

SUPPORTING INFORMATION

for

Interchain Helically π -Stacked Assembly of Cationic Chiral
Poly(*para*-phenylene) Derivatives Enforced by Anionic
 π -Conjugated Molecules through Both Electrostatic and π - π
Interactions

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1. Materials.

All the chemicals were purchased from Aldrich Chemical Co. Ltd., Tokyo Kasei Co. Ltd., and Wako Co. Ltd. Solvents were dried and distilled before use. Disodium succinate (**A2**) was used without further purification. 2,6-Naphthalenedisulfonic acid disodium salt (**A3**) was recrystallized from water–EtOH before use.

2. Measurements.

NMR spectra were obtained with JEOL JNM-AL400 or JNM-EX400. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) or (trimethylsilyl) propionic-2,2,3,3-*d*4 acid sodium salt (TSP-*d*4) as internal standards. Elemental analyses were performed by 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), JEOL JMS-MS700 (EI), Thermo Fisher Scientific EXACTIVE (ESI), and Thermo Fisher Scientific MALDI DUO orbitrapXL (MALDI).

Size exclusion chromatography (SEC) results were obtained with a system consisting of a TOSOH HLC-8320GPC instrument and TOSOH TSKgel G6000+3000PW_{XL}-CP columns. A mixture of 0.2 M NaNO₃ aq., 0.2 M CH₃COOH aq., and methanol (30 wt.%) was used as an eluent and the flow rate was 1.0 mL/min. Static light scattering (SLS) was performed with an Otsuka electronics DLS-8000 super-dynamic light scattering spectrophotometer.

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 and FP-6500 spectrofluorometers. 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. Optical purities of chiral compounds were evaluated with the specific rotation measured by JASCO P-2300 polarimeter.

Scanning electron microscopy (SEM) was performed with JEOL JSM-7500F. The samples were coated with Pt-Pd alloy by using JEOL JFC-1600 ion coater before measurements of SEM.

3. Synthesis

All syntheses were carried out under argon atmosphere. All synthetic routes are shown in Schemes S1 and S2.

1,4-Diiodo-2,5-dimethoxybenzene (1). To a stirred solution of 1,4-dimethoxybenzene (30.5 g, 221 mmol) in acetic acid (600 mL), water (22.5 mL), and sulfuric acid (98 %, 7.5 mL) was added iodine (59.1 g, 233 mmol) and potassium iodate (23.6 g, 110 mmol), and then the mixture was refluxed for 6 h. After cooled to 0 °C, water (300 mL) was added to the reaction mixture. The insoluble solid was collected by filtration and the residue was refined by recrystallization (chloroform/ethanol) to obtain **1** as a white solid (62.9 g, 73.1 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.83 (s, 6H, OCH₃), 7.20 ppm (s, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ =

57.2, 85.5, 121.6, 153.4 ppm; HRMS (EI, m/z): $[M^+]$ calcd for $C_8H_8I_2O_2$: 389.8614; Found: 389.8617; Anal calcd for $C_8H_8I_2O_2$: C 24.64, H 2.07, I 65.09; Found: C 24.63, H, 2.11, I 65.23.

2,5-Diiodohydroquinone (2). To a stirred solution of **1** (17.7 g, 45.4 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of boron tribromide (25.0 g, 99.8 mmol) in CH_2Cl_2 (40 mL), and then the mixture was refluxed at 40 °C for 24 h. After cooled to RT, the reaction mixture was poured into ice-water (800 mL) and the precipitate was collected by filtration to obtain **2** as a white powder (16.0 g, 97.4 %): 1H NMR (400 MHz, $DMSO-d_6$, TMS): δ = 7.15 (s, 2H, Ar-*H*), 9.80 ppm (s, 2H, OH); ^{13}C NMR (100 MHz, $DMSO-d_6$, TMS): δ = 84.2, 123.5, 150.3 ppm; HRMS (EI, m/z): $[M^+]$ calcd for $C_6H_4I_2O_2$ 361.8301; Found: 361.8298; Anal calcd for $C_6H_4I_2O_2$: C 19.91, H 1.11, I 70.13; Found: C 19.79, H 1.23, I 70.05.

(R)-3-Hydroxybutyl tosylate [(R)-3]. The mixed solution of *para*-toluenesulfonyl chloride (11.7 g, 61.4 mmol) and (*R*)-(-)-1,3-butanediol (5.27 g, 58.4 mmol) in pyridine (40 mL) was stirred at 0 °C for 3 h. After adding water to the reaction mixture, the product was extracted with Et_2O (40 mL \times 4), washed with saturated aqueous solution of copper (II) sulfate (100 mL \times 6), water, and brine, dried by Na_2SO_4 , and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 1/1) to obtain **(R)-3** as a colorless liquid (8.22 g, 57.6 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.19 (d, 3H, J = 5.4 Hz, $CHCH_3$), 1.69–1.84 (m, 3H, $CHCH_2$, OH), 2.45 (s, 3H, Ar- CH_3), 3.94 (m, 1H, $CHCH_3$), 4.17 (dq, 2H, J = 47.2 Hz, 5.4 Hz, $TsOCH_2$), 7.35 (d, 2H, J = 8.4 Hz, Ar-*H*), 7.80 ppm (d, 2H, J = 8.4 Hz, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.7, 23.6, 37.9, 64.1, 67.8, 127.9, 129.9, 133.0, 144.9 ppm; HRMS (EI, m/z): $[M^+]$ calcd for $C_{11}H_{16}O_4S$: 244.0769; Found: 244.0766; Anal calcd for $C_{11}H_{16}O_4S$: C 54.08, H 6.60, S 13.12; Found: C 54.17, H 6.62, S 13.21.

(S)-3-Hydroxybutyl tosylate [(S)-3] The same procedure with **(R)-3** by using (*S*)-(+)-1,3-butanediol (5.37 g, 59.6 mmol), *p*-toluenesulfonyl chloride (11.73 g, 61.5 mmol), and pyridine (40 mL) (5.96 g, 41.0 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.19 (d, 3H, J = 5.4 Hz, $CHCH_3$), 1.67–1.83 (m, 3H, $CHCH_2$, OH), 2.45 (s, 3H, Ar- CH_3), 3.94 (m, 1H, $CHCH_3$), 4.17 (dq, 2H, J = 47.2 Hz, 5.4 Hz, $TsOCH_2$), 7.35 (d, 2H, J = 8.4 Hz, Ar-*H*), 7.80 ppm (d, 2H, J = 8.4 Hz, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.7, 23.6, 37.9, 64.1, 67.9, 127.9, 129.9, 132.9, 144.9 ppm; HRMS (FAB, m/z): $[M+H^+]$ calcd for $C_{11}H_{16}O_4S$: 245.0849; Found: 245.0853; Anal calcd for $C_{11}H_{16}O_4S$: C 54.08, H 6.60, S 13.12; Found: C 53.79, H 6.62, S 13.16.

(R)-(-)-1-Bromo-3-butanol [(R)-4]. After dehydrating lithium bromide monohydrate (9.88 g, 94.2 mmol) in vacuo at 85 °C for 3 h, **(R)-3** (7.32g, 30.0 mmol) and tetrahydrofuran (THF, 45 mL) were added and then the mixture was refluxed at 70 °C for 40 h. After removing THF, the residue was dissolved in water, extracted with CH_2Cl_2 (30 mL \times 5), dried by Na_2SO_4 , and

concentrated under reduced pressure. The crude product was distilled at 50 °C under reduced pressure to obtain **(R)-4** as a colorless liquid (2.78 g, 60.6 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.25 (d, 3H, *J* = 6.2 Hz, CHCH₃), 1.88 (s, 1H, OH), 1.98 (q, 2H, *J* = 6.2 Hz, BrCH₂CH₂), 3.53 (m, 2H, BrCH₂) 4.04 ppm (sext, 1H, *J* = 6.2 Hz, CHOH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 23.5, 30.3, 41.5, 66.1 ppm; HRMS (EI, *m/z*): [M-H⁺] calcd for C₄H₉BrO: 150.9764; Found: 150.9764; Anal calcd for C₄H₉BrO: C 31.40, H 5.93, Br 52.22; Found: C 30.98, H 5.73, Br 52.18; [α]_D²² -40.9° (*c* 1.11, CHCl₃).

(S)-(+)-1-Bromo-3-butanol [(S)-4]. The same procedure with **(R)-4** by using lithium bromide monohydrate (6.78 g, 64.7 mmol), **(S)-3** (5.05 g, 20.7 mmol), and THF (40 mL) to give **(S)-4** as a colorless liquid (1.72 g, 54.5 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.25 (d, 3H, *J* = 6.2 Hz, CHCH₃), 1.89 (s, 1H, OH), 1.98 (q, 2H, *J* = 6.2 Hz, BrCH₂CH₂), 3.53 (m, 2H, BrCH₂) 4.03 ppm (sext, 1H, *J* = 6.2 Hz, CHOH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 23.5, 30.3, 41.5, 66.0 ppm; HRMS (EI, *m/z*): [M-H⁺] calcd for C₄H₉BrO: 150.9764; Found: 150.9765; Anal calcd for C₄H₉BrO: C 31.40, H 5.93, Br 52.22; Found: C 31.12, H 5.94, Br 52.26; [α]_D²¹ +41.0° (*c* 1.03, CHCl₃).

