Supporting Information

Self-encapsulation or picket-fence? An answer to molecular designs of highly solid-state luminescent conjugated polymers

Tsuneaki Sakurai,*[1] Kyota Ohkura,[1] Teruyoshi Ikeda[1], Rin Terao,[1] Yoshiki Kamimura,[1] Mitsuo Hara,[2] and Masaki Shimizu[1]

[1] *Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology, Hashikami-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.*

[2] *Faculty of Engineering and Design, Kagawa University, 2217-20, Hayashi-cho, Takamatsu 761-0396, Japan.*

*Correspondence and requests for materials should be addressed to Tsuneaki Sakurai (sakurai@kit.ac.jp).

1. General

All the chemicals were purchased from Tokyo Chemical Industry, Fujifilm Wako Pure Chemical, Nacalai Tesque, Kanto Chemical, or Merck (Sigma-Aldrich®), and used as received. Anhydrous tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and toluene were purchased from Kanto Chemical, and passed through an AS ONE Glass Contour system equipped with two packed columns of neutral alumina and copper oxide under nitrogen before use. Other anhydrous solvents were purchased from Fujifilm Wako Pure Chemical or Merck (Sigma-Aldrich®) and used as received. Triethylamine was distilled over CaH_2. Reactions using microwave were performed using a Biotage Initiator+ microwave reactor. 0.5–2 mL microwave vials with a vial cap were used as a closed reaction vessel. Slow addition of solutions was controlled by using a CHEMYX fusion 101A syringe pump. TLC analyses were performed on a glass coated with Silica gel 70 F_{254} purchased from Fujifilm Wako Pure Chemical Co. Column chromatography was performed on PSQ60B silica gel (spherical) purchased from Fuji Silysia Chemical. Preparative gel permeation chromatography (GPC) was performed on a YMC LC-forte/R multiple preparative HPLC system equipped with Japan Analytical Industry JAIGEL-2.5HR/2.5HR columns (d = 40 mm, l = 600 mm) at a flow rate of 40 mL min^{-1} for the purification of monomers and JAIGEL-2.5HH/3HH columns (d = 20 mm, l = 600 mm) at a flow rate of 7.5 mL min^{-1} for the fractionation of polymers.

^1H and ^{13}C NMR spectra were recorded in chloroform-d ($CDCl_3$), dichloromethane-d_2 (CD_2Cl_2), or 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) on a Varian Mercury 400 spectrometer, operating at 400 and 100 MHz, respectively, where chemical shifts were determined with respect to tetramethylsilane (TMS, δ 0.00) or $CHCl_3$ (CH_2Cl_2, $C_2H_2Cl_4$) as an internal reference. Average molecular weights of the polymers were determined by size exclusion chromatography (SEC) on a SHIMADU HPLC system composed of a CBM-20A system controller, SIL-20A auto sampler, LC-20AD solvent delivery pump, DGU-20A3 degasser, and column oven CTO-20A, equipped with TOSOH TSKgel GMHHR-H HT column. 1,2-dichlorobenzene was used as an eluent at a flow rate of 0.75 mL min^{-1} at 80 °C. Absorption at 365 nm was monitored by a SPD-20A detector and used for detecting the elution peaks. Average molecular weights were estimated by calibration using polystyrene standards purchased from Merck (Sigma-Aldrich®).

Electronic absorption spectra were recorded on a JASCO V-730 UV/VIS/NIR spectrophotometer equipped with a JASCO ETCS-761 Peltier thermostatted single position cell holder. Fluorescence spectra were measured on a JASCO FP-8500 fluorescence spectrophotometer. Absolute fluorescence quantum yields (Φ) were evaluated on this spectrometer with a JASCO ILF-835 fluorescence integrate sphere unit. The excitation

wavelength was set at 320, 405, and 365 nm for **SE-PP**/**PF-PP**, **SE-PPV**/**PF-PPV$_L$**/**PF-PPV$_S$** and **SE-PPB**/**PF-PPB$_L$**/**PF-PPB$_S$**, respectively. Fluorescence lifetimes were evaluated on a Hamamatsu Photonics Quantaurus-τ using 280, 365, or 405 nm LED excitation pulses. Fluorescence decay profiles were obtained by averaging 20 nm range around the peak wavelength. The solution samples for spectroscopic measurements, otherwise noted, were prepared at 2×10^{-5} M in a 1 × 1 cm quartz cell. Spin-coated films of **SE-PP** and **PF-PP**, suitable for absorption and fluorescence spectroscopic measurements, were fabricated from their $CHCl_3$ solutions (ca. 20 μL) onto a quartz substrate spun at 800–1500 rpm for 60 sec using a Mikasa MS-A-100 spin-coater. Spin-coated films of **SE-PPV**, **PF-PPV$_L$**, and **PF-PPV$_S$** were fabricated from their PhCl solutions at 1500 rpm for 60 sec. Spin-coated films of **SE-PPB**, **PF-PPB$_L$**, and **PF-PPB$_S$** were fabricated by solubilizing them in PhCl at 100 ºC and casting these solutions onto a quartz substrate spun at 500–800 rpm for 90 sec. PPV derivatives MEH-PPV and Super Yellow as reference luminescent polymers were purchased from Merck (Sigma-Aldrich®).

Dynamic light scattering (DLS) measurements were performed with an Otsuka Electronics ELSZ-1000 particle size analyzer. Solutions of **SE-PPB** and **PF-PPB$_L$** in PhCl at 2×10^{-5} M in a quartz cell with a 10 mm optical path length were used as samples.

Powder X-ray diffraction (PXRD) experiments of the polymers were carried out using a Rigaku MiniFlex600 X-ray diffractometer (λ = 1.54 Å) with a D/teX Ultra semiconductor detector. The sample was mounted on a silicon non-reflecting plate. Wide-angle X-ray scattering (WAXS) measurements were performed on a Rigaku ATX-G diffractometer with incident X-ray wavelength of 1.54 Å. The sample films were fabricated by dropcast from the $CHCl_3$ solution at r.t. or PhCl solution at 60 ºC onto a quartz plate.

Atomic force microscopy (AFM) measurements were carried out using a Seiko Instruments Inc. SPI-4000 atomic force microscope equipped with a Bruker Instrument Scanasyst-Air silicon cantilever.

An oligomer model of **SE-PPB** was generated by connecting the four molecules of **SE-M3** (dodecyl chains were omitted for clarity) optimized at S_0 in advance, through C–C bonds between terminal alkynes. For structural optimization, density functional theory (DFT) calculations using Gaussian 16 package was used with B3LYP/6-31G(d) level.

2. Synthesis Details

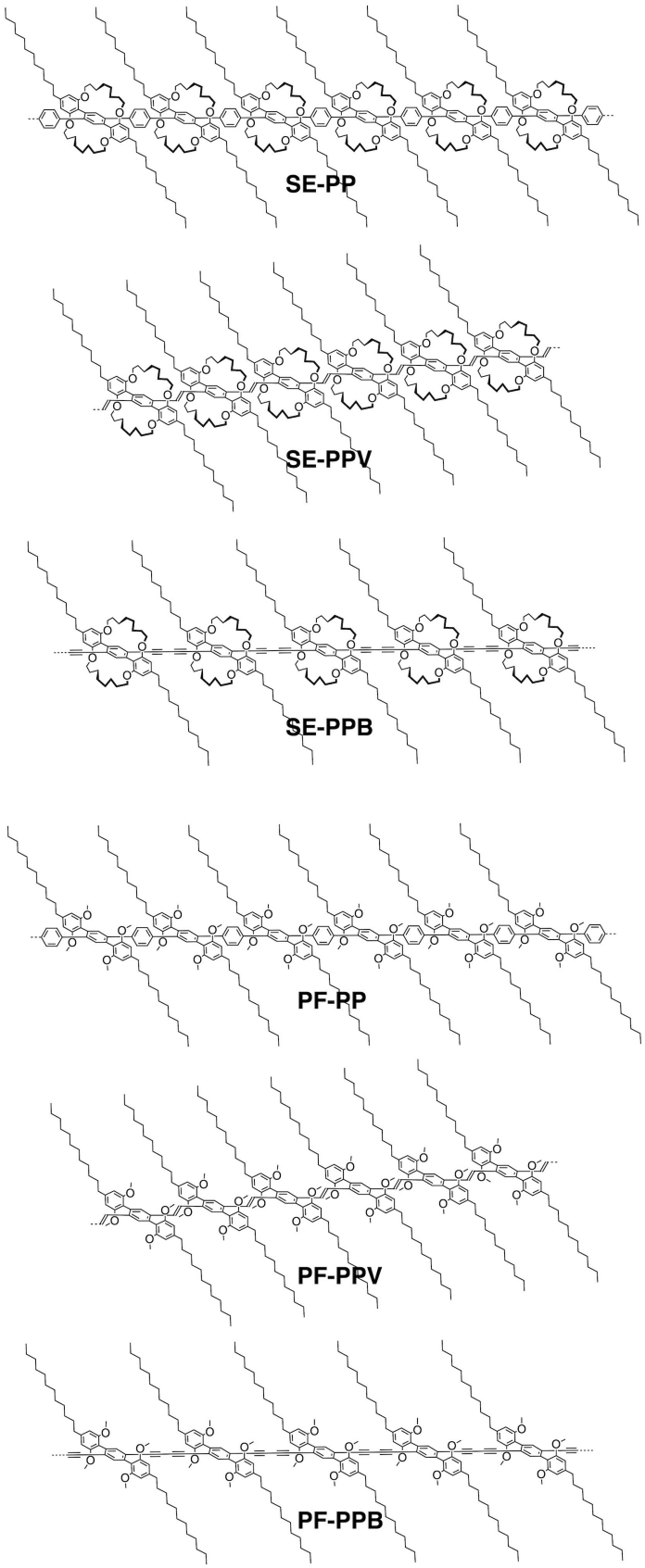


Figure S1. Full description of chemical structures of the target polymers.

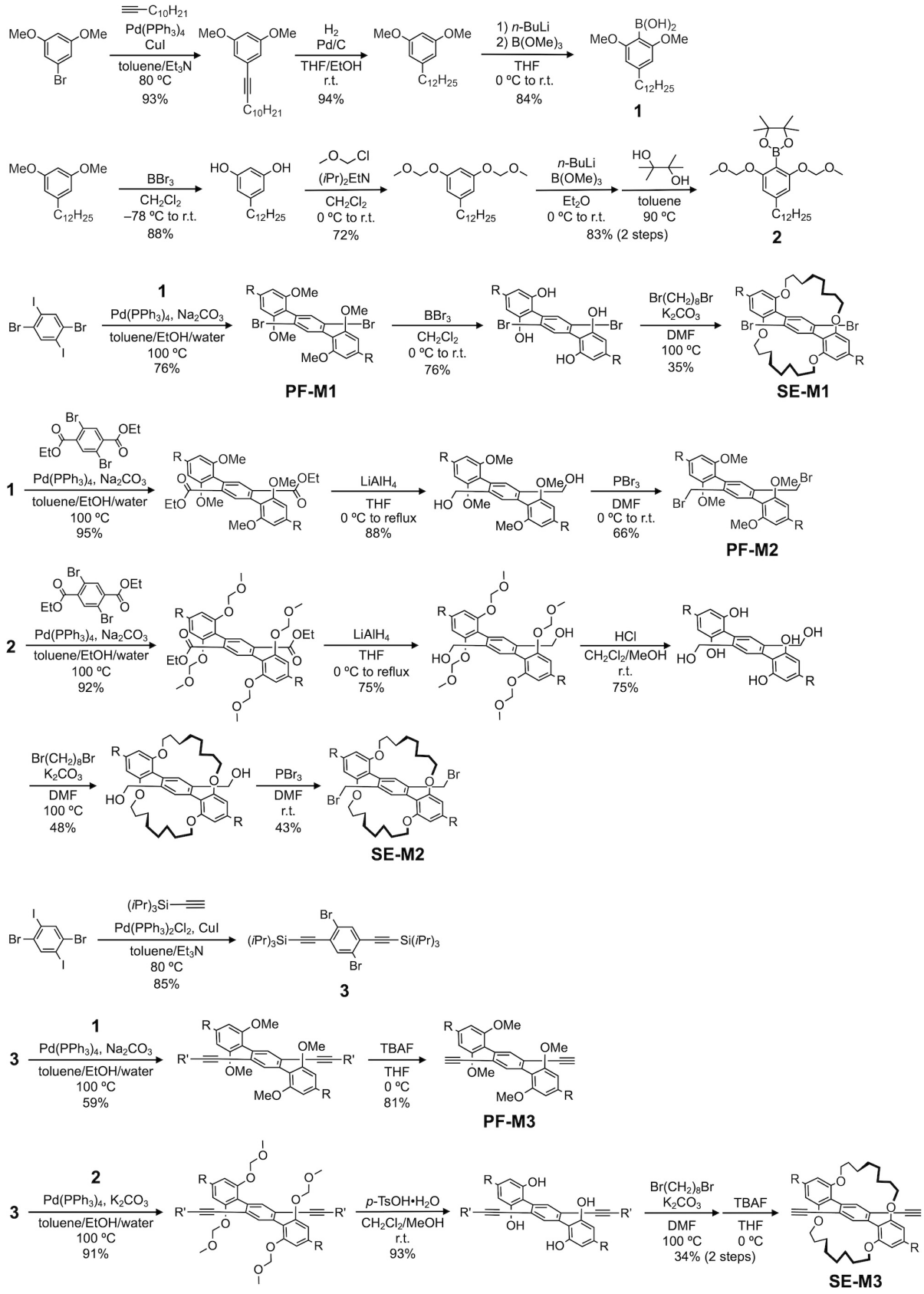
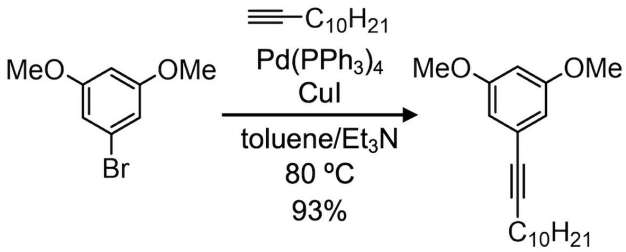
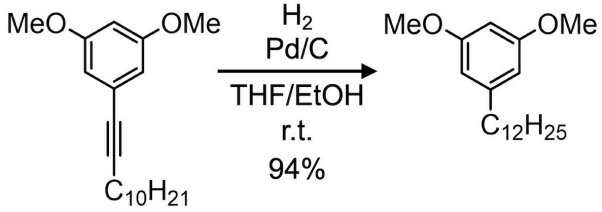


Figure S2. Full synthetic routes of monomers **PF-M1**, **SE-M1**, **PF-M2**, **SE-M2**, **PF-M3**, and **SE-M3** (R = $C_{12}H_{25}$, R' = Si(*i*Pr)$_3$).

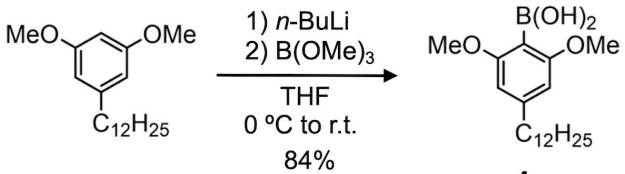
2.1. Synthesis of PF-M1



5-(Dodecyn-1-yl)-1,3-dimethoxybenzene: To an anhydrous toluene/Et_3N solution (50 mL, 1/1 v/v) of 1-bromo-3,5-dimethoxybenzene (2.17 g, 10 mmol), CuI (191 mg, 1 mmol), and $Pd(PPh_3)_4$ (351 mg, 0.5 mmol) was added 1-dodecyne (2.6 mL, 12 mmol), and the mixture was degassed by freeze-pump-thaw cycles for 3 times. The mixture was stirred at 80 ºC under Ar for 13 h, and then cooled down to r.t. The mixture was diluted with toluene, filtered off from an insoluble fraction through a pad of celite, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/toluene (3/1 v/v) as an eluent, to allow isolation of the target compound as a white solid (2.91 g, 9.31 mmol, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 3H, C≡C$(CH_2)_9CH_3$), 1.27–1.33 (m, 14H, C≡C$CH_2CH_2(CH_2)_7CH_3$), 1.56–1.63 (m, 2H, C≡C$CH_2CH_2(CH_2)_7CH_3$), 2.39 (t, J = 6.8 Hz, 2H, C≡C$CH_2(CH_2)_8CH_3$), 3.77 (s, 6H, OCH_3), 6.40 (s, 1H, Ar-H), 6.55 (s, 2H, Ar-H).

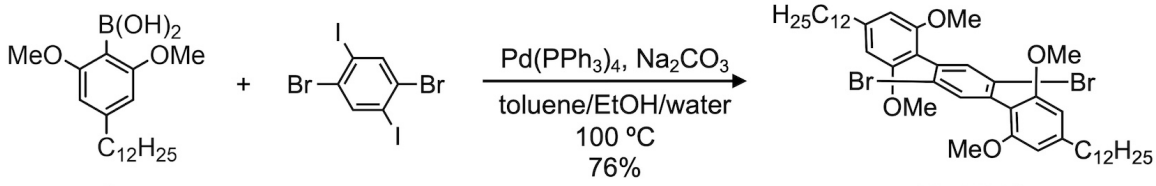


5-Dodecyl-1,3-dimethoxybenzene: To an anhydrous THF/EtOH solution (60 mL, 1/1 v/v) of 5-(dodecyn-1-yl)-1,3-dimethoxybenzene (1.47 g, 4.85 mmol) was added Pd/C (147 mg, 10 wt%), and the mixture was stirred at r.t. under H_2 for 46 h. After the H_2 atmosphere was replaced with Ar, the mixture was filtered through a pad of celite, and evaporated to dryness under reduced pressure, to allow the isolation of the target compound as a white solid (1.40 g, 4.56 mmol, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 3H, $CH_2(CH_2)_{10}CH_3$), 1.26–1.30 (m, 18H, $CH_2CH_2(CH_2)_9CH_3$), 1.59–1.62 (m, 2H, $CH_2CH_2(CH_2)_9CH_3$), 2.54 (t, J = 8.0 Hz, 2H, $CH_2(CH_2)_{10}CH_3$), 3.80 (s, 6H, OCH_3), 6.30 (s, 1H, Ar-H), 6.34 (s, 2H, Ar-H).



