

Chiroptical Properties of Helical Aromatic Conjugated Polymers Synthesized by Electrochemical Polymerization in Chiral Nematic Liquid Crystals

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ABSTRACT

We synthesized several highly fluorescent fluorene derivatives, in which thiophene, biphenylthiophene, ethylenedioxythiophene (EDOT), or biphenyl EDOT moieties were attached at both ends of the fluorene moiety, and polymerized them via electrochemical polymerization in chiral nematic liquid crystals (N*-LCs) providing asymmetric reaction environments. The resulting aromatic conjugated polymers showed induced chirality due to the formation of interchain helically π -stacked structures and hence exhibited circular dichroism (CD). The absorption dissymmetry factors (g_{abs}) were in the range 10^{-4} – 10^{-2} and depended strictly on the moieties in the polymer chains. Some of the polymers exhibited circularly polarized luminescence (CPL) with luminescence dissymmetry factors (g_{lum}) of approximately 10^{-3} . This is the first example of CPL from polymer films prepared by asymmetric electrochemical polymerization.

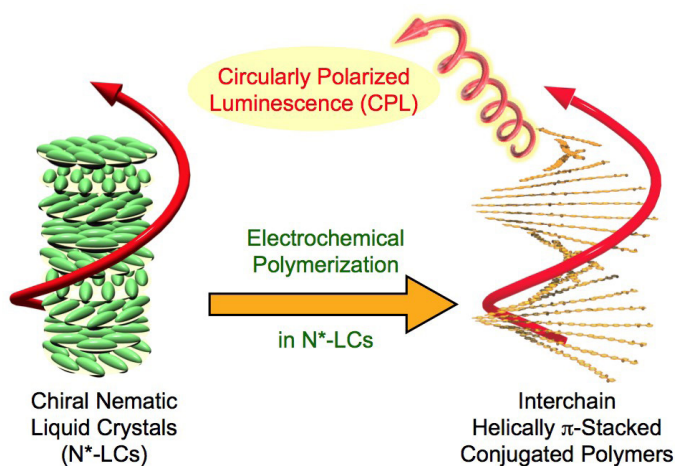
Keywords

Aromatic Conjugated Polymer, Asymmetric Polymerization Reaction Field, Chiral Nematic Liquid Crystal, Circularly Polarized Luminescence, Electrochemical Polymerization, Helical Conjugated Polymers.

Introduction

It is well known that chemical or electrochemical polymerizations of achiral monomers in chiral nematic liquid crystals (N*-LCs) providing asymmetric reaction fields yield polymers with peculiar structures and/or morphologies that resemble the helices of the reaction environments [1-8]. Furthermore, N*-LCs are easily prepared by adding chiral dopants to nematic liquid crystals (N-LCs) [9-16]. Previously, helical poly(3,4-ethylenedioxythiophene) films were synthesized by electrochemical polymerization in N*-LC, and we found that the polymers exhibited induced chirality due to the formation of interchain helically π -stacked structures and hence exhibited circular dichroism (CD) [2,17-20]. However, there is no report of synthesizing luminescent helical conjugated polymers by electrochemical polymerization in an N*-LC field.

When chirality is imparted to a luminescent conjugated polymer, chirality is also induced in the emitted light, resulting in circularly polarized luminescence (CPL) [3,6-8]. The aim of this study was to synthesize helical fluorescent conjugated polymers exhibiting CPL as well as CD and to control the chirality of the CPL. Herein, we synthesized several highly fluorescent fluorene derivatives, in which thiophene, biphenylthiophene, ethylenedioxythiophene (EDOT), or biphenyl EDOT moieties were attached at both ends of the fluorene moiety. The thiophene and EDOT moieties were confirmed to be useful in electrochemical polymerization because of their low oxidation potentials. These fluorene derivatives were electrochemically polymerized in N*-LCs serving as asymmetric solvents. The synthesized polymers were subjected to chiroptical measurements. The polymers exhibited induced chirality due to the interchain helically π -stacked structures, affording CD and CPL properties with dissymmetry factors of approximately 10^{-4} – 10^{-2} (g_{abs}) and 10^{-3} (g_{lum}), respectively. The schematic representation of screwed structures of N*-LCs and interchain helically π -stacked conjugated polymers is given in Scheme 1.



Scheme 1: Schematic representation of screwed structures of N*-LCs and interchain helically π -stacked conjugated polymers.

Results and Discussion

Synthesis of Achiral Monomers for Electrochemical Polymerization

Figure 1 shows the synthetic routes for the seven achiral, monomeric fluorene derivatives TF-H, TF-Oc, EF-H, EF-Me, EF-Oc, TBPF-Oc, and EBPF-Oc, which were used for electrochemical polymerization (see Supplementary materials).

Synthesis of Helical Conjugated Polymers using Chiral Nematic Liquid Crystals

N*-LCs were prepared by adding an axially chiral binaphthyl derivative (*R* or *S*) to a mixture of N-LCs containing cyanobiphenyl-, cyanocyclohexylphenyl-, and cyanocyclohexylbiphenyl-based LCs (Figure 2). POM observations during the cooling process showed that a phase transition from the isotropic to the N*-LC phase occurred at 82 °C and that the N*-LC phase was preserved below -30 °C.

Subsequently, 1 mol% of the monomer and 0.1 mol% of the supporting electrolyte (tetrabutylammonium perchlorate: TBAP) were added to the N*-LC for preparation of the polymerized samples. The samples were inserted into cells with spacer thicknesses of 35 μm , in which 2 sheets of ITO glass (1 cm \times 3 cm) were superimposed. The temperature was raised to 110 °C (isotropic phase) with a temperature controller, and then lowered to 60 °C at 1 °C/min. After the sample was allowed to stand for 30 min, a potential of 4 V was applied to the cell for 30 min with a DC power supply (Figure 2).

