

## Synthesis and Chemical Properties of Electrochromic $\pi$ -Conjugated Polyphenylenes with Pendant Viologen-TCNQ Salts

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**ABSTRACT:** Polyphenylene (PP) with  $\text{NH}_2$  side groups, namely, **PFluNH<sub>2</sub>**, was synthesized by the Pd-catalyzed reaction of 2,5-dibromoaniline with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester. The reaction of **PFluNH<sub>2</sub>** with 1-hexyl-1'-(2,4-dinitrophenyl)-4,4'-bipyridinium diiodide (**SaltBPy(I<sup>-</sup>)**) eliminated 2,4-dinitroaniline to yield PPs with viologen (1,1'-disubstituted 4,4'-bipyridinium dications), **PFluBPy(I<sup>-</sup>)**. The reaction of **PFluBPy(I<sup>-</sup>)** with  $\text{Li}^+\text{TCNQ}^-$  resulted in anion exchange between  $\text{Cl}^-$  and  $\text{TCNQ}^-$ , and yielded **PFluBPy(TCNQ<sup>-</sup>)**. The reaction of **PFluBPy(TCNQ<sup>-</sup>)** with the neutral  $\text{TCNQ}^0$  resulted in an interaction between  $\text{TCNQ}^-$  and  $\text{TCNQ}^0$ , and yielded **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**. Cyclic voltammetry measurements suggested that an electrochemical reduction of the viologen moiety and oxidation of the polymer backbone within **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**. Furthermore, this reaction was accompanied by electrochromism. The electric conductivities ( $\sigma$ ) of the pellets molded from **PFluBPy(TCNQ<sup>-</sup>)** to **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** were  $2.7 \times 10^{-4}$  and  $4.2 \times 10^{-4} \text{ Scm}^{-1}$ , respectively; these  $\sigma$  values were higher than that observed for **PFluNH<sub>2</sub>** ( $\sigma < 10^{-8} \text{ Scm}^{-1}$ ) due to the self-doping in the polymers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 397–403, 2013

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### INTRODUCTION

Polyphenylenes (PPs) have been extensively studied because they can be useful materials for the development of electronic and photoelectronic devices.<sup>1–6</sup> It is known that PPs can undergo a reductive (*n*-type) or an oxidative (*p*-type) of doping; the *p*-doping of PPs effectively converts them into conducting materials.<sup>1–6</sup> As a means of finding a milder environment for doping, we explored the use of viologen, a well-known redox agent, to convert PPs from an insulating to a conducting state. Recently, we have reported self-doped PPs containing a viologen side group with both  $\text{Br}^-$  and  $\text{Cl}^-$  anions.<sup>7</sup> The self-doping nature of PPs that contain a viologen side group can be explained by the electron transfer from the polymer backbone to the viologen. The chemical properties of  $\pi$ -conjugated polymers with pendant viologen groups are a subject of recent interest.<sup>8–10</sup>

Electrochromic materials change color as a result of oxidation or reduction when an appropriate electric potential is applied.<sup>11</sup> The electrochromic properties of viologens are well documented, and viologens have received significant attention because of their electrical and electrochromic properties and good environmental stability.<sup>12–15</sup> The effects of the chemical

structures of the *N*-substituents on the electrochromic properties of viologens have been investigated. However, less attention has been paid to the effect of anionic species on the electrochromic behavior of viologens. Investigation of these affects would facilitate both a better understanding of the electrochromic behavior of viologens and the development of new electrochromic materials. TCNQ is used as an acceptor in organic charge-transfer complexes and can be converted into a radical anion ( $\text{TCNQ}^-$ ) by treatment with alkaline metal halides.<sup>16</sup> In addition,  $\text{TCNQ}^-$  in ammonium or pyridinium salts interacts with neutral  $\text{TCNQ}^0$  to yield complexes with high-electric conductivity ( $\sigma$ ).<sup>16,17</sup> Thus, PPs containing viologens with  $\text{TCNQ}^-$  will exhibit unique electrochromic behavior based on the electrochemically active polymer backbone and side groups. To the best of our knowledge, there has been no report on viologens with  $\text{TCNQ}^-$ . This study is the first example of  $\pi$ -conjugated polymers bearing viologen- $\text{TCNQ}^-$  side groups. To obtain PPs bearing viologen side groups with  $\text{TCNQ}^-$ , PP with a reactive  $\text{NH}_2$  side group (**PFlu-NH<sub>2</sub>**) was used as the starting material because the reaction of Zincke salts (highly electrophilic species formed by the reaction between a pyridine derivative and 1-chloro-2,4-dinitrobenzene) with primary amines yields

pyridinium salts.<sup>18–20</sup> In this study, an anion exchange reaction between  $I^-$  from a BPy( $I^-$ ) side group of PP containing viologen and  $Li^+TCNQ^-$  was also used to yield a PP containing a viologen with  $TCNQ^-$ . Furthermore, PP containing viologen side groups with a  $TCNQ^-$ - $TCNQ^0$  structure was also synthesized.

Herein, we report the synthesis of novel Zincke salts and PPs containing the viologen with  $I^-$ ,  $TCNQ^-$ , and  $TCNQ^-$ - $TCNQ^0$ . In addition, we describe their optical, electrochromic, and electric properties.

