Control over Chiroptical and Electronic Properties of Poly(9,9'-bifluorenylidene) Bearing Chiral Side Chains

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Experimental section

Materials. All chemicals were purchased from Aldrich, Tokyo Chemical Industry, Kanto Chemical, or Wako Pure Chemical Industries and used as received without further indication. Air and water sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques.

General Procedures. NMR spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer by using tetramethylsilane (0 ppm for ¹H NMR) as an internal standard. MALDI/TOF-MS measurements were performed on an AXIMA-CFR Plus (Shimadzu) with dithranol as a matrix. Gel permeation chromatography (GPC) for polymers was performed in tetrahydrofuran (THF) solution using a TOSHO GPC system (HLC-8320GPC EcoSEC) equipped with two TSK gel Super-Multipore HZ-M columns and a UV detector (254 nm). The molecular weight (M_n) and polydispersity index (PDI) of polymers were calculated on the basis of a polystyrene calibration. Thermogravimetric analysis (TGA) was conducted with Rigaku Thermo plus 8120 at heating rate of 10 °C/min under flowing argon gas. UV-vis absorption spectra were recorded on a JASCO V-670 spectrophotometer in a quartz cuvettes of 1 mm path length. Circular dichroic (CD) spectroscopic analysis was performed on a JASCO J-725 using 1 mm length quartz cuvettes in the wavelength range from 250 nm to 700 nm with a scan rate of 200 nm/min. For variable-temperature UV-vis and CD spectra: the initial UV-vis and CD spectra were recorded at 25 °C. Then the temperature was increased at 2 °C /min from 25 °C to 50 °C in chloroform (CHCl₃) and 25 °C to 90 °C in methylcyclohexene (MCH). The thin films were fabricated using spin-coating method by depositing 5 mg/mL CHCl₃ solution on a clean glass or quartz substrate and spinning at 500 rpm for 20s and 3000 rpm for 10s. The ionization potentials of solid samples obtained by spin-coating from 5 mg/mL CHCl₃ solution at 500 rpm for 60s were determined by a photoelectron yield spectrometer (Riken Keiki AC-3).

Theoretical Calculations. Computational analysis was carried out with Gaussian 09, Revision E.01 suite of programs^[S1] with default thresholds and algorism. Geometry optimization of model compound were conducted at the M06-2X/6-31G(d) level of theory. ^[S2] The Cartesian coordinates of model compound are given in Table S2. The time-dependent density functional theory (TDDFT) calculations at the optimized geometries were conducted at the same level of theory.

[S1] Gaussian 09 (Revision E.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[S2] Y. Zhao, D. G. Truhlar, Acc. Chem. Res. 2008, 41, 157.

Synthesis of compound 1:

4-Bromoveratrol (5 g, 23.0 mmol) was dissolved in anhydrous THF (65 mL) by stirring under argon. The reaction temperature was reduced to -78 °C by using a slush bath (ethyl acetate/liq. N₂) and continued stirring for 10 minutes. 2.65 M n-BuLi solution in hexane (10.4 mL, 27.6 mmol) was added dropwise and the mixture was stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.75 g, 36.3 mmol) was added rapidly to the reaction mixture, then the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel) with hexane: CHCl₃ (2:1) as eluent to provide the pure product as white powder (4.31 g, 71%). 1 H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 1.34 (s, 12H), 3.88 (s, 3H), 3.90 (s, 3H), 6.88 (d, 1H, J = 8.2 Hz), 7.28 (d, 1H, J = 8.2 Hz), 7.42 (d, 1H, J = 8.2 Hz). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 24.61, 24.82, 55.71, 55.81, 83.61, 110.48, 116.56, 128.53, 148.33, 151.63. MALDI/TOF-MS: m/z calcd 264.13; found 265.11.

Synthesis of compound 2:

A 50 mL two-necked round bottom flask was charged with 2,7-dibromo-9-fluorenone (400 mg, 1.18 mmol) and compound **1** (681 mg, 2.58 mmol), sodium carbonate (740 mg, 7 mmol), then evacuated and back-filled with argon gas three times. Then 12.0 mL of dry toluene, 3.0 mL EtOH and 3.0 mL of water which were already deaerated for 30 min were added under argon. The mixture was stirred vigorously at 90 °C, tetrakis(triphenylphosphine)palladium (40.58 mg, 0.1 mmol) was then added to the reaction mixture. After the stirring overnight, the mixture was then allowed to cool down to room temperature and the solvent was evaporated by reduced pressure. Water was poured into the reaction mixture and extracted by CHCl₃ for three times, the combined organic layer was washed by brine and dried over anhydrous MgSO₄. The crude product was purified by column chromatography (silica gel) with hexane: CHCl₃ (2:1) as the eluent, affording the pure product as an orange powder (368.4 mg, 69%). ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 3.95 (s, 6H), 3.98 (s, 6H), 6.97 (d, 2H, *J* = 8 Hz), 7.13 (d, 2H, *J* = 8 Hz), 7.19 (d, 2H, *J* = 8 Hz), 7.57 (d, 2H, *J* = 8 Hz), 7.70 (d, 2H, *J* = 8 Hz), 7.89 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298