1

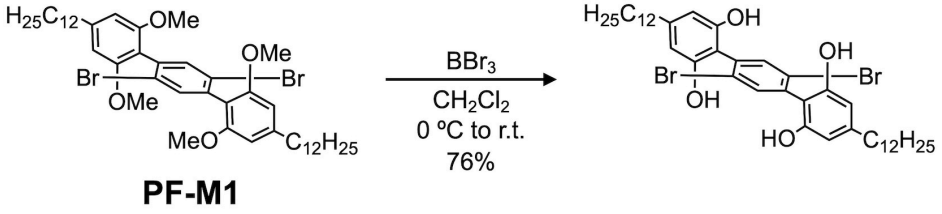
4-Dodecyl-2,6-dimethoxy-4-dodecylbenzeneboronic acid (1): To an anhydrous THF solution (5.4 mL) of 5-dodecyl-1,3-dimethoxybenzene (0.30 g, 0.98 mmol) was added a 1.50 M hexane solution of *n*-BuLi (0.82 mL, 1.22 mmol) at 0 ºC under Ar, and the mixture was stirred at 0 ºC for 4 h. Then, trimethoxyborane ($B(OMe)_3$, 0.11 mL, 0.98 mmol) was added at 0 ºC, and the resultant mixture was stirred at r.t. for 1 h. The reaction mixture was quenched by addition of aq. HCl and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was recrystallized from hexane, to allow isolation of **1** as white solid (0.28 g, 0.82 mmol, 84%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.26–1.32 (m, 18H), 1.60–1.63 (m, 2H), 2.60 (t, J = 8.0 Hz, 2H, $ArCH_2$), 3.90 (s, 6H, OCH_3), 6.45 (s, 2H, Ar-H), 7.18 (s, 2H, $B(OH)_2$).



1 **PF-M1**

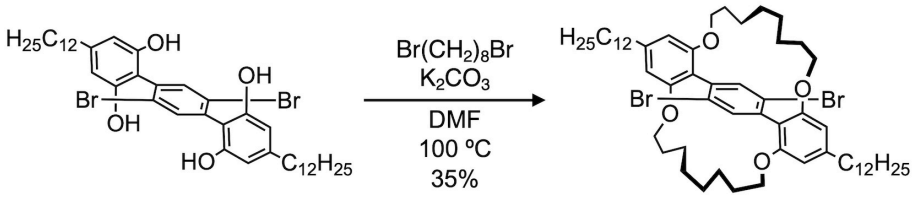
2,5-Bis(2,6-dimethoxy-4-dodecylphenyl)-1,4-dibromobenzene (PF-M1) [S1]**:** To a toluene/EtOH/water solution (13.2 mL, 4/1/1 v/v/v) of **1** (1.05 g, 3.0 mmol), 1,4-dibromo-2,5-diiodobenzene (0.67 g, 1.36 mmol), and Na_2CO_3 (0.87 g, 8.2 mmol) was added $Pd(PPh_3)_4$ (0.47 g, 0.41 mmol), and the mixture was degassed by freeze-pump-thaw cycles (×3). The mixture was stirred at 100 ºC for 46 h under Ar. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (20/1 v/v) as an eluent, to allow isolation of **PF-M1** as white solid (0.88 g, 1.04 mmol, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.27–1.37 (m, 36H), 1.65–1.70 (m, 4H), 2.65 (t, J = 7.8 Hz, 4H, $ArCH_2$), 3.76 (s, 12H, OCH_3), 6.46 (s, 4H, Ar-H), 7.48 (s, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.17, 22.73, 29.40, 29.59, 29.67, 29.69, 29.72, 31.45, 31.96, 36.91, 55.87, 104.05, 115.11, 123.69, 135.54, 136.17, 145.16, 157.45.

2.2. Synthesis of SE-M1



PF-M1

2,5-Bis(2,6-dihydroxy-4-dodecylphenyl)-1,4-dibromobenzene [S1]**:** To an anhydrous CH_2Cl_2 solution (1.2 mL) of 2,5-bis(4-dodecyl-2,6-dimethoxyphenyl)-1,4-dibromobenzene (**PF-M1**: 0.50 g, 0.59 mmol) was added a 1 M CH_2Cl_2 solution of boron tribromide (BBr_3; 3.6 mL, 3.6 mmol) at 0 ºC under Ar, and the mixture was stirred at r.t. for 8 h. The reaction mixture was quenched with the addition of sat. aq. $NaHCO_3$ and extracted with CH_2Cl_2. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (5/1 v/v) as an eluent, to allow isolation of the target compound as white solid (0.36 g, 0.45 mmol, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 7.2 Hz, 6H, CH_3), 1.27–1.33 (m, 36H), 1.60–1.65 (m, 4H, OH), 2.56 (t, J = 8.0 Hz, 4H, $ArCH_2$), 6.42 (s, 4H, Ar-H), 7.76 (s, 2H, Ar-H).

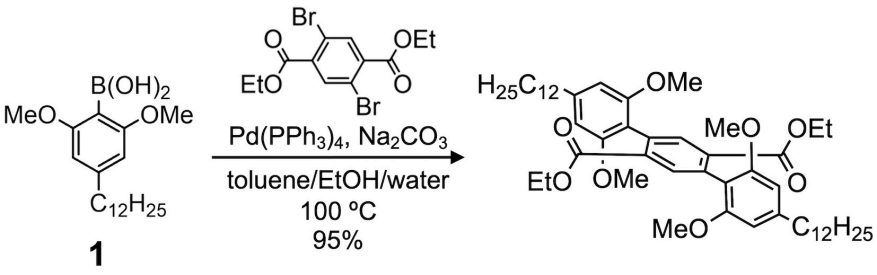


SE-M1

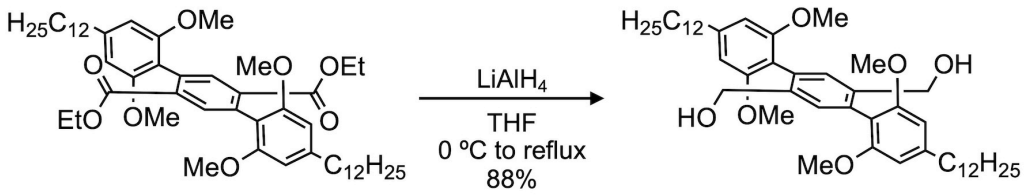
SE-M1: To an anhydrous DMF solution (15 mL) of K_2CO_3 (0.10 g, 0.72 mmol) vigorously stirred at 100 ºC under Ar was added an anhydrous DMF solution (4.6 mL) of 2,5-bis(2,6-dihydroxy-4-dodecylphenyl)-1,4-dibromobenzene (0.14 g, 0.18 mmol) and 1,8-dibromooctane (66 μL, 0.36 mmol) slowly via syringe at 2.3 mL h^{-1}, and the mixture was stirred at 100 ºC for 18 h under Ar. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (40/1 v/v) as an eluent and evaporated to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2/MeOH, to allow isolation of **SE-M1** as white solid (64 mg, 0.063 mmol, 35%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.27–1.37 (m, 54H), 1.59–1.67 (m, 10H), 2.62 (t, J = 7.2 Hz, 4H, $ArCH_2$), 3.93 (s, 8H, OCH_2), 6.40

(s, 4H, Ar-H), 7.50 (s, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.14, 22.71, 24.03, 27.22, 29.14, 29.38, 29.56, 29.64, 29.68, 29.70, 31.42, 31.95, 36.90, 68.43, 103.76, 114.66, 123.45, 135.49, 136.07, 144.80, 157.07.

2.3. Synthesis of PF-M2

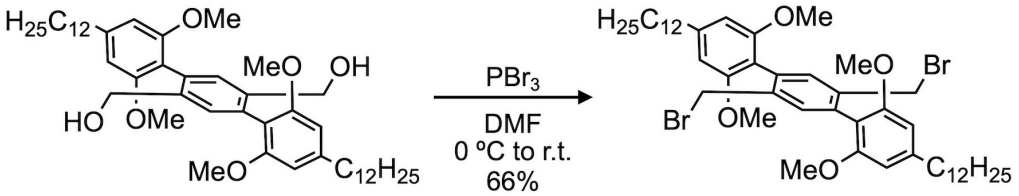


Diethyl 2,5-bis(4-dodecylphenyl-2,6-dimethoxy)terephtalate: To a toluene/EtOH/water solution (2.2 mL, 4/1/1 v/v/v) of diethyl 2,5-dibromotelephthalate (0.075 g, 0.20 mmol), **1** (0.17 g, 0.47 mmol), and Na_2CO_3 (0.83 mg, 0.79 mmol) was added $Pd(PPh_3)_4$ (0.023 g, 0.020 mmol), and the mixture was degassed by freeze-pump-thaw cycles (×3). The mixture was stirred at 100 ºC for 20 h under Ar. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (9/1 v/v) as an eluent, to allow isolation of target compound as white solid (0.16 g, 0.19 mmol, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 0.99 (t, J = 7.2 Hz, 6H, CH_3), 1.27–1.44 (m, 36H), 1.63–1.70 (m, 4H), 2.63 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.70 (s, 12H, OCH_3), 4.06 (q, J = 7.2 Hz, 4H, OCH_2CH_3), 6.44 (s, 4H, Ar-H), 7.84 (s, 2H, Ar-H).



2,5-Bis(hydroxymethyl)-1,4-bis(2,6-dimethoxy-4-dodecylphenyl)benzene: To an anhydrous THF (1.0 mL) solution of diethyl 2,5-bis(2,6-dimethoxy-4-dodecylphenyl)terephthalate (0.14 g, 0.17 mmol) was added a 1.0 M THF solution of $LiAlH_4$ (0.67 mL, 0.67 mmol) at 0 ºC under Ar, and the mixture was refluxed for 22 h. Then, the reaction mixture was cooled down to 0 ºC and poured into water. The mixture was extracted with EtOAc. The organic extract was washed

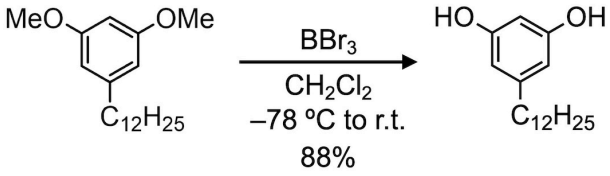
with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (3/1 v/v) as an eluent, to allow isolation of target compound as white solid (0.110 g, 0.15 mmol, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.28–1.37 (m, 36H), 1.65–1.70 (m, 4H), 2.32 (t, J = 6.4 Hz, 2H, OH), 2.65 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.73 (s, 12H, OCH_3), 4.36 (d, J = 6.0 Hz, 4H, CH_2OH), 6.50 (s, 4H, Ar-H), 7.32 (s, 2H, Ar-H).



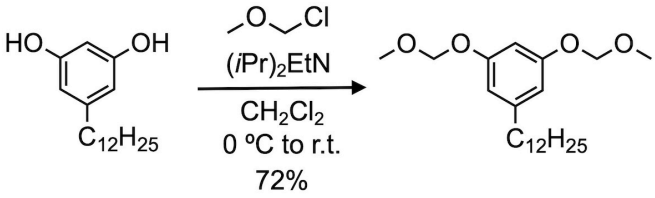
PF-M2

2,5-Bis(bromomethyl)-1,4-bis(4-dodecyl-2,6-dimethoxyphenyl)benzene (PF-M2): To an anhydrous DMF solution (2.4 mL) of 1,4-bis(4-dodecyl-2,6-dimethoxyphenyl)-2,5-bis(hydroxymethyl)benzene (96 mg, 0.13 mmol) was added PBr_3 (27 μL, 0.28 mmol) at 0 ºC under Ar, and the mixture was stirred at r.t. for 15 h. The reaction mixture was quenched by addition of water and extracted with CH_2Cl_2. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (10/1 v/v) as an eluent, where the fraction was collected and evaporated to dryness under reduced pressure. The residue was subjected to preparative size exclusion chromatography (SEC) using $CHCl_3$ as an eluent and JAIGEL-2.5HR/2.5HR (ϕ = 4 cm, l = 60 cm) as SEC columns, where the 2nd fraction was collected and evaporated to dryness under reduced pressure. The residue was reprecipitated from hexane, to allow isolation of **PF-M2** as white solid (75 mg, 0.086 mmol, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.27–1.37 (m, 36H), 1.67–1.71 (m, 4H), 2.65 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.74 (s, 12H, OCH_3), 4.33 (s, 4H, CH_2Br), 6.48 (s, 4H, Ar-H), 7.34 (s, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.12, 22.69, 29.37, 29.54, 29.57, 29.65, 29.70, 31.45, 31.93, 32.63, 36.80, 55.84, 104.34, 114.13, 133.25, 133.47, 136.22, 144.73, 157.58.

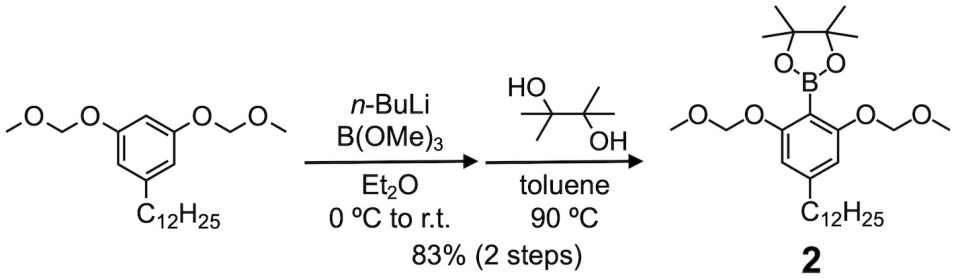
2.4. Synthesis of SE-M2



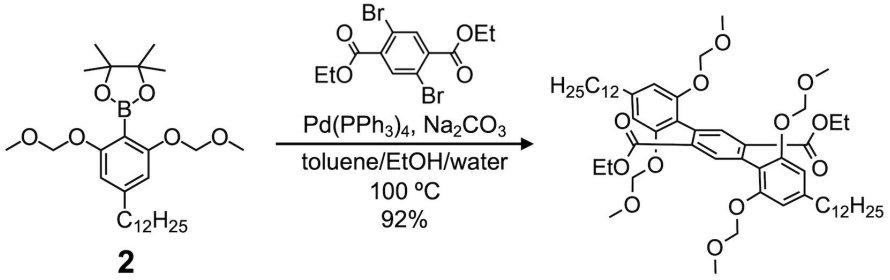
5-Dodecylresorcinol: To an anhydrous CH_2Cl_2 solution (28 mL) of 1-dodecyl-3,5-dimethoxybenzene (3.0 g, 9.8 mmol) was added a 1 M CH_2Cl_2 solution of BBr_3 (25 mL, 25 mmol) at –78 ºC under Ar, and the mixture was stirred at r.t. for 7 h. The reaction mixture was poured into sat. aq. $NaHCO_3$ solution, and the resulting precipitate was filtered and washed with hexane. The residue was dried in vacuo, to allow isolation of the target compound as white solid (2.4 g, 8.7 mmol, 88%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.25–1.29 (m, 18H), 1.53–1.58 (m, 2H), 2.48 (t, J = 8.0 Hz, 2H, $ArCH_2$), 4.71 (s, 2H, OH), 6.17 (s, 1H, Ar-H), 6.24 (s, 2H, Ar-H).



3,5-Bis(methoxymethoxy)-1-dodecylbenzene: To an anhydrous CH_2Cl_2 solution (9.5 mL) of 5-dodecylresorcinol (1.0 g, 3.6 mmol) and chloromethyl methyl ether (0.82 mL, 10.8 mmol) was added *N*,*N*-diisopropylethylamine (2.5 mL, 14.4 mmol) at 0 ºC under Ar, and the mixture was stirred at r.t. for 24 h. The reaction mixture was quenched with the addition of water and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (10/1 v/v) as an eluent, to allow isolation of the target compound as colorless liquid (0.95 g, 2.6 mmol, 72%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 3H, CH_3), 1.25–1.30 (m, 18H), 1.56–1.60 (m, 2H), 2.53 (t, J = 8.0 Hz, 2H, $ArCH_2$), 3.48 (s, 6H, OCH_3), 5.15 (s, 4H, OCH_2O), 6.53 (s, 2H, Ar-H), 6.56 (s, 1H, Ar-H).

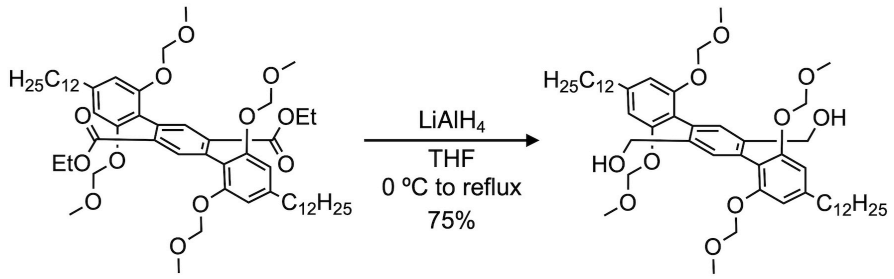


2,6-Bis(methoxymethoxy)-4-dodecyl-benzeneboronic acid pinacol ester (2): To an anhydrous Et_2O solution (4 mL) of 3,5-bis(methoxymethoxy)-1-dodecylbenzene (0.15 g, 0.40 mmol) was added a 1.50 M hexane solution of *n*-BuLi (0.32 mL, 0.48 mmol) at 0 ºC under Ar, and the mixture was stirred at 0 ºC for 4 h. Then, trimethoxyborane (0.067 mL, 0.61 mmol) was added at 0 ºC, and the resultant mixture was stirred at r.t. for 1 h. The Et_2O was removed by distillation. To the residue were added pinacol (0.047 g, 0.40 mmol) and toluene (4 mL), and the mixture was stirred at 90 ºC for 16 h. The reaction mixture was quenched with the addition of water and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (5/1 v/v) as an eluent, to allow isolation of **2** as colorless liquid (0.17 g, 0.34 mmol, 83%). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.27–1.33 (m, 20H), 1.39 (s, 12 H, CH_3), 2.52 (t, J = 6.8 Hz, 2H, $ArCH_2$), 3.46 (s, 6H, OCH_3), 5.12 (s, 4H, OCH_2O), 6.49 (s, 2H, Ar-H).