## EXPERIMENTAL

### General

Solvents were dried, distilled, and stored under nitrogen. **PFluNH<sub>2</sub>** and 1-hexyl-1'-2,4-dinitrophenyl-4,4'-bipyridinium bromide chloride were prepared according to the literatures.<sup>7,21</sup> Other reagents were purchased and used without further purification. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer and a JEOL AL-400 spectrometer, respectively. Elemental analysis was carried out on a Yanagimoto MT-5 CHN recorder. UV-vis and PL spectra were obtained by a JASCO V-560 spectrometer and a JASCO FP-6200, respectively. Quantum yield was calculated by using a diluted ethanol solution of 7-dimethylamino-4-methylcoumarin as the standard. Molecular weights were obtained by gel permeation chromatography (GPC) with Waters 150C with polystyrene gel columns using dimethylformamide (DMF) containing 0.006M LiBr as an eluent. Cyclic voltammetry was performed in an acetonitrile solution containing 0.10M  $[Et_4N]BF_4$  with a Hokuto Denko HSV-110. Ag wire was used as a reference electrode in an acetonitrile solution of  $AgNO_3$  and  $[Et_4N]BF_4$  (0.10M). Electric conductivity measurements were conducted on the molded pellets of the polymers by an Advantest R8340A ultra high resistance meter with a two-probe method.

### Synthesis of SaltBPy( $I^-$ )

After an aqueous solution (20 mL) of 1-hexyl-1'-2,4-dinitrophenyl-4,4'-bipyridinium bromide chloride (0.70 g, 4.7 mmol) and sodium iodide (0.73 g, 3.6 mmol) was stirred at room temperature for 1 h, the precipitate from the reaction solution was collected by filtration, washed with acetone, and dried under vacuum to give **SaltBPy( $I^-$ )** as an orange powder (0.52 g, 39%). <sup>1</sup>H NMR [400 MHz, dimethyl sulfoxide (DMSO)-*d*<sub>6</sub>]:  $\delta$  9.71 (d, *J* = 5.6 Hz, 2H), 9.46 (d, *J* = 5.2 Hz, 2H), 9.18 (s, 1H), 9.08 (d, *J* = 5.6 Hz, 2H), 9.04 (d, *J* = 5.6 Hz, 1H), 8.92 (d, *J* = 4.8 Hz, 2H), 8.46 (d, *J* = 8.4 Hz, 1H), 4.73 (s, 2H), 2.01 (s, 2H), 1.33 (s, 6H), 0.89 (s, 3H). Calcd for  $C_{22}H_{24}N_4I_2O_4$ : C, 39.90; H, 3.65; N, 8.46. Found: C, 40.30; H, 3.55; N, 8.46.

### Synthesis of PFluBPy( $I^-$ )

To a DMSO solution (5 mL) of **SaltBPy( $I^-$ )** (0.16 g, 0.24 mmol) was added to a  $CHCl_3$  solution (5 mL) of **PFluNH<sub>2</sub>** (0.085 g, 0.18 mmol). After the reaction solution was stirred at 80°C for 30 h, the solvents were removed under vacuum. The resulting solid was washed with water, methanol, and chloro-

form. **PFluBPy( $I^-$ )** was collected by filtration, dried under vacuum, and obtained as a deep red powder (0.045 g, 36%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.68 (2H), 9.46 (2H), 8.95 (4H), 7.25–8.43 (9H), 4.70 (2H), 1.94 (2H), 1.29 (6H), 1.02 (4H), 0.85 (16H), 0.70 (3H), 0.64 (6H). Calcd for  $(C_{47}H_{56}I_2N_2 \bullet 2H_2O)_n$ : C, 60.13; H, 6.44; N, 2.98. Found: C, 59.97; H, 6.40; N, 2.79.

### Synthesis of PFluBPy( $TCNQ^-$ )

After an aqueous solution (10 mL) of **PFluBPy( $I^-$ )** (0.045 g, 0.047 mmol) and  $Li^+TCNQ^-$  (0.040 g, 0.19 mmol) was stirred at room temperature for 6 h, the precipitate from the reaction solution was collected by filtration, washed with acetone, and dried under vacuum to give **PFluBPy( $TCNQ^-$ )** as a black powder (0.030 g, 72%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.65 (2H), 9.40 (2H), 8.87 (4H), 6.76–8.31 (9H), 4.67 (2H), 1.91 (2H), 1.27 (6H), 1.01 (4H), 0.84 (16H), 0.67 (9H). Calcd for  $(C_{71}H_{64}N_{10} \bullet H_2O)_n$ : C, 79.30; H, 6.19; N, 13.03. Found: C, 79.14; H, 6.31; N, 12.80.

### Synthesis of PFluBPy( $TCNQ^-$ - $TCNQ^0$ )

After a DMSO solution (20 mL) of **PFluBPy( $TCNQ^-$ )** (0.030 g, 0.028 mmol) and  $TCNQ$  (0.036 g, 0.18 mmol) was stirred at 80°C for 8 h, the solvent was removed under vacuum. The resulting solid was washed with chloroform, dissolved in DMSO, and poured into chloroform to give precipitate. **PFluBPy( $TCNQ^-$ - $TCNQ^0$ )** was collected by filtration, dried under vacuum, and obtained as a black powder (0.030 g, 97%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.67 (2H), 9.43 (2H), 8.92 (4H), 6.84–8.32 (25H), 4.68 (2H), 1.91 (2H), 1.28 (6H), 1.02 (4H), 0.84 (16H), 0.70 (3H), 0.63 (6H). Calcd for  $(C_{95}H_{72}N_{18} \bullet 1.5H_2O)_n$ : C, 76.54; H, 4.94; N, 16.91. Found: C, 76.22; H, 4.59; N, 17.41.

