

## Supporting Information

### Particle dispersion system consisting of helically assembled liquid crystalline poly(*para*-phenylene) derivatives with reproducible chiroptical properties

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#### 1. Materials.

All the chemicals were commercially available and used as received. (*R*)- and (*S*)-1,1'-bi-2-naphthol were purchased from Kankyo Kagaku Center Co. Ltd. 1,4-Phenylenediboronic acid was purchased from Lancaster Co. Ltd. All other chemicals were purchased from Aldrich Chemical Co. Ltd., Tokyo Kasei Co. Ltd. and Wako Co. Ltd. Solvents were dried and distilled before use.

#### 2. Measurements.

NMR spectra were obtained with JEOL AL-400 or Bruker AVANCE-600. Chemical shifts are

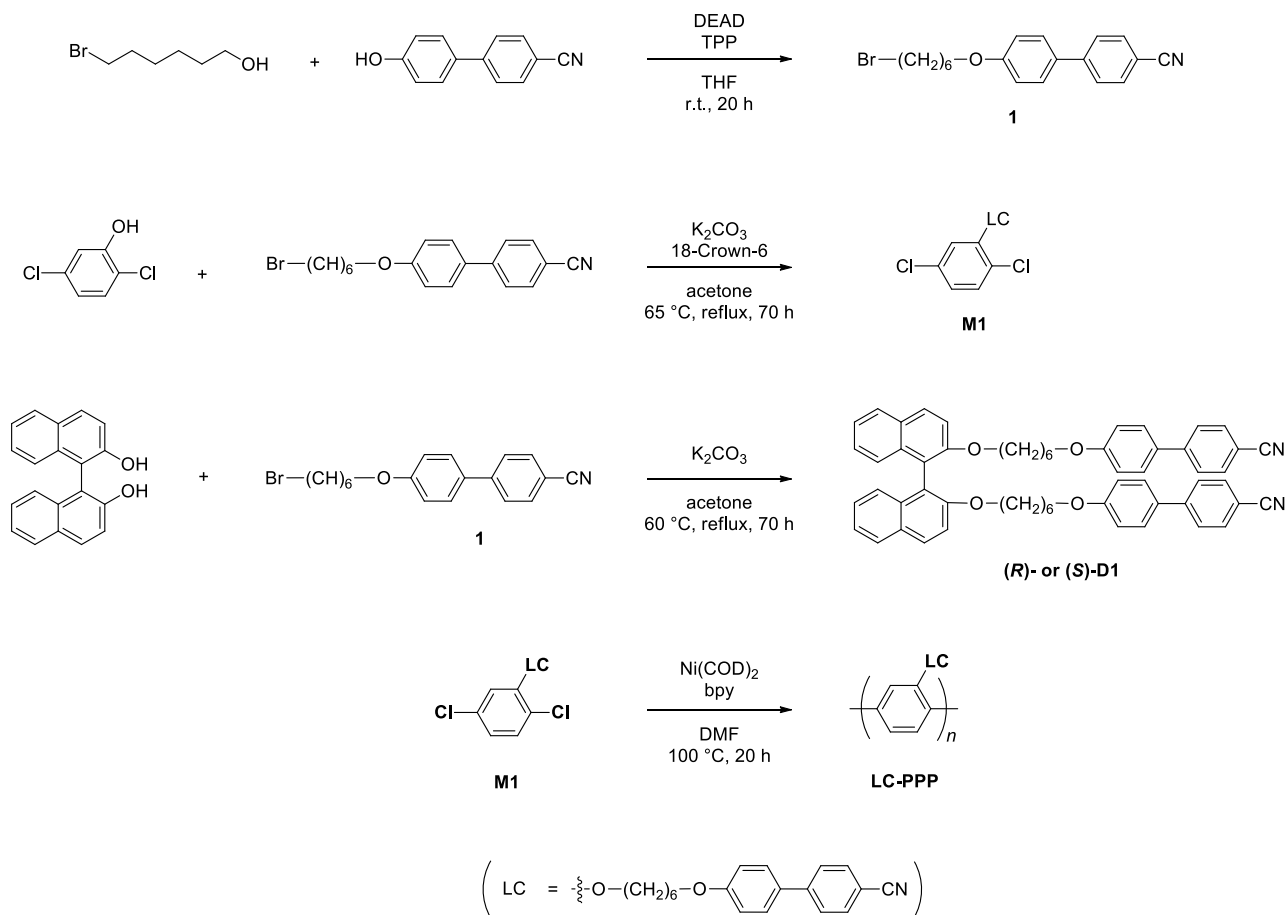
represented in parts per million downfield from tetramethylsilane (TMS) as internal standards. Elemental analyses were performed by Perkin-Elmer 2400 CHN Elemental Analyzer, Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100 and Dionex ICS-1500. High-resolution mass spectra (HRMS) were obtained by using JEOL JMS-HX110A (FAB), Thermo Fisher Scientific EXACTIVE (ESI), and Thermo Fisher Scientific MALDI DUO orbitrapXL (MALDI). Molecular weights of the polymers were evaluated through gel permeation chromatography (GPC) calibrated by polystyrene standard at 40 °C. Tetrahydrofuran (THF) was used as an eluent and the flow rate was 1.0 mL/min. Ultraviolet–visible (UV–vis) absorption spectra were measured with JASCO V-570 UV/VIS/NIR spectrophotometer. Photoluminescence (PL) spectra were measured with JASCO FP-750 spectrofluorometer. Circular dichroism (CD) spectra were measured with JASCO J-820 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were measured with JASCO CPL-200S spectrometer. All optical measurements were performed using a quartz cell. Dynamic light scattering (DLS) measurements were performed using Otsuka Electronics ELSZ-2Plus. Scanning electron microscopy (SEM) was performed with JEOL JSM-7500F. The samples were coated with Pt-Pd alloy using JEOL JFC-1600 ion coater before measurements of SEM. Fluorescence microscopy was performed by using Nikon eclipse TE2000-U with a mercury-vapor lamp (Excitation wavelength: 365 nm) and a fluorescent filter (transmission  $\geq$  420 nm). Thermal behavior of LC-PPP was investigated in a heating run at a heating rate of 10 °C/min in flowing nitrogen gas, using thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60,

