



Post-functionalization of alternating π -conjugated copolymers containing fluorene moieties via anodic chlorination using AlCl_3

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Abstract

Fluorene (Fl) derivatives are representative emitting motifs; thus, they are often installed into alternating π -conjugated copolymers (P(Fl-Ar)) as soluble polymeric emitters. Many researchers have focused on modifying the combined arylene units in P(Fl-Ar) derivatives to tune their optoelectronic properties; however, P(Fl-Ar) derivatives that contain fluorene units with functional groups at their sp^2 carbons remain limited. Here, we synthesize P(Fl-Ar) derivatives comprising sp^2 -chlorinated fluorene units via anodic chlorination using aluminum chloride (AlCl_3). The introduced chlorine atoms affect the optoelectronic properties of the pristine P(Fl-Ar) derivatives. Compared with the precursor P(Fl-Ar) derivatives, chlorinated P(Fl-Ar) derivatives exhibit longer maximum emission wavelengths.

Introduction

Fluorene derivatives with a methylene-bridged biphenyl structure are among the best known polycyclic aromatic hydrocarbons. Various functional groups can be introduced into the 9-position of a fluorene ring via treatment with appropriate electrophiles under basic conditions because of the relatively high acidity of the protons at its 9-position [1–4]. With these benefits, many functional molecules that contain 9-position-functionalized fluorene rings have been developed [5–7]. Among them, 9,9-dialkylfluorene derivatives are often installed into the main chains in π -conjugated polymers (CPs) because the introduced fluorene units can

impart solubility in organic solvents and emission properties to the CPs [8, 9]. The emitting colors of the CPs containing 9,9-dialkylfluorene units can be tuned by changing other components in the CPs. In this context, alternating π -conjugated copolymers with a 9,9-dialkylfluorene unit and another arylene unit (i.e., poly(9,9-dialkylfluorene-*alt*-arylene) (P(Fl-Ar)) derivatives) exhibit a wide range of emission colors due to the combination of these units [7, 9].

To design the structure and emission properties of P(Fl-Ar) derivatives, transition metal-catalyzed polycondensation between 9,9-dialkylfluorene monomers and other arylene monomers with functional groups is often used. This approach is widely accepted for their synthesis; however, multiple steps are required to prepare the corresponding monomers, and troublesome optimization of the polymerization conditions limits the facile synthesis of P(Fl-Ar) derivatives. In this context, introducing functional units into the readily accessible precursor via post-functionalization methods is practical [10–13]. Various synthetic protocols are applicable to synthesize P(Fl-Ar) derivatives via the post-functionalization of precursor CPs [14–28]. P(Fl-Ar) derivatives with various functionalities can be prepared using either of the above approaches, where the modification of the arylene unit in the P(Fl-Ar) derivatives is focused; i.e., P(Fl-Ar) derivatives are synthesized from 9,9-dialkylfluorene and an arylene unit with functional groups (P(Fl-(Ar-FG))) (Fig. 1a).

Although the introduction of functional units into the aromatic moieties of the fluorene units in the P(Fl-Ar) derivatives (P((Fl-FG)-Ar)) is expected to tune the emission

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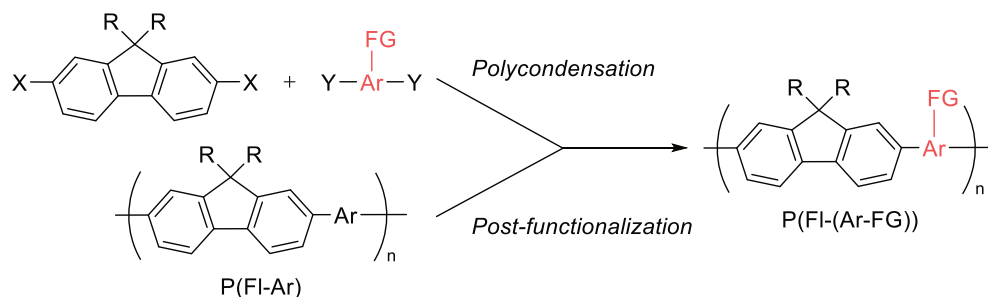
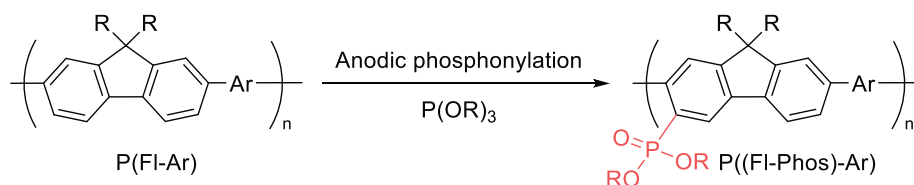
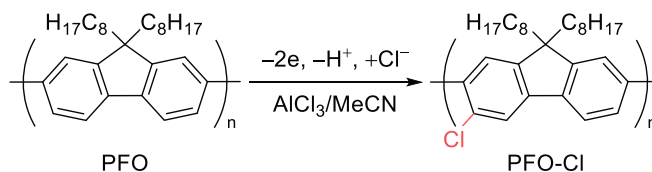
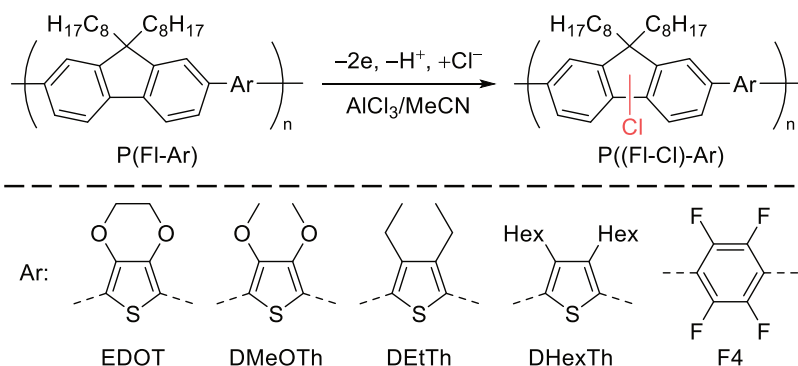
(a) Synthesis of P(FI-(Ar-FG)) via polycondensation or post-functionalization**(b) Synthesis of P((FI-FG)-Ar) via anodic C-H phosphonylation [32]****(c) Anodic C-H chlorination of poly(9,9-dioctylfluorene) (PFO) [37]****(d) This work: Synthesis of P((FI-Cl)-Ar) via anodic C-H chlorination of P(FI-Ar)**

