

Cathodic Hydrodefluorination of a π -Conjugated Alternating Copolymer Consisting of 9,9-Dioctylfluorene and Tetrafluorophenylene

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1. Material

1,2,4,5-Tetrafluorobenzene, di-tert-butyl(methyl)phosphonium tetrafluoroborate ($\text{P}^t\text{Bu}_2\text{Me-HBF}_4$), monofluorobenzene (PhF), and tetrabutylammonium tetrafluoroborate (tBu_4NBF_4) were purchased from Tokyo Chemical Industry Co., Ltd. Palladium(II) acetate ($\text{Pd}(\text{OAc})_2$), potassium carbonate (K_2CO_3), anhydrous acetonitrile (MeCN), and anhydrous *N,N*-dimethylacetamide (DMAc) were purchased from FUJIFILM Wako Pure Chemical Corporation. Acetone and methanol (MeOH) were purchased from Godo. Chloroform- d_1 (CDCl_3), ethylenediaminetetraacetic acid (EDTA), and magnesium carbonate (MgSO_4) were purchased from Kanto Chemical. CHCl_3 was purchased from Shinetsu. All reagents and solvents were used without purification otherwise noted.

2. General

NMR analysis

^1H and ^{19}F NMR spectra were recorded on a Bruker model AVACE III 400A spectrometer (400.13 MHz for ^1H , and 376.31 MHz for ^{19}F), and ^{13}C NMR spectra were recorded on a Bruker model AVANCE III HD-500 spectrometer (125.76 MHz for ^{13}C) using CDCl_3 as a solvent at room temperature. The chemical shifts for ^1H and ^{13}C are given in δ (ppm) upfield from residual CHCl_3 (^1H NMR: 7.26 ppm), and internal tetramethylsilane (^{13}C NMR: 0 ppm), and PhF (^{19}F NMR: -113.5 ppm), respectively.

Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) analyses were performed on a Shimadzu LC-10AS equipped with Tosoh TSK-Gel GMH_{HR}-N tandem columns using chloroform as an eluent. Polystyrene standards were used for calibration.

UV-vis absorption spectra

UV-vis absorption spectra were obtained on a Shimadzu UV-1900 spectrophotometer. Spectra in solution were obtained from a 10^{-5} M CHCl_3 solution. Film-state spectra were obtained from as-spun thin films prepared via spin-coating of a 1.0 mg/mL CHCl_3 solution onto a quartz substrate at 2000 rpm for 60 seconds.

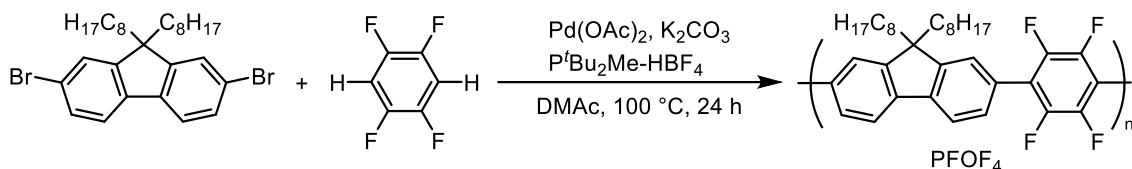
Fluorescence (FL) spectra

Fluorescence spectra were obtained on a SHIMADZU RF-6000 spectrophotometer. Spectra in solution were obtained from a 10^{-5} M CHCl_3 solution. Film-state spectra were obtained from as-spun thin films prepared via spin-coating of a 1.0 mg/mL CHCl_3 solution onto quartz substrates at 2000 rpm for 60 seconds. All fluorescence spectra were collected under the excitation at maximum absorption wavelength.

Cyclic voltammetry (CV) measurements

An ALS Instruments model 2325CV was used to perform CV measurements and record voltammograms. All CV measurements were carried out in anhydrous acetonitrile (MeCN) solutions containing 0.1 M $n\text{Bu}_4\text{NBF}_4$ as supporting electrolytes using a platinum (Pt) disk electrode ($\phi = 3$ mm) or a zinc (Zn) plate (1 cm \times 1 cm) as a working electrode (WE), a Pt plate (1 cm \times 1 cm) as a counter electrode (CE), and an Ag wire as a reference electrode (RE) at a scan rate of 50 mV/sec.

3. Synthesis of Poly(9,9-dioctylfluorene-2,7-diyl-*alt*-1,2,4,5-tetrafluorobenzene-3,6-diyl) (PFOF₄)¹



2,7-Dibromo-9,9-dioctylfluorene (1096.9 mg, 2.0 mmol), Pd(OAc)₂ (22.4 mg, 0.10 mmol), P'Bu₂Me-HBF₄ (49.6 mg, 0.20 mmol), and K₂CO₃ (552.8 mg, 4.0 mmol) were loaded into a two-neck Schlenk flask with a reflux condenser. After the flask was vacuumed and then replaced with Ar gas, 1,2,4,5-tetrafluorobenzene (300.2 mg, 2.0 mmol) and anhydrous DMAc (2.0 mL) were added to the flask. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was poured into 0.1 M EDTA·4Na aqueous solution. The resulting mixture was extracted with CHCl₃. The organic layer was washed with 1 M HCl aqueous solution, and brine. The organic layer was dried using anhydrous MgSO₄, and then filtered through a plug of celite to remove insoluble materials. The filtrate was concentrated under reduced pressure, and precipitated into MeOH. The precipitation was collected by filtration, and dried under vacuum, resulting in gray solid PFOF₄ (690.2 mg, 46%). ¹H NMR (400.13 MHz, CDCl₃, ppm): δ = 7.91 (br, Ar-H), 7.57 (br, Ar-H), 2.05 (br, -CH₂(CH₂)₆CH₃), 1.23–1.12 (br, -CH₂(CH₂)₆CH₃), 0.83 (br, -CH₂(CH₂)₆CH₃); ¹³C NMR (125.76 MHz, CDCl₃, ppm): δ = 151.4, 144.3 (d, $J_{\text{C-F}}$ = 235.2 Hz), 141.2, 129.1, 126.5, 125.1, 120.3, 119.85, 55.5, 40.1, 31.8, 30.9, 30.0, 29.2, 23.8, 22.6, 14.1; ¹⁹F NMR (376.31 MHz, CDCl₃, ppm): δ = -144.6 (Ar-F). M_n = 46,000, M_w = 175,000, PDI = 3.8 (SEC relative to polystyrene standards).

