

Supplementary Material (ESI) for Chemical Communications  
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## Supporting Information

### Optically Active, Lyotropic Liquid Crystalline Poly(diphenylacetylene) Derivative: Hierarchical Chiral Ordering from Isotropic Solution to Anisotropic Solid Film

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## Experimental Methods

### 1) Materials:

(*S*)-2-Methylbutyl bromide ( $[\alpha]_D^{21} = +4.5^\circ$ ,  $c = 5$  in chloroform) was purchased from Sigma-Aldrich and used as received. Dichlorodimethylsilane (TCI), magnesium (turnings, Wako), *n*-butyllithium (in hexane, 1.6 mol/L, Sigma-Aldrich), tantalum(V)chloride (Sigma-Aldrich) and tetrabutyltin(IV) (Wako) were purchased and used as received. All solvents were dried with nitrogen gas prior to use.

### 2) Synthesis of Monomer:

Chlorodimethyl-(*S*)-2-methylbutylsilane (**1**): A 300-mL round-bottomed flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar. After the flask was flushed with nitrogen, Mg turnings (3.2 g, 0.13 mol) and dry tetrahydrofuran (THF, 50 mL) with a small amount of iodine were placed in the flask. (*S*)-2-Methylbutyl bromide (17.0 g, 0.11 mol) was added dropwise to the resulting solution under moderate reflux for 1 hour. And then, the fresh Grignard reagent was added dropwise to a solution of dichlorodimethylsilane (13.0 g, 0.10 mol) in dry THF (50 mL) at 60 °C, and allowed to react for 2 hours. After adding 100 mL of *n*-hexane to the reaction mixture, a yellow clear solution was collected by reduced filtration under nitrogen flow. The solvents and unreacted dichlorodimethylsilane were evaporated. The crude product was distilled under reduced pressure to give a colorless liquid in 66% (10.9 g) yield. The purity was determined to be 99% by gas chromatography analysis.

1-phenyl-2-(*p*-bromophenyl)acetylene (**2**): This compound was synthesized according to

previously reported method. (Teraguchi, M.; Masuda, T. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 2721-2725.)

1-phenyl-2-(*p*-dimethyl-(*S*)-2-methylbutylsilyl)phenylacetylene (**2MB-DPA**): A 300-mL round bottomed flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar. After purging the flask with nitrogen, a solution of 1-phenyl-2-(*p*-bromophenyl)acetylene in diethyl ether (100 mL) was placed in the flask at 0 °C. A hexane solution of *n*-butyllithium (20 mL, 1.6M, 46 mmol) was added dropwise, and the reaction mixture was left for 1 hour. A solution of compound **1** (7.74 g, 47 mmol) in diethyl ether (25 mL) was added dropwise, and stirred for an additional 5 hours at room temperature. After confirming reaction completion by TLC, ice-water (25 ml) was added. The crude product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. The diethyl ether was evaporated, and the crude product was purified by flash column chromatography (eluene, hexane) to give a colorless liquid. Yield: 4.6 g, 32%; Purity: > 99% (<sup>1</sup>H-NMR); IR: 3060(C–H, Aromatic), 2830~3000(C–H, Stretching), 2220 (C≡C), 1600(C=C, Aromatic), 1450(C=C, Aromatic), 1250(SiC–H), 1110(Si–C), and 690~900(C–H, Aromatic) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.2–7.2 (9H, aromatic), 0.2–0.3 (6H, dimethyl), and 0.6–1.5 (11H, (*S*)-2-methylbutyl) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 140.9, 133.1, 131.5, 130.8, 128.3, 123.3, 89.7, 33.0, 31.6, 23.6, 22.6, 11.4 and -2.1 ppm; Anal. Calcd for C<sub>21</sub>H<sub>11</sub>Si: C 82.29, H 8.55%; Found: C 82.08, H 8.68%. [ $\alpha$ ]<sub>D</sub> = +11.75° (*c* = 1.00 g/dL in CHCl<sub>3</sub>).

