Electronic Supplementary Information (10 pages) to:

Molecular Chirality Induction to an Achiral π-Conjugated Polymer by Circularly Polarized Light

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Materials and irradiation experiments. PDOF was used as purchased (Aldrich); Mn was 60,500 and Mw/Mn was 3.72 as determined by SEC with reference to polystyrenes. Thin-film samples were prepared by drop casting a tetrahydrofuran solution of the polymer (3.0 g/L) on to a quartz plate (1 cm x 2 cm x 0.1 cm). The film thickness was ca. 0.05 μm as measured using a Keyence VK8700 laser microscope. CPL was generated by passing light from an Ushio Optical Modulex SX-UID500MAMQQ 500-W Hg-Xe lamp through a Gran-Taylor prism and a glass-construction Fresnel Rhomb (50 mW ($Jsec^{-1}$)). LPL was generated using a Gran-Taylor prism only. Irradiation experiments were conducted under N_2 atmosphere at ambient temperature (ca. 23°C) or an elevated temperature. For details of sunlight-based irradiation experiments, see the caption of **Fig. S1**.

Measurements. The ^{1}H NMR spectra were recorded on a JEOL JNM-ECP400 spectrometer (400 MHz for ^{1}H measurement) and a JEOL JNM-EX270 spectrometer (270 MHz for ^{1}H measurement). SEC was carried out using a chromatographic system consisting of a Hitachi L-7100 chromatographic pump, a Hitachi L-7420 UV detector (254 nm), and a Hitachi L-7490 RI detector equipped with two PL-PolyPore columns (30 x 0.72 (i.d.) cm) (Polymer Laboratories) connected in series (eluent THF, flow rate 1.0 mL/min). Absorption spectra were measured with a JASCO V-560 spectrophotometer. FT-IR spectra were measured using a ThermoFischer Scientific Nexus 870 spectrometer. Polarized optical micrographs were taken using a Nikon Eclipse E600 POL microscope. X-ray diffraction (XRD) profiles were obtained using a Rigaku RINT-TTR diffractometer with monochromated Cu-Kα radiation. CD spectra were taken with a JASCO J-820 spectrometer. The spectra were obtained by averaging those recorded at eight (45° interval) or two (180° interval) different film orientations (angles) with the film face positioned vertically to the incident light beam for measurement. Linear dichroism contributions were thus minimized to afford true CD spectra. The anisotropy factor (g_{CD}) was calculated according to $g_{CD} = \Delta Abs/Abs$ = (Ellipticity/32980)/Abs.

