

Electronic Supplementary Information for:

**Synthesis and Efficient Circularly Polarized Light Emission of An Optically Active
Hyperbranched Poly(fluorenevinylene) Derivative**

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Experimental Details

Materials. (-)- Menthol (TCI), *p*-toluenesulfonyl chloride (tosyl chloride) (Wako), fluorene (TCI), *n*-BuLi (1.57 M hexane solution) (Kanto), 1-iodopentane (Aldrich), HBr (33 wt%, acetic acid solution) (Wako), pyridine (Wako), CHCl₃ (TCI), methanol (Wako), benzylbromide (TCI), *t*-BuOK (TCI), acetone (Wako), and Silica-gel 60 N (neutral) (Kanto) were used as purchased. Paraformaldehyde (TCI) was dried under vacuum in the presence of P₂O₅. Tetrahydrofuran (THF) (Wako) was dried with sodium benzophenone ketyl and distilled immediately before use.

Menthyl tosylate. This compound was synthesized according to the reported method [Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermihle, D.; Krieger, C.; Nolte, M.; Werne, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590] with modifications. To a solution of (-)-menthol (20.00 g, 0.127 mol) in 41 mL of pyridine cooled at 0°C was slowly added tosyl chloride (26.60g, 0.139 g) dissolved in 60mL of CHCl₃. The reaction mixture was warmed to room temperature and was stirred for 3 h. Removal of solvents gave a crude product. Recrystallization of the crude material from a mixture of methanol and water afforded colorless crystals. Yield 34.2 g (87.1%).

9-Neomenthylfluorene. This compound was synthesized according to the reported method [A. Gutnov, H.-J. Drexler, A. Spannenberg, G. Oehme and B. Heller, *Organometallics* 2004, **23**, 1002] with modifications. The reactions were carried out under nitrogen atmosphere. To a solution of fluorene (26.07 g, 0.157 mol) in 120 mL of THF cooled at 0°C was slowly added 100 mL (0.157 mol) of *n*-BuLi (1.57 M in hexane solution). The reaction mixture was stirred for 25 min at 0°C. After the reaction system was cooled to -78°C, menthyl tosylate (24.00 g, 0.0774 mol) dissolved in 120 mL of tetrahydrofuran was added in several portions. The reaction mixture was stirred at room temperature for 30 min and then under reflux for 15 h. The reaction mixture was poured into a large excess of water, and the crude product was extracted with CHCl₃. 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. Yield 5.25 g (22.3 %).

9-Neomenthyl-9-pentylfluorene. The reactions were conducted under nitrogen atmosphere. To a solution of 9-neomenthylfluorene (4.00 g, 0.0132 mol) in 70 mL of tetrahydrofuran cooled at 0°C was slowly added 10.0 mL (0.0157 mol) of *n*-BuLi (1.57 M in hexane solution). The reaction system was stirred at 0°C for 24 h. 1-Iodopentane (3.90 g, 0.0197 mol) dissolved in 10 mL of tetrahydrofuran was slowly added to the reaction mixture. The resulting mixture was warmed to room temperature and was stirred for 24 h. The reaction mixture was poured into a large excess of water, and the crude product was extracted with CHCl₃. 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 4.58 g (92.4 %). Anal: ¹H NMR (270 MHz, CDCl₃, TMS, 25°C): δ 7.71-7.19 (m, 8H, ArH), 2.61-2.55 (m, 1H, -CH-), 2.19-0.07 (m, 29H); HRMS (EI) Calcd for C₂₈H₃₈ 374.29735, found 374.29675; [α]_D²⁵ -51° (CDCl₃, 1 g/dL, 1-dm cell).

