxy)ethoxy)ethyl

Scheme S1. Synthesis of poly[(\(o\)-phenyleneethynylene)-\(alt\)-(\(p\)-phenyleneethynylene)] derivatives.
Reagents and conditions: a) Cl\(\text{CH}_2\text{CH}_3\), NEt\(_3\)/THF, r.t., b) 10, Pd(PPh\(_3\))\(_2\)Cl\(_2\), CuI, NEt\(_3\)/THF, r.t., c) TBAF, acetic acid, THF, 0 °C, d) 3, Pd(PPh\(_3\))\(_4\), CuI, \(^3\)Pr\(_2\)NH/THF, 35 °C, e) fractionation by SEC using CHCl\(_3\) as eluent, f) aqueous KOH/THF, r.t., g) 4, Pd(PPh\(_3\))\(_4\), CuI, \(^3\)Pr\(_2\)NH/THF, 35 °C.
3. To a suspension of 4,5-diiodophthalic acid (3.00 g, 7.18 mmol) in THF (60.0 mL) and NEt3 (3.00 mL) was slowly added chloromethyl methyl ether (1.65 mL, 21.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated to dryness under reduced pressure. The residue was dissolved in EtOAc, and the solution was washed with 5% aqueous NaHCO3, brine, and dried over MgSO4. The solvent was then evaporated in vacuo to afford 3 (2.60 g, 71.6% yield) as a white solid. Mp: 144–146 °C. 1H NMR (500 MHz, CDCl3, 25 °C): δ 8.21 (s, 2H, ArH), 5.45 (s, 4H, OCH2), 3.54 (s, 6H, OCH3). 13C NMR (125 MHz, CDCl3, 30 °C): δ 165.14, 139.40, 132.09, 112.18, 92.37, 58.33. IR (KBr, cm−1): 1716 (νC=O). Anal. Calcd for C12H12I2O6: C, 29.42; H, 2.50. Found: C, 29.42; H, 2.45.

8. Into a two-neck round bottom flask containing 3 (600 mg, 1.19 mmol), 10 (1.01 g, 3.56 mmol), Pd(PPh3)2Cl2 (34 mg, 0.048 mmol), PPh3 (9.3 mg, 0.036 mmol) and CuI (14 mg, 0.071 mmol) were added NEt3 (9.0 mL) and THF (1.2 mL) under Ar. The reaction mixture was stirred at room temperature overnight, and the solvent was then removed by evaporation. The residue was dissolved in CHCl3 and the solution was washed with 0.1 M aqueous HCl, brine, and dried over MgSO4. After evaporation, the residue was purified by column chromatography on silica-gel (n-hexane/EtOAc (4/1, v/v) as eluent) to afford 8 (0.71 g, 73% yield) as a white solid. Mp: 153–154 °C. 1H NMR (500 MHz, CDCl3, 25 °C): δ 7.94 (s, 2H, ArH), 7.49 (m, 8H, ArH), 5.48 (s, 4H, OCH2), 3.57 (s, 6H, OCH3), 1.14 (m, 42H, Si(iPr)3). 13C NMR (125 MHz, CDCl3, 30 °C): δ 165.96, 132.43, 132.29, 131.70, 131.01, 128.68, 124.52, 122.21, 106.51, 96.69, 93.79, 92.25, 88.58, 58.28, 18.79, 11.42. IR (KBr, cm−1): 2214 (νC≡C), 2153 (νC≡C), 1735 (νC=O). HRMS(ESI-MS): m/z calcd for [M(C50H62O6Si2) + Na]+, 837.3983; found 837.3988.

5. To a solution of 8 (0.70 g, 0.85 mmol) in THF (5 mL) was added a 0.1 M solution of AcOH in THF (33 mL) at 0 °C. To this was slowly added a 0.2 M solution of TBAF in THF (15 mL, 3.0 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and to this was then added 30 mL toluene. After most of THF was removed under reduced pressure, the solution was washed with brine and dried over MgSO4. After evaporation, the residue was purified by column chromatography on silica-gel (n-hexane/EtOAc (3/1, v/v) as eluent) to afford 5 (0.39 g, 91% yield) as a white solid. Mp: 105–106 °C. 1H NMR (500 MHz, CDCl3, 25 °C): δ 7.95 (s, 2H, ArH), 7.50 (m, 8H, ArH), 5.49 (s, 4H, OCH2), 3.57 (s, 6H, OCH3), 3.22 (s, 2H, C≡CH). 13C NMR (125 MHz, CDCl3, 30 °C): δ 165.91, 132.47, 132.36, 131.78, 131.08, 128.59, 123.10, 122.80, 96.37, 92.26,
88.67, 83.11, 79.75, 58.28. IR (KBr, cm⁻¹): 2212 (νC≡C), 2109 (νC≡C), 1735 (νC=O). Anal. Calcd for C₃₂H₂₂O₆: C, 76.48; H, 4.41. Found: C, 76.49; H, 4.22.

