Electronic Supplementary Information

Chiral optofluidics: Gigantic circularly polarized light enhancement of *all-trans*-poly(9,9-di-*n*-octylfluorene-2,7-vinylene) during mirror-symmetry-breaking aggregation by optically tuning fluidic media

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Experimental section

Instrumentation

The CD/UV-vis spectra of the solutions were recorded simultaneously at 25 °C on JASCO J-725 and J-820 spectropolarimeters equipped with a Peltier-controlled housing unit using a synthetic quartz (SQ)-grade cuvette with a path length of 10 mm (with a scanning rate of 100 nm/min, a bandwidth of 1 nm and a response time of 1 s, using a single accumulation). The UV-vis spectra were measured independently on a JASCO UV-570 UV-vis-NIR and UV-550 UV-vis spectrophotometer at 25 °C (with a scanning rate of 100 nm/min, a bandwidth of 2 nm and a response time of 1 sec). The photoluminescence (PL) spectra were measured on a JASCO FP-6500 spectrofluorometer at 25 °C (with a scanning rate of 50 and 100 nm/min, an excitation bandwidth of 1 and 3 nm, a monitoring bandwidth of 1 and 3 nm, a response time of 1 sec and a sampling interval of 0.2 and 0.5 nm). The PL quantum yield relative to **PFV** (Φ ~100 % in chloroform) was evaluated.[23] The CPL spectrum was recorded on a JASCO CPL-200 spectrofluoropolarimeter with a path length of 10 mm, a scanning rate of 100 nm/min, a slit width for excitation of 10 nm, a slit width for monitoring of 10 nm and a response time of 1 sec at room temperature, while the instrument was designed to obtain a high S/N ratio by adjusting the angle between the incident and travelling light to 0° with a notch filter. The optical rotation at the Na-d line was measured with a JASCO P-1020 polarimeter with a path length of 1 cm at room temperature (~25 °C). The ^{1}H NMR spectra were recorded with a Bruker AV500 spectrometer (500.13 MHz) and all chemical shifts are given in ppm and are referenced to $SiMe_4$. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted.

The weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index ($PDI = M_w/M_n$) were evaluated using gel permeation chromatography (GPC) on a Shimadzu A10 instrument with ShimPAC (Shimadzu) GPC-806, 804 and 802 as the columns and HPLC-grade THF as the eluent at 40 °C (calibrated with polystyrene standards). The enantiopurity of each limonene was checked by the polarimeter. Refractive index of polymers (in chloroform) and liquids were determined by ATAGO refractometer DR-M2 with water-controlled circulator (ATAGO 60-C4) at four wavelengths (486, 546, 589 and 656 nm) at 25 °C. Fluorescent optical micrographs excited at 450 nm were taken with a Nikon Eclipse E400 optical microscope equipped with a Nikon CCD camera. The time-resolved PL emission spectra and PL lifetime experiment were measured on a streak camera using a femtosecond laser pulse (~150 fsec) from an optical parametric amplifier (Hamamatsu Photonics C4780). The centre wavelength of 450 nm was used as the excitation light source (Coherent Mira, Usho KEC-160, mode-locked Ti: Sapphire laser 100 KHz repetition, LBO crystal (370-450 nm) used as SHG unit), and the centre wavelength at 480-490 nm was monitored. In the case of **PFE**, the centre wavelengths for excitation and monitoring were 390 nm and 440 nm, respectively.

Materials

Spectroscopic-grade chloroform and methanol (Dojindo, Kumamoto, Japan) were used to prepare the polymer solutions and for measurements. **1*R*** and **1*S*** were obtained from Wako (Tokyo, Japan) and purified by distillation under reduced pressure prior to use. Limonene oxides (**2*R*** and **2*S***) were purchased from Sigma-Aldrich and used as received. **1*R***: $[\alpha]_{27}^{589}$ = +100.03˚ (neat). **1*S***: $[\alpha]_{27}^{589}$ = –101.78˚ (neat). **2*R***: $[\alpha]_{27}^{589}$ = +63.81˚ (neat). **2*S***: $[\alpha]_{27}^{589}$ = –63.88˚ (neat). **PFE** purchased from Aldrich was used as received. **PFV** was provided by Nomura *et al.*, and details of the synthesis and characterisation were given in *ref.* 23. The ^{1}H-NMR spectrum in $CDCl_3$ is shown in Fig. S1. The **PFV** exploited in this work were provided by Nomura's group, who synthesised *via* acyclic diene metathesis (ADMET) polymerisation using Grubbs second generation, Ru catalyst, $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ [Ru, Cy = cyclohexyl, $IMesH_2$ =1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene], under optimised conditions (monomer/catalyst molar ratios, initial monomer concentration).[23]

Preparation of optically active polymer particles

The most typical procedure for the production of **PFV** aggregates in a **1*R***/chloroform/methanol tersolvent is described below. First, 2.0 mL of **1*R*** was added to 0.3 mL of a chloroform stock solution containing **PFV** ($\sim 1 \times 10^{-4}$ M as a repeating unit) in the SQ-cuvette, placed in the Peltier apparatuses of JASCO J725 and J820 spectropolarimeters at 25 °C and stirred for 10 sec. A bluish, turbid solution of **PFV** particles dispersed in the solvent was instantly formed by adding 0.7 mL methanol at room temperature to the solution and gently shaking it manually. After stirring for approximately 10–30 sec, this solution was used for the CD/UV-vis and CPL/PL measurements without further stirring. The typical size of the **PFV** particles ranged from 5 μm to 10 μm, as measured by fluorescent optical microscopy.