### 3) Polymerization of 2MB-DPA:

The manipulation and reaction were carried out under dry nitrogen in glove box. A monomer solution (1.5 g, 5.2 mmol) in toluene (5mL) was placed in a Schlenk tube. Another Schenk tube was charged with TaCl<sub>5</sub> (71 mg, 0.20 mmol), *n*-Bu<sub>4</sub>Sn (0.13 mL, 0.40 mmol), and toluene (4.9 mL). This catalyst solution was aged at 80 °C for 10 min. Subsequently, the monomer solution was added to the catalyst solution. Therefore, the polymerization conditions were adjusted to [Monomer] = 0.50 M, [TaCl<sub>5</sub>] = 20 mM, and [*n*-Bu<sub>4</sub>Sn] = 40 mM. Polymerization was carried out at 80 °C for 24 h, which was quenched with a mixture of toluene and methanol (1 mL, volume ratio 4:1). The polymerization mixture was diluted with toluene (100 mL) and poured into methanol (1 L) under stirring to precipitate the formed polymer. The polymer product was isolated by filtration and dried to give an orange solid (yield: 0.636 g, 40%). The weight-average molecular weight (*M*<sub>w</sub>) was determined to be 4.2 x 10<sup>6</sup> g/mol by GPC and the polydispersity index (*PDI*, *M*<sub>w</sub>/*M*<sub>n</sub>) was 4.9. IR: 3060(C–H, Aromatic), 2830~3000(C–H, Stretching), 1600(C=C, Aromatic), 1450(C=C, Aromatic), 1250(SiC–H), 1110(Si–C), and 690~900(C–H, Aromatic) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.2–7.6 (9H, aromatic) and 0.2–1.4 (17H, alkyl) ppm.

### 4) Measurements:

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were measured in CDCl<sub>3</sub> containing tetramethylsilane as the internal standard using a *Bruker* Advance Digital 400 (400 MHz). The FT-IR spectra were measured on a *JASCO* 620 spectrometer using the transmission method with a 16 cm<sup>-1</sup> resolution. The weight-average molecular weight (*M*<sub>w</sub>) and number-average molecular weight (*M*<sub>n</sub>) of all polymers were evaluated by gel permeation chromatography (GPC, Shimadzu