## RESULTS AND DISCUSSION

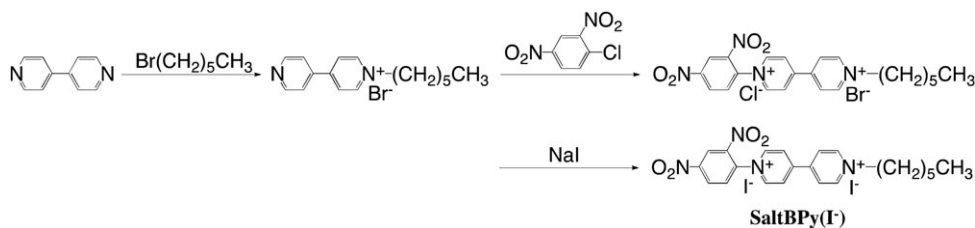
### Synthesis

The introduction of the viologen side group in PP was carried out by the reaction between Zincke salts and PP with  $NH_2$  groups. The new Zincke salt used in this study, **SaltBPy( $I^-$ )**, was synthesized by the two-step *N*-alkyl and *N*-aryl reactions of 4,4'-bipyridyl, followed by the anion exchange reaction (Scheme 1).

The Pd-catalyzed polycondensation of 2,5-dibromoaniline with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester resulted in 98% yield of the PP **PFluNH<sub>2</sub>**, as shown in Scheme 2(a). The reaction of **PFluNH<sub>2</sub>** with **SaltBPy( $I^-$ )** caused the elimination of 2,4-dinitroaniline and yielded **PFluBPy( $I^-$ )** with the viologen moiety in 36% yield [Scheme 2(b)]. The reaction of **PFluBPy( $I^-$ )** with  $Li^+TCNQ^-$  resulted in the anion exchange between  $Cl^-$  and  $TCNQ^-$ , and produced **PFluBPy( $TCNQ^-$ )** in 72% yield [Scheme 2(b)]. Treatment of **PFluBPy( $TCNQ^-$ )** with neutral  $TCNQ^0$  resulted in an interaction between  $TCNQ^-$  and  $TCNQ^0$  and produced **PFluBPy( $TCNQ^-$ - $TCNQ^0$ )**. The synthesis results are summarized in Table I.

### <sup>1</sup>H NMR Spectra

Figure 1 shows the <sup>1</sup>H NMR spectra of **PFluNH<sub>2</sub>**, **PFluBPy( $TCNQ^-$ )**, and **PFluBPy( $TCNQ^-$ - $TCNQ^0$ )** in DMSO-*d*<sub>6</sub>. The presence of the three peaks assigned to the amine protons at  $\delta$  5.09, 5.05, and 4.85 suggests that **PFluNH<sub>2</sub>** has the



**Scheme 1.** Synthesis of 1-hexyl-1'-2,4-dinitrophenyl-4,4'-bipyridinium salts.

three types of coupling units as depicted in Figure 2. These peaks can be assigned to the  $\text{NH}_2$  protons in the tail-to-tail (TT), head-to-tail (HT), and head-to-head (HH) units, respectively. This assignment is related to the chemical shifts of the  $\text{NH}_2$  groups in the previously reported model compounds, **Model-a** ( $\delta = 4.74$ ), **Model-b** ( $\delta = 5.16$ ), and **Model-c** ( $\delta = 5.11$ ), shown in Figure 3.<sup>7</sup> The molar ratio of the TT, HT, and HH units in **PFluNH<sub>2</sub>** was determined to be 0.11 : 0.06 : 0.83 from the peak integrals of H-atoms of the  $\text{NH}_2$  group.