9. To a two-neck round bottom flask containing 4 (0.40 g, 0.49 mmol), Pd(PPh₃)₂Cl₂ (13.7 mg, 19.6 µmol), PPh₃ (3.85 mg, 14.7 µmol), CuI (5.60 mg, 29.4 µmol) and 10 (0.42 g, 1.5 mmol) were added THF (5.0 mL) and NEt₃ (5.0 mL) under Ar. The reaction mixture was stirred at room temperature overnight. The solvent was then removed by evaporation, the residue was dissolved in CHCl₃, and the solution was washed with 0.1 M aqueous HCl, brine, and dried over MgSO₄. After evaporation, the residue was purified by column chromatography on silica-gel (EtOAc/MeOH (10/1, v/v) as eluent) to afford 9 (0.39 g, 85% yield) as a pale yellow solid. Mp: 229–230 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 7.78 (s, 2H, ArH), 7.48 (m, 8H, ArH), 7.30 (d, J = 7.9 Hz, 2H, NH), 4.33–4.26 (m, 2H, CH), 3.68–3.54 (m, 24H, OCH₂), 3.52–3.47 (m, 4H, CH₂), 3.32 (s, 6H, OCH₃), 1.29 (d, J = 6.8 Hz, 6H, CH₃), 1.18–1.11 (m, 42H, Si(iPr)₃). ¹³C NMR (125 MHz, CDCl₃, 30 °C): δ 167.34, 134.67, 132.24, 131.95, 131.58, 127.07, 124.22, 122.49, 106.54, 95.48, 93.56, 88.96, 73.94, 71.97, 70.84, 70.67, 70.65, 70.64, 70.54 59.05, 46.14, 18.77, 17.55, 11.39. IR (KBr, cm⁻¹): 3247 (νN-H), 2152 (νC≡C), 1636 (νC=O). HRMS(ESI-MS): m/z calcd for [M(C₆₆H₉₆N₂O₁₀Si₂) + Na]⁺, 1155.6501; found 1155.6447.

6. To a solution of 9 (0.39 g, 0.35 mmol) in THF (5 mL) was added a 0.1 M solution of AcOH in THF (8.0 mL) at 0 °C. To this was slowly added a 0.1 M solution of TBAF in THF (8.0 mL, 0.80 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and then to this was added 50 mL toluene. After most of THF was removed under reduced pressure, the solution was washed with brine and dried over MgSO₄. After evaporation, the residue was purified by column chromatography on silica-gel (EtOAc/MeOH (8/1, v/v) as eluent) to afford 6 (0.25 g, 86% yield) as a pale yellow solid. Mp: 173–174 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 7.79 (s, 2H, ArH), 7.49 (m, 8H, ArH), 7.29 (d, J = 7.9 Hz, 2H, NH), 4.33–4.26 (m, 2H, CH), 3.68–3.54 (m, 24H, OCH₂), 3.52–3.47 (m, 4H, CH₂), 3.33 (s, 6H, OCH₃), 3.21 (s, 2H, C≡CH), 1.29 (d, J = 6.8 Hz, 6H, CH₃). ¹³C NMR (125 MHz, CDCl₃, 30 °C): δ 167.28, 134.71, 132.25, 131.89, 131.62, 126.89, 123.07, 122.74, 95.08, 89.09, 83.10, 79.60, 73.89, 71.89, 70.74, 70.59, 70.58, 70.57, 70.45, 58.98, 46.06, 17.45. IR (KBr, cm⁻¹): 3239 (νN-H), 2152 (νC≡C), 1636 (νC=O). Anal. Calcd for C₄₈H₅₆N₂O₁₀: C, 40.79; H, 5.62; N, 3.40. Found: C, 40.81; H, 5.53, N, 3.32.
To a solution of **5** (80 mg, 0.16 mmol) in THF (1.3 mL) was added aqueous KOH (0.72 mmol, 1.3 mL). The reaction mixture was stirred at room temperature for 24 h. The solution was then diluted with 5% aqueous NaHCO₃, and the resulting solution was washed with CHCl₃. The aqueous layer was acidified to pH 1–2 by 1 M aqueous HCl. The resulting precipitate was collected, washed with distilled water, and dried under vacuum to afford **7** (41 mg, 62% yield) as a pale yellow solid. Mp: 185 °C (dec.). ¹H NMR (500 MHz, DMSO-d₆, 25 °C): δ 7.96 (s, 2H, ArH), 7.64–7.55 (m, 8H, ArH), 4.41 (s, 2H, C≡CH). ¹³C NMR (125 MHz, DMSO-d₆, 25 °C): δ 167.22, 133.00, 132.30, 132.07, 131.84, 126.41, 122.79, 121.92, 95.20, 88.56, 83.40, 82.91. IR (KBr, cm⁻¹): 3404 (νO-H), 2208 (νC=C), 2106 (νC=C), 1707 (νC=O). HRMS(ESI-MS): m/z calcd for [M(C₂₈H₄₈O₄) – H]⁺, 413.0814; found 413.0815.