4. Cyclic Voltammetry (CV) Measurements for PFOF₄

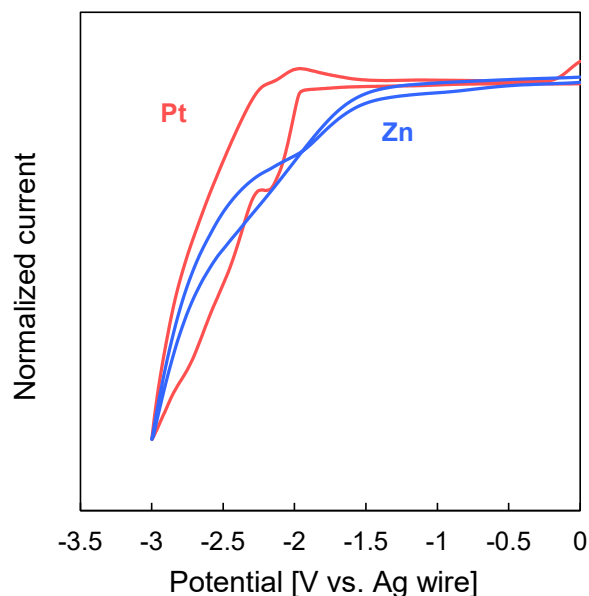
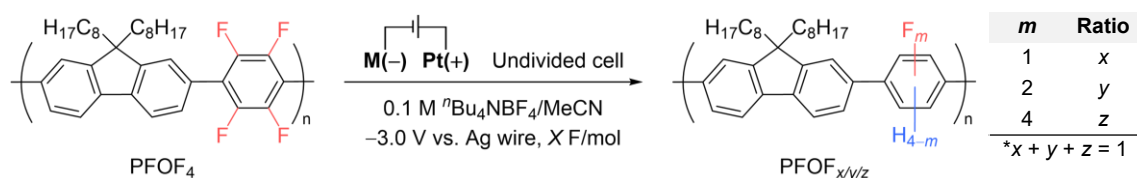


Figure S1. Cyclic voltammograms of the film state PFOF₄ on a Pt disk electrode ($\phi = 3$ mm) (orange line) or a Zn plate (1 cm \times 1 cm) (blue line) measured in 0.1 M ⁿBu₄NBF₄/MeCN at scan rate of 50 mV/s.

5. General Procedure for Cathodic Hydrodefluorination of PFOF₄



A CHCl₃ solution containing 5 mg/mL of PFOF₄ was cast onto a metal (M: Pt or Zn) plate (2 cm \times 2 cm), which was used as a WE for the cathodic hydrodefluorination. 10 mL of 0.1 M ⁿBu₄NBF₄/MeCN was prepared in an undivided cell equipped with the WE, a Pt plate (2 cm \times 2 cm) as a CE, and a silver (Ag) wire as a reference electrode. The constant-potential electrolysis (3.0 V vs. Ag wire) was carried out at room temperature. After the electrolysis, the obtained polymer (PFOF_{x/y/z}, where *x*, *y*, and *z* represent the component ratio of mono, di, and tetra-fluorine substituted repeating units, respectively, and *x* + *y* + *z* = 1) films were washed with MeCN. Then, the resultant polymer was de-doped in 0.1 M Bu₄NBF₄/MeCN by applying the constant potential (0 V vs. Ag wire) to the polymer-coated electrode. The dedoped polymer film was washed with MeCN and MeOH, and then dried. The degree of hydrodefluorination of the obtained polymer was determined by comparing ¹⁹F NMR integral signals.

6. ^1H NMR Spectra of $\text{PFOF}_{x/y/z}$ Obtained from Cathodic Hydrodefluorination of PFOF_4 Using a Pt or Zn Plate as a WE with Different Amount of Charge

Figures S2 show the stacked ^1H NMR spectra showing the enlarged aromatic regions of the $\text{PFOF}_{x/y/z}$ obtained from the cathodic hydrodefluorination of PFOF_4 with different amount of charge passed using either a Pt plate (Figure S2(a)) or a Zn plate (Figure S2(b)) as a WE. ^1H NMR spectra show that the appearance of new signals, denoted as # and \$ with different colors (black and red), as the amount of charge passed increased. These denoted signals are derived from the fluorene moieties adjacent to hydrodefluorinated phenylene moieties. In addition, the proton signals of di- and monofluoro phenylene moieties are also observed around 7.3–7.4 ppm and 7.8 ppm, respectively.