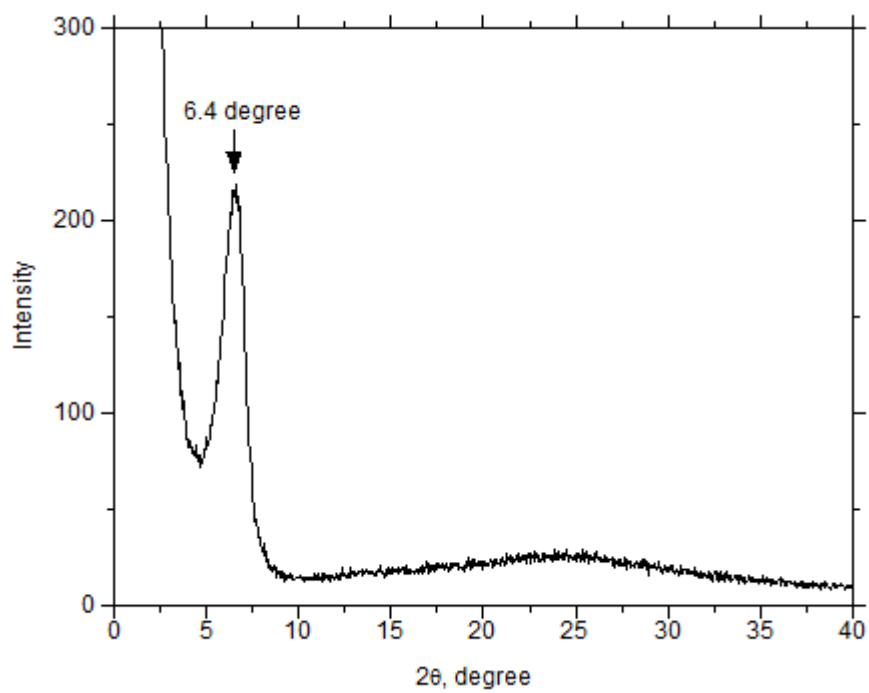
A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column, and HPLC-grade tetrahydrofuran as the eluent at 40 °C), based on a calibration with polystyrene standards. The CD/UV-vis spectra of the solution (an SQ-grade cuvette, with a path length of 1 mm) and films were measured simultaneously at 25 °C on a JASCO J-715, J-725, and J-820 spectropolarimeters equipped with a Peltier-controlled housing unit (with a scanning rate of 100 nm min<sup>-1</sup>, bandwidth of 1 nm and response time of 1 s, using a single accumulation). LD spectra were measured on a JASCO J-715 spectropolarimeter with an LD attachment (with a scanning rate of 100 nm min<sup>-1</sup>, bandwidth of 2 nm and accumulation time of 3 s). Polarized UV-vis spectra of the sheared film were measured independently on a JASCO UV-550 spectrophotometer at 25 °C. The CPL/PL spectra of the solution (an SQ-grade cuvette, with a path length of 1 mm) and films were recorded on a JASCO CPL-200 spectrofluoropolarimeter, with a path length of 1 mm at room temperature. 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 (with a scanning rate of 100 nm min<sup>-1</sup>, a slit width for excitation of 3000 μm, a slit width for monitoring of 3000 μm and a response time of 1 s). The PL spectra were recorded independently on a JASCO ETC-273 spectrofluorometer at 25 °C. DLS experiment was conducted on a Malvern Zetasizer Nano ZS90 spectrometer equipped with a He-Ne laser operating at a wavelength of 633 nm and a collecting angle of 90°. The optical microscope CCD images were recorded on a Nikon Eclipse E600 fluorescence microscope equipped with a Nikon DS-Fi1 digital camera and a super-high-pressure 100-W Hg lamp (OSRAM, HBO103W/2). Morphology of film was observed by a field-emission scanning electron microscope (FE-SEM, Hitachi S-4300, Japan). For FE-SEM analysis, the samples were sputter-coated with gold. XRD measurements were performed at room temperature using a X-ray diffractometer (PANalytical X'Pert PRO-MPD) in Korea Basic Science Institute (Daegu). The samples were mounted directly into the diffractometer. The experiment was carried out using CuK<sub>α</sub>(1.54Å) radiation operating at 40kV and 25mA. High resolution transmission electron microscopy (HR-TEM) images were obtained on a Philips Tecnai G2 F20 S-TWINN Electron Microscope operating at 200 kV. The TEM specimen was prepared by gently casting the dilute polymer solution on carbon-coated copper grid. For measuring exciton lifetimes, Time-Correlated Single Photon Counting (TCSPC) was performed. The second harmonic (SHG = 420 nm) of a tunable Ti:sapphire laser (Mira900, Coherent) with ~150 fs pulse width and 76MHz repetition rate was used as an excitation source. The PL emission was spectrally resolved by using some collection optics and a monochromator (SP-2150i, Acton). The TCSPC module (PicoHarp, PicoQuant) with a MCP-PMT (R3809U, Hamamatsu) was used for ultrafast detection. The total instrument response function (IRF) for PL decay was less than 150 ps, which provided the temporal resolution less than 10 ps. The deconvolution of actual fluorescence decay and IRF was performed by using a fitting software (FlouFit, PicoQuant) to deduce the time constant associated with each exponential decay.

### 5) Chiroptical analysis:

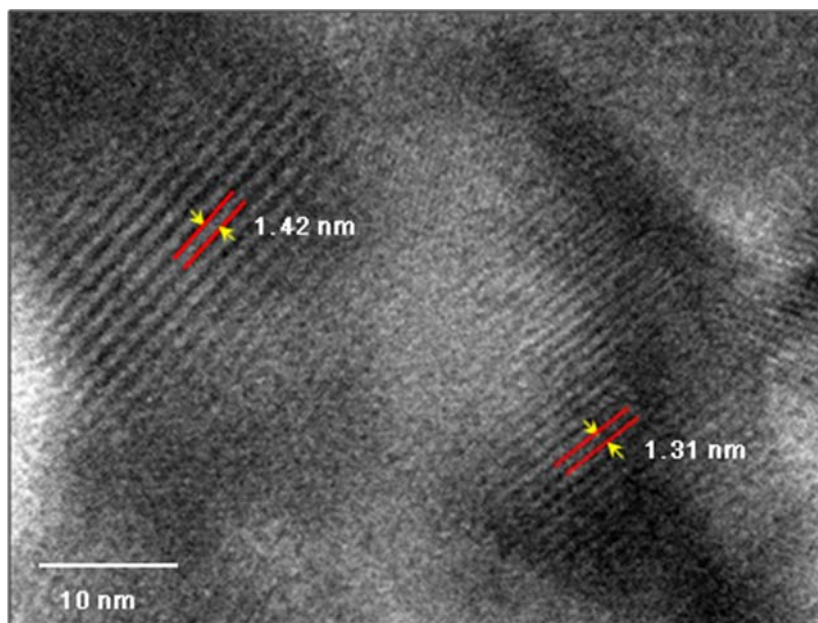
The magnitude of the circular polarization at ground state is defined as  $g_{CD} = 2 \times (\varepsilon_L - \varepsilon_R) / (\varepsilon_L + \varepsilon_R)$ , where  $\varepsilon_L$  and  $\varepsilon_R$  denote the extinction coefficients for left and right circularly