**poly-1-MOM.** Into a Schlenk tube containing **3** (302 mg, 0.597 mmol), **5** (300 mg, 0.597 mmol), CuI (3.41 mg, 17.9 μmol) and Pd(PPh₃)₄ (13.8 mg, 11.9 μmol) were added degassed THF (7.8 mL) and Pr₂NH (1.95 mL) at room temperature under Ar. The flask was subjected to three evacuation/Ar fill cycles, and the reaction mixture was stirred at 35 °C overnight. To this was then added Et₂O (20 mL), and the resulting precipitate was washed in CHCl₃ and the solution was washed with 0.1 M aqueous HCl, brine, and dried over MgSO₄. The solvent was evaporated in vacuo to afford poly-1-MOM (381 mg, 83.7% yield) as a yellow solid. Mp: 205 °C (dec.). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 7.96–7.04 (m, ArH), 5.43 (br, OCH₂), 3.53 (br, OCH₃). ¹³C NMR (125 MHz, CDCl₃, 30 °C): δ 165.64, 132.55–130.59, 128.22, 123.24, 96.18, 92.25, 89.65, 58.26. IR (KBr, cm⁻¹): 2212 (νC=C), 1718 (νC=O). Anal. Calcd for (C₂₂H₄₈O₄)₆: C, 70.21; H, 4.29. Found: C, 70.19; H, 4.28. A part of the polymer (88 mg) was used to further separate into a higher molecular weight fraction (poly-1H-MOM, 54 mg) and a low molecular weight fraction (poly-1L-MOM, 34 mg) by a recycle-SEC using two SEC columns (2 × JAIGEL-2H (1 × 60 cm)) in series (CHCl₃ as eluent).

**poly-1L and poly-1H.** To a solution of poly-1L-MOM (23.0 mg) in THF (0.50 mL) was added aqueous KOH (0.27 mmol, 0.50 mL), and the reaction mixture was stirred at room temperature for 24 h. The solution was then diluted with 5% aqueous NaHCO₃, and the resulting solution was washed with CHCl₃. The aqueous layer was acidified to pH 1–2 by 1 M aqueous HCl. The resulting precipitate was collected, washed with distilled water, and dried under vacuum to afford poly-1L (13.2 mg, 73.2% yield) as a brown solid. Poly-1L: Mp: 171.5-172 °C (dec.). ¹H NMR (500 MHz, DMSO-d₆, 25 °C): δ 8.07–7.30 (br, ArH). ¹³C NMR (125 MHz, DMSO-d₆, 25 °C): δ 167.06,
133.10, 132.57, 131.90, 126.34, 122.48, 95.14, 89.24. IR (KBr, cm\(^{-1}\)): 3434 (\(\nu_{\text{O-H}}\)), 2211 (\(\nu_{\text{C=C}}\)), 1710 (\(\nu_{\text{C=O}}\)). Anal. Calcd for (C\(_{18}\)H\(_{12}\)O\(_{4}\))\(_{n}\): C, 75.00; H, 2.80. Found: C, 74.96, H, 2.81. In the same way, poly-1H was obtained from poly-1H-MOM in 75.6% yield. poly-1H: Mp: 265 °C (dec.).