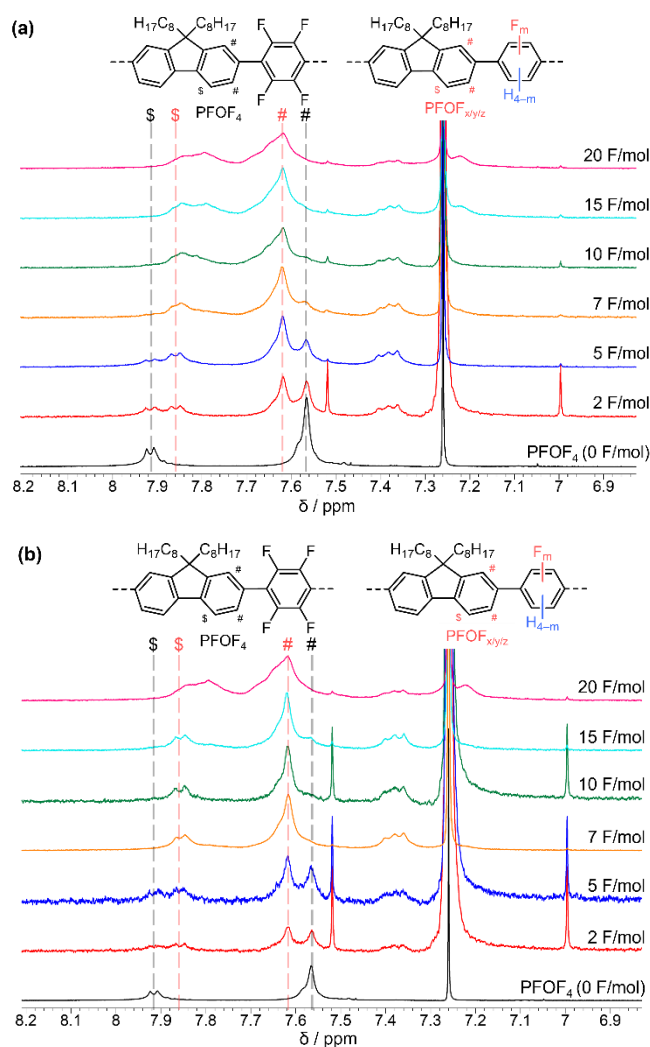


Figure S2. Stacked partial ^1H NMR spectra of $\text{PFOF}_{x/y/z}$ obtained from the cathodic hydrodefluorination using either (a) a Pt plate or (b) a Zn plate as the WE with different amounts of charge passed.

7. ^{19}F NMR Spectra of $\text{PFOF}_{x/y/z}$ Obtained from Cathodic Hydrodefluorination of PFOF_4 Using a Zn Plate as a WE with Different Amount of Charge

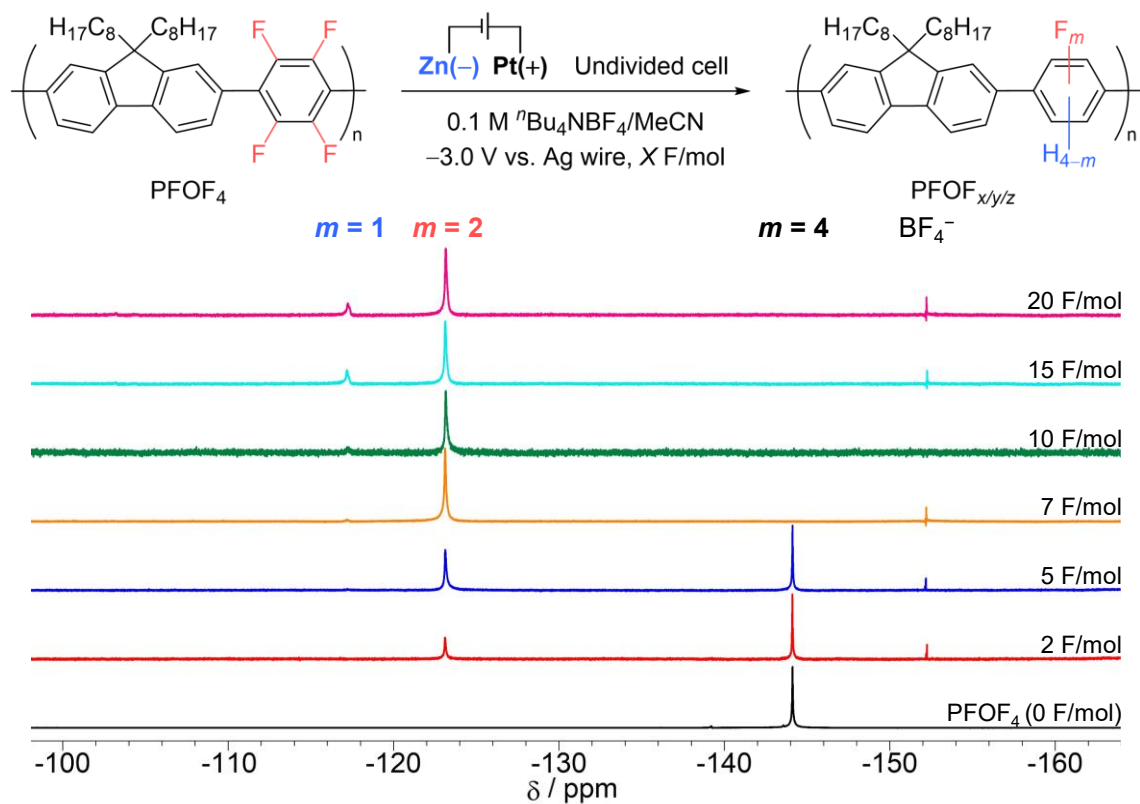


Figure S3. Stacked partial ^{19}F NMR spectra of $\text{PFOF}_{x/y/z}$ obtained from the cathodic hydrodefluorination using a Zn plate as WE with different amounts of charge passed.