The polymers P(TF-H), P(TF-Oc), P(EF-H), P(EF-Me), P(EF-Oc), P(TBPF-Oc), and P(EBPF-Oc) were synthesized by electrochemical polymerization of the fluorene-based monomers in N*-LCs. Since the polymer films were oxidized after the electrochemical polymerizations, they were reduced after washing with acetonitrile with electrochemical dedoping. The number- and weight-average molecular weights, molecular weight dispersion, and degrees of polymerization are summarized in Table 1. It is

evident that the present polymers have narrow molecular weight dispersions, suggesting uniform effective conjugation lengths of the polymers. Although the degrees of polymerization are low due to the relatively large sizes of the monomers, the degrees of polymerization were evaluated in terms of the number of aromatic conjugated rings from 16 to 24. This implied that the present polymers have sufficiently long main chains to be regarded as polymers or oligomers with long chain lengths.

Table 1: Number-average (M_n) and weight-average (M_w) molecular weights, molecular weight dispersion (M_w/M_n), and degrees of polymerization (D.P.).^[a]

Polymer	M_n	M_w	M_w/M_n	D.P. ^[b]
P(TF-H)	1420	1450	1.02	4 (16)
P(TF-Oc)	2320	2400	1.03	4 (16)
P(EF-H)	2490	2580	1.03	6 (24)
P(EF-Me)	2380	2700	1.13	5 (20)
P(EF-Oc)	2600	2960	1.13	4 (16)
P(TBPF-Oc)	2800	2900	1.04	3 (24)
P(EBPF-Oc)	2830	2920	1.03	3 (24)

[a] Measurement of THF-soluble portion by gel permeation chromatography (GPC) [b] Degree of polymerization (number of aromatic rings).

Chiroptical Properties of the Helical Conjugated Polymers

Figure 3 shows the UV-Vis and CD spectra of P(TF-H) and P(TF-Oc) as well as the absorption asymmetry factors (g_{abs}). Both polymer films showed broad absorption bands in the wavelength range 300–500 nm. In the CD spectra, bisignate Cotton effects of the mirror image were observed for P(TF-H), and the g_{abs} was relatively large, such as 1.3×10^{-2} . On the other hand, for P(TF-Oc), only a small CD band with a g_{abs} less than 1.0×10^{-4} was observed. This was probably because the dioctyl groups substituted at the 9 position of the fluorene moieties inhibited the formation of helically π -stacked structures due to steric hindrance. Both polymer films showed faint orange fluorescence but gave no CPL (see Table 2).

Table 2: Chiroptical properties of the synthesized polymers.^[a]

Polymer	Absorption wavelength (nm)	$ g_{\text{abs}} $	Emission wavelength (nm)	Fluorescence quantum yield Φ (%) ^[b]	$ g_{\text{lum}} $
P(TF-H)	354	1.3×10^{-2}	570	< 1	N.D.
P(TF-Oc)	362	1.0×10^{-4}	575	5	N.D.
P(EF-H)	448	8.0×10^{-3}	N.D.	N.D.	N.D.
P(EF-Me)	369	3.3×10^{-4}	N.D.	N.D.	N.D.
P(EF-Oc)	364	N.D.	N.D.	N.D.	N.D.
P(TBPF-Oc)	351	4.8×10^{-3}	451	2	1.3×10^{-3}
P(EBPF-Oc)	352	3.3×10^{-3}	498	< 1	N.D.

[a] Results in N*-LC fields containing (*R*)-chiral compound.

[b] Measurement with an integrating sphere.

Figure 4 shows the UV-Vis and CD spectra, and the g_{abs} values for P(EF-H), P(EF-Me), and P(EF-Oc). As the alkyl chains at the 9-position of the fluorene moiety became longer, the absorption bands became sharper and shifted to shorter wavelengths in the UV-Vis spectra. In the CD spectra, the bisignate Cotton effects of the mirror image were observed in the region corresponding to the absorption wavelength, and the $|g_{\text{abs}}|$ values were 8.0×10^{-3} and