Shimadzu) with alumina pan. Phase transition temperatures were determined using a TA Instrument Q-100 differential scanning calorimeter (DSC) with a constant heating/cooling rate of 2 °C/min, and texture observations were carried out under crossed nicols by using a Zeiss AxioImager M1m polarizing microscope equipped with a Zeiss AxioCam MRc5 digital camera and a Linkam TH-600PM heating and cooling stage with temperature control. X-ray diffraction (XRD) measurement was performed with Rigaku ultra X18 diffractometer. XRD pattern was recorded with an X-ray generator with Nickel filtered CuK  $\alpha$  radiation (40 kV/300 mA:  $\lambda = 0.154$  nm) and a flat plate camera (RINT2500, Rigaku).

## Syntheses.

All syntheses were carried out under argon atmosphere. All synthetic routes are shown in

Schemes S1.



Scheme S1 Synthesis routs of LC-PPP and (R)- or (S)-D1.

#### **4'-[(6-Bromohexan-1-yl)oxy]-[1,1'-biphenyl]-4-carbonitrile (1).**

To a stirred solution of 4-cyano-4'-hydroxybiphenyl (10.00 g, 51.2 mmol), triphenylphosphine (TPP, 20.80 g, 79.3 mmol) and 6-bromo-1-hexanol (7.0 mL, 51.4 mmol) in tetrahydrofuran (THF, 40 mL) was added dropwise a solution of diethyl azodicarboxylate (DEAD, 26 mL, 40 wt% in toluene, 57.2 mmol) in THF (25 mL) at 0 °C. The reaction mixture was stirred at RT for 18 h. The residue was dissolved in chloroform, and washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The crude product was recrystallized from chloroform/methanol to give **1** as a white solid (12.47 g, 68.0 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.51–1.57 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.82–1.94 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub> and BrCH<sub>2</sub>CH<sub>2</sub>), 3.43 (t, 2H, *J* = 6.8 Hz, BrCH<sub>2</sub>), 4.02 (t, 2H, *J* = 6.2 Hz, OCH<sub>2</sub>), 6.99 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.53 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.64 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.69 (d, 2H, *J* = 8.0 Hz, Ar-*H*) ppm (TMS). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 25.30, 27.91, 29.05, 32.67, 33.74, 67.91, 110.10, 115.10, 119.10, 127.10, 128.35, 131.40, 132.57, 145.28, 159.73 ppm (TMS). HRMS (APCI, *m/z*): [M+H<sup>+</sup>] calcd for C<sub>19</sub>H<sub>20</sub>BrNO: 358.0801; Found: 358.0795. Anal Calcd for C<sub>19</sub>H<sub>20</sub>BrNO: C, 63.70; H, 5.63; Br, 22.30. Found: C, 63.56; H, 5.69; Br, 22.18.

#### **1,4-Dichloro-2-({6-[(4'-cyanobiphenyl-4-yl)oxy]hexan-1-yl}oxy)benzene (M1).**

A mixture of 2,4-dichlorophenol (2.50 g, 15.35 mmol), **1** (5.00 g, 13.96 mmol), potassium carbonate (7.71 g, 55.8 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (36.9 mg, 0.14 mmol)

in acetone (70 mL) were stirred at 65 °C for 70 h. After removing the insoluble solid by filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in chloroform, and washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The crude product was recrystallized from chloroform/methanol to give **M1** as a white solid (5.28 g, 78.2 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.58–1.60 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.82–1.94 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 4.01–4.05 (m, 4H, OCH<sub>2</sub>), 6.87 (dd, 1H, *J* = 8.4 Hz, *J* = 2.4 Hz, Ar-*H*), 6.90 (d, 2H, *J* = 2.4 Hz, Ar-*H*), 6.99 (d, 2H, *J* = 9.2 Hz, Ar-*H*), 7.26 (d, 1H, *J* = 8.4 Hz, Ar-*H*), 7.52 (d, 2H, *J* = 8.4 Hz, Ar-*H*), 7.64 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.69 (d, 2H, *J* = 8.8 Hz, Ar-*H*) ppm (TMS). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 25.74, 25.76, 28.88, 29.12, 67.97, 69.23, 110.09, 113.81, 119.12, 121.12, 121.39, 127.10, 128.35, 130.69, 131.37, 132.58, 133.02, 145.31, 155.06, 159.77 ppm (TMS). HRMS (ESI, *m/z*): [M+NH<sub>4</sub><sup>+</sup>] calcd for C<sub>25</sub>H<sub>23</sub>Cl<sub>2</sub>NO<sub>2</sub>: 457.1444; Found: 457.1437. Anal Calcd for C<sub>25</sub>H<sub>23</sub>Cl<sub>2</sub>NO<sub>2</sub>: C, 68.19; H, 5.26; N, 3.18; Cl, 16.10. Found: C, 67.91; H, 5.33; N, 3.15; Cl, 16.24.