(R,R)-1,4-Diiodo-2,5-bis(1-methyl-3-bromopropoxy)benzene [(R,R)-5]. To a stirred solution of triphenylphosphine (TPP, 1.82 g, 6.94 mmol) in THF (5 mL) was added dropwise a solution of diethyl azodicarboxylate (DEAD, 40 wt% in toluene, 3.15 mL, 6.93 mmol) and **(S)-4** (1.06 g, 6.93 mmol) in THF (15 mL) at 0 °C. Then, to the mixture was slowly added dropwise a solution of **2** (1.14 g, 3.15 mmol) in THF (15 mL), and then the reaction mixture was stirred at RT for 24 h. After removing a precipitate by filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in chloroform, washed with water and brine, dried by Na₂SO₄, and concentrated. The crude product was purified by column chromatography (silica gel, chloroform) to give **(R,R)-5** as a white solid (0.99 g, 49.5 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.34 (d, 6H, *J* = 6.0 Hz, OCHCH₃), 2.23 (dm, 4H, *J* = 87.6 Hz, CH₂CH₂Br), 3.60 (m, 4H, CH₂Br), 4.51 (m, 2H, OCHCH₃), 7.25 ppm (s, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 19.5, 29.8, 39.6, 74.9, 88.1, 124.8, 151.9 ppm; HRMS (FAB, *m/z*): [M⁺] calcd for C₁₄H₁₈Br₂I₂O₂: 629.7763; Found: 629.7778; Anal calcd for C₁₄H₁₈Br₂I₂O₂: C 26.61, H 2.87, Br 25.29, I 40.17; Found: C 26.78, H 2.90, Br 24.62, I 40.21; [α]_D²³ -49.4° (*c* 0.61, CHCl₃).

(S,S)-1,4-Diiodo-2,5-bis(1-methyl-3-bromopropoxy)benzene [(S,S)-5]. The same procedure with **(R,R)-5** by using **2** (1.81 g, 5.00 mmol), **(R)-4** (1.68 g, 11.0 mmol), TPP (2.89 g, 11.0 mmol), DEAD (40 wt% in toluene, 5.00 mL, 11.0 mmol), and THF (65 mL) to give **(S,S)-5** as a white solid (0.87 g, 27.4 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.34 (d, 6H, *J* = 6.4 Hz, OCHCH₃), 2.26 (dm, 4H, *J* = 86.0 Hz, CH₂CH₂Br), 3.58 (m, 4H, CH₂Br), 4.50 (m, 2H, OCHCH₃), 7.25 ppm (s, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 19.5, 29.8, 39.6, 74.8, 88.1,

124.8, 151.9 ppm; HRMS (MALDI, m/z): $[M^+]$ calcd for $C_{14}H_{18}Br_2I_2O_2$: 629.7763; Found: 629.7767; Anal calcd for $C_{14}H_{18}Br_2I_2O_2$: C 26.61, H 2.87, Br 25.29, I 40.17; Found: C 26.99, H 2.86, Br 21.78, I 41.58; $[\alpha]_D^{27} +48.4^\circ$ (c 1.00, $CHCl_3$).

(*R,R*)-1,4-Diiodo-2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]benzene dibromide [(*R,R*)-6]. A solution of (*R,R*)-5 (0.42 g, 0.67 mmol) and trimethylamine (30 wt% in water, 1.41 g, 7.16 mmol) in THF (15 mL) was stirred at RT for 72 h. After adding Et_2O (70 mL) to the reaction mixture, the product was extracted with water (40 mL \times 5), washed Et_2O (50 mL \times 1), and concentrated under reduced pressure. The residue was dried in vacuo at 100 °C for 6 h to give (*R,R*)-6 as a white powder (0.49 g, 98.9 %): 1H NMR (400 MHz, D_2O , TSP- d_4): δ = 1.40 (d, 6H, J = 6.7 Hz, $OCHCH_3$), 2.27 (q, 4H, J = 6.7 Hz, $CH_2CH_2N^+(CH_3)_3$), 3.20 (s, 18H, $N^+(CH_3)_3$), 3.60 (m, 4H, $CH_2CH_2N^+(CH_3)_3$), 4.60 (sext, 2H, J = 6.7 Hz, OCH), 7.52 ppm (s, 2H, *Ar-H*); ^{13}C NMR (100 MHz, D_2O , TSP- d_4): δ = 21.4, 31.9, 55.8, 66.2, 77.6, 90.7, 128.3, 154.1 ppm; HRMS (ESI, m/z): $[M-Br^-]$ calcd for $C_{20}H_{36}Br_2I_2N_2O_2$: 669.0044; Found: 669.0044; Anal calcd for $C_{20}H_{36}Br_2I_2N_2O_2$: C 32.02, H 4.84, Br 21.30, I 33.84, N 3.73; Found: C 31.74, H 4.75, Br 18.64, I 32.85, N 3.72; $[\alpha]_D^{23} -32.3^\circ$ (c 0.61, MeOH).

(*S,S*)-1,4-Diiodo-2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]benzene dibromide [(*S,S*)-6]. The same procedure with (*R,R*)-6 by using (*S,S*)-5 (0.79 g, 1.25 mmol), trimethylamine (30 wt% in water, 2.54 g, 12.89 mmol), and THF (20 mL) to give (*S,S*)-6 as a white powder (0.91 g, 96.4 %): 1H NMR (400 MHz, D_2O , TSP- d_4): δ = 1.40 (d, 6H, J = 7.1 Hz, $OCHCH_3$), 2.27 (q, 4H, J = 7.1 Hz, $CH_2CH_2N^+(CH_3)_3$), 3.19 (s, 18H, $N^+(CH_3)_3$), 3.62 (m, 4H, $CH_2CH_2N^+(CH_3)_3$), 4.60 (sext, 2H, J = 7.1 Hz, OCH), 7.52 ppm (s, 2H, *Ar-H*); ^{13}C NMR (100 MHz, D_2O , TSP- d_4): δ = 21.4, 31.9, 55.8, 66.5, 77.7, 90.8, 128.5, 154.3 ppm; HRMS (ESI, m/z): $[M-Br^-]$ calcd for $C_{20}H_{36}Br_2I_2N_2O_2$: 669.0044; Found: 669.0044; Anal calcd for $C_{20}H_{36}Br_2I_2N_2O_2$: C 32.02, H 4.84, Br 21.30, I 33.84, N 3.73; Found: C 31.89, H 4.78, Br 20.60, I 33.60, N 3.73; $[\alpha]_D^{27} +32.1^\circ$ (c 1.01, MeOH).

1,4-Phenylenediboronic acid bis(1,3-propanediol) cyclic ester (7). A suspension of 1,4-phenylenediboronic acid (5.00 g, 30.2 mmol) and 1,3-propanediol (5.63 g, 74.0 mmol) in CH_2Cl_2 (190 mL) was refluxed for 24 h. The solvent was removed under reduced pressure, and the residue was washed with ethanol to give **3** as a white powder (6.94 g, 93.6 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.05 (quint, 4H, J = 5.4 Hz, OCH_2CH_2), 4.16 (t, 8H, J = 5.4 Hz, OCH_2), 7.73 ppm (s, 4H, *Ar-H*); ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ = 27.4, 61.9, 132.5 ppm; HRMS (ESI, m/z): $[M+H^+]$ calcd for $C_{12}H_{16}B_2O_4$: 247.1307; Found: 247.1302; Anal calcd for $C_{12}H_{16}B_2O_4$: C 58.62, H 6.56; Found: C 58.36, H 6.49.

(*R,R*)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-1,

4-phenylene) dibromide [(R,R)-PPP1]. A solution of **(R,R)-6** (0.385 g, 0.512 mmol), **7** (0.126 g, 0.512 mmol), palladium(II) acetate (5.77 mg, 0.026 mmol), and Na₂CO₃ (0.459 g, 4.33 mmol) in *N,N*-dimethylformamide (DMF, 10 mL) and deionized water (10 mL) was stirred at 95 °C for 72 h. After removing a black insoluble powder by filtration, the filtrate was poured into a diluted HBr aqueous solution (300 mL) and vigorously stirred overnight in the presence of ethylenediamine-tetraacetic acid (EDTA, 1 g). Then the mixture was filtered and the residue was washed with hot methanol. The filtrate was concentrated to about 100 mL under reduced pressure, dropped into a large amount of acetone (500 mL), and vigorously stirred overnight. The resulting precipitate was collected by filtration and dissolved in deionized water. The above processes were repeated twice to purify the polymer. Subsequently, the aqueous solution of the polymer passed through an ion exchange resin (Amberlite® IRA-402, regenerated by NaOH aq.) to exchange the anionic species ($X^- \rightarrow OH^-$), and then neutralized by HBr. Finally, low molecular weight fractions, oligomers, and impurities were removed by a dialysis treatment (Spectra/Por® Dialysis Membrane 6, MWCO: 8,000) in deionized water for a month. The resulting solution was freeze-dried to obtain **(R,R)-PPP1** as a pale green solid (0.175 g, 59.6 %): ¹H NMR (400 MHz, DMSO-*d*₆, TMS): $\delta = 1.27$ (br, 6H, OCH(CH₃)CH₂), 2.10 (br, 4H, OCHCH₂), 3.13 (br, 18H, N⁺CH₃), 3.53 (br, 4H, CH₂N⁺(CH₃)₃), 4.57 (br, 2H, OCH), 7.21 (s, 2H, Ar-*H*), 7.78 ppm (br, 4H; Ar-*H*); ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): $\delta = 19.3, 29.5, 52.6, 62.8, 73.1, 118.5, 126.3, 129.3, 130.1, 131.6, 136.6, 148.8$ ppm.

(S,S)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-1,4-phenylene) dibromide [(S,S)-PPP1]. The same procedure with **(R,R)-PPP1** by using **(S,S)-6** (0.444 g, 0.591 mmol), **7** (0.145 g, 0.591 mmol), palladium(II) acetate (7.13 mg, 0.032 mmol), Na₂CO₃ (0.508 g, 4.79 mmol), DMF (12 mL), and deionized water (12 mL) to give **(S,S)-PPP1** as a pale green solid (0.267 g, 78.7 %): ¹H NMR (400 MHz, DMSO-*d*₆, TMS): $\delta = 1.27$ (br, 6H, OCH(CH₃)CH₂), 2.09 (br, 4H, OCHCH₂), 3.14 (br, 18H, N⁺CH₃), 3.55 (br, 4H, CH₂N⁺(CH₃)₃), 4.57 (br, 2H, OCH), 7.21 (s, 2H, Ar-*H*), 7.77 ppm (br, 4H, Ar-*H*); ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): $\delta = 19.3, 29.4, 52.5, 62.7, 73.1, 118.4, 126.1, 129.1, 129.9, 131.4, 136.4, 148.6$ ppm.