K): δ (ppm) 56.10, 56.13, 109.95, 111.57, 119.26, 120.77, 122.76, 132.83, 133.01, 135.26, 142.02, 142.77, 149.22, 149.39, 194.20. MALDI/TOF–MS: m/z calcd 452.5; found 453.79.

Synthesis of compound 3:

The compound **3** was synthesized according to literature procedures. ^[S3] A 50 mL two-necked round bottom flask charged with a mixture of 2,7-dibromo-9-fluorenone (250 mg, 0.74 mmol) and hydrazine monohydrate (5.5 mL) in ethanol (10 mL) were heated at reflux overnight. After cooling down to room temperature, the reaction was quenched by water and resulting aqueous solution was extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous MgSO₄. After removal of solvent under reduced pressure, the crude product was obtained as a yellow powder and used for the next reaction without further purification (247.5 mg, 95%). ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 6.54 (s, 4H), 7.47–7.51 (m, 4H), 7.58–7.63 (m, 4H), 7.87 (s, 2H), 8.03 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 120.93, 121.45, 121.77, 122.16, 124.09, 128.29, 131.31, 132.40, 136.15, 138.97, 139.40, 142.38.

Synthesis of compound 4:

The compound **4** was synthesized according to literature procedures. ^[S3] A 50 mL two-necked round bottom flask was charged with compound **3** (200 mg, 0.568 mmol) with THF (5 mL). The activated MnO₂ (3.13 mmol, 272 mg) was added in one portion. Stirring was continued for 30 min, and then the mixture was filtered through a plug of Celite[®] pad and washed with CHCl₃. After removal of solvent under reduced pressure, the crude product was obtained quantitatively as a pink solid (198 mg, quantitatively). ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 7.44 (d, 2H, *J* = 8 Hz), 7.64 (s, 2H), 7.76 (d, 2H, *J* = 8 Hz). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 120.53, 122.06, 122.13, 127.92, 129.33, 134.45.

[S3] J. Bauer, L. Hou, J. C. M. Kistemaker and B. L. Feringa, J. Org. Chem., 2014, 79, 4446.

Synthesis of compound 5:

The compound 5 was synthesized according to literature procedures. ^[S4] A 50 mL

two-necked round bottom flask was charged with the compound 2 (55 mg, 0.122 mmol) and Lawesson's reagent (25 mg, 0.061 mmol) was added with 5 mL of toluene. The solution was heated up to 90 °C under the flow of argon gas for 4 h, during which the mixture turned dark green. After the compound 2 was completely reacted, compound 4 (0.244 mmol, 85.4 mg) dissolved in 3 mL toluene was injected into mixture rapidly. The solution turned into dark red. After the stirring overnight, the mixture was then allowed to cool down to room temperature and the solvent was extracted by water and CHCl₃ for three times, the combined organic layer was washed with brine and dried over anhydrous MgSO₄. The crude product was purified by column chromatography (silica gel) with CHCl₃ as the eluent, affording the pure product as a dark red solid (63.8 mg, 69%). ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 3.93 (s, 6H), 3.98 (s, 6H), 6.95 (d, 2H, J = 8 Hz) 7.12–7.13 (m, 2H), 7.19–7.22 (m, 2H), 7.49 (d, 2H, *J* = 8 Hz), 7.56–7.59 (m, 4H), 7.72 (d, 2H, *J* = 8 Hz), 8.49 (s, 2H), 8.71 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 55.97, 56.25, 109.94, 111.49, 119.57, 120.40, 120.75, 121.31, 125.47, 128.98, 129.19, 131.89, 133.71, 138.62, 139.72, 140.36, 148.80, 149.20. MALDI/TOF-MS: m/z calcd 758.49; found 758.95.

[S4] D. Pijper, B. L. Feringa, Angew. Chem. Int. Ed., 2007, 46, 3693.

