Synthesis of 9-Substituted Fluorene Copolymers via Chemical and Electrochemical Polymer Reaction and Their Optoelectronic Properties

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ABSTRACT: Through Suzuki–Miyaura coupling polymerization and subsequent polymer reactions, we prepared three novel series of poly(fluorene) alternating copolymers consisting of 9-fluorenone (**PreP1**), 9,9-bis(*p*-isopropylphenylsulfanyl)fluorene (**P1**), and 9,9-difluorofluorene (**P2**) with 9,9-dioctylfluorene. Electrochemical fluorodesulfurization was found to be the key step to convert **P1** to **P2**. This technique provided the selectively and efficiently fluorinated product without undesired side reactions, and could tune the substitution ratio by controlling the quantity of charge passed. The obtained copolymers, **PreP1**, **P1** and **P2** were revealed to have the intramolecular charge transfer (ICT) interaction between the electron donor and acceptor moieties, which was supported by DFT calculations. The large stokes shift of **P2** (ca.170 nm) observed by optical analyses indicated the large structural difference between its ground-state and excited-state derived from intermolecular excimer formation. Furthermore, the band gap and energy level of the polymers could be tuned by changing the bridged structure at the 9-position of the fluorene unit.

Introduction

Selective and effective modifications and substitutions for polymers have been of much utility toward construction of various functional materials such as graft,[1,2] block,[3–5] pendant[6–8] and network polymers.[9–11] Thermal, optical and other properties of polymers can be enriched by proper modifications of the polymer chain. Especially, the introduction of fluorine atom into polymers is of great interest due to the specific features derived from its small atomic size, high electronegativity, and the high stability of C–F bonds.[7,12–14] For example, fluorine-containing polymers generally show high thermal stability, low dielectric constant, low surface free energy, and improved chemical resistance. They can be directly synthesized via polymerization of fluorinated monomers[12–14] or polymer reaction (postpolymerization modification).[7] However, conventional techniques for both routes require usually severe reaction conditions at the fluorination step.

In our previous works, electrochemical fluorination of organic compounds has been developed using stable ionic liquids containing hydrogen fluoride (HF) (Et_4NF–nHF ($n = 3$–5)) as a fluorine source and a supporting electrolyte.[15–17] This synthetic methodology utilizes reactive species generated by electron transfer between substrate and electrode. Therefore, it can be carried out under mild and safe conditions without oxidants or reductants. Recently, we reported the first detailed example of electrochemical fluorination of a polymer by polymer reaction, namely, anodic fluorodesulfurization of a poly(fluorene) derivative in Et_4NF–4HF.[18] The facile and selective fluorinating process for polymers is notable to produce functional polymers with environmentally benign system. In general, controlled introduction of substituents at 9-position of poly(fluorine)s by polymer reaction is sometime difficult because undesired side reactions occur under severe reaction conditions using lithium diisopropylamide (LDA), butyllithium, and etc.[19,20] Therefore, the novel process to supply selectively 9-substituted poly(fluorene)s by polymer reaction under mild conditions without side reactions has been of growing interest.

Difluoromethylene bridged biphenyl (9,9-difluorofluorene)[21–24] and bithiophene[25] have been synthesized and found to show unique properties. In the case of difluoromethylene bridged bithiophene, LUMO level was lowered due to the strongly electron withdrowing difluoromethylene bridge.[25] Although the meta-bridged difluoromethylene structure is expected to show unique properties if incorporated into conjugated polymer backbone, there have been no report on conjugated polymers having 9,9-difluorofluorene unit.

In this paper, we report synthesis of novel 9-substituted poly(fluorene) derivatives including a 9,9-difluorofluorene unit through Suzuki–Miyaura coupling polymerization and subsequent selective and effective polymer reactions employing the electrochemical technique. We also investigated optoelectronic properties of the alternating copolymers stemmed from the single parent polymer. Such conjugated electron donor–acceptor copolymers are of growing interest in semiconductor applications owing to their good charge separation properties.[26–31]

Experimental Section

Materials. Dry solvents were used as received. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, 2,7-dibromofluorenone, tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), *p*-isopropylbenzenethiol, boron trifluoride–ether complex, nitrosonium tetrafluoroborate ($NO^+BF_4^-$) and pyridinium poly(hydrogen fluoride) (PPHF) containing 60% hydrogen fluoride were used as received. Et_4NF–4HF and Et_4NF–5HF were kindly supplied by Morita Chemical Industries Co. Ltd. (Japan). Although these HF salts are easily handled, proper safety precautions should be taken at all times. Therefore, it is recommended to use hand protection.