Fig. 1 a Synthetic procedures for P(FI-(Ar-FG)). b Anodic C-H phosphonylation of P(FI-Ar). c Anodic C-H chlorination of PFO. d This work: anodic C-H chlorination of P(FI-Ar)

properties of the P(FI-Ar) derivatives, there are few P((FI-FG)-Ar) polymers. Only Leclerc and Beaupré [29] has reported the polycondensation between alkoxy-substituted fluorene monomers and arylene monomers, where a multi-step synthesis is required for sp²-alkoxylated fluorene monomers. Therefore, the post-functionalization of aromatic C-H bonds on fluorene units is more practical to synthesize P((FI-FG)-Ar). Electrochemical C-H post-

functionalization (ePF) is a powerful and promising method to replace the aromatic C-H bonds of the main chain of CPs with various functional groups under mild conditions [30, 31]. ePF is triggered by the electrochemical doping of CPs in the presence of reactive dopants or reagents and their subsequent chemical reaction with the electrochemically doped CPs. Recently, we successfully synthesized phosphonylated fluorene-containing P(FI-Ar)

derivatives (P((Fl-Phos)-Ar)) via an electrochemical C–H phosphonylation of fluorene moieties with trialkyl phosphite (P(OR)₃) as a phosphonate source (Fig. 1b) [32]. The introduced phosphonate groups affect their optoelectronic properties depending on the degree of phosphonylation. Nonetheless, the relationship between the optoelectronic properties of P((Fl-FG)-Ar) and the introduced functional units remains unknown.

Here, we expand the library of sp^2 -functionalized fluorene-containing P(Fl-Ar) derivatives via the anodic C–H chlorination protocol. Anodic chlorination is a typical electrochemical post-functionalization for CPs [33–36], where chloride (Cl[−]) serves as a dopant and a chlorine source. Previously, we achieved high-efficiency anodic chlorination of CPs in acetonitrile (MeCN) containing aluminum chloride (AlCl₃) as the chlorine source, electrolyte, and Lewis acid [37]. The developed electrolysis system (i.e., the AlCl₃/MeCN system) enables the C–H chlorination of the 3-position of a fluorene unit in poly(9,9-dioctylfluorene) (PFO) (Fig. 1c). Encouraged by this discovery, we performed anodic chlorination of P(Fl-Ar) using the AlCl₃/MeCN system in this work (Fig. 1d). Various P(Fl-Ar) derivatives were prepared via Pd-catalyzed direct C–H arylation polycondensation and subjected to anodic chlorination. The sp^2 -chlorinated fluorene-containing P(Fl-Ar) (P((Fl-Cl)-Ar)) derivatives were carefully characterized, and their optoelectronic properties were investigated.

Experimental procedure

General procedure for the anodic chlorination of P(Fl-Ar) derivatives

A CHCl₃ solution (1 mL) containing 5 mg of P(Fl-Ar) derivatives was cast onto a Pt plate (2 cm × 2 cm), which was used as a working electrode (WE) for the anodic chlorination. First, 10 mL of 0.2-M AlCl₃/MeCN solution was prepared in an undivided cell with the WE and a Pt plate (2 cm × 2 cm) used as a counter electrode (CE). Anodic chlorination was performed under constant-current electrolysis ($j = 0.5 \text{ mA/cm}^2$) at room temperature. After the desired amount of charge has been passed, the obtained polymer films were washed with MeCN. Then, the resulting polymer was de-doped in 0.1-M Bu₄NPF₆/MeCN by applying a negative potential (−0.2 V vs. SCE) to the polymer-coated electrode. The de-doped polymer film was washed with MeCN, distilled water, and MeOH and subsequently dried. The degree of chlorination of the obtained polymer was determined by comparing the ¹H NMR integral signals of (1) the aromatic protons and (2) the protons derived from the η -methylene protons and terminal methyl protons of the side chains of the fluorene units (i.e., −CH₂CH₃).

Results and discussion

Preparation of P(Fl-Ar) derivatives and their electrochemical properties

In accordance with the reported literature, P(Fl-Ar) derivatives were prepared via direct C–H arylation polycondensation between 2,7-dibromo-9,9-dioctylfluorene and another arylene unit [38, 39]. We prepared five types of P(Fl-Ar) derivatives based on the availability of monomers, structures, and electron densities, where Ar represents 3,4-ethylenedioxythiophene (EDOT), 3,4-dimethoxythiophene (DMeOTh), 3,4-diethylthiophene (DEtTh), 3,4-dihexylthiophene (DHexTh), or 1,2,4,5-tetrafluorobenzene (F4). The electrochemical properties of the P(Fl-Ar) derivatives were investigated via cyclic voltammetry (CV) measurements in an MeCN solution, which contained tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) or AlCl₃ (Fig. S1). Because there was Lewis acidic AlCl₃, the oxidation onset potential of P(Fl-Ar) derivatives in an AlCl₃/MeCN solution shifted in the negative direction from that observed in a Bu₄NPF₆/MeCN solution. This trend is consistent with the effects of AlCl₃ on the homopolymers [37]. The oxidation onset potential of P(Fl-F4) in an AlCl₃/MeCN solution could not be determined because P(Fl-F4) appeared to be oxidized outside the potential window of the AlCl₃/MeCN solution. Table 1 summarizes the polycondensation results and oxidation onset potentials of the P(Fl-Ar) derivatives.