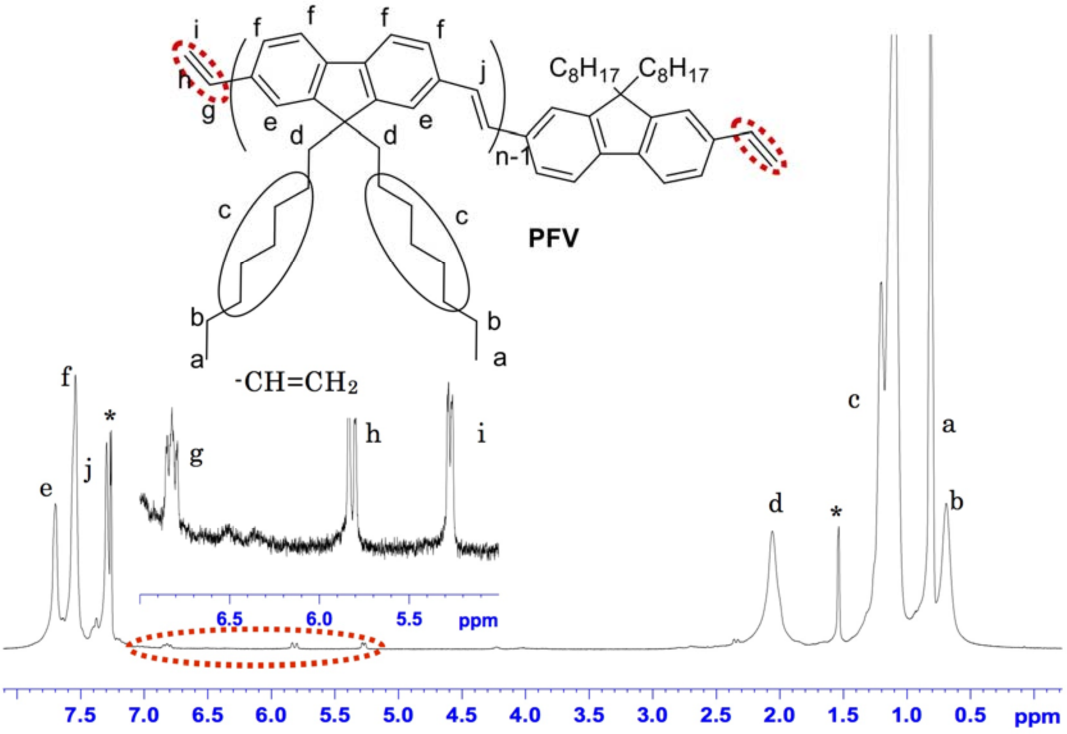


Fig. S1 ^{1}H-NMR spectra of **PFV** and in chloroform-d_1 at room temperature.

Gaussian03 calculation[42]

Electronic state calculations, including the parent polysilane, **TFV** and **TFE**, as models of **PFV** and **PFE**, were employed using the time-dependent density function theory (TD-DFT) Gaussian03 program (B3LYP, 3-21G basis sets) running on Apple iMac (IntelCoreDuo2, 2.0 GHz, 4GB memory, MacOS ver.10.4.11). For the calculations, the geometries of **TFV** and **TFE** with dihedral angles varying from 180° to 0° were optimised by the PM3-MM level of Gaussian03 using initial standard parameters (default).

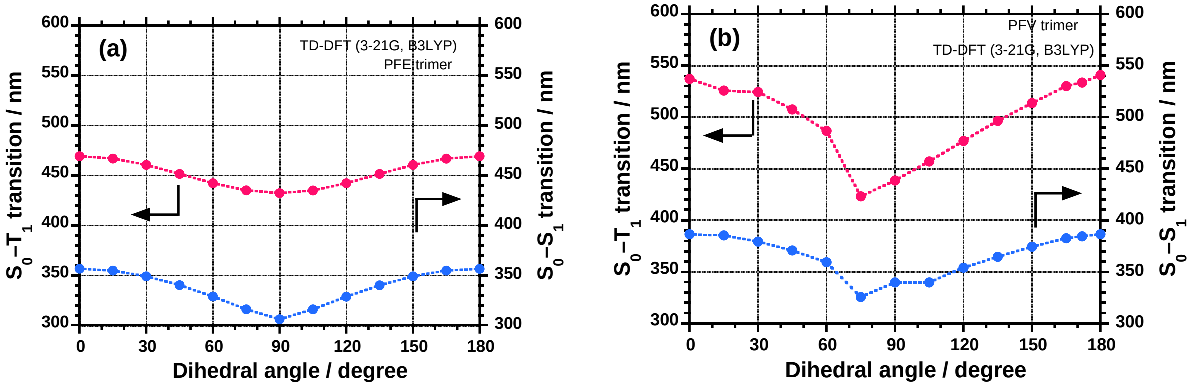


Fig. S2 The S_0–S_1 and S_0–T_1 transition energies (in nm) of (*a*) **TFV** and (*b*) **TFE** as a function of dihedral angle.[42]