Synthesis of compound 6:

The compound **6** was synthesized according to literature procedures. ^[S5] A 50 ml twonecked round bottom flask was charged with compound **5** (50 mg, 0.066 mmol), and evacuated and back-filled with argon three times. Anhydrous DCM (10 ml) was added to the flask via syringe, BBr₃ (5 ml, 0.4 mmol) was added to the reaction mixture slowly at 0 °C and the solution was stirred overnight at room temperature. Methanol was then added slowly to quench the reaction and the solvent was removed by evaporation under reduced pressure. The resulting dark brown powder was washed by water and extracted with ethyl acetate (EtOAc) for three times. Then combined organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was evaporated and the obtained oil residue was purified through column chromatography (silica gel) with hexane: EtOAc (2:1) as the eluent to afford pure compound **6** as a red powder (46 mg, quantitatively). ¹H NMR (THF-d₈, 400 MHz, TMS, 298 K): δ (ppm) 6.89 (t, 2H, *J* = 8 Hz) 7.12–7.20 (m, 4H), 7.64–7.71 (m, 4H), 7.83–7.89 (m, 4H), 8.03–8.06 (m, 2H), 8.17–8.20 (m, 2H), 8.64 (d, 2H, J = 7.6 Hz), 8.85 (d, 2H, J = 8 Hz). ¹³C NMR (THF-d₈, 100 MHz, TMS, 298 K): δ (ppm) 113.55, 115.37, 118.03, 120.18, 120.66, 121.49, 124.90, 128.64, 129.10, 131.83, 132.30, 138.27, 139.02, 139.64, 145.50, 145.80. MALDI/TOF–MS: m/z calcd 702.39; found 702.78. Elemental analysis: Anal. Calcd for C₃₈H₂₂Br₂O₄•1.5H₂O₁ C, 62.52; H, 3.43; Found: C, 62.11; H, 3.03.

[S5] C. Pan, K. Sugiyasu, Y. Wakayama, A. Sato, M. Takeuchi, *Angew. Chem. Int. Ed.* **2013**, *52*, 10775.

Synthesis of (*R*)-2-methyloctyl-*p*-toluenesulforate:

The compound was synthesized according to literature. ^[S6] A 50 mL two-necked round bottom flask was charged with solution of (R)-(–)-2-nonanol (315 mg, 2.19 mmol) in pyridine (5 mL), while keeping the solution at –5 °C in an ice/salt bath under the argon atmosphere. Subsequently, *p*-toluenesulfonyl chloride (502 mg, 2.63 mmol) was added to the mixture, which was kept stirring overnight at 0 °C. The excess of *p*-toluenesulfonyl chloride was slowly quenched by cold water. Then the mixture was extracted by CHCl₃ three times. The organic layer was collected and washed with 1 M H₂SO₄, and 0.4 M CuSO₄ until no color change was observed in the copper sulfate, then the solution was washed once with water. The organic layer was dried over anhydrous MgSO₄, filtration and concentration of the filtrate gave (*R*)-2-methyloctyl-*p*-toluenesulforate as colorless oil (221.5 mg, 34%).

¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 0.88 (t, 3H, J = 6.8 Hz), 1.18– 1.28 (m, 12H), 1.47–1.63 (m, 3H), 2.46 (s, 3H), 4.59–4.64 (m, 1H), 7.34 (d, 2H, J = 8 Hz), 7.81 (d, 2H, J = 8 Hz). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 14.03, 20.83, 21.57, 22.57, 24.83, 29.02, 29.04, 31.63, 36.44, 80.69, 127.68, 129.65, 134.54, 144.32. MALDI/TOF–MS: m/z calcd 282.44; found 283.11.

Synthesis of (S)-2-methyloctyl-p-toluenesulforate:

(S)-2-methyloctyl-*p*-toluenesulforate was synthesized in a similar fashion as the description above and obtained as colorless oil (232.8 mg, 36%)

¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 0.88 (t, 3H, J = 6.8 Hz), 1.17– 1.29 (m, 12H), 1.46–1.61 (m, 3H), 2.45 (s, 3H), 4.59–4.63 (m, 1H), 7.34 (d, 2H, J = 8Hz), 7.80 (d, 2H, J = 8 Hz). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 14.00, 20.78, 21.52, 22.53, 24.78, 29.00, 31.60, 31.75, 36.40, 80.64, 127.63, 129.62, 134.49, 144.31. MALDI/TOF–MS: m/z calcd 282.44; found 282.34.

