Electronic Supplementary Material (ESI) for Chemical Science

Electronic Supplementary Information

Stereoselective Supramolecular Polymerization of C_n-Symmetric Bowl-Shaped Chiral Macrocycles: Preferential Chiral Self-Sorting

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1. General

Unless otherwise noted, all commercial reagents were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL model GSX270 spectrometer, operating at 270.05 and 67.80 MHz for ^{1}H and ^{13}C NMR, respectively, where chemical shifts were determined with respect to tetramethylsilane as an internal reference. Matrix-assisted laser deposition ionization time-of-flight (MALDI–TOF) mass spectrometry was performed in the reflector mode on a Brucker autoflex TM speed spectrometer using dithranol as a matrix. Electronic absorption and circular dichroism (CD) spectra were recorded on a JASCO model U-best V-560 spectrometer and a JASCO Type J-820 spectropolarimeter, respectively, using quartz cells of 10 and 1 mm optical path lengths. Analytical size-exclusion chromatography (SEC) was performed at 25 °C, using a 7.8 mm x 300 mm polystyrene gel column (TOSOH TSKgel G3000H_{HR}) on a JASCO Type PU-2080i Plus equipped with a JASCO Type MD-2015 Plus variable-wavelength UV-Vis detector and a JASCO Type CD-2095A variable-wavelength CD detector. All of the calculations were performed with the Gaussian 09[S1] program package.

(S1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.

2. ^{1}H and ^{13}C NMR Spectroscopy of (*R*)-1 and (*R*)-2

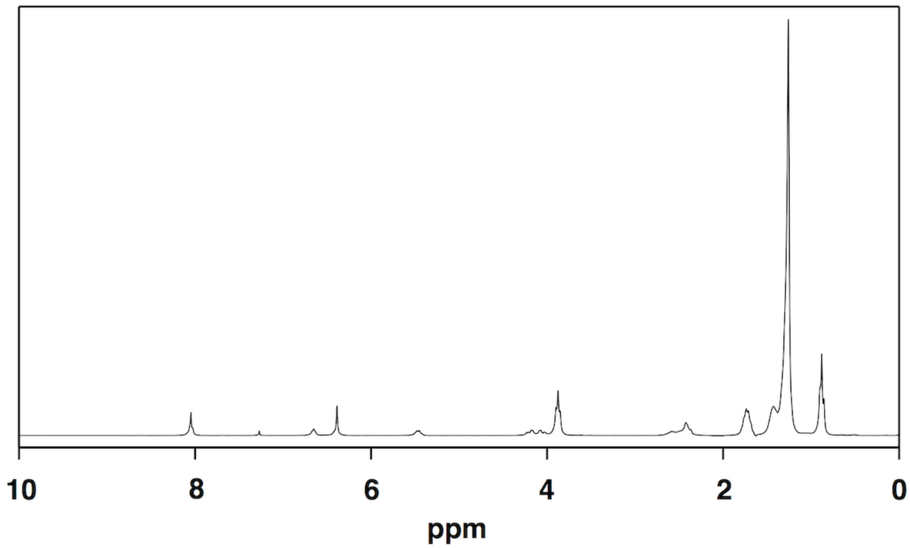

Fig. S1. ^{1}H NMR spectrum (270.05 MHz) of (*R*)-**1** in $CDCl_3$ at 25 °C. δ (ppm) 8.02 (s, 4H), 8.00 (d, *J* = 8.5 Hz, 4H), 6.62 (t, 4H), 6.36 (s, 8H), 5.45–5.42 (m, 4H), 4.18–4.04 (m, 8H), 3.85 (t, 24H), 2.55–2.39 (m, 16H), 1.74–1.68 (m, 24H), 1.43–1.37 (m, 24H), 1.23 (m, 192H), 0.85 (t, 36H).