Synthesis of PreP1 by Suzuki–Miyaura Coupling Polymerization. 2,7-Dibromofluorenone (68 mg, 0.20 mmol) and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (110 mg, 0.20 mmol) were dissolved in 2 mL of dry toluene under argon. To the solution, K_2CO_3 (aq) (2.0 M, 1.4 mL), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) were added. After stirring for 48 h at 100 °C, the reaction mixture was reprecipitated into a large amount of methanol. **PreP1** was collected by filtration, dried under vacuum, and obtained as an orange powder (92 mg). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.1–7.6 (*Ar–H*, br), 2.11 ($CH_2(CH_2)_6CH_3$, br), 1.25–0.77 ($CH_2(CH_2)_6CH_3$, br).^{13}C NMR (67.8 MHz, $CDCl_3$): δ 151.9, 142.9, 142.5, 142.4, 140.5, 138.7, 135.2, 133.4, 133.3, 125.7, 123.0, 121.0, 120.9, 120.7, 120.2, 55.6, 40.5, 31.8, 30.1, 29.3, 23.9, 22.7, 14.2. IR (NaCl): 2916, 2846, 1695, 1496, 1450, 772 cm^{-1}. Anal. Calcd for $(C_{42}H_{46}O)_n$: C, 88.68; H, 8.51; O, 2.81. Found: C, 87.95; H, 8.24; O, 3.34.

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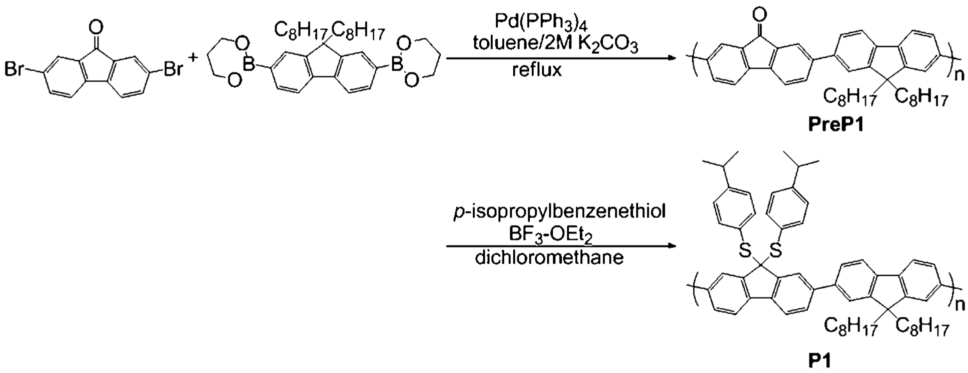
Scheme 1. Synthesis of PreP1 and P1



Synthesis of P1 by Dithioacetal Formation. PreP1 (60 mg) was dissolved in 5 mL of dry dichloromethane under argon atmosphere. *p*-Isopropylbenzenethiol (0.68 mL, 4.5 mmol) and boron trifluoride-ether complex (0.30 mL, 2.4 × 10^{-4} mmol) were added to the solution. After the mixture was stirred for 24 h at room temperature, the polymer was reprecipitated into methanol. **P1** was collected by filtration, dried under vacuum, and obtained as a pale yellow powder (61 mg). Dithioacetal was quantitatively formed judging from ^{1}H NMR spectrum. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.9−6.8 (*Ar*−*H*, br), 2.82 (C*H*(CH_3)$_2$, br), 2.11 (CH_2(CH_2)$_6$$CH_3$, br), 1.25−0.77 (alkyl, br). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 151.6, 150.4, 150.1, 146.8, 139.8, 136.3, 128.9, 128.1, 127.4, 127.1, 126.4, 123.9, 121.3, 120.1, 120.1, 119.8, 55.4, 40.5, 33.9, 33.8, 32.0, 31.9, 30.2, 30.1, 29.8, 29.4, 24.0, 23.9, 23.8, 22.7, 14.2. IR (NaCl): 2927, 2858, 1727, 1446, 1272, 1022, 829 cm^{-1}. Anal. Calcd. for $(C_{60}H_{68}S_2)_n$: C, 84.45; H, 8.03; S, 7.52. Found: C, 82.43; H, 7.23; S, 7.74; Br, 0.94.

Chemical Fluorodesulfurization of P1. P1 (30 mg, ca. 0.035 mmol of dithioacetal unit) dissolved in 1.0 mL of dry dichloromethane was added dropwise to a solution of NO^+ BF_4^- (11 mg, 0.090 mmol) and 60% PPHF (0.30 mL) or $Et_4NF-4HF$ (0.30 mL) in 2 mL of dry dichloromethane, in a plastic bottle at 0 °C under argon. The mixture was stirred at room temperature for 2 h. After purification by reprecipitation into methanol, a gelated product was obtained. Any fluorinated product was not detected by ^{1}H and ^{19}F NMR analyses of the slightly soluble part of the product in $CDCl_3$.