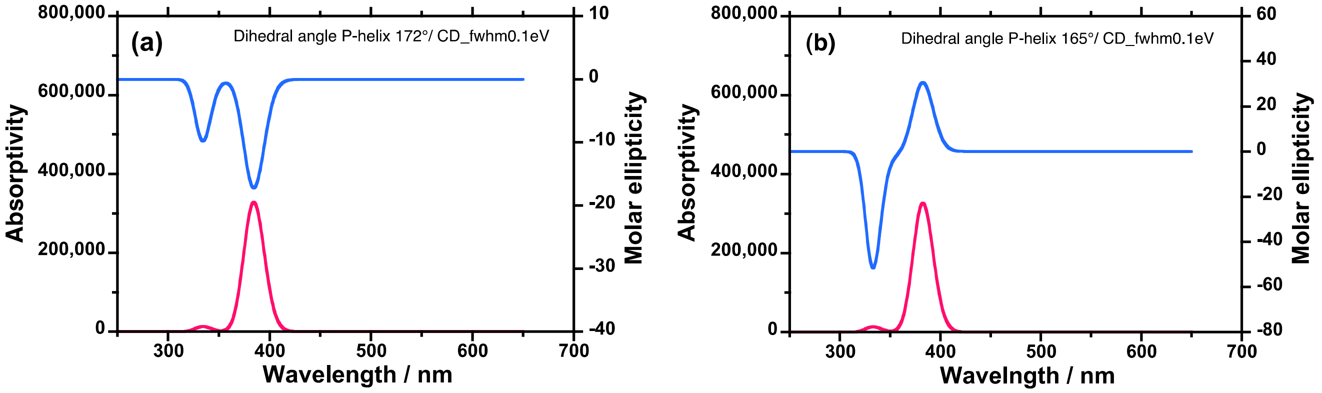


Fig. S3 UV-vis (bottom red line) and CD (upper blue line) spectra (*fwhm* = 0.10 eV) of **TFV** as simulated by Gaussian03 (TD-DFT, B3LYP, 3-21G basis set). (*a*) *P*-helix with a dihedral angle of 172° and (*b*) *P*-helix with a dihedral angle of 165°.

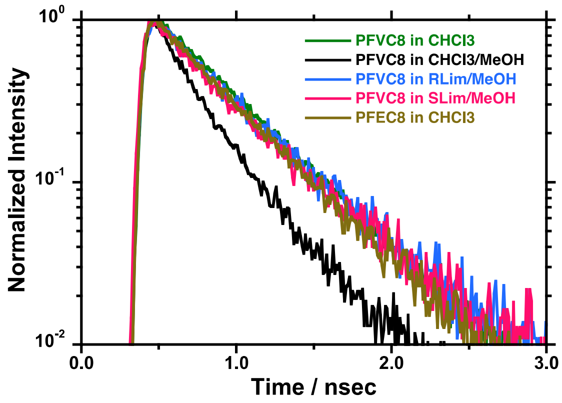


Fig. S4 A comparison of the PL lifetime in nsec of **PFV**. Typical PL decay curves in semi-log scales as a function of time (**PFV** in chloroform, aggregates in chloroform/methanol = 0.3/2.7 (v/v), aggregates in chloroform/**1*R***/methanol = 0.3/0.8/1.9 (v/v/v), aggregates in chloroform/**1*S***/methanol = 0.3/0.8/1.9 (v/v/v) and **PFE** in chloroform).

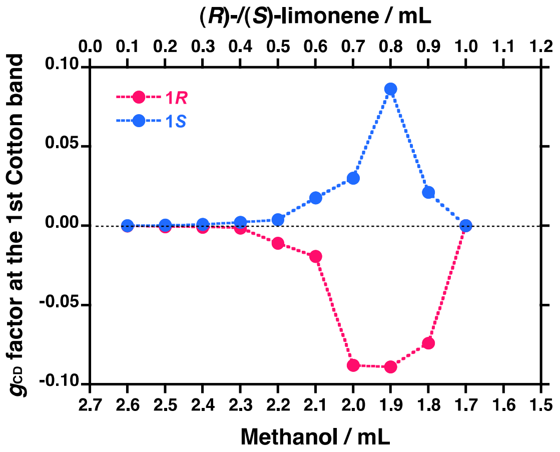


Fig. S5 The g_{CD} value of **PFV** aggregates due to the chiral tersolvents as function of volume fraction of methanol and limonenes with fixed volumes of chloroform 0.3 mL and total volume 3.0 mL.