8. Optical Properties of PFOF_{x/y/z} with Various Fluorine-Containing Levels

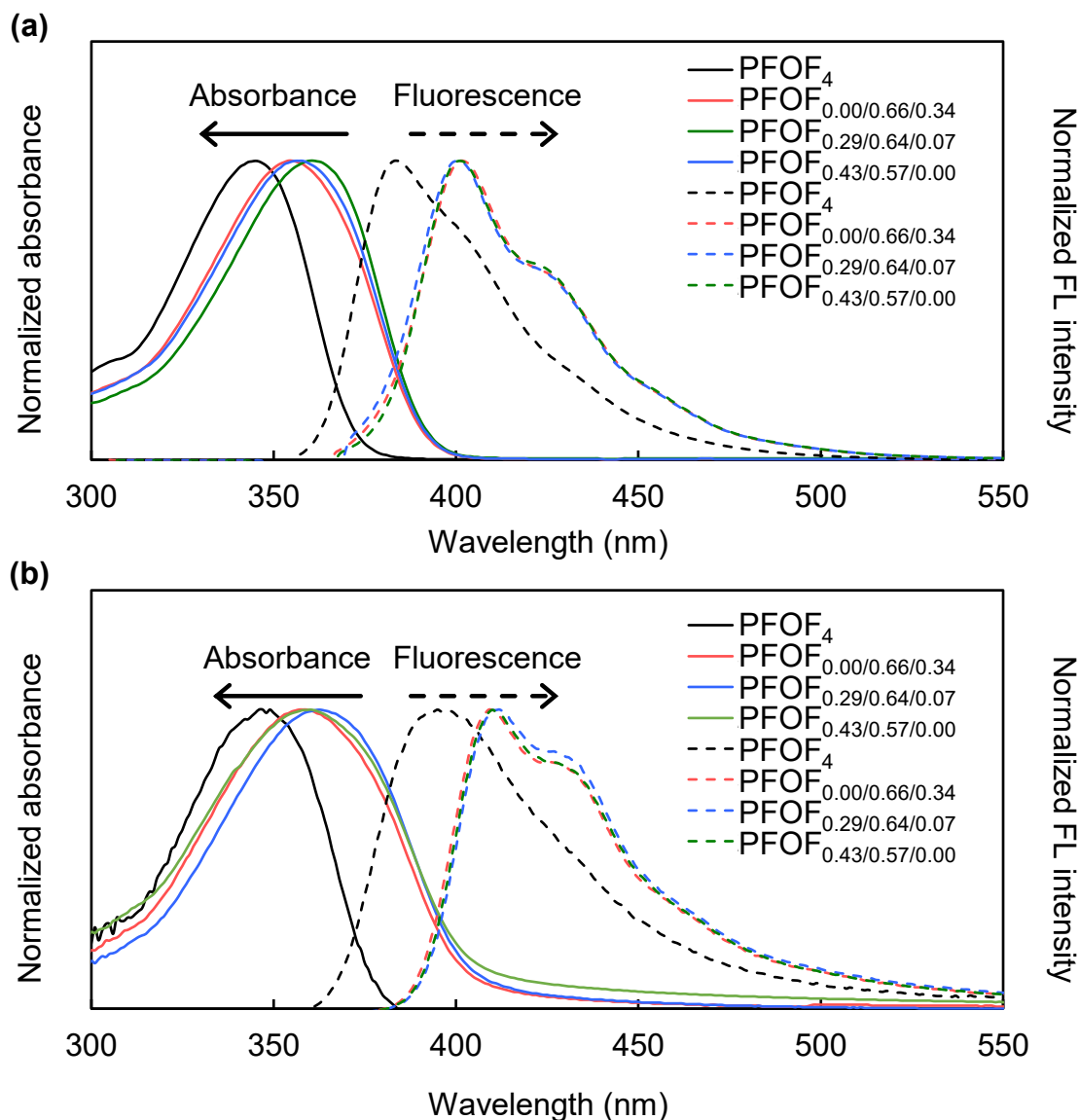


Figure S4. UV-vis (Solid lines) and fluorescence (dashed lines) spectra of PFOF₄ (black line) and PFOF_{x/y/z} in (a) CHCl₃ solution (10⁻⁵ M), and (b) the thin-film state. *x*, *y*, and *z* represent the component ratio of mono-, di-, and tetrafluorophenylene moieties in PFOF_{x/y/z}, respectively. Each PFOF_{x/y/z} sample was obtained from the cathodic hydrodefluorination of PFOF₄ using a Pt plate as a WE with different amount of charge passed: 5 (red line), 10 (blue line), or 20 (green line) F/mol. The optical data was summarized in Table 1.

