Synthesis and Characterization of Fluorene-Based Polymers Having Azine Unit for Blue Light Emission

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Abstract. Two types of donor-acceptor copolymers were designed and synthesized by combination of an electron donor unit of fluorene sequences and an electron acceptor azine unit such as 1,2,4,5-tetrazine and 1,3,5-triazine. They were well soluble in common organic solvents with the number average molecular weight (M_n) of 7.0 and 14.5 kg mol⁻¹, respectively, and have good thermal stability showing about at 360 °C with 5 wt% loss in TGA. Two copolymers exhibited intense blue photoluminescence with emission peak maxima at 437 and 421 nm in CHCl₃, and 451 and 422 nm in the film state, respectively. These polymers exhibited good fluorescence quantum efficiencies in CHCl₃ (ϕ_f = 0.63, 0.97). Energy levels of the highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels estimated by cyclic voltammetry were to be -5.83, -6.0 eV and -2.85, -2.88 eV, respectively.

1. Introduction

Conjugated polymers have gained large interest through various organic electronic applications such as organic light emitting diodes (OLEDs) [1-3], light emitting electrochemical cells (LECs) [4-6], organic solar cells [7,8] and organic thin-film transistors [9]. Blue light-emitting materials are of great significance for their unique applications in flat-panel displays and high-density information storage. Especially in full-color displays, the short-wavelength emission can serve as an excitation source for emission over the whole visible range [10]. Therefore, development of high-efficiency blue emitting materials is important. However, to develop stable pure blue polymeric emitters with their color coordinates in the Commission Internationale de L'Eclairage (CIE) chromaticity diagram within the standard blue (CIE: $x < 0.15$; $y < 0.1$) are still rare since the large energy bandgap (E_g) of these materials makes the achievement of high efficiency and a good charge balance difficult [11]. In this framework, the rational design of p-type conjugated polymers by incorporating electron-withdrawing groups, such as azine unit, seems to be a straightforward strategy to tune carrier injection and transporting properties of known materials [12]. A new donor-acceptor (D-A) system has been designed, which is expected to lower both the energy level of the highest occupied molecular orbital (E_{HOMO}) and energy level of the lowest unoccupied molecular orbital (E_{LUMO}), giving rise to a series of intriguing properties such as improved resistance to oxidation, facilitated electron injection, and ambipolar characteristics, which could simplify device fabrication and operation.

In this paper, the synthesis, characterization and photoluminescence properties of fluorene-based polymers, **PF-tetrAz** or **PF-triAz**, shown in Fig.1 were investigated. Herein, the

fluorene sequences were selected as D for the reason of good thermal and electrochemical stability, high fluorescence yield and facile chemical functionalization [13,14], while 1,2,4,5-tetrazine (**tetrAz**) and 1,3,5-triazine (**triAz**) were chosen as A for their electron deficiency [12].

Fig. 1. Chemical structures of **PF-tetrAz** and **PF-triAz**

Scheme 1. Synthetic routes of **PF-tetrAz** and **PF-triAz**.

2. Experimental

2.1 Materials

Two polymers (**PF-tetrAz** and **PF-triAz**) were synthesized according to the Scheme 1. 7-Bromo-9,9-bis(2-ethylhexyl)-9H-fluorene-2-carbonitrile **1**, 2,4-dichloro-6-(octyloxy)-1,3,5-triazine **4** and 2,2'-(9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis-1,3,2-dioxaborolane were synthesized according to the procedures reported previously [15-17]. Reagents and solvents were purchased from Kanto Chemical, Tokyo Chemical Industry, Aldrich and Nacalai Tesque Inc. Dimethylformamide (DMF) distilled after drying with CaH_2 was stored under an argon atmosphere. Tetrahydrofuran (THF) distilled after drying with sodium was stored under an argon atmosphere. The other solvents and all commercially available reagents were used without further purification.