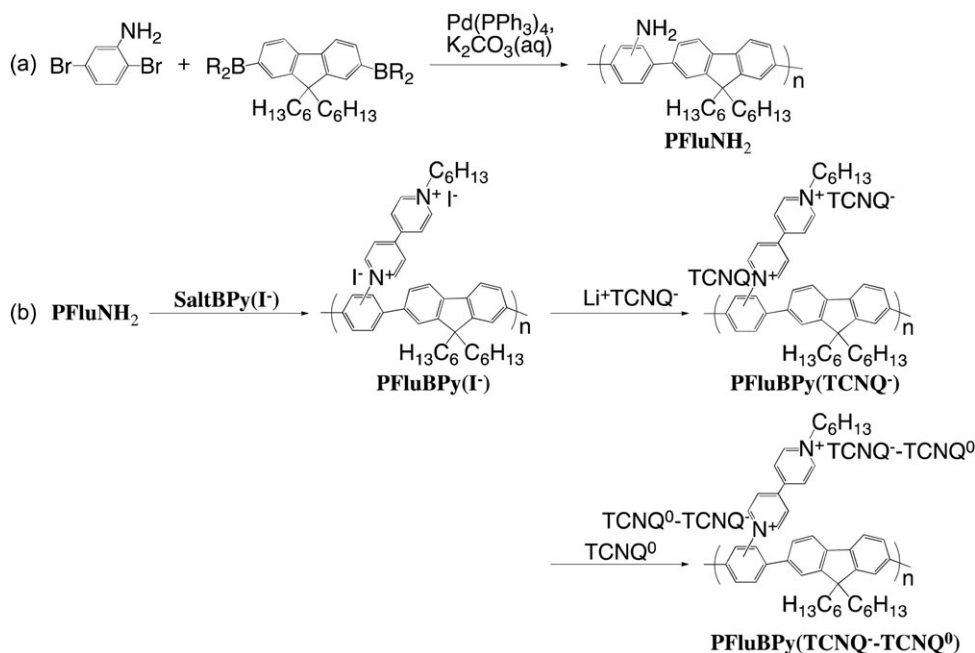
The signals due to aliphatic and aromatic protons of **PFluNH<sub>2</sub>** were observed in the ranges of  $\delta$  0.72–2.08 and  $\delta$  7.47–7.91, respectively. The observed areas of the signals due to amine, aliphatic, and aromatic protons were in good agreement with the structure of **PFluNH<sub>2</sub>** as shown in Scheme 2(a). Data from the elemental analysis also agreed with the structure of **PFluNH<sub>2</sub>** with hydration water; the presence of the hydrophilic  $\text{NH}_2$  groups in the polymers appeared to be the reason for the hydration.

The disappearance of the peaks due to the  $\text{NH}_2$  protons in the  $^1\text{H}$  NMR spectrum of **PFluBPy(TCNQ<sup>-</sup>)** suggests that the reaction of **PFluNH<sub>2</sub>** with **SaltBPy(I<sup>-</sup>)** proceeded completely. The peak integral ratio of the aliphatic and aromatic protons also supports this assumption. The peaks corresponding to the

H-atoms of the radical anion  $\text{TCNQ}^-$  in the polymers disappeared in the  $^1\text{H}$  NMR spectrum. In contrast, the peaks corresponding to the H-atoms of the neutral  $\text{TCNQ}^0$  of **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** were observed at  $\delta$  6.85 and 7.64. The peak integral ratio of the H-atoms of the neutral  $\text{TCNQ}^0$  and the benzene rings in the polymer backbone suggested that all the  $\text{TCNQ}^-$  molecules interacted with  $\text{TCNQ}^0$ .

### IR Spectra

Figure 4 depicts the IR spectra of **PFluNH<sub>2</sub>**, **PFluBPy(TCNQ<sup>-</sup>)**, and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**. The IR spectrum of **PFluNH<sub>2</sub>** exhibits two distinct peaks due to  $\nu(\text{N-H})$  at 3455 and 3376  $\text{cm}^{-1}$ . A peak assignable to  $\delta(\text{N-H})$  of **PFluNH<sub>2</sub>** was observed at 1611  $\text{cm}^{-1}$ . Because of the introduction of the viologen unit, the absorption due to the  $\text{NH}_2$  group disappeared and a new strong absorption due to  $\nu(\text{C=N})$  in the viologen unit appeared at 1632  $\text{cm}^{-1}$  in the IR spectra of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**. Peaks due to  $\nu(\text{C}\equiv\text{N})$  of  $\text{TCNQ}^-$  of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** were observed at 2130  $\text{cm}^{-1}$  and 2172  $\text{cm}^{-1}$ , respectively. These wave numbers were shifted as compared with the corresponding  $\nu(\text{C}\equiv\text{N})$  of  $\text{TCNQ}$  itself (2223  $\text{cm}^{-1}$ ). These observations are consistent with the observation that  $\text{Et}_3\text{N}^+\text{H}-\text{TCNQ}^-$  exhibited



**Scheme 2.** Synthesis of polyphenylenes containing  $\text{NH}_2$  side group and viologen and pyridinium units.

**Table I.** Synthesis Results and Optical, Electrochemical, and Electric Properties of Polymers

	Yield (%)	$M_n^a$	$M_w^a$	$\eta_{sp}c^{-1}$ (dLg <sup>-1</sup> ) <sup>b</sup>	Absorption (nm) <sup>c</sup>	$\lambda_{em}$ (nm) <sup>d</sup>	Oxidation potential (V) <sup>e</sup>	Reduction potential (V) <sup>e</sup>			$\sigma$ (Scm <sup>-1</sup> ) <sup>f</sup>	
								$E_{pc}(1)$	$E_{pc}(2)$	$E_{pa}(1)$		$E_{pa}(2)$
<b>PFluNH<sub>2</sub></b>	98	11,200	34,000	0.19	368	461 (0.10)	1.48	$E_{pc}(1)$	$E_{pc}(2)$	$E_{pa}(1)$	$E_{pa}(2)$	$<10^{-8}$
<b>PFluBPy(I<sup>-</sup>)</b>	36			1.88	366, 400		1.50	-0.59	-1.07	-0.40	-0.82	$6.0 \times 10^{-6}$
<b>PFluBPy(TCNQ<sup>-</sup>)</b>	72			1.90	363, 500		1.60	-0.68	-1.35	-0.60	-1.09	$2.7 \times 10^{-4}$
<b>PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)</b>	97				362, 489		1.23	-0.81	-1.13	-0.66	-0.96	$4.2 \times 10^{-4}$

<sup>a</sup>Determined by GPC (eluent = DMF containing 0.006 M LiBr vs. polystyrene standards).