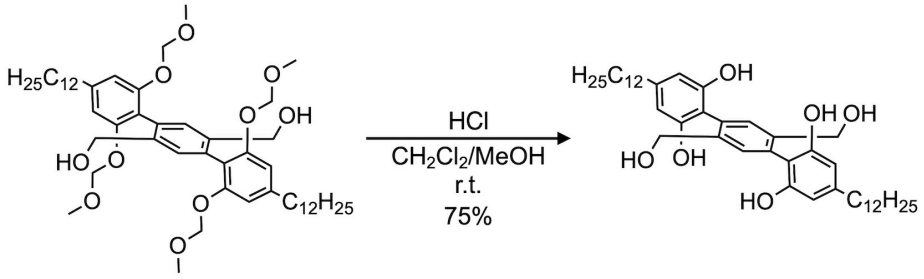


Diethyl 2,5-bis[2,6-bis(methoxymethoxy)-4-dodecylphenyl]terephthalate: To a toluene/EtOH/water solution (16.4 mL, 7/2/2 v/v/v) of diethyl 2,5-dibromotelephtalate (0.40 g, 1.05 mmol), **2** (1.04 g, 2.11 mmol), and Na_2CO_3 (0.67 g, 6.31 mmol) was added $Pd(PPh_3)_4$ (122 mg, 0.11 mmol), and the mixture was degassed by freeze-pump-thaw cycles (×3). The mixture was stirred at 100 ºC for 20 h under Ar. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (5/1 v/v) as an eluent, to allow isolation of

target compound as white solid (0.92 g, 0.97 mmol, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 0.98 (t, J = 7.2 Hz, 6H, CH_3), 1.27–1.40 (m, 36H), 1.60–1.70 (m, 4H), 2.61 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.30 (s, 12H, OCH_3), 4.06 (q, J = 7.2 Hz, 4H, OCH_2CH_3), 4.97–5.05 (m, 4H, OCH_2O), 6.69 (s, 4H, Ar-H), 7.92 (s, 2H, Ar-H).

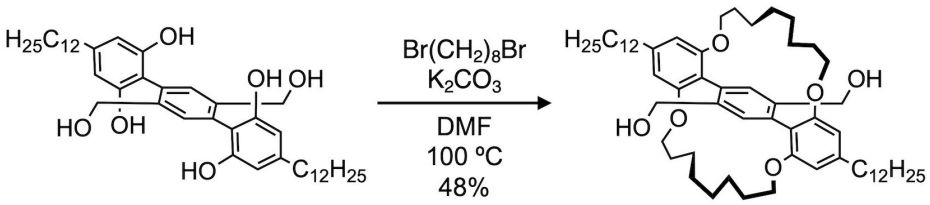


1,4-Bis[2,6-bis(methoxymethoxy)-4-dodecylphenyl]-2,5-bis(hydroxymethyl)benzene: To an anhydrous THF solution (5.0 mL) of $LiAlH_4$ (73 mg, 1.92 mmol) was added an anhydrous THF solution (5.0 mL) of diethyl 2,5-bis[2,6-bis(methoxymethoxy)-4-dodecylphenyl]terephthalate (0.76 g, 0.80 mmol) at 0 ºC under Ar, and the mixture was refluxed for 16 h. Then, the reaction mixture was cooled down to 0 ºC and quenched by slow addition of water. The resulting mixture was extracted with EtOAc, and the organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2/MeOH to allow isolation of target compound as white solid (0.52 g, 0.60 mmol, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.27–1.35 (m, 36H), 1.63–1.70 (m, 4H), 2.64 (t, J = 8.0 Hz, 2H, $ArCH_2$), 2.65 (t, J = 6.8 Hz, 4H, OH), 3.20 (s, 12H, OCH_3), 4.40 (d, J = 6.4 Hz, 4H, CH_2OH), 4.97–5.01 (m, 8H, OCH_2O), 6.73 (s, 4H, Ar-H), 7.36 (s, 2H, Ar-H).

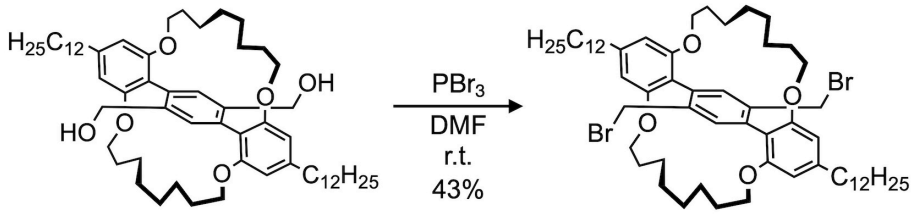


1,4-Bis(2,6-dihydroxy-4-dodecylphenyl)-2,5-bis(hydroxymethyl)benzene: To an anhydrous CH_2Cl_2/MeOH solution (10 mL, 1/1 v/v) of 1,4-bis[2,6-bis(methoxymethoxy)-4-dodecylphenyl]-2,5-bis(hydroxymethyl)benzene (0.52 g, 0.60 mmol) was added 4 M dioxane solution of HCl (1.8 mL, 7.2 mmol) at r.t. under Ar, and the mixture was stirred at r.t. for 14 h.

Then, the reaction mixture was cooled down to 0 ºC, poured into water, and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2/MeOH to allow isolation of the target compound as white solid (0.31 g, 0.45 mmol, 75%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.86 (t, J = 6.8 Hz, 6H, CH_3), 1.25–1.32 (m, 36H), 1.52–1.57 (m, 4H), 2.41 (t, J = 8.0 Hz, 4H, $ArCH_2$), 2.60 (t, J = 5.6 Hz, 2H, OH), 4.72 (d, J = 5.2 Hz, 2H, CH_2OH), 6.23 (s, 4H, Ar-H), 7.14 (s, 2H, Ar-H), 8.81 (s, 4H, ArOH).



SE-M2': To an anhydrous DMF solution (25 mL) of K_2CO_3 (0.11 g, 0.76 mmol) vigorously stirred at 100 ºC under Ar was added an anhydrous DMF solution (5.5 mL) of 1,4-bis(2,6-dihydroxy-4-dodecylphenyl)-2,5-bis(hydroxymethyl)benzene (0.15 g, 0.22 mmol) and 1,8-dibromooctane (80 μL, 0.43 mmol) slowly via syringe at 3.7 mL h^{-1}, and the mixture was stirred at 100 ºC for 17 h under Ar. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (10/1 v/v) as an eluent, to allow isolation of the target compound as white solid (95 mg, 0.10 mmol, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 7.2 Hz, 6H, CH_3), 1.27–1.36 (m, 36H), 1.49–1.54 (m, 4H), 1.65–1.68 (m, 4H), 2.29 (t, J = 6.0 Hz, 2H, OH), 2.61 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.86–3.96 (m, 8H, OCH_2), 4.33 (d, J = 6.0 Hz, 4H, CH_2OH), 6.43 (s, 4H, Ar-H), 7.25 (s, 2H, Ar-H).

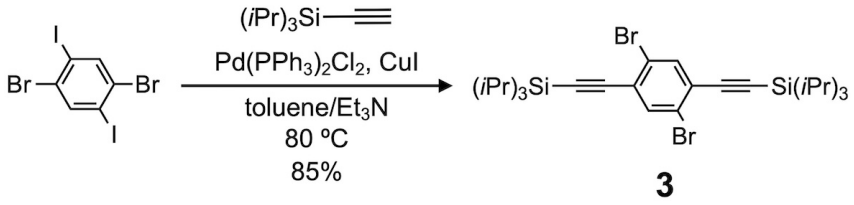


SE-M2

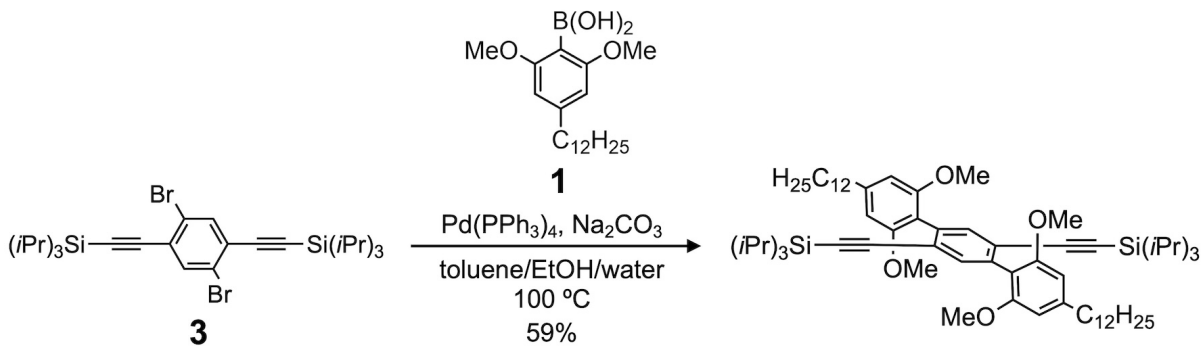
SE-M2: To an anhydrous DMF solution (1.7 mL) of **SE-M2'** (77 mg, 0.084 mmol) was added PBr_3 (18 μL, 0.19 mmol) at 0 ºC under Ar, and the mixture was stirred at r.t. for 16 h. Then, the reaction mixture was extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was

subjected to column chromatography on silica gel using hexane/EtOAc (30/1 v/v) as an eluent, where the target fraction was collected and evaporated to dryness under reduced pressure. The residue was subjected to preparative SEC using $CHCl_3$ as an eluent and JAIGEL-2.5HR/2.5HR (ϕ = 4 cm, l = 60 cm) as SEC columns, where the 2nd fraction was collected and evaporated to dryness under reduced pressure, to allow isolation of **SE-M2** as white solid (0.037 g, 0.036 mmol, 43%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 0.87 (t, J = 6.8 Hz, 6H, CH_3), 1.26–1.35 (m, 60H), 1.64–1.68 (m, 4H), 2.62 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.85–3.94 (m, 8H, OCH_2), 4.33 (s, 4H, CH_2Br), 6.44 (s, 4H, Ar-H), 7.23 (s, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.14, 22.71, 23.98, 27.17, 29.09, 29.38, 29.54, 29.58, 29.65, 29.68, 29.72, 31.50, 31.95, 33.07, 36.83, 68.34, 103.93, 113.79, 132.99, 133.60, 136.11, 144.34, 157.17.

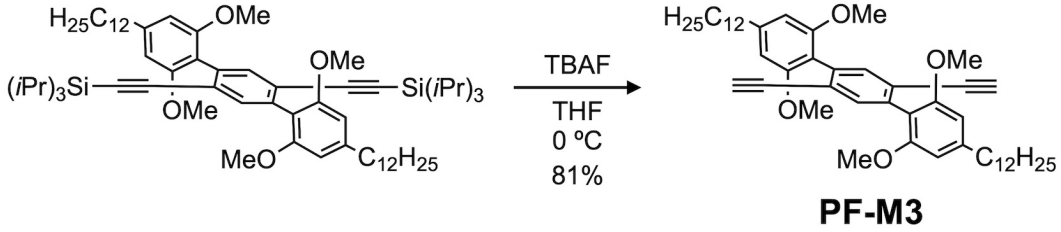
2.5. Synthesis of PF-M3



2,5-Bis(triisopropylsilylethynyl)-1,4-dibromobenzene: To an anhydrous toluene/Et_3N solution (15 mL, 1/1 v/v) of 1,4-dibromo-2,5-diiodobenzene (1.46 g, 3.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.21 g, 0.30 mmol) and CuI (0.12 g, 0.6 mmol) was added (triisopropylsilyl)acetylene (1.4 mL, 6.3 mmol), and the mixture was degassed by freeze-pump-thaw cycles (×3). The mixture was stirred at 80 ºC for 8 h under Ar. After being cooled down to r.t., the mixture was filtered off from an insoluble fraction through a pad of celite, and the filtrate was evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane as an eluent, to allow isolation of the target compound as white solid (1.52 g, 2.6 mmol, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.10–1.13 (m, 42H), 7.67 (s, 2H, Ar-H).



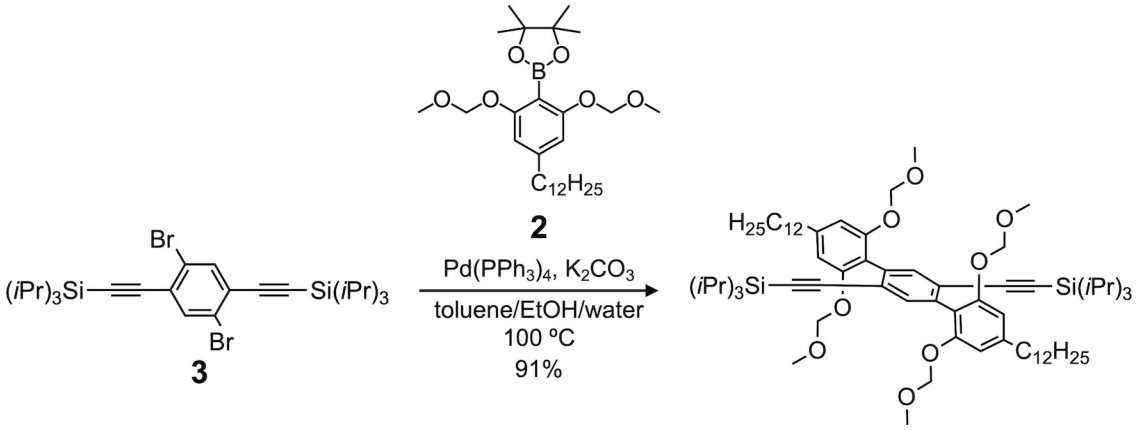
1,4-Bis(4-dodecyl-2,6-dimethoxyphenyl)-2,5-bis(triisopropylsilylethynyl)benzene: To a toluene/EtOH/water solution (10 mL, 4/1/1 v/v/v) of **1** (0.46 g, 1.3 mmol), **3** (0.26 g, 0.44 mmol), and Na_2CO_3 (0.28 g, 2.6 mmol) was added $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), and the mixture was degassed by freeze-pump-thaw cycles (×3). The mixture was stirred at 100 ºC for 48 h under Ar. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (20/1 v/v) as an eluent, to allow isolation of the target compound as white solid (0.27 g, 0.26 mmol, 59%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.87–0.91 (m, 48H), 1.27–1.37 (m, 36H), 1.60–1.64 (m, 4H), 2.59 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.71 (s, 12H, OCH_3), 6.41 (s, 4H, Ar-H), 7.37 (s, 2H, Ar-H).



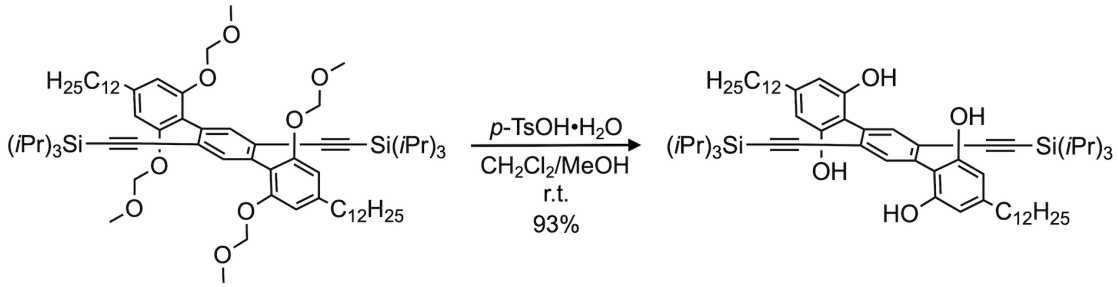
PF-M3

2,5-Bis(4-dodecyl-2,6-dimethoxyphenyl)-1,4-diethynylbenzene (PF-M3): To an anhydrous THF solution (13 mL) of 1,4-bis(4-dodecyl-2,6-dimethoxyphenyl)-2,5-bis(triisopropylsilylethynyl)benzene (0.18 g, 0.17 mmol) was added a 1 M THF solution of tetrabutylammonium fluoride (0.51 mL, 0.51 mmol) at 0 ºC, and the mixture was stirred at 0 ºC for 45 min. The reaction mixture was quenched by addition of water and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (20/1 v/v) as an eluent, to allow isolation of **PF-M3** as white solid (0.10 g, 0.14 mmol, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 1.27–1.36 (m, 36H), 1.64–1.71 (m, 4H), 2.64 (t, J = 8.0 Hz, 4H, $ArCH_2$), 2.89 (s, 2H, CH), 3.74 (s, 12H, OCH_3), 6.46 (s, 4H, Ar-H), 7.46 (s, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.16, 22.72, 29.40, 29.59, 29.68, 29.72, 31.43, 31.94, 36. 85, 55.84, 79.00, 83.38, 104.18, 114.71, 123.23, 135.51, 136.21, 144.56, 157.68.

2.6. Synthesis of SE-M3

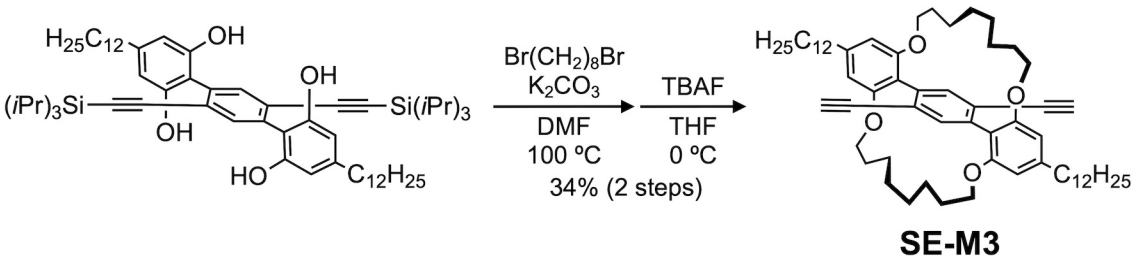


1,4-Bis[4-dodecyl-2,6-bis(methoxymethoxy)phenyl]-2,5-bis(triisopropylsilylethynyl)-benzene: To a toluene/EtOH/water (11 mL, 4/1/1 v/v/v) solution of **2** (371 mg, 0.75 mmol), **3** (180 mg, 0.30 mmol), and K_2CO_3 (250 mg, 1.81 mmol) was added $Pd(PPh_3)_4$ (0.035 mg, 0.030 mmol), and the mixture was degassed by freeze-pump-thaw cycles (×3). The mixture was stirred at 100 ºC for 48 h under Ar. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (20/1 v/v) as an eluent, to allow isolation of the target compound as white solid (320 mg, 0.27 mmol, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88–0.90 (m, 48H), 1.28–1.35 (m, 36H), 1.57–1.61 (m, 4H), 2.57 (t, J = 8.0 Hz, 4H, $ArCH_2$), 3.32 (s, 12H, OCH_3), 4.97 (d, J = 6.4 Hz, 4H, OCH_2O), 5.10 (d, J = 6.4 Hz, 4H, OCH_2O), 6.67 (s, 4H, Ar-H), 7.44 (s, 2H, Ar-H).