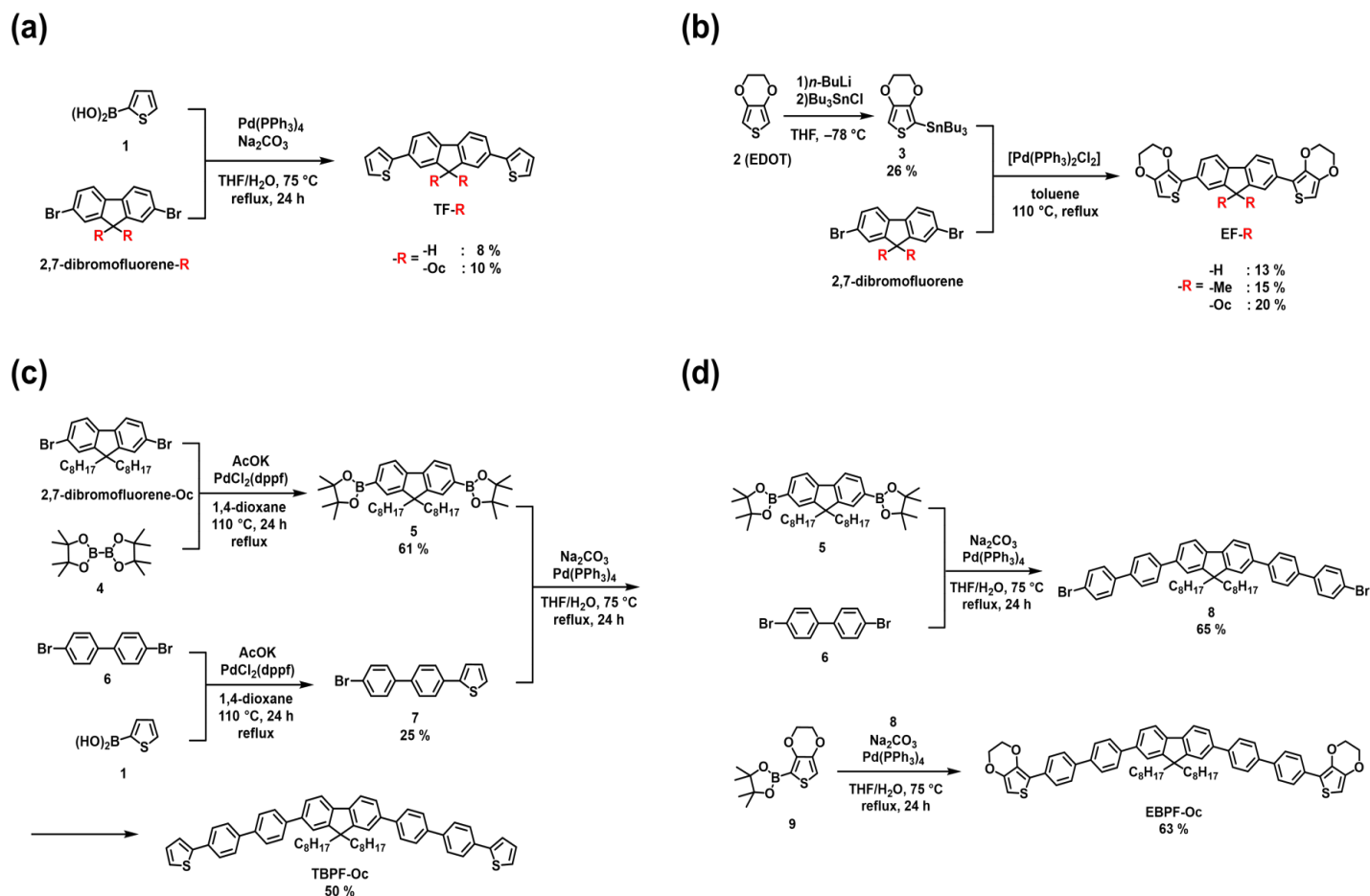


Figure 1: Synthetic routes to the achiral monomers; (a) TF-R, (b) EF14- R, (c) TBPF-Oc, and (d) EBPF-Oc.

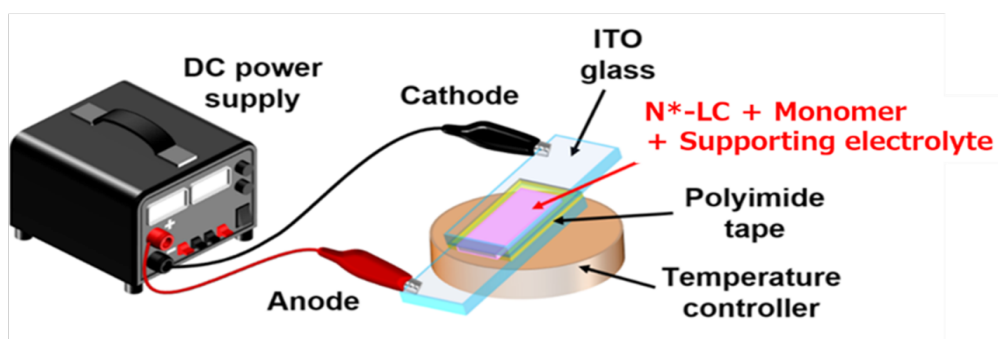
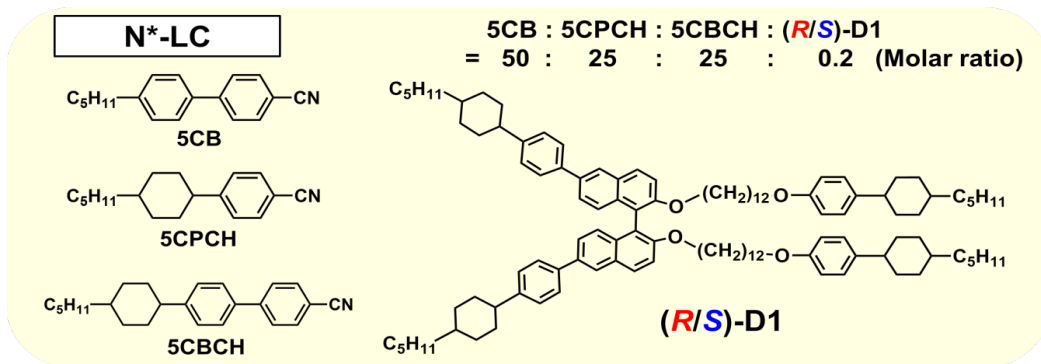


Figure 2: Electrochemical polymerization system for syntheses of polymer films in N*-LC.

