Supplementary Information for:

Gigantic Chiroptical Enhancements in Polyfluorene Copolymers Bearing Bulky Neomenthyl Group: Importance of Alternating Sequence of Chiral and Achiral Fluorene Units

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General Methods:

Materials. Tetrahydrofuran (THF) (Wako Pure Chemical) was dried on sodium benzophenone ketyl and distilled immediately before use. The other chemicals listed as follows were used without purification: *l*-menthol, pyridine, chloroform, *n*-butyllithium (1.57 M in *n*-hexane solution) 1-iodopentane, bromine, iodine, dichloromethane, dimethyl sulfoxide, magnesium (turnings), 1,2-dibromoethane, and potassium carbonate (Kanto Chemical); 1,4-dioxane (Nacalai Tesque); triphenylphosphine, and *p*-toluenesulfonyl chloride (Wako Pure Chemical Industries, Ltd.); fluorene, hydrazine monohydrate, and dichloro[1,3-bis(diphenylphosphino)propane]nickel(II)) (Tokyo Chemical Industry); palladium(II) chloride, 2,7-dibromo-9,9-dioctylfluorene, and 9,9-dioctylfluoren-2,7-diboronic acid bis(1,3-propanediol) ester) (Sigma-Aldrich).

Measurements. ¹H NMR spectra were recorded on a JEOL JNM-ESC400 spectrometer (400 MHz for ¹H). 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 TOSOH TSK gel G3000H HR and G6000H HR columns (30 x 0.72 (i.d.) cm) connected in series (eluent THF, flow rate 1.0 mL/min). SEC was also performed using Wyatt Technology Dawn EOS-N MALLS detector and Viscotek Model TDA300 on-line RI and viscometric detectors. Right-angle scattering information was obtained from the MALLS detector and integrated into the TDA detector system to calculate molar masses and Mark-Houwink-Sakurada constants. Absorption spectra were measured at room temperature with a JASCO V-570 spectrophotometer. CD and LD spectra were taken on a JASCO J-820 spectrometer. Fluorescent spectra were taken on a JASCO FP-8500 fluorescence spectrophotometer attached with an ILF-835 100-mm φ integral sphere unit. FT-IR spectra were measured using a Thermo

Fischer Scientific Nexus 870 spectrometer. Optical rotation was measured with a JASCO P-1030 digital polarimeter. DSC analyses were performed on Rigaku Thermo plus TG8120 and DSC8230 apparatuses using Thermo plus 2 software for data analyses. Polarized optical microscopic observations were conducted using a Nikon Eclipse E600 POL microscope. CPL-fluorescent spectra were taken on a JASCO CPL-200 (NAIST, Japan). X-ray diffraction (XRD) profiles were obtained using a Rigaku Miniflex diffractometer.

Film fabrication. Polymer films were fabricated by drop-casting a CHCl₃ solution (8 mg/mL, 20 μ L) onto a quartz plate (size: 1 cm × 2 cm, thickness: 1 mm). The film thickness was in a range from ca. 0.33 to 1.31 μ m, which was taken on a Keyence laser scanning microscope VK 9700.

Monomer synthesis:

Menthyltosylate. This compound was synthesized according to the literature [G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermühle, C. Krüger, M. Nolte, S. Werner, *J. Am. Chem. Soc.* 1993, *115*, 4590–4601] with modifications.

p-Toluenesulfonyl chloride (26.6 g, 0.14 mol) dissolved in 60 mL of CHCl₃ was slowly added to a solution of *l*-menthol (20.0 g, 0.13 mol) in 41 mL of pyridine cooled at 0 °C. The reaction mixture was stirred at room temperature for 3 h. Removal of solvents gave a crude product. The crude material was dissolved in MeOH, and water was slowly added to the solution. This process yielded colorless crystals (m.p. 89 °C). Yield: 34.2 g (87%).

9-Neomenthylfluorene. This compound was synthesized according to the literature [A. Gutnov, H.-J. Drexler, A. Spannenberg, G. Oehme, and B. Heller, *Organometallics*, **2004**, *23*, 1002–1009] with modifications.