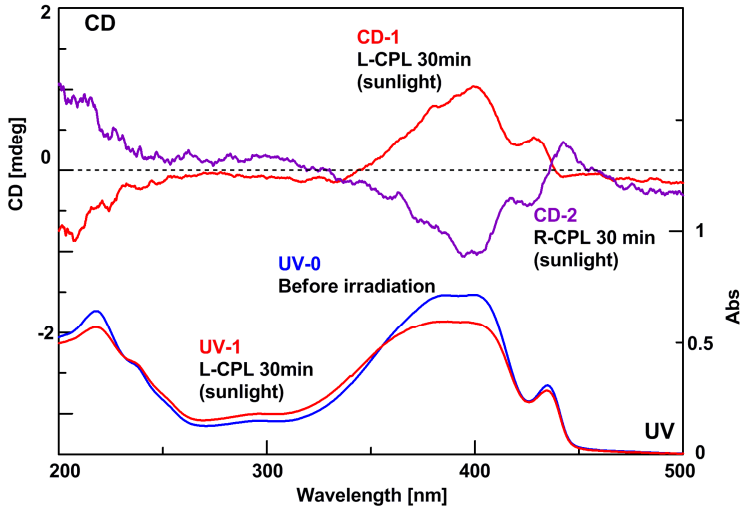

Fig. S1. CD (top) spectra of PDOF in film upon irradiation using L-CPL (red, CD-1) from sunlight for 30 min and R-CPL (purple, CD-2) from sunlight for 30 min and UV (bottom) spectra before irradiation (blue, UV-0) and after L-CPL irradiation for 30 min (red, UV-1). The intensity of CD-2 was normalized for UV abs. 0.60 at 385 nm. The UV absorbance at 385 nm of the original spectrum after R-CPL irradiation was 0.48. L-CPL irradiation and R-CPL irradiation were conducted at 8.0°C and 2.5°C, respectively. Relevant experiments were conducted outdoors to avoid any polarizing effects of window glass. CPL was generated by passing sunlight through a Gran-Taylor prism and a glass-construction Fresnel Rhomb. Although the CD intensity was not as high as that obtained by CPL from a Hg-Xe lamp, the two spectra obtained with L- and R-CPL were nearly symmetrical. This is the first clear example of chiral induction to an organic molecule using natural sunlight. The relatively low CD intensity can be reasonably ascribed to the relatively weak sunlight intensity (exact intensity unknown) and relatively outdoor temperature (8°C and 2.5°C for L- and R-CPL experiments, respectively) in Sapporo, Hokkaido, where the sunlight experiments were conducted in March 2011.

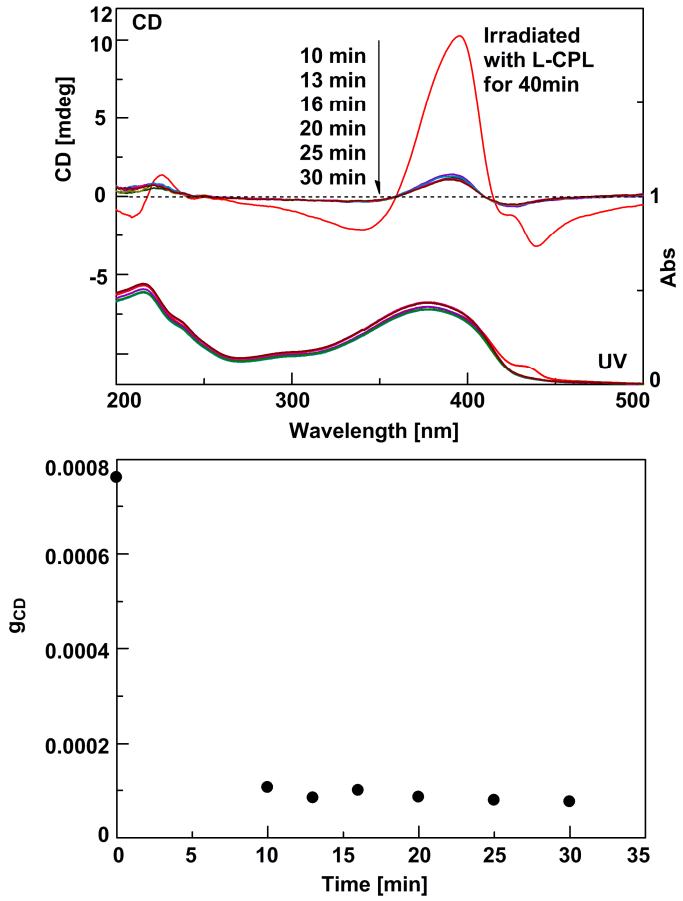

Fig. S2. CD and UV spectral changes on heating PDOF film at 160°C for 10-30 min after inducing chirality by L-CPL irradiation for 40 min using a 500-W Hg-Xe lamp (top) and g_{CD}-vs.-heating time plot (bottom). g_{CD} is based on maximum CD intensity at 391 nm.

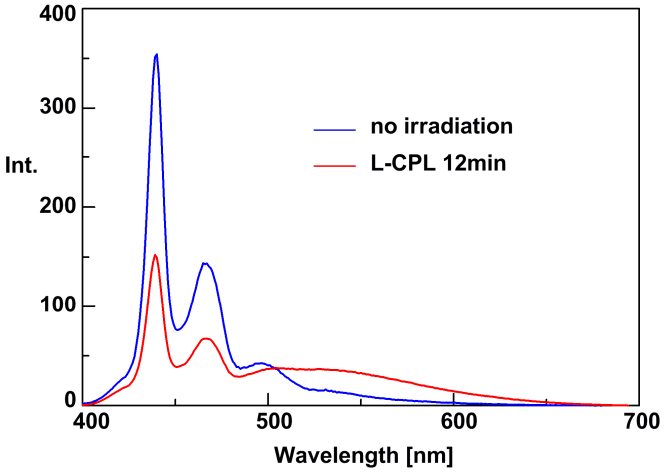

Fig. S3. Emission spectra of PDOF film before and after irradiation with L-CPL from a 500-W Hg-Xe lamp for 12 min [λ_{ex} = 385 nm, range 300 V].