polarized light, respectively. [Dekker, H. P. J. M. In *Circular Dichroism: Principles and Applications*, ed. Berova, N.; Nakanishi, K.; Woody, R. W., Wiley-VCH, New York, 2<sup>nd</sup> ed, 2000, Ch. 7.] The magnitude of the circular polarization at excited state is defined as  $g_{\text{CPL}} = 2 \times (I_{\text{L}} - I_{\text{R}}) / (I_{\text{L}} + I_{\text{R}})$ , where  $I_{\text{L}}$  and  $I_{\text{R}}$  indicate the output signals for left and right circularly polarized light, respectively. Experimentally, the value of  $g_{\text{CD}}$  is determined by  $\Delta\epsilon/\epsilon$  at the wavelength with CD extremum. Also, the value of  $g_{\text{CPL}}$  is determined by  $\Delta I/I$  at the wavelength with CPL maximum intensity.

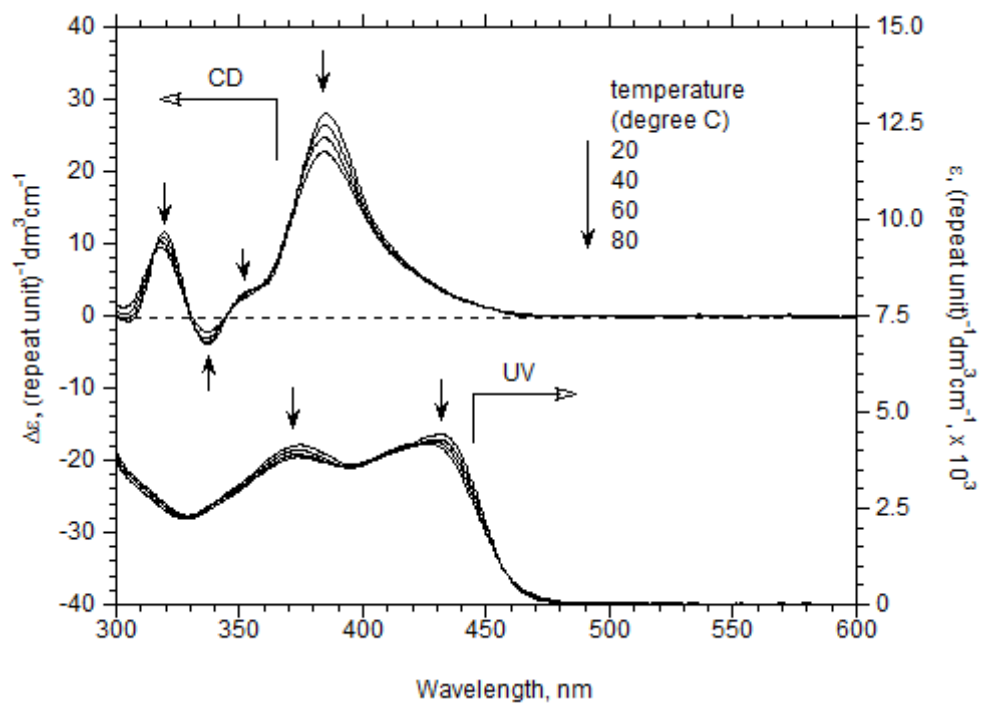
**Fig. S1** XRD pattern of 2MB-PDPA in drop-cast film.



