

## Supporting Information

### **Regulable Chiral Amplification Effects in Copoly(phenylacetylene)s and Bidirectional Manipulation for Helix Preferences**

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## Experimental Section

### Materials

4-Ethynylbenzoic acid, 1-decanol, *L*-alanine, *D*-alanine, 1-Hydroxybenzotriazole monohydrate (HOBt), *N,N'*-dicyclohexylcarbodiimide (DCC), anhydrous *N,N*-dimethylacetamide (DMA) and [(norborene)rhodium(I) chloride]<sub>2</sub> ([Rh(nbd)Cl]<sub>2</sub>) were purchased from Aladdin Reagent Company. *L*-Homocysteine thiolactone hydrochloride, coumarin 120 (7-amino-4-methylcoumarin) and tetrahydrofuran (THF, water content < 50 ppm) were obtained from Aldrich. All other solvents and reagents were of analytical grade and used as received. Milli-Q water (18.2MΩ cm) was used in all cases. The *L*- / *D*-Alanine decyl ester was prepared according to a previously reported method.<sup>[1]</sup> 4-Ethynylbenzoyl-*L*-Alanine decyl ester (*L*-1, *D*-1) and 4-ethynylbenzoyl-*L*-homocysteine thiolactone (*L*-2) were prepared according to Scheme S1.

### Measurements

<sup>1</sup>H-NMR characterizations were recorded in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> (J&K) on a Bruker Avance 400 MHz. The NMR spectra were analyzed and processed using MestReNova-6.1.1-6384 software. The molecular weights were determined by a gel permeation chromatography (GPC) performed at 35 °C with three linear Styragel columns and a Waters 2414 differential refractive index (RI) detector. THF or DMF was utilized as eluent, polystyrenes were used as standard. UV source was provided by a WFH-204B UV lamp. Circular dichroism (CD) spectra were characterized by using JASCO CD

spectrometer J-1500. VCD spectra for solvated samples were measured by JASCO FVS-6000 spectrometer, 150 or 500  $\mu\text{m}$  Teflon spacer was used and about 10000 scans. Circularly polarized photoluminescence spectra of the samples were obtained by a JASCO CPL-300 spectrophotometer.

#### **4-Ethynylbenzoyl-Alanine Decyl Ester (*L-1*, *D-1*).**

HOBt (1.05 g, 7.78 mmol) and DCC (1.45 g, 7.03 mmol) were added to a solution of 4-ethynylbenzoic acid (1 g, 6.84 mmol) in dry DMA (8 mL). After the reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 1 h under nitrogen, the *L*-alanine decyl ester (or *D*-alanine decyl ester, 1.67 g, 6.84 mmol), which had been prepared from *L*-alanine (or *D*-alanine) and 1-decanol by the conventional method,<sup>[1]</sup> was added to the mixture. The dispersion solution was stirred at room temperature for 12 h. After filtration, the solvent was removed by evaporation. The crude product was purified by silica gel chromatography with chloroform as the eluent and then recrystallized from hexane to give a white crystalline solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, rt, 400 MHz):  $\delta$  0.88 (t, CH<sub>3</sub>, 3H), 1.26-1.32 (m, CH<sub>2</sub>, 14H), 1.52 (d, CH<sub>3</sub>, 3H), 1.62-1.70 (m, CH<sub>2</sub>, 4H), 3.20 (s,  $\equiv\text{CH}$ , 1H), 4.18 (t, CH<sub>2</sub>, 2H), 4.78 (m, -CH, 1H), 6.75 (br, NH, 1H), 7.55 (d, aromatic, 2H), 7.76 (d, aromatic, 2H).