Synthesis of (*R*)–BF:

The compound (*R*)–**BF** was synthesized according to literature. ^[S6] A 50 mL roundbottom flask was charged with compound **6** (50 mg, 0.0712 mmol) and K₂CO₃ (98 mg, 0.712 mmol). The flask was evacuated and refilled with argon gas three times. After addition of DMSO (10 mL), the mixture was stirred at 80 °C for 2 hours. The (*S*)-2-methyloctyl-*p*-toluenesulforate (90.5 mg, 0.3205 mmol) was added, the mixture was stirred at 80 °C for 2 days. After the completion of reaction, the mixture was allowed to cool down to the room temperature. The solvent was distilled under reduced pressure. The resulting solid was extracted with water and CH₂Cl₂ three times. The combined organic layer was washed with brine and dried over anhydrous MgSO₄. The crude product was purified by column chromatography (silica gel) with Hexane: CHCl₃ (1:1) as the eluent. (*R*)–**BF** was obtained as a red powder (86 mg, 53%).

¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 0.84–0.91 (m, 12H), 1.29–1.34 (m, 32H), 1.80–1.86 (m, 8H), 4.01–4.04 (m, 4H), 4.07–4.10 (m, 4H), 6.96 (d, 2H, J = 8 Hz), 7.14-7.20 (m, 4H), 7.48 (d, 2H, J = 8 Hz), 7.54–7.58 (m, 4H), 7.70 (d, 2H, J = 8 Hz), 8.50 (s, 2H), 8.72 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 14.10, 19.90, 22.67, 25.63, 29.35, 29.69, 29.76, 31.84, 36.72, 36.76, 117.13, 117.72, 120.33, 120.44, 120.84, 121.21, 125.50, 128.87, 129.28, 131.80, 134.07, 138.55, 138.90, 139.67, 140.30, 149.19, 149.32. MALDI/TOF–MS: m/z calcd 1207.37; found 1208.87. Elemental analysis: Anal. Calcd for C₇₄H₉₄Br₂O₄•3H₂O₁ C, 70.40; H, 7.93; Found: 70.92; H, 7.64.

Synthesis of (S)–BF:

The compound (S)–BF was synthesized similarly and obtained as a red powder (94 mg, 58%).

¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 0.84–0.89 (m, 12H), 1.25–1.30 (m, 40H), 1.41–1.48 (m, 9H), 1.74–1.81 (m, 3H), 4.33–4.37 (m, 2H), 4.40–4.45 (m, 2H), 6.96 (d, 2H, J = 8 Hz), 7.14–7.20 (m, 4H), 7.48 (d, 2H, J = 8 Hz), 7.54–7.58 (m, 4H), 7.70 (d, 2H, J = 8 Hz), 8.49 (s, 2H), 8.72 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 14.10, 19.87, 22.67, 25.63, 29.35, 29.69, 31.84, 36.72, 36.76,

117.13, 117.72, 120.33, 120.44, 120.84, 121.21, 125.50, 128.87, 129.28, 131.80, 134.07, 138.55, 138.90, 139.67, 140.24, 140.30, 149.19, 149.32. MALDI/TOF–MS: m/z calcd 1207.37; found 1207.74. Elemental analysis: Anal. Calcd for C₇₄H₉₄Br₂O₄•3H₂O₅C, 70.40; H, 7.93; Found: C, 70.22; H, 7.88.

[S6]: P. J. M. Stals, M. M. J. Smulder, R. M. Rapun, A. R. A. Palmans and E. W. Meijer, *Chem. Eur. J.* **2009**, *15*, 2071.

Synthesis of C8–BF:

The **C8–BF** was synthesized according to the literature, ^[S7] and obtained as a red powder.

¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ (ppm) 0.87–0.90 (m, 12H), 1.29–1.34 (m, 32H), 1.80–1.86 (m, 8H), 4.01–4.04 (m, 4H), 4.07–4.10 (m, 4H), 6.94 (d, 2H, J = 8 Hz), 7.14–7.19 (m, 4H), 7.46–7.49 (m, 2H), 7.55–7.58 (m, 4H), 7.70 (d, 2H, J = 8 Hz), 8.49 (s, 2H), 8.71 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS, 298 K): δ (ppm) 14.12, 22.68, 26.04, 26.09, 29.31, 29.38, 29.43, 29.70, 31.83, 69.33, 69.59, 112.70, 114.04, 119.74, 120.33, 120.77, 121.24, 125.46, 128.91, 129.24, 131.80, 133.68, 137.94, 138.56, 138.91, 139.70, 140,30, 140.35, 143.98, 149.04, 149.35. MALDI/TOF–MS: m/z calcd 1151.24; found 1151.36. Elemental analysis: Anal. Calcd for C₇₀H₈₆Br₂O₄•H₂O₁C, 71.86; H, 7.36; Found: C, 71.12; H, 7.17.