2,4,7-Tris(bromomethyl)-9-neomenthyl-9-pentylfluorene. To a mixture of 9-neomenthyl-9-pentylfluorene (3.78, 0.0101 mol) and paraformaldehyde (20.2 g, 0.250 mol) cooled at 0°C was added dropwise 43.1 mL of 33 wt% HBr (20.2 g, 0.250 mol) in acetic acid solution. The reaction mixture was warmed to 70°C and was stirred for 36 h. The mixture was poured into a large excess of water, and the crude product was extracted with CHCl₃. The organic layer was dried on MgSO₄. The crude product was purified by silica-gel column chromatography using a mixture of toluene and *n*-hexane (1/5, v/v) as eluent to remove the di-substituted compound from the mixture of di-, tri- and tetra-substituted products. The mixture of tri- and tetra-substituted products obtained by chromatography was dissolved in a small amount of CHCl₃. To this solution was added a large excess of methanol. On removal of solvents from the soluble part, the target compound appeared as white precipitates which were collected by filtration. Yield 2.20 g (33.5 %). Anal: ¹H NMR (270 MHz, CDCl₃, TMS, 25°C): δ 7.9-7.27 (m, 5H, ArH), 4.91-4.76 (m, 2H, CH₂Br at 4-position of fluorene), 4.62-4.55 (m, 4H, CH₂Br at 2- and 7-position of fluorene), 2.57-2.53 (m, 1H, -CH-), 2.2-0.94 (m, 29H); HRMS (EI) Calcd for C₃₁H₄₁Br₃ 650.0758, found 650.0758; [α]_D²⁵ -58° (CDCl₃, 1 g/dL, 1-dm cell). *The 9-position carbon of the fluorene ring of this compound is a center of chirality unlike that of 9-neomenthylfluorene or 9-neomenthyl-9-pentylfluorene. Hence, two diastereomers are possible. The ratio of the two diastereomers was estimated to be 56/44 on the basis of the peak intensity ratio of the two groups of signals centered at 2.52 ppm and 2.57 ppm, respectively, based on the methine proton at the 1-position of the neomenthyl group. The absolute configurations of the diastereomers are not known.*

Polymerization. To a dry tetrahydrofuran solution (30 mL) of 2,4,7-tris(bromomethyl)-9-neomenthyl-9-pentylfluorene (0.400 g, 0.615 mmol) and benzylbromide (0.092 g, 0.54 mmol) was added *t*-BuOK (0.200 g, 1.79 mmol) dissolved in dry tetrahydrofuran (10

mL). The mixed solution was stirred at room temperature for 12 h. *t*-BuOK (0.200 g, 1.79 mmol) and benzylbromide (15.3 g, 90.0 mmol) were then added in this order to the reaction mixture. The reaction system was further stirred at 50°C for 24 h. Water (2 mL) was added to the mixture to quench the reaction. The quenched reaction mixture was poured into a large excess of methanol. Precipitated polymer was collected with a centrifuge and dried at 60°C for 2h. Yield 0.25 g, (61%). Mn 29800, Mw 249500 (vs. PSt). The obtained polymer was dissolved in 2 mL of tetrahydrofuran and poured into a large excess of acetone. The acetone-insoluble and -soluble parts were separated with a centrifuge. Acetone-insoluble, higher-molecular-weight part (58%): Mn 74300, Mw 352400 (vs. PSt), $[\alpha]_D -64^\circ$ (in CDCl₃, 1 g/dL, 0.1-dm cell). Acetone-soluble, lower-molecular-weight part: Mn 7300, Mw 27100 (vs. PSt), $[\alpha]_D -67^\circ$ (in CDCl₃, 1 g/dL, 0.1-dm cell).

Fabrication of polymer into a film form. The acetone-insoluble polymer (10 mg) was dissolved in CHCl₃ (1 mL). A drop of the solution (ca. 0.05 mL) was placed on a 1-mm thick quartz plate (1 cm x 2 cm), and then the plate was spun at 1000 rpm for 1 min to form a spin-coated film on the quartz plate. The film was dried under vacuum at room temperature for 2 h.

Measurements. The ¹H NMR spectra were recorded on a JEOL JNM-ECP600NK spectrometer (600 MHz for ¹H measurement) and a JNM-EX270 spectrometer (270 MHz for ¹H 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 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). Absorption and emission spectra were measured at room temperature with a JASCO V-560 spectrophotometer. Fluorescent spectra were taken on a JASCO FP-777W fluorescence spectrophotometer. Samples for fluorescent measurements were degassed by N₂ bubbling for 10 min. CD spectra were taken on a JASCO J-820 spectrometer. FT-IR spectra were measured using a ThermoFischer Scientific Nexus 870 spectrometer. Optical rotation was measured with a JASCO P-1030 digital polarimeter. Spin-coating was preformed using an apparatus designed by Sapporo Nambu Mechatro Machinery. DT-TGA and 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 measurements. CPL-fluorescent spectra of the polymer films were measured using a pulsed laser diode at 375 nm (LDH-P-C-375 and PDL800-B, PicoQuant) as an excitation light. The film was irradiated with the excitation light from the surface normal. The collinearly transmitted photoluminescence was collected by a pair of achromatic doublet lenses, and the circular polarization was separated by the combination of achromatic quarter-wave plate and linear polarizer. Finally, the circularly polarized photoluminescence spectra were taken on a high-sensitive charge-coupled device (CCD) spectrometer (SR-303i and iDus420A, Andor