1,4-Bis(4-dodecyl-2,6-dihydroxyphenyl)-2,5-bis(triisopropylsilylethynyl)benzene [S2]**:** To an anhydrous CH_2Cl_2/MeOH (4.0 mL, 1/1 v/v) solution of 1,4-bis[4-dodecyl-2,6-bis(methoxymethoxy)phenyl]-2,5-bis(triisopropylsilylethynyl)benzene (0.32 g, 0.27 mmol) was added *p*-toluenesulfonic acid monohydrate (0.63 g, 3.3 mmol) under Ar, and the mixture was stirred at r.t. for 9 h. The reaction mixture was quenched by addition of sat. aq. $NaHCO_3$

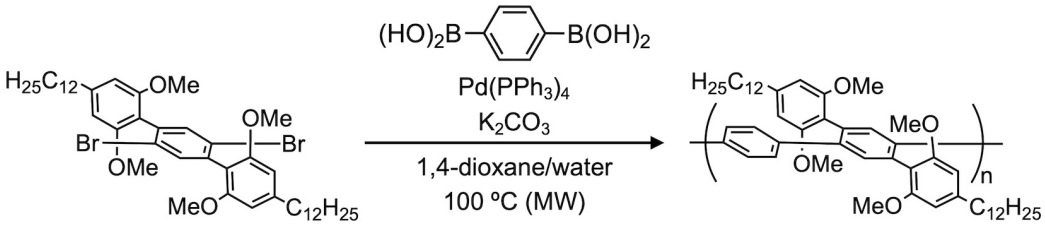
solution and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (5/1 v/v) as an eluent, to allow isolation of the target compound as white solid (0.24 g, 0.24 mmol, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 6H, CH_3), 0.95 (m, 42H), 1.26–1.33 (m, 36H), 1.58–1.63 (m, 4H), 2.52 (t, J = 7.6 Hz, 4H, $ArCH_2$), 4.77 (s, 4H, OH), 6.41 (s, 4H, Ar-H), 7.67 (s, 2H, Ar-H).



SE-M3

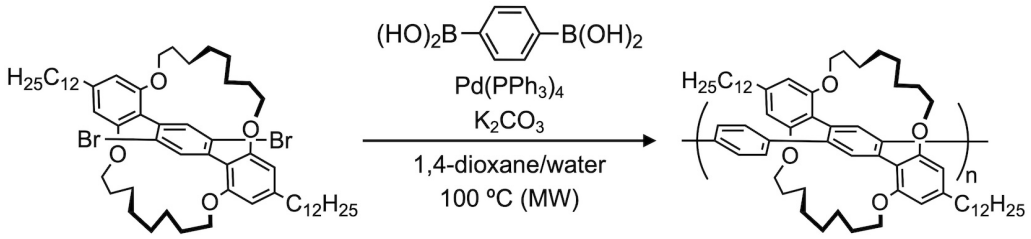
SE-M3: To an anhydrous DMF solution (6.0 mL) of K_2CO_3 (49 mg, 0.35 mmol) under vigorous stirring at 100 ºC was added an anhydrous DMF solution (6.0 mL) of 1,4-bis(2,6-dihydroxy-4-dodecylphenyl)-2,5-bis(triisopropylsilylethynyl)benzene (0.10 g, 0.10 mmol) and 1,8-dibromooctane (37 µL, 0.20 mmol) slowly via syringe at 4.0 mL h^{-1} under Ar, and the mixture was stirred at 100 ºC for 90 h. Then, the reaction mixture was cooled down to r.t. and extracted with EtOAc. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (10/1 v/v) as an eluent, where the 1st fraction was collected and evaporated to dryness under reduced pressure, to allow the crude product. To an anhydrous THF solution (2 mL) of the crude product was added a THF solution of tetrabutylammonium fluoride (16 µL, 0.16 mmol) at 0 ºC under Ar, and the mixture was stirred at 0 ºC for 1 h. The reaction mixture was quenched by addition of water and extracted with EtOAc. The organic extract was washed with water, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (20/1 v/v) as an eluent, to allow isolation of **SE-M3** as white solid (30 mg, 0.034 mmol, 34%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, J = 7.6 Hz, 6H, CH_3), 1.27–1.43 (m, 60H), 1.56–1.64 (m, 4H), 2.60 (t, J = 7.2 Hz, 4H, $ArCH_2$), 2.83 (s, 2H, CH), 3.88 (m, 4H, OCH_2), 3.95 (m, 4H, OCH_2), 6.40 (s, 4H, Ar-H), 7.48 (s, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.13, 22.70, 24.22, 27.30, 29.21, 29.37, 29.56, 29.67, 29.70, 31.40, 31.94, 36.86, 68.27, 78.59, 84.06, 103.76, 114.06, 123.08, 135.62, 136.03, 144.17, 157.27.

2.7. Synthesis of Polymers



PF-M1 **PF-PP**

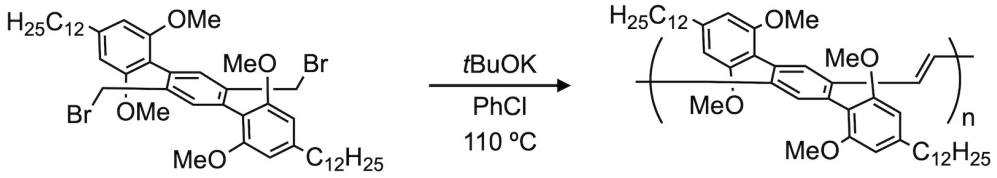
PF-PP: To a 1,4-dioxane/water (1.0 mL, 4/1, v/v) solution of **PF-M1** (30 mg, 0.036 mmol), 1,4-benzenediboronic acid (6.0 mg, 0.036 mmol), and K_2CO_3 (23 mg, 0.21 mmol) was added $Pd(PPh_3)_4$ (2 mg, 5 mol%) under Ar flow, and the vial was sealed with a crimp cap. The mixture was stirred under heating by microwave at 100 ºC for 24 h. After cooling down to r.t., the mixture was poured into toluene and a trace amount of sodium *N*,*N*-diethyldithiocarbamate trihydrate was added. The mixture was stirred at 100 ºC for 12 h. Then, the reaction mixture was cooled down to r.t. and extracted with toluene. The organic extract was washed with water and concentrated to a volume of ca. 1 mL under reduced pressure. The solution was reprecipitated by addition of MeOH to give **PF-PP** as white solid (20 mg, 75%).



SE-M1 **SE-PP**

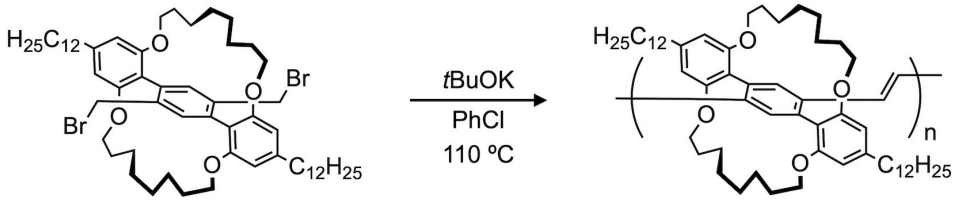
SE-PP: To a 1,4-dioxane/water (0.75 mL, 2/1, v/v) solution of **SE-M1** (25 mg, 0.025 mmol), 1,4-benzenediboronic acid (4.0 mg, 0.025 mmol), and K_2CO_3 (21 mg, 0.15 mmol) was added $Pd(PPh_3)_4$ (1.4 mg, 5 mol%) under Ar flow, and the vial was sealed with a crimp cap. The mixture was stirred under heating by microwave at 100 ºC for 24 h. After cooling down to r.t., the mixture was poured into toluene and a trace amount of sodium *N*,*N*-diethyldithiocarbamate trihydrate was added. The mixture was stirred at 100 ºC for 12 h. Then, the reaction mixture was cooled down to r.t. and extracted with toluene. The organic extract was washed with water and concentrated to a volume of ca. 1 mL under reduced pressure. The solution was reprecipitated by addition of MeOH to give the target polymer as white solid. Due to the low molecular weight, the polymer was subjected to preparative SEC using $CHCl_3$ as an eluent under a flow rate of 7.5 mL min^{-1} and JAIGEL-2.5HH/3HH (ϕ = 2 cm, l = 60 cm) as SEC

columns, where the fraction except low molecular weight oligomers was collected and evaporated to dryness under reduced pressure, to give **SE-PP** as white solid (5.0 mg, 22%) that was used for the evaluation of physical properties.



PF-M2 **PF-PPV$_L$ and PF-PPV$_S$**

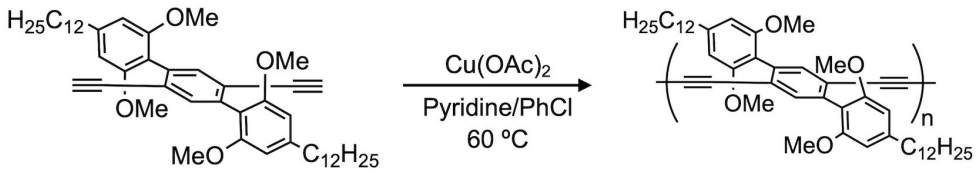
PF-PPV$_L$ and **PF-PPV$_S$:** An anhydrous PhCl solution (0.3 mL) of **PF-M2** (20 mg, 0.023 mmol) was degassed by freeze-pump-thaw cycles (×3), and the solution was added to an anhydrous PhCl solution (1.7 mL) of potassium *tert*-butoxide (13 mg, 0.12 mmol). The solution was further degassed by freeze-pump-thaw cycles (×3), and then stirred at 110 ºC under Ar for 18 h. After being cooled down to r.t., the mixture was diluted with chlorobenzene and concentrated to a volume of ca. 1 mL under reduced pressure. The residue was reprecipitated by addition of MeOH to allow the target polymer as yellow solid (10 mg, 59%). Due to the bimodal peaks in analytical SEC, the polymer was subjected to preparative SEC using $CHCl_3$ as an eluent under a flow rate of 7.5 mL min^{-1} and JAIGEL-2.5HH/3HH (ϕ = 2 cm, l = 60 cm) as SEC columns, where bimodal peaks were observed. The former peak was targeted, where two fractions with relatively large and small molecular weights were collected and evaporated to dryness under reduced pressure each. The residue was reprecipitated from $CHCl_3$/MeOH each, to give **PF-PPV$_L$** and **PF-PPV$_S$** as yellow solid. Both of the polymers were used for the evaluation of physical properties.



SE-M2 **SE-PPV**

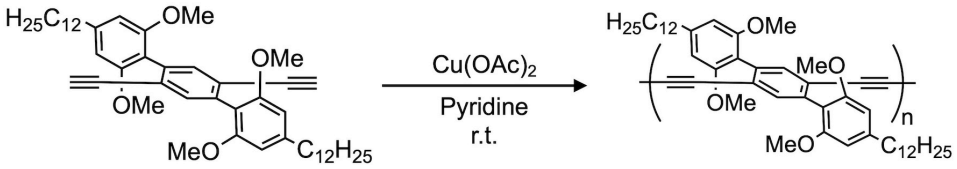
SE-PPV: An anhydrous PhCl solution (0.5 mL) of **SE-M2** (20 mg, 0.019 mmol) was degassed by freeze-pump-thaw cycles (×3), and the solution was added to an anhydrous PhCl solution (1.0 mL) of potassium *tert*-butoxide (11 mg, 0.096 mmol). The mixture was further degassed by freeze-pump-thaw cycles (×3), and then stirred at 110 ºC under Ar for 23 h. After being cooled down to r.t., the mixture was concentrated to a volume of ca. 1 mL under reduced

pressure. The solution was reprecipitated by addition of MeOH to give **SE-PPV** the target polymer as yellow solid (14 mg, 76%).



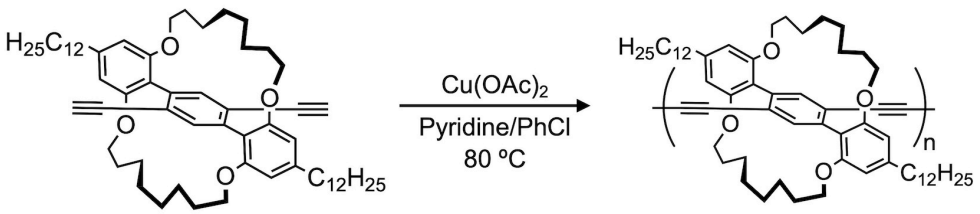
PF-M3 **PF-PPB$_L$**

PF-PPB$_L$: To an anhydrous pyridine/PhCl (2.7 mL, 1/1, v/v) solution of **PF-M3** (20 mg, 0.027 mmol) was added copper (II) acetate (27 mg, 0.14 mmol), and the mixture was stirred at 60 ºC under Ar for 39 h. After being cooled down to r.t., the reaction mixture was reprecipitated by addition of MeOH to give **PF-PPB$_L$** as yellow solid (18 mg, 92%). Due to the low solubility of the polymer, no NMR spectrum with a sufficient S/N ratio was obtained in $CDCl_3$, CD_2Cl_2, or $C_2D_2Cl_4$.



PF-M3 **PF-PPB$_S$**

PF-PPB$_S$: To an anhydrous pyridine (2.4 mL) solution of **PF-M3** (18 mg, 0.024 mmol) was added copper (II) acetate (24 mg, 0.12 mmol), and the mixture was stirred at r.t. under Ar for 39 h. After being cooled down to r.t., the reaction mixture was reprecipitated by addition of MeOH to give **PF-PPB$_S$** as yellow solid (17 mg, 92%).



SE-M3 **SE-PPB**

SE-PPB: To an anhydrous pyridine/PhCl (1.2 mL, 1/1, v/v) solution of **SE-M3** (11 mg, 0.012 mmol) was added copper (II) acetate (12 mg, 0.060 mmol), and the mixture was stirred at 80 ºC under Ar for 24 h. After being cooled down to r.t., the reaction mixture was reprecipitated by addition of MeOH to give **SE-PPB** as yellow solid (9.0 mg, 91%).

2.8. ^{1}H and ^{13}C NMR Spectra of Monomers

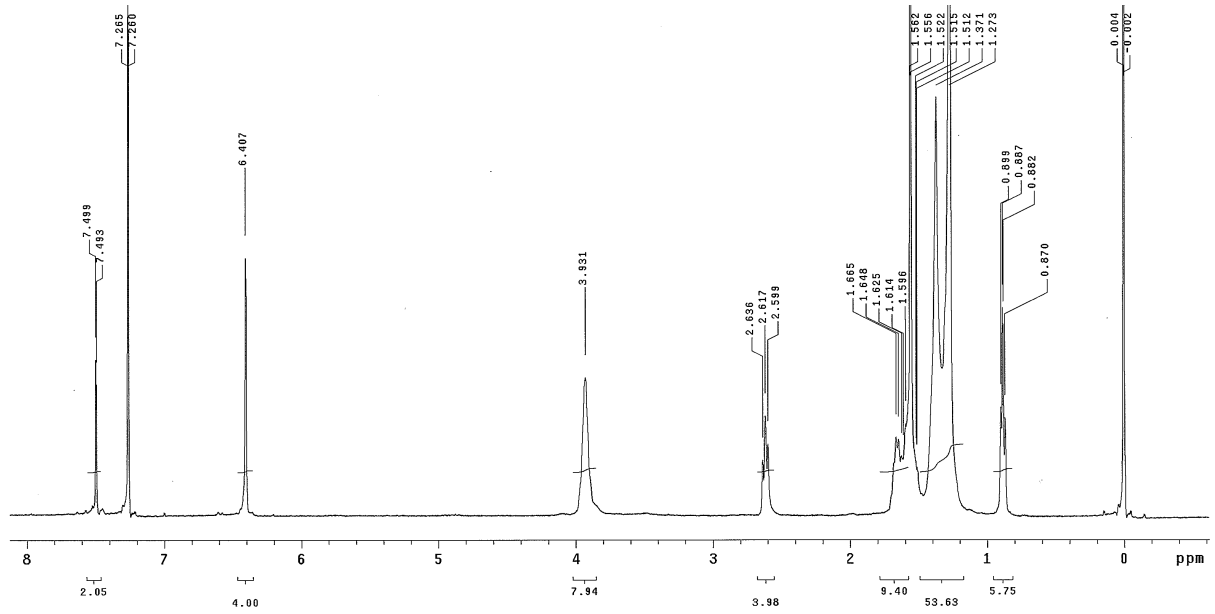


Figure S3. ^{1}H NMR spectrum of **SE-M1** in $CDCl_3$ at r.t.