General Procedure for Anodic Fluorination by Constant Current Electrolysis. A chloroform solution containing 1 mg of **P1** was casted on the platinum plate electrode (1 cm × 1 cm) and dried under reduced pressure. $Et_4NF-4HF$ or $Et_4NF-5HF$ (3 mL) was added into plastic test tube, and deaerated by argon bubbling. The platinum electrode coated with polymer film was introduced as an anode and a bare platinum plate electrode (1 cm × 1 cm) was used as a cathode. Constant current (10 mA/cm^2) was passed at room temperature with Metronnix Corp. (Tokyo) constant current power supply model 5944 from 2 F/mol to 24 F/mol monitored with Hokutodenko Coulomb/Amoperehour meter HF-201. The polymer film was washed with methanol and subsequently dried in vacuo. All optical and electrochemical properties of **P2** were measured with the most reacted sample (fluorodesulfurization ratio = ca. 90%) prepared by passage of 24 F/mol charge in $Et_4NF-5HF$. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.9−7.0 (*Ar*−*H*, br), 2.82 (C*H*(CH_3)$_2$, br), 2.11 (CH_2(CH_2)$_6$$CH_3$, br), 1.25−0.77 (alkyl, br).^{19}F-NMR (270 MHz, $CDCl_3$): δ −33.7 (>CF_2, inner unit), −34.1 (>CF_2, terminal unit). IR (NaCl): 2931, 2866, 1713, 1546, 1470, 1230, 775 cm^{-1}.

Measurement. NMR spectra were recorded on a Jeol EX-270 spectrometer. UV−vis spectra were obtained on a Shimadzu UV-1600 spectrophotometer. IR spectra were taken on a Jasco FT/IR-410 infrared spectrometer by casting the sample from a chloroform solution on a NaCl plate. Photoluminescence (PL) spectra were obtained on a Shimadzu RF-5300PC spectrophotomerter. GPC analyses were performed by a Shimadzu Prominence GPC system (Shim-pack GPC 803C column), using chloroform as the eluent after calibration with polystyrene standards. Cyclic voltammetry measurements were recorded on an ALS 600A Electrochemical Analyzer. EDX analysis was performed with Genesis XM2 (Keyence). Film thickness was estimated by a Keyence Laser Focus Displacement Meter LT-8100. DFT calculation was performed using Gaussian 03 suit of programs by optimization with using the B3LYP/6-31G(d,p) method. The orbital diagrams were generated by using the GaussView program.

Results and Discussion

Synthesis of Alternating Fluorene Copolymers via Suzuki−Miyaura Coupling Polymerization and Chemical Polymer Reactions. Poly(9-fluorenone-*alt*-9,9-dioctylfluorene), **PreP1**, was prepared by Suzuki−Miyaura coupling polymerization of 9,9-dioctylfluorene-2,7diboronic acid ester and 2,7-dibromofluorenone with tetrakis(triphenylphosphine)palladium catalyst ($Pd(PPh_3)_4$) in a toluene/2 M potassium carbonate solution (Scheme 1). After purification by reprecipitation into methanol, **PreP1** was obtained as an orange-colored powder. Poly[9,9-bis(*p*-isopropylphenylsulfanyl)fluorene-*alt*-9,9-dioctylfluorene], **P1**, was prepared via dithioacetal formation of **PreP1** with *p*-isopropylbenzenethiol (Scheme 1). After removal of excess thiol, quantitatively dithiolated **P1** was obtained as a pale yellow-colored powder. In ^{1}H NMR spectra of before and after dithioacetal formation of **PreP1**, the peak of the methyne proton of the isopropyl group was observed (Figure 1a, top and middle, respectively). The relative intensity of the methyne proton was good agreement with the theoretical value, when the methylene proton of the octyl group in the dioctylfluorene unit was used as a standard. This indicated the conversion of ketone group to dithioacetal group was almost quantitative. GPC measurements were conducted to provide the relative molecular weight to polystyrene standards and polydispersity index. Before and after polymer reaction, molecular weight of **PreP1** (M_n = 5100, M_w = 10 100, M_w/M_n = 2.01) was increased (**P1**, M_n = 6400, M_w = 19 300, M_w/M_n = 3.02).