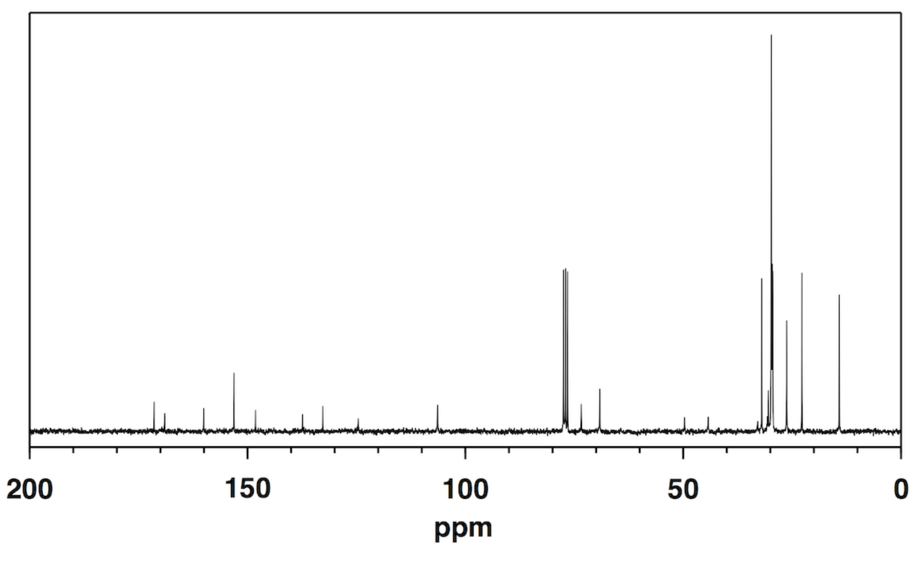

Fig. S2. ^{13}C NMR spectrum (67.80 MHz) of (*R*)-**1** in $CDCl_3$ at 25 °C. δ (ppm) 171.4, 169.0, 153.1, 148.2, 137.4, 132.7, 124.6, 106.4, 73.4, 69.1, 49.7, 44.2, 32.9, 32.0, 30.4, 29.7, 29.6, 29.4, 26.3, 22.8, 14.2.

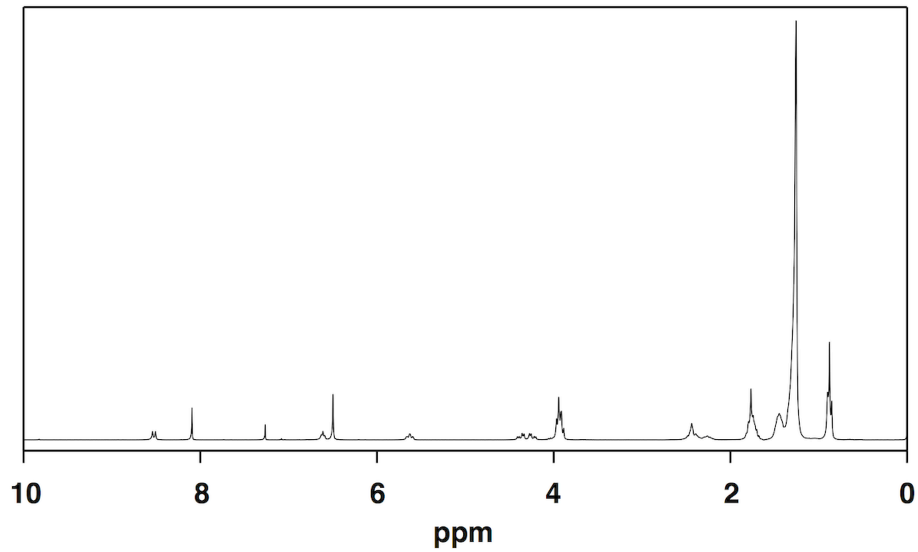

Fig. S3. ^{1}H NMR spectrum (270.05 MHz) of (*R*)-**2** in $CDCl_3$ at 25 °C. *δ* (ppm) 8.49 (d, *J* = 8.9 Hz, 3H), 8.07 (s, 3H), 6.58 (t, 3H), 6.47 (s, 6H), 5.60 (t, 3H), 4.37–4.26 (m, 6H), 3.91–3.86 (m, 18H), 2.45–2.20 (m, 12H), 1.77–1.67 (m, 18H), 1.45–1.39 (m, 18H), 1.23 (m, 144H), 0.85 (t, 27H).

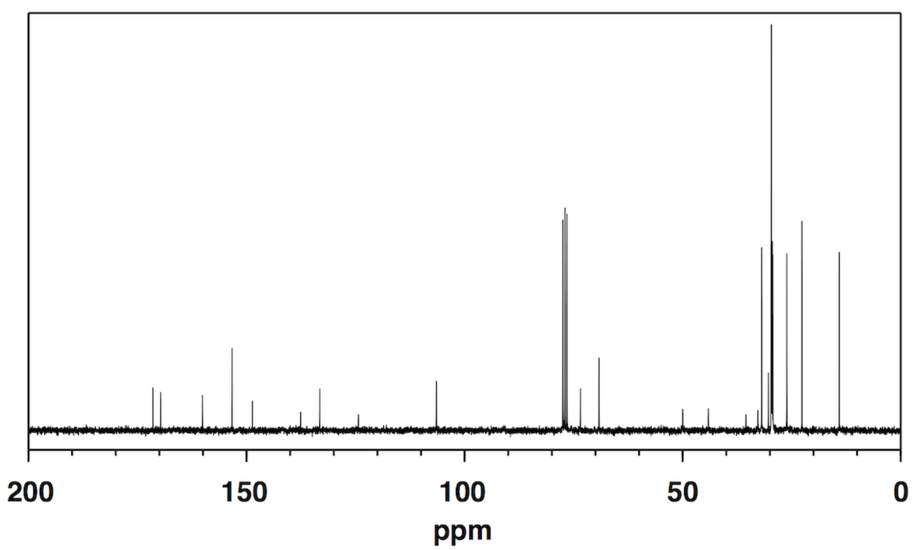

Fig. S4. ^{13}C NMR spectrum (67.80 MHz) of (*R*)-**2** in $CDCl_3$ at 25 °C. *δ* (ppm) 171.5, 169.7, 160.1, 153.3, 148.6, 137.6, 133.2, 124.3, 106.5, 73.4, 69.2, 50.0, 44.1, 35.5, 32.7, 31.9, 30.3, 29.7, 29.7, 29.4, 29.4, 26.1, 22.7, 14.1.

