Supporting Information for

Chirality induction in metal-induced achiral polythiophene aggregates assisted by optically active amines and polythiophene†

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1. Experimental Procedures

1-1. Instruments

The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The NMR spectra were obtained using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C using tetramethylsilane (TMS) or the solvent residual peaks as the internal standards. The DOSY experiments were carried out by using pulsed field gradient with the BPPSTE pulse sequence.[1] The hydrodynamic diameters (d_h) were calculated from the diffusion constants (D) obtained by DOSY measurements according to the Einstein-Stokes equation, $d_h = k_B T/3\pi\eta_0 D$ (k_B: Boltzmann constant; T: absolute temperature; η_0: solvent viscosity; D: diffusion constant). The electron spray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-T100CS spectrometer (Akishima, Japan). The absorption and CD spectra were measured in a 2- or 5-mm 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 (–5 to 55 °C). The elemental analyses were performed by the Analytical Laboratory in the Graduate School of Bioagricultural Sciences, Nagoya University. The size exclusion chromatography (SEC) was performed with a JASCO PU-980 liquid chromatograph equipped with a JASCO DG-980-50 degasser and a UV-visible detector (254 nm; JASCO UV-970) at 40 °C. An SEC column (Tosoh TSK-GEL Multipore H_{XL}-M: 30 x 0.78 cm (i.d.): pore size, 0.01–0.6 μm; bead size, 5 μm) was connected, and $CHCl_3$ was used as eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh).

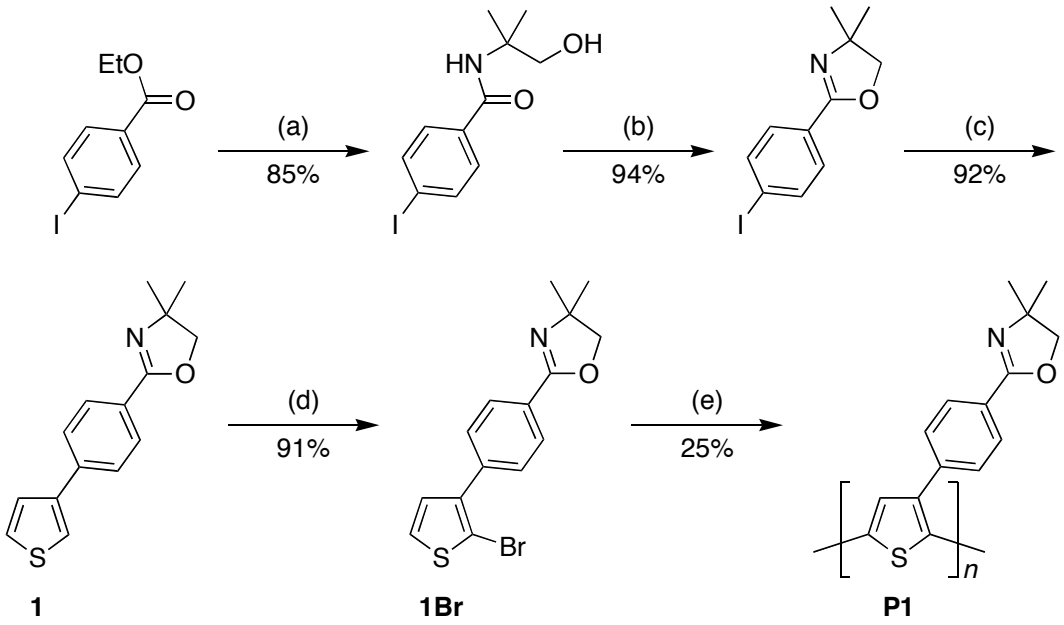
1-2. Materials

All starting materials and dehydrated solvents were purchased from Sigma-Aldrich (St. Louis, Missouri, USA), Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Triethylamine was distilled over CaH_2 under Ar after being stirred with KOH pellets overnight. The deuterium solvents were purchased from Merck (Darmstadt, Germany) or Cambridge Isotope Laboratories (Andover, Massachusetts, USA) and degassed with Ar and used throughout all the experiments. Silica gel (SiO_2) for the flash chromatography was purchased from Merck. An optically active regioregular polythiophene, poly[3-[4-((*R*)-4-ethyl-2-oxazolin-2-yl)phenyl]thiophene] (PEOPT) (M_n = 5.3 x 10^3, DP_n = 21, M_w/M_n = 1.25),[2] and achiral regioregular poly(3-hexylthiophene) (PHT) (M_n = 8.2 x 10^3, DP_n = 49, M_w/M_n = 1.80)[3] were synthesized according to the previously reported methods.

1-3. Synthetic procedures

The polythiophene derivative bearing an achiral oxazoline group (**P1**) was synthesized according to Scheme S1.[2] The reaction progresses were monitored by TLC or ESI-MS.

Scheme S1. Synthesis of regioregular polythiophene (**P1**) bearing an achiral oxazoline group[a]



[a]Reagents and conditions: (a) 2-amino-2-methyl-1-propanol, Me_3Al, toluene, reflux, 2 days; (b) 4-toluenesulfonyl chloride, Et_3N, CH_2Cl_2, rt, 6 days; (c) 3-thiopheneboronic acid, $Pd(PPh_3)_4$, K_3PO_4, toluene, reflux, 2 days; (d) NBS, DMF, rt, 3 days, (e) (i) LDA, THF, -98 °C; (ii) $MgBr_2$•Et_2O, -98 °C, 10 min; (iii) $Ni(dppp)Cl_2$, -98 °C (15 min), -60 °C (1 h), rt (2.5 h), and then reflux (20 h).

2-[*N*-(4-Iodobenzoyl)amino]-2-methyl-1-propanol. To a toluene (100 mL) solution of 2-amino-2-methyl-1-propanol (11.0 mL, 115 mmol) was added dropwise trimethylaluminium in *n*-hexane (1.56 M) (100 mL, 156 mmol) at 0 °C via a cannula within 40 min under nitrogen. The reaction mixture was then allowed to warm to room temperature and further stirred for 1 h. A toluene (150 mL) solution of ethyl 4-iodobenzoate (25.0 g, 90.6 mmol) was added dropwise to the mixture via a dropping funnel within 50 min at that temperature, and the mixture was then refluxed for 2 days. After cooling to room temperature, 20% aqueous solution of Rochelle salt (100 mL) was added. After filtration, the filtrate was dissolved in ethanol and the solvent was removed by evaporation. The crude product was purified by recrystallization with ethanol (10 mL) and *n*-hexane (20 mL) to give the desired product as a slightly yellow needle crystal (24.6 g, 77.1 mmol, 85.1% yield). IR (KBr, cm^{-1}): 3375, 3301, 3081, 2968, 2873, 1639, 1587, 1543, 1331, 1049, 877, 715. ^1H NMR ($CDCl_3$): δ 1.00 (s, CH_3, 6H), 2.33 (s, OH, 1H), 3.70 (s, OCH_2, 2H), 6.22 (s, NH, 1H), 7.48 (d, Ph-H_2, J = 8.4 Hz, 2H), 7.77 (d, Ph-H_3, J = 8.4 Hz, 2H).