To a solution of fluorene (26.1 g, 0.16 mol) in 120 mL of THF cooled at 0 °C was slowly added 100 mL (0.16 mol) of *n*-BuLi (1.57 M in *n*-hexane solution). The reaction mixture was stirred for 30 min at 0 °C. After the reaction system was cooled to -78 °C, menthyltosylate (24.0 g, 0.08 mol) dissolved in 120 mL of THF was added in several portions. The reaction mixture was stirred at room temperature for 30 min and for additional 15 h under reflux, and then was poured into a large excess of iced water. The crude product was extracted with CHCl₃, and the organic layer was dried on MgSO₄. The crude material was first purified by silica-gel column chromatography with a mixture of toluene and *n*-hexane (1/10, v/v) as eluent and was then recrystallized from methanol to afford colorless crystals (m.p. 63–65 °C). Yield: 5.3 g (22%).

9-Neomenthyl-9-*n***-pentylfluorene**. This compound was synthesized by the method of the literature [J.-M. Yu, T. Sakamoto, K. Watanabe, S. Furumi, N. Tamaoki, Y. Chen, and T. Nakano, *Chem. Commun.*, **2011**, *47*, 3799–3801].

To a solution of 9-neomenthylfluorene (4.0 g, 13.2 mol) in 70 mL of THF cooled at 0 °C was slowly

added 10.0 mL (15.7 mol) of *n*-BuLi (1.57 M in *n*-hexane solution). After the reaction system was stirred at 0 °C for 1 h, 1-iodopentane (3.9 g, 19.7 mol) dissolved in 10 mL of THF was slowly added. The resulting mixture was warmed to room temperature, was stirred for 24 h, and was poured into a large excess of iced water. The crude product was extracted with CHCl₃, and the organic layer was dried on MgSO₄. The crude material was purified by silica-gel column chromatography with a mixture of toluene and *n*-hexane (1/5, v/v) as eluent to afford a colorless oily product. Yield: 4.6 g (92%); $[\alpha]_D^{25}$ –51 (c. 1.00, CHCl₃).

2,7-Dibromo-9-neomenthyl-9-*n***-pentylfluorene (DBNPF)**. This compound was synthesized according to the literature [R. Kannan, B. A. Reinhardt, and L.-S. Tan, U.S. Patent, 6,300,5, Oct 9, 2001] with modifications.

To a solution of **NPF** (10.3 g, 27.4 mmol) and iodine (83.5 mg, 0.3 mmol) in 52 mL of CH₂Cl₂ was added dropwise bromine (3.0 mL, 58.6 mmol). After the reaction system was stirred at room temperature for 1.5 h, it was poured into an excess of aq. NaHSO₃. The crude product was extracted with CH₂Cl₂. The organic layer was washed with brine and was dried on MgSO₄. The crude product was purified by recrystallization with *n*-hexane to afford colorless crystals (m.p. 145 °C). Yield: 12.4 g (85%); $[\alpha]_D^{26}$ +9.0 (c. 1.00, CHCl₃).

Polymerization

Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄). This compound was synthesized according to the literature [D. R. Coulson, *Inorg. Synth.*, **1972**, *13*, 121–124; *ibid*, **1990**, *28*, 107–109].

In a two-necked flask, $PdCl_2$ (1.5 g, 8.5 mmol) and triphenylphosphine (11.1 g, 42.3 mmol) were dissolved in 105 mL of dimethyl sulfoxide (DMSO). After the reaction mixture was stirred at 150 °C for 15 min, hydrazine monohydrate (1.7 mL, 33.9 mmol) was added dropwise to the system. The reaction system was then cooled to room temperature. The product was separated from the reaction mixture as yellow powder by filtration and was washed with EtOH and Et₂O in this order. Yield: 9.1 g (93%).