Technology). CPL-fluorescent spectra of the solution samples were taken on a JASCO CPL-200 (NAIST, Japan). CPL transmission spectra were acquired on an optical spectrometer (USB2000, Ocean Optics) through broad-band $\lambda/4$ plates and a linear polarizer using a 500-W halogen lamp as the light source.

Supporting Results and Discussions

^1H NMR spectra of the polymers and estimation of DB. DB values were estimated from the ^1H NMR spectra (Fig. S1) according to the following calculations. The hyperbranched polymers are considered to consist dendritic or branching units (D), linear units (L), and terminal units (T) (Chart S1). The L and T units can consist of multiple isomeric structures, i.e., L1-L3 and T1-T4. In the NMR spectra, unreacted Br-CH₂- groups show signals around 4.5-5 ppm among which the higher-magnetic-field peak and the lower-magnetic-field peak are based on those at the 2- and 7-positions and at the 4-position, respectively. In addition, a methine proton of the neomenthyl group shows a peak around 2.5 ppm. From the relative signal intensities of these peaks, one can obtain information on the [2- or 7-CH₂Br]/[4-CH₂Br] ratio and the [-CH₂Br] / [neomenthyl] ratio, where [2- or 7-CH₂Br] + [4-CH₂Br] = [-CH₂Br]. With this information, [D]/[L]/[T] ratios for the polymers can be estimated, and degree of branching (DB) can be calculated according to the definition, $\text{DB} = ([\text{D}] + [\text{T}])/([\text{D}] + [\text{T}] + [\text{L}])$. Because each individual fraction of L1-L3 and T1-T4 cannot be identified in the NMR spectra, we assume that [L1] = [L2] = [L3] and [T1] = [T2] = [T3] = [T4] for simplicity. With this assumption, the sum concentration of linear units (L1-L3) and that of terminal units (T1-T4) can be determined according to $[\text{L}] = 2[2\text{- or }7\text{-CH}_2\text{Br}] + [4\text{-CH}_2\text{Br}]$ and $[\text{T}] = 4[2\text{- or }7\text{-CH}_2\text{Br}] + 3[4\text{-CH}_2\text{Br}]$.

For the acetone-insoluble polymer, we know the followings from the peak intensities giving [2- or 7-CH₂Br], [4-CH₂Br], and [neomenthyl]:

$$[2\text{- or }7\text{-CH}_2\text{Br}]/[4\text{-CH}_2\text{Br}] = 1/1 \text{ (ratio of the two -CH}_2\text{Br signals)}$$

$$[\text{D}] + [\text{L}] + [\text{T}] = 1 \text{ (intensity of the methine signal of the neomenthyl group)}$$

$$2[\text{L}] + 4[\text{T}] = 2.63 \text{ (intensity of the 2 or 7-CH}_2\text{Br signal)}$$

By resolving the simultaneous equations, we obtain [D]/[L]/[T] = 0.23/0.23/0.54 and DB = 0.77.

For the acetone-soluble polymer, we know the followings from the peak intensities giving [2- or 7-CH₂Br], [4-CH₂Br], and [neomenthyl]:

$$[2\text{- or }7\text{-CH}_2\text{Br}]/[4\text{-CH}_2\text{Br}] = 1/1.12 \text{ (ratio of the two -CH}_2\text{Br signals)}$$

$$[\text{D}] + [\text{L}] + [\text{T}] = 1 \text{ (intensity of the methine signal of the neomenthyl group)}$$

$$2[\text{L}] + 4[\text{T}] = 3.06 \text{ (intensity of the 2 or 7-CH}_2\text{Br signal)}$$

By resolving the simultaneous equations, we obtain [D]/[L]/[T] = 0.10/0.27/0.63 and DB = 0.73.