#### **4-Ethynylbenzoyl-*L*-Homocysteine Thiolactone (*L-2*).**

*L*-Homocysteine thiolactone hydrochloride (250 mg) and NaHCO<sub>3</sub> (300 mg) were added to the 30 mL mixed solvent of ethyl acetate and H<sub>2</sub>O (1/1, v/v) under nitrogen atmosphere. After the reaction mixture was stirred for a while, the 4-Ethynylbenzoyl

chloride (1.67 g, 6.84 mmol), which had been prepared from 4-Ethynylbenzoyl according to a previously reported method,<sup>[2]</sup> was slowly added to the mixture. The dispersion solution was stirred at room temperature for 12 h. After the reaction, the reaction solution was diluted with saturated brine, extracted with ethyl acetate. The organic layer solution was collected then dried with anhydrous magnesium sulfate. The crude product was purified by silica gel chromatography with ethyl acetate and petroleum ether (1/4, v/v) as the eluent to give a white crystalline solid. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, rt, 400 MHz):  $\delta$  2.28 (m, CH<sub>2</sub>, 1H), 2.46 (m, CH<sub>2</sub>, 1H), 3.32 (m, CH<sub>2</sub>, 1H), 3.46 (m, CH<sub>2</sub>, 1H), 4.41 (s,  $\equiv$ CH, 1H), 4.82 (m, -CH, 1H), 7.59 (d, aromatic, 2H), 7.85 (d, aromatic, 2H), 8.85 (br, NH, 1H).

### **Polymerization.**

Polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere with [Rh(nbd)Cl]<sub>2</sub> as the catalyst in a similar way to previously reported.<sup>[3]</sup> A typical polymerization procedure is described below. Monomer (*L*-1, *D*-1, *L*-2, or a mixture of the two) was placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. Then dry THF, rhodium catalyst THF solution and triethylamine were added with a syringe. After 12 h, the resulting polymer was precipitated into a large amount of methanol, collected by centrifugation, and then dried in vacuo at room temperature overnight to give the polymer or copolymer. Poly-[1(*L*),-co-1(*D*)<sub>1-r</sub>] series have similar <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t. 400 MHz):  $\delta$  0.86 (s, CH<sub>3</sub>, 3H), 1.24 (broad, CH<sub>2</sub>, 14H), 1.56 (broad, CH<sub>3</sub>, 3H), 2.26 (broad, CH<sub>2</sub>, 2H), 4.08 (broad,

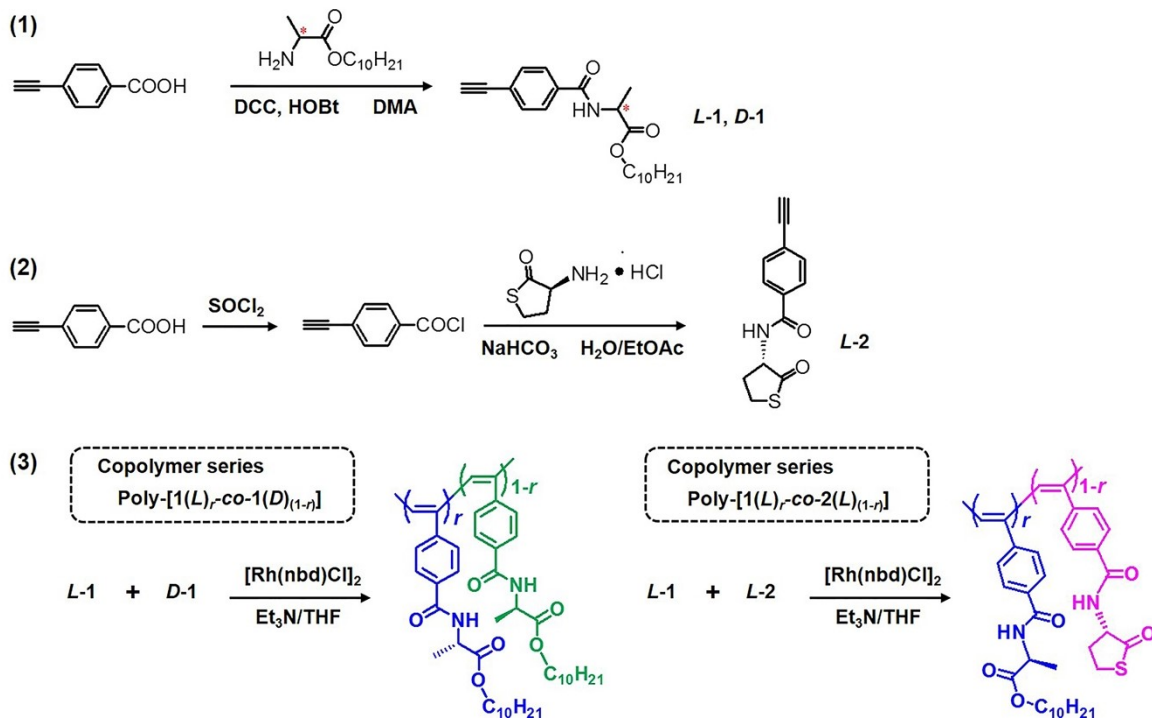
CH<sub>2</sub>, 2H), 4.66 (broad, CH, 1H), 5.54 (broad, =CH, 1H), 5.8-7.2 (broad, aromatic, 4H), 7.4-8.0 (broad, NH, 1H). Poly-2(*L*) <sup>1</sup>H NMR (d<sub>7</sub>-DMF, r.t. 400 MHz):  $\delta$  2.93-2.38 (m, CH<sub>2</sub>, 4H) 4.94 (broad, -CH, 1H), 5.95 (broad, =CH, 1H), 6.84 (broad, aromatic, 2H), 7.62 (broad, aromatic, 2H), 8.48 (broad, NH, 1H).