2-(4-Iodophenyl)-4,4-dimethyl-2-oxazoline. To a solution of 2-[*N*-(4-iodobenzoyl)amino]-2-methyl-1-propanol (24.5 g, 76.8 mmol) prepared above in CH_2Cl_2 (200 mL) and triethylamine (60 mL, 430 mmol) was added dropwise a CH_2Cl_2 (20 mL) solution of 4-toluenesulfonyl chloride (22.0 g, 116 mmol) at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and further stirred for 6 days. The mixture was then poured into saturated aqueous NH_4Cl (100 mL) and extracted with $CHCl_3$. The extract was washed with water and brine and dried over anhydrous Na_2SO_4. After evaporation, the crude product was purified by SiO_2 chromatography with *n*-hexane/ethyl acetate (9/1, vol/vol) as the eluent to give the desired product as a colorless needle crystal (21.8 g, 72.4 mmol, 94.3% yield). IR (KBr, cm^{-1}): 2956, 2930, 2872, 1645, 1588, 1483, 1460, 1393, 1348, 1332, 1071, 1007, 897, 829, 728. ^1H NMR ($CDCl_3$): δ 0.99 (s, CH_3, 6H), 4.06 (s, OCH_2, 2H), 7.67 (d, Ph-H_2, J = 6.8 Hz, 2H), 7.76 (d, Ph-H_3, J = 6.8 Hz, 2H).

3-[4-(4,4-Dimethyl-2-oxazolin-2-yl)phenyl]thiophene (1). To a mixture of 3-thiopheneboronic acid (10.3 g, 80.5 mmol), tetrakis(triphenylphosphine)palladium(0) (2.53 g, 2.19 mmol), and potassium phosphate (25.4 g, 120 mmol) in toluene (285 mL) was added 2-(4-iodophenyl)-4,4-dimethyl-2-oxazoline (21.3 g, 70.7 mmol) at room temperature under nitrogen. The mixture was refluxed under nitrogen for 2 days. After cooling to room temperature, the mixture was poured into saturated aqueous NH_4Cl (200 mL) and extracted with $CHCl_3$. The extract was washed with water and brine and dried over anhydrous Na_2SO_4. After evaporation, the crude product was purified by SiO_2 chromatography with *n*-hexane/ethyl acetate (9/1, vol/vol) as the eluent to give **1** as a white plate crystal (16.7 g, 64.9 mmol, 91.8% yield). Mp: 123–125 °C. IR (KBr, cm^{-1}): 3102, 2969, 2926, 2896, 1643, 1608, 1357, 1320, 1304, 1185, 1068, 963, 849, 784, 740, 631. ^1H NMR ($CDCl_3$): δ 1.39 (s, CH_3, 6H), 4.11 (s, OCH_2, 2H), 7.39 (dd, Th-H_4, J = 5.0, 3.0 Hz, 2H), 7.42 (dd, Th-H_5, J = 5.0, 1.5 Hz, 2H), 7.52 (dd, Th-H_2, J = 3.0, 1.5 Hz, 2H), 7.62 (d, Ph-H_2, J = 8.5 Hz, 2H), 7.96 (d, Ph-H_3, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.40, 67.56, 79.05, 121.24, 126.09, 126.13, 126.46, 126.62, 128.73, 138.30, 141.41, 161.79. ESI-MS (CH_3OH/CH_2Cl_2 (80/20, vol/vol), positive): Calcd for $C_{15}H_{16}NOS$ [**1**+H]$^+$: m/z = 258.10. Found: m/z = 258.08. Elemental Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44. Found: C, 69.97; H, 5.92; N, 5.29.

2-Bromo-3-[4-(4,4-dimethyl-2-oxazolin-2-yl)phenyl]thiophene (1Br). *N*-Bromosuccinimide (11.7 g, 65.7 mmol) was added to a solution of **1** (16.7 g, 64.9 mmol) in DMF (100 mL) at room temperature, and the mixture was stirred for 3 days under shielded light. After the solvent was evaporated under reduced pressure, the mixture was poured into saturated aqueous NH_4Cl (100 mL) and extracted with diethyl ether. The extract was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation, and the crude product was purified by SiO_2 chromatography with *n*-hexane/ethyl

acetate (10/1, vol/vol) as the eluent to give **1Br** as a slightly yellow solid (19.9 g, 59.2 mmol, 91.2% yield). Mp: 56–57 °C. IR (KBr, cm^{-1}): 3106, 2966, 2926, 2891, 1648, 1612, 1352, 1315, 1301, 1184, 1061, 1018, 988, 967, 876, 849, 717, 688. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, CH_3, 6H), 4.12 (s, OCH_2, 2H), 7.04 (d, Th-H_4, J = 5.5 Hz, 2H), 7.31 (d, Ph-H_5, J = 5.5 Hz, 2H), 7.59 (d, Ph-H_2, J = 8.5 Hz, 2H), 8.00 (d, Ph-H_3, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 28.38, 67.60, 79.14, 109.27, 126.13, 127.15, 128.25, 128.48, 128.88, 137.73, 140.36, 161.76. ESI-MS (CH_3OH/CH_2Cl_2 (80/20, vol/vol), positive): Calcd for $C_{15}H_{15}BrNOS$ [**1Br**+H]$^+$: m/z = 338.00. Found: m/z = 337.99. Elemental Anal. Calcd for $C_{15}H_{14}BrNOS$: C, 53.58; H, 4.20; N, 4.17. Found: C, 53.64; H, 4.29; N, 4.04.