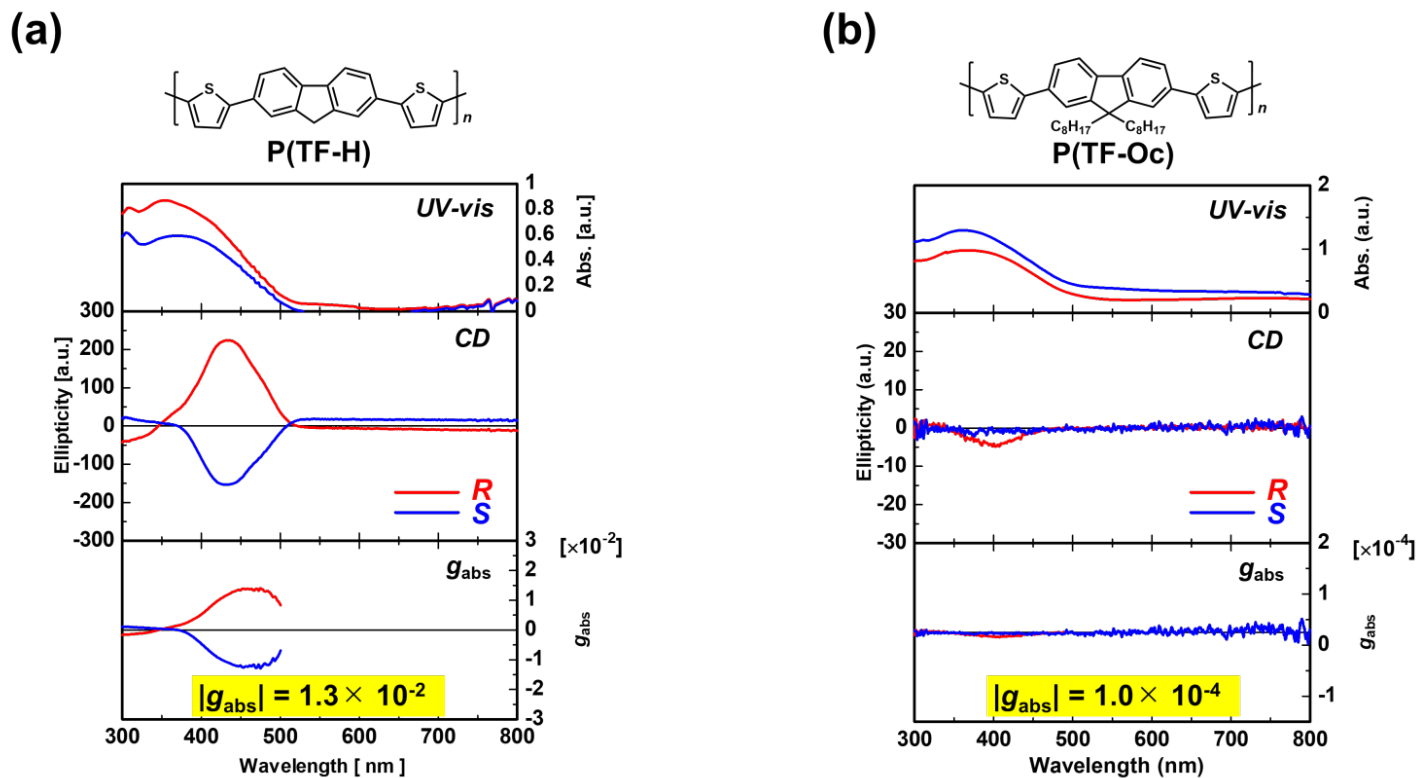


Figure 3: UV-vis and CD spectra of (a) P(TF-H) and (b) P(TF-Oc).

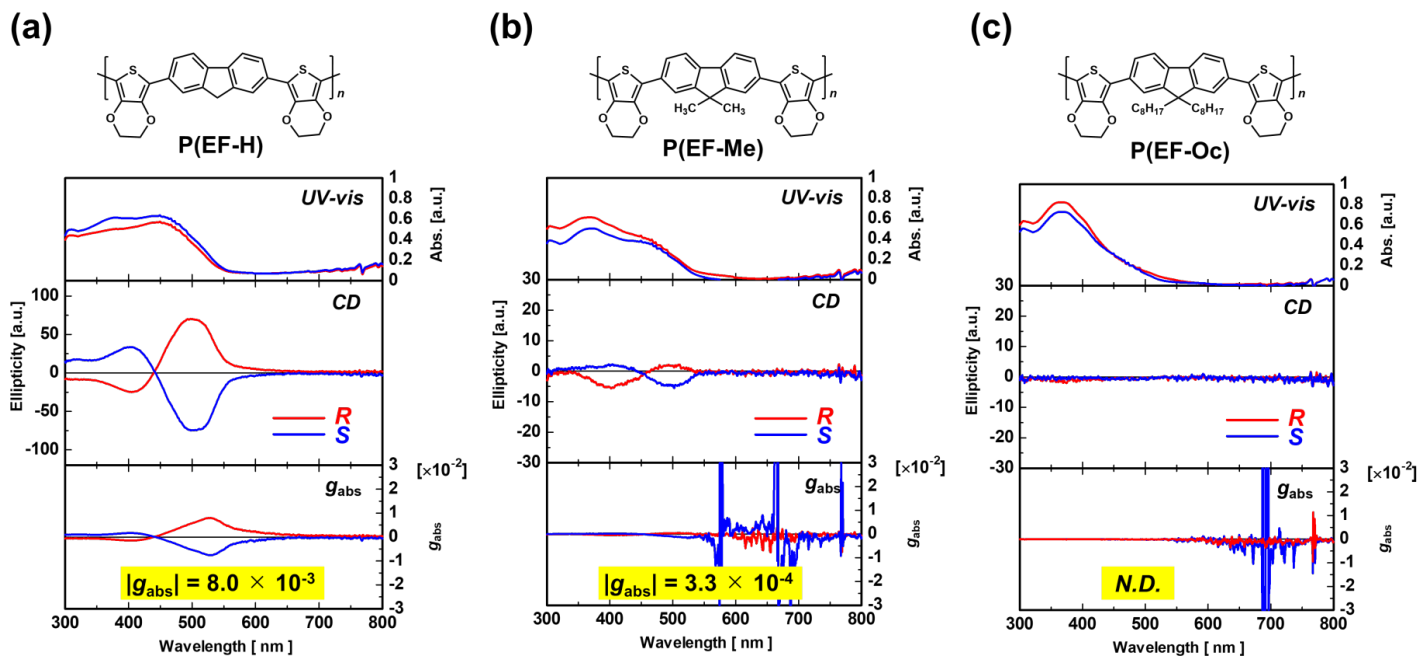


Figure 4: UV-vis and CD spectra of (a) P(EF-H), (b) P(EF-Me) and (c) P(EF-Oc).