Anodic chlorination of P(Fl-Ar) derivatives

Anodic chlorination of P(Fl-Ar) was performed under identical conditions to the anodic chlorination of PFO in our previous report (Fig. 2) [37]. P(Fl-Ar) films were prepared on a platinum (Pt) plate (2 cm × 2 cm) with a 5-mg/mL CHCl₃ solution. The polymer-coated Pt plate was used as a WE for the reaction. Figure 2 shows the reaction profile as a function of the amount of charge passed through the electrode. The ¹H NMR-based degree of chlorination was calculated by comparing the signals derived from the aromatic protons at 7.6–7.9 ppm and the signals derived from the η -methylene protons and terminal methyl protons of the side chains of the fluorene units (i.e., −CH₂CH₃) at approximately 0.8 ppm. The total number of protons of P(Fl-DHexTh) observed at approximately 0.8 ppm is different from that of other P(Fl-Ar) derivatives because the protons of the two methyl groups of the side chains of DHexTh had overlapping signals.

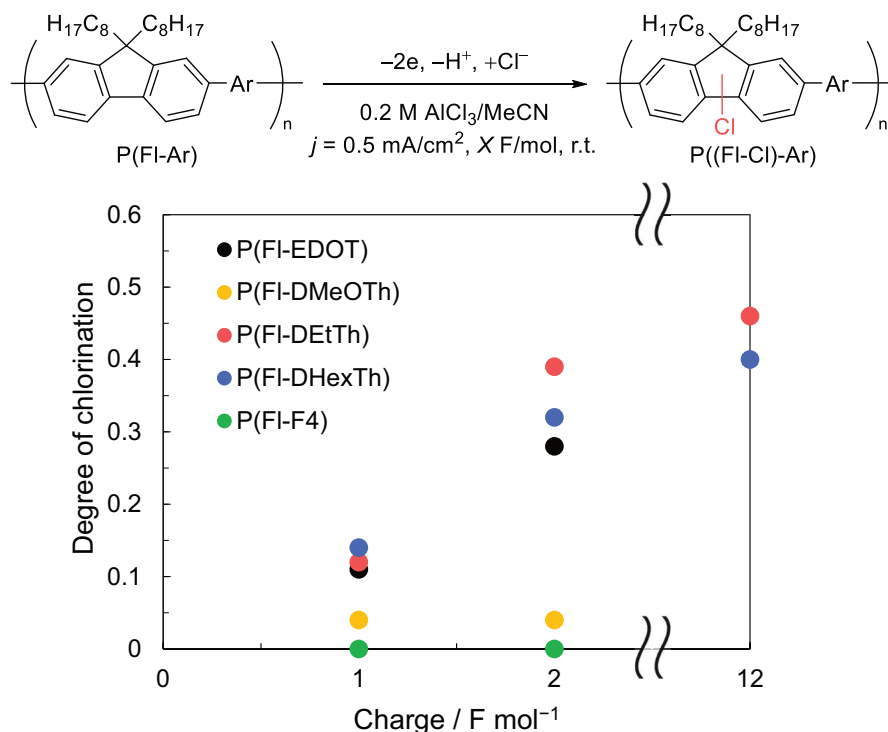
The P(Fl-Ar) derivatives containing 3,4-dialkoxy-substituted thiophene units (i.e., EDOT or DMeOTh) were dissolved during the reaction. Hence, the degree of chlorination of the obtained polymers was estimated by

Table 1 P(FI-Ar) precursors

P(FI-Ar)	Yield [%] ^a	M_n^b	M_w^b	PDI ^c	E_{onset}^{Ox} [V vs. SCE] ^d
P(FI-EDOT)	67	82,400	474,800	5.8	0.99 (0.89)
P(FI-DMeOTh)	52	10,500	54,600	5.2	1.19 (1.07)
P(FI-DEtTh)	54	9,900	21,110	2.1	1.30 (1.12)
P(FI-DHexTh)	97	16,500	115,400	7.0	1.35 (1.24)
P(FI-F4)	32	34,300	214,300	6.3	1.97 (n.d.) ^e

^aIsolated yield^bDetermined by size exclusion chromatography (SEC, CHCl₃ eluent, polystyrene standard)^cPDI is the polydispersity index and is defined as M_w/M_n ^dCV measurements were performed in 0.1-M Bu₄NPF₆/MeCN and 0.1-M AlCl₃/MeCN. The numbers in parentheses are E_{onset}^{Ox} of the P(FI-Ar) derivatives in 0.1-M AlCl₃/MeCN^eNot determined because of the high oxidation tolerance of P(FI-F4)

Fig. 2 Traces of the degree of chlorination of the P((FI-Cl)-Ar) derivatives as a function of charge passed. The degree of chlorination of P(FI-Ar) derivatives was determined via ^1H NMR