**(R)-(+)-2,2'-Bis({6-[(4'-cyanobiphenyl-4-yl)oxy]hexan-1-yl}oxy)-1,1'-binaphthyl ((R)-D1).**

A mixture of [1,1'-binaphthalene]-2,2'-diol (1.00 g, 3.49 mmol), **1** (2.69 g, 7.51 mmol) and potassium carbonate (1.93 g, 14.0 mmol) in acetone (40 mL) were stirred at 60 °C for 70 h. After removing the insoluble solid by filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in chloroform, and washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The crude product was purified by column chromatography (silica gel, chloroform) to give **(R)-D1** as a yellow oil (1.98 g, 67.5 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.91–0.97 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.09–1.14 (m, 4H,  $\text{OCH}_2\text{CH}_2$ ), 1.40–1.50 (m, 8H,  $\text{OCH}_2\text{CH}_2$ ), 3.78(t, 8H,  $\text{OCH}_2$ ), 3.87–4.03 (m, 4H,  $\text{OCH}_2$ ), 6.93 (d, 4H,  $J = 8.8$  Hz, Ar-*H*), 7.14–7.21 (m, 4H, Ar-*H*), 7.27–7.30 (m, 2H, Ar-*H*), 7.40 (d, 2H,  $J = 8.8$  Hz, Ar-*H*), 7.51 (d, 4H,  $J = 8.0$  Hz, Ar-*H*), 7.63 (d, 4H,  $J = 8.4$  Hz, Ar-*H*), 7.68 (d, 4H,  $J = 8.4$  Hz, Ar-*H*), 7.82 (d, 2H,  $J = 8.0$  Hz, Ar-*H*), 7.90 (d, 2H,  $J = 8.8$  Hz, Ar-*H*) ppm (TMS).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.38, 25.40, 28.93, 29.30, 67.85, 69.65, 109.99, 114.97, 115.84, 118.91, 120.75, 123.35, 125.38, 125.92, 126.90, 127.62, 128.13, 128.92, 129.19, 131.12, 132.40, 134.09, 145.08, 154.35, 159.59 ppm (TMS). HRMS (ESI,  $m/z$ ):  $[\text{M}+\text{NH}_4^+]$  calcd for  $\text{C}_{58}\text{H}_{52}\text{N}_2\text{O}_4$ : 858.4265; Found: 858.4245. Anal Calcd for  $\text{C}_{58}\text{H}_{52}\text{N}_2\text{O}_4$ : C, 82.83; H, 6.23; N, 3.33. Found: C, 82.86; H, 6.11; N, 3.39.  $[\alpha]_{\text{D}}^{27} +15.60^\circ$  ( $c$  1.04,  $\text{CHCl}_3$ )

**(*S*)-(-)-2,2'-Bis({6-[(4'-cyanobiphenyl-4-yl)oxy]hexan-1-yl}oxy)-1,1'-binaphthyl ((*S*)-D1).**

A mixture of [1,1'-binaphthalene]-2,2'-diol (1.00 g, 3.49 mmol), **1** (2.69 g, 7.51 mmol) and potassium carbonate (1.93 g, 14.0 mmol) in acetone (40 mL) were stirred at 60 °C for 70 h. After removing the insoluble solid by filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in chloroform, and washed with water and brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The crude product was purified by column chromatography (silica gel, chloroform) to give (*S*)-**D1** as a white powder (2.42 g, 73.1 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.92–0.97 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.09–1.16 (m, 4H,  $\text{OCH}_2\text{CH}_2$ ), 1.40–1.50 (m, 8H,  $\text{OCH}_2\text{CH}_2$ ), 3.78(t, 8H,  $\text{OCH}_2$ ), 3.79–4.02 (m, 4H,  $\text{OCH}_2$ ), 6.93 (d, 4H,  $J = 8.8$

Hz, Ar-*H*), 7.14–7.19 (m, 4H, Ar-*H*), 7.26–7.30 (m, 2H, Ar-*H*), 7.40 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.51 (d, 4H, *J* = 8.8 Hz, Ar-*H*), 7.62 (d, 4H, *J* = 8.4 Hz, Ar-*H*), 7.67 (d, 4H, *J* = 8.4 Hz, Ar-*H*), 7.82 (d, 2H, *J* = 8.4 Hz, Ar-*H*), 7.90 (d, 2H, *J* = 9.2 Hz, Ar-*H*) ppm (TMS). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 25.38, 25.40, 28.93, 29.30, 67.85, 69.64, 109.99, 114.97, 115.84, 118.92, 120.75, 123.36, 125.38, 125.93, 126.90, 127.63, 128.13, 128.93, 129.19, 131.11, 132.40, 134.10, 145.08, 154.35, 159.59 ppm (TMS). HRMS (ESI, *m/z*): [M+NH<sub>4</sub><sup>+</sup>] calcd for C<sub>58</sub>H<sub>52</sub>N<sub>2</sub>O<sub>4</sub>: 858.4265; Found: 858.4244. Anal Calcd for C<sub>58</sub>H<sub>52</sub>N<sub>2</sub>O<sub>4</sub>: C, 82.83; H, 6.23; N, 3.33. Found: C, 82.67; H, 6.18; N, 3.14. [α]<sub>D</sub><sup>26</sup> –15.79° (*c* 1.01, CHCl<sub>3</sub>)

### **LC-PPP.**

Ni(cod)<sub>2</sub> (3.43 g, 12.49 mmol) and 2,2'-bipyridyl (1.95 g, 12.49 mmol) were dissolved in DMF (7 mL). The reaction mixture was warmed up to 80 °C for 1 h. To the solution was added **M1** (5.00 g, 11.35 mmol) at 80 °C. The reaction mixture was stirred at 100 °C for 20 h. The reaction mixture was then poured into HCl/methanol (300 mL, 1:9 v/v) and stirred at RT for 1h. The precipitate was filtered and washed exhaustively with methanol and water. To the solution of the residue in THF (60 mL) was added the solution of sodium cyanide (2.00 g, 40.81 mmol) in H<sub>2</sub>O (10 mL) at RT and stirred for 1 h. The solution was then poured into methanol (300 mL) and soon the precipitate was filtered. To remove the low-molecular compounds, Soxhlet extraction was used for the residue in acetone (100 mL) for 6 days. Subsequently, the residue was extracted in THF to obtain the THF soluble parts of **LC-PPP**. After 2 days of Soxhlet extraction, the solution was