[S7] M. Kaller, S. Tussetschlager, P. Fischer, C. Deck, A. Baro, F. Giesselmann and S. Laschat, *Chem. Eur. J.* **2009**, *15*, 9530.

Polymerization



General procedure for polymerization of monomer:

The monomer (50 mg, 0.0435 mmol), Ni(COD)₂ (19.2 mg, 0.07 mmol), 2,2'-bipyridyl (10.87 mg, 0.07 mmol) were placed in a flask under argon atmosphere. A solution of COD (0.07 mmol) in DMF (0.2 mL) and toluene (0.5 mL) were added, and the reaction mixture was stirred at 90 °C for three days. After cooling down to the room temperature, the reaction mixture was diluted with CHCl₃ and the organic layer was washed with sat. EDTA aq. (3 times), 3 M HCl aq. (3 times) and water (3 times). The organic layer was dried over anhydrous MgSO₄ and then removed by evaporation under reduced pressure. The resultant solid was purified by precipitation using CHCl₃/methanol mixture and collected by centrifugation (6000 rpm, 60 min), corresponding polymers were obtained as dark red powder.

The random copolymers poly(C8-BF(x)-co-(S)-BF(y)) were synthesized in a similar method and feeding ratio of each random copolymers were summarized in Table S1.

Table S1. Synthesis of random copolymers poly(C8-BF(x)-co-(S)-BF(y)) via Yamamoto coupling polymerization.

| [C8–BF] / [(S)–BF] (mol%) in feed | random copolymers | | | |
|--------------------------------------|-------------------------------|--|--|--|
| 83/17 | poly(C8–BF(86)-co-(S)–BF(14)) | | | |
| 67/33 | poly(C8-BF(59)-co-(S)-BF(41)) | | | |
| 50/50 | poly(C8-BF(43)-co-(S)-BF(57)) | | | |

Poly((*R***)–BF)**: ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ 0.78–0.95 (m, 12H), 1.09–1.29 (m, 60H), 3.97 (2H), 4.11 (2H), 6.53 (broad, 2H), 6.90 (broad, 2H), 7.00–7.03 (m, 2H), 7.41–7.52 (m, 6H), 7.70–7.72 (m, 2H), 8.70 (s, 2H), 8.86 (s, 2H) ppm. GPC (polystyrene as standard): $M_n = 10.0$ kDa, PDI = 1.6.

Poly((S)–BF): ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ 0.77–0.94 (m, 12H), 1.09–1.29 (m, 60H), 3.97 (2H), 4.10 (2H), 6.54 (broad, 2H), 6.85 (broad, 2H), 7.03 (broad, 2H), 7.46–7.56 (m, 6H), 7.70 (m, 2H), 8.70 (s, 2H), 8.86 (s, 2H) ppm. GPC (polystyrene as standard): M_n = 9.3 kDa, PDI = 1.2.

Poly(C8–BF): ¹H NMR (CDCl₃, 400 MHz, TMS, 298 K): δ 0.75–0.90 (m, 12H), 1.10–1.29 (m, 40H), 1.43–1.55 (m, 16H), 3.59–3.83 (m, 4H), 6.49–7.00 (m, 6H), 7.52–7.73 (m, 8H), 8.60 (s, 2H), 8.86 (s, 2H) ppm.

GPC (polystyrene as standard): $M_n = 11.4$ kDa, PDI = 1.7.



Fig. S1 ¹H NMR spectrum of C8–BF (400 MHz, in CDCl₃)



Fig. S2 ¹³C NMR spectrum of C8–BF (100 MHz, in CDCl₃)



Fig. S3 ¹H NMR spectrum of (S)–BF (400 MHz, in CDCl₃)



Fig. S4 ¹³C NMR spectrum of (S)–BF (100 MHz, in CDCl₃)



Fig. S5 ¹H NMR spectrum of (*R*)–BF (400 MHz, in CDCl₃)



Fig. S6 ¹³C NMR spectrum of (*R*)–BF (100 MHz, in CDCl₃)



Fig. S7 ¹H NMR spectrum of poly(C8–BF) (400 MHz, in CDCl₃).



Fig. S8 ¹H NMR spectrum of poly((*R*)–BF) (400 MHz, in CDCl₃).