(R,R)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-{4,4'-biphenylene}) dibromide [(R,R)-PPP2]. The same procedure with **(R,R)-PPP1** by using **(R,R)-6** (0.375 g, 0.500 mmol), 4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (0.189 g, 0.500 mmol), palladium(II) acetate (6.02 mg, 0.027 mmol), Na₂CO₃ (0.439 g, 4.14 mmol), DMF (10 mL), and deionized water (10 mL) to give **(R,R)-PPP2** as a pale green solid (0.302 g, 93.0 %): ¹H NMR (400 MHz, DMSO-*d*₆, TMS): $\delta = 1.26$ (d, 6H, $J = 6.0$ Hz, OCH(CH₃)CH₂), 2.06 (br, 4H, OCHCH₂), 3.10 (br, 18H, N⁺CH₃), 3.46 (t, 4H, $J = 8.0$ Hz, CH₂N⁺(CH₃)₃), 4.54 (sext, 2H, $J = 6.0$ Hz, OCH), 7.20 (s, 2H, Ar-*H*), 7.76 (br, 4H, Ar-*H*), 7.86 ppm (br, 4H, Ar-*H*); ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): $\delta = 19.3, 29.4, 52.6, 62.8, 73.1,$

118.6, 126.3, 126.5, 129.0, 130.1, 131.6, 137.0, 138.6, 148.8 ppm.

(*S,S*)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-{4,4'-biphenylene}) dibromide [(*S,S*)-PPP2]. The same procedure with (*R,R*)-PPP1 by using (*S,S*)-6 (0.375 g, 0.500 mmol), 4,4'-biphenyldiboric acid bis(neopentyl glycol) cyclic ester (0.189 g, 0.500 mmol), palladium(II) acetate (5.78 mg, 0.026 mmol), Na₂CO₃ (0.430 g, 4.06 mmol), DMF (10 mL), and deionized water (10 mL) to give (*S,S*)-PPP2 as a pale green solid (0.231 g, 71.2 %): ¹H NMR (400 MHz, DMSO-*d*₆, TMS): δ = 1.26 (d, 6H, *J* = 6.0 Hz, OCH(CH₃)CH₂), 2.06 (br, 4H, OCHCH₂), 3.10 (br, 18H, N⁺CH₃), 3.46 (t, 4H, *J* = 8.0 Hz, CH₂N⁺(CH₃)₃), 4.53 (sext, 2H, *J* = 6.0 Hz, OCH), 7.20 (s, 2H, Ar-*H*), 7.76 (br, 4H, Ar-*H*), 7.85 ppm (br, 4H, Ar-*H*); ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): δ = 19.3, 29.4, 52.5, 62.7, 73.0, 118.4, 126.1, 126.4, 128.8, 129.9, 131.4, 136.9, 138.4, 148.6 ppm.

Sodium 3-(2-naphthyloxy)propylsulfonate (SNap). To a solution of 2-naphthol (2.89 g, 20.1 mmol) in EtOH (50 mL) was added dropwise a solution of NaOH (0.95 g, 23.6 mmol) in EtOH (50 mL) at RT. Then, 1,3-propanesultone (2.61 g, 21.4 mmol) and EtOH (50 mL) were added to the mixture, and the reaction mixture was stirred at RT for 24 h. The resulting precipitate was filtered, washed with EtOH, and recrystallized from water–EtOH to give **SNap** as a white solid (4.37 g, 75.5 %): ¹H NMR (400 MHz, D₂O, TSP-*d*₄): δ = 2.09 (quint, 2H, *J* = 7.1 Hz, OCH₂CH₂), 2.95 (t, 2H, *J* = 7.1 Hz, CH₂SO₃Na), 3.79 (t, 2H, *J* = 7.1 Hz, OCH₂), 6.92 (s, 1H, Ar-*H*), 6.95 (dd, 1H, *J* = 8.8 and 2.4 Hz, Ar-*H*), 7.30 (t, 1H, *J* = 8.0 Hz, Ar-*H*), 7.39 (t, 1H, *J* = 8.0 Hz, Ar-*H*), 7.58–7.61 (m, 2H, Ar-*H*), 7.67 ppm (d, 1H, *J* = 8.0 Hz, Ar-*H*); ¹³C NMR (400 MHz, D₂O, TSP-*d*₄): δ = 27.0, 50.7, 69.0, 109.8, 121.0, 126.5, 129.1, 129.4, 130.2, 131.4, 132.0, 136.8, 158.5 ppm; HRMS (ESI) calcd for C₁₃H₁₃NaO₄S [M – Na⁺]: 265.0540; Found: 265.0539; Anal calcd for C₁₃H₁₃NaO₄S: C 54.16, H 4.55; Found: C 53.97, H 4.55.

Diethylene glycol bis(3-sulfonatepropyl) ether disodium salt (A1). To a solution of diethylene glycol (1.071 g, 10.1 mmol) in THF (70 mL) was added NaH (0.583 g, 24.3 mmol) at 0 °C, and then the mixture was stirred at RT for 1.5 h. After that, a solution of 1,3-propanesultone (2.95 g, 24.2 mmol) in THF (30 mL) was added dropwise. The reaction mixture was stirred at RT for 24 h. After quenching residual NaH with water, THF solvent was removed under reduced pressure. The resulting aqueous solution was washed by chloroform 4 times, and then water was removed. The residue was recrystallized from water–EtOH to give **A1** as a white solid (3.84 g, 96.5 %): ¹H NMR (400 MHz, D₂O, TSP-*d*₄): δ = 2.03 (quint, 4H, *J* = 6.8 Hz, CH₂CH₂SO₃Na), 2.99 (t, 4H, *J* = 6.8 Hz, CH₂SO₃Na), 3.63–3.70 ppm (m, 12H, CH₂OCH₂CH₂O); ¹³C NMR (100 MHz, D₂O, TSP-*d*₄): δ = 27.1, 50.7, 71.9, 72.0, 72.4 ppm; HRMS (ESI) calcd for C₁₀H₂₀Na₂O₉S₂ [M – Na⁺]: 371.0441; Found: 371.0439; Anal calcd for C₁₀H₂₀Na₂O₉S₂: C 30.46, H 5.11, S 16.26; Found: C 29.93, H 5.27, S 15.18.

2,6-Bis(3-sulfonatepropoxy)naphthalene disodium salt (A4). A solution of NaOH (0.900 g, 22.5 mmol) in EtOH (50 mL) was added dropwise to a solution of 2,6-dihydroxynaphthalene (1.602 g, 10.0 mmol) in EtOH (120 mL) at RT, and then the mixture was refluxed at 80 °C for 1 h. After adding 1,3-propanesultone (2.69 g, 22.1 mmol), the reaction mixture was refluxed at 80 °C for 3.5 h. The resulting precipitate was filtrated and recrystallized from water–EtOH 3 times to give **A4** as light reddish white powder (2.325 g, 51.9 %): ¹H NMR (400 MHz, D₂O, TSP-*d*₄): δ = 2.24 (quint, 4H, *J* = 5.7 Hz, OCH₂CH₂), 3.11 (t, 4H, *J* = 5.7 Hz, CH₂SO₃Na), 4.15 (t, 4H, *J* = 5.7 Hz, OCH₂), 7.15 (d, 2H, *J* = 8.4 Hz, Ar-*H*), 7.21 (s, 2H, Ar-*H*), 7.69 ppm (d, 2H, *J* = 8.4 Hz, Ar-*H*); ¹³C NMR (100 MHz, D₂O, TSP-*d*₄): δ = 27.1, 50.8, 69.6, 110.7, 121.7, 131.3, 132.5, 157.5 ppm; HRMS (ESI) calcd for C₁₆H₁₈Na₂O₈S₂ [M + Na⁺]: 471.0131; Found: 471.0127; Anal calcd for C₁₆H₁₈Na₂O₈S₂: C 42.86, H 4.05, S 14.30; Found: C 42.65, H 3.88, S 14.31.

