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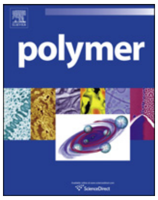

π-Conjugated poly(anthracene-*alt*-fluorene)s with X-shaped repeating units: New blue-light emitting polymers

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ABSTRACT

A series of new π-conjugated poly(anthracene-*alt*-fluorene)s with X-shaped repeating units were synthesized. The polymers were easily soluble in common organic solvents and had good film-forming abilities. They showed high absolute PL quantum yields in the solid state. The electroluminescent devices based on the three X-shaped polymers with a configuration of ITO/PEDOT:PSS/polymer/LiF/Ca/Al emitted blue light with high brightness and low turn-on voltages.

1. Introduction

π-Conjugated polymers have attracted a great deal of attention in the past few decades due to their potential application in opto-electronic area including polymer light-emitting diode (PLED) [1], organic solar cell [2] and organic field-effect transistor (OFET) [3]. Among the π-conjugated polymers used as electroluminescent materials, the linear conjugated polymers have been extensively studied, such as polyfluorene, poly(*p*-phenylenevinylene) and so on [1a,4,5]. To improve the performance of devices, conjugated polymers with new structures have also been developed. For example, the study on the polymers with hyperbranch structure has been very active in the past few years, because the 3D structures of such polymers can suppress inter-chain interactions [6]. However, the structures of hyperbranched polymers are very complicated, and cannot be easily controlled. Undoubtedly, the exploration and development of the conjugated polymers with novel structures are of great interest.

Recently, there has been an increasing interest in the synthesis and characterization of the full π-conjugated compounds with topologically special structure such as cruciform or X-shaped [7–14]. The compounds displayed high electrochemical and photoluminescent activities and are expected to be useful as the components in non-linear optical device [7,8], light-emitting diodes [9,10], organic field-effect transistors [11] and chemical sensors [12,13]. Moreover, the X-shaped molecules have 3D structure and are desirable to be introduced to polymers as a unit, which may decrease intermolecular aggregation. Nevertheless, a few of work has been reported on π-conjugated polymers containing the X-shaped repeating units (X unit) [15]. In this paper, we develop a kind of π-conjugated polymers with the new structures and explore their potential applications in PLED. We choose anthracene as a building unit, because anthracene-based derivatives especially 9,10-substituted have been widely used as organic optoelectronic materials due to their high fluorescence quantum yields [16]. In 9,10-substituted anthracene derivatives, there are large dihedral angles between the anthracene unit and substitutes at 9,10-positions, which make the molecule has a 3D structure and fit to be used as an X unit. Several groups have reported polymers composed of 9,10-linked anthracene derivatives [17]. Extending the polymer along the 2,6-positions of anthracene not only can make the backbone of polymer full π-conjugated, but also keeps the 3D structure of X unit, suggesting that the development of these types of the polymers are very necessary. However, to our knowledge, only a few polymers and oligomers containing 2,6-anthrylene structure have been reported [18a–c]. Lately, Geng group reported the first soluble conjugated poly(2,6-anthrylene) [18d]. In this contribution, we report a series of new π-conjugated poly(anthracene-*alt*-fluorene)s with X-shaped repeating units. These polymers were synthesized by the polycondensation between 2,6-dibromo-9,10-di(9,9-dioctylfluorenyl-2-yl)-anthracene (**DBDFA**) and 2,7-bis(trimethylene boronates) in the presence of palladium catalyst. Here, **DBDFA** was used as the new X-shaped monomer. To investigate the properties of the polymers containing such

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a unit, the different molar ratios between the X unit and the fluorene unit were used, and the influence of these on the thermal, optical and electrochemical and electroluminescent (EL) properties of the new polymers were also investigated. The results showed that π-conjugated polymers containing X unit exhibited high absolute PL efficiency in the solid state. The devices based on these polymers showed low turn-on voltages and emitted bright blue light.

2. Experimental section

2.1. Materials

Fluorene was an industrial product and was recrystallized from ethanol before use. 2,7-Dibromo-9*H*-fluorene (**1**) [19a], 2,7-dibromo-9,9-dioctyl-fluorene (**2**) [19b], 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (**3**) [19c], 2-bromo-9*H*-fluorene (**4**) [19d], 2-bromo-9,9-dioctyl-fluorene (**5**) [6d], and 2,6-diaminoanthraquinone (**6**) [19e] were prepared as previously reported. $[Bu_4N]ClO_4$ (Bu = butyl) was an industrial product and purified by recrystallizing three times from a mixture of ethyl acetate and cyclohexane and dried over P_2O_5 under vacuum at room temperature for three days. All solvents were dehydrated and distilled under an inert atmosphere before use.