### **Theoretical Calculations**

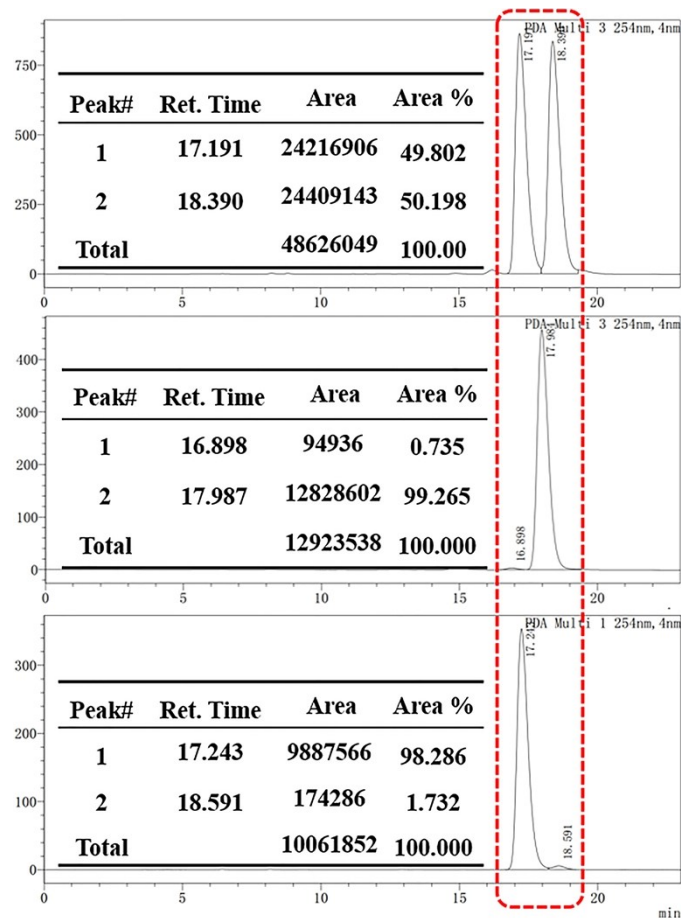
The Gaussian 09 suite of programs was used to carry out Density Functional Theory (DFT) calculations. The hybrid exchange-correlation functional b3lyp and 6-31+G(d,p) basis set were used in all calculations. The theoretical infrared and VCD spectra were obtained from the frequency calculations.

### **CPL measurement**

A CPL-active system was constructed in which the coumarin 120 CHCl<sub>3</sub> solution (about 0.001 mg mL<sup>-1</sup>) was responsible for the fluorescence and the helical copolymer solutions served as a “filter” (about 0.1 mg mL<sup>-1</sup> in THF and CHCl<sub>3</sub>, respectively). CPL measurement were carried out arranging the coumarin 120 solution and helical copolymer solution side-by-side, and fluorescent substance placed in front.