3,6-Bis(7-bromo-9,9-bis(2-ethylhexyl)-9H-fluorene-2-yl)-1,2-dihydro[1,2,4,5] tetrazine (2). To suspension of **1** (0.2 g, 0.41 mmol) in 1 mL ethanol was quickly added hydrazine (0.019 mL, 0.615 mmol) and sulfur (0.008 g, 0.25 mmol). The mixture was refluxed for 3h with stirring and then

placed in an ice bath for further solidification. The orange precipitate was collected by filtration and washed with cold ethanol (2 x 10 mL) to give a crude dihydrotetrazine, which was used in the next step without further purification.

3,6-Bis(7-bromo-9,9-bis(2-ethylhexyl)-9H-fluorene-2-yl)-[1,2,4,5]tetrazine (3). The orange solid of **2** was dissolved in acetic acid (1 mL) at room temperature with stirring. NaNO₂ (0.028 g, 0.41 mmol) was added to the solution at 0 °C. The purple precipitate signified the completion of the reaction was collected by filtration and washed with methanol (2 × 5 mL) to give a dark purple solid (0.176 g, 84.6%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.08 (s, 2H), 8.01 (d, J= 8.25 Hz 2H), 7.78 (d, J= 8.25 Hz 2H), 7.62 (d, J= 8.25 Hz 2H), 7.56 (s, 2H), 7.50 (d, J= 8.25 Hz 2H), 2.12-2.03 (m, 8H), 1.28-1.25 (m, 4H), 0.91-0.77 (m, 32H), 0.56-0.50 (m, 24H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm]: 177.3, 157.7, 153.3, 144.7, 138.2, 130.5, 130.4, 128.4, 127.6, 127.5, 122.0, 120.3, 55.5, 44.2, 34.7, 33.6, 28.0, 27.1, 22.6, 14.1, 10.3.

2-Octyloxy-4,6-bis(7-bromo-9,9-bis(2-ethylhexyl)-9H-fluorene-2-yl)-1,3,5-triazine(5).

9,9-Bis(2-ethylhexyl)-2,7-dibromofluorene (0.44 g, 0.80mmol) was dissolved in dry THF (4 mL) and cooled to -78 °C under nitrogen atmosphere, in which 1.6 M n-BuLi/hexane solution (0.56 mL, 0.9 mmol) was added dropwise with stirring. The mixture was kept at -78 °C for 1 h and **4** (0.11 g, 0.4 mmol) was slowly added. The reaction mixture was stirred for another 15 min at -78 °C. Afterward, the solution was allowed to warm up to room temperature and stirred for 24 h, and quenched with addition of water. After extraction with CH₂Cl₂, drying over MgSO₄ and the solvent evaporation, the crude product was purified by column chromatography (silica gel, CH₂Cl₂/hexane, 1:2, as eluent) to afford a yellow oil (0.088g, 51%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.66 (s, 4H), 7.82 (d, J= 7.78 Hz 2H), 7.65 (d, J= 7.78 Hz 2H), 7.58 (d, J= 7.78 Hz 2H), 7.51 (d, J= 7.79 Hz 2H), 4.66 (m, 2H), 2.13-1.90 (m, 10H), 1.32-0.82 (m, 42H), 0.58-0.52 (m, 27H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm]: 173.5, 170.3, 153.9, 150.4, 144.5, 139.4, 134.5, 130.1, 128.4, 127.5, 124.6, 121.7, 121.6, 119.6, 68.1, 55.3, 44.3, 34.7, 33.5, 31.8, 29.4, 29.1, 28.8, 28.1, 27.1, 26.0, 22.7, 22.6, 14.1, 14.0, 10.4.