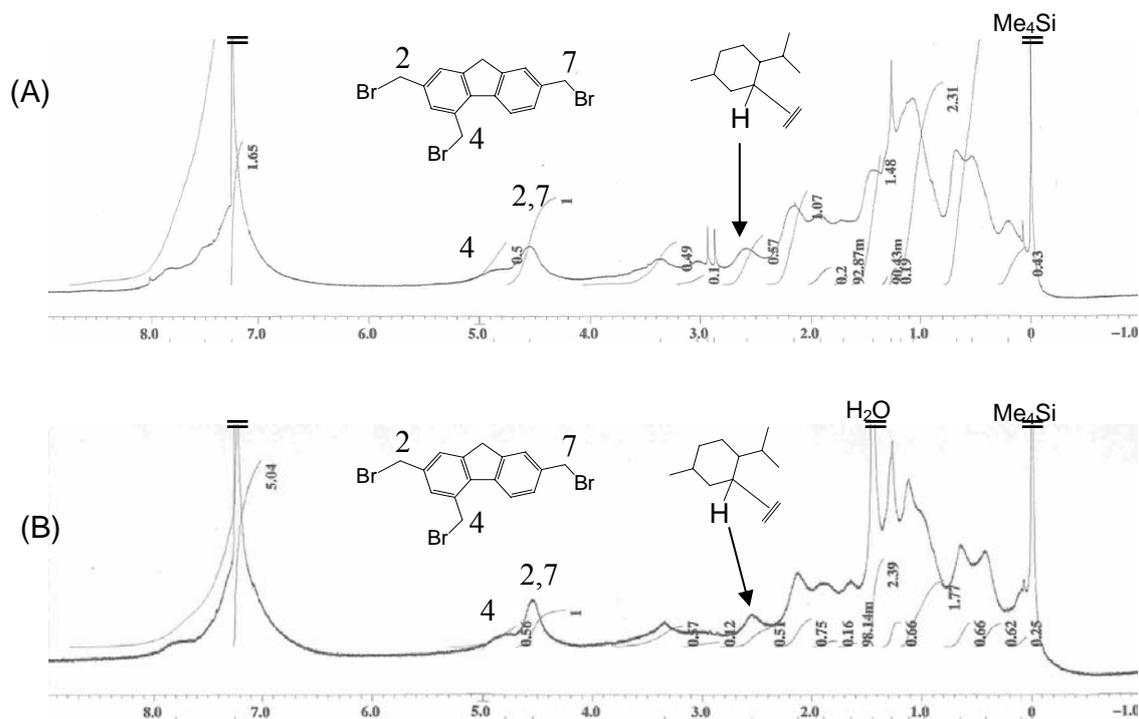


Fig. S1 ^1H NMR spectra of the acetone-insoluble polymer (A) and the acetone-soluble polymer (bottom). [600 MHz, CDCl_3 , 60°C]