NMR Spectra

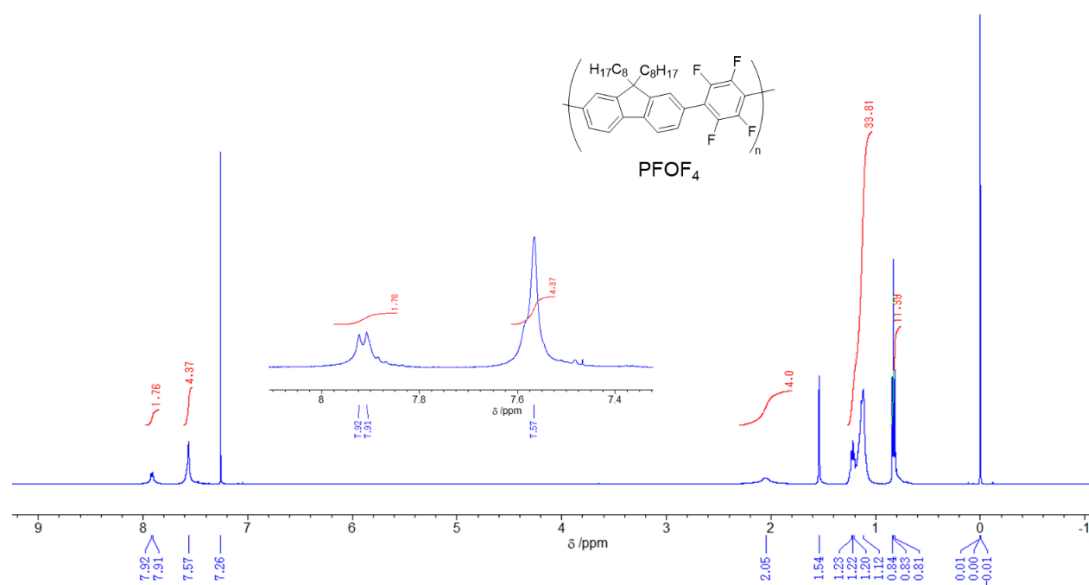


Figure S5. ¹H NMR spectrum (400.13 MHz, CDCl₃) of poly(9,9-dioctylfluorene-2,7-diyl-*alt*-1,2,4,5-tetrafluorophenylene-3,6-diyl) (PFOF₄).

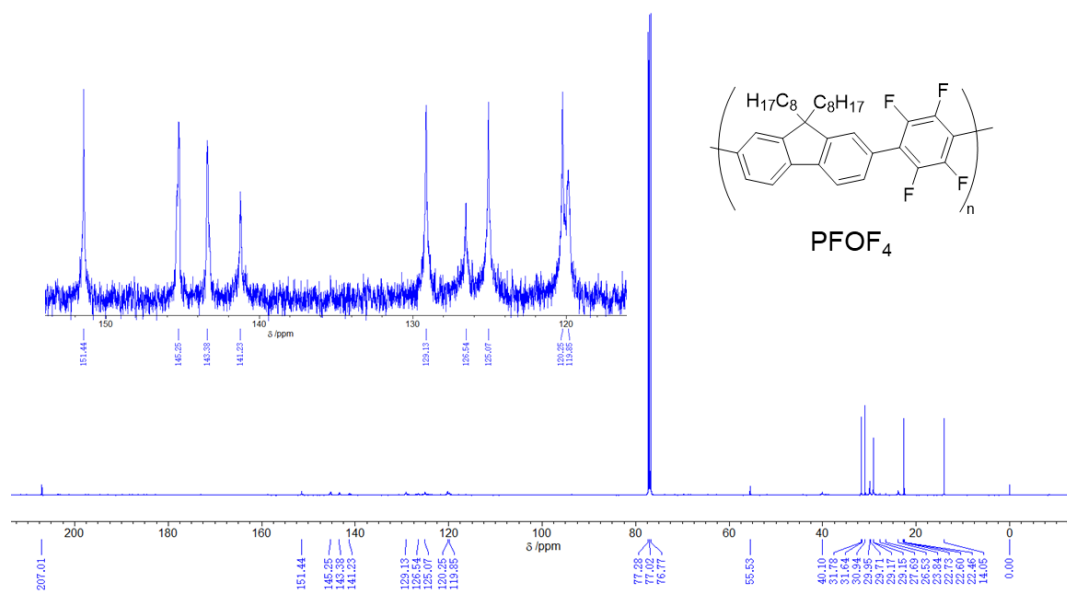


Figure S6. ¹³C NMR spectrum (125.76 MHz, CDCl₃) of PFOF₄.

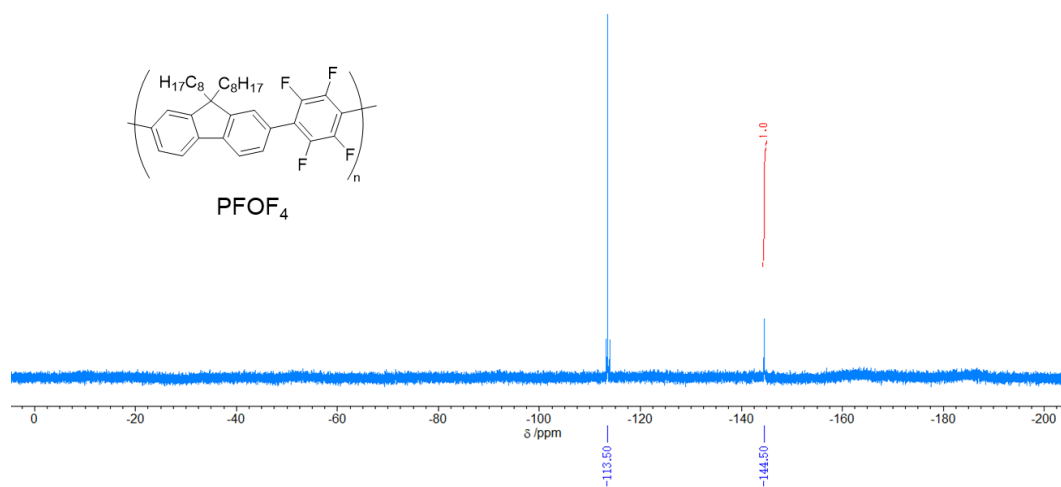


Figure S7. ¹⁹F NMR spectrum (376.31 MHz, CDCl₃) of PFOF₄.