3. MALDI–TOF Mass Spectrometry of (*R*)-1 and (*R*)-2

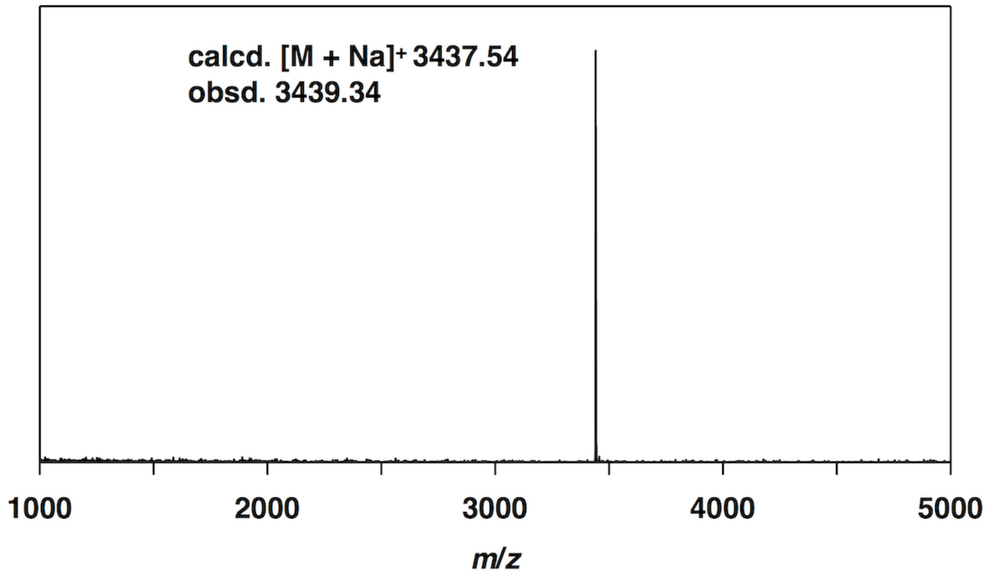

Fig. S5. MALDI–TOF mass spectrum of (*R*)-**1**.

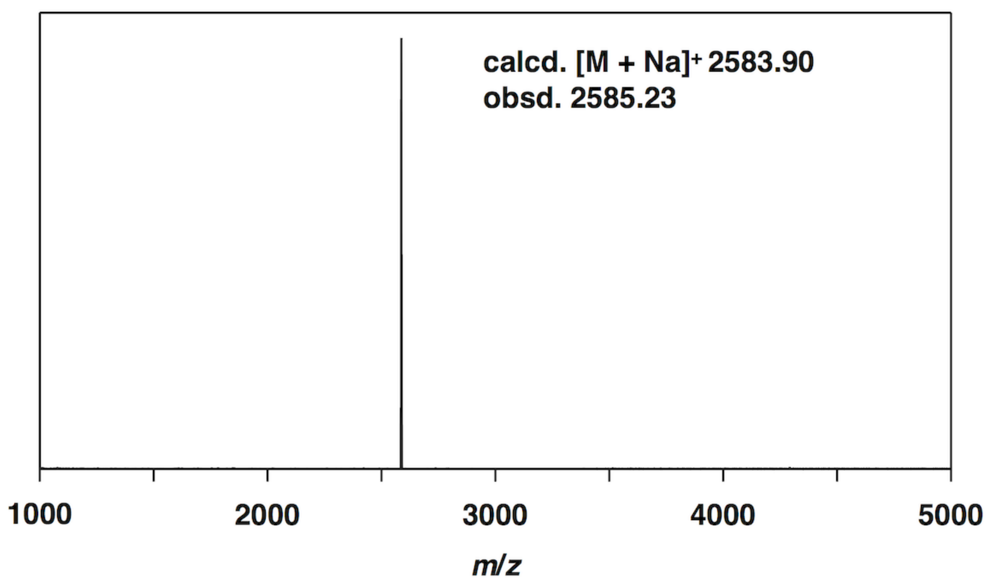

Fig. S6. MALDI–TOF mass spectrum of (*R*)-**2**.