evaporated under vacuum and re-precipitated in methanol (300 mL). The precipitated product was filtered and dried under vacuum to give the THF soluble part of **LC-PPP** as a pale yellow powder (1.62 g, 38.6 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.49–1.78 (m, 8H,  $\text{OCH}_2\text{CH}_2$  and  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 3.92–4.06 (m, 4H,  $\text{OCH}_2$ ), 6.89–7.66 (m, 11H, Ar-*H*) ppm (TMS).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.80, 26.09, 29.17, 29.22, 67.91, 68.54, 110.12, 111.63, 114.20, 114.82, 115.05, 119.05, 119.77, 122.23, 127.05, 127.95, 128.31, 130.02, 131.32, 132.54, 132.57, 145.20, 159.7 ppm (TMS). Anal Calcd for: C, 79.99; H, 6.18; N, 3.73; Cl, 1.57. Found: C, 78.96; H, 6.38; N, 3.22; Cl, 1.98. GPC (tetrahydrofuran vs. polystyrene):  $M_n = 4.5 \times 10^3$  g/mol,  $M_w = 8.2 \times 10^3$  g/mol,  $M_w/M_n = 1.8$ .

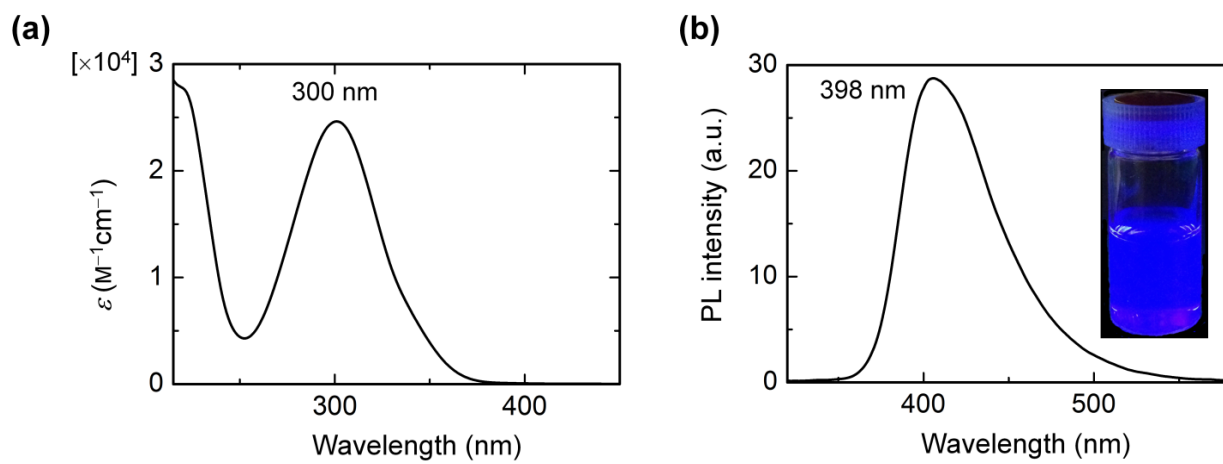


Fig. S1 (a) UV-vis and (b) PL spectra of LC-PPP in  $\text{CHCl}_3$  ( $2.0 \times 10^{-5}$  M).

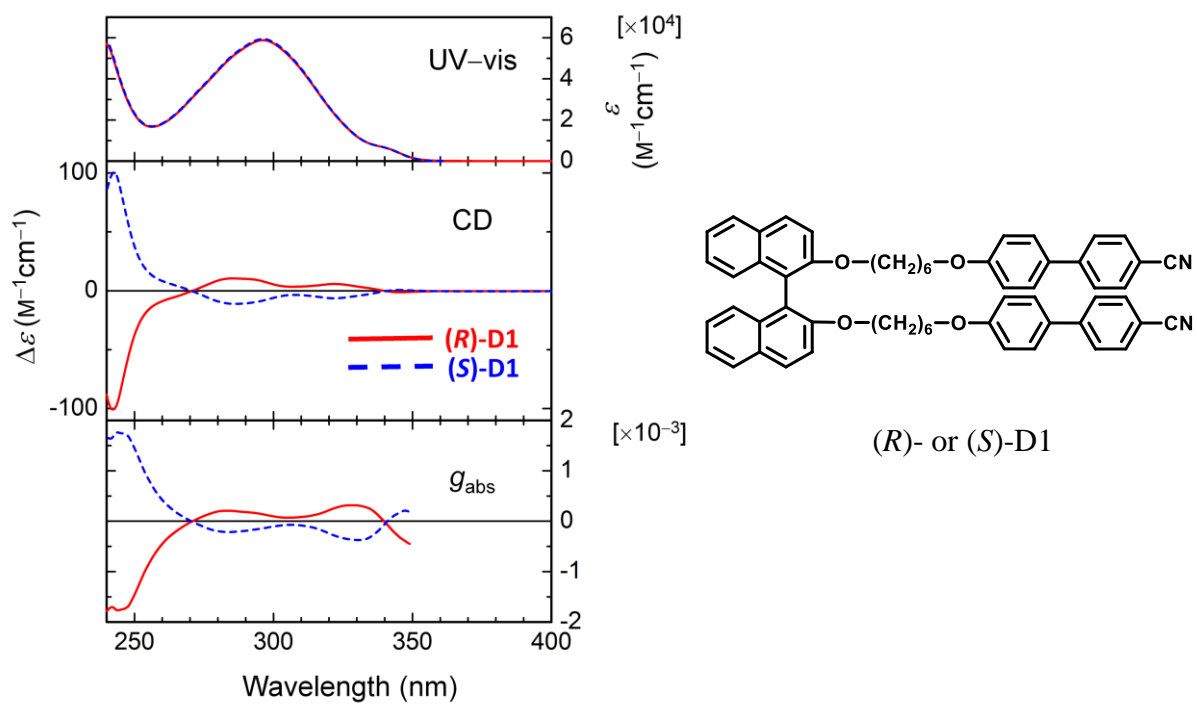


Fig. S2 UV-vis and CD spectra of (R)- or (S)-D1 in  $CHCl_3$  ( $2.0 \times 10^{-5}$  M).