Next, we carried out the chemical fluorodesulfurization of **P1** according to the previous report.[23] **P1** was subjected to a dichloromethane solution of 60% pyridinium poly(hydrogen fluoride) (PPHF) or $Et_4NF-4HF$ with NO^+ BF_4^- under argon. After purification, a gelated product was obtained. Any fluorinated product was not detected by ^{1}H and ^{19}F NMR analyses of the slightly soluble part of the product in $CDCl_3$. Therefore, chemical 9-fluorination of **P1** was found to be very difficult by chemical polymer reaction.

Electrochemical Polymer Reaction of P1. A chloroform solution containing 1 mg of **P1** including electroreactive group was coated on a platinum electrode (1 cm × 1 cm) and slowly dried under reduced pressure. By using laser focus displacement meter, film thickness was estimated as ca. 40 μm. For the electrochemical polymer reaction, 3 mL of ionic liquid hydrogen

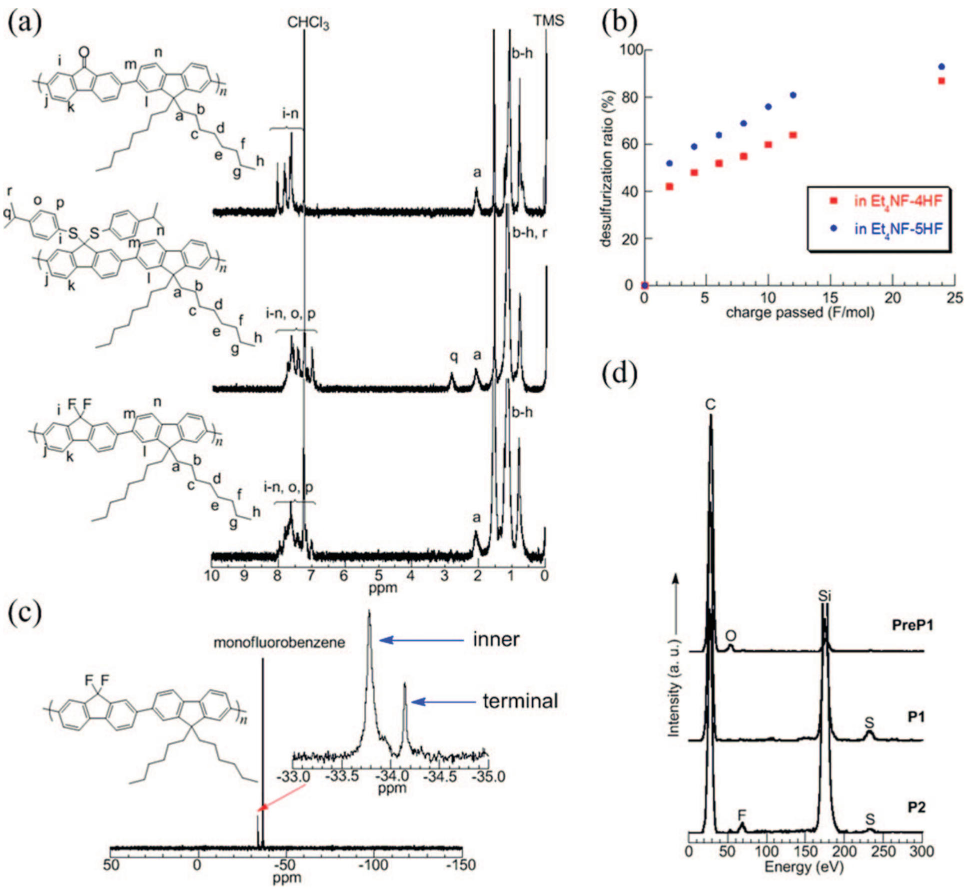
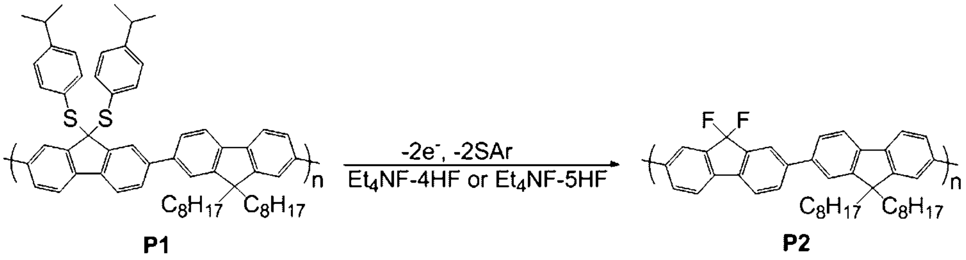


Figure 1. (a) ^{1}H NMR spectra of **PreP1** (top), **P1** (middle), and **P2** (24 F/mol charge passed in Et$_4$NF−5HF) (bottom) in CDCl$_3$. (b) Plots of desulfurization ratios of Et$_4$NF−4HF and Et$_4$NF−5HF estimated by ^{1}H NMR. (c) ^{19}F-NMR spectrum of **P2** (24 F/mol charge passed in Et$_4$NF−5HF) in CDCl$_3$ with monofluorobenzene as a standard. (d) EDX profiles of **PreP1** (top), **P1** (middle), and **P2** (24 F/mol charge passed in Et$_4$NF−5HF) (bottom) with a Si wafer-supported thin film.