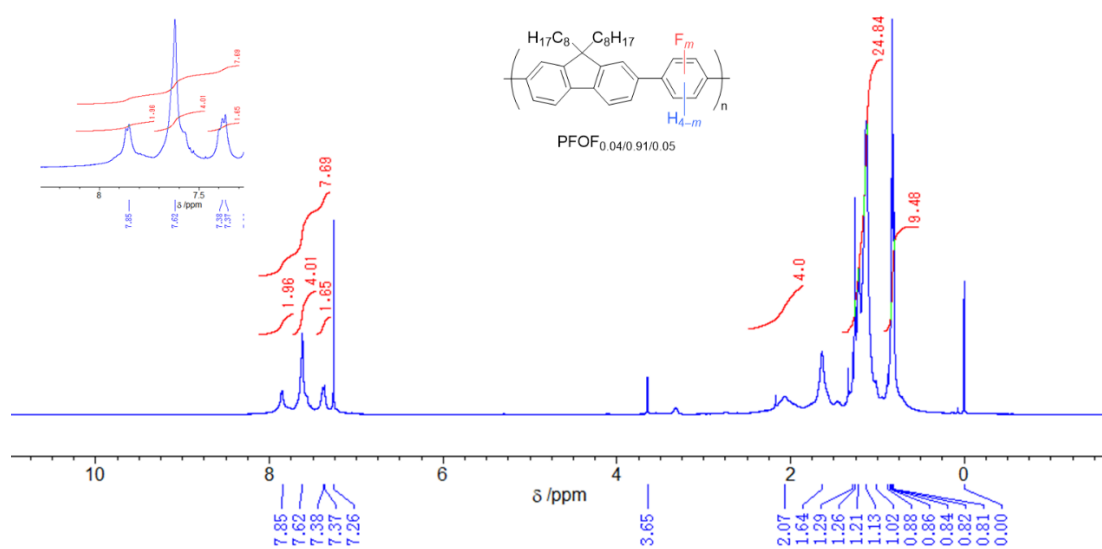


Figure S8. ¹H NMR spectrum (400.13 MHz, CDCl₃) of PFOF_{0.04/0.91/0.05}.

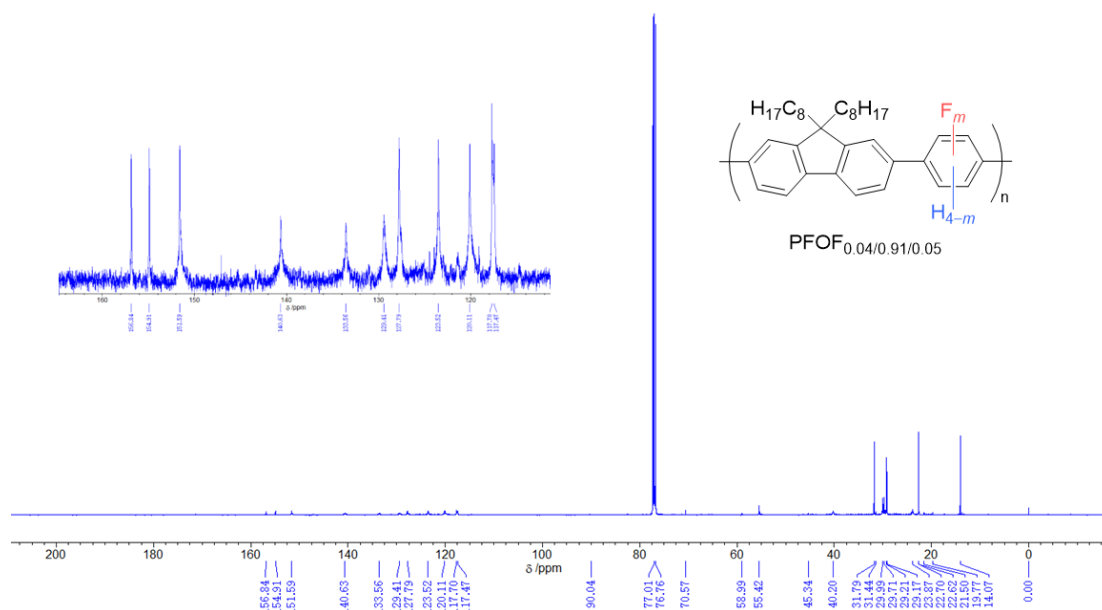


Figure S9. ¹³C NMR spectrum (125.76 MHz, CDCl₃) of PFOF_{0.04/0.91/0.05}.

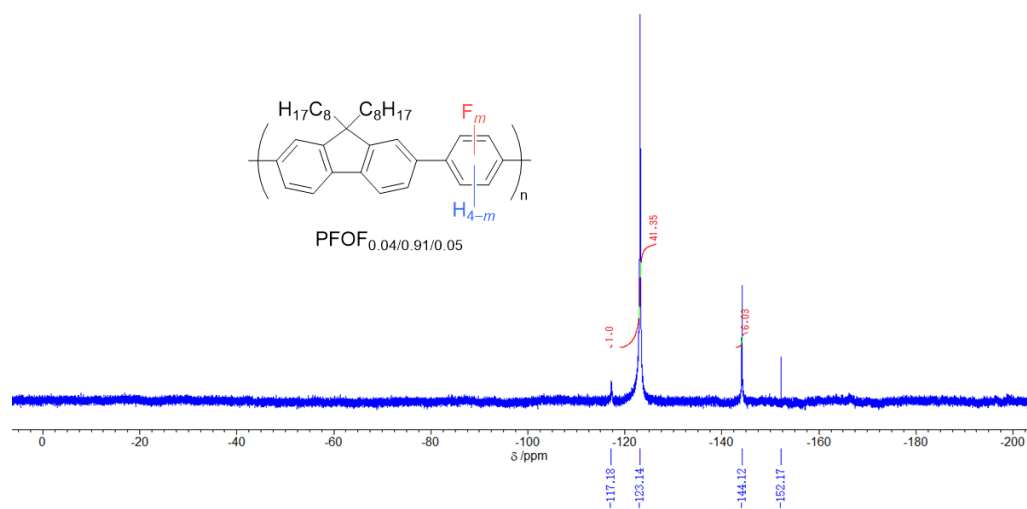
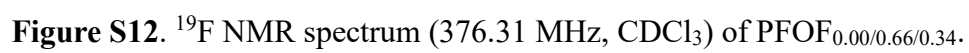
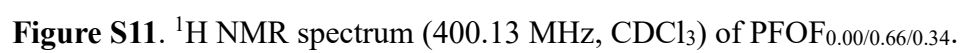