Poly[3-[4-(4,4-dimethyl-2-oxazolin-2-yl)phenyl]thiophene] (P1). Polymerization of **1Br** was carried out according to the reported method.[2,3] **1Br** (2.00 g, 5.95 mmol) and $MgBr_2$•Et_2O (1.84 g, 7.14 mmol) weighed under nitrogen were placed in a two-necked flask equipped with a magnetic stirrer bar and a three-way stopcock under dry nitrogen, and THF (38 mL) was then added by a syringe. The mixture was cooled to -98 °C, and to this suspension solution was added lithium diisopropylamide solution (6.8 mmol based on *n*-BuLi) in THF (12 mL) via a cannula under dry nitrogen -98 °C. After stirring for 10 min at that temperature, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl_2) (32 mg, 68 μmol) was added, and the mixture was allowed to warm to -60 °C over 15 min. After the further addition of Ni(dppp)Cl_2 (32 mg, 68 μmol), the mixture was gradually allowed to warm to room temperature, whereupon the solution became clear within 1 h. Ni(dppp)Cl_2 (32 mg, 68 μmol) was added to the mixture at room temperature. After stirring for 2.5 h, the solution was refluxed under stirring for 20 h, giving the purple suspension. After cooling to room temperature, the solvent was removed by evaporation and the dark purple suspension was poured into a large amount of CH_3OH. The purple precipitate was collected by centrifugation, washed with CH_3OH and THF, and dried *in vacuo* at room temperature overnight. The polymer was then dissolved in $CHCl_3$ and the solution was washed with saturated aqueous EDTA and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the polymer was again dissolved in $CHCl_3$ and the solution was poured in a large amount of *n*-hexane. The precipitate was collected by centrifugation and dried *in vacuo* at room temperature overnight to afford **P1** as a dark purple powder (0.37 g, 1.46 mmol, 24.5% yield). M_n = 5.8 x 10^3, DP_n = 23, M_w/M_n = 1.27. IR (KBr, cm^{-1}): 3063, 2964, 2927, 2893, 1650, 1609, 1352, 1314, 1300, 1189, 1063, 1018, 967, 830, 689. ^{1}H NMR ($CDCl_3$): δ 1.32–1.44 (br, CH_3, 6H), 4.04–4.18 (br, OCH_2, 2H), 6.85–6.93 (br, Th-H_4, 1H), 7.31–7.57 (d, Ph-H_2, 2H), 7.86–8.01 (d, Ph-H_3, 2H). ^{13}C NMR ($CDCl_3$): δ 28.39, 67.59, 79.10, 127.37, 128.42, 129.15, 129.89, 131.55, 134.08, 138.21, 138.60, 161.77. Elemental Anal. Calcd for $(C_{15}H_{13}NOS•0.3H_2O)_n$: C, 69.10; H, 5.26; N, 5.37. Found: C, 69.00; H, 5.23; N, 5.12.

1-4. Measurements

Absorption and CD measurements of P1 in the presence of various chiral amines and metal salts. A typical experimental procedure is described below. Stock solutions of **P1** (2.6 mg/5 mL, 2 mM) and (1*R*,2*S*)-1-amino-2-indanol [(1*R*,2*S*)-**2**] (3.0 mg/5 mL, 4 mM) in $CHCl_3$ and silver trifluoromethanesulfonate (AgOTf) (10.3 mg/1 mL, 40 mM) in CH_3CN were prepared in a dry box (NX1-M00320, Vacuum Atmosphere Company, Hawthorne, USA) under an argon atmosphere. The stock solutions of **P1** (400 μL) and (1*R*,2*S*)-**2** (200 μL) were transferred to a 0.2-cm quartz cell with a stopcock using Hamilton microsyringes. To this was added $CHCl_3$ (180 μL) and the stock solution of AgOTf (20 μL) subsequently. After the mixture was allowed to stand for 30 min, the absorption and CD spectra were recorded. In a similar manner, the absorption and CD spectra of **P1** in the presence of other chiral amines and metal salts were performed.

^{1}H NMR and DOSY measurements of P1 in the presence of (1*R*,2*S*)-2 and AgOTf. Stock solutions of **P1** (3.4 mg/3 mL, 4.4 mM) and (1*R*,2*S*)-**2** (2.0 mg/3 mL, 4.4 mM) in $CDCl_3$, and AgOTf (10.3 mg/1 mL, 40 mM) in CD_3CN were prepared in a dry box under an argon atmosphere. The stock solutions of **P1** (270 μL), (1*R*,2*S*)-**2** (270 μL), and AgOTf (30 μL) were transferred to a 5-mm NMR tube using microsyringes. After the mixture was allowed to stand for 30 min, the ^{1}H NMR and DOSY measurements were performed.

Absorption and CD titrations of P1 with AgOTf–(1*R*,2*S*)-2 mixture. Stock solutions solution of **P1** (2.7 mg/10 mL, 1.05 mM) and (1*R*,2*S*)-**2** (11.9 mg/1 mL, 80 mM) in $CHCl_3$ and AgOTf (20.6 mg/1 mL, 80 mM) in CH_3CN were prepared in a dry box under an argon atmosphere. The stock solutions of (1*R*,2*S*)-**2** (500 μL) and AgOTf (500 μL) were mixed in a vessel equipped with a stopcock using microsyringes to prepare a 1:1 mixture solution of AgOTf and (1*R*,2*S*)-**2**. The stock solution of **P1** (760 μL) was transferred to a 0.2-mm quartz cell, and its initial absorption spectrum was recorded. To this was added increasing volumes of the AgOTf–(1*R*,2*S*)-**2** solution (0–40 μL, 0–2 equiv.), and their absorption and CD spectra were recorded for each addition after the mixtures had been allowed to stand for 30 min.

Absorption and CD measurements of P1–PEOPT mixtures in the presence of metal salts. A typical experimental procedure is described below. Stock solutions of **P1** (2.6 mg/50 mL, 0.20 mM) and PEOPT (2.6 mg/50 mL, 0.20 mM) in $CHCl_3$ and copper(II) trifluoromethanesulfonate ($Cu(OTf)_2$) (14.5 mg/2 mL, 20 mM) in CH_3CN were prepared in a dry box under an argon atmosphere. The stock solutions of **P1** (0–2 mL) and PEOPT (0–2 mL) were transferred to a 0.5-cm quartz cell with a stopcock using Hamilton microsyringes, keeping the total volume to be 2 mL. To this was added the stock solution of $Cu(OTf)_2$ (20 μL). After the mixtures were allowed to stand for 3 h, the absorption and CD spectra were

recorded (Fig. 2a). In a similar manner, the absorption and CD spectra of **P1**–PEOPT mixtures in the presence of other metal salts were performed.