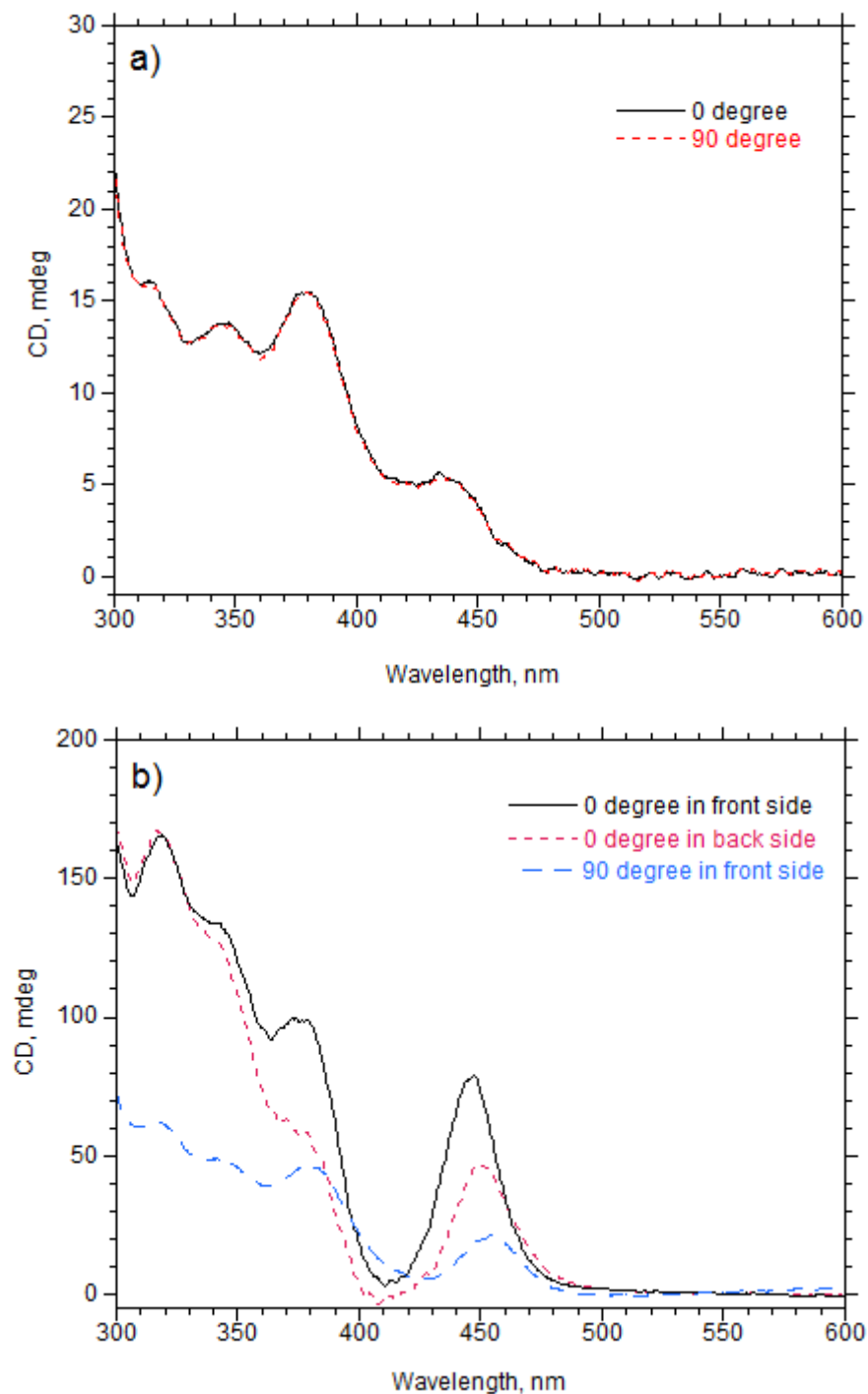
**Fig. S2** HR-TEM image of 2MB-PDPA in drop-cast film.