Poly[(9,9,9',9'',9'''-hexaxis(2-ethylhexyl)[2,2':7',2''-ter-9H-fluorene]-7,7''-diyl)-([1,2,4,5]tetrazine-3,6-diyl)] (PF-tetrAz). A mixture of 2,2'-(9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis-1,3,2-dioxaborolane (0.037 g, 0.07 mmol), tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄, 4.1 mg), aqueous K₂CO₃ (2M, 0.7 mL) and **3** (0.071 g, 0.07 mmol) in toluene (1.0 mL) was refluxed with vigorous stirring for three days under argon atmosphere. After the reaction solution was cooled to room temperature, the resultant polymer was precipitated from methanol/HCl aq, and reprecipitated from methanol/NH₃ aq and from methanol, respectively. The precipitate was successively extracted with acetone, hexane and CHCl₃ by Soxhlet extraction. The CHCl₃ extract was again precipitated from methanol. **PF-tetrAz** was obtained as an orange solid (0.077g, 80%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.12 (br, 4H), 7.82 (br, 4H), 7.70-7.59 (m, 8H), 7.49 (br, 1H), 7.36 (br, 1H), 2.17-2.0 (m, 12H), 1.11-0.80 (m, 54H), 0.63-0.57 (m, 36H). C₈₉H₁₂₂N₄ (1246.89): Calcd. C 85.66, H 9.85, N 4.49; Found. C 83.48, H 9.33, N 4.38.

Poly[(9,9,9',9'-tetrakis(2-ethylhexyl)-9H-fluorene-7,7'-diyl)-9,2-octyloxy-1,3,5-triazine-4,6-diyl)] (PF-triAz). Under an argon atmosphere, a solution of bis(1,5-cycloocta- -diene)nickel(0) (Ni(cod)₂) (0.110 g, 0.40 mmol), 2,2'-bipyridine (bpy) (0.070 g, 0.448mmol) and 1,5-cyclooctadiene (cod) (0.10 g, 0.92 mmol) in DMF (1 mL) was heated for 30 min at 80 °C. To the DMF solution was

added **5** (0.083 g, 0.184 mmol) dissolved in THF (1 mL) under argon. The reaction solution was heated for 3 days at 80 °C. After the reaction solution was cooled to room temperature, the resultant polymer was precipitated from methanol/HCl aq, and reprecipitated from methanol/NH₃ aq and from methanol, respectively. The precipitate was successively extracted with acetone, hexane and CHCl₃ by Soxhlet extraction. The CHCl₃ extract was again precipitated from methanol. **PF-triAz** was obtained as a white solid (0.060g, 83%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.73 (s, 4H), 7.90 (s, 4H), 7.70 (s, 4H), 4.69 (s, 2H), 2.17 (s, 8H), 1.97 (m, 2H), 0.93-0.87 (m, 42H), 0.68-0.60 (m, 27H). C₇₁H₁₀₃N₃O (1013.70): Calcd. C 84.05, H 10.23, N 4.14; Found. C 82.23, H 9.66, N 3.84.

2.2 General Method and Instrumentation

All synthetic manipulations were performed by a standard technique using a Schlenk tube under an argon atmosphere. Column chromatography was performed using a silica gel (Kanto Chem., 60 N, 63–120 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS 400 spectrometer. ¹H and ¹³C chemical shifts are given in units of δ (ppm) relative to δ (TMS) = 0.00 and δ(CDCl₃) = 77.0 ppm, respectively. Photoabsorption in the range of ultraviolet-visible (UV-vis) and photoluminescence (PL) measurements of the polymer samples in CHCl₃ and in a form of a thin film coating on a quartz glass were performed using a Shimadzu UV-1800 spectrophotometer and an F-4500 fluorescence spectrophotometer (Hitachi). The fluorescence quantum yield in CHCl₃ were relative to 9,10-diphenylanthracene in cyclohexane (ϕ_f = 0.90) as a standard. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymers were estimated by gel permeation chromatography (GPC) system (Shimadzu, LCsolution) using polystyrene standards with CHCl₃ as an eluent. Cyclic voltammetry (CV) of polymers in thin film on a Pt disk was performed at a scan rate of 50 mV/s in acetonitrile containing 0.1 M Et₄NBF₄ at room temperature under Ar using a saturated calomel electrode (SCE) as the reference and a platinum wire as the counter electrode. The electrochemical data (vs SCE) obtained by cyclic voltammetry were made a correction with the redox potential (4.8 eV) of ferrocene/ferricinium [18, 19]. Elemental analyses were carried out with a Perkin-Elmer type 2400 apparatus. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out by an Extra 6000 TG/DTA (Seiko) analyzer at a heating rate of 10 °C min⁻¹ in an argon atmosphere.