Absorption and CD measurements of PHT–PEOPT mixtures in poor solvents. A typical experimental procedure is described below. Stock solutions of PHT (1.7 mg/10 mL, 1.0 mM) and PEOPT (2.6 mg/10 mL, 1.0 mM) in $CHCl_3$ were prepared. The stock solutions of PHT (0–0.4 mL) and PEOPT (0–0.4 mL) were transferred to a 0.5-cm quartz cell with a stopcock using Hamilton microsyringes, keeping the total volume to be 0.4 mL. To this was added CH_3CN (1.6 mL). After the mixtures were allowed to stand for 15 min, the absorption and CD spectra were recorded (Fig. S8). In a similar manner, the absorption and CD spectra of PHT–PEOPT mixtures in $CHCl_3$/CH_3OH (20/80, vol/vol) were performed.

Molecular Modeling and Calculations. Molecular modeling and molecular mechanics calculations were performed using the Dreiding Force Field as implemented in the Materials Studio software (version 3.0; Accerlys Inc.). The polymer model (20 repeating monomer units) of **P1** was constructed with Polymer Builder in the Materials Studio. Charges on the atoms of **P1** were calculated by using the charge equilibration (QEq) in the Materials Studio; the total charge of the molecule was set to zero. The starting main-chain conformation of a polymer model was defined as a rotational conformation of a single bond between neighboring thiophene rings. The initial dihedral angles of a single bond from planarity were set to 120 (*s-trans*) and 20° (*s-cis*) to give polymer models with a twisted helical conformation. The energy minimization was accomplished by the conjugate gradient method and further continued until the root-mean-square (rms) value became less than 0.1 kcal mol^{-1} $Å^{-1}$.

2. Chiral aggregate formation of P1 with chiral metal complexes

2-1. Absorption titration of P1 with Ag(I)

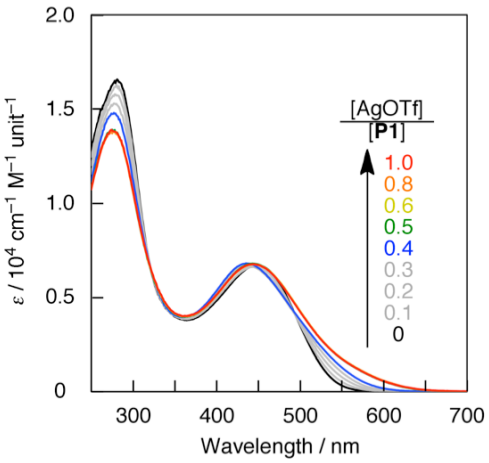


Fig. S1. Absorption spectral changes of **P1** in $CHCl_3$ upon the addition of AgOTf in CH_3CN ($CHCl_3/CH_3CN$ = 100/0 to 97.5/2.5, vol/vol) at 25 °C; [**P1**] = 1 mM unit^{-1}, [AgOTf]/[**P1**] = 0–1. The spectra were measured after the mixtures had been allowed to stand for 30 min at rt.

2-2. Time dependent CD intensity changes of P1 with chiral Ag(I) complex

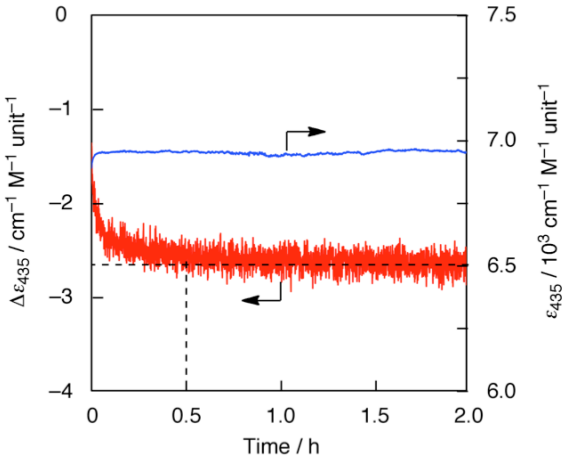


Fig. S2. Time dependent changes of the molar circular dichroism ($\Delta\varepsilon_{435}$) and molar absorptivity (ε_{435}) at 435 nm of **P1** upon the addition of AgOTf–(1*R*,2*S*)-**2** complex in $CHCl_3/CH_3CN$ (97.5/2.5, vol/vol) at 25 °C; [**P1**] = 1 mM unit^{-1}, [**P1**]:[AgOTf]:[(1*R*,2*S*)-**2**] = 1:1:1.