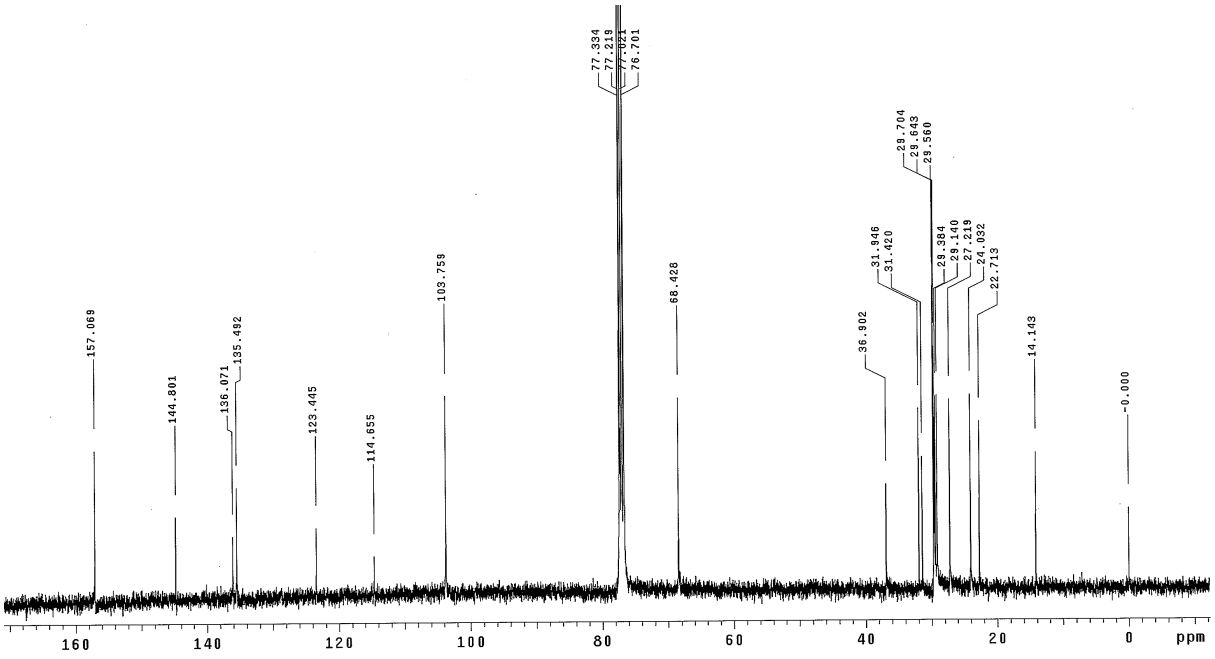


Figure S4. ^{13}C NMR spectrum of **SE-M1** in $CDCl_3$ at r.t.

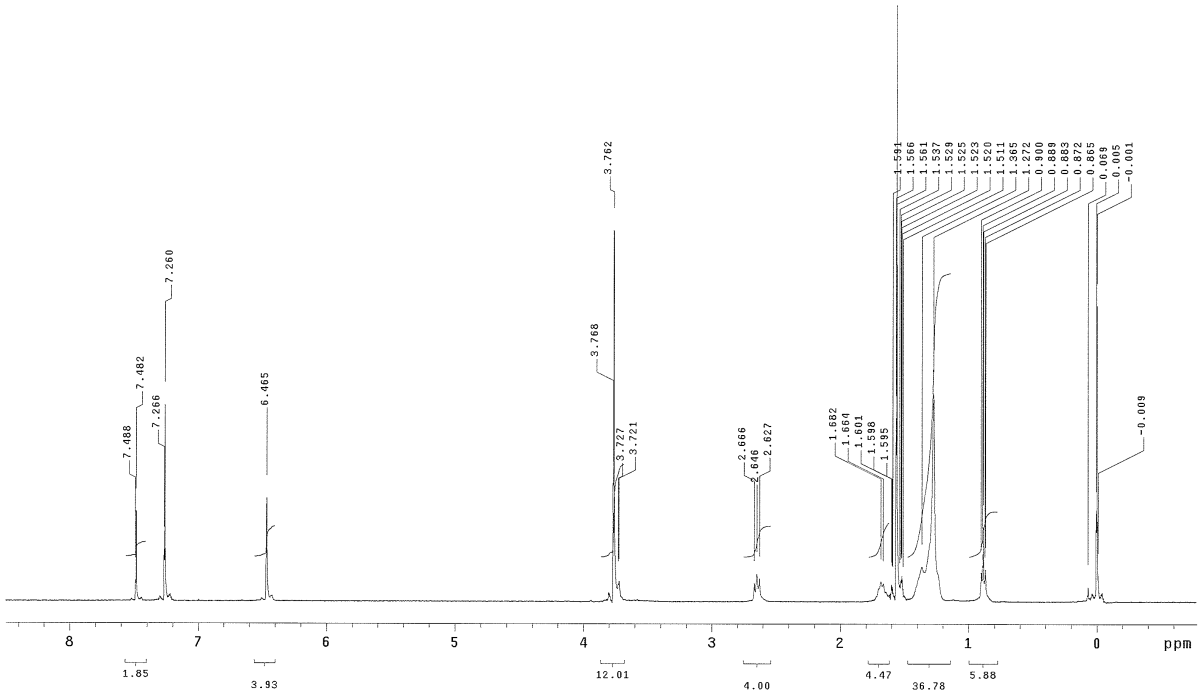


Figure S5. ^{1}H NMR spectrum of **PF-M1** in $CDCl_3$ at r.t.

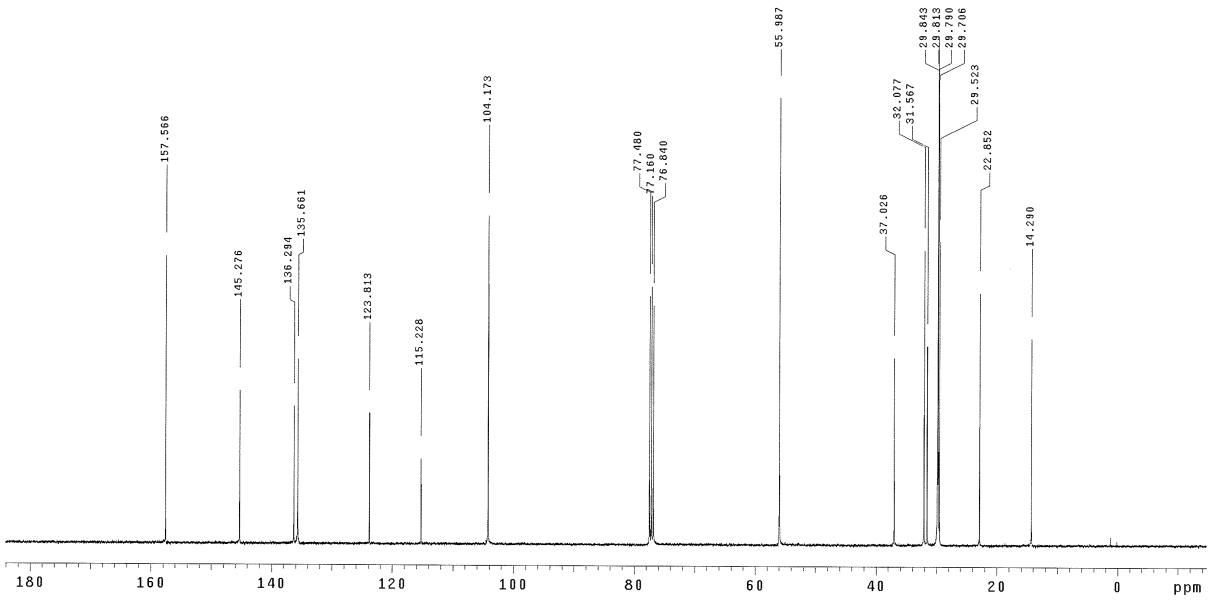


Figure S6. ^{13}C NMR spectrum of **PF-M1** in $CDCl_3$ at r.t.

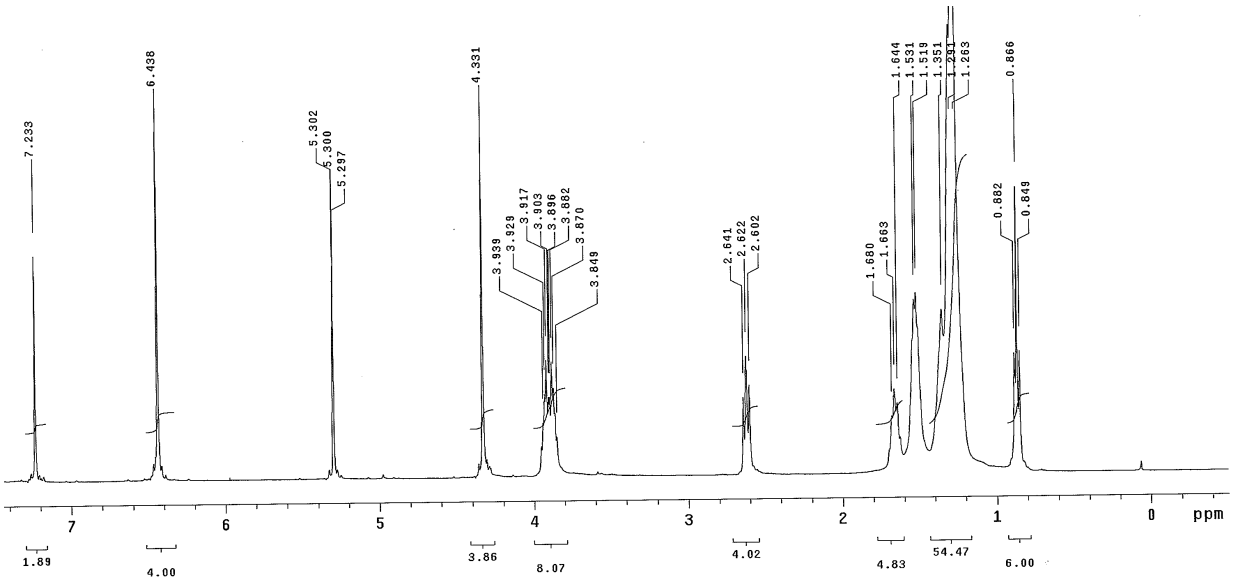


Figure S7. ^{1}H NMR spectrum of **SE-M2** in CD_2Cl_2 at r.t.

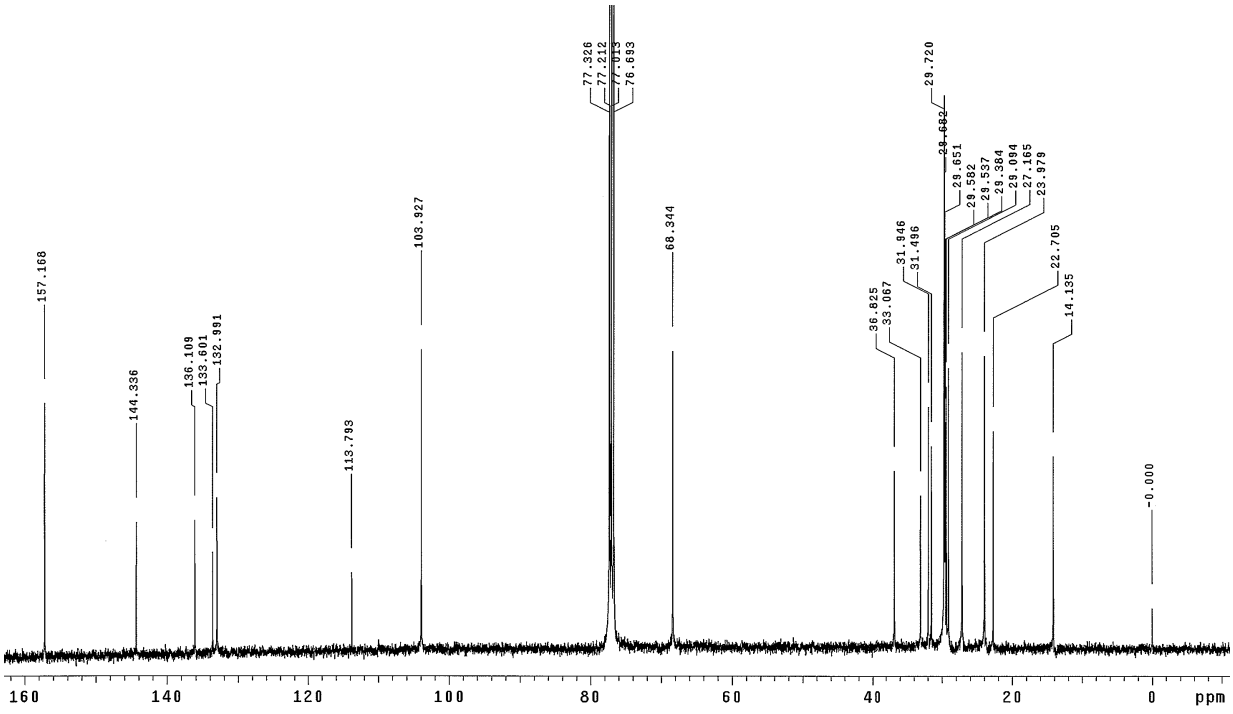


Figure S8. ^{13}C NMR spectrum of **SE-M2** in $CDCl_3$ at r.t.

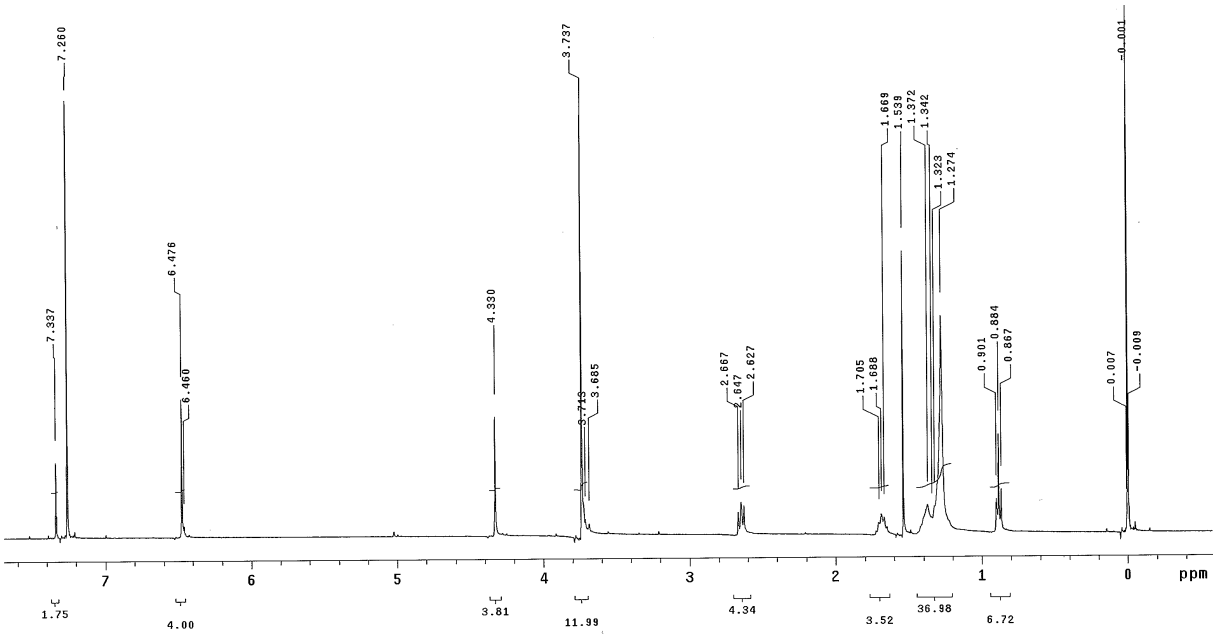


Figure S9. ^{1}H NMR spectrum of **PF-M2** in $CDCl_3$ at r.t.

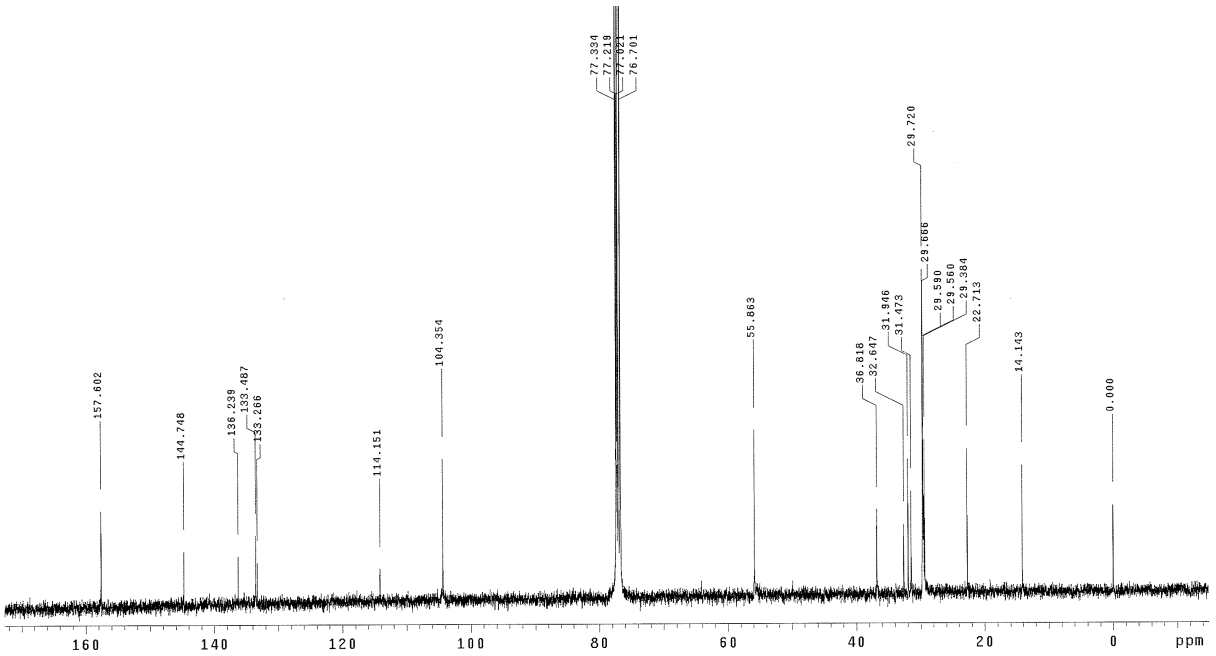


Figure S10. ^{13}C NMR spectrum of **PF-M2** in $CDCl_3$ at r.t.