**Fig. S3** Temperature-variable CD and UV-vis spectra of 2MB-PDPA in solution ( $c = 5.0 \times 10^{-4} \text{ molL}^{-1}$  in toluene)

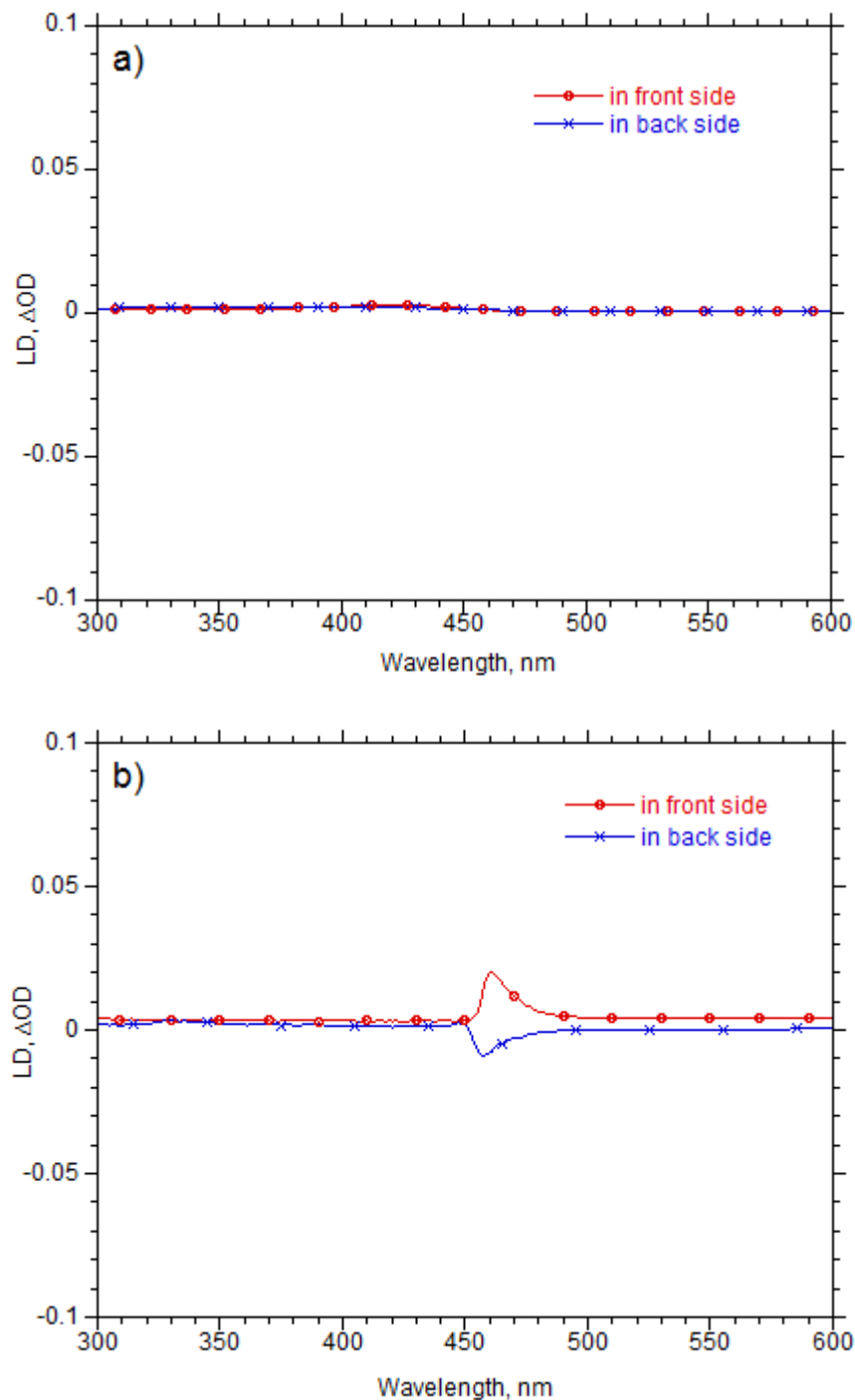


**Fig. S4** CD spectra of 2MB-PDPA in a) spin- and b) cast-films with rotating and/or turning inside out. Spin-cast film does not show any change. The changes in spectral shape and relative intensity of the CD bands of cast-film are negligibly small.