**Scheme 1.** Synthesis of chiral monomers and copolymer series.

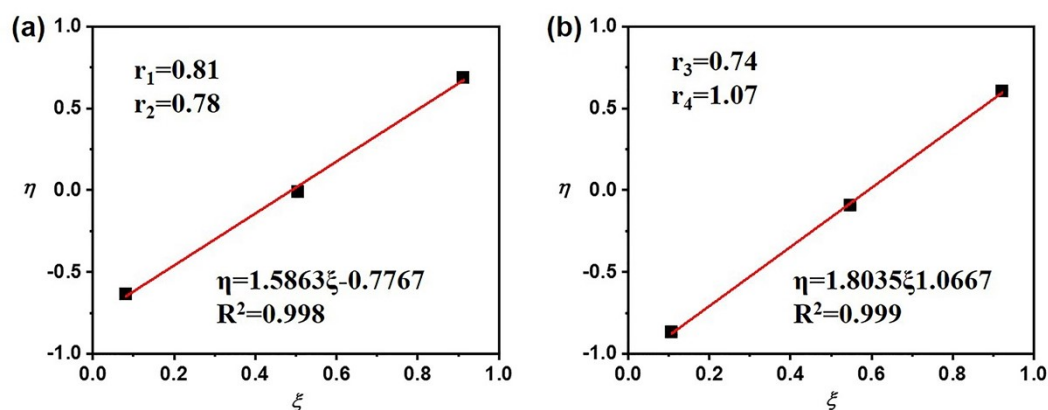


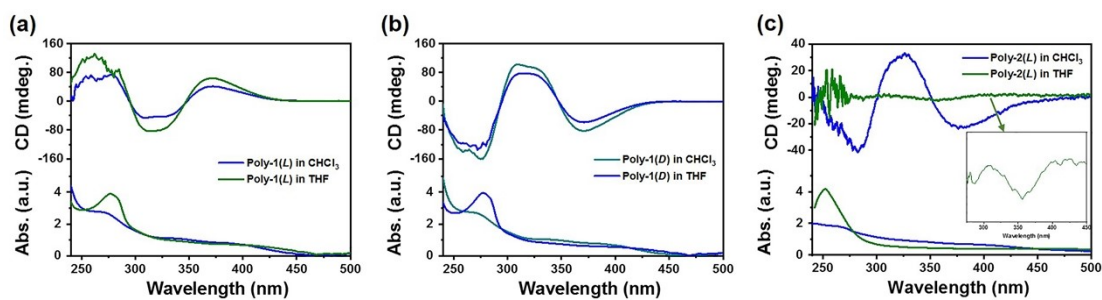
**Figure S1.** HPLC spectra of the racemic monomer, *L*-1 and *D*-1, respectively.