4. Sample Preparation

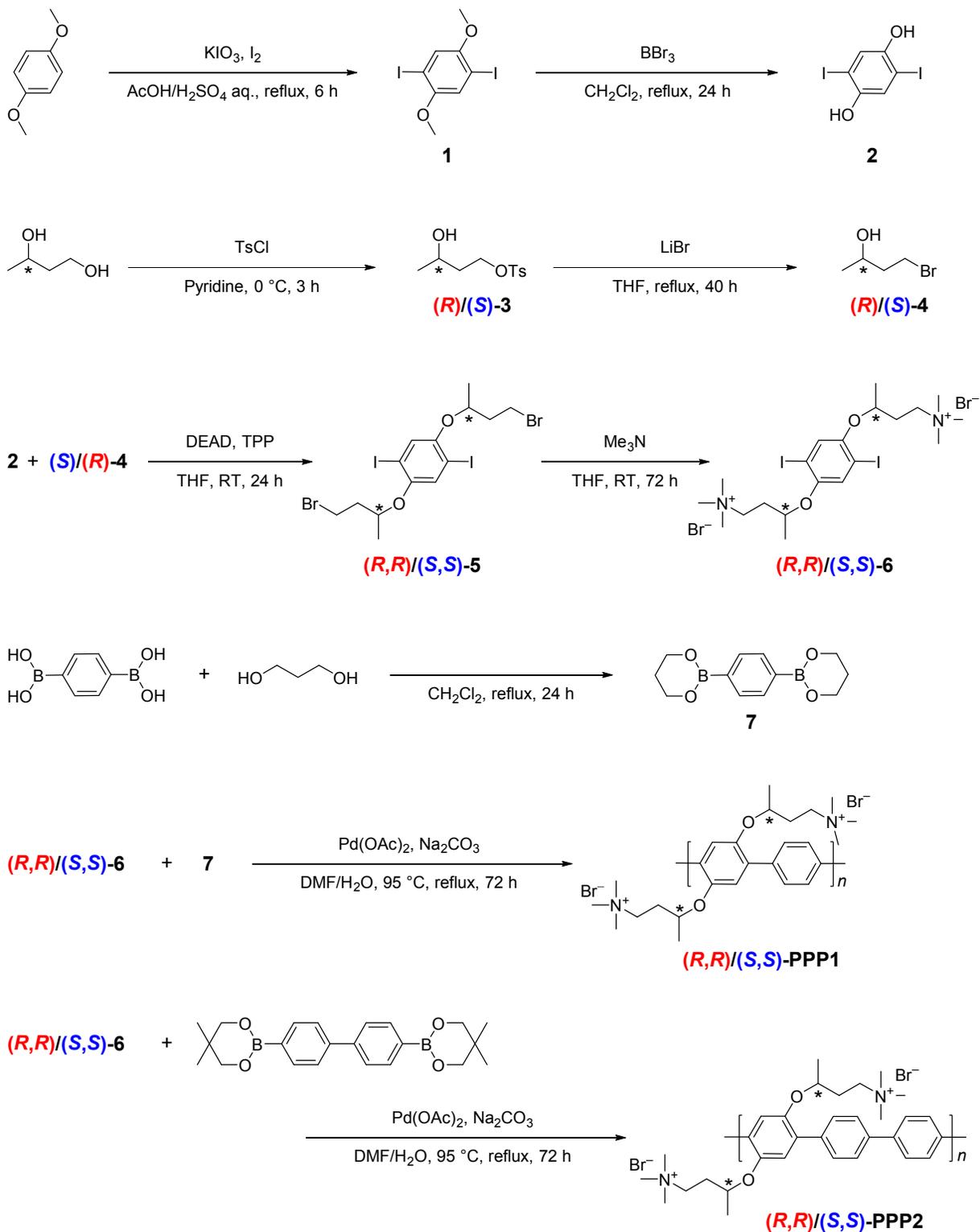
4.1. Optical measurements for the cationic polymers. The cationic polymers (**PPP1** or **PPP2**) were dissolved in water, methanol, and mixtures of water and methanol at the concentration of 2.0×10^{-5} M, respectively.

4.2. Optical measurements for mixtures of the cationic polymers and the anionic additives. The cationic polymers (**PPP1** or **PPP2**) and the anionic additives (**A1**, **A2**, **A3**, or **A4**) were separately dissolved in water at the concentration of 1.0×10^{-3} M, and then the solutions were mixed with various molar ratios at RT. Exceptionally, the concentration of **SNap** was kept at 2.0×10^{-3} M to adjust a concentration of the anionic moiety to the other anionic additives. Subsequently, the mixtures were diluted with water to give a concentration of the polymer = 2.0×10^{-5} M. All ϵ and $\Delta\epsilon$ in UV–vis absorption and CD spectra were evaluated in terms of the concentrations of the polymers. The heating treatment to **PPP2–SNap** was performed by using a Peltier-type thermostat attached in JASCO J-820 spectropolarimeter.

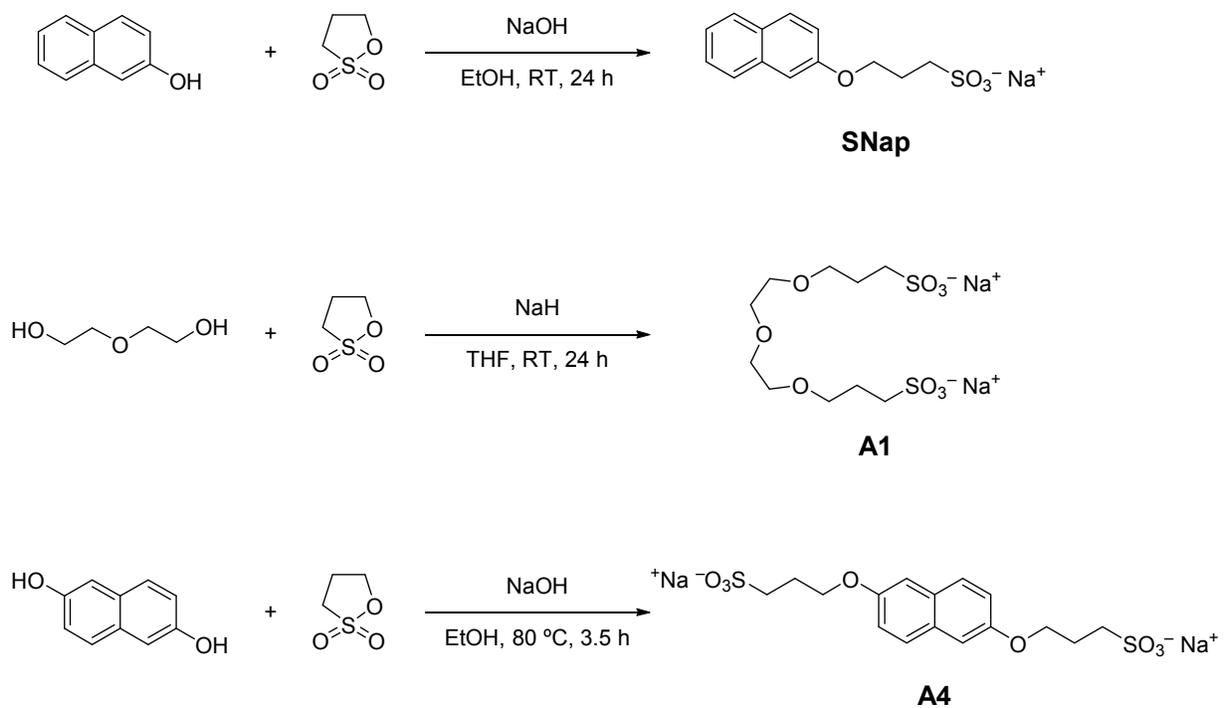
4.3 SEM measurements. According to the above procedure, a mixed solution of **PPP1** and **SNap** was prepared with the molar ratio of 1:4. The mixed solution was dried at RT on a sample stage to give a solid sample for the SEM measurement.

5. Average Molecular Weights of Cationic Polymers

To evaluate the average molecular weights of the polymers, we performed size exclusion chromatography (SEC) using a cation-coated column, where the column packing material used as a stationary phase possessed cationic groups to prevent adsorption of cationic polymers. However all chromatograms of the SEC measurements showed broad peaks, indicating quite high polydispersity indices. Moreover, the SEC results were less reproducible. This is because the polymers were partially adsorbed to the column packing material despite the cation-coating on the column packing material. In addition, it was difficult to evaluate the molecular weight of water-soluble conjugated polymers using the SEC equipment because the hydrophobic polymer main chains tend to aggregate each other in polar solvent via interchain π - π interactions. Hence, we found that the results of the SEC measurements for the ionic conjugated polymers were less reliable. Subsequently, we performed static light scattering (SLS) measurements in water to estimate the absolute molecular weights of the polymers through Zimm plot analysis. However, the required polymer concentration (10 mg/mL in water) was too high to dissolve the polymers completely. The M_w values were only estimated to be 9.9×10^5 – 7.5×10^6 , which suggests an occurrence of aggregation of the polymers. This may be rationalized with the argument that the conjugated hydrophobic backbones tend to aggregate via hydrophobic and π - π interactions. As a result, we were not able to quantitatively evaluate the average molecular weights of the polymers.



Scheme S1. Synthetic routes of cationic chiral poly(*para*-phenylene) derivatives (**PPP1** and **PPP2**).



Scheme S2. Synthetic route of anionic additives (**SNap**, **A1**, and **A4**).

Table S1. Optical properties of (*R,R*)-**PPP1** in water, methanol, and the mixtures.

Solvent	UV-vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a (%)
	λ_{\max} (nm)	ε (M ⁻¹ cm ⁻¹)	λ_{\max} (nm)	$\Delta\varepsilon$ (M ⁻¹ cm ⁻¹)	g_{abs}^b ($\times 10^{-4}$)	Em _{max} (nm)	Ex (nm)	
methanol	341	2.00×10^4	289	+1.89	+1.74	405	344	32.4
			247	-3.22	-2.90			
methanol-water = 75:25	341	2.00×10^4	222	+5.19	+2.64	407	342	36.1
			288	+2.27	+1.86			
			246	-4.60	-3.69			
methanol-water = 50:50	339	1.90×10^4	221	+4.89	+2.25	411	342	32.8
			286	+3.14	+2.89			
			245	-4.90	-4.28			
methanol-water = 25:75	337	1.86×10^4	221	+6.92	+3.55	415	339	24.9
			284	+4.15	+3.59			
			244	-6.39	-5.17			
water	335	1.79×10^4	286	+4.98	+3.75	418	342	10.5
			243	-6.57	-4.84			
			220	+12.6	+5.34			

^a Quantum yield was estimated by using an integral sphere.

^b Dissymmetry factor in absorbance

^c The concentration of (*R,R*)-**PPP1** is 5.0×10^{-5} M.

Table S2. Optical properties of (*S,S*)-**PPP1** in water, methanol, and the mixtures.