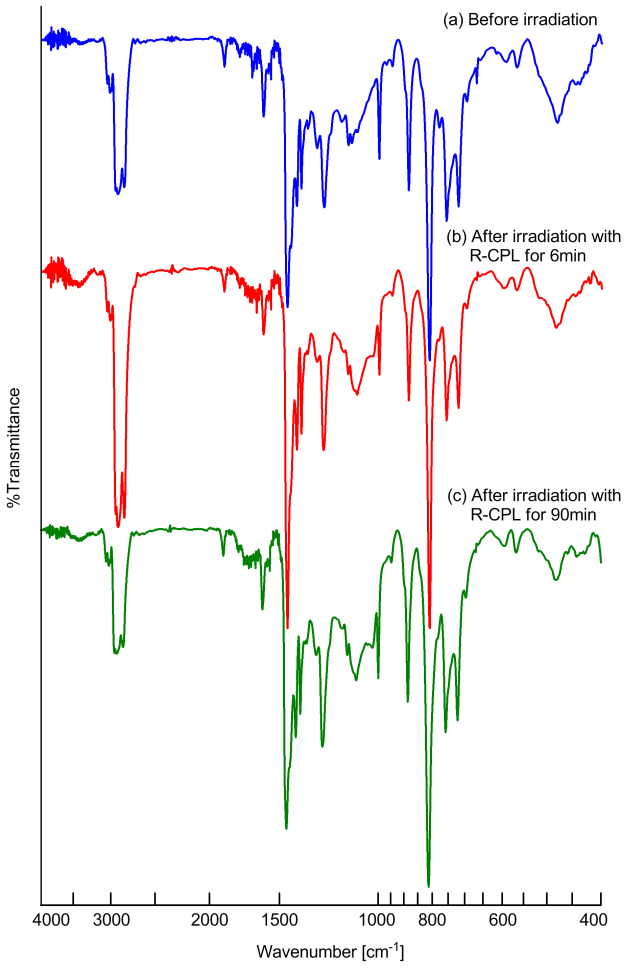

Fig. S4. FT-IR spectra of PDOF before (a) and after irradiation for 6 min (b) and 90 min (c) with R-CPL from a 500-W Hg-Xe lamp [KBr pellet]. PDOF was irradiated in film, removed and collected by washing the quartz plate with $CHCl_3$, and recovered by removing the solvent. After irradiation, signals due to fluorenone units (keto defects) were observed at around 1735 cm^{-1}.