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4. Calculated Structures and Energies

Computational calculation was carried out using the structures shown in Figure S5. The structures were optimized with B3LYP/6-31G* followed by frequency calculation at the same level. Both structures were confirmed to have zero imaginary frequencies. Then, single-point energy and frequency calculations were carried out with M06-2X/6-31G** level using the optimized geometries. The energies shown in the main text are calculated using Gibbs free energies of the results of final single-point calculations containing zero-point, thermal, and entropy effects at 298.15 K.

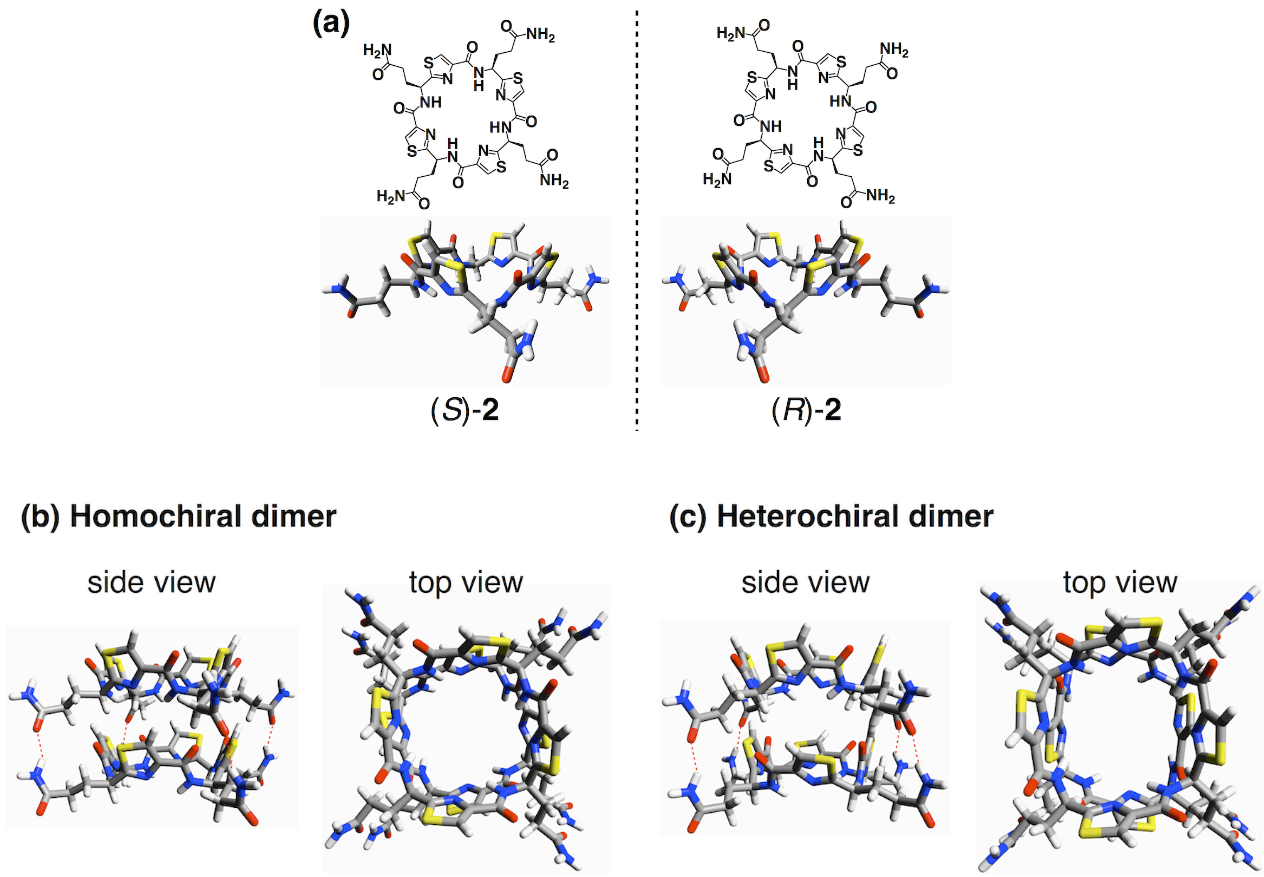

Fig. S7. (a) Energy minimized models of monomers (*S*)-**2** and (*R*)-**2**, and their (b) homochirally and (c) heterochirally self-assembled dimers.

Homochiral dimer

E (M06-2X/6-31G**//B3LYP/6-31G*) = -8183.5768696 a.u.