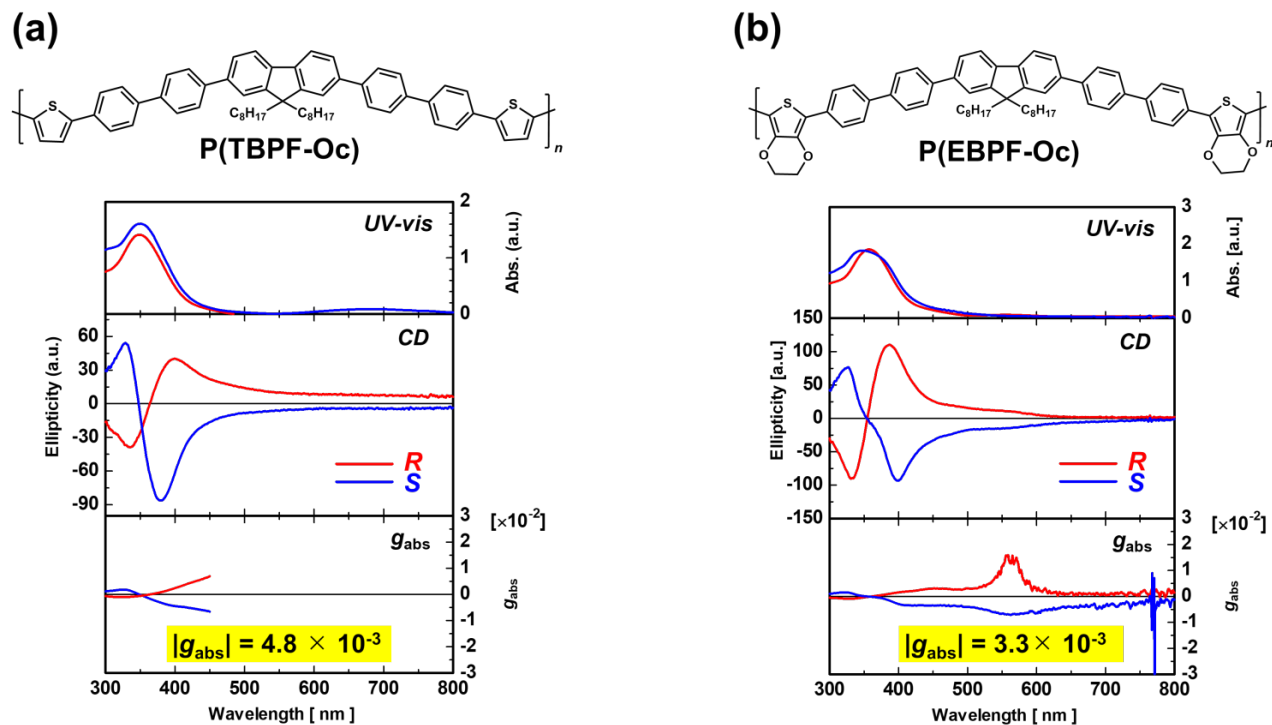


Figure 5: UV-vis and CD spectra of (a) P(TBPF-Oc) and (b) P(EBPF-Oc).

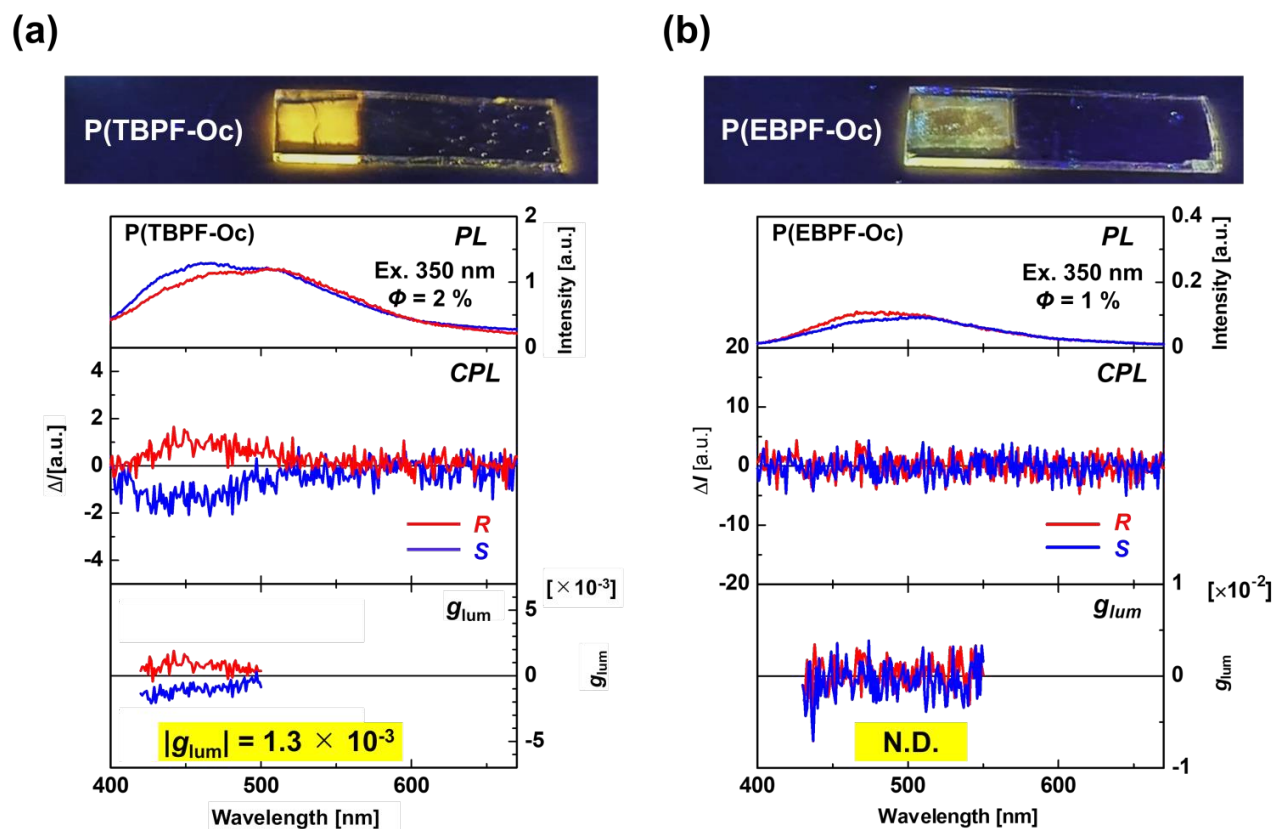


Figure 6: PL and CPL spectra of (a) P(TBPF-Oc) and (b) P(EBPF-Oc).