Scheme 2. Electrochemical Fluorodesulfurization of P1



fluoride salt (Et$_4$NF−4HF or Et$_4$NF−5HF) was used as the supporting electrolyte, reaction medium and fluorine source immediately after deaeration by argon bubbling in a plastic test tube. Constant current electrolysis (10 mA/cm^2) was carried out using the polymer-coated platinum anode and a bare platinum cathode (1 cm × 1 cm) at room temperature (Scheme 2). The polymer film of **P2** was subsequently purified by washing with methanol and finally dried in vacuo. Then, **P2** was redissolved in chloroform (or CDCl$_3$) to be conducted for spectroscopic analyses.

Figure 1a shows the ^{1}H NMR spectra of **P1** (middle) and **P2** (bottom: after 24 F/mol charge passed) in CDCl$_3$. In the spectrum of **P1**, the peak of the α-methylene protons of the 9,9-dioctylfluorene unit and the methyne protons of 9,9-bis(*p*-isopropylphenylsulfanyl)fluorene unit were observed at 2.11 ppm and 2.82 ppm, respectively. After a charge of 4 F/mol was passed, desulfurization was confirmed by the decrease of the methyne peak. After 24 F/mol, the desulfurization of **P1** was mostly complete. The desulfurization ratio could be estimated by comparing the intensities of the methyne protons in the leaving group and the α-methylene protons of the octyl groups. The estimated desulfurization ratios were gradually increased by increasing of electronic charge passed between 2−24 F/mol in both Et$_4$NF−4HF and Et$_4$NF−5HF (Figure 1b). This result indicates that the reaction ratio could be electrically controlled. From Figure 1b, Et$_4$NF−5HF is found to be the more suitable electrolytic medium because of the higher contents of fluoride anion.

In ^{19}F-NMR spectra (internal standard: monofluorobenzene at −36.5 ppm) of **P2**, peaks were observed at −33.7 and −34.1 ppm as shown in Figure 1c. These peaks were attributed to the 9,9-difluorofluorene unit in **P2** (inner and terminal units, respectively) by comparing the spectrum of the model compound, 9,9-difluorofluorene (−34.9 ppm). Peaks derived from byproduct such as monofluorinated fluorene unit and Ar−F unit were not detected at all. Energy dispersive X-ray (EDX) analysis of **P2** provided information on the substitution level before and after polymer reactions (Figure 1d). A comparison between the

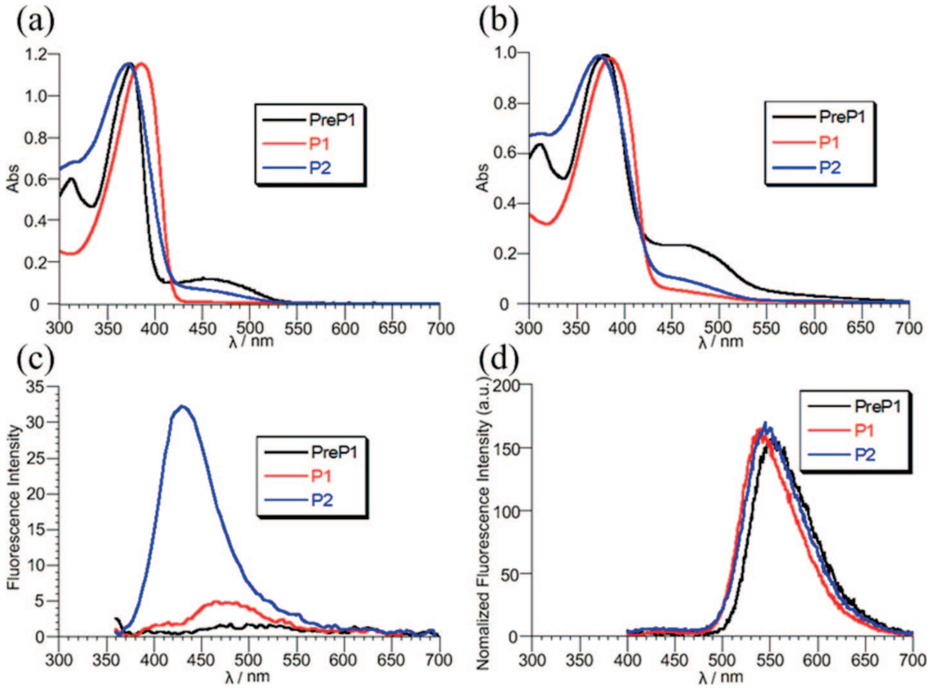


Figure 2. UV−vis absorption spectra of **PreP1**, **P1**, and **P2** in a dilute chloroform solution (a) and in a film state (b). PL spectra in a dilute chloroform solution (c) and in a film state (d).