3. Results and Discussion

3.1. Synthesis.

The general synthetic routes toward the monomer and polymer **PF-tetrAz** and **PF-triAz** are outlined in Scheme 1. Dihydropyridazine intermediate **2**, cyclized of **1** with anhydrous hydrazine by heating, was oxidized instantly into the fully aromatic tetrazine **3** for its instability. Tetrazine **3** was polymerized by Suzuki coupling reaction with 2,2'-(9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis-1,3,2-dioxaborolane to give **PF-tetrAz**. 2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene reacted with **4** to give **5**. Homopolymerization of **5** by the Yamamoto reaction [20] afforded **PF-triAz** as a white solid. All the copolymers had good solubility in common organic solvents such as CHCl₃, chlorobenzene, and *o*-dichlorobenzene. The polymers were identified by NMR and elemental analyses. The GPC results were summarized in Table 1. The M_n of **PF-tetrAz** and **PF-triAz** were 7.0 and 14.5 kg/mol, respectively. TGA results are shown in Fig. 2. Observed temperatures for 5wt % loss were 363 and 387 °C, respectively, which suggest that both have good thermal stability comparable to polyfluorenes [21].

Table 1. GPC and TGA results of the polymers.

Polymer	M_n ($\text{kg}\cdot\text{mol}^{-1}$)	M_w ($\text{kg}\cdot\text{mol}^{-1}$)	M_w/M_n	T_d ($^{\circ}\text{C}$) ^a
PF-tetrAz	7.0	7.6	1.08	363
PF-triAz	14.5	21.9	1.52	387

^aTemperature of 5% weight loss determined by TGA under an argon atmosphere.

Fig. 2. Thermal gravimetric analysis (TGA) curves of the polymers.

3.2. Optical properties.

The photophysical properties of dilute solution and thin films of all the polymers were investigated with UV-vis and PL, and the results are shown in Fig. 3. The UV-vis absorption and the emission spectra data for polymer were summarized in Table 2.

Fig. 3. UV-vis absorption spectra and photoluminescence (PL) of the polymers in CHCl_3 (a) and film state (b).

Table 2. Optical properties, energy gaps and levels of the polymers.

Polymer	Abs. $\lambda_{\max}$ (nm)		Em. $\lambda_{\max}$ (nm)		ϕ_{fl}	$E_{\text{g}}^{\text{opt}}$ (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{g}^{ec} (eV)
	CHCl_3	film	CHCl_3	film					
PF-tetrAz	390	393	437	451	0.63	2.80	−5.83	−2.85	2.96
PF-triAz	394	395	421	422	0.97	2.98	−6.0	−2.88	3.12

Absorption and PL spectra of **PF-tetrAz** and **PF-triAz** in CHCl_3 are shown in Fig. 3a. The absorption maxima in wavelength ($\lambda_{\max}$) at 390 nm for **PF-tetrAz** and 394 nm for **PF-triAz** are due to π - π^* transition of the conjugated main chains. The absorption $\lambda_{\max}$ of **PF-triAz** is in long wavelengths compared with that of **PF-tetrAz**, which indicates that π -conjugation of **PF-triAz** is longer than that of **PF-tetrAz**. The emission peaks in solution were observed at 437 nm for **PF-tetrAz** and 421 nm for **PF-triAz**. Stokes shifts of **PF-triAz** in the solution was 27 nm, which was much smaller than that of **PF-tetrAz** (47 nm). These small Stokes shifts also support **PF-triAz** having rigid and regular conformation, which enabled utilization of absorbed energy to PL efficiently.