Random Copolymerization of DBNPF with 2,7-Dibromo-9,9-dioctylfluorene (DBDOF) and Homopolymerization of DBNPF. In a Schlenk tube, magnesium (turnings, 70 mg, 2.9 mmol) was activated with 1,2-dibromoethane (188 mg, 1.0 mmol) in 1 mL of THF. For a random copolymerization, prescribed amounts of **DBNPF** and **DBDOF** dissolved in 3 mL of THF was added in several potions to activated magnesium, and the mixture was stirred at 60 °C for 1 h (see Table S1 for the amounts of the monomers). Ni(dppp)Cl₂ (20.4 mg, 0.04 mmol) was added to the system, the mixture was stirred at 60 °C for 24 h, and the reaction was quenched by adding 7 mL of 0.1 M aq. HCl. The crude product was extracted with $CHCl_3$ and the organic layer was dried on MgSO₄. Removal of $CHCl_3$ afforded the crude polymer as yellow, crude powder. The crude material was dissolved in 20 mL of $CHCl_3$, and the solution was poured into 600 mL of MeOH. The precipitates were collected with a centrifuge. Homopolymerization was conducted in the same manner as random copolymerization. Amounts of monomers used for reactions are shown in Table S1.

Entry	Polymerization	DBNPF		DBDOF		Molar	Obtained
	Туре	Amount	Molar	Amount	Molar	Ratio	Polymer
1	Homopolymerization	1.00 g	1.90 mmol	-	-	1/0	Homo.
2	Random copolymerization	0.90 g	1.71 mmol	0.10 g	0.19 mmol	9/1	Ran9/1
3	Random copolymerization	0.50 g	0.95 mmol	0.52 g	0.95 mmol	1/1	Ran1/1
4	Random copolymerization	0.10 g	0.19 mmol	0.93 g	1.71 mmol	1/9	Ran1/9

Table S1. Amounts of monomers used for random copolymerization and homopolymerization.

Homo.: 77% yield; $[\alpha]_D^{25}$ -0.5 (c. 4.00, THF); M_n 11,800 (estimated by SEC on the basis of polystyrene standards); M_w/M_n 4.15 (estimated by SEC on the basis of polystyrene standards); M_n 10,400 (determined by SEC-VISC-RALS); M_w/M_n 1.56 (determined by SEC-VISC-RALS); T_g 127 °C; T_d 314 °C; ¹H NMR (400 MHz, CDCl₃, 293 K) δ 7.83–7.31 (m), 2.77 (brd), 2.66 (brd), 2.24 (brd), 2.06 (brd), 1.75 (brd), 1.54 (brd), 1.36 (brd),1.18 (brd),1.15 (brd), 1.13 (brd), 0.87 (brd), 0.83 (brd), 0.73 (brd), 0.72 (brd), 0.68 (brd), 0.59 (brd), 0.52 (brd), 0.50 (brd), 0.28 (brd), 0.24 (brd), 0.21 (brd), 0.16 (brd) ppm; IR (KBr) υ 2954, 2927, 2861, 1608, 1457, 1377, 1260, 1095, 1022, 888, 811, 743 cm⁻¹.

Ran.-9/1: 72% yield; $[\alpha]_D^{25}$ –0.6 (c. 4.00, THF); M_n 19,500 (estimated by SEC on the basis of polystyrene standards); M_w/M_n 3.45 (estimated by SEC on the basis of polystyrene standards); M_n 10,000 (determined by SEC-VISC-RALS); M_w/M_n 1.57 (determined by SEC-VISC-RALS); T_g 120 °C; T_d 298 °C; ¹H NMR (400 MHz, CDCl₃, 293 K) δ 7.83–7.31 (m), 2.77 (brd), 2.66 (brd), 2.24 (brd), 2.06 (brd), 1.76 (brd), 1.54 (brd), 1.24 (brd), 1.18 (brd), 1.13 (brd), 0.81 (brd), 0.73 (brd), 0.69 (brd), 0.68 (brd), 0.59 (brd), 0.52 (brd), 0.50 (brd), 0.28 (brd), 0.24 (brd), 0.16 (brd) ppm; IR (KBr) υ 2954, 2929, 2864, 1609, 1459, 1379, 1260, 1095, 1018, 889, 814, 742 cm⁻¹.