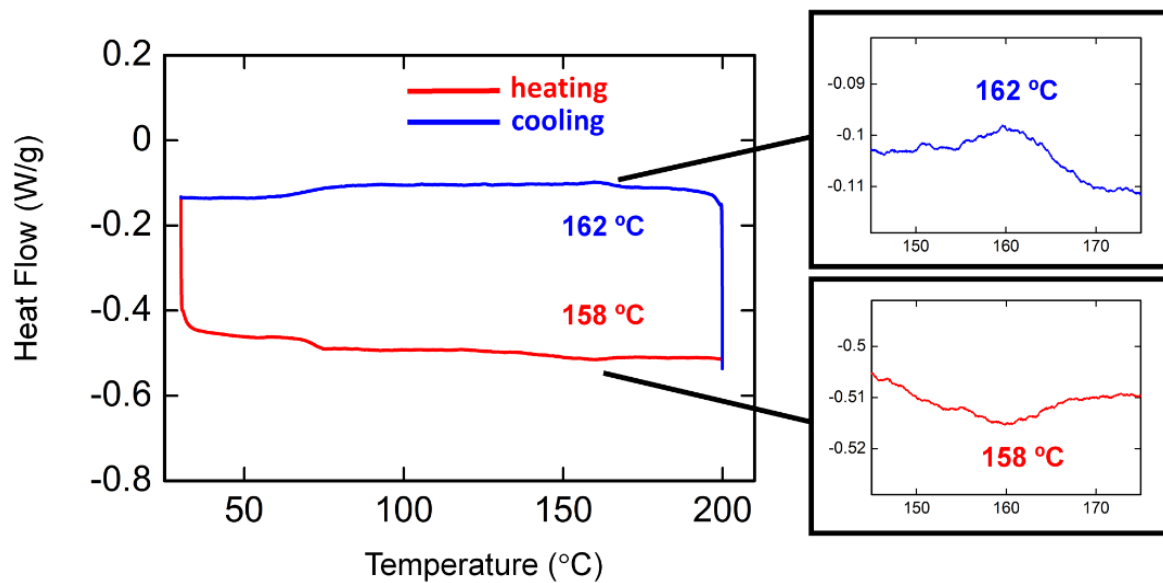


Fig. S3 DSC curves of LC-PPP.

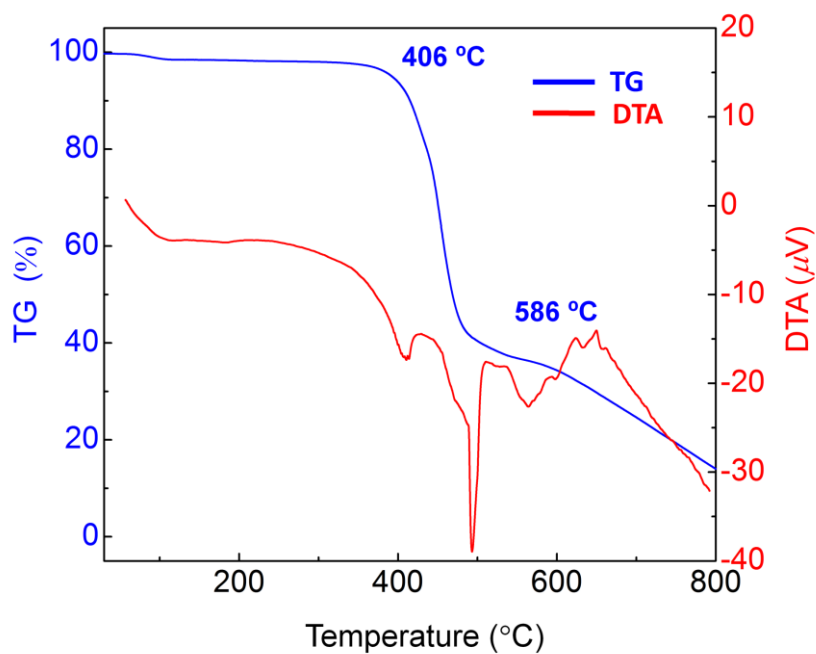


Fig. S4 TG and DTA curves of LC-PPP.

Table S1 Reproducibility of mean diameters of particles determined by DLS.

System	Mean diameter (nm)	
	1st trial	2nd trial
R10	294 ± 181	296 ± 144
S1	233 ± 73	315 ± 121
S2	296 ± 170	251 ± 64
S5	191 ± 29	196 ± 41
S10	232 ± 82	308 ± 137