G (M06-2X/6-31G**//B3LYP/6-31G*) = -8182.307283 a.u. (N_{imag} = 0)

C	1.483020	4.494684	-1.004150
C	2.773350	3.392211	-2.764162
N	1.509171	3.447697	-3.082342
C	4.059885	-0.771598	-2.091250
C	4.494652	-1.482975	-1.004198
C	3.392197	-2.773270	-2.764248
N	3.447675	-1.509081	-3.082395
C	-0.771588	-4.059872	-2.091360
C	-1.482964	-4.494620	-1.004298
C	-2.773246	-3.392095	-2.764308
N	-1.509069	-3.447640	-3.082493
C	-4.059917	0.771659	-2.091301
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N	-3.447683	1.509158	-3.082419
C	0.771667	4.059913	-2.091216
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S	4.115612	-3.142902	-1.200263
S	3.142956	4.115668	-1.200191
S	-4.115743	3.142965	-1.200316
C	3.829751	2.704399	-3.615654
N	3.821500	1.255586	-3.364475
C	4.214854	0.702707	-2.191650
O	4.679101	1.366477	-1.257470
C	2.704410	-3.829667	-3.615764
N	1.255596	-3.821464	-3.364576
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C	-3.829649	-2.704290	-3.615804
N	-3.821486	-1.255485	-3.364565
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C	3.355448	-5.222482	-3.466609
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C	-3.386416	7.666102	-4.068120
N	-3.283078	8.347891	-2.894651
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C	7.666123	3.386521	-4.068013
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H	4.362254	-5.158019	-3.896869
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N	2.263294	3.087584	2.603237
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C	-1.233500	6.684325	1.249101
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N	-1.778022	8.917067	2.069215
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C	1.233459	-6.684348	1.248983
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N	1.777874	-8.917098	2.069149
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H	-6.232811	-1.076498	0.268808
H	-8.666358	-1.335693	2.940732
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H	1.076516	-6.232778	0.268774
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H	6.232761	1.076522	0.268887
H	6.785393	0.266189	1.755320
H	8.666283	1.335696	2.940836
H	9.833677	2.193418	1.979762

Heterochiral dimer

E (M06-2X/6-31G**//B3LYP/6-31G*) = -8183.57568902 a.u.

G (M06-2X/6-31G**//B3LYP/6-31G*) = -8182.303569 a.u. (N_{imag} = 0)

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C	-1.508533	-3.318744	-1.925773
C	-0.991475	-3.794950	-0.752053
C	0.501802	-3.857802	-2.687103
N	-0.660231	-3.366225	-3.015821
C	4.284804	-1.554888	-2.309605
C	5.348469	-1.369891	-1.468607
C	4.751315	0.532500	-2.887323
N	3.965733	-0.481679	-3.113277
C	1.508560	3.318758	-1.925717
C	0.991484	3.794950	-0.751999
C	-0.501763	3.857827	-2.687071
N	0.660275	3.366253	-3.015778
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S	0.625411	-4.318084	-0.990169
S	-5.984190	-0.214096	-1.669769
S	-0.625398	4.318088	-0.990134
C	-4.601726	-1.873634	-3.592502
N	-3.298596	-2.473289	-3.285441
C	-2.887025	-2.769612	-2.027557
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C	4.601778	1.873671	-3.592417
N	3.298644	2.473321	-3.285369
C	2.887054	2.769628	-2.027487
C	-1.680177	3.996527	-3.631887
N	-2.647310	2.910590	-3.412903
C	-3.501253	2.820498	-2.360115
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C	-3.570487	5.574086	-4.427281
C	-4.011516	7.037867	-4.534183
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C	5.645183	4.163139	-4.094030
C	6.913865	5.023300	-4.095407
N	7.469735	5.272646	-2.878898

C	3.570552	-5.574042	-4.427286
C	4.011584	-7.037821	-4.534197
N	4.401641	-7.623269	-3.368695
C	-5.645126	-4.163096	-4.094153
C	-6.913809	-5.023255	-4.095557
N	-7.469696	-5.272616	-2.879059
O	-4.006564	7.633194	-5.605667
O	7.377009	5.469002	-5.138964
O	4.006649	-7.633136	-5.605687
O	-7.376940	-5.468944	-5.139126
H	-5.762732	2.083314	-0.771363
H	-1.453025	-3.842163	0.222967
H	5.762747	-2.083307	-0.771305
H	1.453019	3.842151	0.223029
H	-4.562439	-1.649796	-4.664496
H	-2.614535	-2.580986	-4.023839
H	1.276308	-3.821565	-4.633697
H	2.553783	-2.070494	-3.972340
H	4.562506	1.649844	-4.664415
H	2.614594	2.581028	-4.023775
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H	-2.553726	2.070533	-3.972356
H	5.895974	3.008368	-2.272794
H	6.698056	2.317194	-3.685306
H	-1.518722	6.098533	-3.964367
H	-2.497917	5.699310	-2.557510
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C	-4.597902	1.293923	4.926255