Ran.-1/1: 84% yield; $[\alpha]_D^{25}$ +0.6 (c. 4.00, THF); M_n 13,400 (estimated by SEC on the basis of polystyrene standards); M_w/M_n 4.17 (estimated by SEC on the basis of polystyrene standards); M_n 8,800 (determined by SEC-VISC-RALS); M_w/M_n 1.70 (determined by SEC-VISC-RALS); T_g 67 °C;

 $T_{\rm d}$ 297 °C; ¹H NMR (400 MHz, CDCl₃, 293 K) δ 7.82–7.32 (m), 2.75 (brd), 2.65 (brd), 2.25 (brd), 2.10 (brd), 1.76 (brd), 1.55 (brd), 1.24 (brd), 1.13 (brd), 0.87 (brd) 0.81 (brd), 0.79 (brd), 0.72 (brd), 0.71 (brd), 0.59 (brd), 0.52 (brd), 0.28 (brd), 0.21 (brd) 0.15 (brd) ppm; IR (KBr) υ 2937, 2927, 2855, 1609, 1459, 1404, 1377, 1259, 1096, 1024, 887, 814, 743 cm⁻¹.

Ran.-1/9: 84% yield; $[\alpha]_D^{25}$ +0.3 (c. 4.00, THF); M_n 18,400 (estimated by SEC on the basis of polystyrene standards); M_w/M_n 5.11 (estimated by SEC on the basis of polystyrene standards); M_n 16,400 (determined by SEC-VISC-RALS); M_w/M_n 1.82 (determined by SEC-VISC-RALS); T_g 32 °C; T_d 301 °C; ¹H NMR (400 MHz, CDCl₃, 293 K) δ 7.84–7.28 (m), 2.75 (brd), 2.11 (brd), 2.03 (brd), 1.76 (brd), 1.55 (brd), 1.26 (brd), 1.24 (brd), 1.13 (brd), 0.81 (brd), 0.72 (brd), 0.59 (brd), 0.52 (brd), 0.27 (brd), 0.21 (brd), 0.15 (brd) ppm; IR (KBr) υ 2926, 2853, 1610, 1459, 1405, 1375, 1259, 1096, 1024, 886, 814, 742 cm⁻¹.

Alternating copolymerization of DBNPF with 9,9-dioctylfluoren-2,7-diboronic acid **bis(1,3-propanediol) ester.** In a flask equipped with a reflux condenser, **DBNPF** (240 mg, 0.45 mmol) and 2,7-di(1,3,2-dioxaborolan-2-vl)-9,9-di-n-octylfluorene (250 mg, 0,45 mmol) were dissolved in 4 mL of 1,4-dioxane. Pd(PPh₃)₄ (52 mg, 0.05 mmol), K₂CO₃ (0.43 g, 3.08 mmol), and 1.5 mL of water were added to the flask. After the reaction mixture was stirred at 110 °C for 2.5 h, 7 mL of 0.1 M aq. HCl was added to the system. The crude product was extracted with $CHCl_3$, and the organic layer was dried on MgSO₄. Removal of CHCl₃ afforded the crude material as yellow solid. The crude material was dissolved in 20 mL of CHCl₃, and the solution was poured into 600 mL of MeOH. The precipitates were collected with a centrifuge to give Alt.; 72% yield; $\left[\alpha\right]_{D}^{25}$ +0.9 (c. 4.00, THF); M_n 25,300 (estimated by SEC on the basis of polystyrene standards); M_w/M_n 5.27 (estimated by SEC on the basis of polystyrene standards); M_n 22,300 (determined by SEC-VISC-RALS); M_w/M_n 2.35 (determined by SEC-VISC-RALS); T_g 85 °C; T_d 304 °C; ¹H NMR (400 MHz, CDCl₃, 293 K) δ 7.83–7.31 (m), 2.77 (brd) 2.25 (brd), 2.10 (brd), 1.78 (brd), 1.56 (brd), 1.13 (brd), 0.87 (brd), 0.80 (brd), 0.72 (brd), 0.59 (brd), 0.50 (brd), 0.26 (brd), 0.20 (brd) ppm; IR (KBr) υ 2927, 2855, 1608, 1458, 1403, 1378, 1256, 1115, 889, 814, 750, 727, 696 cm⁻¹.