2-3. CD and absorption titrations of P1 with chiral Ag(I) complex

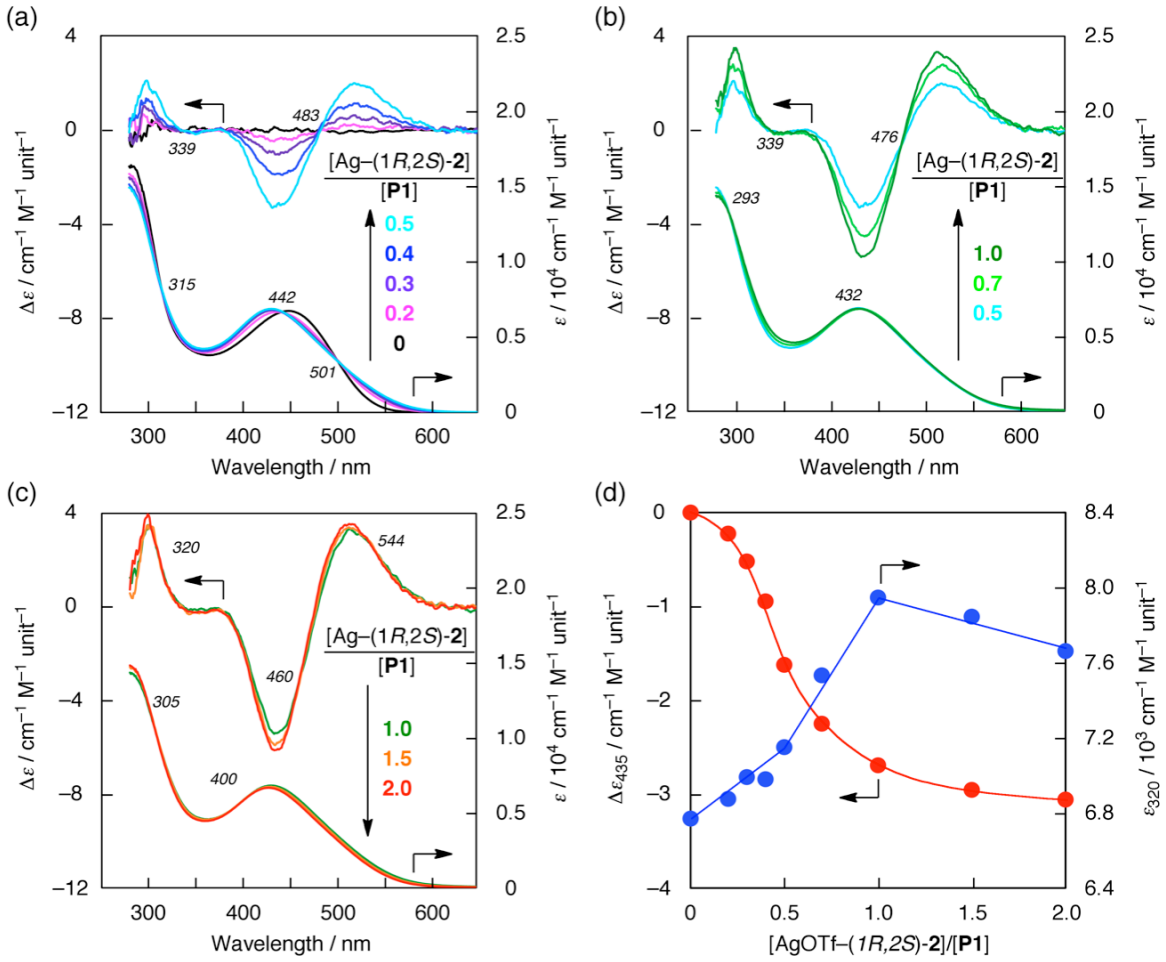


Fig. S3. CD and absorption spectra of **P1** in the presence of AgOTf–(1*R*,2*S*)-**2** complex in $CHCl_3/CH_3CN$ (97.5/2.5, vol/vol) at 25 °C; [**P1**] = 1 mM unit^{-1}, [AgOTf–(1*R*,2*S*)-**2**]/[**P1**] = 0–0.5 (a), 0.5–1 (b), and 1–2 (c). These spectra were measured after the mixtures had been allowed to stand for 30 min at rt. (d) Plots of the molar circular dichroism at 435 nm ($\Delta\varepsilon_{435}$) and the molar absorptivities at 320 nm (ε_{320}) of **P1** upon the addition of AgOTf–(1*R*,2*S*)-**2** complex.

2-4. ^{1}H NMR spectra of P1 with chiral Ag(I) complexes

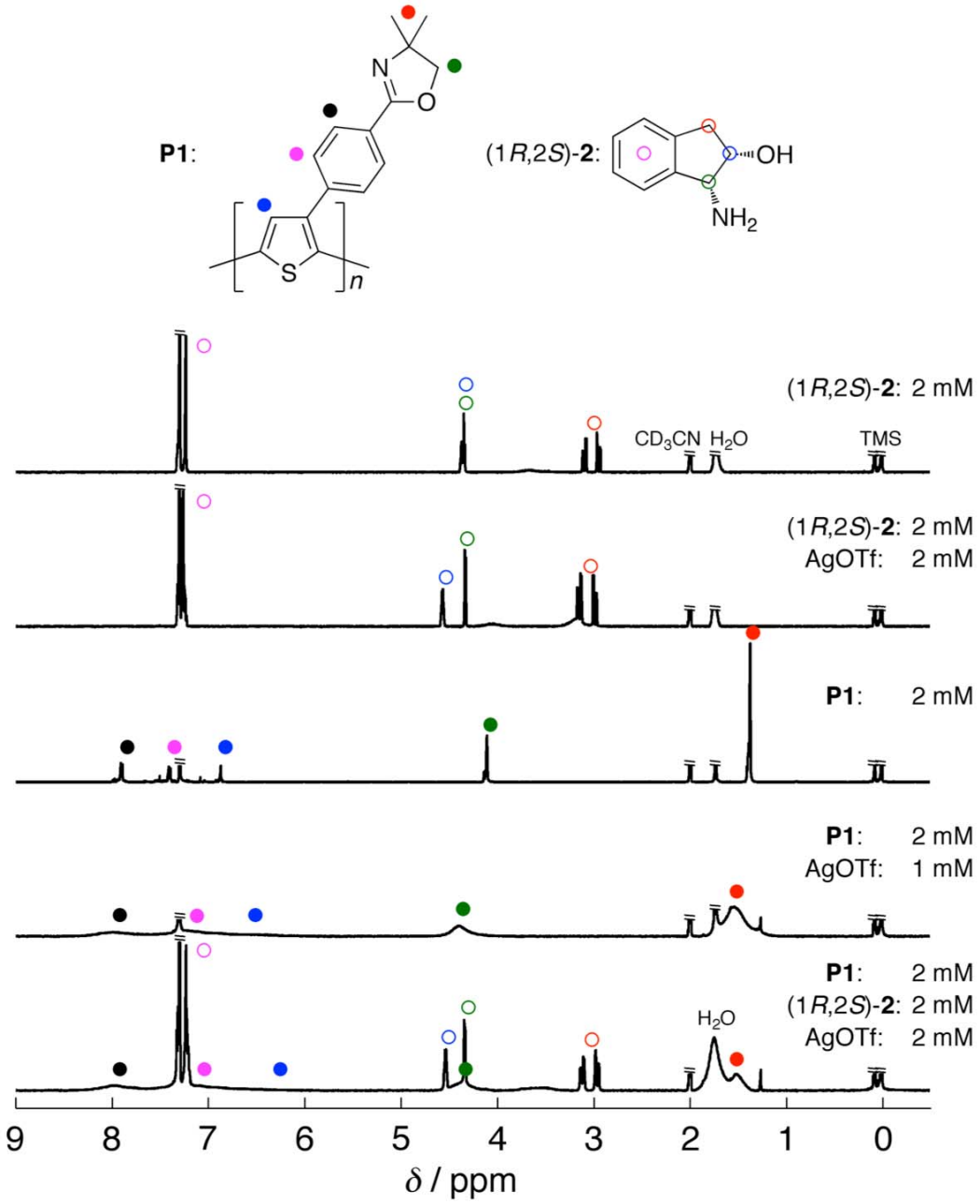


Fig. S4. ^{1}H NMR spectra of **P1**, (1*R*,2*S*)-**2**, and their complexes in $CDCl_3/CD_3CN$ (10/1, vol/vol) at 25 °C; [**P1**] = 2 mM unit^{-1}.