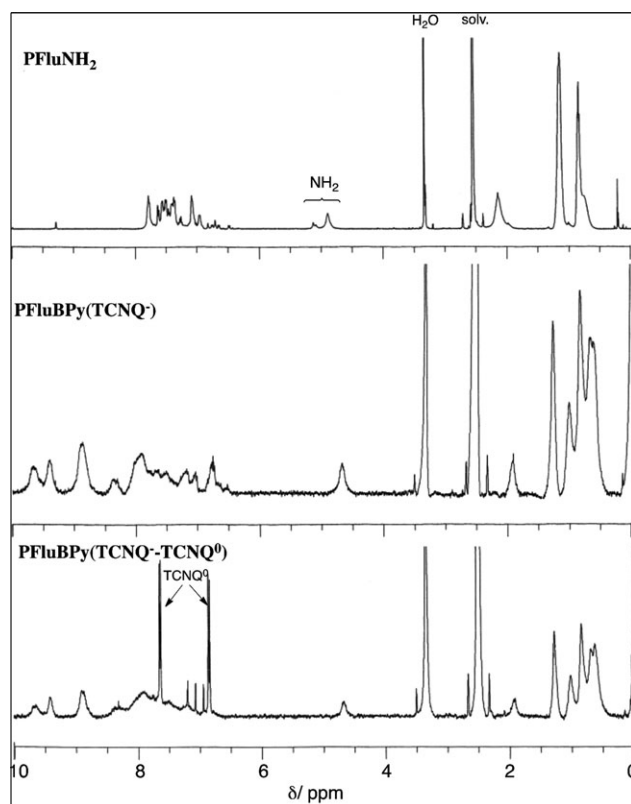
<sup>b</sup>Measured at the concentration of 0.10 g dL<sup>-1</sup> in DMF at 30°C.

<sup>c</sup>In DMF.

<sup>d</sup>Photoluminescence (PL) peak in DMF. Quantum yield of PL was shown in parenthesis.

<sup>e</sup>Measured by cyclic voltammetry in an acetonitrile solution of [Et<sub>4</sub>N]BF<sub>4</sub> (0.10 M).

<sup>f</sup>Measured with a two-probe method.

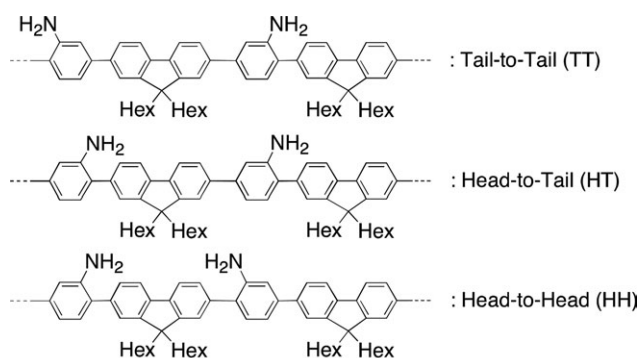
**Figure 1.** <sup>1</sup>H NMR spectra of PFluNH<sub>2</sub>, PFluBPy(TCNQ<sup>-</sup>), and PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>) in DMSO-*d*<sub>6</sub>.

absorptions due to  $\nu(C\equiv N)$  of TCNQ<sup>-</sup> at shorter wavenumbers than those observed for neutral TCNQ.<sup>16</sup>

### Molecular Weights and Viscosities

PFluNH<sub>2</sub> was completely soluble in both less-polar organic solvents such as toluene and chloroform and polar organic solvents such as DMF and DMSO. In contrast to PFluNH<sub>2</sub>, PFluBPy(TCNQ<sup>-</sup>) and PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>) were soluble in DMF and DMSO but insoluble in toluene and chloroform. GPC measurements suggested that the  $M_n$  and  $M_w$  values of PFluNH<sub>2</sub> were 11,200 and 34,000, respectively.

DMSO solution of PFluNH<sub>2</sub> afforded an intrinsic viscosity of 0.19 dLg<sup>-1</sup>. The  $\eta_{sp}c^{-1}$  values of PFluBPy(TCNQ<sup>-</sup>) in DMSO

**Figure 2.** Structurally non-equivalent diads in PFluNH<sub>2</sub>.



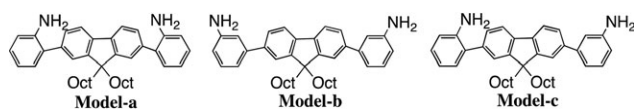


Figure 3. Structures of model compounds.

increased when its concentration ( $c$ ) was reduced, suggesting that the polymer behaved as a polymeric electrolyte in the dilute solutions.<sup>22</sup> The  $\eta_{sp}c^{-1}$  values of **PFluBPy(TCNQ<sup>-</sup>)** in DMSO at 30°C were significantly larger than those of the starting polymer **PFluNH<sub>2</sub>**. This is apparently due to the expanded structure of **PFluBPy(TCNQ<sup>-</sup>)**. These structures were induced by the static repulsion between the cationic viologen and pyridinium side groups in the dilute solutions.