Fig. S9 ¹H NMR spectrum of **poly((S)–BF)** (400 MHz, in CDCl₃).



Fig. S10 Thermal gravity analysis (TGA) of (a) poly(C8-BF), (b) poly((S)-BF), (c)poly((R)-BF) under flowing argon gas. The arrow indicates the temperature where2%ofthesampleweightislost.



Fig. S11 The molecular orbitals and electronic transitions of model compound of (R)–BF, which has (R)-1-methylpropyloxy groups, calculated at the M06-2X/6-31G(d)//M06-2X/6-31G(d) level.



Fig. S12 Variable-temperature ¹H NMR spectra of (S)–BF (0.237 mM) in CDCl₃.



Fig. S13 Simulated UV-vis absorption (upper) and CD (bottom) spectra of model compound of (R)–BF, which has (R)-1-methylpropyloxy groups calculated at the M06-2X/6-31G(d)//M06-2X/6-31G(d) level. According to the structural optimization of (R)–BF model compound, (M) form of 9,9'-BF unit is most stable conformation in gas phase (inset of saturated UV-vis absorption spectrum), simulated CD spectrum of which is consistent with that obtained for (R)–BF. Simulated spectra were plotted by using 0.25 eV of half width at half maximum.



Fig. S14 (a) Concentration dependent UV-vis spectra of **C8–BF** in CHCl₃ at 25 °C; (b) the absorbance at 468 nm as a function of its concentration; (c) the absorbance at 321 nm as a function of its concentration.



Fig. S15 Concentration dependent UV-vis absorption spectra of (a) **poly((S)–BF)** and (b) **poly((R)–BF)** in the range from 5×10^{-6} M to 5×10^{-4} M in CHCl₃ at 25 °C.



Fig. S16 Powder X-ray diffraction profiles of **poly(C8–BF)** (black), **poly((S)–BF)** (red) and **poly((R)–BF)** (blue).



Fig. S17 Photoelectron yield spectra of (a) **poly(C8–BF)**, (b) **poly((S)–BF)**, (c) **poly((R)–BF)** spin-coating pristine films. The substrates are ITO-coated glasses.



Fig. S18 ¹H NMR spectra of random copolymers poly(C8-BF(43)-co-(S)-BF(57)), poly(C8-BF(59)-co-(S)-BF(41)) and poly(C8-BF(86)-co-(S)-BF(14)) in CDCl₃. The percentages of (S)-BF units were calculated to be 57%, 41% and 14%, respectively, according to the integration of α -proton signal of alkoxy groups (indicated by red arrows) from ¹H NMR spectra described above. The ¹H NMR spectra of poly((S)-BF) and poly(C8-BF) were also included for comparison.



Fig. S19 Photoelectron yield spectra of (a) poly(C8-BF(86)-co-(S)-BF(14)), (b) poly(C8-BF(59)-co-(S)-BF(41)) and (c) poly(C8-BF(43)-co-(S)-BF(57)) spin-coating pristine films. The substrates are ITO-coated glasses.



Fig. S20 (a) UV-vis absorption and (b) CD spectra of poly(C8–BF(43)-co-(S)– BF(57)) (orange line), poly(C8–BF(59)-co-(S)–BF(41)) (green line) and poly(C8– BF(86)-co-(S)–BF(14)) (blue line) in MCH. The concentrations of polymers are 0.5 mM based on the molecular weight of repeating unit. The path length is 1 mm.