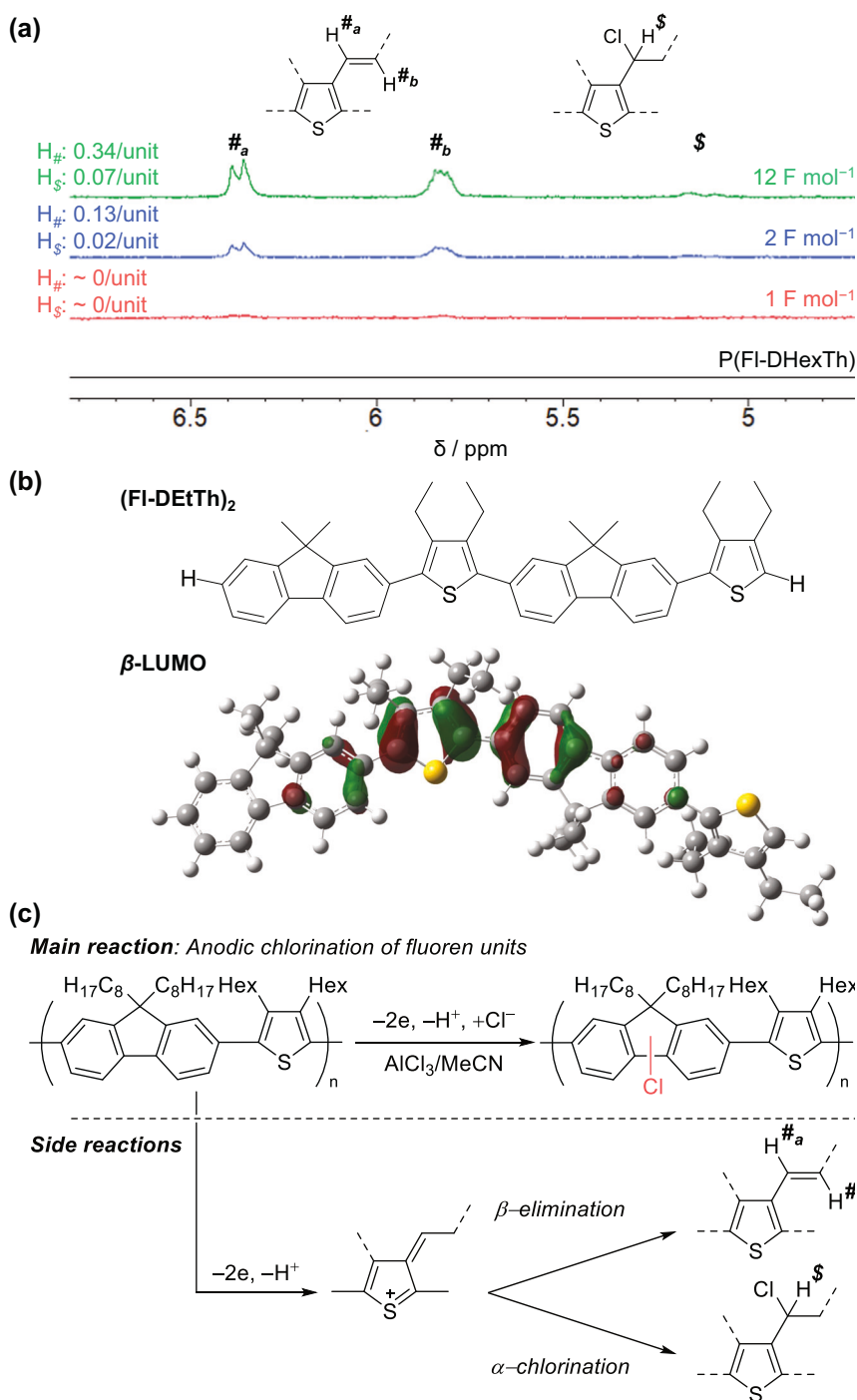
collecting the polymer films that remained on the electrode after the reaction. The P(FI-EDOT) film began to dissolve in the electrolyte after the passage of 1 F/mol of charge, whereas the P(FI-DMeOTh) film immediately began to dissolve in the electrolyte at the initial stage of anodic chlorination. As a result, the degree of chlorination of P(FI-EDOT) increased with increasing amount of charge passed, whereas that of P(FI-DMeOTh) hardly changed for 1 F/mol and 2 F/mol of charge passed. With 2 F/mol of charge passed, the degree of chlorination of P((FI-Cl)-EDOT) was approximately 0.3. The difference in anodic chlorination between P(FI-EDOT) and P(FI-DMeOTh) was presumably due to the difference in molecular weights (Table 1). The dissolution of the polymer films during the reaction hampered efficient electron transfer between polymer film and working electrode, which was believed to decrease the degree of chlorination. P(FI-EDOT) has a much greater molecular weight than P(FI-DMeOTh), which increases the tolerance of P(FI-EDOT) to dissolution during the reaction and results in a greater degree of chlorination. This trend in the effects of the molecular weight on the efficiency of the ePF is consistent with our previous work [40].

The P(FI-Ar) derivatives containing 3,4-dialkylthiophene units (i.e., DEtTh or DHexTh) were successfully chlorinated while maintaining their film state after passing 12 F/mol of charge. The degree of chlorination of these polymers gradually increased with increasing amount of charge passed, which follows the same trend as the reported anodic chlorination of CPs [24, 25, 37]. With 12 F/mol of charge