C	-3.601207	2.601472	3.110069
N	-3.629703	1.331302	2.815172
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C	4.181937	-0.582998	3.833841
C	4.597826	-1.293973	4.926311
C	3.601161	-2.601503	3.110095
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C	-0.408685	-4.167236	3.741626
S	2.712933	4.017984	4.805076
S	-4.262919	2.969143	4.701837
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C	-3.513899	-2.822464	2.295131
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C	-3.014842	3.639339	2.167479
N	-1.576268	3.821031	2.420607
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N	1.576233	-3.821056	2.420591
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C	4.174328	-7.122313	0.748823
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C	5.866655	3.018961	1.334841
C	7.042655	3.945138	1.062546
N	7.842167	4.212164	2.132398
C	-3.320302	5.885957	1.000338
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C	-5.866676	-3.018970	1.334726
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O	-4.509455	7.471032	-0.380913
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H	3.075919	-3.186309	1.173277
H	0.941377	-3.237841	1.888883
H	5.225898	3.708533	3.304415
H	4.576157	4.649596	1.956768
H	4.862055	-4.698830	1.948888
H	3.749535	-5.446234	3.101980
H	-4.576185	-4.649613	1.956648
H	-5.225944	-3.708569	3.304298
H	-3.749578	5.446204	3.101981
H	-4.862082	4.698813	1.948865
H	3.300328	-5.340052	0.056282
H	2.296233	-6.218225	1.216388
H	4.176159	-7.636362	2.768101
H	5.033644	-8.709202	1.708611
H	6.236669	2.075977	1.755493
H	5.401728	2.801825	0.372481
H	7.692277	3.790339	3.036726
H	8.638842	4.820456	2.005568
H	-3.300326	5.340053	0.056289
H	-2.296248	6.218214	1.216419
H	-4.176194	7.636335	2.768119
H	-5.033663	8.709187	1.708627
H	-5.401736	-2.801821	0.372375
H	-6.236695	-2.075992	1.755385
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5. ^{1}H NMR Spectroscopy upon Dilution

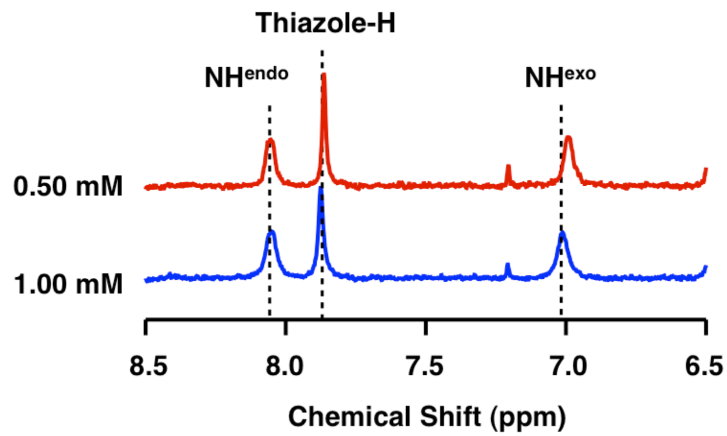

Fig. S8. ^{1}H NMR spectra of (*R*)-**1** at 70 °C in C_6D_{12} at 1.00 mM (blue) and 0.50 mM (red). Upon 2-fold dilution of (*R*)-**1**, the exocyclic amide proton (NH^{exo}) signal shows upfield shift, indicating that intermolecular hydrogen bonds are weakened.

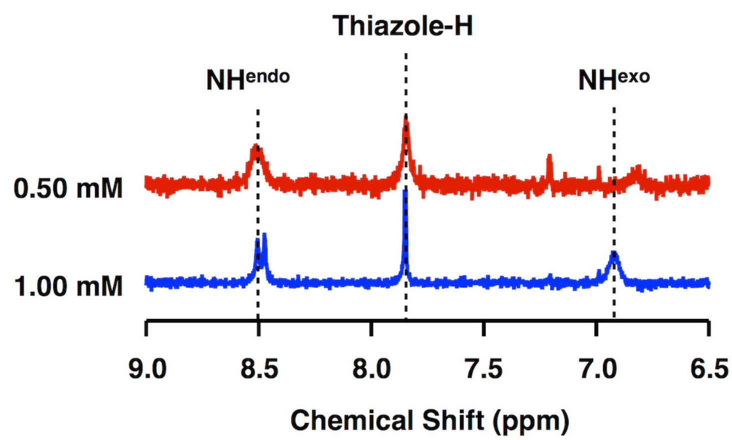

Fig. S9. ^{1}H NMR spectra of (*R*)-**2** at 70 °C in C_6D_{12} at 1.00 mM (blue) and 0.50 mM (red). Upon 2-fold dilution of (*R*)-**2**, the exocyclic amide proton (NH^{exo}) signal shows upfield shift, indicating that intermolecular hydrogen bonds are weakened.