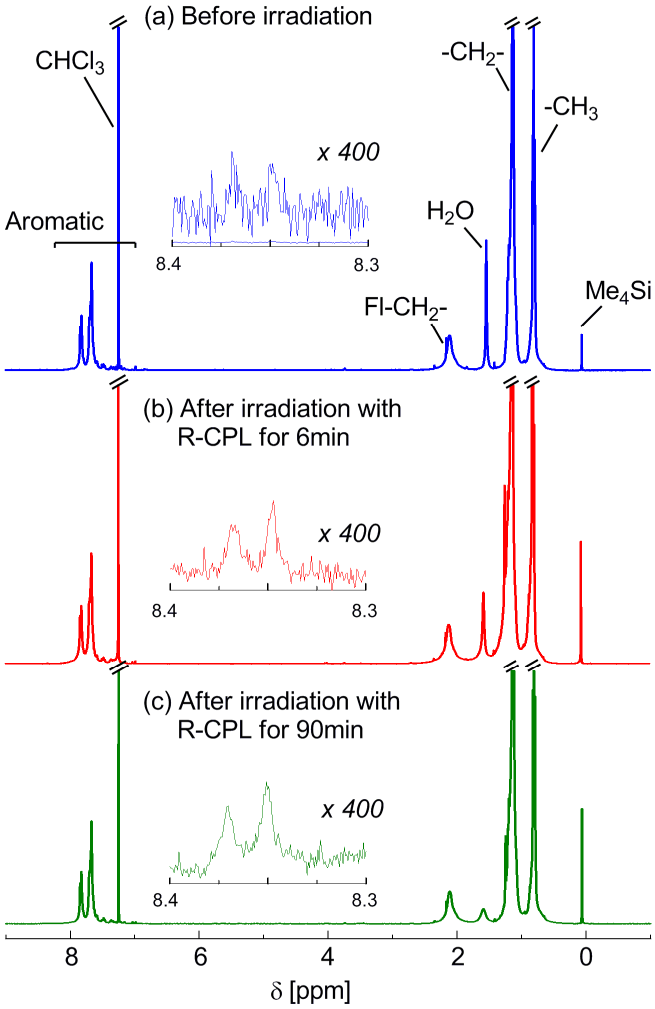

Fig. S5. 400 MHz ^{1}H NMR spectra of PDOF before (a) and after irradiation for 6 min (b) and 90 min (c) with R-CPL from a 500-W Hg-Xe lamp [$CDCl_3$, r.t.]. PDOF was irradiated in film, removed and collected by washing the quartz plate with $CHCl_3$, and recovered by removing the solvent. The content of fluorenone units (keto defects) was estimated to be ca. 0.3% and ca. 0.5% after irradiation for 6 min and 90 min, respectively, from the intensity ratio of the signals at around 8.35 ppm due to the ketone units and the other aromatic signals due to DOF units.

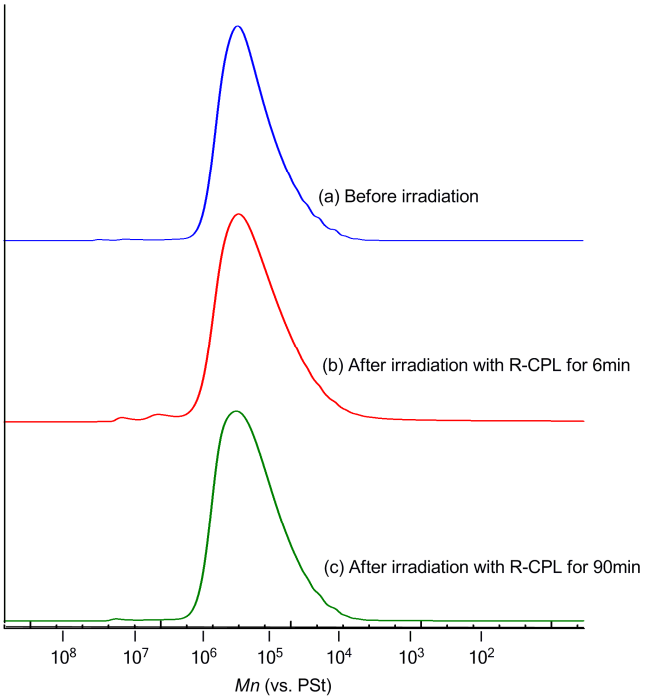

Fig. S6. SEC curves of PDOF before (a) and after irradiation for 6 min (b) and 90 min (c) with R-CPL from a 500-W Hg-Xe lamp [in THF]. The curves were obtained using a UV detector at 400 nm. PDOF was irradiated in film, removed and collected by washing the quartz plate with THF, and recovered by removing the solvent.

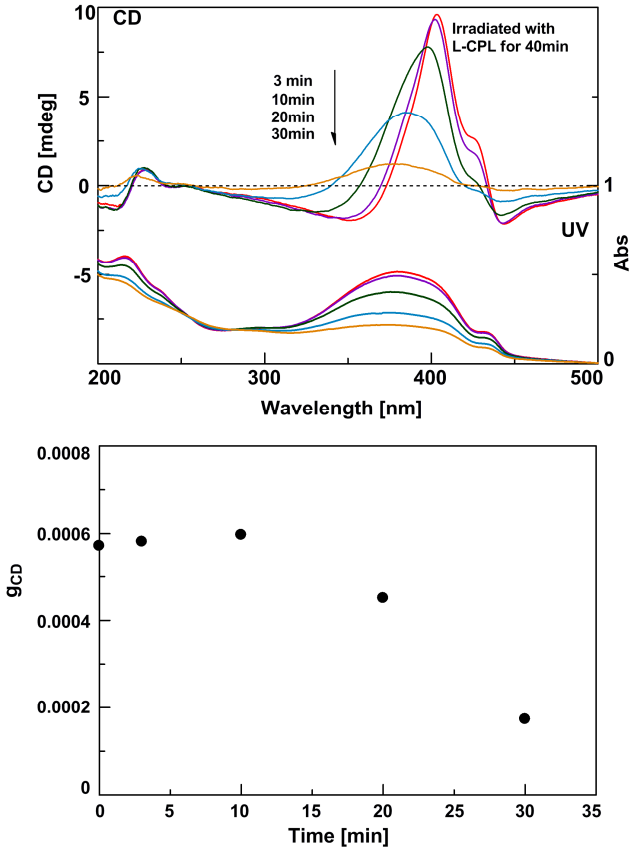

Fig. S7. CD and UV spectral changes on linearly polarized light (LPL) irradiation to PDOF film after inducing chirality by L-CPL irradiation for 40 min using a 500-W Hg-Xe lamp (top) and g_{CD}-vs.-LPL irradiation time plot (bottom). g_{CD} is based on maximum CD intensity in the range of 381-403 nm.