3.3×10^{-4} for P(EF-H) and P(EF-Me), respectively. These polymers showed the same tendency in their chiroptical properties, as shown in Figure 3. Namely, the longer alkyl chains at the 9 position of the fluorene moiety notably decrease the CD intensity because they inhibited interchain helical π -stacking. Meanwhile, these polymer films showed no fluorescence.

Finally, the UV-Vis and CD spectra and g_{abs} values for P(TBPF-Oc) and P(EBPF-Oc) were examined, as shown in Figure 5. Both polymer films showed relatively sharp absorption bands at approximately 300–450 nm. They also showed Cotton effects of the mirror image in the region corresponding to the absorption bands. The $|g_{\text{abs}}|$ values were 4.8×10^{-3} and 3.3×10^{-3} for P(TBPF-Oc) and P(EBPF-Oc), respectively.

As shown in Figure 6, the P(TBPF-Oc) and P(EBPF-Oc) polymer films exhibited yellow fluorescence with quantum yields of approximately 2 % and 1 %, respectively. Furthermore, the P(TBPF-Oc) film exhibited a CPL band at approximately 400–500 nm with a $|g_{\text{lum}}|$ value of 1.3×10^{-3} . It should be emphasized that the signs of CPL bands observed for the P(TBPF-Oc) film were rigorously controlled by the chirality of N*-LC containing the axially chiral binaphthyl dopant. However, P(EBPF-Oc) gave no detectable CPL band. The PL and CPL results for the present polymers are also summarized in Table 2.

It is worth noting that although the thiophene and EDOT moieties provide active sites for electrochemical polymerization because of their relatively low oxidation potentials, they strongly depressed the fluorescence intensity. In particular, the degree of fluorescence depression by the EDOT moiety was apparently larger than that of the thiophene moiety. This decreased or quenched fluorescence may be due to energy transfer, in which a photon generated upon excitation of the fluorene moiety is transferred to the excited thiophene or EDOT moiety through intersystem crossing, resulting in a nonradiative transition from the excited to ground state of the thiophene or EDOT. In addition, the presence of a biphenylene moiety between the fluorene and the thiophene or EDOT moiety may have contributed to a slight decrease in fluorescence from the thiophene or EDOT moiety, as seen in the CPL result for the P(TBPF-Oc) film.

Conclusion

We synthesized a series of fluorene-based conjugated polymer films, P(TF-H), P(TF-Oc), P(EF-H), P(EF-Me), P(EF-Oc), P(TBPF-Oc), and P(EBPF-Oc), by electrochemical polymerization in N*-LCs serving as asymmetric solvent. Most of the polymer films showed bisignate Cotton effects in the CD spectra, indicating the formation of interchain helically π -stacked structures. The absorption dissymmetry factors ($|g_{\text{abs}}|$) were in the range 10^{-4} – 10^{-2} , and they depended strictly on the molecular moieties in the polymer chains. It is important to emphasize that the P(TBPF-Oc) films exhibited CPL with luminescence dissymmetry factors ($|g_{\text{lum}}|$) of 1.3×10^{-3} . This is the first example of CPL generated by polymer films prepared via asymmetric electrochemical polymerization. It was confirmed that electrochemical polymerizations in N*-LCs

asymmetric polymerization fields show promise in synthesizing chiroptical helical conjugated polymers from achiral or racemic monomers.

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Supplementary Information

Chiroptical Properties of Helical Aromatic Conjugated Polymers Synthesized by Electrochemical Polymerization in Chiral Nematic Liquid Crystals

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Measurements

Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-d using JEOL ECS-400 NMR spectrometer. Elemental analysis was performed at the Center for Organic Elemental Microanalysis of Kyoto University. Optical absorption spectra were measured using a JASCO V-570 spectrometer and CD spectra were obtained with JASCO J-820 spectrometer with quartz cell. Texture observations were carried out under crossed nicols by using a Zeiss AxioImager M1m polarizing optical microscope (POM) equipped with a Zeiss AxioCam MRc5 digital camera and a Linkam THMS600 heating and cooling stage with temperature control. The samples for observations with POM were sandwiched between two cover glasses.

Synthesis

TF-H

Under an argon atmosphere, 2,7-dibromofluorene-H (1.00 g, 3.09 mmol) and 2-thiophene boronic acid [**1**] (0.78 g, 6.17 mmol) were placed in a 300 mL three-necked flask and dissolved in THF (50 mL). To the THF solution, a basic aqueous solution of Na₂CO₃ (1.64 g, 15.4 mmol) dissolved in 20 mL of pure water and one spatula of Tetrakis(triphenylphosphine) palladium (0) was added, and reflux at 75 °C for 24 hours. bottom. The reaction solution was transferred to a separating funnel and extracted with chloroform. The extracted organic layer was separated with pure water and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it and the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using a developing solvent of chloroform: *n*-hexane=1:1. Further, the solvent was evaporated under reduced pressure, and recrystallization was performed with chloroform and methanol to obtain white solid **TF-H** (8.5 mg, 8 %).

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.78 -7.66 (m, 4H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 2.9 Hz, 2H), 7.22 (d, *J* = 5.0 Hz, 2H), 7.04 (dd, *J* = 4.9, 3.7 Hz, 2H), 3.91 (s, 2H).