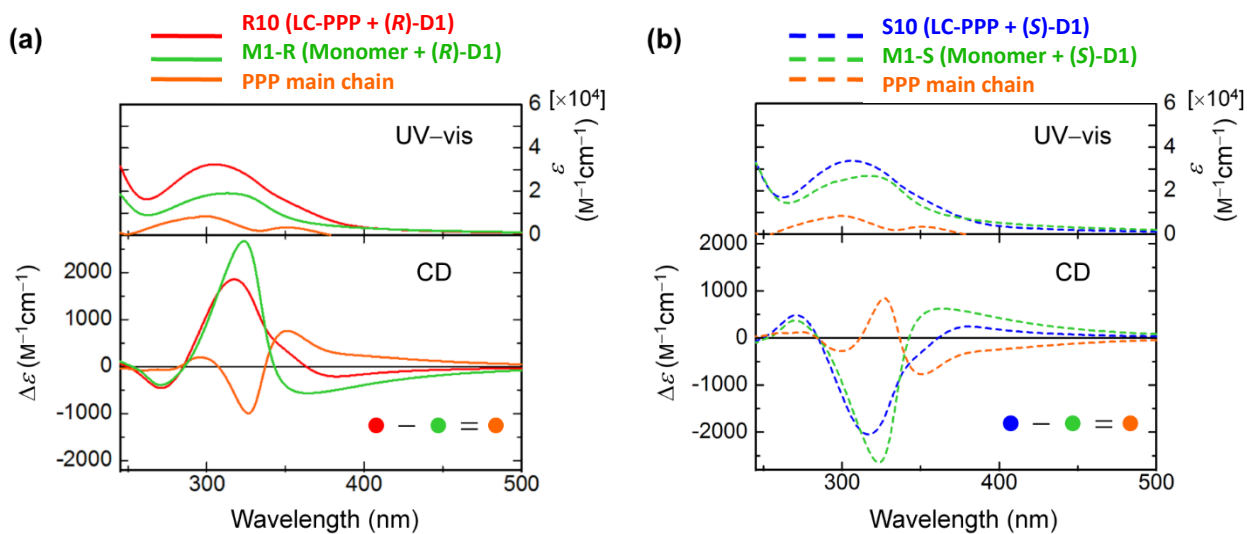


Fig. S5 UV-vis and CD spectra of (a) the system R10, the system M1-R, and the difference spectrum corresponding to PPP main chain obtained by subtracting the spectrum of M1-R from that of the system R10, and (b) the system S10, the system M1-S, and the difference spectrum corresponding to PPP main chain obtained by subtracting the spectrum of M1-S from that of the system S10

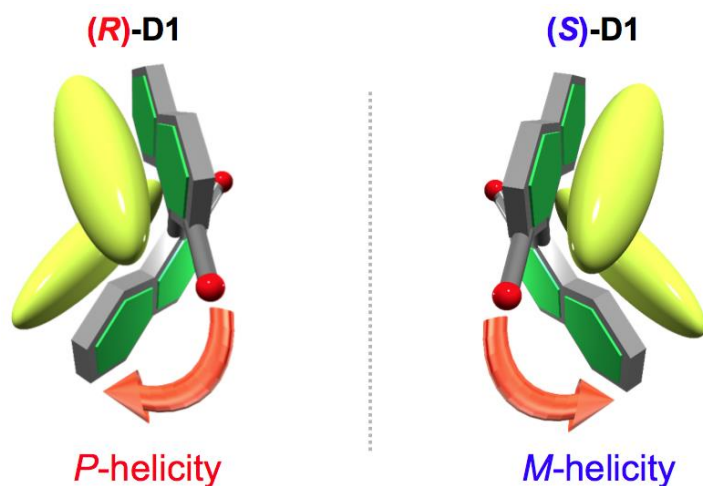


Fig. S6 Schematic representation of helicity induction from a binaphthyl chiral dopant to a cyanobiphenyl molecule.

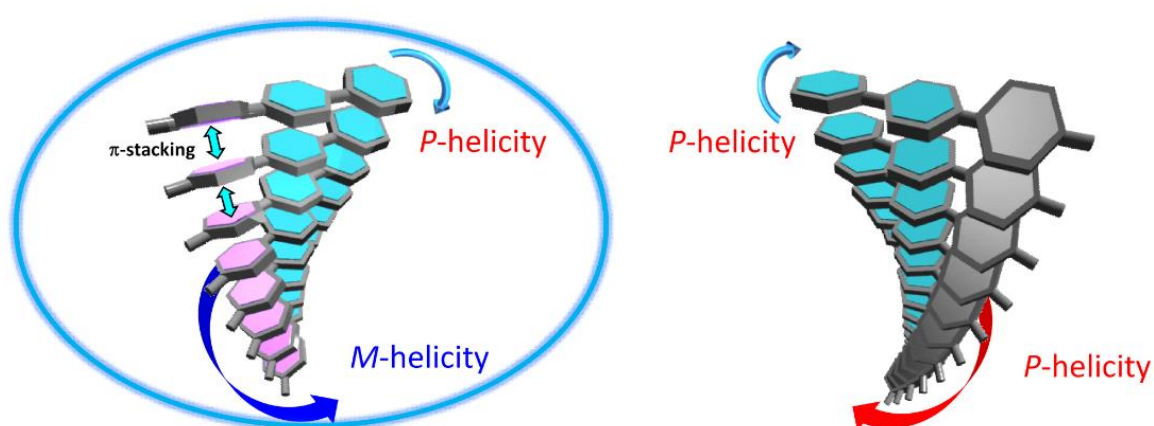


Fig. S7 Schematic representation of helically  $\pi$ -stacked phenylene rings.

Left figure: The right-handed twisted phenylene rings (*P*-helicity) favorably form the left-handed helical  $\pi$ -stacking structure (*M*-helicity). Right figure: However, the right-handed twisted phenylene rings (*P*-helicity) is unfavorable for the right-handed helical  $\pi$ -stacking structure (*M*-helicity). That is, the opposite relationship in helical handedness between the intrachain twisted structure and interchain  $\pi$ -stacking structure is suitable for the formation of stable  $\pi$ -stacked structure.