2.2. Instrumentation

Elemental analysis was taken with a Carlo Erba 1106 elemental analyzer. ^1H NMR and ^{13}C NMR spectra were carried out on a Bruker DRX 300 spectrometer. The molecular weight was measured by GPC with a Perkin–Elmer Series 200 GPC system equipped with a UV detector using THF as the eluent. The data were relative to polystyrene standards. UV–vis absorption and photoluminescence spectra were measured with a Hitachi U-2810 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammetry (CV) for the cast films were measured in an acetonitrile solution of $[Bu_4N]ClO_4$ (0.10 M, Bu = butyl) using (0.10 M $AgNO_3$)/Ag and platinum wires as reference and counter electrodes, respectively. A CHI 600B analyzer was used for the measurements. Thermal stability was determined with a TA 2000 thermogravimetric analyzer at a heating rate of 20 °C min^{-1} in nitrogen.

2.3. LED device fabrication

On a clean ITO glass, a layer PEDOT–PSS (50 nm, Bayer AG) was applied. A layer of polymer (15 mg mL^{-1} in cyclohexane) was then spin-coated on the substrate. After drying for 2 h in the glove box at 60 °C, LiF, Ca (120 nm) and Al (100 nm) were deposited on the polymer films by thermal evaporation, respectively, under a vacuum of 10^{-4} torr. The luminance-voltage and current-voltage properties of the devices are measured at room temperature in air. The EL spectra were recorded on a photometer PR 705.

2.4. Synthesis of the monomers

2.4.1. Synthesis of 2,6-dibromo-9,10-di(9,9-dioctylfluorenyl-2-yl)-9,9,10,10-tetrahydro-9,10-dihydroxyl-anthracene (*7*)

A solution of *n*-BuLi (2.5 M, 6.15 mL, 15.4 mmol) in hexane was added slowly to a solution of **5** (5.77 g, 12.3 mmol) in anhydrous THF (50 mL) at −78 °C, and the mixture was stirred for 1 h at such temperature. Then, a suspension of **6** (1.50 g, 4.1 mmol) in anhydrous THF (40 mL) was added to the mixture. The reactants were allowed to slowly warm to room temperature and stirred for 24 h. A large amount of water (300 mL) was added to the mixture for extraction with ethyl acetate. The organic extracts were washed with brine and dried over Na_2SO_4. Column chromatography over silica gel with hexane:ethyl acetate (15:1) as the eluent afford **7** (2.82 g, yield 60%) as a carmine glassy crude product. ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, $J = 3.0$ Hz, 2H), 7.61 (s, 2H), 7.56 (d, $J = 7.8$ Hz, 2H), 7.46 (d, $J = 1.8$ Hz, 2H), 7.34–7.37 (m, 8H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 3.48 (s, 2H), 1.99–2.03 (m, 8H), 1.08–1.23 (m, 40H), 0.83 (t, $J = 9.3$ Hz, 12H), 0.66–0.70 (m, 8H).

2.4.2. Synthesis of 2,6-dibromo-9,10-di(9,9-dioctylfluorenyl-2-yl)-anthracene (*8*)

A mixture of **7** (2.78 g, 2.42 mmol), potassium iodide (4.02 g, 24.2 mmol) and sodium hypophosphite hydrate (5.14 g, 48.5 mmol) was stirred in acetic acid (50 mL) for 15 h at 120 °C. After cooling to room temperature, the mixture was filtered and washed with water. The residue was purified by column chromatography on silica gel using a mixture of hexane and CH_2Cl_2 (8:1, v/v) as the eluent to yield **8** as a white-yellow powder (1.38 g, yield 51%). Mp 161–163 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.92 (s, 2H), 7.85 (d, $J = 6.9$ Hz, 2H), 7.66 (d, $J = 9.0$ Hz, 2H), 7.40 (m, 12H), 1.98–2.07 (m, 8H), 1.02–1.18 (m, 40H), 0.71–0.83 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.22, 151.02, 141.14, 140.71, 137.35, 136.26, 131.15, 129.76, 129.71, 129.17, 128.99, 127.50, 127.00, 125.95, 122.97, 120.24, 119.96, 55.30, 40.41, 31.85, 30.19, 30.02, 29.31, 24.13, 23.99, 22.59. Anal. calcd for $C_{130}H_{168}Br_2$: C, 77.68; H, 7.97; Br, 14.35; Found: C, 77.59; H, 8.06; Br, 14.44. MALDF-TOF: *m*/*z* 1115.6 (M^+).