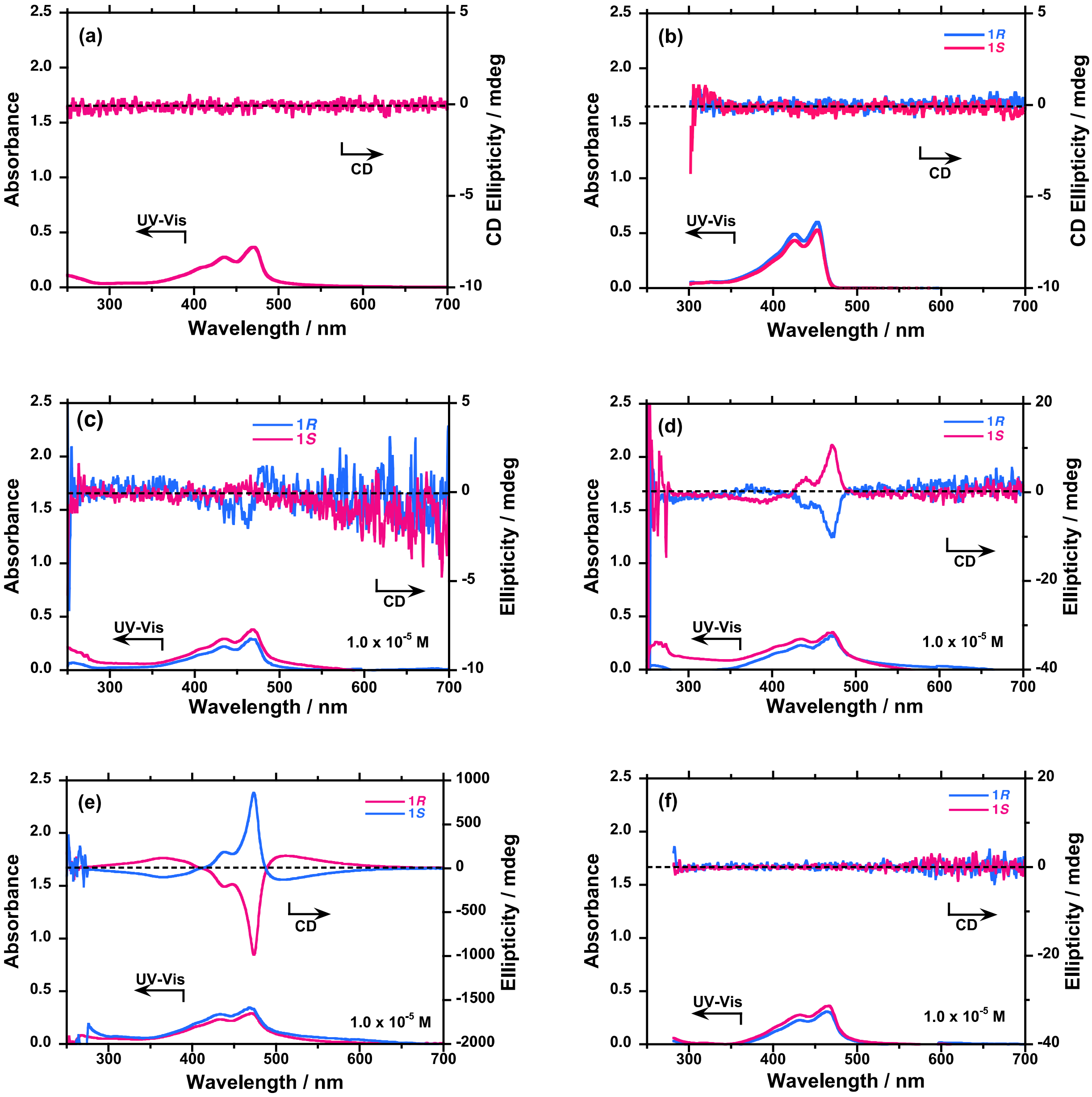


Fig. S6 UV-vis (lower lines) and CD (top lines) spectra of **PFV** (1.0 x 10^{-5} M) in a series of cosolvents and tersolvents at 25 °C. (a) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.0/2.7 (v/v/v), (b) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/2.7/0.0 (v/v/v), (c) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.1/ 2.6 (v/v/v), (d) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.3/2.4 (v/v/v), (e) chloroform/(**1*R*** or **1*S***)/ methanol = 0.3/0.8/1.9 (v/v/v), and (f) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/1.0/1.7 (v/v/v).

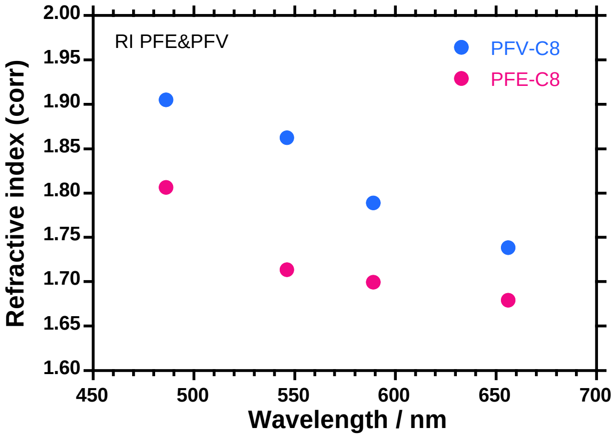


Fig. S7 Refractive indices of **PFV** and **PFE** at four wavelengths (486, 546, 589 and 656 nm) in chloroform at 25 °C.