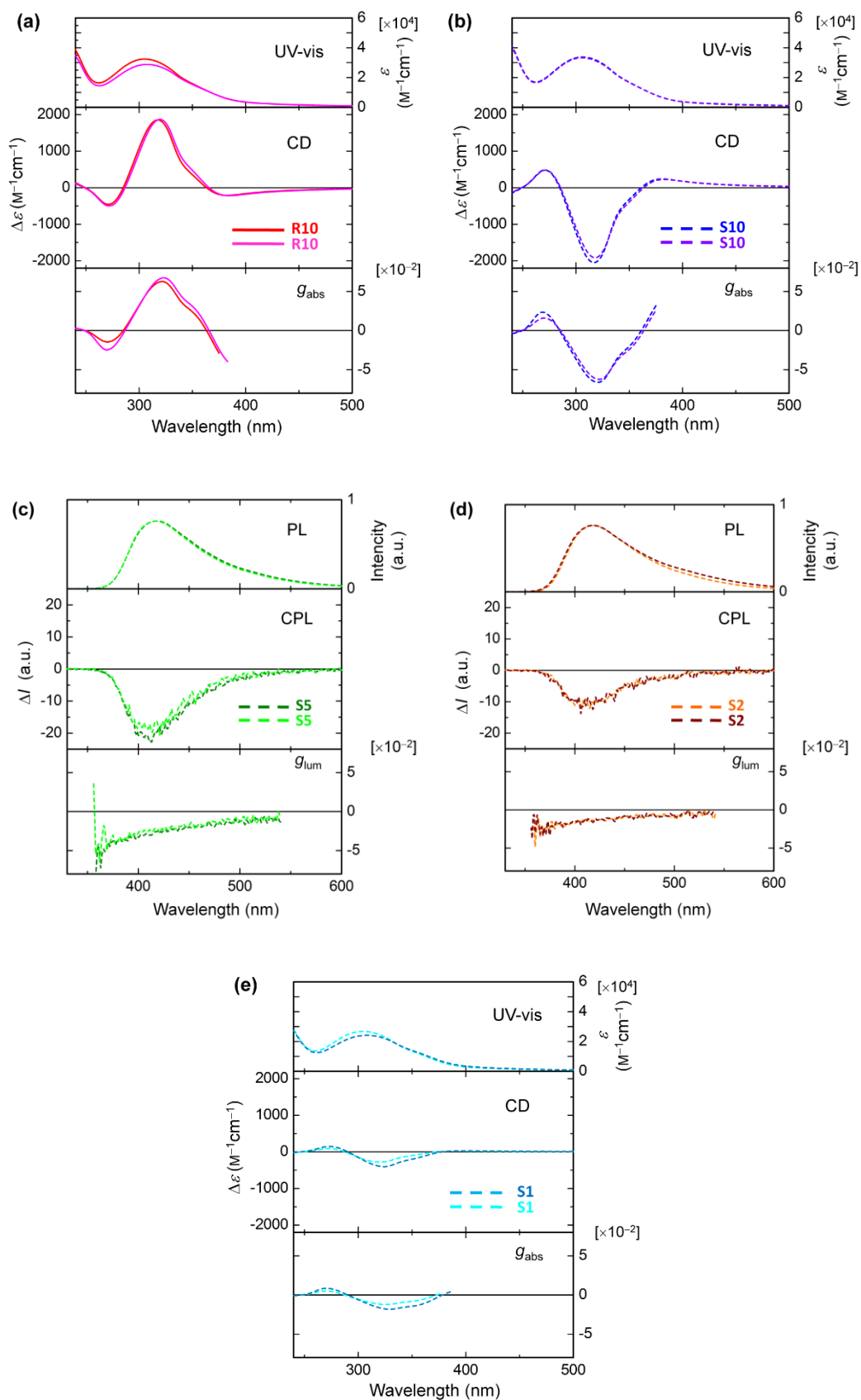


Fig. S8 Reproducibility of UV-vis and CD spectra of system S1, S2, S3, S10, and S12.