**Table S1.** Homo-/copolymerization results.<sup>a</sup>

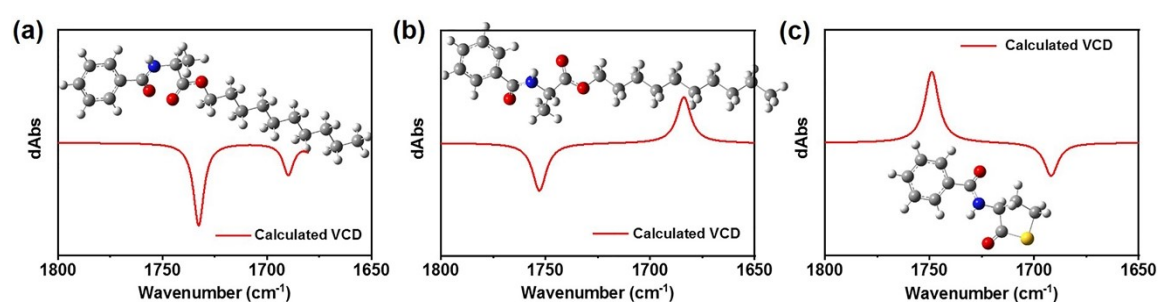
Run	Copolymer	L-1 (mmol)	D-1 (mmol)	L-2 (mmol)	Yield (%)	Mn	PDI
1	poly-1(L)	200	0	-	93	89800	2.00
2	poly-[1(L) <sub>0.95</sub> -co-1(D) <sub>0.05</sub> ]	190	10	-	94	88500	2.27
3	poly-[1(L) <sub>0.85</sub> -co-1(D) <sub>0.15</sub> ]	170	30	-	89	91000	2.13
4	poly-[1(L) <sub>0.75</sub> -co-1(D) <sub>0.25</sub> ]	150	50	-	92	88100	2.20
5	poly-[1(L) <sub>0.65</sub> -co-1(D) <sub>0.35</sub> ]	130	70	-	91	95700	2.11
6	poly-[1(L) <sub>0.55</sub> -co-1(D) <sub>0.45</sub> ]	110	90	-	88	87200	2.10
7	poly-[1(L) <sub>0.5</sub> -co-1(D) <sub>0.5</sub> ]	100	100	-	95	99700	2.18
8	poly-[1(L) <sub>0.45</sub> -co-1(D) <sub>0.55</sub> ]	90	110	-	90	94500	2.12
9	poly-[1(L) <sub>0.35</sub> -co-1(D) <sub>0.65</sub> ]	70	130	-	93	84600	2.11
10	poly-[1(L) <sub>0.25</sub> -co-1(D) <sub>0.75</sub> ]	50	150	-	93	86200	2.25
11	poly-[1(L) <sub>0.15</sub> -co-1(D) <sub>0.85</sub> ]	30	170	-	91	105800	1.99
12	poly-[1(L) <sub>0.05</sub> -co-1(D) <sub>0.95</sub> ]	10	190	-	93	83700	2.32
13	poly-1(D)	0	200	-	89	98200	2.15
14	poly-[1(L) <sub>0.9</sub> -co-2(L) <sub>0.1</sub> ]	180	-	20	94	177300	1.99
15	poly-[1(L) <sub>0.7</sub> -co-2(L) <sub>0.3</sub> ]	140	-	60	92	231200	1.87
16	poly-[1(L) <sub>0.5</sub> -co-2(L) <sub>0.5</sub> ]	100	-	100	91	265200	1.69
17	poly-[1(L) <sub>0.3</sub> -co-2(L) <sub>0.7</sub> ]	60	-	140	90	254600	1.62
18	poly-[1(L) <sub>0.1</sub> -co-2(L) <sub>0.9</sub> ]	20	-	180	91	273800	1.83
19	poly-2(L)	0	-	200	88	215600	1.52

<sup>a</sup> Carried out in THF at 30 °C under a N<sub>2</sub> atmosphere for 12 h.

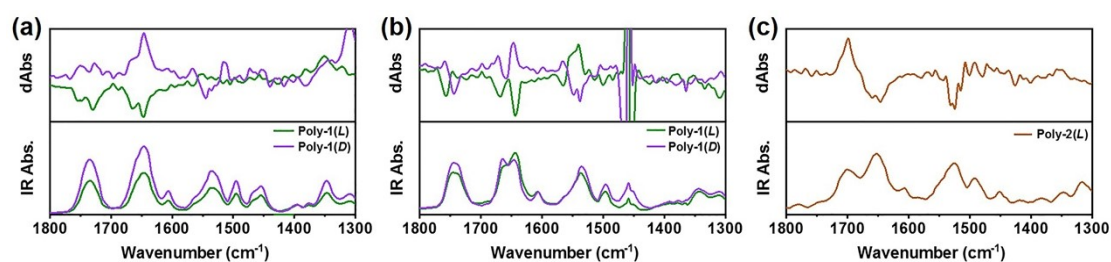
**Figure S2.** Kelen-Tüdös plots for the copolymerizations of L-1 with D-1 (a) and L-1 with L-2 (b).



**Figure S3.** CD and UV-Vis spectra of (a) poly-1(*L*), (b) poly-1(*D*) and (c) poly-2(*L*) in  $\text{CHCl}_3$  and THF solution at 25 °C.