\(\text{\(^{1}\)H NMR (500 MHz, DMSO-}\text{d}_6, 25 ^\circ\text{C}}\): \(\delta\) 8.17–7.40 (br, ArH). \(\text{\(^{13}\)C NMR (125 MHz, DMSO-}\text{d}_6, 25 ^\circ\text{C}}\): \(\delta\) 167.26, 132.88, 132.01, 131.93, 126.53, 122.55, 95.30, 89.28. IR (KBr, cm\(^{-1}\)): 3422 (\(\nu_{\text{O-H}}\)), 2209 (\(\nu_{\text{C≡C}}\)), 1717 (\(\nu_{\text{C=O}}\)). Anal. Calcd for (C\(_{18}\)H\(_{12}\)O\(_{4}\))\(_{n}\): C, 75.00; H, 2.80. Found: C, 74.95, H, 2.79.

**poly-2.** Into a Schlenk tube containing 4 (201 mg, 0.244 mmol), 6 (200 mg, 0.244 mmol), CuI (1.39 mg, 7.30 \(\mu\)mol) and Pd(PPh\(_3\))\(_4\) (5.64 mg, 4.88 \(\mu\)mol) were added degassed THF (3.2 mL) and \(\text{\(^{3}\)Pr}_2\text{NH (0.80 mL}}\) at room temperature under Ar. The flask was subjected to three evaporation/Ar fill cycles, and the reaction mixture was stirred at 35 °C overnight. To this was then added Et\(_2\)O (20 mL), and the resulting precipitate was dissolved in CHCl\(_3\) and the solution was washed with 0.1 M aqueous HCl, brine, and dried over MgSO\(_4\). The solvent was evaporated in vacuo to afford crude poly-2 (290 mg, 85.3% yield) as a yellow solid, which was further purified by a recycle-SEC using two SEC columns (2 × JAIGEL-2H (1 × 60 cm)) in series (CHCl\(_3\) as eluent) to afford poly-2 (190 mg, 56.0% yield) as a yellow solid. Mp: 180 °C (dec.). \(\text{\(^{1}\)H NMR (500 MHz, CDCl}_3, 25 ^\circ\text{C}}\): \(\delta\) 9.14-6.17 (br, ArH), 4.48-2.92 (br, Tg proton), 1.48–1.03 (br, CH\(_3\)). \(\text{\(^{13}\)C NMR (125 MHz, CDCl}_3, 25 ^\circ\text{C}}\): \(\delta\) 166.85, 133.41, 131.74-129.85, 126.88, 123.04, 94.67, 90.04, 74.13, 72.21-70.27, 70.05, 59.19, 46.22, 17.55. IR (KBr, cm\(^{-1}\)): 3263 (\(\nu_{\text{O-H}}\)), 2211 (\(\nu_{\text{C=C}}\)), 1636 (\(\nu_{\text{C=O}}\)). Anal. Calcd for (C\(_{38}\)H\(_{52}\)N\(_2\)O\(_{10}\))\(_{n}\): C, 65.69; H, 7.25; N, 4.03. Found: C, 65.69, H, 7.29, N, 3.86.

The molecular modeling was performed on a Windows 7 PC with the ArgusLab software. The initial structure of poly-1 (9mer) was constructed based on its related structures of o-PE and o-PE-alt-p-PE oligomers that have been reported to adopt a 3_1-helical conformation (three monomer units per turn). The initial model was then fully optimized by the semi-empirical molecular orbital (MO) calculations (PM6 method in MOPAC2012). The calculated CD spectrum for the resultant energy-minimized structure as shown in Fig. 3 was obtained using ZINDO method in Gaussian 09 software (Gaussian, Inc., Pittsburgh, PA). Gaussian bands with a half-bandwidth of 0.19 eV were used to generate the CD spectrum. Computer resource for the ZINDO calculation was provided by the Information Technology Center of Nagoya University.

Supporting References

(S4) M. Thompson, ArgusLab, Planaria Software LLC, Seattle, WA (1996).
Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
### Supporting Data

**Table S1.** Yield and molecular weight data for poly-1-MOM, poly-1H-MOM, poly-1L-MOM and poly-2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_n \times 10^{-3}$</th>
<th>$M_w/M_n$</th>
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<td>poly-1-MOM</td>
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<td>2.6</td>
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<tr>
<td>poly-2</td>
<td>56.0</td>
<td>9.9</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^a\) A part of poly-1-MOM was separated into two fractions, a higher molecular weight polymer (poly-1H-MOM) and a low molecular weight polymer (poly-1L-MOM) by SEC using CHCl\(_3\) as eluent. \(^b\) Determined by SEC (polystyrene standards using THF with 0.5 wt% TBAB as eluent).