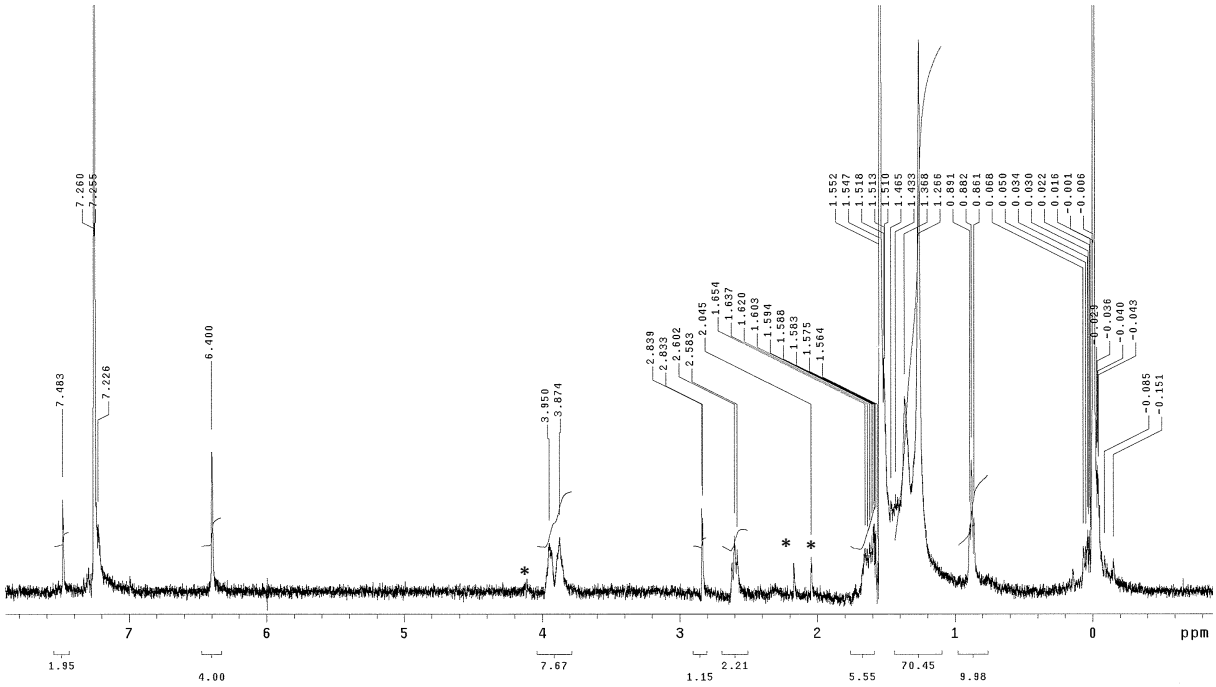


Figure S11. ^{1}H NMR spectrum of **SE-M3** in $CDCl_3$ at r.t. The peaks with an asterisk represent the residual solvent peaks of EtOAc and acetone.

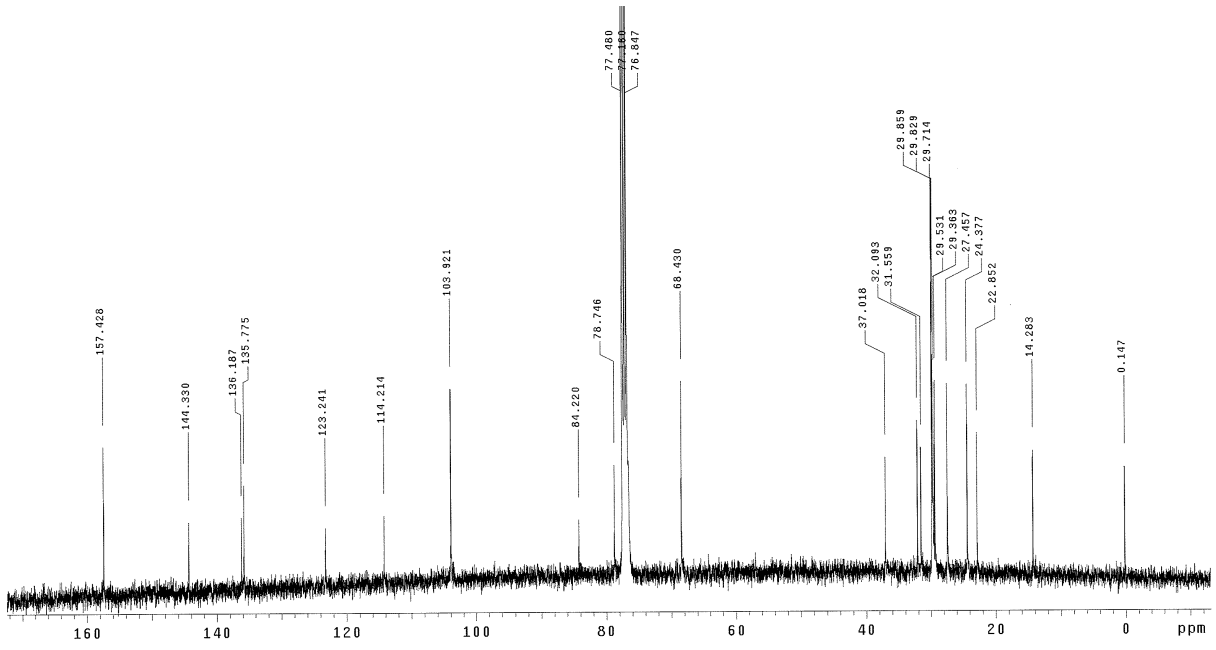


Figure S12. ^{13}C NMR spectrum of **SE-M3** in $CDCl_3$ at r.t.

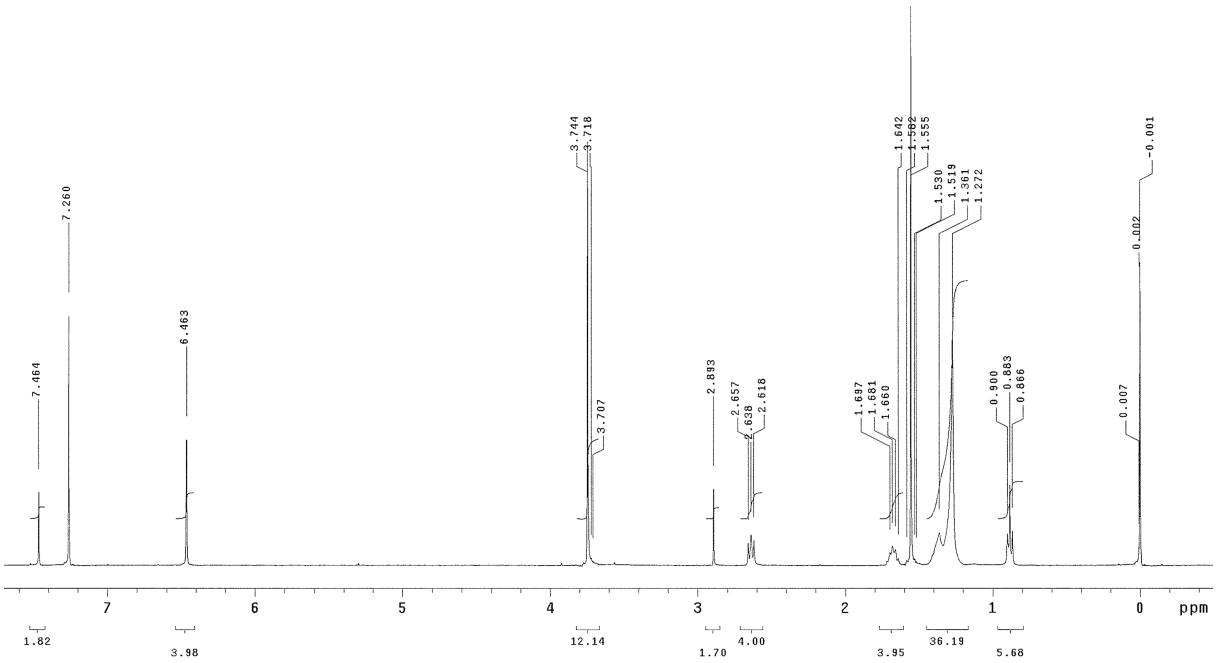


Figure S13. ^{1}H NMR spectrum of **PF-M3** in $CDCl_3$ at r.t.

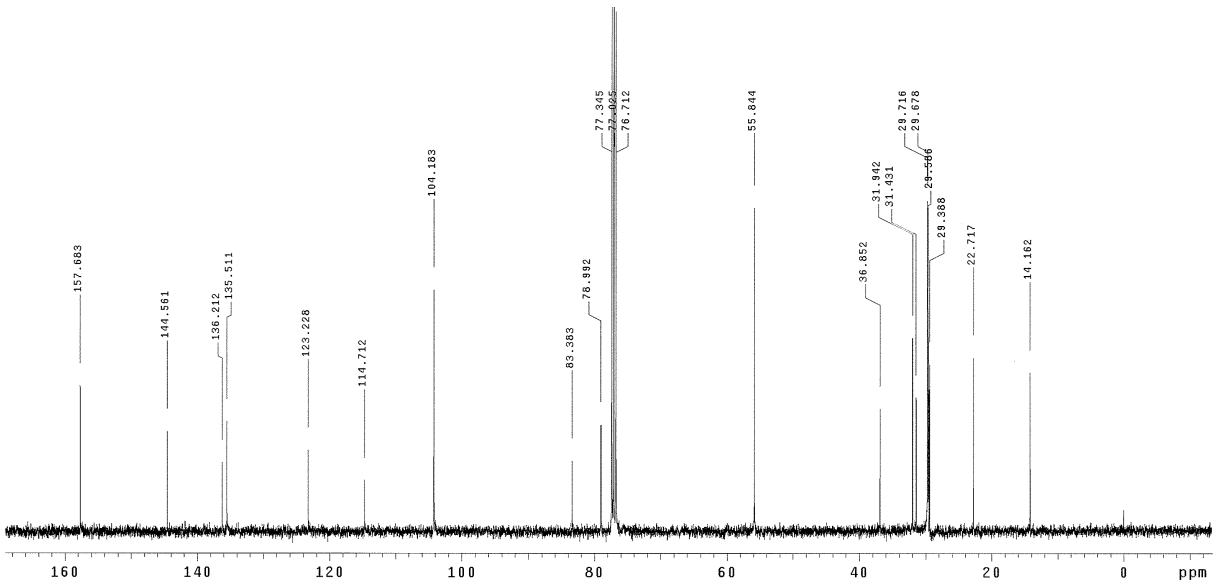


Figure S14. ^{13}C NMR spectrum of **PF-M3** in $CDCl_3$ at r.t.

2.9. ^{1}H NMR Spectra of Polymers

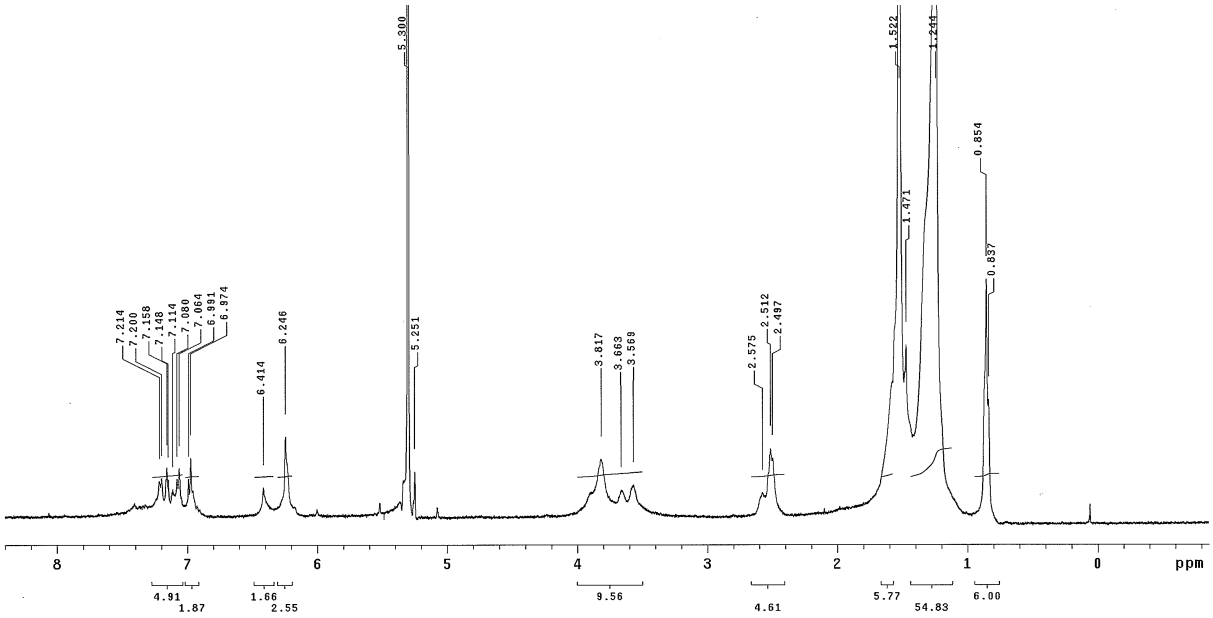


Figure S15. ^{1}H NMR spectrum of **SE-PP** in CD_2Cl_2 at r.t.

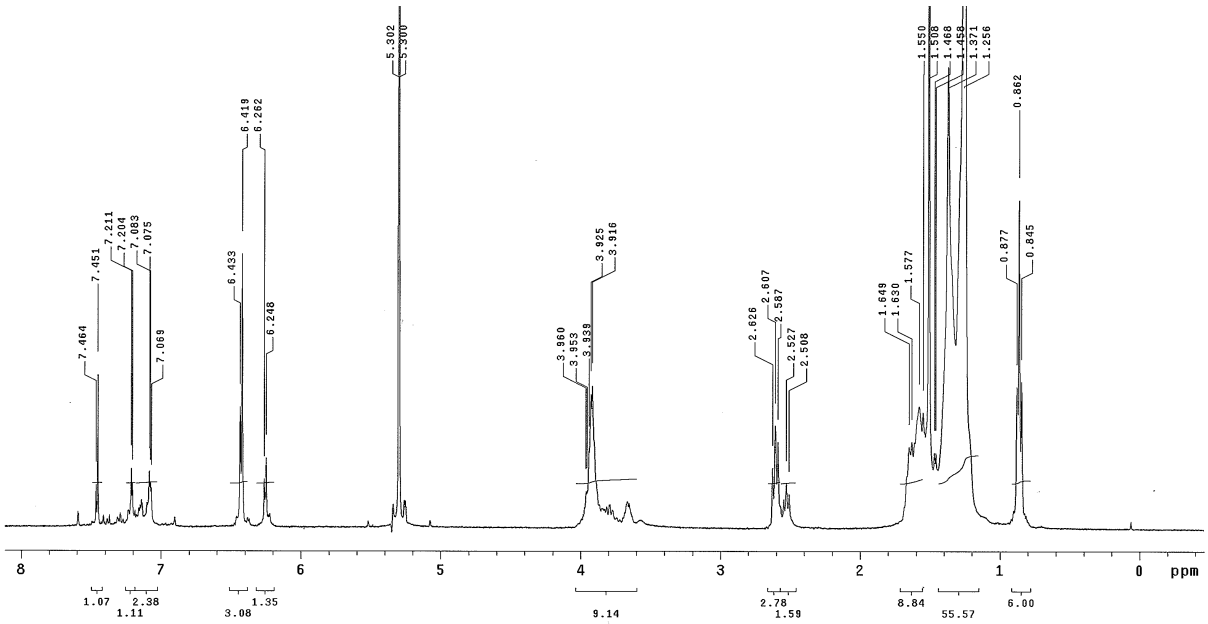


Figure S16. ^{1}H NMR spectrum of **PF-PP** in CD_2Cl_2 at r.t.

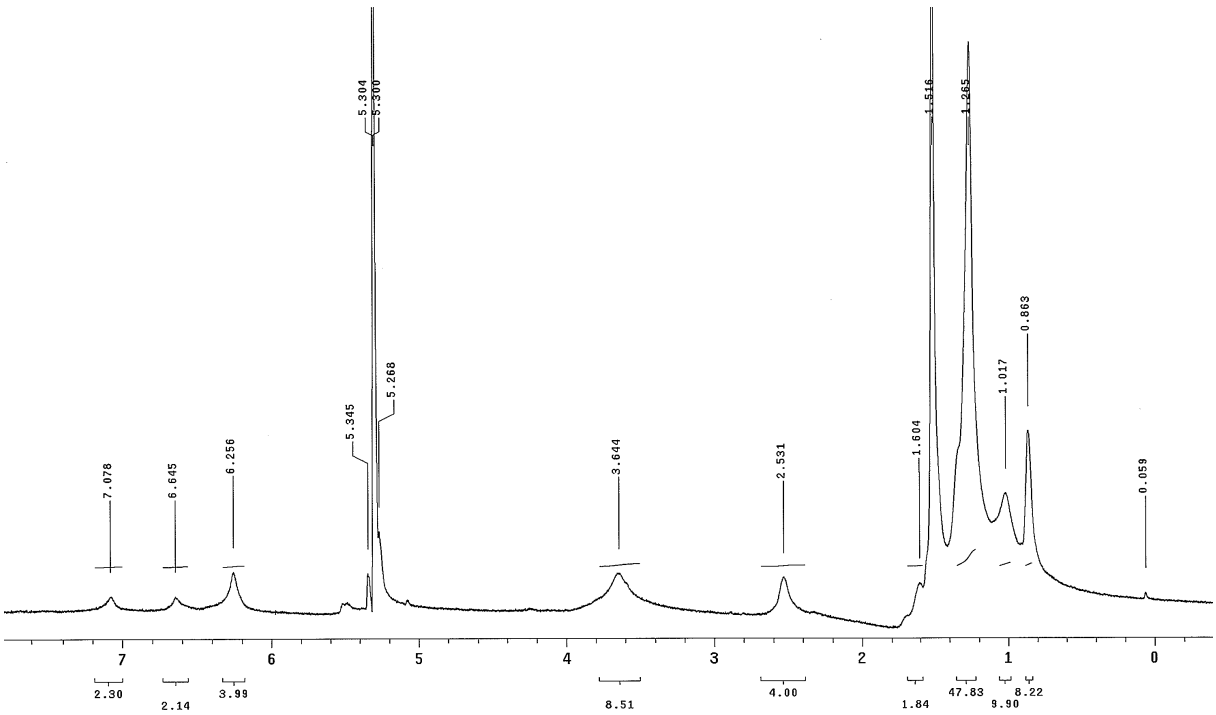


Figure S17. ^{1}H NMR spectrum of **SE-PPV** in CD_2Cl_2 at r.t.