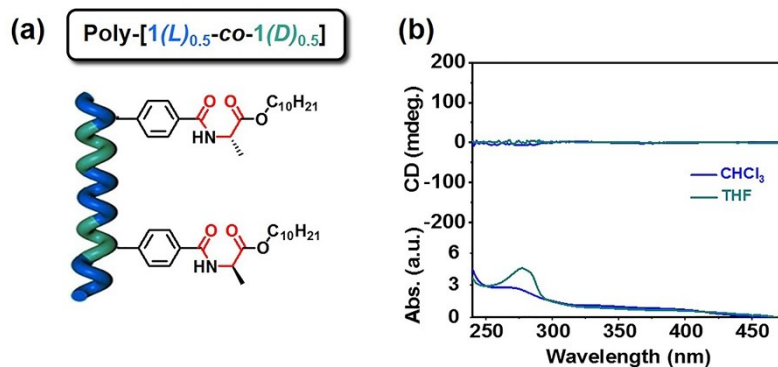


**Figure S4.** Calculated VCD spectra of possible conformations by varying the OC-N-C-CO dihedral angle and maintaining unchanged the rest of geometrical parameters of the optimal conformation in  $\text{CHCl}_3$ : (a) *L*-1 monomeric pendant with *syn* conformer (OC-N-C-CO dihedral angle is  $-20^\circ$ ), (b) *L*-1 monomeric pendant with *anti* conformer (OC-N-C-CO dihedral angle is  $125^\circ$ ), and (c) *L*-2 monomeric pendant with *anti* conformer (OC-N-C-CO dihedral angle is  $132^\circ$ ).

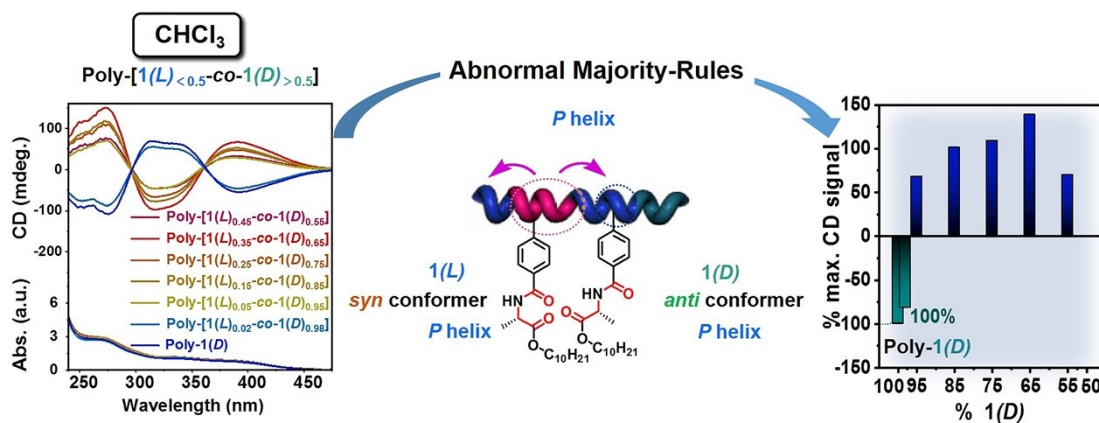


**Figure S5.** Infrared and VCD spectra of poly-1(*L*) and poly-1(*D*) in  $\text{CHCl}_3$  (a), THF (b) and poly-2(*L*) in  $\text{CHCl}_3$  (c).