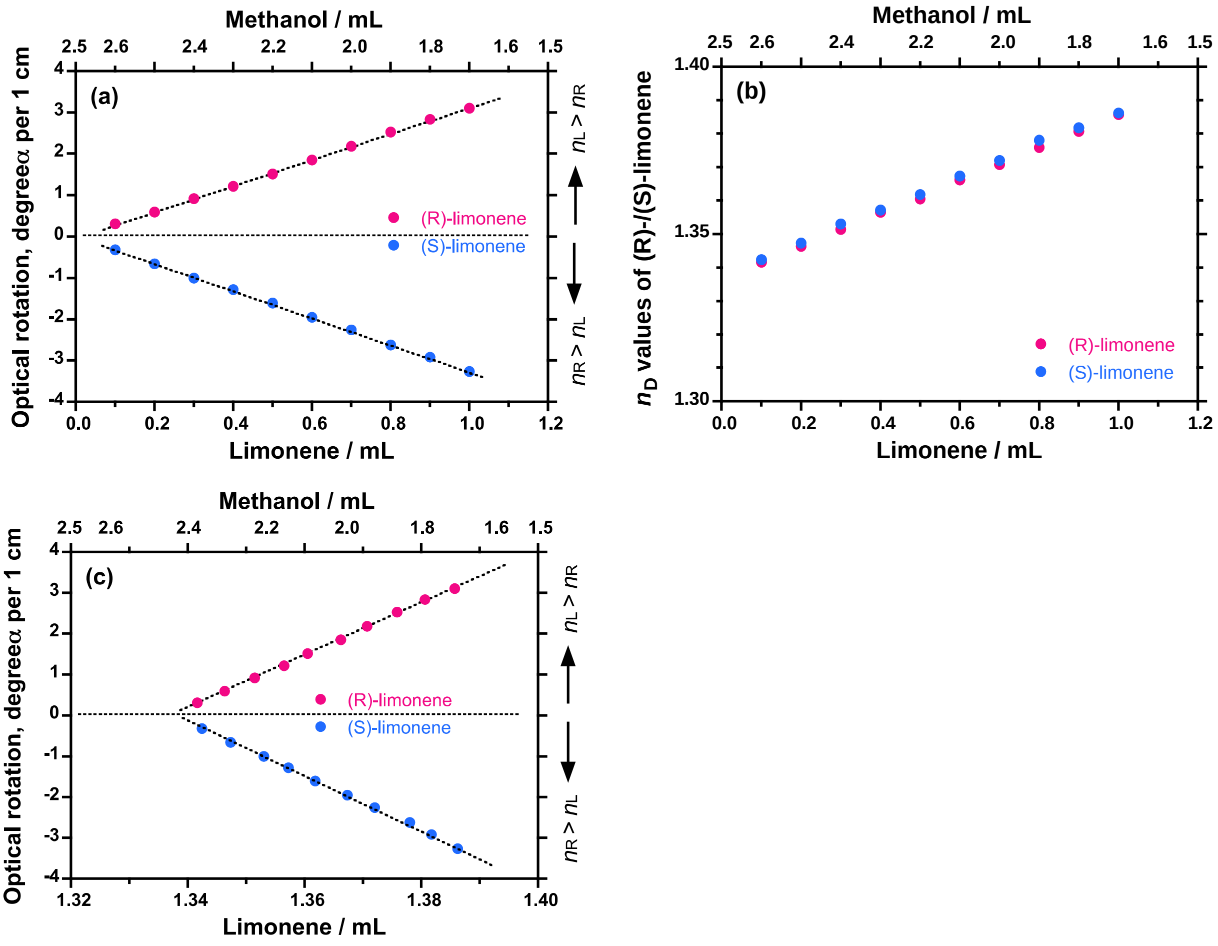


Fig. S8 (a) Optical rotation at 589 nm (~25 °C) and (b) refractive index of the chiral tersolvents as functions of volume fractions of limonenes and methanol at 25 °C (chloroform 0.3 mL and total volume 3.0 mL). (c) Optical rotation at 589 nm and refractive index of the tersolvents. Note that the refractive index (n_F) at 436 nm of the chiral tersolvents was very slightly high compared to that at 589 nm (n_D). For this reason, we used RI and [α] values at Na-d line (589 nm). The tersolvent (total 3.0 mL) consisted of limonene (1.0–0.1 mL), chloroform (0.3 mL, fix) and methanol (1.7–2.6 mL).

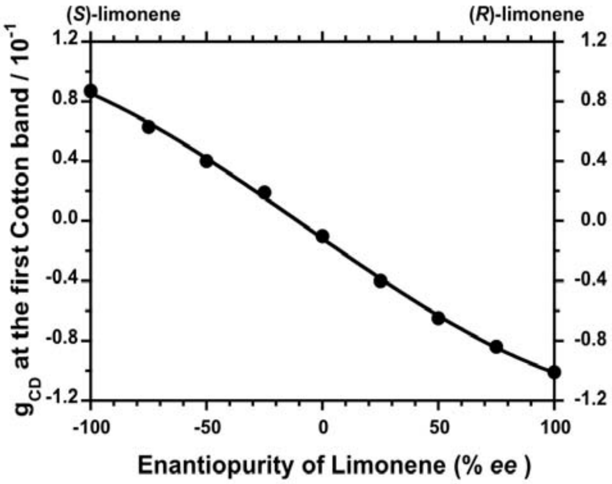


Fig. S9 The g_{CD} value of **PFV** aggregates at ~470 nm as a function of the enantiopurity of **1*R*** and **1*S*** in the tersolvents chloroform/(**1*R*** and **1*S***)/methanol = 0.3/0.8/1.9 (v/v/v).