TF-Oc

Under an argon atmosphere, 2,7-dibromofluorene-Oc (1.00 g, 1.82 mmol) and [1] (0.44 g, 3.64 mmol) were placed in a 300 mL three-necked flask and dissolved in THF (50 mL). To the THF solution, a basic aqueous solution of Na₂CO₃ (0.46 g, 5.46 mmol) dissolved in 20 mL of pure water and one spatula of Tetrakis(triphenylphosphine) palladium (0) was added, and reflux at 75 °C for 24 hours. The reaction solution was transferred to a separating funnel and extracted with chloroform. The extracted organic layer was separated with pure water and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it and the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using a developing solvent of chloroform: *n*-hexane=1:1. Further, the solvent was evaporated under reduced pressure and obtained **TF-Oc** as yellow viscous liquid.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.67 (d, *J* = 7.9 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.56 (d, *J* = 1.2 Hz, 2H), 7.38 (dd, *J* = 3.6, 1.1 Hz, 2H), 7.33 – 7.24 (m, 2H), 7.14 – 7.06 (m, 2H), 2.16 – 1.88 (m, 4H), 1.21 – 0.97 (m, 20H), 0.81 (dt, *J* = 14.1, 5.5 Hz, 6H), 0.73 – 0.59 (m, 4H).

Tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane [3]

Under argon atmosphere, a solution of 3,4-ethylenedioxythiophene [2] (2.83 g, 19.9 mmol) in dry THF (50 mL) was cooled to –78 °C, and a solution of *n*-BuLi (14.8 mL, 23.8 mmol, 1.6 M in hexane) was added dropwise. The reaction mixture was stirred for 1 h and tributyltin chloride (9.71 g, 29.81 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture poured into hexane and filtrate was extracted with diethyl ether, washed with water and dried over Na₂SO₄. After evaporation of the solvent, the crude product was passed through a chromatography (silica gel, hexane) and colorless liquid (2.26 g, 26 %) was obtained.

EF-H

[3] (2.20 g, 5.10 mmol), 2,7-dibromofluorene-H (0.66 g, 2.0 mmol) were dissolved in dry toluene (30 mL) and bis(triphenylphosphine) palladium(II) chloride (0.03 g, 0.04 mmol) was added in one portion. The reaction mixture was refluxed for 12 h at 110 °C. The reaction mixture poured into hexane and the filtrate which was extracted with chloroform was washed with water, brine and dried over Na₂SO₄. After evaporation of the solvent, the crude product was passed through a chromatography (silica gel, hexane : chloroform = 5 : 1). The crude product was further purified by recrystallization (chloroform and ethanol) to give a solid (0.30 g, yield: 13 %).

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.90 (s, 2H), 7.73 (d, *J* = 1.2 Hz, 4H), 6.31 (s, 2H), 4.35 (m, 4H), 4.27 (m, 4H), 3.96 (s, 2H).

EF-Me

[3] (2.20 g, 5.1 mmol) and 2,7-dibromofluorene-Me (0.81 g, 2.5 mmol) were added to a 300 mL 3-neck flask under an argon atmosphere. Toluene (30 mL) was added there with stirring and Bis (Triphenylphosphine)palladium (II) (0.0514 g, 0.0732 mmol) was added. The mixed solution was heated to 125 °C in an oil bath and refluxed for 12 hours. The solution was taken out from the oil bath to release heat and the organic layer was extracted with chloroform. Then, it was separated with pure water, and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it, the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using a developing solvent of chloroform:*n*-hexane=1:1 under light shielding conditions. At this time, silica gel was mixed with K₂CO₃ (10 wt%, 25 g) to remove residual products generated during the reaction. Further, the solvent was evaporated under reduced pressure, and the residue was purified by recrystallization with chloroform and *n*-hexane to get **EF-Me** (0.24 g, 15 %) as yellow solid.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.73 (s, 2H), 7.69 (dd, *J* = 8.7, 11.2 Hz, 4H), 6.31 (s, 2H), 4.35 (m, 4H), 4.27 (m, 4H), 1.54 (s, 6H).

EF-Oc

[3] (2.20 g, 5.1 mmol) and 2,7-dibromofluorene-Oc (0.81 g, 2.5 mmol) were added to a 300 mL 3-neck flask under an argon atmosphere. Toluene (30 mL) was added there with stirring and Bis (Triphenylphosphine)palladium (II) (0.0514 g, 0.0732 mmol) was added. The mixed solution was heated to 125 °C in an oil bath and refluxed for 12 hours. The solution was taken out from the oil bath to release heat and the organic layer was extracted with chloroform. Then, it was separated with pure water, and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it, the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using a developing solvent of chloroform:*n*-hexane=1:1 under light shielding conditions. At this time, silica gel was mixed with K₂CO₃ (10 wt%, 25 g) to remove residual products generated during the reaction. Further, the solvent was evaporated under reduced pressure, and the residue was purified by recrystallization with chloroform and *n*-hexane to get **EF-Oc** (0.50 g, 20 %) as yellow solid.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.72 (d, *J* = 8 Hz, 1H), 7.64 (t, *J* = 24 Hz, 2H), 7.43 (d, *J* = 4 Hz, 1H), 7.33 (d, *J* = 8 Hz, 1H), 7.15 (t, *J* = 8 Hz, 1H), 2.06 (m, 2H), 1.11 (m, 10H), 0.83 (t, *J* = 12 Hz, 3H), 0.72 (s, 2H).