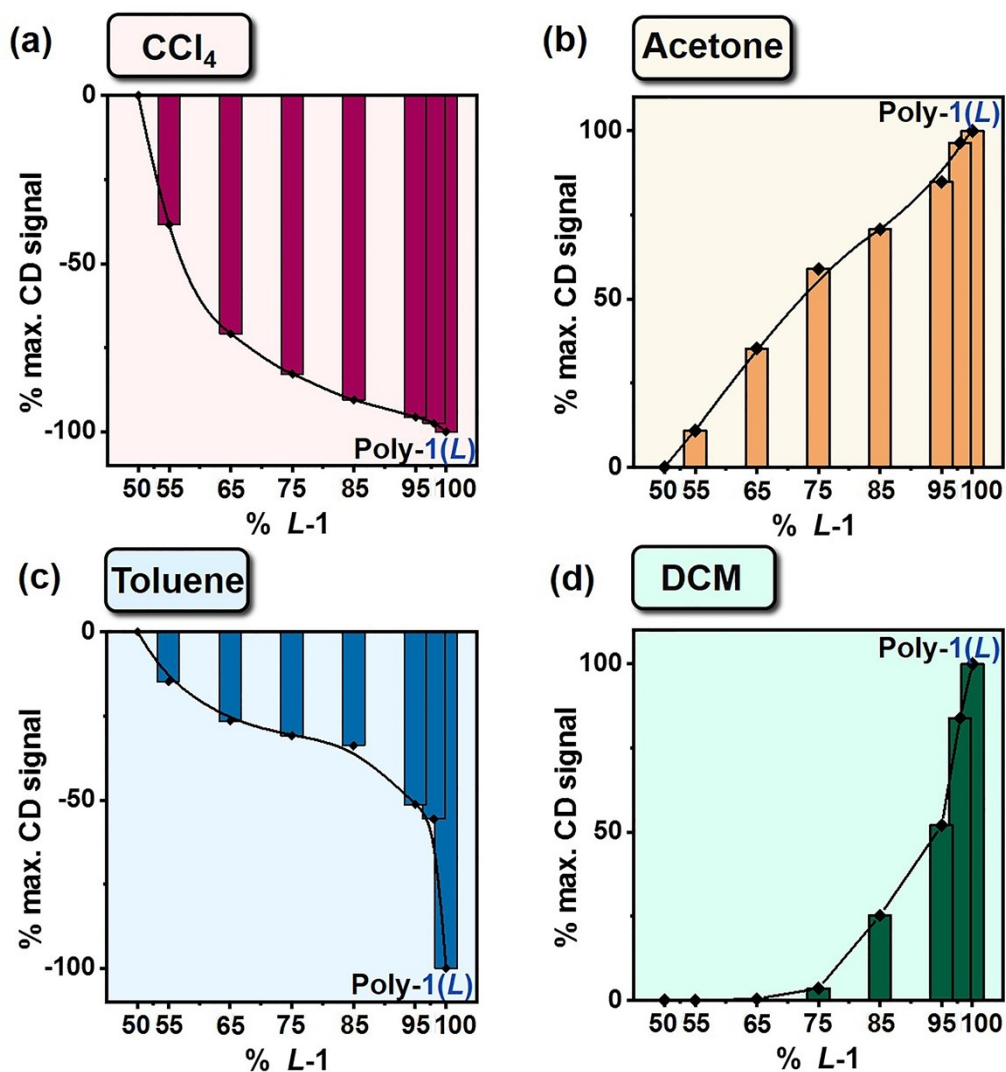




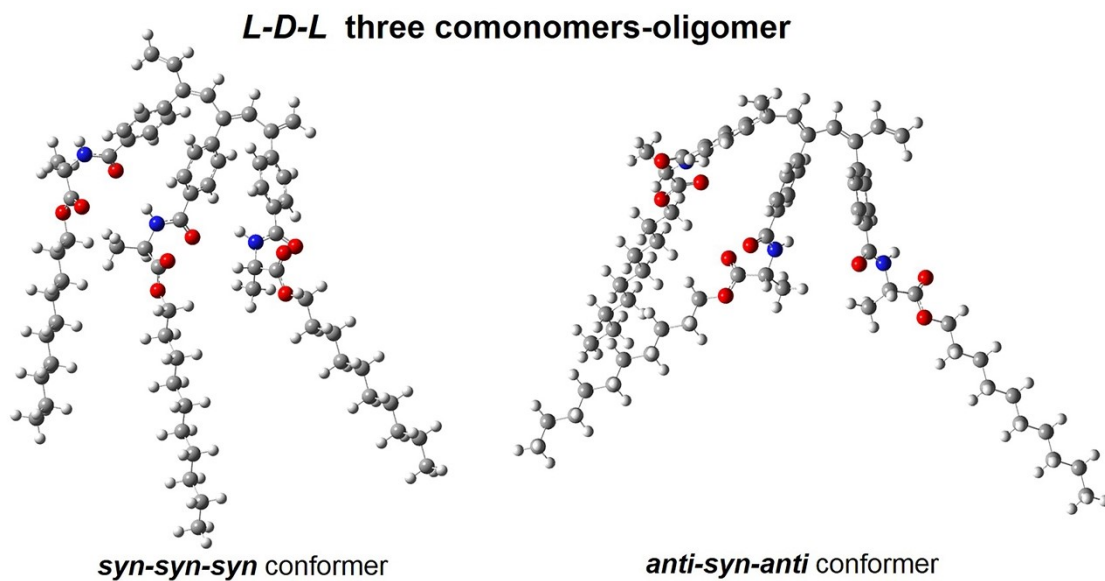
**Figure S6.** (a) The helical structure and the conformations of the poly-[1(L)<sub>0.5</sub>-co-1(D)<sub>0.5</sub>] components and (b) CD and UV-Vis spectra of poly-[1(L)<sub>0.5</sub>-co-1(D)<sub>0.5</sub>] in THF and CHCl<sub>3</sub>. CD and UV-Vis measurements were performed at 25 °C with the concentration of 0.1 mg ml<sup>-1</sup>.