**Fig. S1** (a) CD and absorption spectra of poly-1L in the presence of varying amounts of (S,S)-A1 in DMSO at 25 °C: [poly-1L] = $6.8 \times 10^{-5}$ M per monomer unit. (b) CD and absorption spectra of 7 in the presence of varying amounts of (S,S)-A1 in H\(_2\)O/THF (6.5/3.5, v/v) at 25 °C: [7] = $6.8 \times 10^{-5}$ M.

**Fig. S2** CD and absorption spectra of poly-2 in the absence and presence of 1.5 equiv. of (R,R)-A1 or (S,S)-A1 in H\(_2\)O/THF (6.5/3.5, v/v) at 25 °C: [poly-2] = $9.0 \times 10^{-5}$ M per monomer unit.
**Fig. S3** CD (a, b), absorption (a, b) and fluorescence spectra (c, d; excitation wavelength = 362 nm) of poly-1L in the presence of varying amounts of (S,S)-A1 ([A1]/[poly-1L] = 0–0.19 (a, c) and 0.29–1.3 (b, d)) in H$_2$O/THF (6.5/3.5, v/v) at 25 °C: [poly-1L] = 6.8 × 10$^{-5}$ M per monomer unit.

**Fig. S4** Calculated CD spectrum for the energy-minimized left-handed structure of poly-1 (9mer, see Fig. 3) obtained using the ZINDO method. Gaussian bands with a half-bandwidth of 0.19 eV were used.
Fig. S5 CD (a), absorption (a) and fluorescence spectra (b; excitation wavelength = 362 nm) of poly-1L in the presence of varying amounts of (S)-A3 in H₂O/THF (6.5/3.5, v/v) at 25 °C: [poly-1L] = 6.8 × 10⁻⁵ M per monomer unit.

Fig. S6 CD (a), absorption (a) and fluorescence spectra (b; excitation wavelength = 362 nm) of poly-1L in the presence of varying amounts of (S)-A4 in H₂O/THF (6.5/3.5 v/v) at 25 °C: [poly-1L] = 6.8 × 10⁻⁵ M per monomer unit.
Fig. S7 CD (a), absorption (b) and fluorescence spectra (b; excitation wavelength = 362 nm) of poly-1L in the presence of varying amounts of (S,S)-A2 in H₂O/THF (6.5/3.5, v/v) at 25 °C: [poly-1L] = 6.8 × 10⁻⁵ M per monomer unit. (c) Plots of CD intensity (left axis) at 350 nm, molar absorptivity (right axis I) at 315 nm and fluorescence intensity (right axis II) at 450 nm of poly-1L versus the molar ratio of (S,S)-A2 to poly-1L in H₂O/THF (6.5/3.5, v/v) at 25 °C: [poly-1L] = 6.8 × 10⁻⁵ M per monomer unit. (d) Temperature-dependent CD and absorption spectral changes of poly-1L in the presence of 1.1 equiv. of (S,S)-A2 in H₂O/THF (6.5/3.5, v/v): [poly-1L] = 6.8 × 10⁻⁵ M per monomer unit.
**Fig. S8** CD (a, b), absorption (a, b) and fluorescence spectra (c, d; excitation wavelength = 362 nm) of poly-1H in the presence of varying amounts of (S,S)-A1 ([A1]/[poly-1H] = 0–0.3 (a), 0.5–1.5 (b), 0–0.1 (c) and 0.2–1.5 (d)) measured immediately after the addition of (S,S)-A1 in H₂O/THF (6.5/3.5, v/v) at 25 °C: [poly-1H] = 8.2 × 10⁻⁵ M per monomer unit. (e) Plots of CD intensity (left axis) at 420 and 350 nm, molar absorptivity (right axis I) at 315 nm and fluorescence intensity (right axis II) at 460 nm of poly-1H versus the molar ratio of (S,S)-A1 to poly-1H in H₂O/THF (6.5/3.5 v/v) at 25 °C: [poly-1H] = 8.2 × 10⁻⁵ M per monomer unit.
**Fig. S9** CD (a), absorption (a) and fluorescence spectra (b; excitation wavelength = 362 nm) of poly-1H in the presence of varying amounts of (S,S)-A2 in H$_2$O/THF (6.5/3.5 v/v) at 25 °C: [poly-1H] = 8.2 × 10$^{-5}$ M per monomer unit.