Solvent	UV–vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a (%)
	λ_{\max} (nm)	ε (M ⁻¹ cm ⁻¹)	λ_{\max} (nm)	$\Delta\varepsilon$ (M ⁻¹ cm ⁻¹)	g_{abs}^b ($\times 10^{-4}$)	Em _{max} (nm)	Ex (nm)	
methanol	342	2.13×10^4	288	-2.49	-2.18	405	344	34.2
			246	+3.56	+3.02			
methanol–water = 75:25	341	2.04×10^4	220	-6.74	-3.35	407	342	37.4
			287	-2.36	-2.03			
			246	+4.34	+3.58			
			220	-5.73	-2.70			
methanol–water = 50:50	341	1.95×10^4	288	-3.09	-2.81	410	342	35.7
			245	+5.29	+4.67			
			220	-7.42	-3.78			
methanol–water = 25:75	337	1.86×10^4	286	-4.36	-3.92	416	340	25.9
			244	+6.56	+5.69			
			220	-11.3	-5.70			
water	335	1.78×10^4	288	-4.67	-3.79	417	339	12.2
			243	+6.80	+5.47			
			220	-12.5	-5.84			

^a Quantum yield was estimated by using an integral sphere.

^b Dissymmetry factor in absorbance

^c The concentration of (*S,S*)-**PPP1** is 5.0×10^{-5} M.

Table S3. Optical properties of (*R,R*)-**PPP2** in water, methanol, and the mixtures.

Solvent	UV–vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a (%)
	λ_{\max} (nm)	ε (M ⁻¹ cm ⁻¹)	λ_{\max} (nm)	$\Delta\varepsilon$ (M ⁻¹ cm ⁻¹)	g_{abs}^b ($\times 10^{-4}$)	Em _{max} (nm)	Ex (nm)	
methanol	339	3.29×10^4	292	+2.62	+1.60	408	340	64.3
			238	+2.84	+2.51			
methanol–water = 75:25	339	3.25×10^4	221	-3.00	-1.17	409	340	64.6
			290	+2.81	+1.90			
			237	+3.05	+2.73			
			222	-2.52	-1.09			
methanol–water = 50:50	338	3.19×10^4	290	+3.14	+2.05	413	340	61.4
			237	+2.98	+2.67			
			220	-2.33	-0.92			
methanol–water = 25:75	337	3.06×10^4	292	+3.26	+2.16	419	340	44.2
			236	+2.60	+2.46			
			216	-1.83	-0.64			
water	345	3.00×10^4	298	+3.60	+2.37	419	344	31.5
			249	+2.64	+3.06			
			229	-7.05	-4.73			

^a Quantum yield was estimated by using an integral sphere.

^b Dissymmetry factor in absorbance

^c The concentration of (*R,R*)-**PPP2** is 5.0×10^{-5} M.

Table S4. Optical properties of (*S,S*)-**PPP2** in water, methanol, and the mixtures.

Solvent	UV-vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a (%)
	λ_{\max} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{\max} (nm)	$\Delta\epsilon$ (M ⁻¹ cm ⁻¹)	g_{abs}^b ($\times 10^{-4}$)	Em _{max} (nm)	Ex (nm)	
methanol	338	3.30×10^4	291	-2.68	-1.49	408	340	53.0
			238	-2.93	-2.20			
			222	+3.45	+1.25			
methanol-water = 75:25	338	3.26×10^4	293	-3.21	-1.56	410	341	55.2
			238	-3.54	-2.41			
			221	+3.87	+1.23			
methanol-water = 50:50	337	3.17×10^4	291	-3.78	-1.90	414	339	51.0
			237	-3.68	-2.49			
			221	+3.88	+1.22			
methanol-water = 25:75	336	3.06×10^4	288	-4.08	-2.19	419	340	33.6
			237	-3.10	-2.14			
			220	+2.62	+0.81			
water	343	2.93×10^4	298	-4.30	-2.21	419	346	16.9
			251	-2.50	-2.16			
			227	+5.23	+2.49			

^a Quantum yield was estimated by using an integral sphere.

^b Dissymmetry factor in absorbance

^c The concentration of (*S,S*)-**PPP2** is 5.0×10^{-5} M.

Table S5. Average particle size **PPP1**, **PPP2**, and their polymer assemblies evaluated by DLS measurements.

Sample	Average particle size (nm)
(<i>R,R</i>)-PPP1	334.9 ± 112.5
(<i>R,R</i>)-PPP1-SNap = 1:2	765.1 ± 216.5
(<i>R,R</i>)-PPP1-SNap = 1:4	865.9 ± 236.4
(<i>R,R</i>)-PPP2	223.7 ± 65.2
(<i>R,R</i>)-PPP2-SNap = 1:2	207.4 ± 44.6
(<i>R,R</i>)-PPP2-SNap = 1:4	604.8 ± 149.4
(<i>R,R</i>)-PPP2-SNap = 1:6	444.3 ± 83.5
(<i>R,R</i>)-PPP2-SNap = 1:8	473.7 ± 122.4
(<i>R,R</i>)-PPP2-SNap = 1:10	463.9 ± 94.7
(<i>R,R</i>)-PPP2-SNap = 1:10 after annealing treatment	281.7 ± 116.7

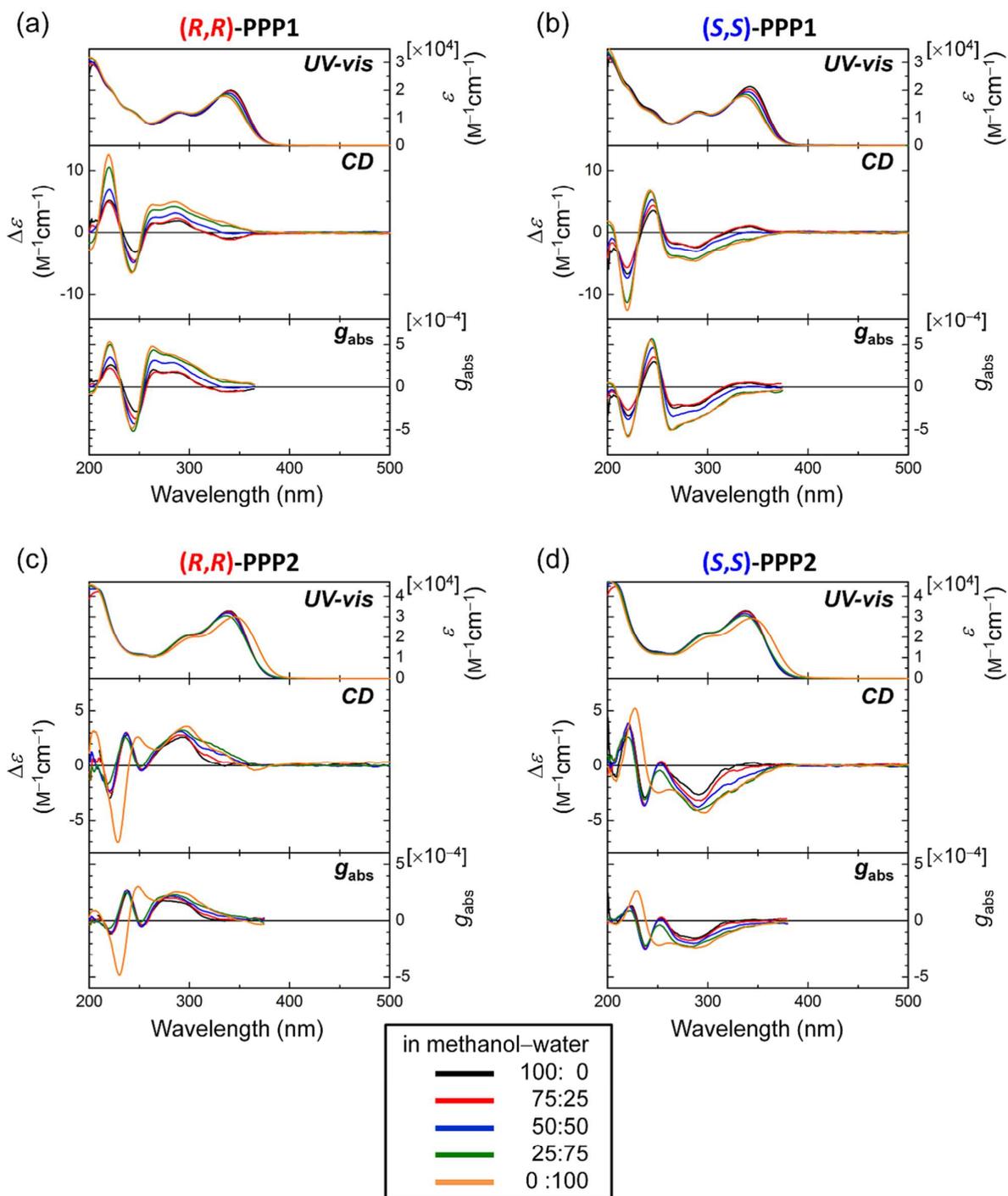


Figure S1. [Solvent dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (a) (R,R) -PPP1, (b) (S,S) -PPP1, (c) (R,R) -PPP2, and (d) (S,S) -PPP2 in methanol, water, and the mixtures ($c = 5.0 \times 10^{-5}$ M).