6. Size Exclusion Chromatography of Polymeric Aggregate of (*R*)-2

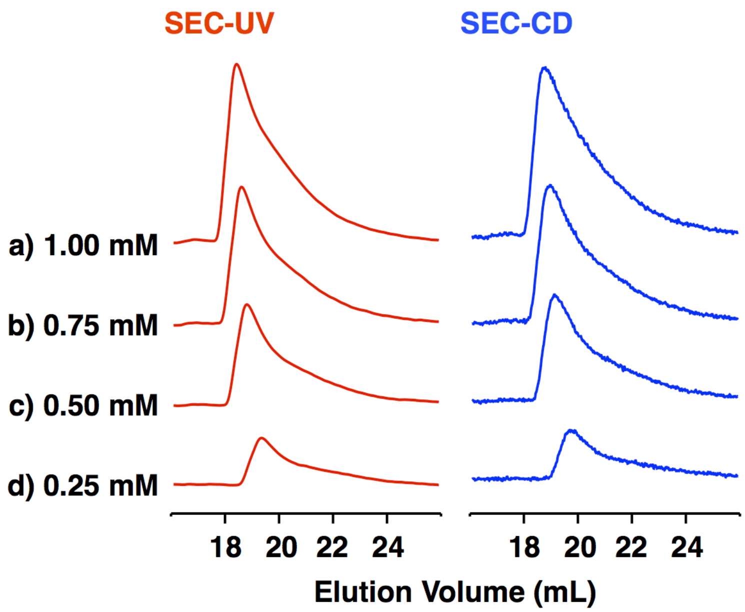

Fig. S10. SEC-UV (red curves) and SEC-CD (blue curves) traces (25 °C, 254 nm) of supramolecular polymerization of (*R*)-**2** at [(*R*)-**2**] = (a) 1.00, (b) 0.75, (c) 0.50 and (d) 0.25 mM. Loading solvent; C_6H_{12}, eluent; $CHCl_3/C_6H_{12}$ (3/7 in v/v), column; TOSOH TSKgel G3000H_{HR}.

7. Circular Dichroism Spectra of 2

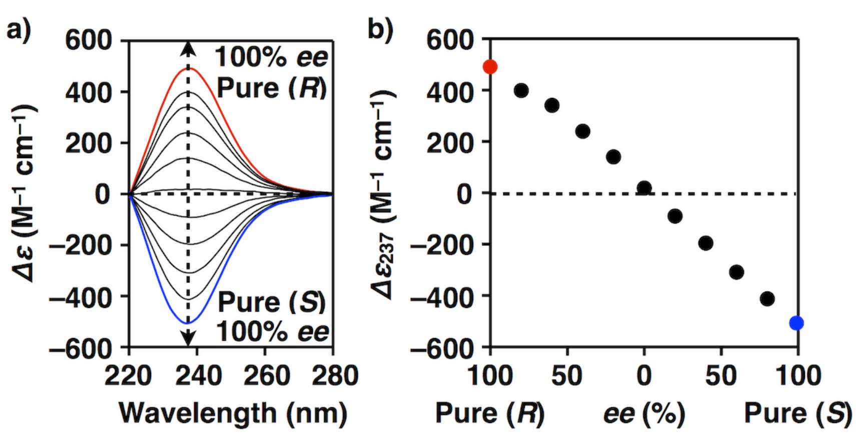

Fig. S11. Stereochemical supramolecular copolymerization of (*S*)-**2** and (*R*)-**2** ([**2**] = 1.00 mM) in cyclohexane (C_6H_{12}) at different enantiomeric excess (*ee*) values. (a) Circular dichroism (CD) spectra in C_6H_{12} at 25 °C and (b) plots of $\Delta\varepsilon$ at 237 nm versus *ee*.