Supporting Figures and Tables



Figure S1. ¹H NMR spectra of the polymers and NPF; Homo. (a), Ran.-9/1 (b), Ran.-1/1 (b), Ran.-1/9 (d), Alt. (e), and NPF (f). [400 MHz, CDCl₃, r.t.]

Note: The peaks at around 2.5–2.8 ppm indicate the methine proton of neomenthyl moiety. While the peak in the spectrum (e, **Alt.**) appears as a unimodal peak, the peaks in the spectra of (a)-(c) of **Homo., Ran.-1/1**, and **Ran.-1/9** appear as bimodal peaks attributed to the polymer tacticity. These results imply that the asymmetric field of the chiral repeating unit on **Alt.** would hardly reach the neighboring chiral units.



Figure S2. Linear dichroism (LD) and UV spectra of the polymers in film before and after thermal annealing; **Homo.** (A), **Ran.-9/1** (B), **Ran.-1/1** (C), **Ran.-1/9** (D), and **Alt** (E).



Figure S3. UV spectra (A) and CD spectra with a representative UV spectrum (B) spectra of the alternating copolymer measured at 1.0×10^{-5} M, 2.0×10^{-5} M, 3.0×10^{-5} M, 4.0×10^{-5} M, 1.0×10^{-4} M, 2.0×10^{-4} M, 3.0×10^{-4} M, 3.0×10^{-4} M, and 4.0×10^{-4} M in THF.

Note: Chain aggregation in THF affecting polymer chirality is ruled out by these spectra. The spectra taken in the concentration range of 1×10^{-5} M to 4×10^{-4} M (per residue) did not show any significant differences.



Figure S4. TG-DTA and DSC profiles of the polymers recorded under N_2 atmosphere; **Homo.** (A), **Ran.-9/1** (B), **Ran.-1/1** (C), **Ran.-1/9** (D), and **Alt.** (E). [sample weight for TD-TGA; 8.8 mg (A), 8.2 mg (B), 7.1 mg (C), 7.3 mg (D), and 3.2 mg (E): sample weight for DSC; 10.7 mg (A), 9.3 mg (B), 10.2 mg (C), 11.7 mg (D), and 8.1 mg (E)].



Figure S5. Changes in UV and CD spectra of the homopolymer and the random copolymer in film via thermal annealing; **Homo.** (A), **Ran.-9/1** (B), **Ran.-1/1** (C), and **Ran.-1/9** (D). [annealing temp. = 150 °C (A), 140 °C (B), 80 °C (C), and 60 °C (D); time* = 0.5 h, 1 h, and 2 h (A–D)] *On thermal annealing at the prescribed temperatures for 0.5 h, spectral changes were observed. However, on further heating for 1 h and 2 h, no changes were confirmed.



Figure S6. ¹H NMR (left) and IR (right) spectra of **Alt.** before (i) and after being annealed (ii). [(thermal annealing) in a film state on a glass plate, 160 °C, 24 h, under air, in the dark; (NMR) in CDCl₃, 400 MHz, r.t.; (IR) KBr pellet, r.t.]

Note: According to ref. 20b, keto defect (fluoren-9-one moiety) in a poly(fluoren-2,7-diyl) derivative shows characteristic peaks at around 7.9 ppm in ¹H NMR spectra that were assigned to the protons on the 1- and 8-positions of the fluoren-9-one ring. The spectrum, (A)-(ii) showed no clear such peaks ruling out the possibility of keto defect generation. This conclusion is supported by IR spectra, (B)-(i) and (B)-(ii), showing no significant changes on annealing at around 1500-1900 cm⁻¹ where an intense ketone C=O stretching band could appear. Thus, the chemical structure of the alternating copolymer in film was not changed by thermal annealing.



Figure S7. UV and PL spectra of the alternating copolymer in a THF solution; (a) as prepared and (b) after being annealed on a film.