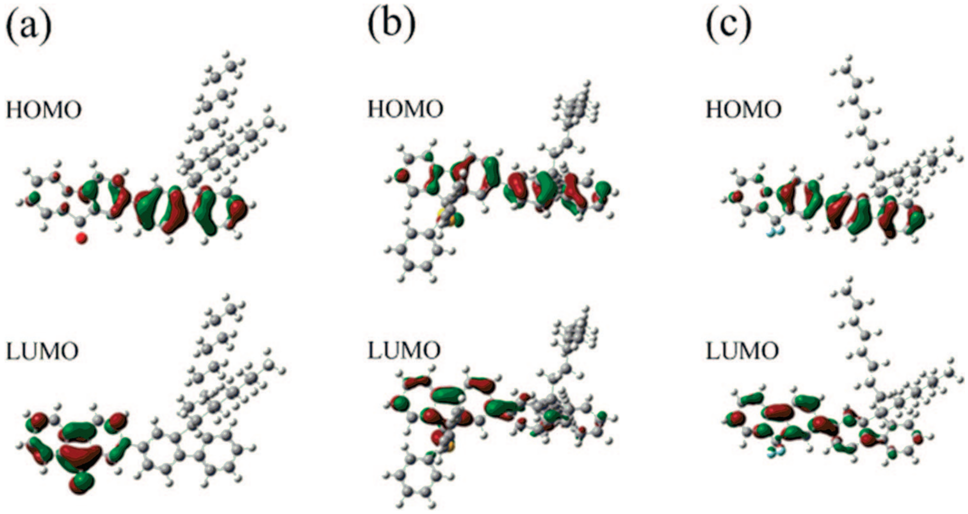


Figure 3. Molecular orbital HOMO and LUMO of (a) **PreP1**, (b) **P1**, and (c) **P2** with a chain length $n = 1$. The molecular orbital surface isovalue is 0.04.

measured F/C ratio (0.066) and the calculated theoretical ratio (0.075) gives fluorination ratio (88%), which is in good agreement with that estimated by the ^{1}H NMR measurement (92%). Moreover, no oxygen peak was observed, indicating that no fluorenone units were produced by undesirable hydrolysis side reactions during electrolysis.

After the electrochemical polymer reaction (24 F/mol charge passed in $Et_4NF-5HF$), the GPC molecular weights of **P2** ($M_n = 5800$, $M_w = 18{,}300$, $M_w/M_n = 3.16$) showed slightly smaller values compared to those of **P1** ($M_n = 6400$, $M_w = 19\ 300$, $M_w/M_n = 3.02$) due to the elimination of thiol (disulfide) unit and the substitution with two fluorine atoms. This result suggested that neither decomposition nor propagation of the polymer occurred even after the excess charge was passed. These foregoing analyses indicated that the electrochemical fluorodesulfurization proceeded selectively and efficiently without side reactions.

Optical Properties and DFT calculations. UV−vis absorption spectra of the copolymers in a dilute chloroform solution and in a film state are shown in Figure 2, parts a and b. In the absorption spectra of **PreP1** and **P2** in chloroform, lower energy absorption band at around 400−530 nm appeared, which were derived from intramolecular charge transfer (ICT) interaction between the electron accepting 9-fluorenone unit in **PreP1** or the 9,9-difluorofluorene unit in **P2** and the electron donating 9,9-dioctylfluorene unit (Figure 2a).[26−31] In the thin film state, all copolymers, **PreP1**, **P1**, and **P2**, exhibited two absorption bands of $\pi-\pi^*$ transition and ICT, even in **P1** having the weakly electron accepting dithioacetal bridged unit (Figure 2b). To understand these optical properties, we carried out the molecular orbital calculations by using quantum mechanical package Gaussian 03. These structures of $n = 1$ (Figure 3) and $n = 2$ (Figure S1) model for **PreP1**, **P1**, and **P2** were obtained from geometry optimization calculations by the density functional theory (DFT) by optimization with the B3LYP functional and the 6-31G basis set.[32] The excitation energies, oscillator strengths (f), and configurations for the polymers with $n = 1$, and $n = 2$ are listed in Table S1. By DFT calculation, the

Table 1. Photophysical Data of POF, PreP1, P1, and P2 in Chloroform and in the Film State

	solution				film			
polymer	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Stokes shift (nm)	Φ_{fl}	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Stokes shift (nm)	E_g^{opt} (eV)[a]
POF	378	416	38	0.84	380	440, 463	60	2.83
PreP1	375, 456			<0.001	383, 463	553	169	2.28
P1	385			0.072	392, 480	540	148	2.36
P2	371, 465	417	46	0.22	274, 469	545	171	2.29

[a] Energy band gaps were estimated from the onset wavelength of the optical absorption.