| atoms | Х | У | z | atoms | Х | У | Z |
|-------|-----------|-----------|-----------|-------|-----------|------------|-----------|
| Н | 0.052896 | -1.311012 | -5.042941 | Br | 3.498207 | 3.951863 | 1.922569 |
| С | 0.033875 | -1.646777 | -4.010082 | 0 | 1.003252 | -8.911903 | -1.174824 |
| С | 0.065792 | -2.534319 | -1.345904 | 0 | -1.003252 | 8.911903 | -1.174824 |
| С | -0.021068 | -0.733031 | -2.966319 | С | -0.107668 | -9.817928 | -1.311960 |
| С | 0.085002 | -3.006284 | -3.714426 | Н | -1.042349 | -9.250821 | -1.214864 |
| С | 0.132152 | -3.466668 | -2.389052 | С | 0.107668 | 9.817928 | -1.311960 |
| С | -0.066349 | -1.177879 | -1.628707 | Н | 1.042349 | 9.250821 | -1.214864 |
| Н | 0.105416 | -3.730266 | -4.523477 | Ο | -0.603729 | -7.503018 | 0.396133 |
| С | 0.021068 | 0.733031 | -2.966319 | 0 | 0.603729 | 7.503018 | 0.396133 |
| С | -0.132152 | 3.466668 | -2.389052 | С | -1.445438 | -6.827784 | 1.332760 |
| С | -0.033875 | 1.646777 | -4.010082 | С | 1.445438 | 6.827784 | 1.332760 |
| С | 0.066349 | 1.177879 | -1.628707 | С | 0.000000 | -10.806173 | -0.166455 |
| С | -0.065792 | 2.534319 | -1.345904 | Н | -0.002232 | -10.258709 | 0.779187 |
| С | -0.085002 | 3.006284 | -3.714426 | Н | 0.934547 | -11.371623 | -0.243705 |
| Н | -0.052896 | 1.311012 | -5.042941 | Н | -0.837365 | -11.50953 | -0.170658 |
| Н | -0.105416 | 3.730266 | -4.523477 | С | 0.000000 | 10.806173 | -0.166455 |
| С | 0.000000 | 0.000000 | -0.733279 | Н | 0.837365 | 11.50953 | -0.170658 |
| С | 0.000000 | 0.000000 | 0.631104 | Н | 0.002232 | 10.258709 | 0.779187 |
| С | -0.680509 | -0.956822 | 1.528251 | Н | -0.934547 | 11.371623 | -0.243705 |
| С | -1.945197 | -2.290847 | 3.63639 | С | -0.042182 | -10.450685 | -2.698366 |
| С | -0.443043 | -0.583135 | 2.868652 | Н | -0.026096 | -9.638671 | -3.436213 |
| С | -1.618175 | -1.94747 | 1.242431 | Н | 0.912973 | -10.982242 | -2.788896 |
| С | -2.222914 | -2.603909 | 2.3061 | С | 0.042182 | 10.450685 | -2.698366 |
| С | -1.056626 | -1.256843 | 3.918628 | Н | -0.912973 | 10.982242 | -2.788896 |
| Н | -0.869651 | -0.971065 | 4.949528 | Н | 0.026096 | 9.638671 | -3.436213 |
| Н | -2.443694 | -2.831886 | 4.432789 | С | -1.209674 | -11.391029 | -2.989956 |
| С | 0.680509 | 0.956822 | 1.528251 | Н | -2.169271 | -10.886631 | -2.83059 |
| С | 1.945197 | 2.290847 | 3.63639 | Н | -1.185391 | -12.275165 | -2.346099 |
| С | 1.618175 | 1.94747 | 1.242431 | Н | -1.184022 | -11.736878 | -4.026791 |
| С | 0.443043 | 0.583135 | 2.868652 | С | 1.209674 | 11.391029 | -2.989956 |
| С | 1.056626 | 1.256843 | 3.918628 | Н | 1.185391 | 12.275165 | -2.346099 |
| С | 2.222914 | 2.603909 | 2.3061 | Н | 1.184022 | 11.736878 | -4.026791 |
| Н | 0.869651 | 0.971065 | 4.949528 | Н | 2.169271 | 10.886631 | -2.83059 |
| Н | 2.443694 | 2.831886 | 4.432789 | С | 0.609293 | 5.956133 | 2.261896 |
| Н | 1.898282 | 2.195524 | 0.225296 | Н | -0.121183 | 6.582532 | 2.783317 |
| Н | -0.17045 | 2.88063 | -0.322404 | Н | 1.241818 | 5.457741 | 3.000482 |
| Н | -1.898282 | -2.195524 | 0.225296 | Н | 0.066656 | 5.182577 | 1.710733 |
| Н | 0.17045 | -2.88063 | -0.322404 | С | -0.609293 | -5.956133 | 2.261896 |
| С | -0.311808 | 4.909326 | -2.093081 | Н | -0.066656 | -5.182577 | 1.710733 |
| С | -0.748679 | 7.61152 | -1.496091 | Н | 0.121183 | -6.582532 | 2.783317 |
| С | 0.306248 | 5.493891 | -0.973454 | Н | -1.241818 | -5.457741 | 3.000482 |
| С | -1.140587 | 5.688302 | -2.899711 | Н | 2.173062 | 6.216259 | 0.783300 |
| С | -1.346413 | 7.033959 | -2.60402 | Н | -2.173062 | -6.216259 | 0.783300 |
| С | 0.079209 | 6.831352 | -0.659291 | С | 2.18515 | 7.941841 | 2.067343 |
| Н | 0.968888 | 4.891978 | -0.357469 | Н | 1.449323 | 8.523744 | 2.636479 |