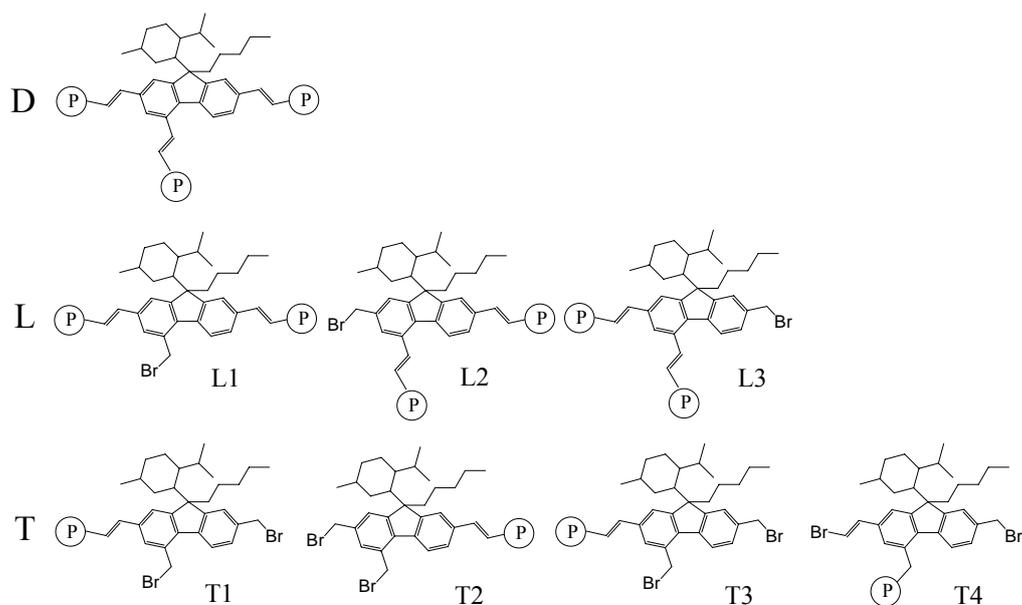
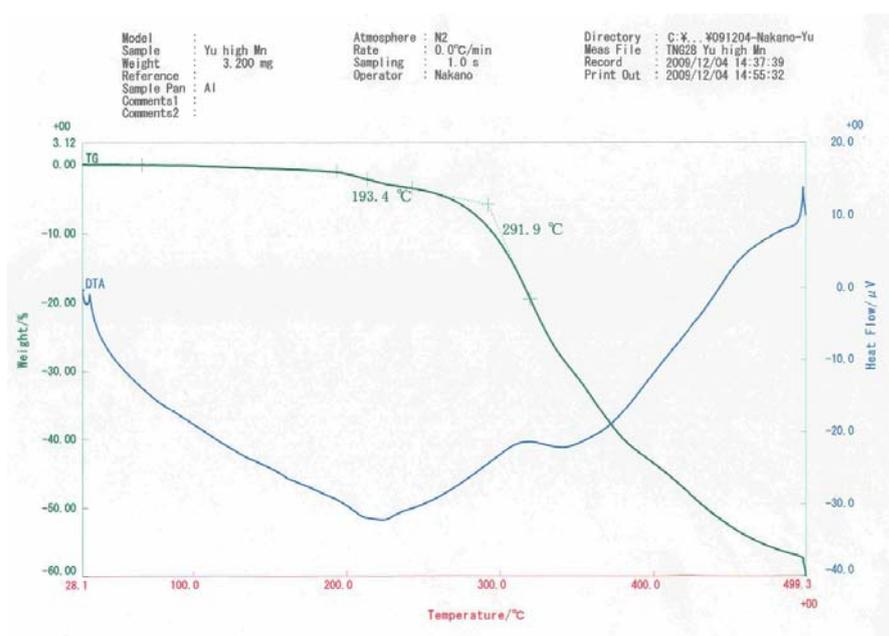


Chart S1. Unit structures in hyperbranched polymers. P represents a polymer chain.

Thermal analyses on the acetone-insoluble polymer. Fig. S2 shows DT-TGA and DSC profiles for the acetone-insoluble polymer. The polymer started to decompose around 190°C in TGA analyses. The polymer indicated no clear exothermic or endothermic transitions in DSC analyses.

A. TG-DTA



B. DSC

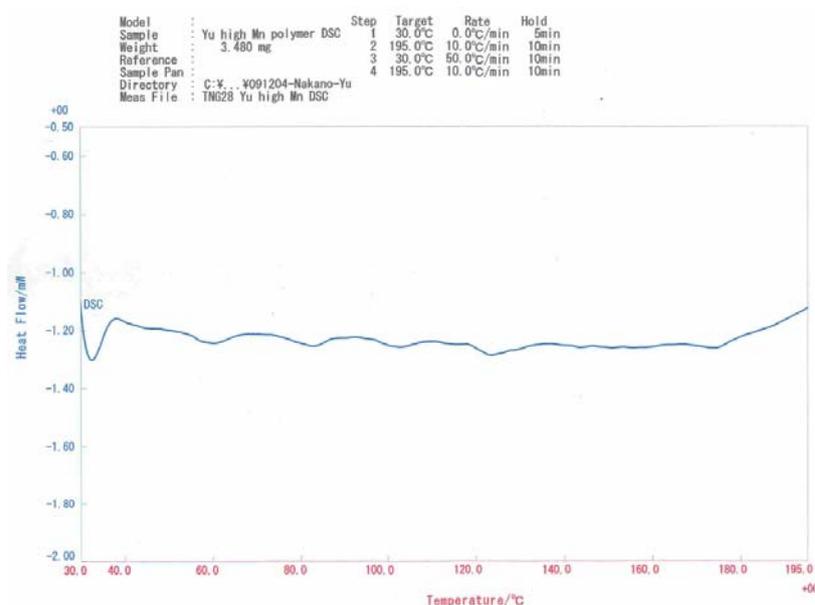


Fig. S2 TG-DTA (A) and DSC (2nd heating run) (B) profiles of the acetone-insoluble polymer. TG-DTA conditions: sample weight = 3.20 mg, heating rate = 10°C/min, atmosphere = nitrogen. DSC conditions: sample weight = 3.48 mg, heating rate = 10°C/min, atmosphere = nitrogen.