### UV-vis Absorption and Photoluminescence

Optical data relating to the polymers are summarized in Table I. Figure 5 shows the UV-vis spectra of **PFluNH<sub>2</sub>**, **PFluBPy(TCNQ<sup>-</sup>)**, and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** in DMF. These polymers showed an absorption maximum ( $\lambda_{max}$ ) at a wavelength longer than those of the model compounds, due to the expansion of the  $\pi$ -conjugated system along the polymer chain. The absorption peak due to the  $\pi$ - $\pi^*$  transition of **PFluNH<sub>2</sub>** was observed at 368 nm; this wavelength was longer than those observed for **PFluBPy(TCNQ<sup>-</sup>)**, **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**, and **PFluPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**. The  $\lambda_{max}$  of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** was shorter than that observed for **PFluNH<sub>2</sub>** due to the steric repulsion between the side groups, which effected the twisting of the polymer backbone. In addition to the absorption due to the  $\pi$ - $\pi^*$  transitions of the polymer backbone, **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** showed absorptions due to **TCNQ<sup>-</sup>** at 500 nm and 489 nm, respectively. The observation that **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** showed absorptions due to the anionic species at a wavelength that was shorter than that at which **PFluBPy(TCNQ<sup>-</sup>)** showed absorption is consistent with the fact that  $[\text{Et}_3\text{NH}^+][\text{TCNQ}^- \cdot \text{TCNQ}^0]$  exhibited an absorption at a shorter wavelength than  $[\text{Et}_3\text{NH}^+][\text{TCNQ}^-]$  did.<sup>16</sup> It has been

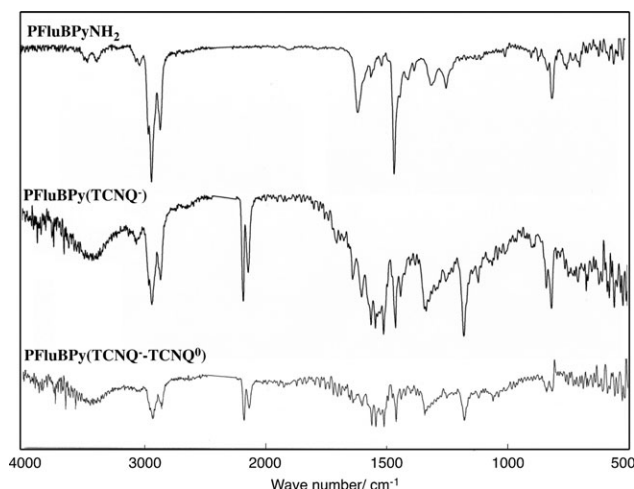


Figure 4. IR spectra of **PFluNH<sub>2</sub>**, **PFluBPy(TCNQ<sup>-</sup>)**, and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**.

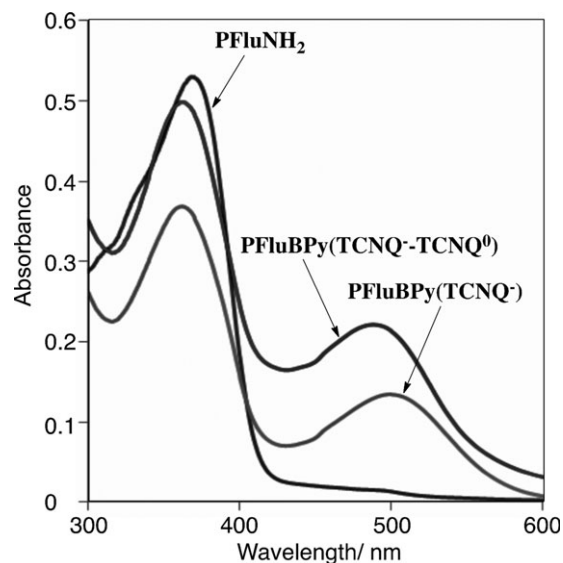


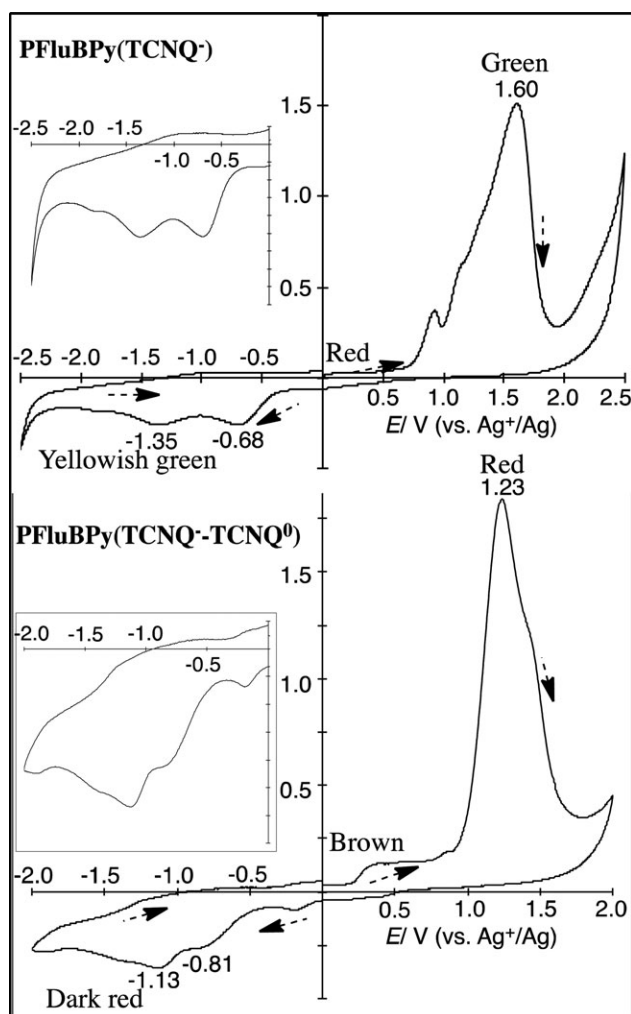
Figure 5. UV-vis spectra of **PFluNH<sub>2</sub>**, **PFluBPy(TCNQ<sup>-</sup>)**, and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** in DMF.