2-5. DOSY measurements

Table S1. Diffusion coefficients (*D*) of **P1**, (1*R*,2*S*)-**2**, and their AgOTf complexes[a]

		D / 10^{-10} m^2 s^{-1}		
sample	conc. / mM	**P1**	(1*R*,2*S*)-**2**	TMS[b]
P1	2	5.25		21.5
(1*R*,2*S*)-**2**	2		13.8	20.2
P1/Ag[c]	2/1	2.09		19.3
Ag/(1*R*,2*S*)-**2**	1/2		9.09	21.0
P1/Ag/(1*R*,2*S*)-**2**	2/2/2	2.50	7.43	19.4

[a]Measured in $CDCl_3/CD_3CN$ (10/1, vol/vol) at 25 °C. [b]TMS was used as the internal standard. [c]After the measurement (*ca*. 4 h), a small amount of an orange-red precipitate derived from the **P1**–AgOTf complex was observed in the NMR tube.

2-6. Temperature effect

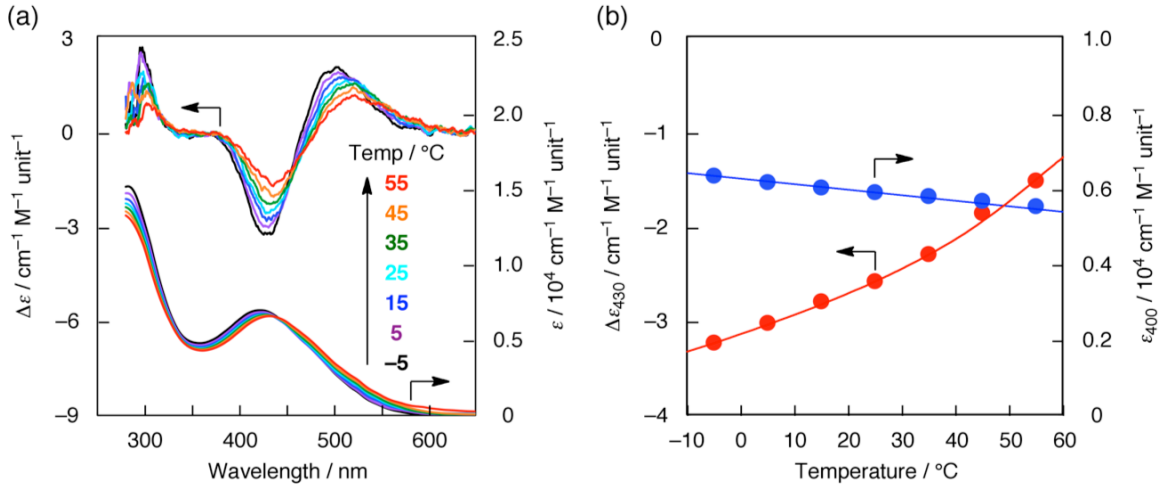


Fig. S5. (a) Temperature dependent absorption and CD spectral changes of **P1**–AgOTf–(1*R*,2*S*)-**2** complex. (b) Plots of the molar circular dichroism at 430 nm ($\Delta\varepsilon_{430}$) and molar absorptivity at 400 nm (ε_{400}) of **P1**–AgOTf–(1*R*,2*S*)-**2** complex in $CHCl_3/CH_3CN$ (97.5/2.5, vol/vol); [**P1**] = 1 mM unit^{-1}, [**P1**]:[AgOTf]:[(1*R*,2*S*)-**2**] = 1:1:1. These spectra were measured after the mixtures had been allowed to stand for 30 min at rt.

2-7. Effect of chiral amines

Table S2. Molar circular dichroisms ($\Delta\varepsilon_{max}$) and molar absorptivities (ε_{max}) of **P1** in the presence of AgOTf–chiral amine complexes[a]

		CD spectra (2nd Cotton)			absorption spectra	
			$\Delta\varepsilon$	λ	ε x 10^{-3}	λ
amine	configuration[b]	sign	/ cm^{-1} M^{-1} $unit^{-1}$	/ nm	/ cm^{-1} M^{-1} $unit^{-1}$	/ nm
none					6.98	449
(1*S*,2*R*)-**2**	*S*	+	2.66	438	6.98	432
(1*R*,2*S*)-**2**	*R*	–	2.71	434	6.83	430
(1*R*,2*S*)-**3**	*S*	+	2.28	441	7.09	441
(1*R*,2*S*)-**4**	*S*	+	1.94	444	6.90	443
(*S*)-**5**	*S*	+	0.72	453	7.19	436
(*S*)-**6**	*S*	–	0.91	438	7.07	441
(1*R*,2*S*)-**7**	*S*	+	0.62	435	6.92	448

[a]Solvent: $CHCl_3$:CH_3CN = 97.5:2.5; temp: 25 °C; cell length: 2 mm; [**P1**] = 1 mM $unit^{-1}$ [**P1**]:[AgOTf]:[chiral amine] = 1:1:1. The spectra were measured after the mixtures had been allowed to stand for 30 min at rt. [b]Absolute configuration of the amino group-bound asymmetric carbon atom.