2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) [5]

2,7-dibromofluorene-Oc (1.50 g, 2.73 mmol), bis(pinacolato)diboron [4] (1.52 g, 6.01 mmol) and AcOK (0.81 g, 8.20 mmol) were added to 300 mL three-necked flask under an argon atmosphere. These were dissolved in 1,4-dioxane (60 mL) and heated to 110 °C by an oil bath. Two spatulas of PdCl₂(dppf) were added and reflux for 24 hours. The reaction solution was transferred to a separating funnel and extracted with chloroform. The extracted organic layer was separated with pure water and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it and the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using chloroform as developing solvent. Further, the solvent was evaporated under reduced pressure, and recrystallization was performed with chloroform and methanol to obtain [5] (1.06 g, 60.7 %) as white crystal.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.81 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 7.0 Hz, 4H), 2.00 (m, 4H), 1.38 (s, 24H), 1.21-1.05 (m, 20H), 0.82 (bs, 6H), 0.61 (bs, 4H).

4-bromo-4'-thienylbiphenyl [7]

4,4'-dibromobiphenyl [6] (1.22 g, 3.91 mmol), [1] (0.50 g, 3.91 mmol) and AcOK (1.18 g, 11.7 mmol) were added to 300 mL three-necked flask under an argon atmosphere. These were dissolved in 1,4-dioxane (60 mL) and heated to 110 °C by an oil bath. Two spatulas of PdCl₂(dppf) were added and reflux for 24 hours. The reaction solution was transferred to a separating funnel and extracted with chloroform. The extracted organic layer was separated with pure water and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it and the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using chloroform and *n*-hexane (1:6) as developing solvent. Further, the solvent was evaporated under reduced pressure, and recrystallization was performed with chloroform and methanol to obtain 4-bromo-4'-thienylbiphenyl [7] (0.30 g, 24.5 %) as white crystal.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.69 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 4H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.37 (m, 1H), 7.31 (d, *J* = 2.8 Hz, 1H), 7.11 (t, *J* = 4.0 Hz, 1H).

TBPF-Oc

Under an argon atmosphere, [5] (0.27 g, 0.42 mmol) and [7] (0.29 g, 0.84 mmol) were placed in a 300 mL three-necked flask and dissolved in THF (50 mL). To the THF solution, a basic aqueous solution of Na₂CO₃ (0.23 g, 2.10 mmol) dissolved in 15 mL of pure water and one spatula of Tetrakis(triphenylphosphine) palladium (0) was added, and reflux at 75°C for 24 hours. The reaction solution was transferred to a separating funnel and extracted with chloroform. The extracted organic layer was separated with pure water and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it and the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using a developing solvent of chloroform:*n*-hexane = 1:8. Further, the solvent was evaporated under reduced pressure, and recrystallization was performed with chloroform and methanol to obtain TBPF-Oc (0.18 g, 50.1%) as white solid.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.82-7.63 (m, 22H), 7.38 (d, *J* = 3.9 Hz, 1H), 7.32 (d, *J* = 5.3 Hz, 1H), 7.12 (t, *J* = 2.9 Hz, 1H), 2.07 (m, 2H), 1.25-1.08 (m, 22H), 0.80 (t, *J* = 6.9 Hz, 3H).

Anal Calcd for C₆₁H₆₂S₂: C 85.26 %, H 7.27 %, S 7.46 %. Found: C 85.12 %, H 7.37 %, S 7.47 %.

2,7-Bis(4'-bromo[1,1'-biphenyl]-4-yl)-9,9-*n*-dioctyl-fluorene [8]

Under an argon atmosphere, [5] (0.30 g, 0.47 mmol) and [6] (0.87 g, 2.80 mmol) were placed in a 300 mL three-necked flask and dissolved in THF (50 mL). To the THF solution, a basic aqueous solution of Na₂CO₃ (0.26 g, 2.33 mmol) dissolved in 10 mL of pure water and one spatula of tetrakis(triphenylphosphine) palladium (0) was added, and reflux at 75°C for 24 hours.

The reaction solution was transferred to a separating funnel and extracted with chloroform. The extracted organic layer was separated with pure water and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it and the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using a developing solvent of chloroform:*n*-hexane = 1:3. Further, the solvent was evaporated under reduced pressure, and recrystallization was performed with chloroform and methanol to obtain [8] (0.26 g, 65.2 %) as white solid.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.80 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 4H), 7.67 (d, *J* = 7.9 Hz, 4H), 7.64 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.61 (m, 4H), 7.60-7.53 (dt, *J* = 19.5, 2.0 Hz, 4H), 7.52 (s, 2H), 2.06 (quin, *J* = 4.3 Hz, 4H), 1.22-1.07 (m, 20H), 0.79 (t, *J* = 7.1 Hz, 6H), 0.73 (bs, 4H).

Anal Calcd for C₅₃H₃₆Br₂: C 74.64 %, H 6.62 %, Br 18.74 %; Found: C 74.64 %, H 6.70 %, Br 18.81 %.

EBPF-Oc

Under an argon atmosphere, **[8]** (0.21 g, 0.25 mmol) and **[9]** (0.14 g, 0.54 mmol) were placed in a 300 mL three-necked flask and dissolved in THF (40 mL). To the THF solution, a basic aqueous solution of Na₂CO₃ (0.12 g, 1.17 mmol) dissolved in 10 mL of pure water and one spatula of tetrakis(triphenylphosphine) palladium (0) was added, and reflux at 75°C for 24 hours. The reaction solution was transferred to a separating funnel and extracted with chloroform. The extracted organic layer was separated with pure water and washed with saturated brine. Na₂SO₄ was added to the resulting solution to dry it and the solvent was evaporated under reduced pressure, and silica gel chromatography was performed using a developing solvent of chloroform. Further, the solvent was evaporated under reduced pressure, and recrystallization was performed with chloroform and methanol to obtain **EBPF-Oc** (0.15 g, 62.5 %) as white solid.

¹H-NMR (400 MHz, CDCl₃, δ from CHCl₃, ppm) δ = 7.83-7.61 (m, 24H), 6.34 (s, 2H), 4.35 (m, 4H), 4.28 (m, 4H), 2.06 (quin, *J* = 4.2 Hz, 4H), 1.22-1.08 (m, 20H), 0.79 (t, *J* = 7.3 Hz, 6H), 0.74 (bs, 4H).