passed, the degree of chlorination of the P((FI-Cl)-Ar) derivatives was approximately 0.4. However, when the amount of charge passed increased, three new signals gradually appeared at approximately 5.1 ppm (labeled as \$), 5.8 ppm (labeled as #_b), and 6.4 ppm (labeled as #_a) in the ^1H NMR spectra. Figure 3a shows the stacked partial ^1H NMR spectra of P(FI-DHexTh) with the corresponding regions after the anodic chlorination with different amounts of charge. The P((FI-Cl)-DEtTh) samples had similar ^1H NMR spectra to the P((FI-Cl)-DHexTh) samples. These signals were due to the unexpected side reactions at the α -carbons of the side chains of the thiophene units. Signal \$ was derived from the chlorination of the α -carbons ($\text{C}_{\alpha\text{-Th-Cl}}$) [41]. The pair of signals # was derived from the formation of carbon-carbon double bonds ($\text{C}=\text{C}$) between α -carbon and β -carbon, whose stereochemistry was trans [42, 43]. These side reactions at the side chains of the thiophene units were not observed in the anodic chlorination of poly(3-hexylthiophene) (P3HT) under identical electrolysis conditions [37]. The degree of chlorination of the α -carbons hardly increased after the passage of 12 F/mol of charge. Negligibly few $\text{C}=\text{C}$ bonds formed when 1 F/mol of charge was passed. Meanwhile, the degree of $\text{C}=\text{C}$ bond formation gradually increased with increasing charge passage. When 12 F/mol of charge was passed, the degree of $\text{C}=\text{C}$ bond formation was approximately 0.3, which is comparable to the desirable anodic sp^2 -chlorination.

To gain insight into the reaction mechanism, density functional theory (DFT) was used to investigate P(FI-

Fig. 3 **a** Stacked partial ^1H NMR spectra of P(FI-DHexTh) and P(FI-Cl)-DHexTh samples obtained from the anodic chlorination with different amounts of charge passed. The degree of side reactions (i.e., C = C bond formation and C–Cl bond formation) is also presented. **b** Chemical structure and molecular orbitals corresponding to the β -LUMO of (FI-DEtTh) $_2$ in the one-electron oxidation state. The molecular orbital surface iso value is 0.04 ($U\omega\text{B97XD}/6\text{-}31\text{G} + (\text{d,p})$). **c** Plausible reaction mechanism of the anodic chlorination of P(FI-DHexTh)

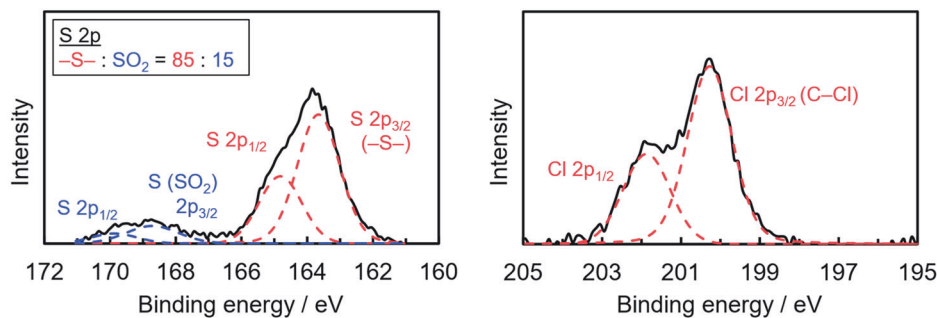


DHexTh) and P(FI-DEtTh) in the one-electron oxidation state. The anodic substitution reaction is often discussed in terms of the lowest unoccupied molecular orbital (LUMO) of the substrate in the one-electron oxidation state, i.e., β -LUMO [32, 44–46]. We used the dimer unit of P(FI-DEtTh) ((FI-DEtTh) $_2$) as a model structure for the DFT calculations. To reduce the calculation cost, the side chains of the fluorene units in (FI-DEtTh) $_2$ were changed from octyl units to methyl groups. Figure 3b shows the molecular

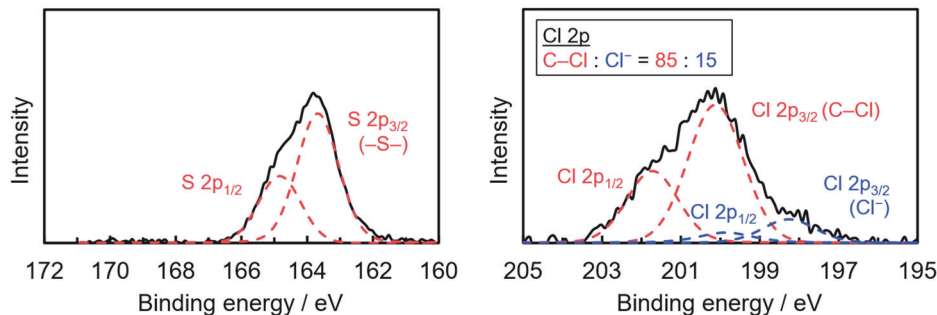
structure of (FI-DEtTh) $_2$ and a diagram of its β -LUMO in the one-electron oxidation state. The β -LUMO coefficient of (FI-DEtTh) $_2$ in the one-electron oxidation state was mainly localized at the thiophene ring between two fluorene rings, which indicates that the thiophene moieties in both P(FI-DHexTh) and P(FI-DEtTh) served as more electron-deficient units than the fluorene moieties during the anodic chlorination. We also investigated the β -LUMO of a tetramer unit of 3-butylthiophene ((3-BuTh) $_4$) in the one-

Fig. 4 XPS spectra of the S 2p and Cl 2p regions: **a** *m*-P((FI-Cl)-EDOT), **b** *m*-P((FI-Cl)-DEtTh), and **c** *m*-P((FI-Cl)-DHexTh). The numbers in the spectra are the atomic ratio of sulfide (–S–) to sulfone (SO₂) or the atomic ratio of C–Cl bonds to Cl[–] ions