Table S2. The Cartesian Coordinates (Å) of Optimized Structure of ModelCompound in the Ground State

| Х | У | Z | atoms | Х | У | Z |
|-----------|---|---|--|--|--|--|
| -1.655537 | 5.236548 | -3.74141 | Н | 2.60258 | 8.61611 | 1.310777 |
| -1.996111 | 7.655256 | -3.21225 | С | -2.18515 | -7.941841 | 2.067343 |
| 0.311808 | -4.909326 | -2.093081 | Н | -1.449323 | -8.523744 | 2.636479 |
| 0.748679 | -7.61152 | -1.496091 | Н | -2.60258 | -8.61611 | 1.310777 |
| 1.140587 | -5.688302 | -2.899711 | С | 3.297138 | 7.444148 | 2.987477 |
| -0.306248 | -5.493891 | -0.973454 | Н | 3.791571 | 8.286899 | 3.477928 |
| -0.079209 | -6.831352 | -0.659291 | Н | 4.057446 | 6.891296 | 2.426403 |
| 1.346413 | -7.033959 | -2.60402 | Н | 2.915839 | 6.780524 | 3.769362 |
| 1.655537 | -5.236548 | -3.74141 | С | -3.297138 | -7.444148 | 2.987477 |
| -0.968888 | -4.891978 | -0.357469 | Н | -4.057446 | -6.891296 | 2.426403 |
| 1.996111 | -7.655256 | -3.21225 | Н | -2.915839 | -6.780524 | 3.769362 |
| -3.498207 | -3.951863 | 1.922569 | Н | -3.791571 | -8.286899 | 3.477928 |
| | x -1.655537 -1.996111 0.311808 0.748679 1.140587 -0.306248 -0.079209 1.346413 1.655537 -0.968888 1.996111 -3.498207 | xy-1.6555375.236548-1.9961117.6552560.311808-4.9093260.748679-7.611521.140587-5.688302-0.306248-5.493891-0.079209-6.8313521.346413-7.0339591.655537-5.236548-0.968888-4.8919781.996111-7.655256-3.498207-3.951863 | xyz-1.6555375.236548-3.74141-1.9961117.655256-3.212250.311808-4.909326-2.0930810.748679-7.61152-1.4960911.140587-5.688302-2.899711-0.306248-5.493891-0.973454-0.079209-6.831352-0.6592911.346413-7.033959-2.604021.655537-5.236548-3.74141-0.968888-4.891978-0.3574691.996111-7.655256-3.21225-3.498207-3.9518631.922569 | x y z atoms -1.655537 5.236548 -3.74141 H -1.996111 7.655256 -3.21225 C 0.311808 -4.909326 -2.093081 H 0.748679 -7.61152 -1.496091 H 1.140587 -5.688302 -2.899711 C -0.306248 -5.493891 -0.973454 H -0.079209 -6.831352 -0.659291 H 1.346413 -7.033959 -2.60402 H 1.655537 -5.236548 -3.74141 C -0.968888 -4.891978 -0.357469 H 1.996111 -7.655256 -3.21225 H -3.498207 -3.951863 1.922569 H | xyzatomsx-1.6555375.236548-3.74141H2.60258-1.9961117.655256-3.21225C-2.185150.311808-4.909326-2.093081H-1.4493230.748679-7.61152-1.496091H-2.602581.140587-5.688302-2.899711C3.297138-0.306248-5.493891-0.973454H3.791571-0.079209-6.831352-0.659291H4.0574461.346413-7.033959-2.60402H2.9158391.655537-5.236548-3.74141C-3.297138-0.968888-4.891978-0.357469H-4.0574461.996111-7.655256-3.21225H-2.915839-3.498207-3.9518631.922569H-3.791571 | xyzatomsxy-1.6555375.236548-3.74141H2.602588.61611-1.9961117.655256-3.21225C-2.18515-7.9418410.311808-4.909326-2.093081H-1.449323-8.5237440.748679-7.61152-1.496091H-2.60258-8.616111.140587-5.688302-2.899711C3.2971387.444148-0.306248-5.493891-0.973454H3.7915718.286899-0.079209-6.831352-0.659291H4.0574466.8912961.346413-7.033959-2.60402H2.9158396.7805241.655537-5.236548-3.74141C-3.297138-7.444148-0.968888-4.891978-0.357469H-4.057446-6.8912961.996111-7.655256-3.21225H-2.915839-6.780524-3.498207-3.9518631.922569H-3.791571-8.286899 |