reported that **PFluBPy(Br<sup>-</sup>,Cl<sup>-</sup>)** exhibits absorption peaks in the range of 500–700 nm corresponding to the viologen radical cation, which is generated by electron transfer from the polymer backbone to the viologen group.<sup>7</sup> However, such absorption corresponding to the viologen radical cation was not observed in the UV-vis spectra of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** under nitrogen. This result suggests the presence of few radical species in the polymer backbone, which, in turn, corresponds to a restriction of electron transfer from the polymer main chain to the viologen group because of twisting between the polymer repeating units induced by bulky **TCNQ<sup>-</sup>** and **TCNQ<sup>-</sup>-TCNQ<sup>0</sup>**. The disappearance of absorption corresponding to the viologen radical cation is also occurred in polypyrrole with viologen pendant group at the *N*-position because of the twisting between the pyrrole ring and viologen group.<sup>8</sup>

**PFluNH<sub>2</sub>** was photoluminescent in solution when irradiated with UV light. The photoluminescence (PL) peak of the polymer appeared at an onset position of its absorption band ( $\lambda_{em} = 373$  nm), as usually observed with photoluminescent PPs.<sup>23</sup> The quantum yield of the PL of **PFluNH<sub>2</sub>** in DMF was 0.10. In contrast to **PFluNH<sub>2</sub>**, **PFluBPy(TCNQ<sup>-</sup>)**, and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** showed no PL in solution. It has reported that the addition of 1,1'-ethyl-4,4'-bipyridyl (ethyl viologen) in the **PFluNH<sub>2</sub>** solution quenched the PL of the polymer.<sup>7</sup> Based on this fact, the quenched PL of the polymer backbones of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** is attributed to the effect of the pendant viologen moiety. This assumption is also consistent with the fact that viologens brought about a quenching effect on photoluminescent compounds.<sup>24</sup>

### Electrochemical and Electric Properties

Figure 6 shows cyclic voltammograms of cast films of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** on a Pt plate. The cast films of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** undergo two-step electrochemical reduction in the viologen moiety and electrochemical oxidation



**Figure 6.** Cyclic voltammograms of cast films of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** on a Pt plate in an acetonitrile solution of [Et<sub>4</sub>N]BF<sub>4</sub> (0.10 M). The scan was started from 0 V with a rate of 50 mVs<sup>-1</sup>. The scan direction is shown with arrows.

of the polymer backbone in an acetonitrile solution of 0.10 M [NEt<sub>4</sub>]BF<sub>4</sub>. The peak potentials are summarized in Table I. As depicted in Figure 6, the cyclic voltammogram of **PFluBPy(TCNQ<sup>-</sup>)** shows the peaks for the first cathode potential ( $E_{pc}(1)$ ) and the second cathode potential ( $E_{pc}(2)$ ) at  $-0.68$  V and  $-1.35$  V versus Ag<sup>+</sup>/Ag, respectively. These were coupled to the anode potentials  $E_{pa}(1)$  and  $E_{pa}(2)$  at  $-0.60$  V and  $-1.09$  V versus Ag<sup>+</sup>/Ag, respectively. An anodic peak at 1.60 V versus Ag<sup>+</sup>/Ag was observed for **PFluBPy(TCNQ<sup>-</sup>)** due to the electrochemical oxidation of the polymer backbone. However, the corresponding reduction (p-dedoping) peak did not appear in the cyclic voltammograms; this is likely due to the formation of a stable adduct between the dicationic viologen moieties of the polymers and BF<sub>4</sub><sup>-</sup>, which prevented electrochemical reduction (p-dedoping). It has been reported that  $\pi$ -conjugated polymers containing a viologen side group display an irreversible electrochemical oxidation.<sup>7</sup>

The color of the red film of **PFluBPy(TCNQ<sup>-</sup>)** changed to yellowish green after the electrochemical reduction and changed

back to red after crossing the  $E_{pa}(2)$  peak. The color of the brown film changed to green after the electrochemical oxidation. While the color of the brown film of **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** changed to dark red after the electrochemical reduction and returned to brown after crossing the  $E_{pa}(2)$  peak, as shown in Figure 6. The color of the brown film changed to red after electrochemical oxidation. The difference in electrochromism of **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** corresponds to the observation that the TCNQ<sup>-</sup>-TCNQ<sup>0</sup> species affects the electrochemical reaction of the viologen moiety and the polymer backbone, as mentioned above. The observation that the peak potential corresponding to electrochemical oxidation of the polymer backbone of **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** is lower than that of **PFluBPy(TCNQ<sup>-</sup>)** corresponds to the assumption that **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** has a larger  $\pi$ -system than **PFluBPy(TCNQ<sup>-</sup>)** in oxidized state. The difference in the  $\pi$ -system of the oxidized polymers may affect significantly on the color of the cast films of the polymers.