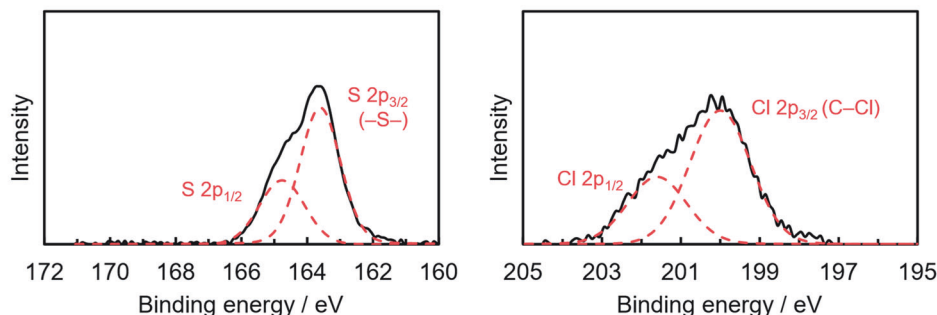
(a) *m*-P((FI-Cl)-EDOT)



(b) *m*-P((FI-Cl)-DEtTh)



(c) *m*-P((FI-Cl)-DHexTh)



electron oxidation state as a model molecule of homopolymers, such as poly(3-hexylthiophene) (P3HT) (Fig. S3a). Compared with (FI-DEtTh)₂, the β -LUMO coefficient of (3-BuTh)₄ in the one-electron oxidation state was delocalized along its main chain, which suggests that the side reactions observed in the anodic chlorination of P(FI-DHexTh) and P(FI-DEtTh) were due to the localization of β -LUMO at the thiophene moieties. In addition, the chlorine atoms that were introduced into the fluorene units were expected to promote the localization of the β -LUMO coefficient on the thiophene units because of their electron-withdrawing nature. Thus, such side reactions were also facilitated by an increase in degree of chlorination of the precursor polymers. The gradual increase in the signals derived from the side reactions supports this idea (Fig. 3a). Based on the above discussion, a plausible reaction mechanism for the anodic chlorination of P(FI-DHexTh) and P(FI-DEtTh) is described in Fig. 3c. The localization of

β -LUMO at the thiophene ring during the anodic chlorination induces deprotonation at the α -position, followed by a C=C bond formation via β -elimination or a C–Cl bond formation via α -chlorination.

P(FI-F4) was not electrochemically chlorinated under the present reaction conditions, as determined by the absence of changes in the ¹H and ¹⁹F NMR spectra of P(FI-F4) before and after the anodic chlorination (Fig. S2). Since the oxidation potential of P(FI-F4) was greater than the potential window of the AlCl₃/MeCN system (Fig. S1), the anodic oxidation of the electrolyte preferentially proceeded and resulted in no chlorination of P(FI-F4) under the present reaction conditions.

Characterization of chlorinated P(FI-Ar) derivatives

Chlorinated P(FI-Ar) derivatives such as P((FI-Cl)-EDOT), P((FI-Cl)-DEtTh) and P((FI-Cl)-DHexTh) were characterized

via NMR analyses, SEC measurements, X-ray photoelectron spectroscopy (XPS) measurements, and energy dispersive X-ray spectroscopy (EDS) analyses. To characterize the P(FI-Cl)-Ar derivatives, anodic chlorination of P(FI-Ar) derivatives was performed under identical reaction conditions to those in Fig. 2 with either four 2-F/mol charge passed (Ar = EDOT) or three 12-F/mol charge passed (Ar = DEtTh or DHexTh). After each reaction, the obtained P(FI-Cl)-Ar samples, which remained in the film state on the electrode, were mixed. The degree of chlorination of the mixed samples (*m*-P(FI-Cl)-Ar), as determined by ¹H NMR, was 0.30 (Ar = EDOT), 0.41 (Ar = DEtTh), and 0.47 (Ar = DHexTh).

The regioselectivity of the anodic chlorination of P(FI-Ar) derivatives was investigated according to a previous report on the anodic chlorination of PFO [37]. Unfortunately, the chlorine-substituted carbon on the fluorene rings was not determined, presumably because the *m*-P(FI-Cl)-Ar derivatives had a lower degree of chlorination than PFO (1.00 degree of chlorination); thus, the regioselectivity of the anodic chlorination was not clarified in the current study. Based on the DFT calculations for the model dimer unit in the one-electron oxidation state (Fig. 3b) and the literature of Swager and Song [47], chlorine would be replaced by hydrogen at the 1- or 3-position of a fluorene ring due to the electron-withdrawing nature of charged thiophene units at the 2-position of fluorene units. In addition, the anodic C–H chlorination of PFO [37] and anodic C–H phosphonylation of P(FI-Ar) [32] selectively provided 3-position-functionalized fluorene moieties. Therefore, we speculate that the anodic C–H chlorination of P(FI-Ar) derivatives also provides 3-chlorinated fluorene units.

Next, XPS analyses of the *m*-P(FI-Cl)-Ar derivatives were conducted to confirm the valence state of sulfur and formation of carbon–chlorine (C–Cl) bonds (Fig. 4). *m*-P(FI-Cl)-Ar films on an indium tin oxide (ITO) substrate were prepared with *m*-P(FI-Cl)-Ar in CHCl₃ and used for the XPS measurements. Interestingly, the S 2p XPS profiles of the *m*-P(FI-Cl)-Ar samples provided different results depending on the incorporated arylene units. An additional peak appeared at approximately 169 eV in the XPS spectra for the S 2p peak of *m*-P(FI-Cl)-EDOT, which resulted from the sulfone formed by the oxidation of a sulfur atom in a thiophene ring (Fig. 4a) [32, 48, 49]. The XPS-based atomic ratio of sulfide (–S–) to sulfone (SO₂) was determined to be 85:15. In contrast, the valence of sulfur in both *m*-P(FI-Cl)-DEtTh and *m*-P(FI-Cl)-DHexTh did not change, since the observed binding energy of S 2p was almost identical to the reported value for thiophene-containing CPs (Fig. 4b and 4c) [32, 37, 50]. DFT calculations for the (FI-EDOT) dimer units in the one-electron oxidation state revealed that the β-LUMO coefficient was relatively localized at the EDOT unit (Fig. S3b). Since P(FI-EDOT) has no α-methylene carbons on the thiophene rings,