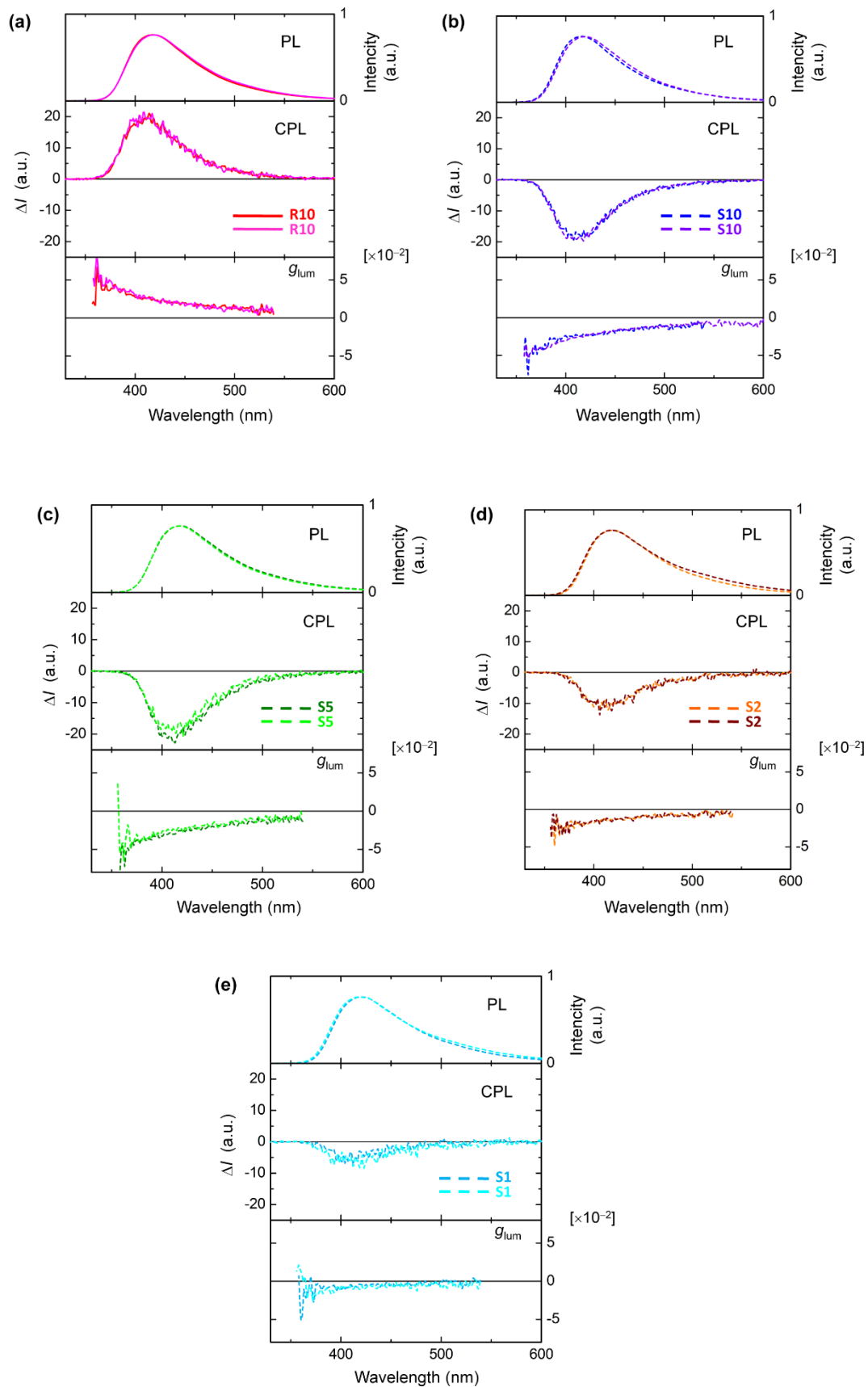


Fig. S9 Reproducibility of PL and CPL spectra of system S1, S2, S3, S10, and S12.

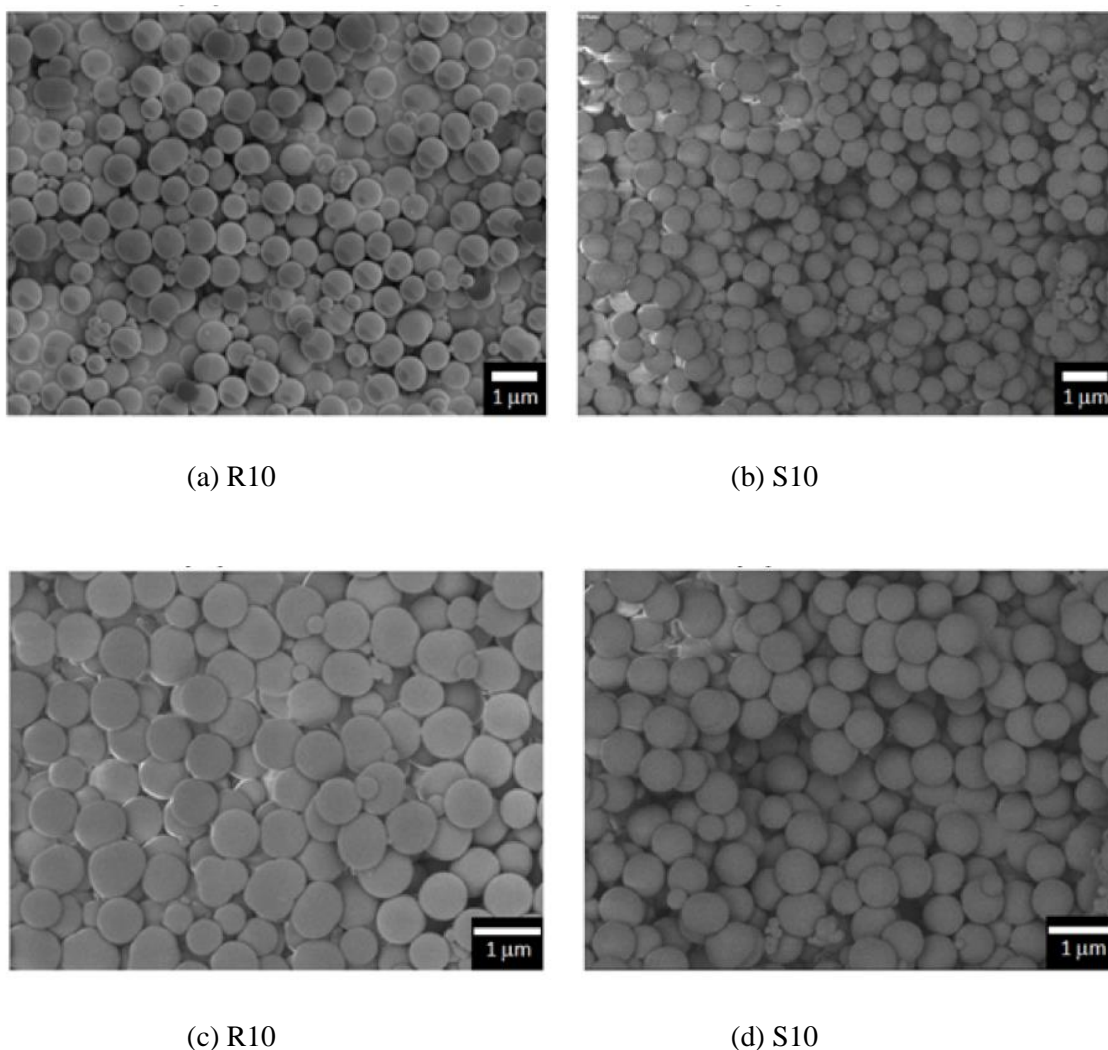


Fig. S10 SEM images of silica-coated polymer particles for systems R10 and S10.

(a) and (b): 10,000 magnification, (c) and (d): 15,000 magnification.

Note that the silica-coating polymer particles are prepared using the so-called “sol-gel” method. Typical procedures are as follows. LC-PPP (2.5 mg) and (*R*)-D1 or (*S*)-D1 (0.1 mole towards LC-PPP) are mixed in  $\text{CHCl}_3$ . Tetraethoxysilane (TEOS, 0.2 ml) is added into the mixture. Ethyl alcohol (20 ml) is added to the mixture followed by addition of aqueous ammonia (5 ml). The mixture begins to turn cloudy white in a few minutes and then is allowed to stand overnight. Particles formed are collected by suction filtration using a fine filter and vacuum dried.