2-8. Effect of metal salts

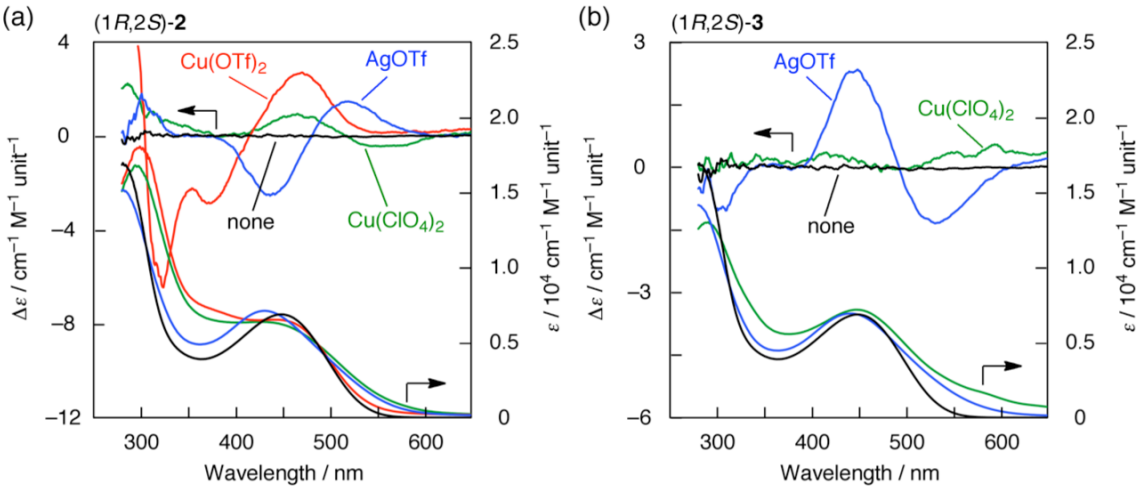


Fig. S6. CD and absorption spectra of **P1** in the presence of metal salt–(1*R*,2*S*)-**2** (a) and –(1*R*,2*S*)-**3** (b) complexes in $CHCl_3/CH_3CN$ (97.5/2.5, vol/vol) at 25 °C; [**P1**] = 1 mM $unit^{-1}$, [**P1**]:[metal salt]:[(1*R*,2*S*)-**2** or (1*R*,2*S*)-**3**] = 1:1:1. These spectra were measured after the mixtures had been allowed to stand for 30 min at rt.

Table S3. Molar circular dichroisms ($\Delta\varepsilon_{max}$) and molar absorptivities (ε_{max}) of **P1** in the presence of metal salt–(1*R*,2*S*)-**2** complexes[a]

	CD spectra			absorption spectra	
		$\Delta\varepsilon$	λ	ε x 10^{-3}	λ
metal salt	sign	/ cm^{-1} M^{-1} $unit^{-1}$	/ nm	/ cm^{-1} M^{-1} $unit^{-1}$	/ nm
$Fe(ClO_4)_2$		n.d.[b]		7.78	438
$Co(ClO_4)_2$		n.d.[b]		7.15	446
$Ni(ClO_4)_2$		n.d.[b]		6.68	448
$Cu(ClO_4)_2$	+	1.06	466	6.37	428
$Cu(OTf)_2$	+	2.89	471	6.52	439
$Zn(OTf)_2$		n.d.[b]		6.62	422
CuOTf		n.d.[b]		6.54	447
AgOTf	–	2.71	434	6.83	430

[a]Solvent: $CHCl_3$:CH_3CN = 97.5:2.5; temp: 25 °C; cell length: 2 mm; [**P1**] = 1 mM $unit^{-1}$, [**P1**]:[metal salt]:[(1*R*,2*S*)-**2**] = 1:1:1. The spectra were measured after the mixtures had been allowed to stand for 30 min at rt. [b]Not detected.

2-9. Chiral Co-aggregate Formation of P1–PEOPT Mixture with Cu(II) and Ag(I)