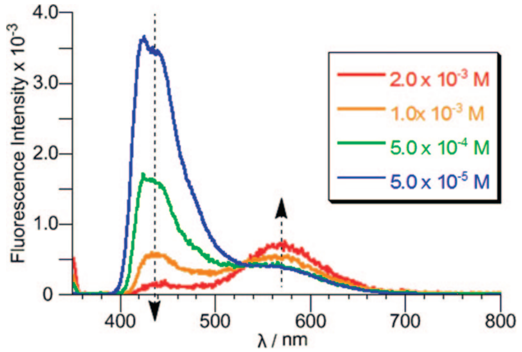


Figure 4. PL spectra of P2 in chloroform at various concentrations.

molecular orbitals of these electron donor and acceptor models were obtained with the localization of the electron density on the donor unit at HOMO and the atomic coefficients on the acceptor unit at LUMO. This indicates the possibility of ICT in the corresponding polymers. Especially, the electron density distribution at LUMO of the polymers becomes highly delocalized near the carbonyl, dithioacetal, and difluoromethylene group, indicating the meta-conjugated[26,33−36] and meta-bridged effect[26,37] (Figure 3).

The optical band gap (E_g^{opt}) was determined from the absorption onset (edge) in the UV−vis spectra of the thin films of the polymers. The absorption onset wavelengths of **PreP1**, **P1** and **P2** (543, 526, and 542 nm) correspond to the band gap of them, 2.28, 2.36, and 2.29 eV, respectively (Table 1). All copolymer showed a lower band gap than poly(9,9-dioctylfluorene), **POF**,[38] as the result of ICT effect between the donor and acceptor moieties in the copolymers.

The quantum yield of fluorescence of the polymers in a dilute chloroform solution (10^{-6} M) was determined on excitation of the polymer at their λ_{max}^{abs} in comparison with the emission of quinine sulfate dehydrate/0.1 M sulfuric acid solution (Φ_{fl} = 0.55) as a standard (Table 1). The photoluminescence (PL) spectrum of **P2** showed a slightly broad emission at 417 nm in a chloroform solution (Figure 2c) and the estimated quantum yield of fluorescence was 0.22. This value is higher than those of **PreP1** and **P1** (<0.1). The PL spectra in the film state were measured by using polymer film coated by drop cast on glass plate (Figure 2d). The spectrum of **P2** in the film state showed an emission peak at 545 nm, which was red-shifted from that in a chloroform solution. A large Stokes shift (171 nm) is derived from large structural differences between its ground-state and excited state.[39,40] It is well-known that the various conjugated polymers show intermolecular excimeric properties.[41−48] In order to confirm the formation of excimer, we carried out the PL measurement of **P2** in chloroform at various concentrations (Figure 4). PL behavior showing the gradual increase of the emission intensity at 545 nm in the course of incleasing of polymer concentration indicates the formation of intermolecular excimers[41−48] in the chloroform solution at high concentrations. The revealed excimer formation in solution strongly supports the aggregation of aromatic units and excimer formation in the film state. Moreover, **PreP1** and **P1** in the film state showed emission peaks at 553 and 540 nm, respectively, while the emissions of **PreP1** and **P1** were hardly detected in a dilute chloroform solution. This result also displays the large structural differences between ground states and excited states of these copolymers.

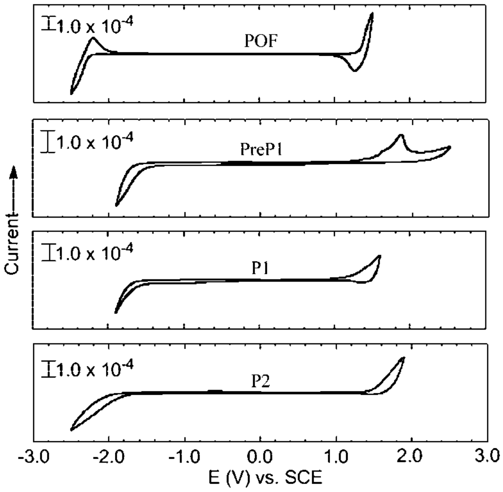


Figure 5. Cyclic voltammograms of **POF**, **PreP1**, **P1**, and **P2**, measured in the film state in 0.1 M $Et_4N\ BF_4$/acetonitrile at a sweep rate of 100 mV/s.