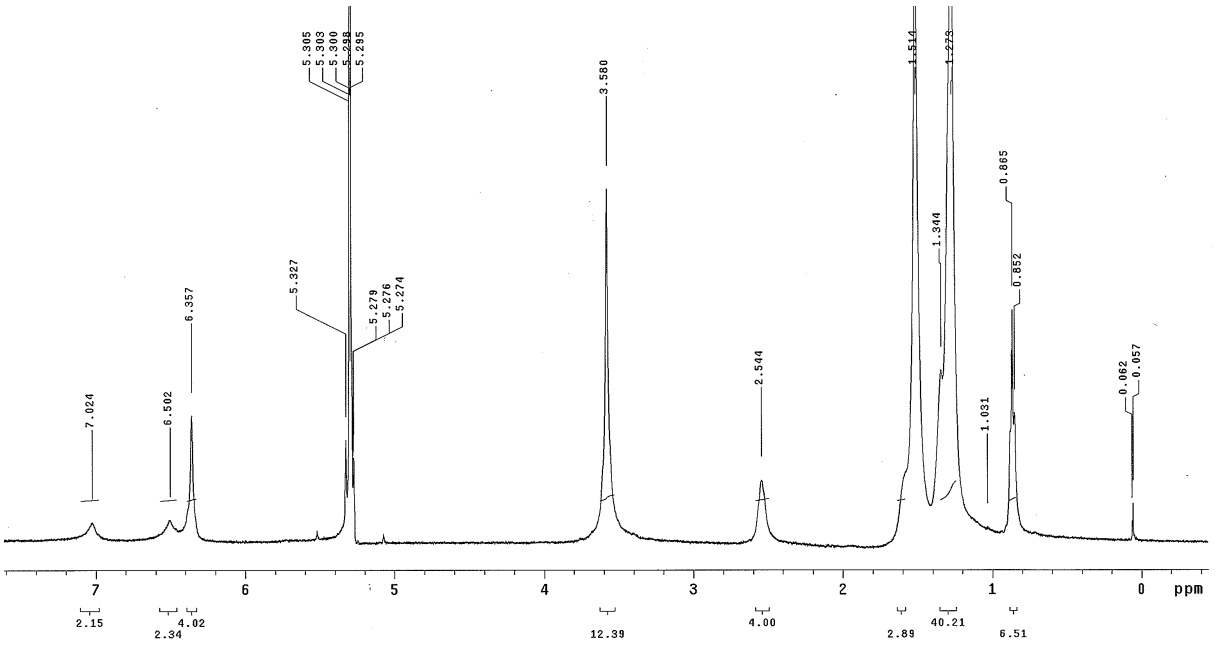


Figure S18. ^{1}H NMR spectrum of **PF-PPV$_L$** in CD_2Cl_2 at r.t.

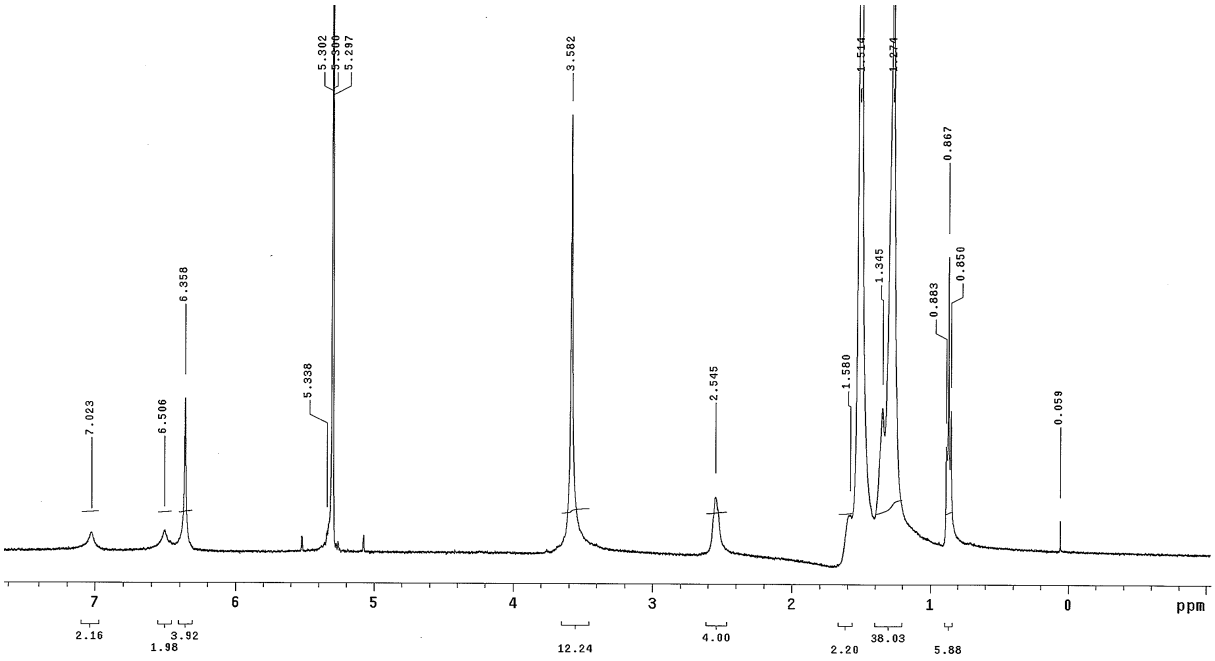


Figure S19. ^{1}H NMR spectrum of **PF-PPVs** in CD_2Cl_2 at r.t.

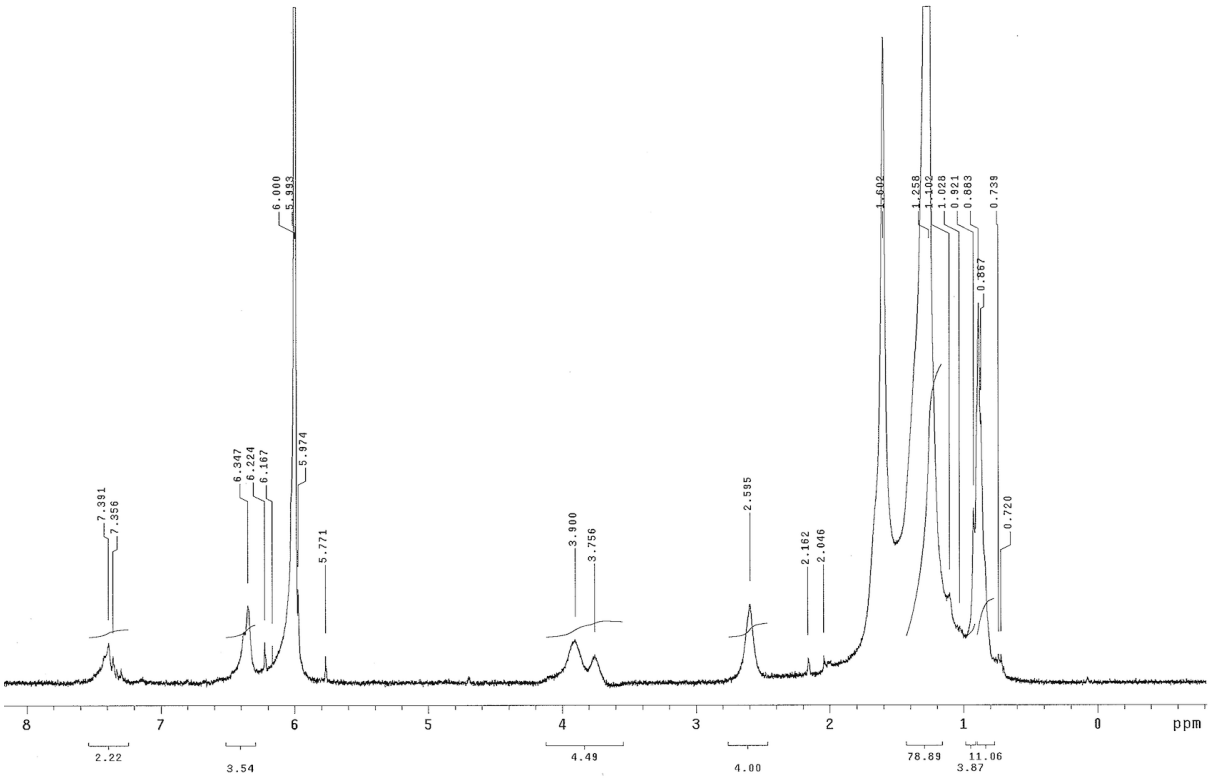


Figure S20. ^{1}H NMR spectrum of **SE-PPB** in $C_2D_2Cl_4$ at r.t.

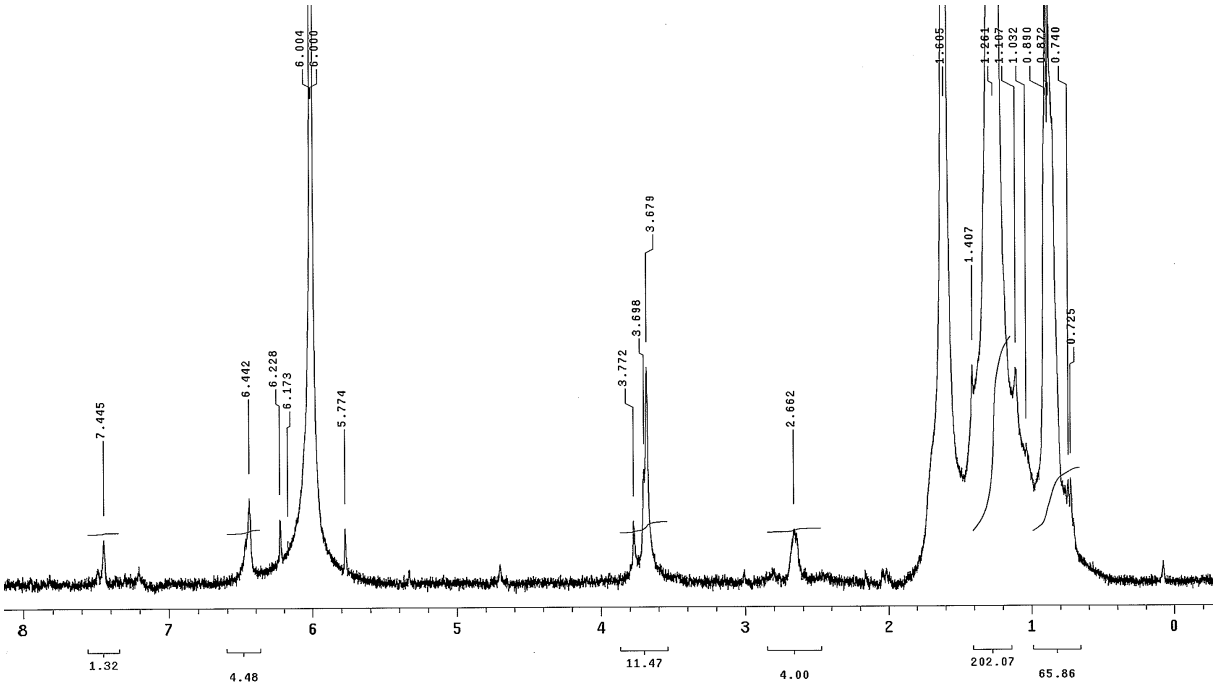


Figure S21. ^{1}H NMR spectrum of **PF-PPBs** in $C_2D_2Cl_4$ at r.t.

2.10. Size-Exclusion Chromatograms of Polymers

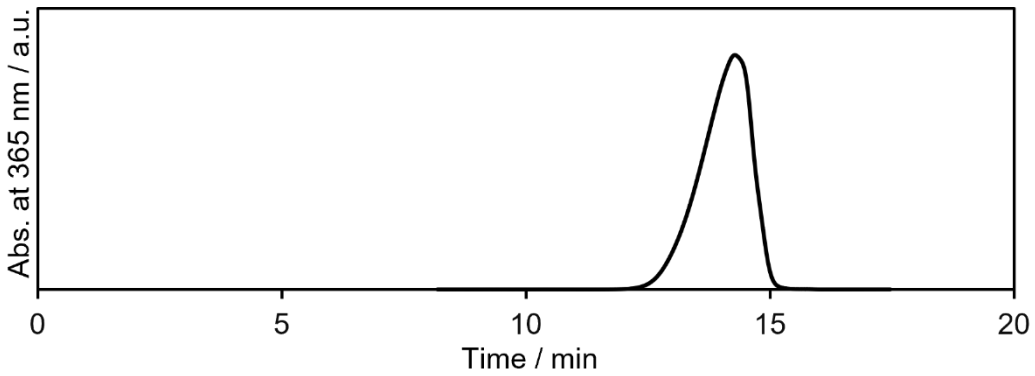


Figure S22. Size exclusion chromatogram of **SE-PP** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

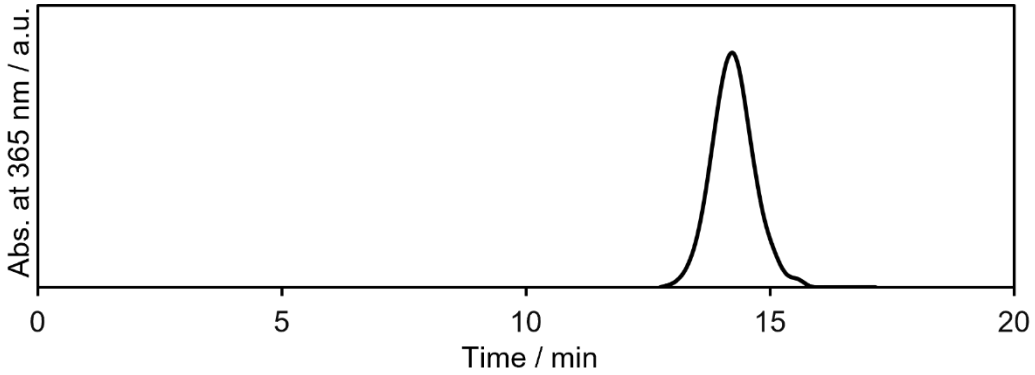


Figure S23. Size exclusion chromatogram of **PF-PP** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

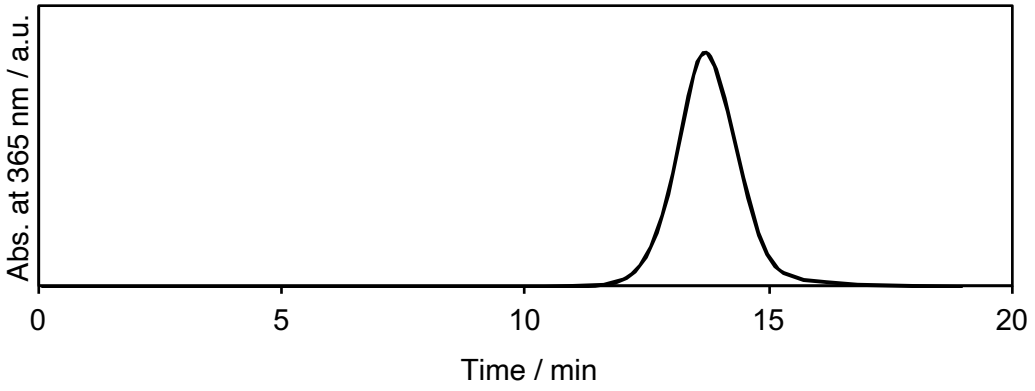


Figure S24. Size exclusion chromatogram of **SE-PPV** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

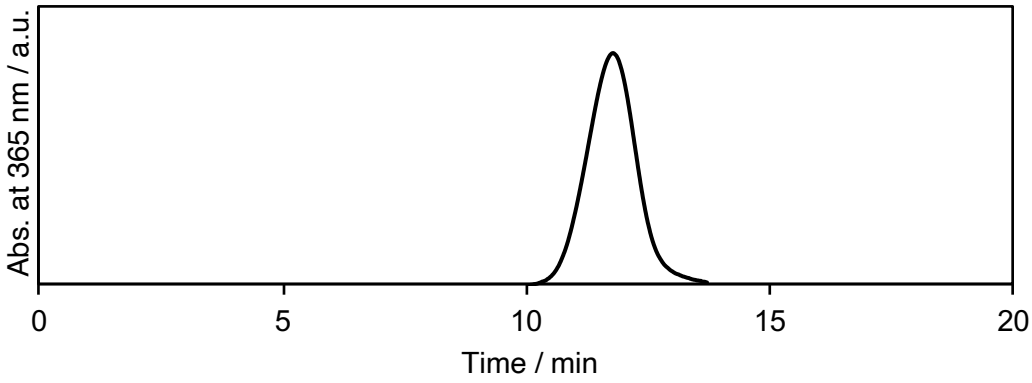


Figure S25. Size exclusion chromatogram of **PF-PPV$_L$** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

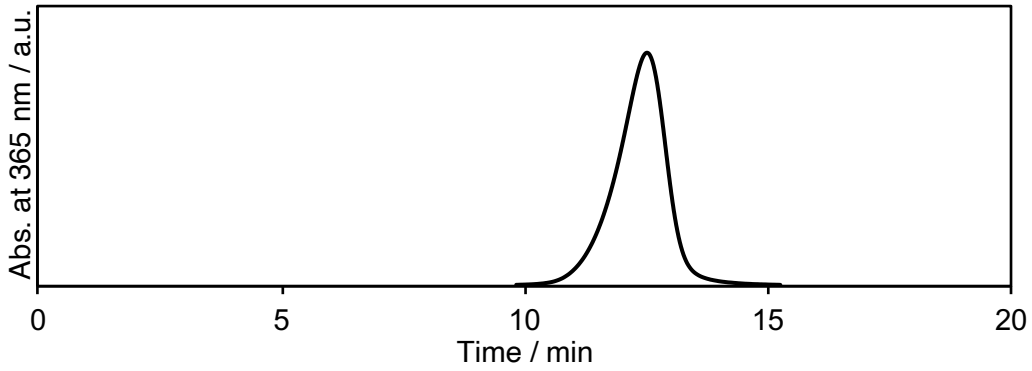


Figure S26. Size exclusion chromatogram of **PF-PPV$_S$** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