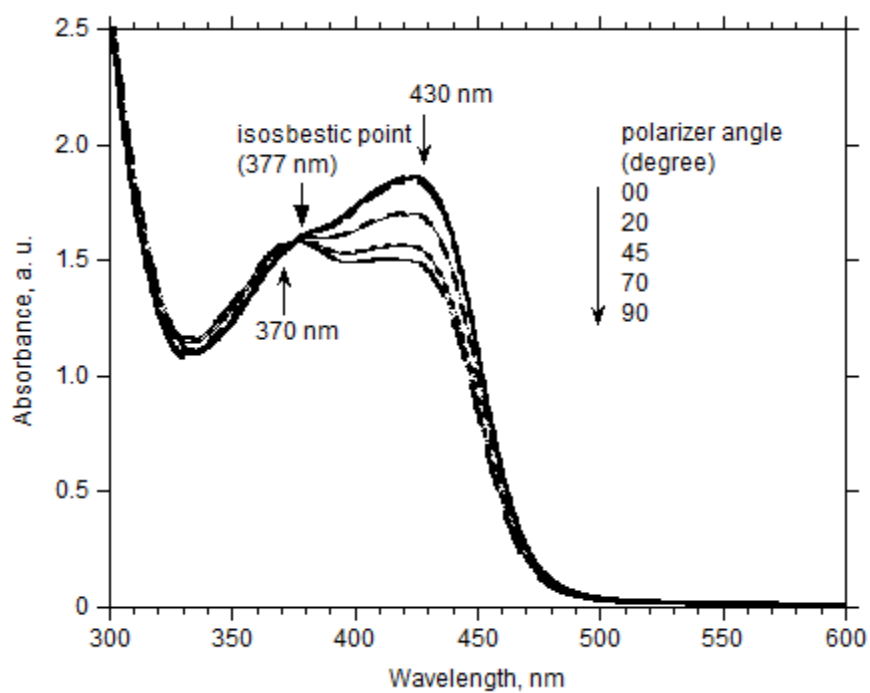




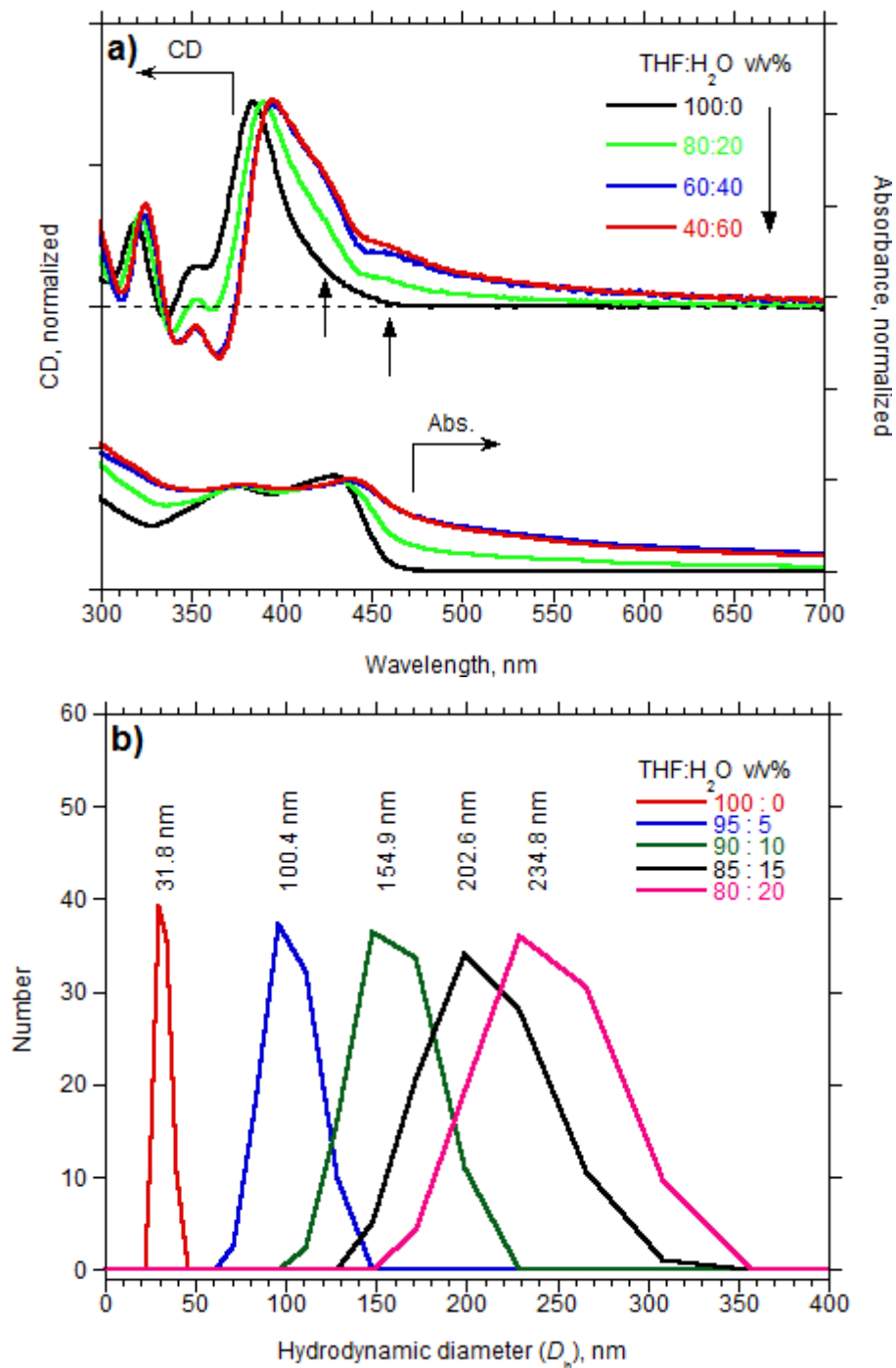
**Fig. S5** LD spectra of 2MB-PDPA in a) spin- and b) cast-films. Both films show no LD signals in the absorption wavelength of polymer chain. Although the LD band of cast-film is shown at 460 nm, which is probably due to the self-assemble and/or aggregate, it does not overlap the absorption band of polymer chain and the signal is negligibly small.



**Fig. S6** Polarized UV-Vis spectra of 2MB-PDPA in sheared film as a function of polarizer angle against shearing direction.



**Fig. S7** Variation in a) CD spectra and b) size distribution curves of 2MB-PDPA in THF upon addition of water ( $c \sim 5.0 \times 10^{-4} \text{ molL}^{-1}$  for CD measurement;  $c \sim 5.0 \times 10^{-6} \text{ molL}^{-1}$  for DLS measurement).



Aggregate is intermediate between solution and solid states although it does not provide a self assemble with well ordered structure. Therefore, CD spectra measurement accompanied with an aggregation experiment may give information of the chirality transfer from solution to solid. **Figure S7a** shows the CD spectra of **2MB-PDPA** in THF/water mixture solvents. The CD signal at 430 nm absorption due to the  $\pi$ - $\pi$  transition of the polyene

backbone increased gradually with increasing water volume fraction, even though the spectral shapes were quite different from those of the films. Simultaneously, the CD signal at 460 nm absorption also increased gradually which is probably due to chiral aggregate phase. Dynamic light scattering (DLS) measurements confirmed that **2MB-PDPA** was dissolved completely in THF (hydrodynamic diameter,  $D_h$ : 31.8 nm in solution with concentration of  $5 \times 10^{-6} \text{ molL}^{-1}$ ) and then gradually assembled into larger size aggregates with increasing water volume fraction ( $D_h$ : 234.8 nm in THF/H<sub>2</sub>O 80/20 vol% mixture) (**Figure S7b**). These results reconfirm that the axial chirality between the main chain and resonant side phenyl rings of a single polymer chain in solution is transferred to the polymer backbone in bulk solid.

**Fig. S8** PL and CPL spectra of 2MB-PDPA in solution ( $c = 5.0 \times 10^{-4} \text{ molL}^{-1}$ , in toluene, excited at 380 nm) and drop-cast film (thickness  $\sim 5 \mu\text{m}$ , excited at 440 nm).