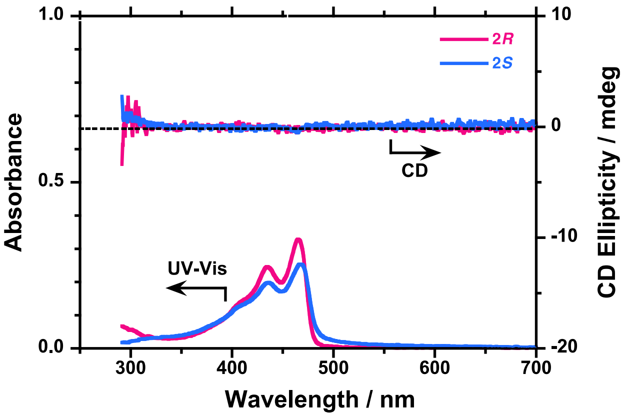


Fig. S10 UV-vis (lower lines) and CD (upper lines) spectra of **PFV** (1.0×10^{-5} M) in tersolvent chloroform/(**2*R*** or **2*S***)/methanol = 0.3/0.8/1.9 (v/v/v) at 25 °C.

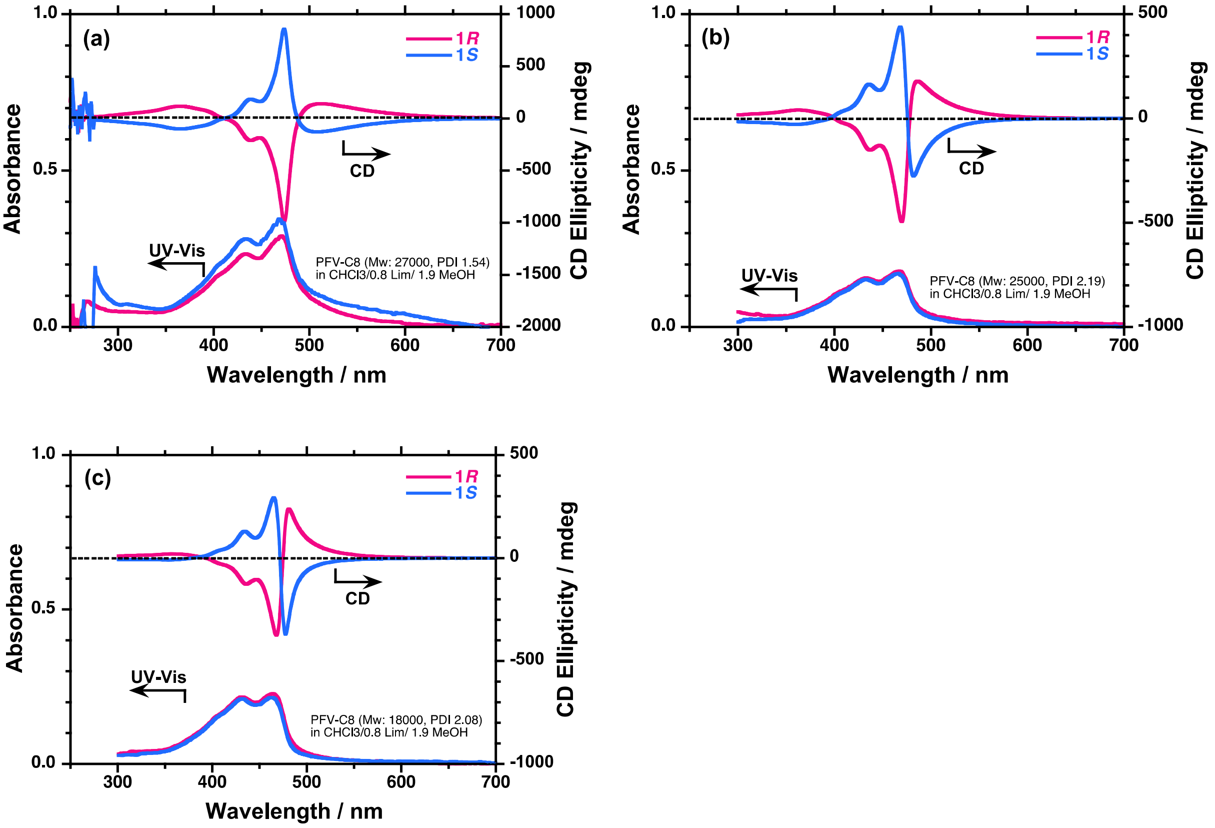


Fig. S11 UV-vis (lower lines) and CD (upper lines) spectra of **PFV** (1.0 x 10^{-5} M) with three different M_w and *PDI* samples in tersolvent chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.8/1.9 (v/v/v) at 25 °C. (*a*) M_w = 27 000, *PDI* = 1.54, (*b*) M_w= 25 000, *PDI* = 2.19 and (*c*) M_w= 18 000, *PDI* = 2.08).