Figure S10. ¹⁹F NMR spectrum (376.31 MHz, CDCl₃) of PFOF_{0.04/0.91/0.05}.



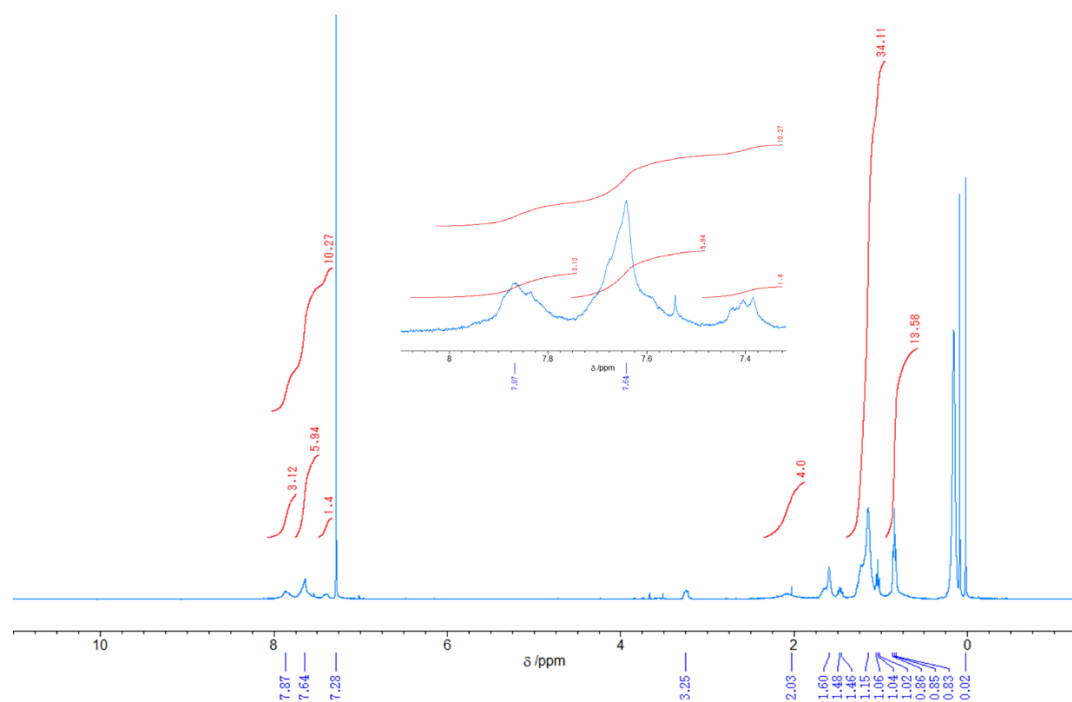


Figure S13. ^1H NMR spectrum (400.13 MHz, CDCl_3) of $\text{PFOF}_{0.29/0.64/0.07}$.

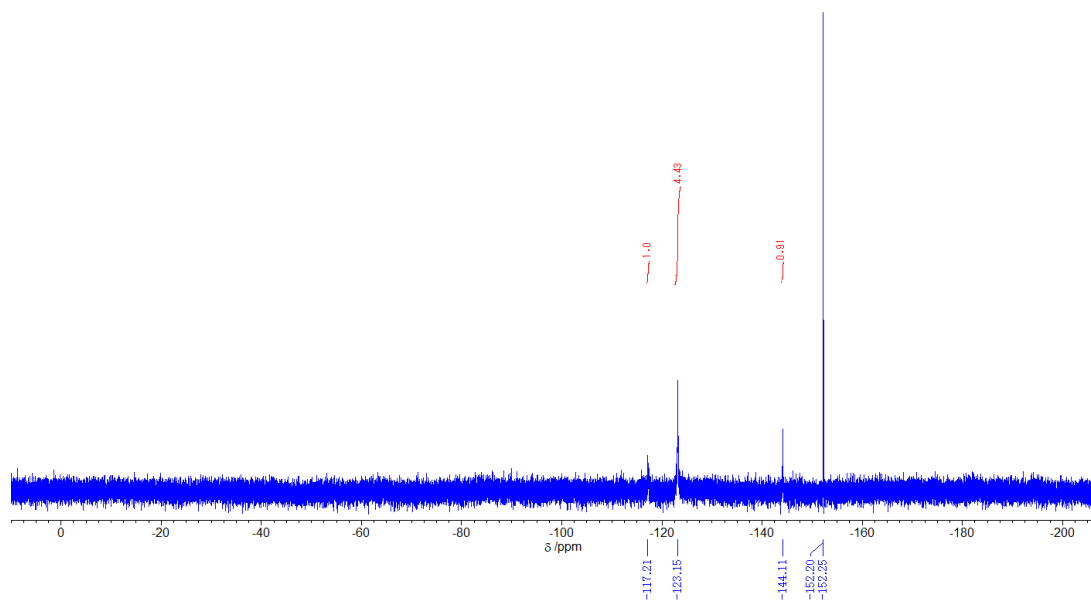


Figure S14. ^{19}F NMR spectrum (376.31 MHz, CDCl_3) of $\text{PFOF}_{0.29/0.64/0.07}$.