CPL transmission spectra. Fig. 3S shows the CPL transmission spectra for the film sample of the acetone-insoluble polymer. The difference observed for right-handed and left-handed CPL transmission was much smaller than that for right-handed and left-handed emission (Figure 3A). G values for CPL transmission are:

at 430 nm

$$g = 2(IL-IR)/(IL+IR) = 2 \times (80.933 - 80.074) / (80.933 + 80.074) = 0.0665$$

at 490 nm

$$g = 2(IL-IR)/(IL+IR) = 2 \times (85.142 - 84.351) / (85.142 + 84.351) = 0.0093$$

These values are smaller than g_{PL} values by the order of 10^{-1} . In addition, L-CPL transmission is larger than R-CPL transmission. These results support the conclusion that the observed CPL emission is not due to ordering in the film.

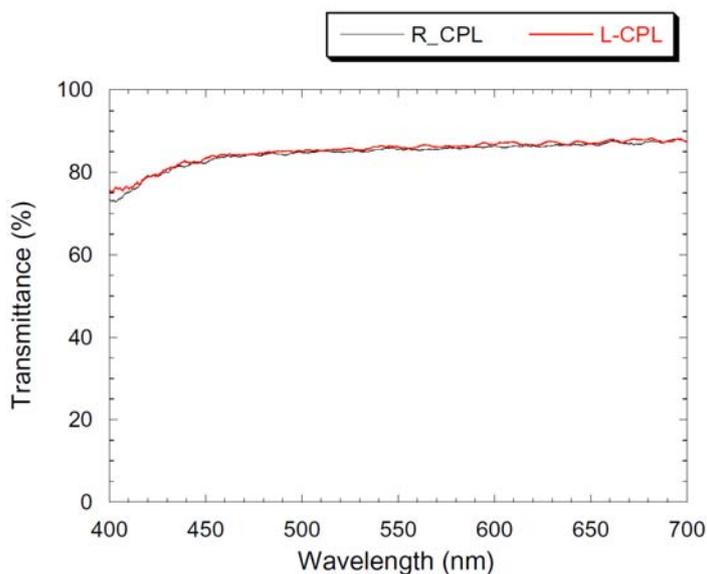
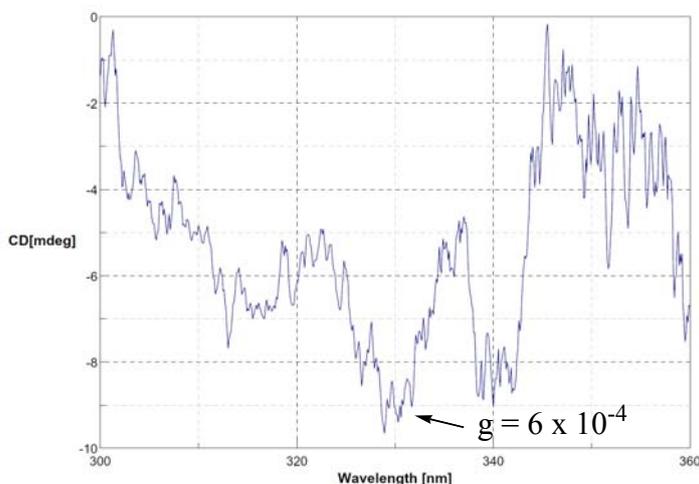


Fig. S3 CPL transmission spectra for the film sample of the acetone-insoluble polymer.

CPL emission from 9-neomenthyl-9-pentylfluorene and the hyperbranched polymer in a THF solution. Fig. S4 indicates CPL emission spectra of 9-neomenthyl-9-pentylfluorene and the hyperbranched polymer in a THF solution. 9-Neomenthyl-9-pentylfluorene showed moderate CPL emission with a g value as high as 6×10^{-4} . The hyperbranched polymer showed only negligible CPL emission. These results mean that observed intense CPL emission from the polymer film is not due to 9-neomenthyl-9-pentylfluorene chromophore inserted into the polymer chain and also that the solid, amorphous state is important in achieving effective CPL emission.