The  $\sigma$  values of the pellets molded from **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** were  $2.7 \times 10^{-4}$  and  $4.2 \times 10^{-4}$ , respectively. These  $\sigma$  values were higher than that for **PFluNH<sub>2</sub>** ( $\sigma < 10^{-8}$  Scm<sup>-1</sup>). This is attributed to the assumption that self-doping based on electron-transfer from the polymer backbone to the electro-withdrawing viologen and pyridinium side groups occurs in **PFluBPy(TCNQ<sup>-</sup>)** and **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)**. These  $\sigma$  values are higher than that of the previously reported **PFluBPy(Br<sup>-</sup>,Cl<sup>-</sup>)** compound, by two orders of magnitude.<sup>7</sup> The observation that **PFluBPy(TCNQ<sup>-</sup>-TCNQ<sup>0</sup>)** had a higher conductivity than **PFluBPy(TCNQ<sup>-</sup>)** is attributed to the presence of the TCNQ<sup>-</sup>-TCNQ<sup>0</sup> structure. This assumption is confirmed by the fact that [C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>Ph]TCNQ<sup>-</sup>-TCNQ<sup>0</sup> showed higher conductivities than [C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>Ph]TCNQ<sup>-</sup>.<sup>17</sup>

## CONCLUSIONS

PPs that contain viologen-TCNQ<sup>-</sup> and viologen-TCNQ<sup>-</sup>-TCNQ<sup>0</sup> side groups were obtained using PP containing an NH<sub>2</sub> side group as a starting material. The viologen side groups in the polymers quenched the PL of the polymer backbone. PPs that contained the viologen-TCNQ<sup>-</sup> or viologen-TCNQ<sup>-</sup>-TCNQ<sup>0</sup> side groups produced electrochemically active films, and the electrochemical reactions were accompanied by electrochromism. This electrochromism depended on the structures of the anionic species in the viologens. The  $\sigma$  values of the pellets molded from the polymers with the viologen moieties were higher than that of **PFluNH<sub>2</sub>**, four orders of magnitude, because of the self-doping nature of the polymers with the viologen moiety. From the results obtained in this study, it can be concluded that the introduction of TCNQ anions in the pendant viologen group of  $\pi$ -conjugated polymers is available to change considerably the chemical properties of the  $\pi$ -conjugated polymer backbone.

## REFERENCES

- List, E. J. W.; Scherf, U. In *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T., Reynolds, J., Eds.; CRC Press: New York, 2007; Vol. 1, Chapter 5, p 847.
- Samuel, I. D. W.; Turnbull, G. A. *Chem. Rev.* 2007, 107, 1272.

3. Coropceanu, V.; Cornil, J.; Filho, D. A. S.; Olivier, Y.; Silbey, R.; Brédas, J. L. *Chem. Rev.* **2007**, *107*, 926.
4. Schwab, P. F. H.; Smith, J. R.; Michl, J. *Chem. Rev.* **2005**, *105*, 1197.
5. Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267.
6. Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.
7. Yamaguchi, I.; Mizoguchi, N. *Macromolecules* **2009**, *42*, 4416.
8. Yamaguchi, I.; Asano, T. *J. Mater. Sci.* **2011**, *46*, 4582.
9. Sato, K.; Nakahodo, T.; Fujihara, H. *Chem. Commun.* **2011**, *47*, 10067.
10. Yamaguchi, I.; Higashi, H.; Sato, M. *React. Funct. Polym.* **2009**, *69*, 864.
11. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*; Cambridge University Press: Cambridge, UK, **2007**.
12. Monk, P. M. S. *Electrochromism in Viologen-based Systems. In the Viologens. Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine*; John Wiley and Sons: New York, **1998**.
13. Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* **1983**, *130*, 1080.
14. Barltrop, J. A.; Jackson, A. C. *J. Chem. Soc. Perkin Trans.* **1984**, *2*, 367.
15. Jain, V.; Khiterer, M.; Montazami, R.; Yochum, H. M.; Shea, K. J. R.; Heflin, J. R. *Appl. Mater. Interfaces* **2009**, *1*, 83.
16. Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.
17. Koßmehl, G.; Kabbeck-Kupijal, D.; Magonov, S. N. *Synth. Met.* **1991**, *42*, 2565.
18. Marvell, E. N.; Caple, G.; Shahidi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5641.
19. Marvell, E. N.; Shahidi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5646.
20. Kunugi, S.; Okubo, T.; Ise, N. *J. Am. Chem. Soc.* **1976**, *98*, 2282.
21. Yamaguchi, I.; Higashi, H.; Shigesue, S.; Shingai, S.; Sato, M. *Tetrahedron Lett.* **2007**, *48*, 7778.
22. Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3*, 246.
23. Yamaguchi, I.; Goto, K. *Macromolecules* **2009**, *42*, 7836.
24. Dwight, S. J.; Gaylord, B. S.; Hong, J. W.; Bazan, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 16850.