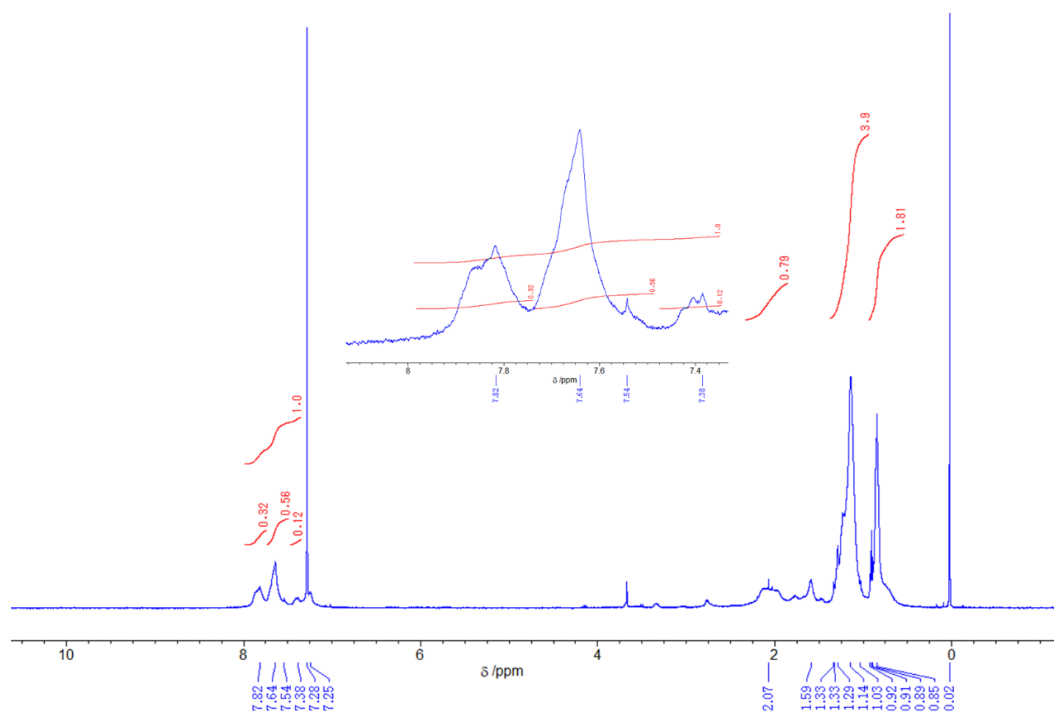


Figure S15. ^1H NMR spectrum (400.13 MHz, CDCl_3) of $\text{PFOF}_{0.43/0.57/0.00}$.

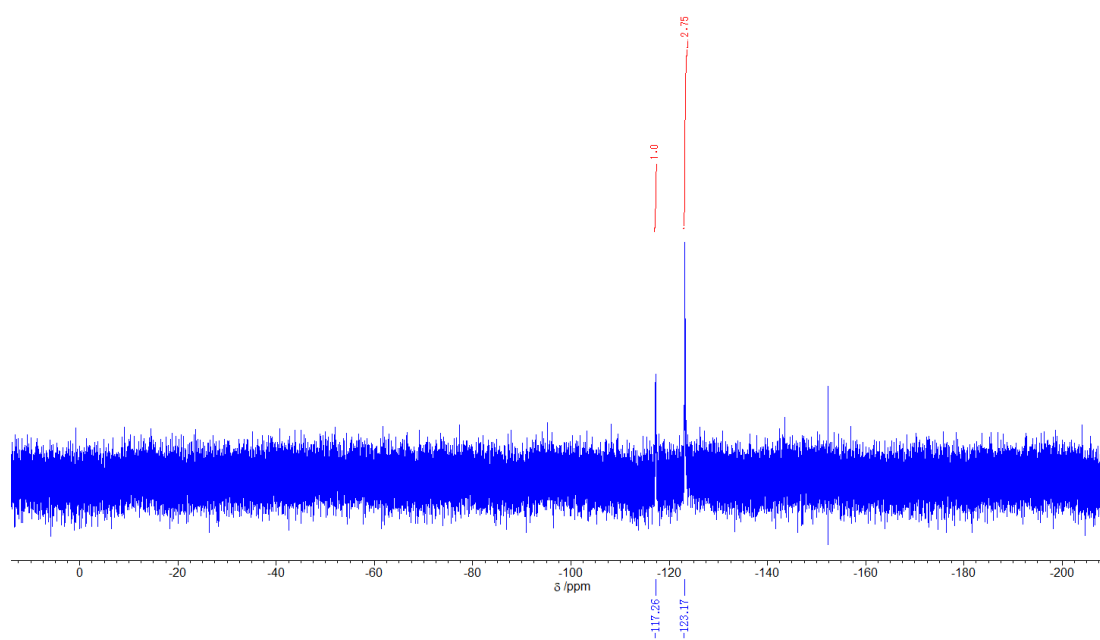


Figure S16. ^{19}F NMR spectrum (376.31 MHz, CDCl_3) of $\text{PFOF}_{0.43/0.57/0.00}$.

Reference

- 1 W. Lu, J. Kuwabara, T. Iijima, H. Higashimura, H. Hayashi, and T. Kanbara, *Macromolecules*, **45**, 4128–4133 (2012).