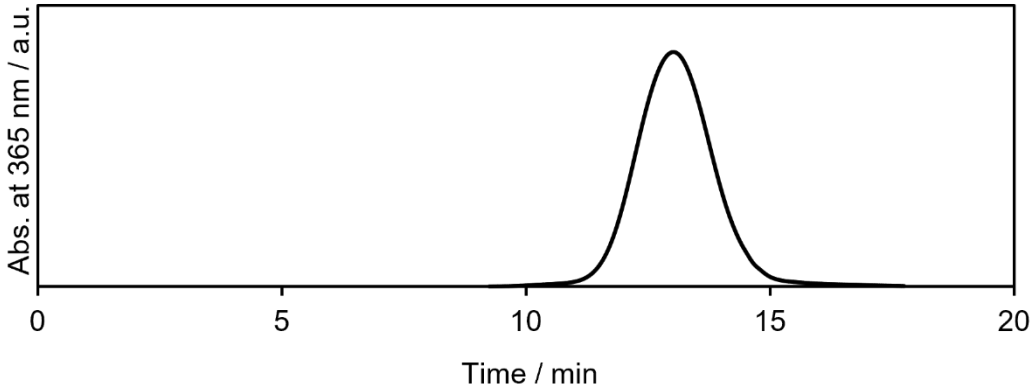


Figure S27. Size exclusion chromatogram of **SE-PPB** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

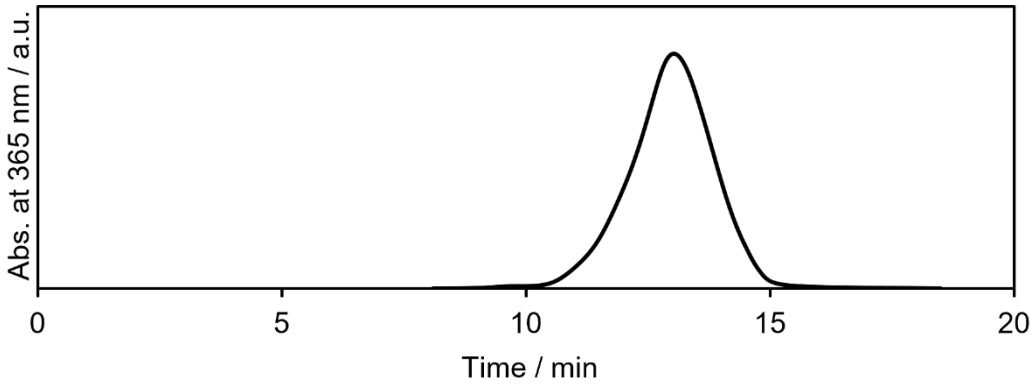


Figure S28. Size exclusion chromatogram of **PF-PPB$_L$** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

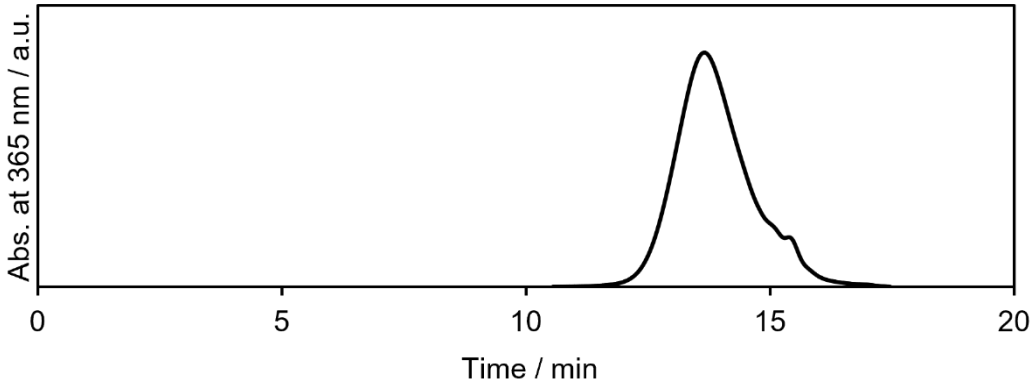


Figure S29. Size exclusion chromatogram of **PF-PPB$_S$** eluted with 1,2-dichlorobenzene at 0.75 mL min^{-1} at 80 ºC.

3. Supporting Figures and Tables

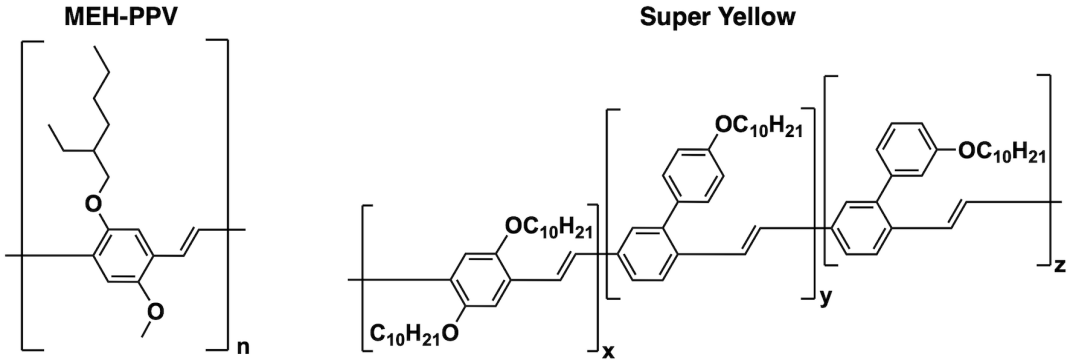


Figure S30. Chemical structures of MEH-PPV and Super Yellow (x = ~0.04, $y = z$ = ~0.48) [S3].

Table S1. Emission maxima (λ_{em}) and photoluminescence quantum yield (Φ) of MEH-PPV and Super Yellow in spin-coated films.

	λ_{em} / nm	Φ_{Film}
MEH-PPV (purchased from Sigma Aldrich)	590	0.14
MEH-PPV (synthesized by our group)	585	0.14
Super Yellow (purchased from Sigma Aldrich)	548	0.28

Table S2. Summary of absorption/emission maxima ($\lambda_{abs}/\lambda_{em}$), photoluminescence quantum yield (Φ) and photoluminescence lifetimes (τ), together with radiative (k_r) and nonradiative (k_{nr}) rate constants. The values of k_r and k_{nr} were calculated from Φ and τ according to the equations (1) and (2) described below. The excitation wavelength of λ_{ex} = 320, 405, and 365 nm were used for the evaluation of Φ for PPs, PPVs, and PPBs, respectively, while λ_{ex} = 280, 405, and 365 nm were used for the evaluation of τ for PPs, PPVs, and PPBs, respectively.

$$\Phi = k_r/(k_r + k_{nr}) \quad \text{.....(1)}$$

$$\tau = 1/(k_r + k_{nr}) \quad \text{.....(2)}$$

		λ_{abs} / nm	λ_{em} / nm	Φ	τ / ns	k_r / 10^8 s^{-1}	k_{nr} / 10^8 s^{-1}
SE-PP	$CHCl_3$	271	386	0.49	0.84	5.8	6.1
	Film	272	387	0.32	0.56	5.7	12
PF-PP	$CHCl_3$	272	384	0.61	1.3	4.7	3.0
	Film	269	386	0.39	0.61	6.4	10
SE-PPV	$CHCl_3$	431	493, 523	0.58	0.64	9.1	6.6
	Film	435	496, 531	0.28	0.28	10	26
PF-PPV$_L$	$CHCl_3$	431	484, 515	0.79	0.56	14	3.8
	Film	441	494, 528	0.25	0.22	11	34
PF-PPV$_S$	$CHCl_3$	431	484, 514	0.83	0.56	15	3.0
	Film	441	493, 528	0.30	0.22	14	32
SE-PPB	PhCl	403, 413, 441	430, 445, 474, 490	0.25	0.43	5.8	17
	Film	401, 411, 440	446, 475, 491	0.09	0.45	2.0	20
PF-PPB$_L$	PhCl	404, 414, 441	434, 449, 477, 493	0.33	0.39	8.5	17
	Film	405, 415, 441	449, 479, 495	0.12	0.48	2.5	18
PF-PPB$_S$	PhCl	390, 409	437, 461	0.38	0.48	7.9	13
	Film	401, 414, 439	446, 477, 494	0.13	0.74	1.8	12

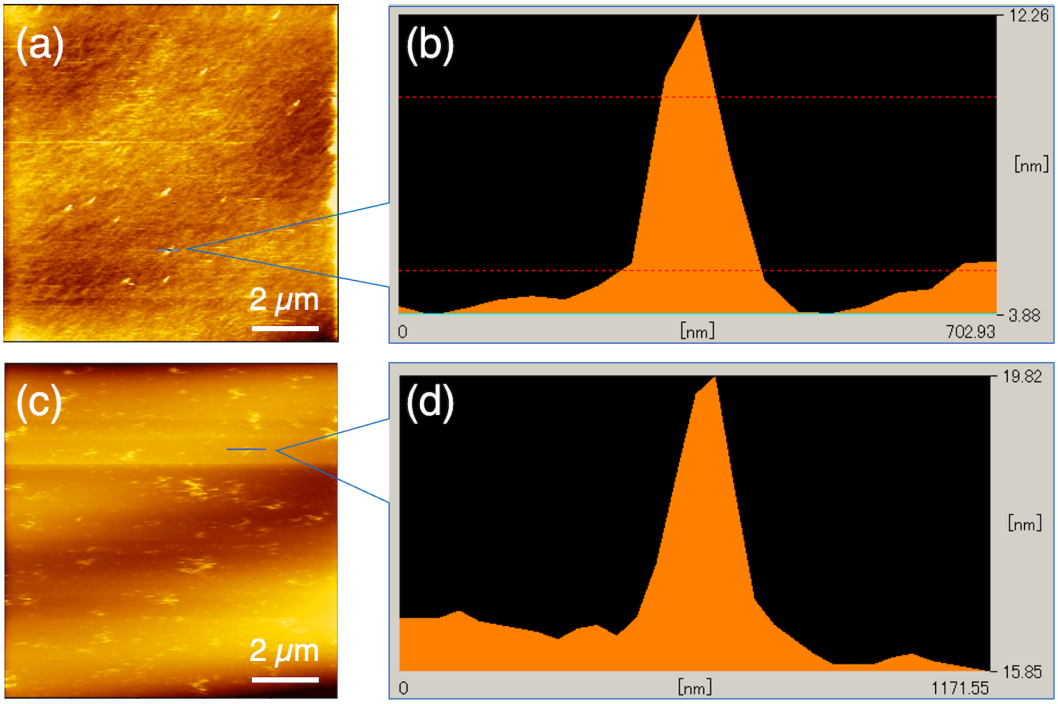


Figure S31. (a,c) AFM topographic images of aggregates and (b,d) cross-sectional profiles of (a,b) **SE-PPB** and (c,d) **PF-PPB**$_L$. The PhCl solutions were dropcast on a silicon substrate and used as samples after drying of PhCl.

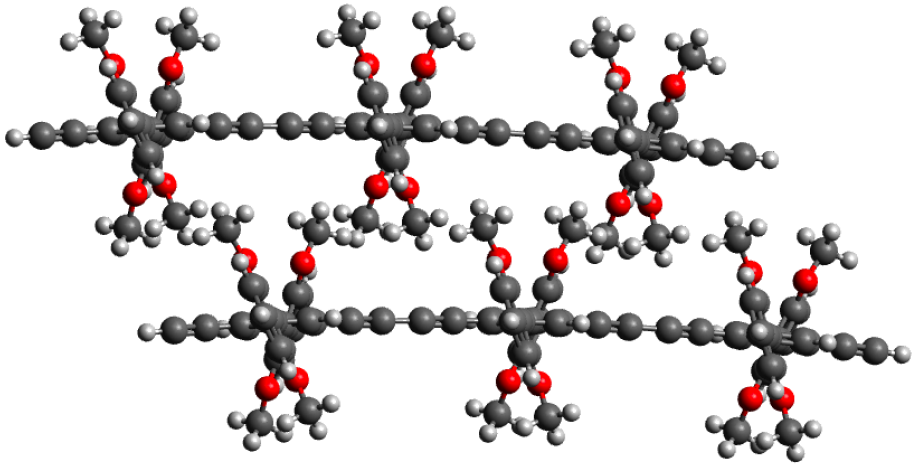


Figure S32. Packing model of two adjacent chains of trimer segments for **PF-PPB** aggregate.

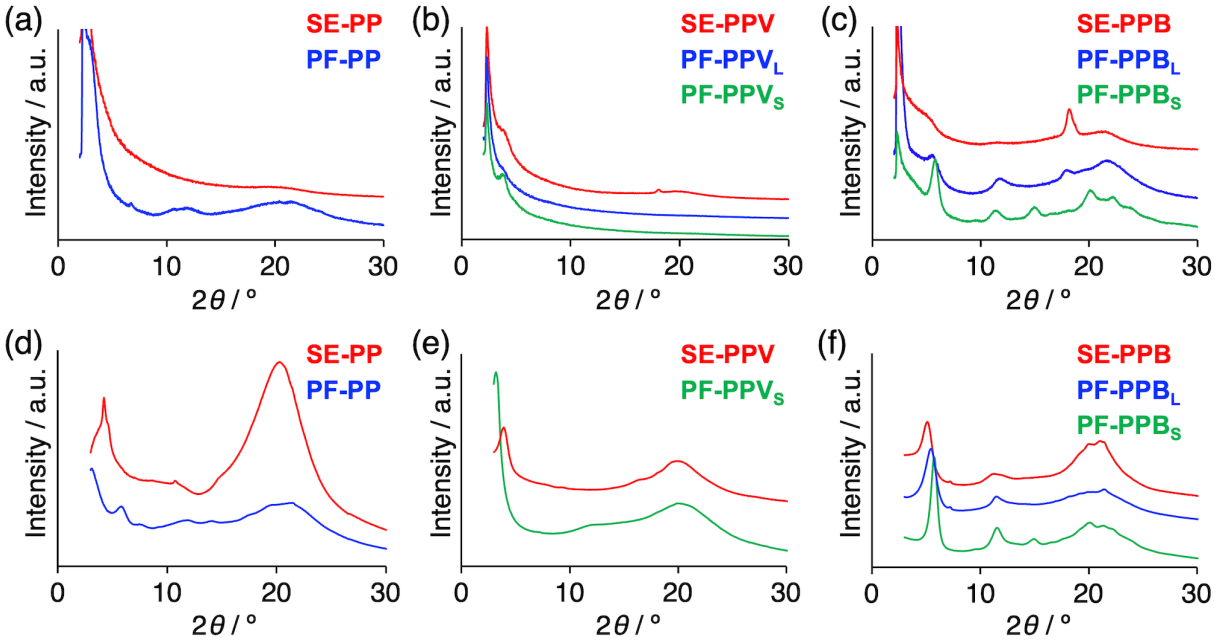


Figure S33. PXRD patterns of (a) **SE-PP** and **PF-PP**, (b) **SE-PPV**, **PF-PPV$_L$** and **PF-PPV$_S$** and (c) **SE-PPB**, **PF-PPB$_L$** and **PF-PPB$_S$**. 1D WAXS profiles of (d) **SE-PP** and **PF-PP**, (e) **SE-PPV** and **PF-PPV$_S$**, and (f) **SE-PPB**, **PF-PPB$_L$** and **PF-PPB$_S$**. The incident X-ray wavelength is 1.54 Å for both experiments.

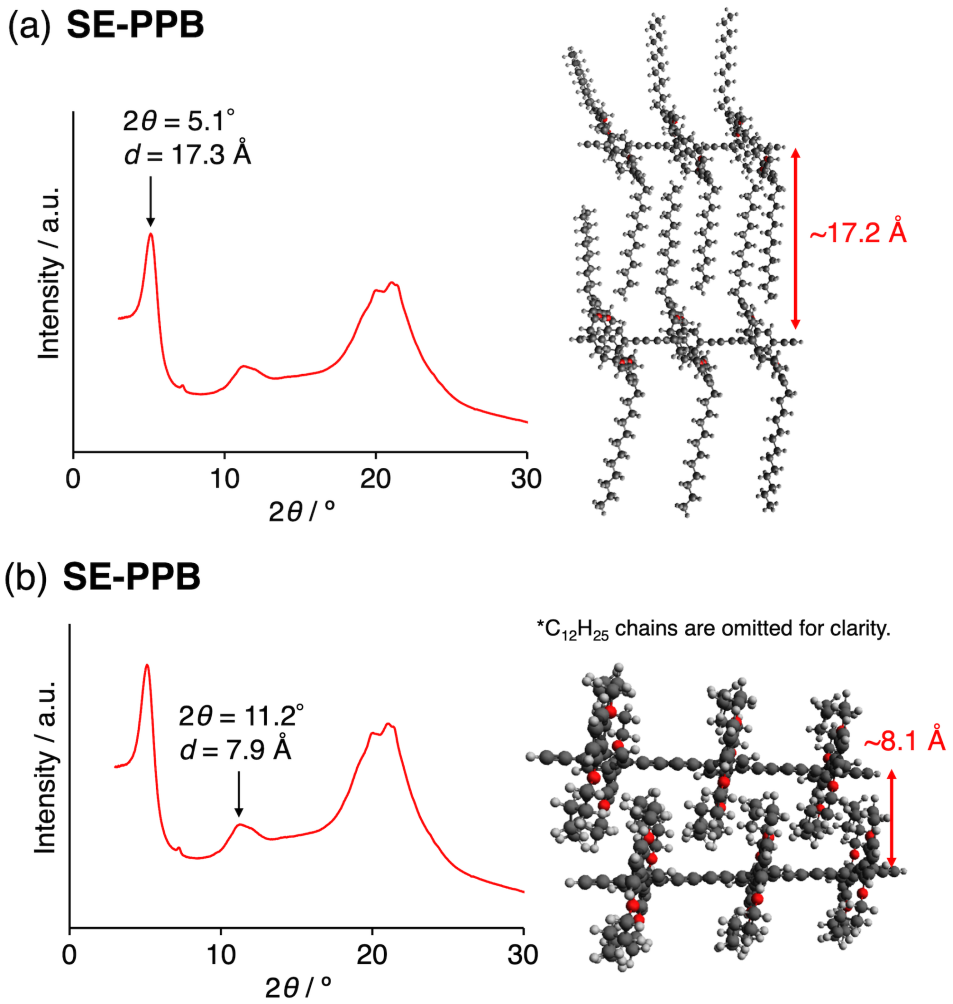


Figure S34. Schematic illustration of plausible aggregate structures of **SE-PPB** and possible assignment to the observed WAXS peaks at 2θ = (a) 5.1° and (b) 11.2°.

5. Supporting References

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