the sulfur atom was oxidized, which generated sulfone during the anodic chlorination. The Cl 2p XPS profiles of the *m*-P(FI-Cl)-Ar derivatives show two peaks derived from C–Cl bonds, which indicates the formation of C–Cl bonds via anodic chlorination. Two minor peaks in the *m*-P(FI-Cl)-DEtTh sample were due to the remaining Cl[–] ions [51]. The XPS-based atomic ratio of C–Cl bonds to Cl[–] ions was determined to be 85:15 (Fig. 4b). The amount of chlorine atoms introduced into the *m*-P(FI-Cl)-Ar samples was also evaluated via EDS measurements. The EDS measurements could not distinguish the chlorine atoms derived from C–Cl bonds from those arising from Cl[–] ions; thus, the atomic ratio of chlorine derived from C–Cl bonds to sulfur (Cl_{C-Cl}/S) was calculated using the XPS-based atomic ratio of Cl_{C-Cl}/Cl_{Cl[–]} (Cl_{C-Cl}/Cl_{Cl[–]} = 85:15). The atomic ratio of Cl_{C-Cl}/S for all *m*-P(FI-Cl)-Ar samples was close to their ¹H NMR-based degrees of chlorination: Cl_{C-Cl}/S = 0.25 (Ar = EDOT), 0.46 (Ar = DEtTh), and 0.45 (Ar = DHexTh). These results suggest that the chlorination of the α-carbons in the side chains of the thiophene units was negligible, which is consistent with the weak signals from chlorinated α-methine, as shown in Fig. 3a.

Finally, the effects of the anodic chlorination on the molecular weights of the *m*-P(FI-Cl)-Ar derivatives were investigated via SEC measurements. Figure S4 displays the SEC traces of the precursor polymers and *m*-P(FI-Cl)-Ar derivatives. The SEC chromatographic peaks of the P(FI-Ar) derivatives (Ar = DHexTh or DEtTh) and *m*-P(FI-Cl)-Ar derivatives were observed at almost identical retention time, which indicates that the molecular weight of the precursor polymers was maintained without degradation and further propagation of their polymer main chain during the reaction. Meanwhile, *m*-P(FI-Cl)-EDOT had a broader SEC chromatogram toward longer retention time than P(FI-EDOT), presumably due to the generation of sulfones in the EDOT moieties. The generated sulfone moieties increased the polarity of P(FI-EDOT), which changed its hydrodynamic volume and decreased the SEC-based molecular weight of P(FI-Cl)-EDOT.

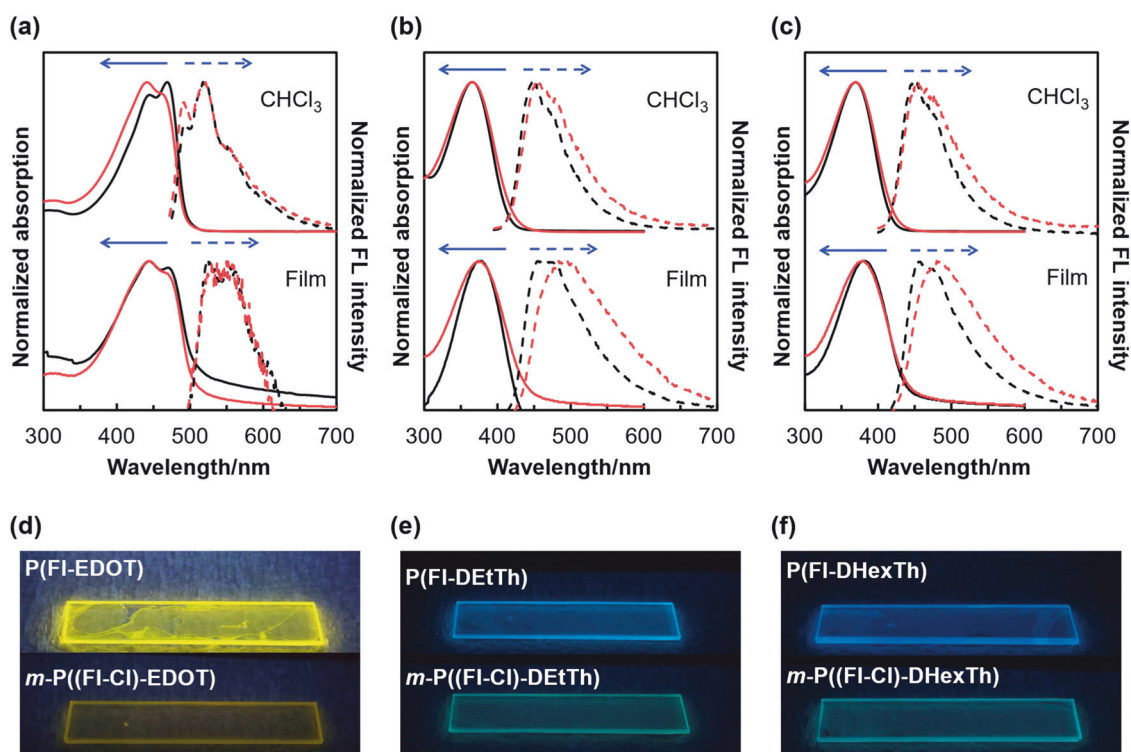
Optoelectronic properties of chlorinated polymers

Finally, the effects of anodic chlorination on their optoelectronic properties were investigated (Table 2). The electrochemical properties of the *m*-P(FI-Cl)-Ar samples were evaluated via CV measurements in 0.1-M Bu₄NPF₆/MeCN (Fig. S5). The oxidation onset potential of the *m*-P(FI-Cl)-Ar samples shifted in the positive direction from that of the pristine precursors because of the electron-withdrawing nature of the substituted chlorine atoms [25, 37].