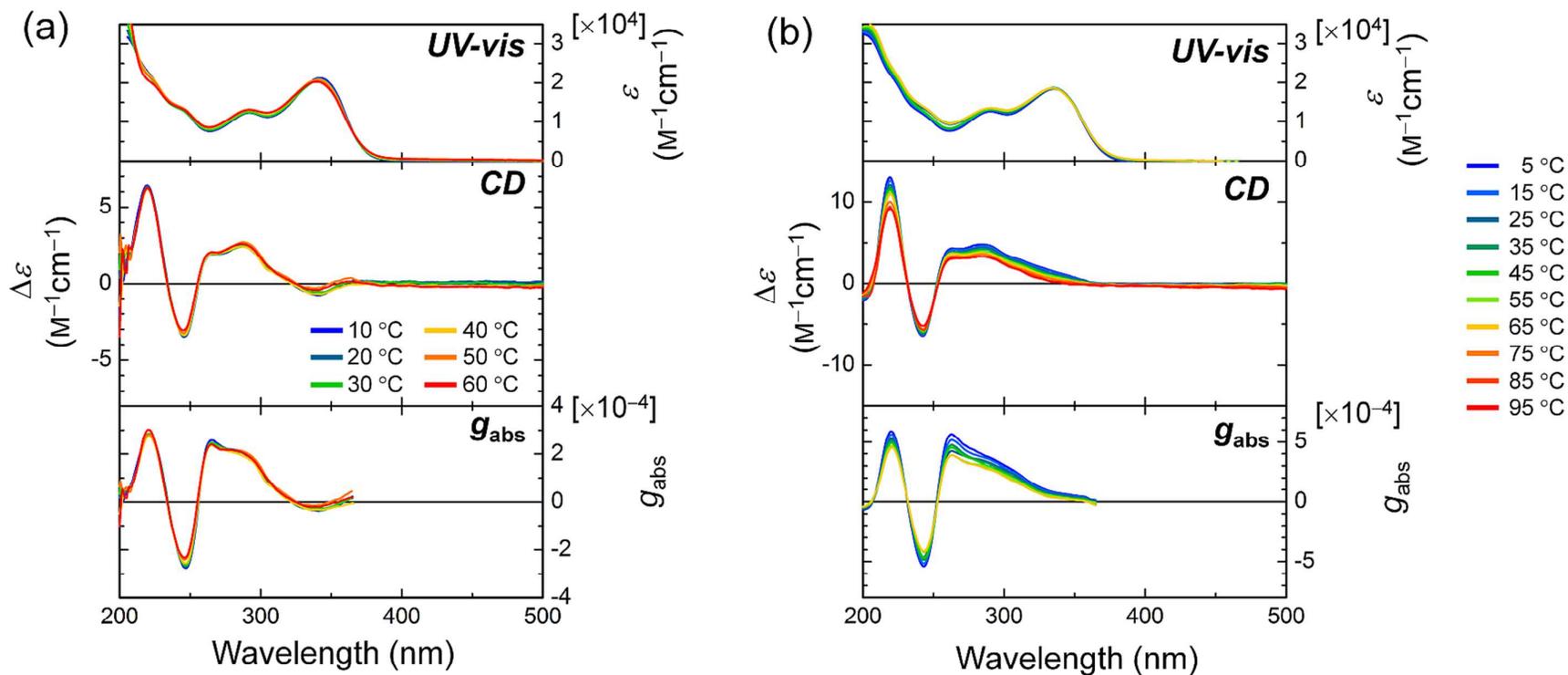


Figure S2. [Temperature dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of *(R,R)*-PPP1 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

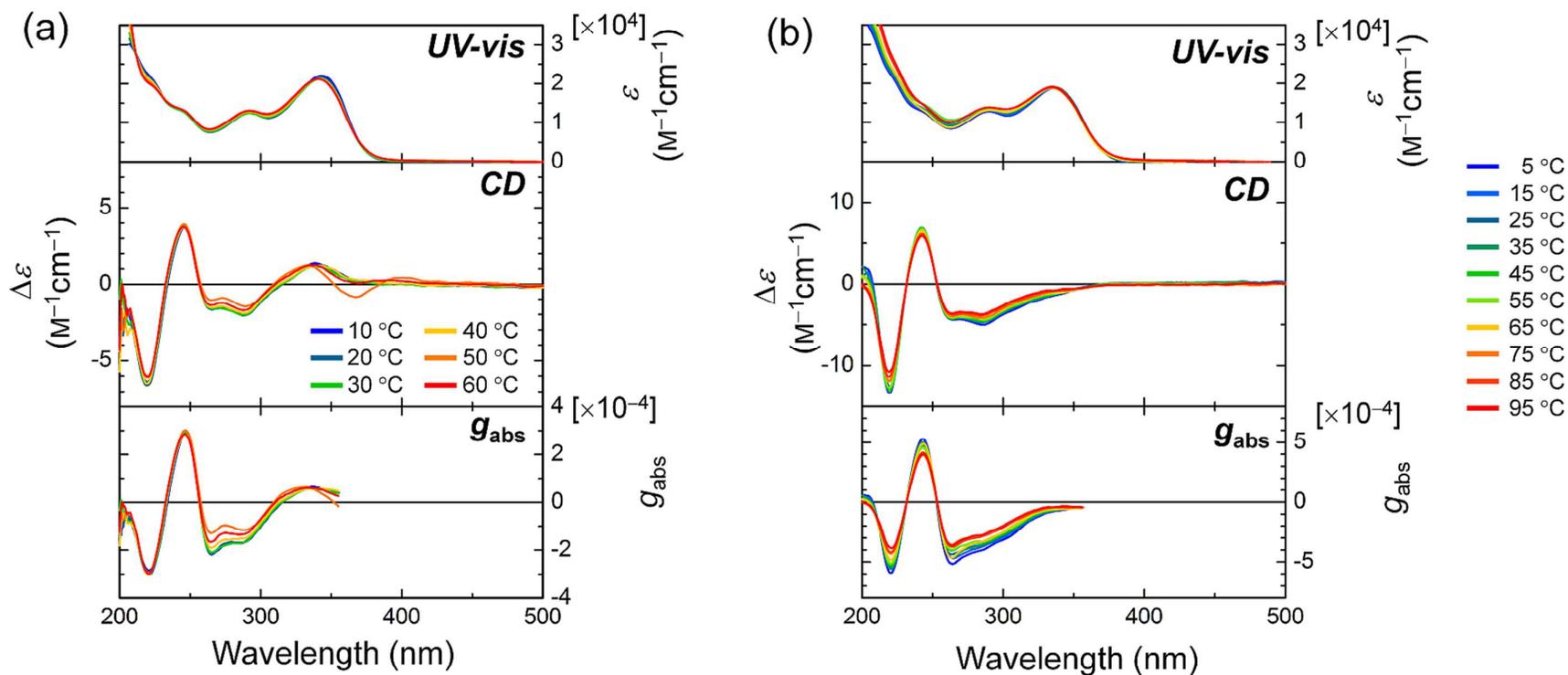


Figure S3. [Temperature dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (S,S)-PPP1 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

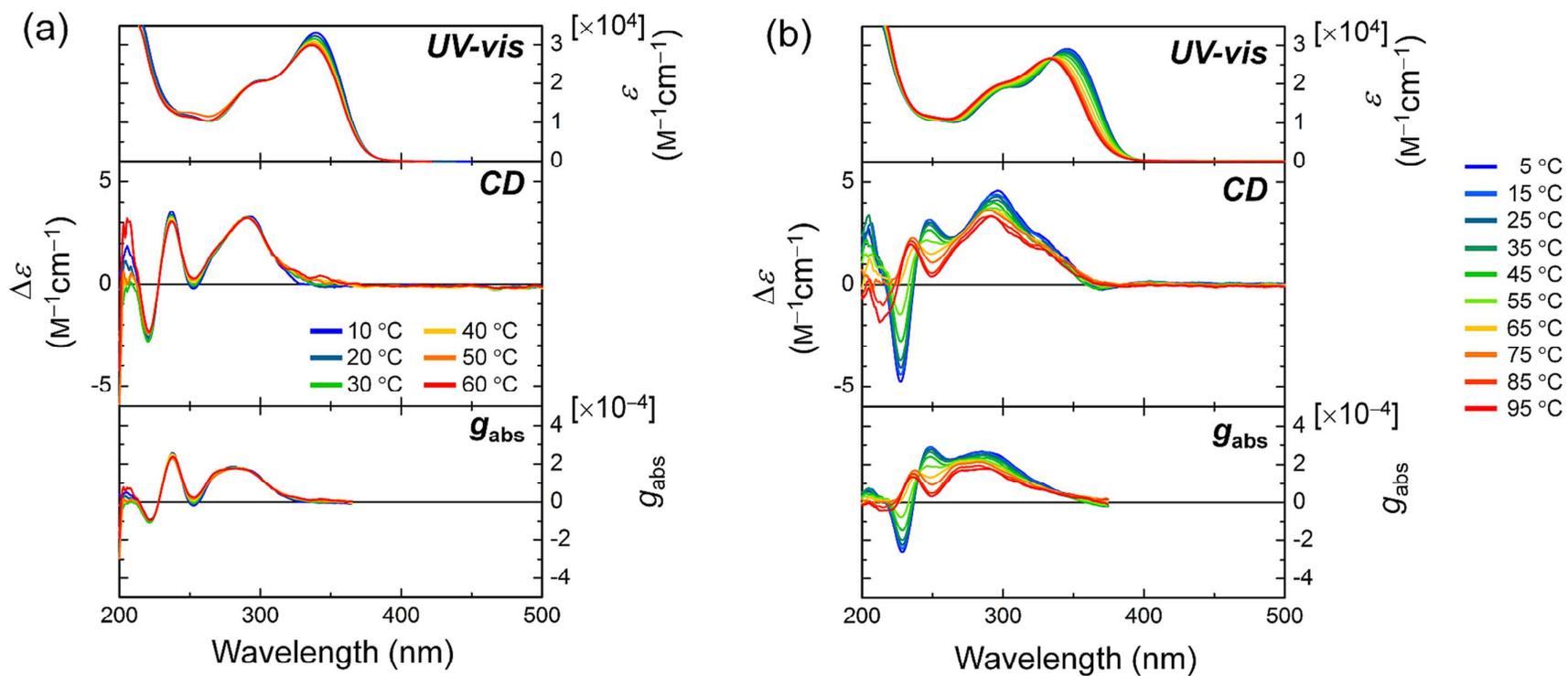


Figure S4. [Temperature dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of *(R,R)*-PPP2 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