8. Stereochemical Size-Exclusion Chromatography of 2

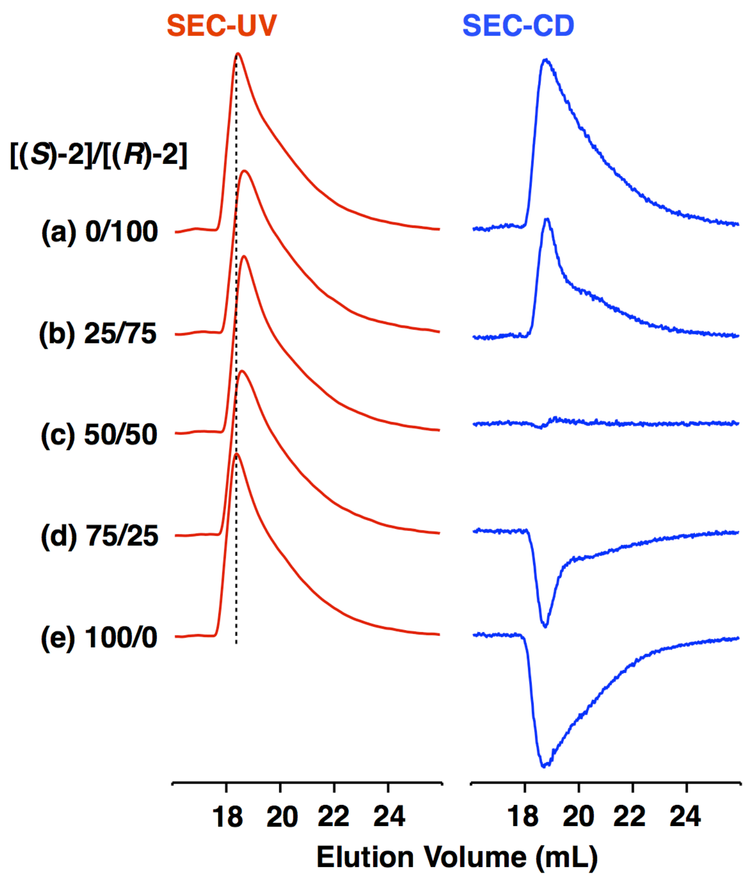

Fig. S12. SEC-UV (red curves) and SEC-CD (blue curves) traces (25 °C, 254 nm) of stereochemical supramolecular copolymerization of (*S*)-**2** and (*R*)-**2** at molar ratios [(*S*)-**2**]/[(*R*)-**2**] of (a) 0/100, (b) 25/75, (c) 50/50, (d) 75/25 and (e) 100/0. Loading solvent; C_6H_{12}, eluent; $CHCl_3/C_6H_{12}$ (3/7 in v/v), column; TOSOH TSKgel G3000H_{HR}.

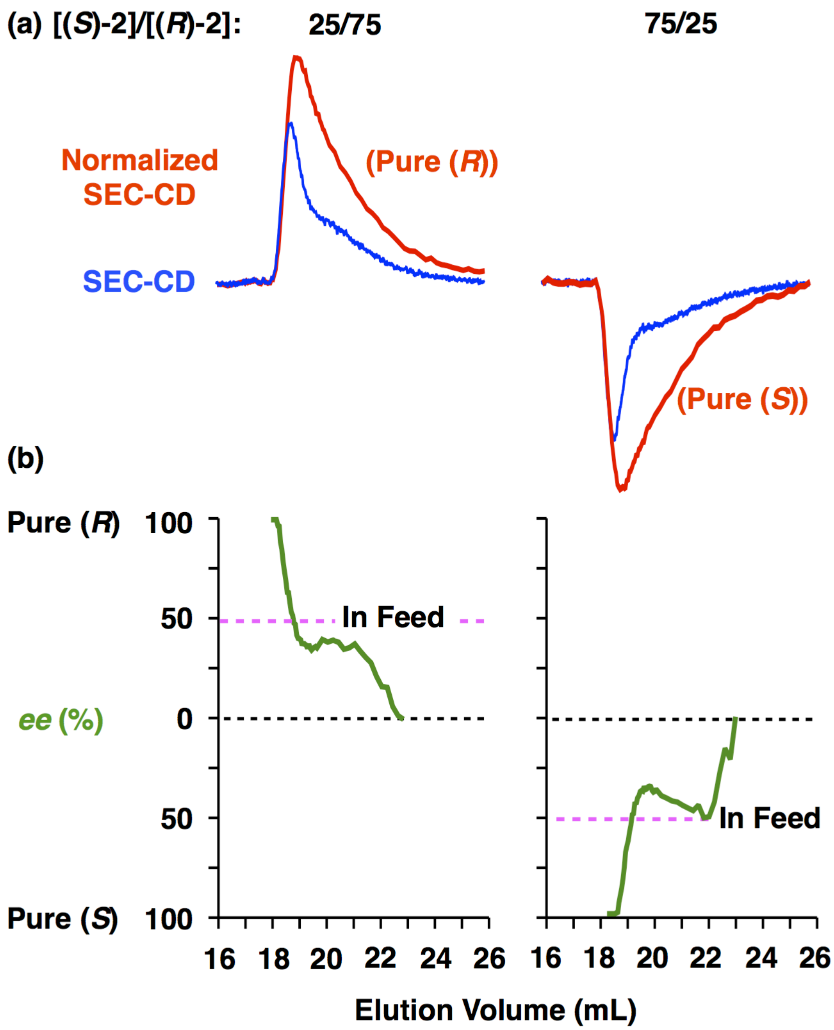

Fig. S13. Stereochemical supramolecular copolymerization of (*S*)-**2** and (*R*)-**2**. (a) SEC-CD traces (25 °C, 254 nm) at [(*S*)-**2**]/[(*R*)-**2**] of 0/100 (red curve) and 25/75 (blue curve) [left] 100/0 (red curve) and 75/25 (blue curve) [right], normalized by their total SEC-UV peak areas. Loading solvent; C_6H_{12}, loading concentration; [**2**] = 1.00 mM, eluent; $CHCl_3/C_6H_{12}$ (3/7 in v/v), column; TOSOH TSKgel G3000H_{HR}. (b) Changes in enantiomeric excess (ee) with SEC volume obtained from (a).