**Fig. S10** CD and absorption spectra of poly-1H in the presence of A1 with different ee values ((S)-rich) measured immediately after the addition of A1 (a) and after 500 h (b) in H$_2$O/THF (6.5/3.5 v/v) at 25 °C: [poly-1H] = 8.2 × 10$^{-5}$ M per monomer unit, [A1]/[poly-1H] = 0.5.
Fig. S11 CD and absorption spectra of poly-1L in the presence of A1 with different ee values (S-rich) in H₂O/THF (6.5/3.5, v/v) at 25 °C: [poly-1L] = 6.8 × 10⁻⁵ M per monomer unit, [A1]/[poly-1L] = 0.19.

Fig. S12 (a) Time-dependent CD and absorption spectral changes of poly-1H in the presence of (S,S)-A1. (b) Plots of CD intensity at 356 nm of poly-1H versus time in H₂O/THF (6.5/3.5, v/v) at 25 °C: [poly-1H] = 8.2 × 10⁻⁵ M per monomer unit and [(S,S)-A1]/[poly-1H] = 0.5.
**Fig. S13** Absorption spectra of a solution of poly-1H with 0.5 equiv. of (S,S)-A1 in H₂O/THF (6.5/3.5, v/v) (225 h after the addition of (S,S)-A1) before (a) and after filtrations through membrane filters with pore size of 0.45 (b), 0.20 (c), 0.10 (d) and 0.02 µm (e): [poly-1H]₀ = 8.2 × 10⁻⁵ M per monomer unit.

**Fig. S14** (a) Time-dependent CD and absorption spectral changes of poly-1L in the presence of (S,S)-A1 in H₂O/THF (6.5/3.5, v/v) at 25 °C: [poly-1L] = 6.8 × 10⁻⁵ M per monomer unit and [(S,S)-A1]/[poly-1L] = 0.19.
**Fig. S15** $^1$H NMR spectrum of 3 in CDCl$_3$ at 25 °C.

**Fig. S16** $^{13}$C NMR spectrum of 3 in CDCl$_3$ at 30 °C.
**Fig. S17** $^1$H NMR spectrum of 5 in CDCl$_3$ at 25 ºC.

**Fig. S18** $^{13}$C NMR spectrum of 5 in CDCl$_3$ at 30 ºC.
**Fig. S19** $^1$H NMR spectrum of 6 in CDCl$_3$ at 25 ºC.

**Fig. S20** $^{13}$C NMR spectrum of 6 in CDCl$_3$ at 30 ºC.
**Fig. S21** $^1$H NMR spectrum of 7 in DMSO-$d_6$ at 25 ºC.

**Fig. S22** $^{13}$C NMR spectrum of 7 in DMSO-$d_6$ at 25 ºC.
**Fig. S23** $^1$H NMR spectrum of 8 in CDCl$_3$ at 25 ºC.

**Fig. S24** $^{13}$C NMR spectrum of 8 in CDCl$_3$ at 30 ºC.
Fig. S25 $^1$H NMR spectrum of 9 in CDCl$_3$ at 25 ºC.

Fig. S26 $^{13}$C NMR spectrum of 9 in CDCl$_3$ at 30 ºC.
**Fig. S27** $^1$H NMR spectrum of poly-1-MOM in CDCl$_3$ at 25 °C.

**Fig. S28** $^{13}$C NMR spectrum of poly-1-MOM in CDCl$_3$ at 30 °C.
**Fig. S29** $^1$H NMR spectrum of poly-1L in DMSO-$d_6$ at 25 ºC.

**Fig. S30** $^{13}$C NMR spectrum of poly-1L in DMSO-$d_6$ at 25 ºC.
Fig. S31 $^1$H NMR spectrum of poly-$\text{1H}$ in DMSO-$d_6$ at 25 °C.

Fig. S32 $^{13}$C NMR spectrum of poly-$\text{1H}$ in DMSO-$d_6$ at 30 °C.
Fig. S33 $^1$H NMR spectrum of poly-2 in CDCl$_3$ at 25 ºC.

Fig. S34 $^{13}$C NMR spectrum of poly-2 in CDCl$_3$ at 30 ºC.