The absorption and PL spectra of **PF-tetrAz** and **PF-triAz** in thin solid film state are shown in Fig. 3b. Compared with absorption spectra in solution, the absorption of **PF-tetrAz** and **PF-triAz** is slightly broaden and red shift compared with their absorption in film. The broadening and red shift of the film absorption spectra indicated that there were some aggregations or interactions of the polymer chains in the solid state. The optical band gap ($E_{\text{g}}^{\text{opt}}$) estimated from the onset of the absorption spectrum in the film state was 2.8 eV for **PF-tetrAz**, which was smaller than that of **PF-triAz** (2.98 eV). Compared with PL spectra of **PF-tetrAz** and **PF-triAz** in solution, a red shift was observed in their film. The PL maximum of **PF-triAz** in the film state was shorter in wavelength than that of **PF-tetrAz**. This can be attributed to the higher polarizability of the **tetrAz** group and restrained intermolecular aggregation [22].

PF-tetrAz and **PF-triAz** showed intense blue PL emission with CIE coordinates ($x, y = 0.16, 0.12$; $0.16, 0.07$, respectively) in the film state and good relative ϕ_{fl} of 0.63, 0.97 in CHCl_3 , which suggest that **PF-tetrAz** and **PF-triAz** are considered to be good polymeric blue emitters superior to a series of polyfluorene derivatives [23].

3.3. Electrochemical Properties.

Electrochemical analysis of the thin-film sample of the polymers was employed to estimate E_{HOMO} and E_{LUMO} . The CV results of **PF-tetrAz** and **PF-triAz** are shown in Fig. 4 and the estimated values are summarized in Table 2. During the anodic scan, both of the compounds showed irreversible oxidation peaks, which are assigned to the oxidation of the fluorene units. **PF-tetrAz** had E_{HOMO} of −5.83 eV, which was higher about 0.17 eV than that of **PF-triAz** (−6.0 eV). This could be caused by the delocalization of the HOMO because of good planarity between the fluorene and **tetrAz** segments. Upon the cathodic sweep, **PF-triAz** exhibited quasireversible reduction waves, whereas **PF-tetrAz** showed weak irreversible reduction waves. The E_{LUMO} of **PF-tetrAz** (−2.85 eV) is slightly lower than that of **PF-triAz** (−2.74 eV), on account of higher electron-deficiency of **tetrAz** compared to **triAz**. The above results suggest that electronegativity of the azine unit is responsible for lowering of both E_{HOMO} and E_{LUMO} of the polymers.

Fig. 4. Cyclic voltammograms of **PF-tetrAz** and **PF-triAz**.

Estimated from the E_{HOMO} and E_{LUMO} , the E_{g}^{ec} values of 2.96 and 3.12 eV are obtained for **PF-tetrAz** and **PF-triAz**, respectively, which are similar to $E_{\text{g}}^{\text{opt}}$. These energy gaps with suitable E_{HOMO} and E_{LUMO} are good for lessening driving voltage and augmenting efficiency of OLEDs [24].

4. Conclusion

In summary, two efficient blue luminescence polymers **PF-tetrAz** and **PF-triAz**, have been developed by combination of the fluorene sequences as a electron-donor and the **tetrAz** or **triAz** core as an electron-acceptor. These polymers were obtained in high yields, and they had a good solubility in common organic solvents and a good thermal stability. In the CHCl_3 solution, they showed similar electronic properties of absorption and emission, the values of $\lambda_{\text{max}}(\text{abs})$ and $\lambda_{\text{max}}(\text{em})$ of each polymer were about 390 and 430 nm, respectively. In the state of the thin films, **PF-triAz** showed deep blue fluorescence with the values of $\lambda_{\text{max}}(\text{em})$ at 422 nm and emission indicatable by CIE coordinates (0.16, 0.07) in the film state. **PF-tetrAz** and **PF-triAz** showed acceptable E_{HOMO} (−5.83, −6.0 eV) for hole transport and proper E_{g} (2.96, 3.12 eV) for blue emission. According to these results, these D-A copolymers have a great potential to be applied in OLEDs and LECs as the blue-light emitting materials.

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