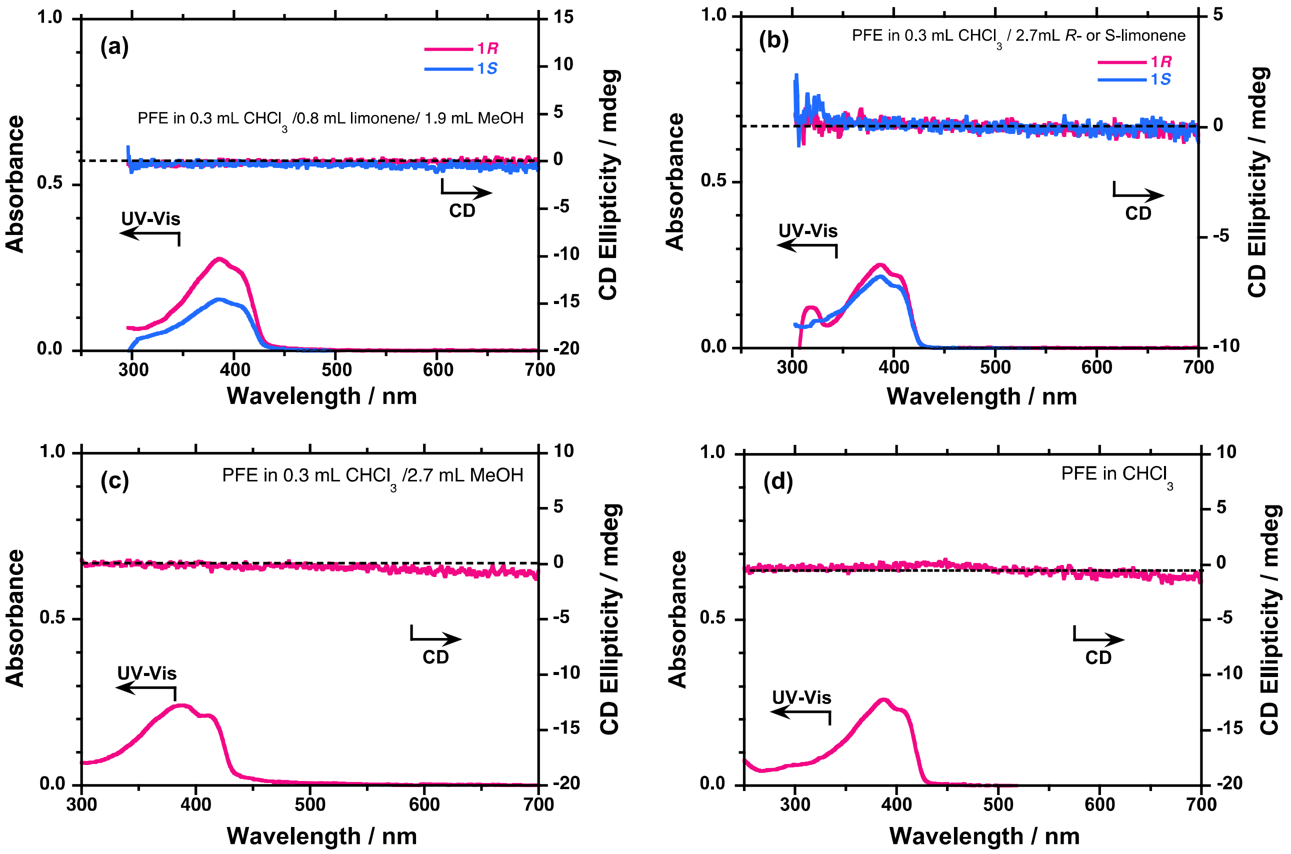
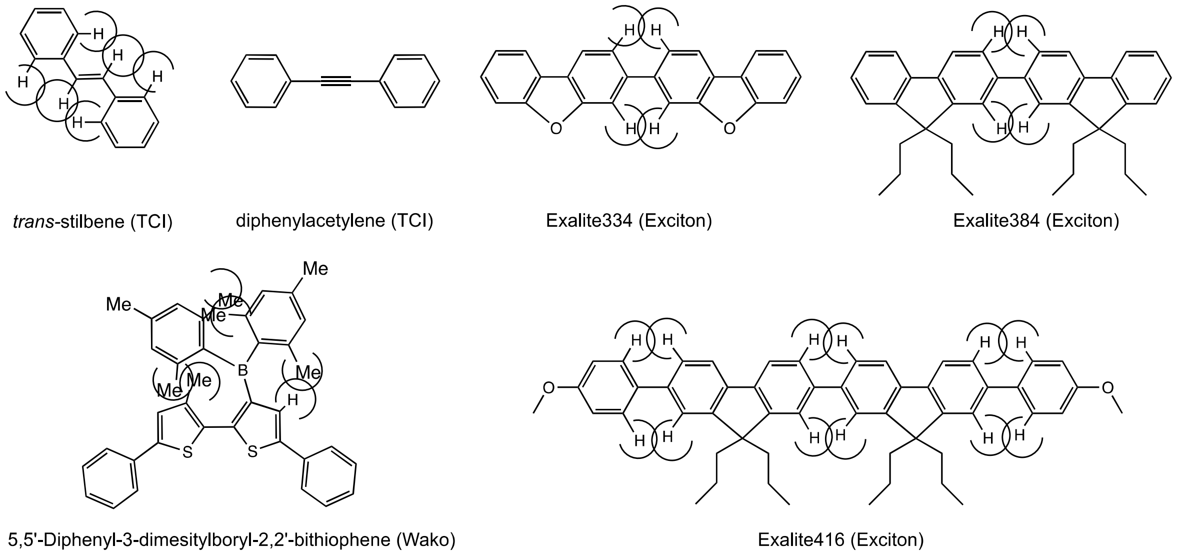


Fig. S12 UV-vis (lower lines) and CD (top lines) spectra of **PFE** (1.0 x 10^{-5} M) in tersolvent, cosolvents and pure solvent at 25 °C. The solvents were (*a*) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.8/1.9 (v/v/v), (*b*) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/2.7/0.0 (v/v/v), (*c*) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.0/2.7 (v/v/v) and (*d*) chloroform/(**1*R*** or **1*S***)/ methanol = 3.0/0.0/0.0 (v/v/v).



trans-stilbene (TCI)

diphenylacetylene (TCI)

Exalite334 (Exciton)

Exalite384 (Exciton)

5,5'-Diphenyl-3-dimesitylboryl-2,2'-bithiophene (Wako)

Exalite416 (Exciton)

Chart S1 Chemical structures of *trans*-stilbene with H–H repulsions as a molecular model of **PFV**, diphenylacetylene without any H–H repulsion as a molecular model of **PFE**, Exalite series (oligofluorenes) with H–H repulsions as molecular models of polyfluorenes and diphenylbithiophene derivative with highly steric repulsions.