Fig. S8. Polarized optical micrographs of PDOF before and after irradiation with L-CPL from a 500-W Hg-Xe lamp for 45 min and for 90 min. Irradiation was conducted on a glass plate.

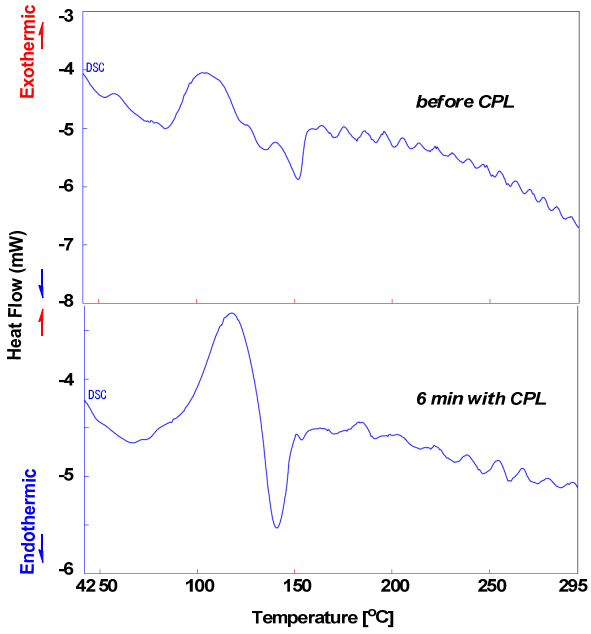

Fig. S9. DSC profiles of PDOF before (top) and after (bottom) irradiation with L-CPL from a 500-W Hg-Xe lamp for 6 min [sample weight 10.6 mg (top), 10.6 mg (bottom)]. Irradiation was conducted in a film form on quartz plate. The irradiated sample was collected as a powder from the surface of quartz plate and transferred into a DSC sample pan.

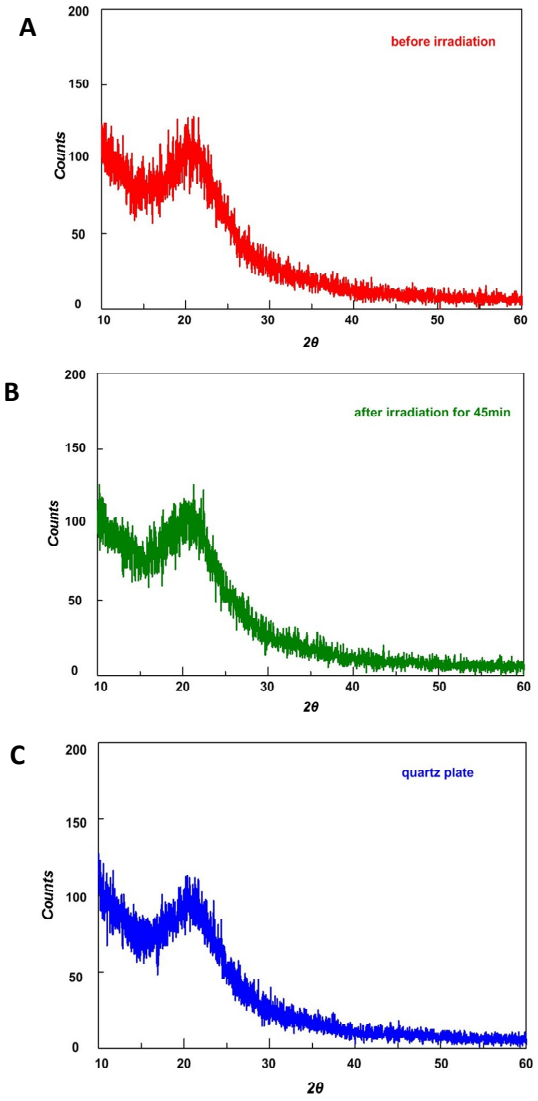

Figure S10. XRD profiles of PDOF before (A) and after (B) irradiation with R-CPL from a 500-W Hg-Xe lamp for 45 min and that of a quartz plate only (control experiment) (C). Irradiation was conducted on a quartz plate, and the sample on the quartz plate was directly subjected to XRD experiments.