The optical properties of the P(FI-Ar) samples and *m*-P(FI-Cl)-Ar samples were also investigated. Figure 5 shows

Table 2 Optoelectronic properties of the P(FI-Ar) derivatives and *m*-P((FI-Cl)-Ar) samples

Polymer	Degree of chlorination ^a	$E_{onset}^{Ox.}$ (vs. SCE) ^b	λ_{max} (CHCl ₃) [nm] ^c		λ_{max} (Film) [nm] ^d		Φ_{FL}^e	
			Abs.	FL	Abs.	FL	CHCl ₃	Film
P(FI-EDOT)	–	0.99	469	518	444	^f	0.15	0.02
<i>m</i> -P((FI-Cl)-EDOT)	0.30 (0.25) ^g	1.01	441	521	445	^f	0.08	~ 0
P(FI-DEtTh)	–	1.30	365	447	376	466	0.20	0.34
<i>m</i> -P((FI-Cl)-DEtTh)	0.41 (0.46) ^g	1.38	364	452	375	484	0.08	0.15
P(FI-DHexTh)	–	1.35	369	449	381	454	0.35	0.33
<i>m</i> -P((FI-Cl)-DHexTh)	0.47 (0.45) ^g	1.49	369	455	378	480	0.07	0.18

^aDetermined by ¹H NMR^bCV measurements were performed in 0.1-M Bu₄NPF₆/MeCN^cAbsorption and fluorescence spectra in solution were obtained from a 0.02-mg/mL CHCl₃ solution^dAbsorption and fluorescence spectra in the film-state were obtained from as-spun thin films prepared via spin-coating of a 5.0-mg/mL CHCl₃ solution^eFluorescence quantum yield^fNot determined because of the weak fluorescence spectra^gNumbers in parentheses are the EDS-based Cl_{C-Cl}/S ratio**Fig. 5** UV/Vis absorption spectra (solid lines) and FL spectra (dotted lines) of P(FI-Ar) (black lines) and *m*-P((FI-Cl)-Ar) (red lines) in CHCl₃ (upper) and in the film state (lower): **a** Ar = EDOT, **b** Ar =DEtTh, and **c** Ar = DHexTh. Photographs of P(FI-Ar) (upper) and *m*-P((FI-Cl)-Ar) (lower) in the film state under UV irradiation ($\lambda = 365$ nm): **d** Ar = EDOT, **e** Ar = DEtTh, and **f** Ar = DHexTh

the ultraviolet/visible (UV/Vis) absorption spectra and fluorescence (FL) spectra of the P(FI-Ar) derivatives and *m*-P((FI-Cl)-Ar) samples in CHCl₃ solutions and in the film state. The introduced chlorine atoms and aforementioned side reactions hardly affected the absorption properties of the P(FI-Ar) derivatives because the P(FI-Ar) derivatives and *m*-

P((FI-Cl)-Ar) samples had almost identical absorption spectra and absorption maximum wavelengths. The *m*-P((FI-Cl)-Ar) samples had different emission properties from the precursor polymers, particularly in the film state. Compared with the pristine P(FI-Ar) derivatives, all chlorinated P(FI-Ar) exhibited a lower fluorescence quantum yield (Φ_{FL}) in both CHCl₃

and the film state. Interestingly, the maximum emission wavelength of *m*-P((Fl-Cl)-Ar) (Ar = DEtTh and DHexTh) was longer than that of the original polymers in both CHCl₃ solution and the film state, which was accompanied by a change in emission color of P(Fl-Ar) in the film state (Ar = DEtTh and DHexTh) (Fig. 5b and 5c). The precursor polymers showed light blue emission under UV irradiation, whereas the chlorinated polymer showed light green emission under UV irradiation. According to the report by Inagi, Fuchigami, and coworkers, the emission wavelength of poly(9,9-dioctylfluorene-*alt*-thiophene-2,5-diyl) was blue-shifted by introducing chlorine atoms into the thiophene units [24, 52]. The present study demonstrated the opposite trend (i.e., a redshift of the emission wavelength), which suggests that this redshift resulted from the partial charge transfer from thiophene units to chlorinated fluorene units and the formation of a C=C bond between α -carbon and β -carbon of the side chains of the thiophene units [53, 54].

Conclusion

The post-functionalization of alternating π -conjugated copolymers (P(Fl-Ar)) that contained 9,9-dioctylfluorene units was successfully achieved via anodic chlorination using the AlCl₃/MeCN system. The reactivity of the P(Fl-Ar) derivatives varied depending on the installed arylene units in the copolymers. When the Ar unit was EDOT or dialkyl-substituted thiophene, the aromatic C–H bonds of the fluorene units in the P(Fl-Ar) derivatives were chlorinated via anodic C–H chlorination. Side reactions occurred because of β -LUMO localization at the thiophene units during the anodic chlorination. The optoelectronic properties of the P(Fl-Ar) derivatives could be modified by anodic chlorination when C–Cl bonds formed at the fluorene units. The introduction of chlorine atoms onto the fluorene unit of P(Fl-DHexTh) or P(Fl-DEtTh) caused a redshift in their emission properties. The electrochemical C–H post-functionalization of the fluorene units enables rapid access to novel fluorene-containing alternating π -conjugated polymers (i.e., P((Fl-FG)-Ar)), which require cumbersome synthetic processes. The developed P((Fl-FG)-Ar) derivatives should be applicable to various organic electronics.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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