Note: According to ref. 20c, an emission band at around 550 nm due to keto defect (fluoren-9-one moiety) was observed in solution for a poly(9,9-di-n-octylfluoren-2,7-diyl) where, for a polymer containing 33% of keto defect, the ratio of emission intensities of di-n-octylfluorene unit to 1/9.5. fluorenone unit was In addition. according to ref. 20d. for poly[9,9-bis(3,7,11-trimethyldodecyl)fluorene-2,7-diyl] containing only 1% of keto defect, the ratio of emission intensities of bis(3,7,11-trimethyldodecyl)fluorene unit to fluorenone unit was 1/6.2. These ratios were estimated by us using relevant figures in the references. Hence, the emission at around 550 nm is a very sensitive probe of keto defect. However, when the annealed alternating copolymer in film was re-dissolved in THF, it did not indicate the signal at around 550 nm in fluorescence due to ketone units at all (Figure S3), strongly supporting that the spectroscopic features observed for the alternating copolymer in this work is not based on keto defect. The emission band of the alternating copolymer at around 550 nm is observed only in film. This means that the band is due to inter-chain excimer formation that occurred only in the solid state.



Figure S8. Polarized micrographs of the polymers in the solid state; at room temperature (top) and at 150 °C (Homo.), 140 °C (Ran.-9/1), 80 °C (Ran.-1/1), 60 °C (Ran.-1/9), and 150 °C (Alt.) (bottom).

Note: **Homo.** and **Ran.-9/1**, **-1/1**, **-1/9** showed textures indicative of liquid crystalline (LC) phase at r.t., but the textures almost disappeared on heating at the prescribed temperatures. On the other hand, while **Alt.** did not show any clear texture and was opaque at room temperature, it exhibited a clear texture at 150 °C. The polymer chains of **Homo.** and **Ran.-m/n** at room temperature seem to be aligned as obtained, and the alignment was not stable at an elevated temperature. In contrast, heating facilitates chain alignment of the alternating copolymer (**Alt.**).

	In a THF solution ^a				In film ^b			
	$\lambda_{Abs.max}$	$g_{ m CD} imes 10^4$	$\lambda_{Em.max}$	$\Phi_{\rm Em}^{\ \ c}$	$\lambda_{Abs.max}$	$g_{ m CD} imes 10^4$	$\lambda_{Em.max}$	$\Phi_{\rm Em}{}^{\rm c}$
Homo.	373	-0.7	415	0.74	368	-1.1	438	0.39
Ran9/1	374	-0.5	415	0.74	369	-1.1	439	0.42
Ran1/1	375	-0.2	416	0.75	370	-0.5	439	0.42
Ran1/9	378	d	417	0.76	376	-0.4	439	0.47
Alt.	384	_d	416	0.53	378	-0.2	422	0.03
Alt. (annealed ^e)	-	-	_	-	393	+260	520	0.04
NPF	270	-3.5	308	0.44	-	_	-	_

Table S2. Optical properties: absorption maximum ($\lambda_{Abs.max}$), anisotropy factor in the ground state (g_{CD}), emission maximum ($\lambda_{Em.max}$), and internal fluorescence quantum yield (Φ_{Em}) of the polymers in a THF solution and in film and **NPF** in a THF solution.

^aConc. = 1.0×10^{-5} M per residue, cell length = 1.0 cm, temp. = room temperature. ^bDrop-cast film on a quartz plate (size 1 cm × 2 cm, thickness 1 mm). ^cInternal fluorescence quantum yield determined by using an integral sphere. ^dUnder the detection limit (CD < \pm 0.04 mdeg). ^eThe film was annealed at 160 °C for 48 h in the dark.

Note: Although the precise reason, why **Alt.** exhibits lower fluorescence quantum yields in both solution and film than the others, is not obvious at the present stage, the reason might come from structural flexibility of **Alt.** The proposed structural flexibility of **Alt.** could facilitate a thermal relaxation of the excitation energy, resulting in the low fluorescence quantum yield of **Alt.**



Figure S9. IR spectra of the homopolymer and the copolymers (KBr); Homo. (A), Ran.-9/1 (B), Ran.-1/1 (C), Ran.-1/9 (D), and Alt. (E).



Figure S10. CPL and fluorescence (PL) spectra of thermally annealed films of the homopolymer and the random copolymers. λ_{ex} : in PL spectra, 366 nm for all the film samples; in CPL spectra, 350 nm for all the polymers.