Table 2. Electrochemical Properties and Energy Levels of POF, PreP1, P1 and P2

polymer	$E_{onset,ox}$ (V)[a]	$E_{onset,red}$ (V)[a]	I_p(HOMO) (eV)[b]	E_a(LUMO) (eV)[b]	E_g^{el} (eV)[c]
POF	1.27	−2.14	−5.67	−2.26	3.41
PreP1	1.36	−1.51	−5.76	−2.89	2.87
P1	0.92	−1.41	−5.32	−2.99	2.33
P2	1.34	−1.58	−5.74	−2.82	2.92

[a] Onset oxidation and reduction potentials measured by cyclic voltammetry. [b] Estimated from the onset oxidation and reduction potentials by using $I_p(\mathrm{HOMO}) = -(E_{onset,ox} + 4.4)$ (eV) and $E_a(\mathrm{LUMO}) = -(E_{onset,red} + 4.4)$ (eV). [c] Energy band gaps determined by using $E_g^{el} = (E_a(\mathrm{LUMO}) - I_p(\mathrm{HOMO}))$ (eV).

Electrochemical Properties. Cyclic voltammetry (CV) measurements were conducted to clarify the electrochemical properties of the conjugated electron donor−acceptor copolymers, **PreP1**, **P1**, and **P2**. A three electrode system equipped with the platinum electrode covered with the copolymers (working electrode), platinum counter electrode and SCE as a reference electrode was used in an electrolytic solution of acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate, Et_4NBF_4. The voltammograms and the onset potentials of oxidation ($E_{onset,ox}$) and reduction ($E_{onset,red}$) are shown in Figure 5 and Table 2. The energy level of HOMO, LUMO and thus the electrochemical band gaps, E_g^{el}, could be estimated according to the empirical relationships shown below.[26−31,37−40]

$$I_p(\mathrm{HOMO}) = -(E_{onset,ox} + 4.4)\ (\mathrm{eV})$$

$$E_a(\mathrm{LUMO}) = -(E_{onset,red} + 4.4)\ (\mathrm{eV})$$

$$E_g^{el} = (E_a(\mathrm{LUMO}) - I_p(\mathrm{HOMO}))\ (\mathrm{eV})$$

Table 2 provides both E_a(LUMO) and I_p(HOMO) levels and the E_g^{el} of **PreP1**, **P1**, and **P2**. The energy levels of LUMO of **PreP1**, **P1** and **P2** were lower than that of **POF** (−2.26 eV) due to the stability of anion in these copolymers. The oxidation potential of **P1** was slightly lower than those of the other copolymers. This can be illustrated by an existence of lone paired electrons on sulfur in dithioacetal group, which affected to the electronic state of the polymer main chain via meta-bridged effect. Energy levels of HOMO of **PreP1** and **P2** were similar values that of **POF** (−5.67 eV). The E_g^{el} of **PreP1**, **P1** and **P2** were determined to be 2.87, 2.33, and 2.92 eV, respectively.

Conclusion

In summary, we have synthesized novel fluorene copolymers including ketone, dithioacetal, and difluoromethylene groups at the 9-position through Suzuki−Miyaura coupling polymerization and subsequent selective polymer reactions. Especially, we have successfully demonstrated electrochemical fluorodesulfurization of the electroreactive poly(fluorene) (**P1**) film coated on anode in ionic liquid HF salts. The conversion from dithioacetal to difluoromethylene reached to 80−90% or more and could be controlled by the charge passed and HF contents of ionic liquids. Moreover, we could investigate optoelectronic properties of the alternating copolymers stemmed from the single parent polymer. These novel copolymers including electron accepting unit showed characteristic optoelectronic properties such as ICT behavior. The 9,9-difluorinated copolymer (**P2**) exhibited the fluorescent behavior in chloroform and clearly showed excimer formation at high concentration and in the film state. From these results, effective and selective polymer reactions of poly(fluorene) would be useful approach to provide functional materials. These meta-bridged donor−acceptor conjugated copolymers have potential for semiconducting applications.

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Supporting Information Available: Figures showing the molecular orbital of **PreP1**, **P1**, and **P2**, UV−vis spectra and PL spectra of **POF**, a scheme showing and text discussing the synthesis of **POF**, and a table showing the electronic transition data of **PreP1**, **P1**, and **P2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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