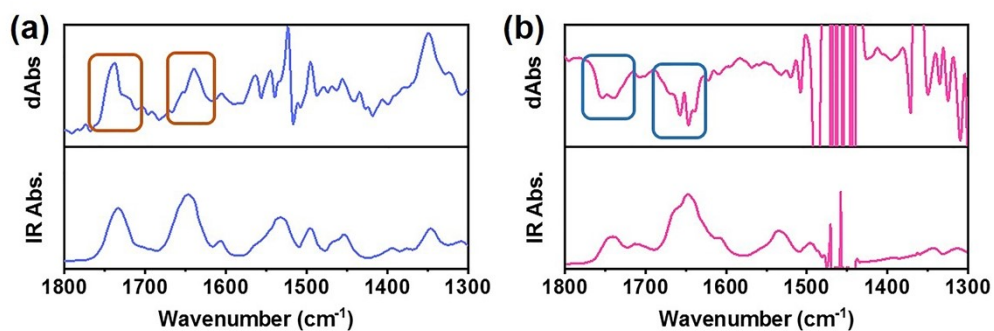
**Figure S7.** CD studies of the poly-[1(L)<sub><0.5</sub>-co-1(D)<sub>>0.5</sub>] series in CHCl<sub>3</sub> and schematic for the conformational composition of the poly-[1(L)<sub><0.5</sub>-co-1(D)<sub>>0.5</sub>] components. CD and UV-Vis measurements were performed at 15 °C with the concentration of 0.1 mg mL<sup>-1</sup>.



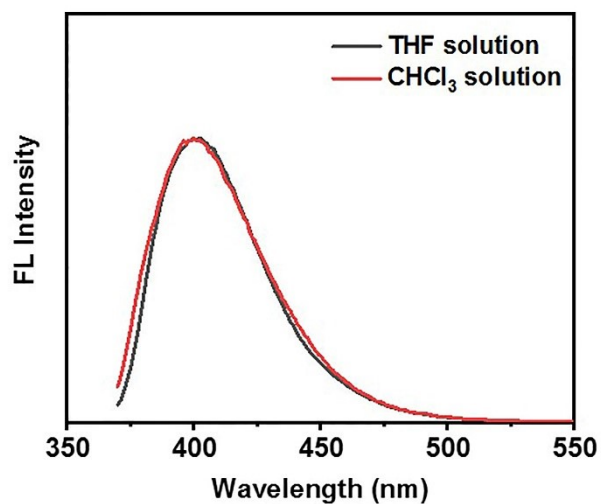
**Figure S8.** The CD intensity of poly-[1(L)<sub>>0.5</sub>-co-1(D)<sub><0.5</sub>] series versus the percentage enantiomeric excess of the copolymer components in different solutions at 25°C with 0.1 mg mL<sup>-1</sup>.



**Figure S9.** The optimal conformation of *L-D-L* three comonomers-oligomer in  $\text{CHCl}_3$  and respective conformational energy with *syn-syn-syn* conformer (left, -2190839.49 kcal/mol) and *anti-syn-anti* conformer (right, -2190845.71 kcal/mol) at the pendant.



**Figure S10.** Infrared and VCD spectra of poly-[1(*L*)<sub>0.9</sub>-co-2(*L*)<sub>0.1</sub>] in (a)  $\text{CHCl}_3$  and (b) THF solution.



**Figure S11.** Photoluminescence (PL) spectra of coumarin 120 excited at 350 nm in THF and CHCl<sub>3</sub>.

### References

- (1) M. Reller, S. Wesp, M. R. M. Koos, M. Reggelin and B. Luy, *Chem. Eur. J.* 2017, **23**, 13351-13359.
- (2) M. Han, K. Guo, F. Wang, Y. Zhu and H. Qi, *Journal of Applied Polymer Science* 2017, **134**, 45141.
- (3) S. I. Sakurai, S. Ohsawa, K. Nagai, K. Okoshi, J. Kumaki and E. Yashima, *Angew. Chem. Int. Ed.* 2007, **46**, 7605-7608.