(A) 9-Neomenthyl-9-pentylfluorene



(B) Hyperbranch polymer

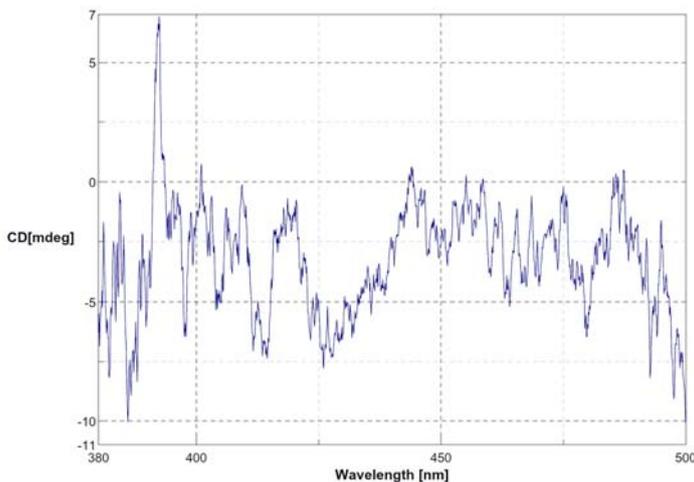


Fig. S4. CPL emission spectra of 9-neomenthyl-9-pentylfluorene (A) and the hyperbranched polymer (B) in a THF solution (conc. 5.9×10^{-5} M). Excitation wavelength was 264 nm for A and was 314 nm for B.

CPL emission from the lower-molecular-weight polymer (film). The lower-molecular-weight polymer (acetone-soluble part, Mn 7300, Mw/Mn 3.71, $[\alpha]_D^{25} -67^\circ$ (CHCl_3 , 1 g/dL, 0.1-dm cell), DB 0.73) showed CPL emission (Fig. S5). However, CPL efficiency was much less than that of the higher-molecular-weight polymer (Mn 74300), indicating that an extended hyperbranched structure is important in achieving efficient CPL emission.

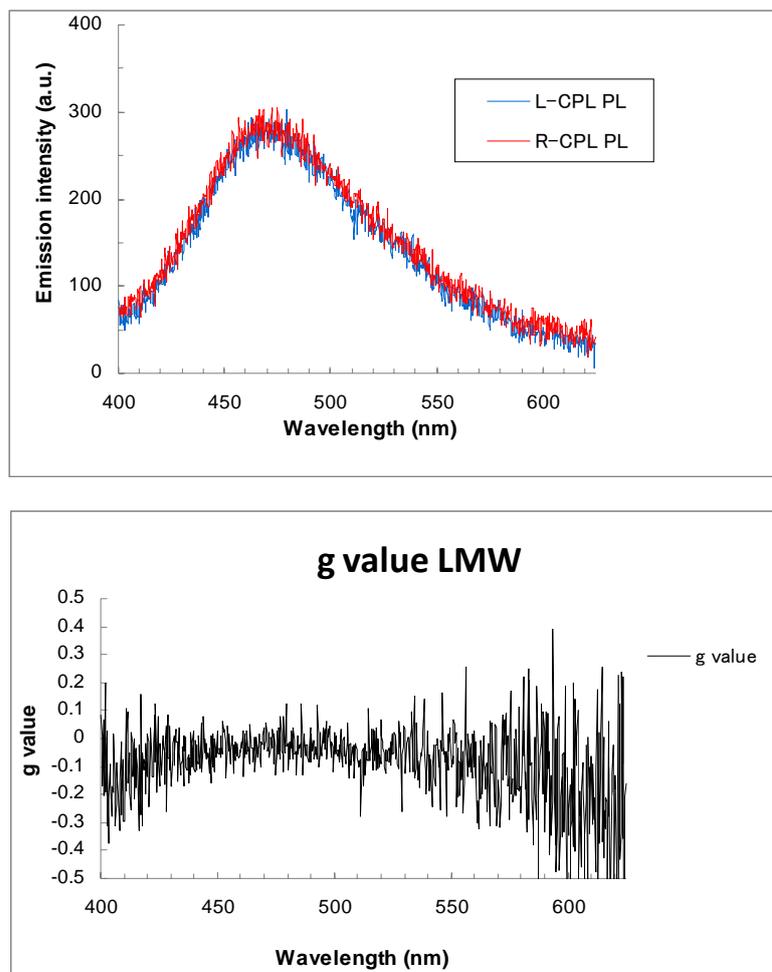


Fig. S5. CPL emission spectrum (top) and g-vs.-WL plots for the lower-molecular-weight polymer (film sample).