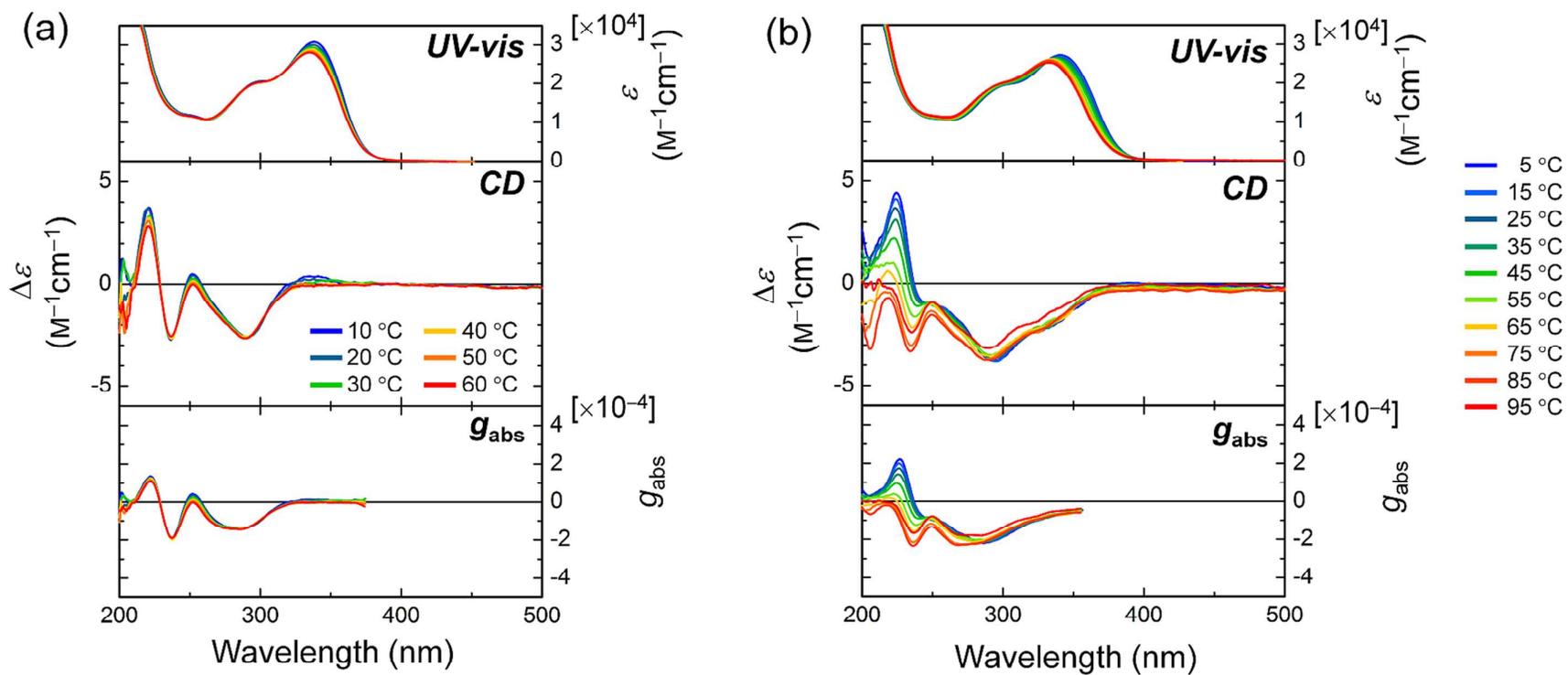


Figure S5. [Temperature dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (*S,S*)-PPP2 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

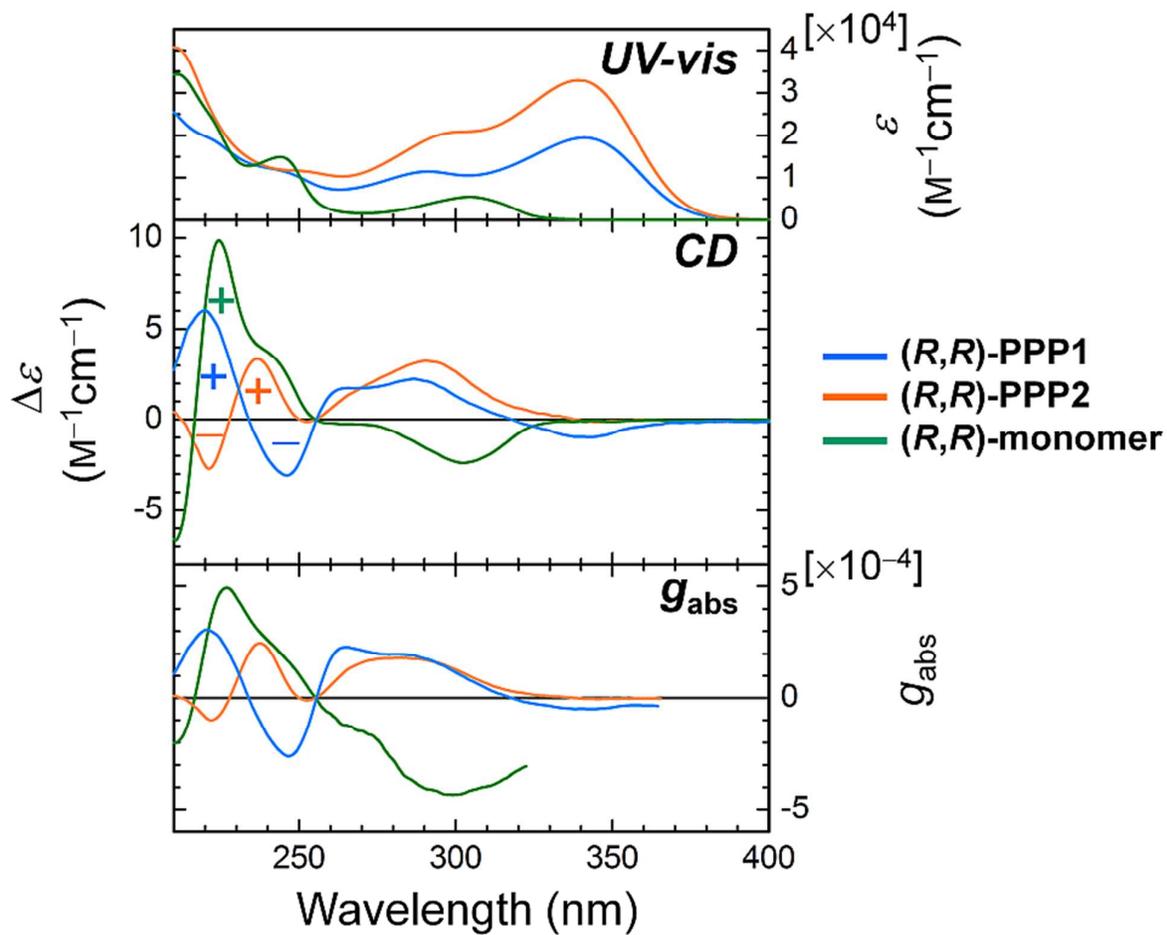


Figure S6. UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (R,R) -PPP1, (R,R) -PPP2, and (R,R) -monomer [(R,R) -6] in methanol [$c = 5.0 \times 10^{-5}$ M for (R,R) -PPP1, 5.1×10^{-5} M for (R,R) -PPP2, and 3.9×10^{-5} M for (R,R) -6].

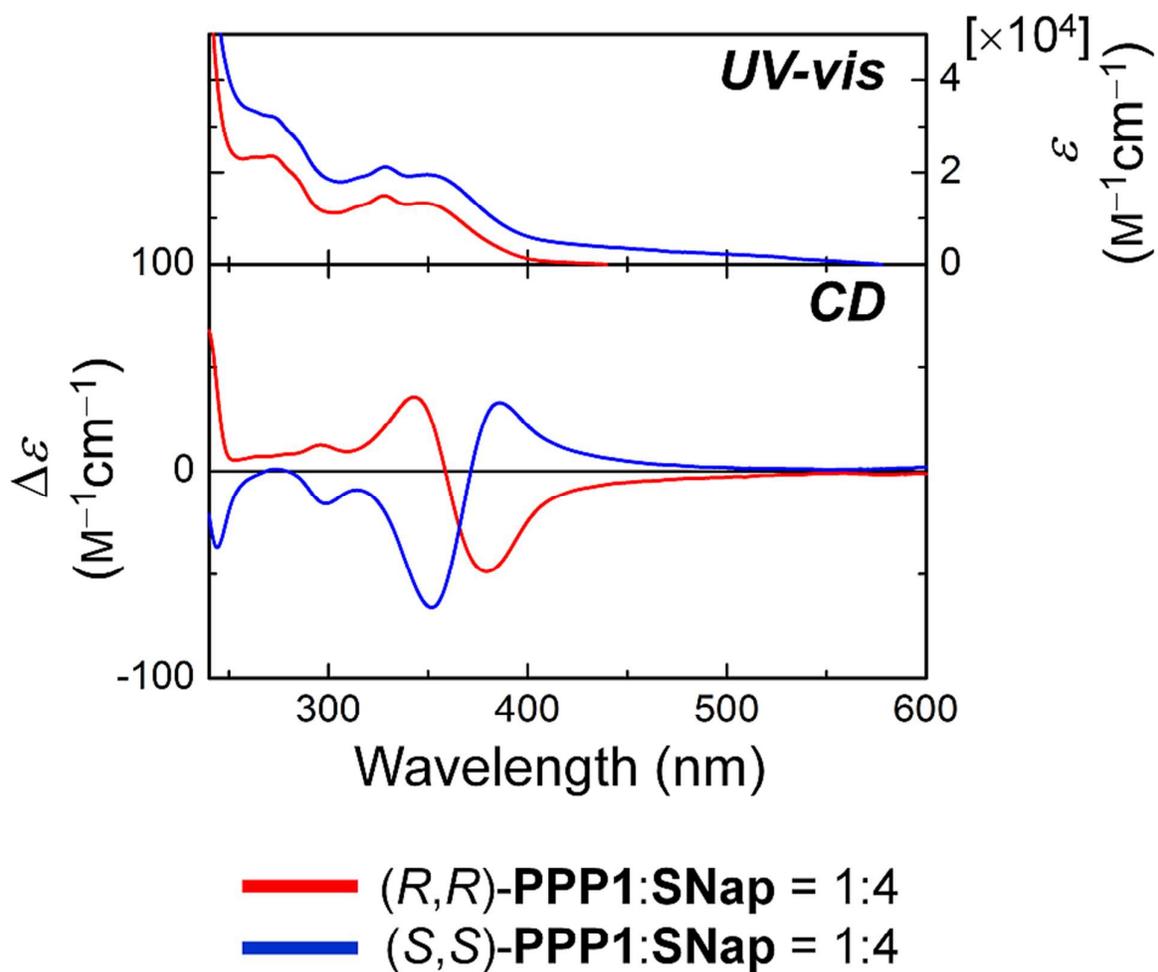


Figure S7. UV–vis absorption (upper) and CD spectra (lower) of the mixtures of **PPP1** and **SNap** (1:4 mol/mol) in water. The concentration of **PPP1** in the mixtures is kept constant at 2.0×10^{-5} M.