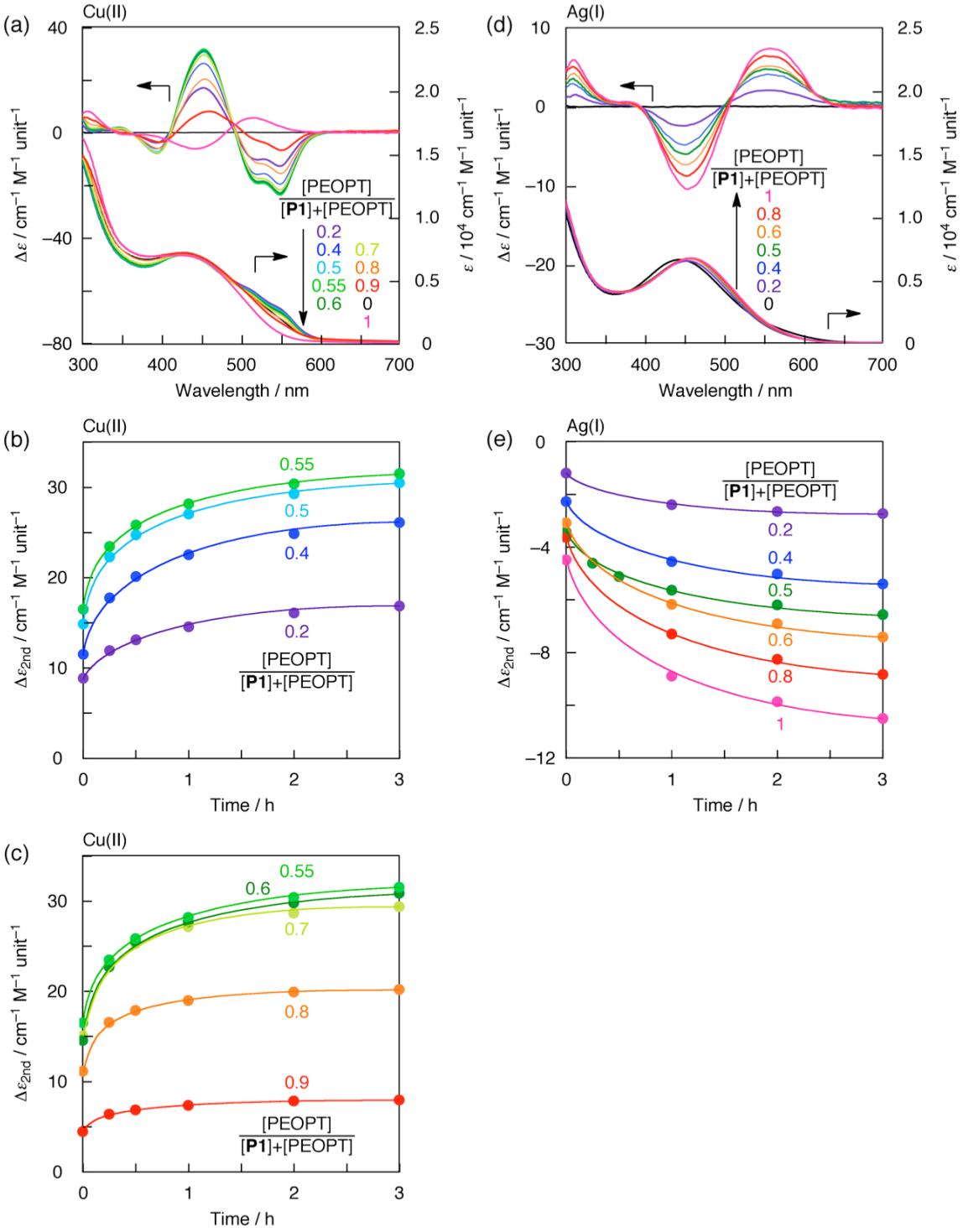


Fig. S7. (a, d) CD and absorption spectra of **P1**–PEOPT mixtures with $Cu(OTf)_2$ (a) and AgOTf (d) in $CHCl_3/CH_3CN$ (99/1, vol/vol) at 25 °C; [**P1**]+[PEOPT] = 0.2 mM unit^{-1}, ([**P1**]+[PEOPT]):[$Cu(OTf)_2$ or AgOTf] = 1:1. These spectra were measured after the mixtures had been allowed to stand for 3 h at rt. (b, c, e) Time-dependent CD intensity changes ($\Delta\varepsilon_{2nd}$) of **P1**–PEOPT mixtures with $Cu(OTf)_2$ (b, c) and AgOTf (e) in $CHCl_3/CH_3CN$ (99/1, vol/vol); [PEOPT]/([**P1**]+[PEOPT]) = 0–0.55 (b), 0.55–1 (c), and 0–1 (e).

2-10. Chiral Co-aggregate Formation of PHT–PEOPT Mixture in Poor Solvent

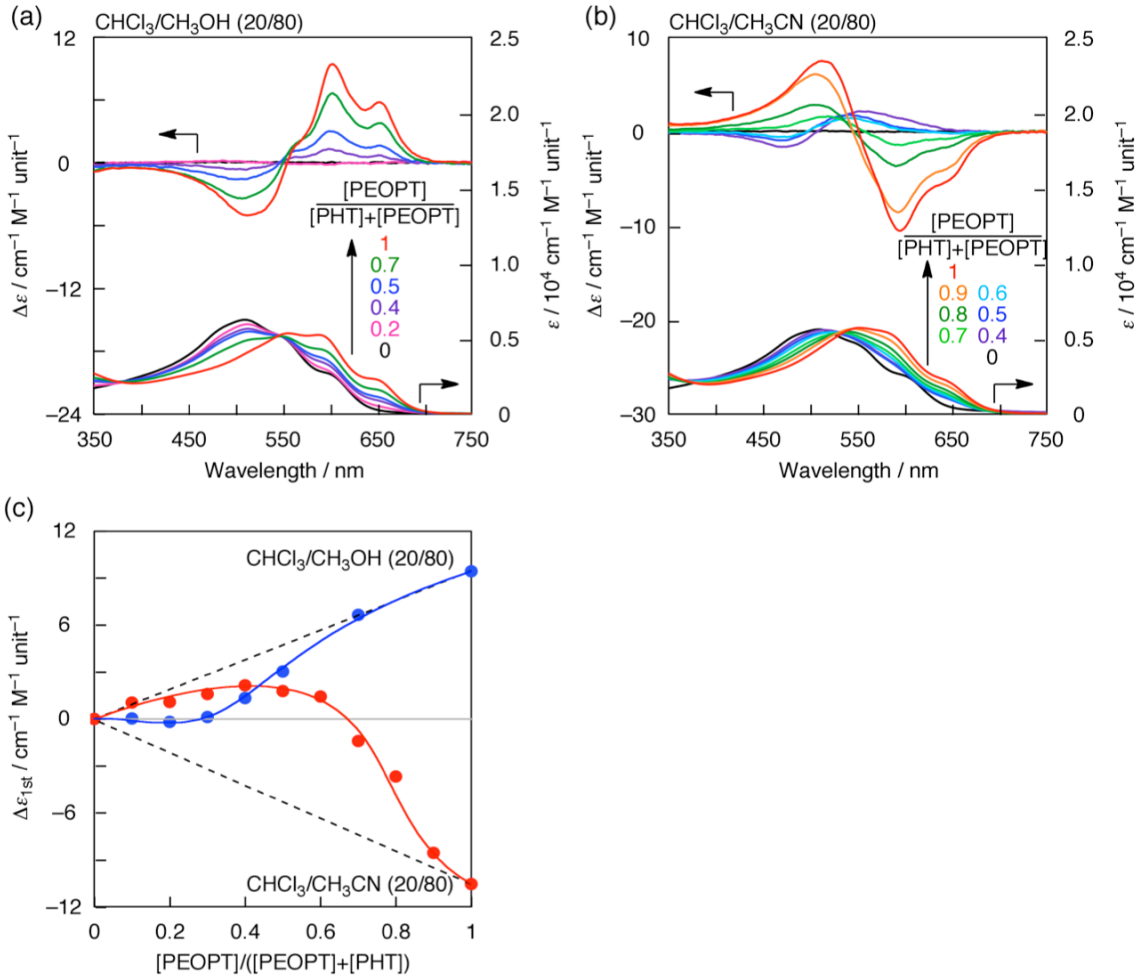


Fig. S8. (a, b) CD and absorption spectra of PHT–PEOPT mixtures in $CHCl_3/CH_3OH$ (20/80, vol/vol) (a) and $CHCl_3/CH_3CN$ (20/80, vol/vol) (b) at 25 °C; [PHT]+[PEOPT] = 0.2 mM unit^{-1}. These spectra were measured after the mixtures had been allowed to stand for 15 min at rt. (c) Plots of the molar circular dichroism (1st Cotton effect) ($\Delta\varepsilon_{1st}$) of PHT–PEOPT mixtures in $CHCl_3/CH_3OH$ (20/80, vol/vol) (blue) and $CHCl_3/CH_3CN$ (20/80, vol/vol) (red) versus PEOPT content; [**P1**]+[PEOPT] = 0.2 mM unit^{-1}. These spectra were measured after the mixtures had been allowed to stand for 15 min at rt.

3. Supporting references

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3. (a) R. D. McCullough, R. D. Lowe, *J. Chem. Soc., Chem. Commun.*, 1992, 70–72.
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   (c) I. Osaka, R. D. McCullough, *Acc. Chem. Res.*, 2008, **41**, 1202–1214.