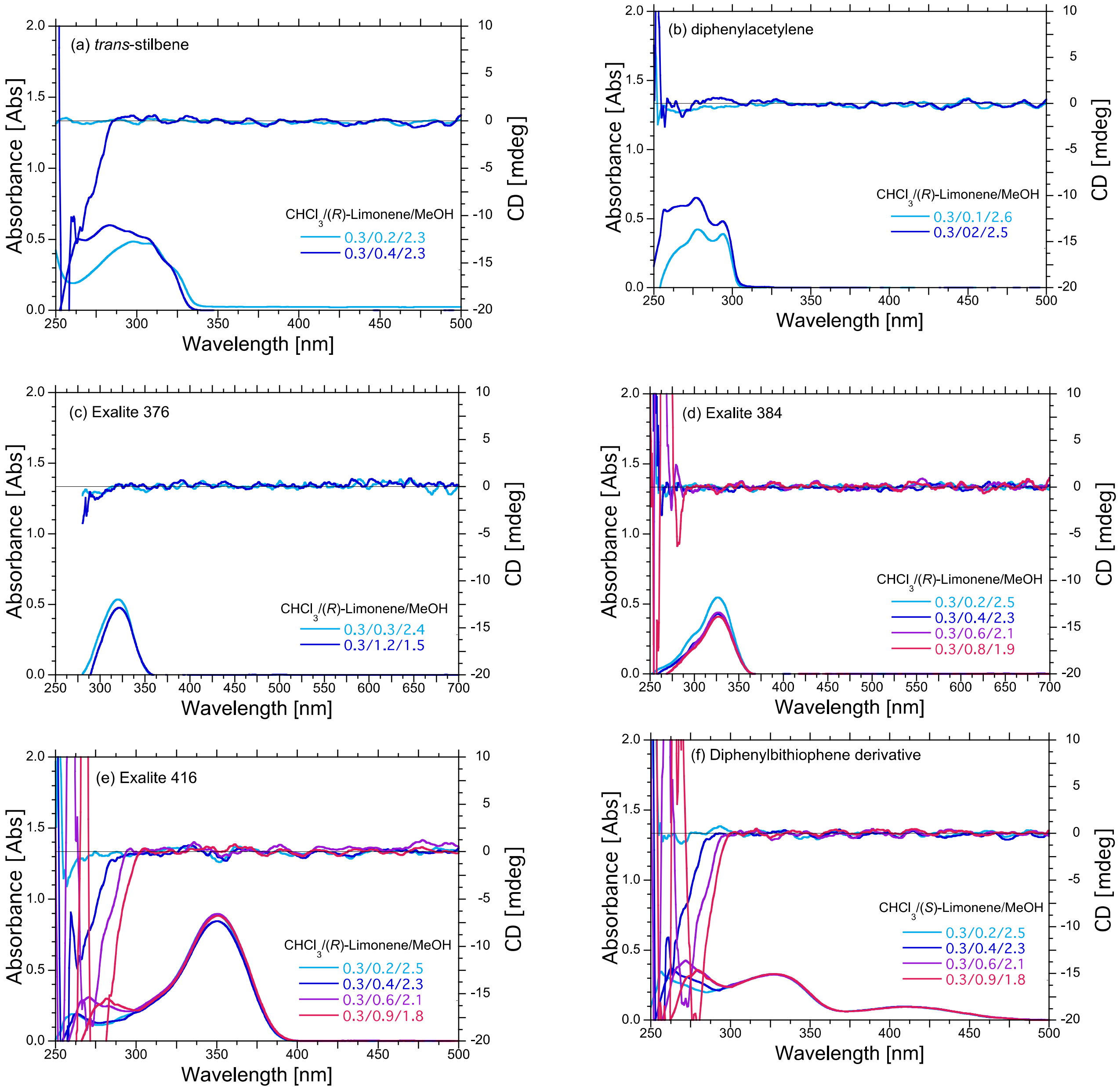


Fig. S13 UV-*vis* (lower lines) and CD (top lines) spectra of aggregates generated from (*a*) *trans*-stilbene, (*b*) diphenylacetylene, (*c*) Exalite376, (*d*) Exalite384, (*e*) Exalite416 and (*f*) diphenylbithiophene derivative with the help of various volume fractions of **1*R*** or **1*S***-based tersolvents at 25 °C. The tersolvents were (i) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.2/2.5 (v/v/v), (ii) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.4/2.3 (v/v/v), (iii) chloroform/(**1*R*** or **1*S***)/methanol = 0.3/0.6/2.1 (v/v/v) and (iv) chloroform/(**1*R*** or **1*S***)/ methanol = 0.3/0.9/1.8 (v/v/v).