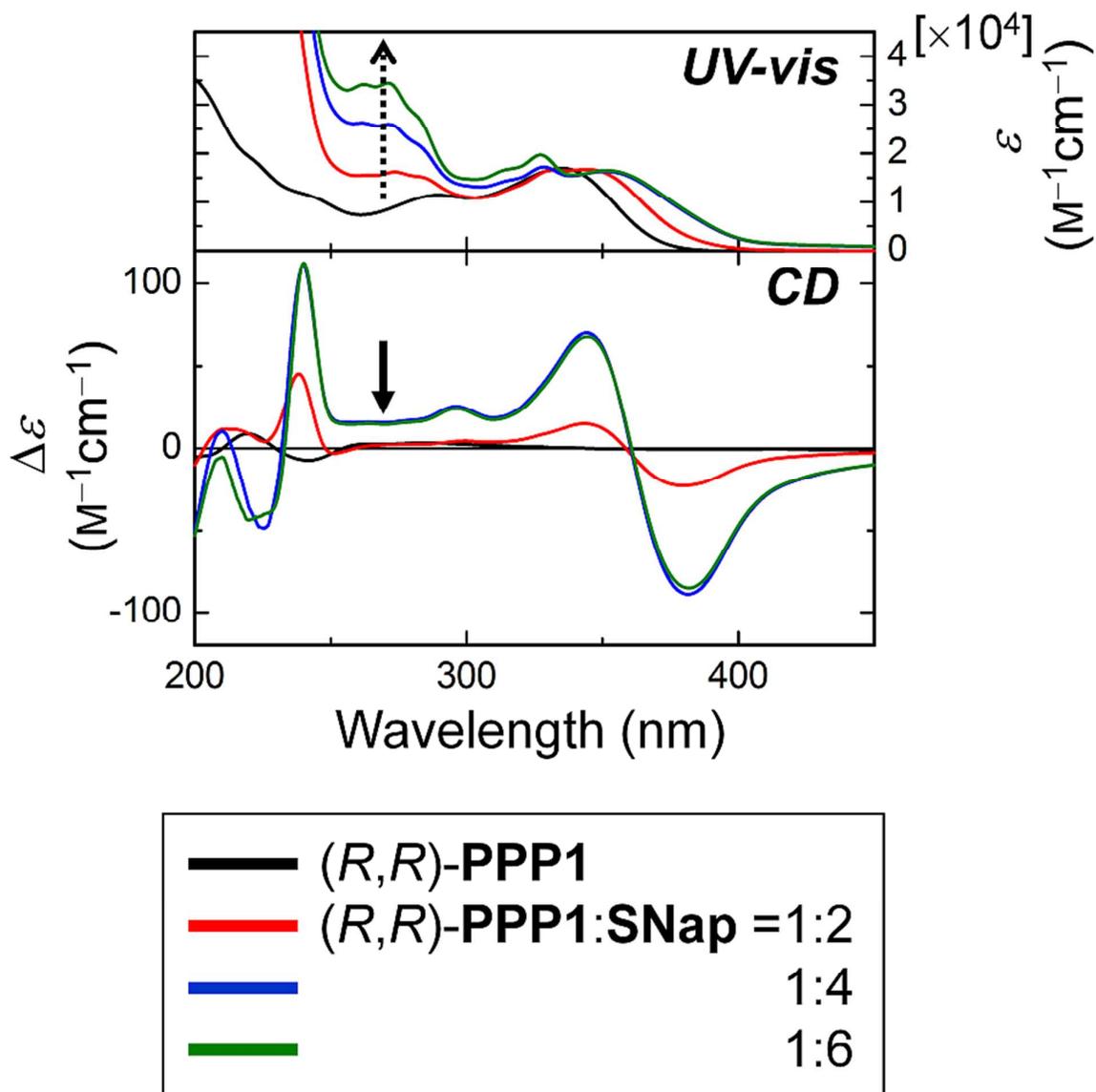


Figure S8. UV-vis absorption (upper) and CD spectra (lower) of the mixtures of *(R,R)*-PPP1 and SNap in water. The concentration of *(R,R)*-PPP1 in the mixtures is kept constant at 2.0×10^{-5} M. In UV-vis spectra, the absorption band of SNap at 270 nm increased in intensity with increasing SNap (expressed by dashed arrow), but no notable change was observed in CD spectra (solid arrow).

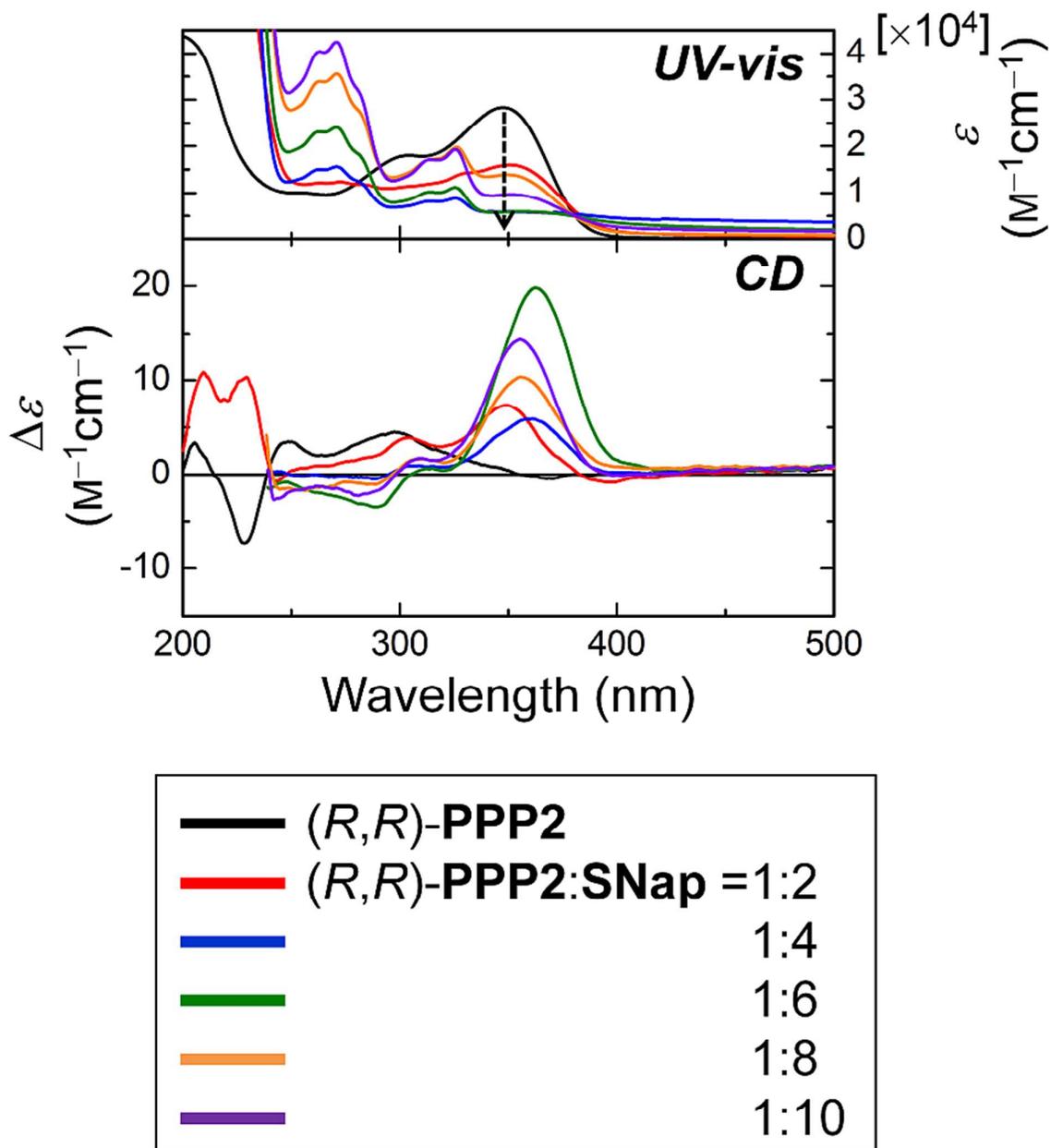


Figure S10. UV–vis absorption and CD spectra of the mixtures of *(R,R)*-PPP2 and SNap in water. Absorbance of PPP2 irregularly decreases in intensity with adding SNap (expressed by dashed arrow), which results from the precipitate of the polymer. The initial concentration of *(R,R)*-PPP2 is kept constant at 2.0×10^{-5} M.