2.5. Synthesis of the polymers

2.5.1. Synthesis of ***XP-3***

This polymer was prepared by using standard Suzuki polycondensation reaction as previously reported [20]. Thus, a mixture of **8** (300 mg, 0.16 mmol), **3** (89 mg, 0.16 mmol), $Pd(PPh_3)_4$ (18 mg, 0.016 mmol) and aq. Na_2CO_3 (2 M, 5 mL) in degassed toluene (20 mL) was stirred for 72 h at 80 °C under an argon atmosphere. After cooling to room temperature, the mixture was diluted with toluene. The organic layer was separated, washed with water, and dried over with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was re-dissolved in a minimum amount of $CHCl_3$. The solution was poured into methanol to give a precipitate that was purified by Soxhlet extraction with acetone for 48 h to obtain a green-yellow powder (225 mg, yield 72%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.06 (s, 2H), 7.94–7.96 (d, 2H), 7.81–7.89 (m, 4H), 7.46–7.67 (m, 10H), 7.40 (m, 6H), 1.80–2.18 (m, 12H), 0.61–1.27 (m, 90H). Anal. calcd for $(C_{101}H_{128})_n$: C, 90.39; H, 9.61; Found: C, 90.17; H, 9.78.

2.5.2. Synthesis of ***XP-1***

XP-1 was synthesized by a similar procedure to the preparation of **XP-3**. Monomer feed ratio: **10** (150 mg, 0.08 mmol), **3** (148 mg, 0.26 mmol), **2** (103 mg, 0.18 mmol). Yield: 83%. ^1H NMR (300 MHz, $CDCl_3$): δ 8.13 (s, 2H), 7.84–8.02 (m, 16H), 7.42–7.69 (m, 44H), 1.89–2.15 (m, 36H), 0.70–1.28 (m, 270H). Anal. calcd for $[(C_{29}H_{40})_{0.85}(C_{72}H_{88})_{0.15}]_n$: C, 89.95; H, 10.05; Found: C, 89.32; H, 10.33.

2.5.3. Synthesis of ***XP-2***

Analogously, **XP-2** was obtained. Monomer feed ratio: **8** (141 mg, 0.126 mmol), **3** (141 mg, 0.25 mmol), **2** (69 mg, 0.126 mmol). Yield: 79%. ^1H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 2H), 7.82–8.00 (m, 8H), 7.40–7.67 (m, 28H), 2.02–2.08 (m, 20H), 0.66–1.28 (m, 150H). Anal. calcd for $[(C_{29}H_{40})_{0.75}(C_{72}H_{88})_{0.25}]_n$: C, 90.11; H, 9.89; Found: C, 88.67; H, 9.97.

3. Results and discussion

3.1. Synthesis and characterization

As shown in Scheme 1, the X-shaped monomer, 2,6-dibromo-9,10-di(9,9-dioctylfluorenyl-2-yl)-anthracene (**8**), was prepared by the aromatization of precursor **7**. For the synthesis of **7**, an approach by employing the reaction between 2,6-dibromoanthranone (**6**) and the Grignard reagent of 2-bromo-9,9-dioctylfluorene (**5**) gave very low yield due to the formation of a complicated mixture that was difficultly purified. However, a higher yield of **7** was obtained when *n*-BuLi was used instead of the Grignard reagent. By employing Suzuki polycondensation, three polymers, **XP-1**–**XP-3**, were prepared. The yields of the three polymers were higher than 70%, and M_n of the polymers, determined by GPC versus polystyrene standards, ranged from 14,000 to 18,000, as shown in Table 1.

XP-1–**XP-3** were easily soluble in common organic solvents such as chloroform, toluene and tetrahydrofuran, and had good film-forming abilities when cast from either chloroform or toluene solutions.

The chemical structures of the three polymers were characterized by ^{1}H NMR spectroscopy and elemental analysis (see Section 2). Hydrogens in the aryl rings are at $\delta = 8.13–7.40$, and the H signals in the alkyl side chains were observed at $\delta = 0.61–2.18$. All the detected peaks and ratios between their peak areas were consistent with the proposed structure.

3.2. Optical and thermal properties of the polymers

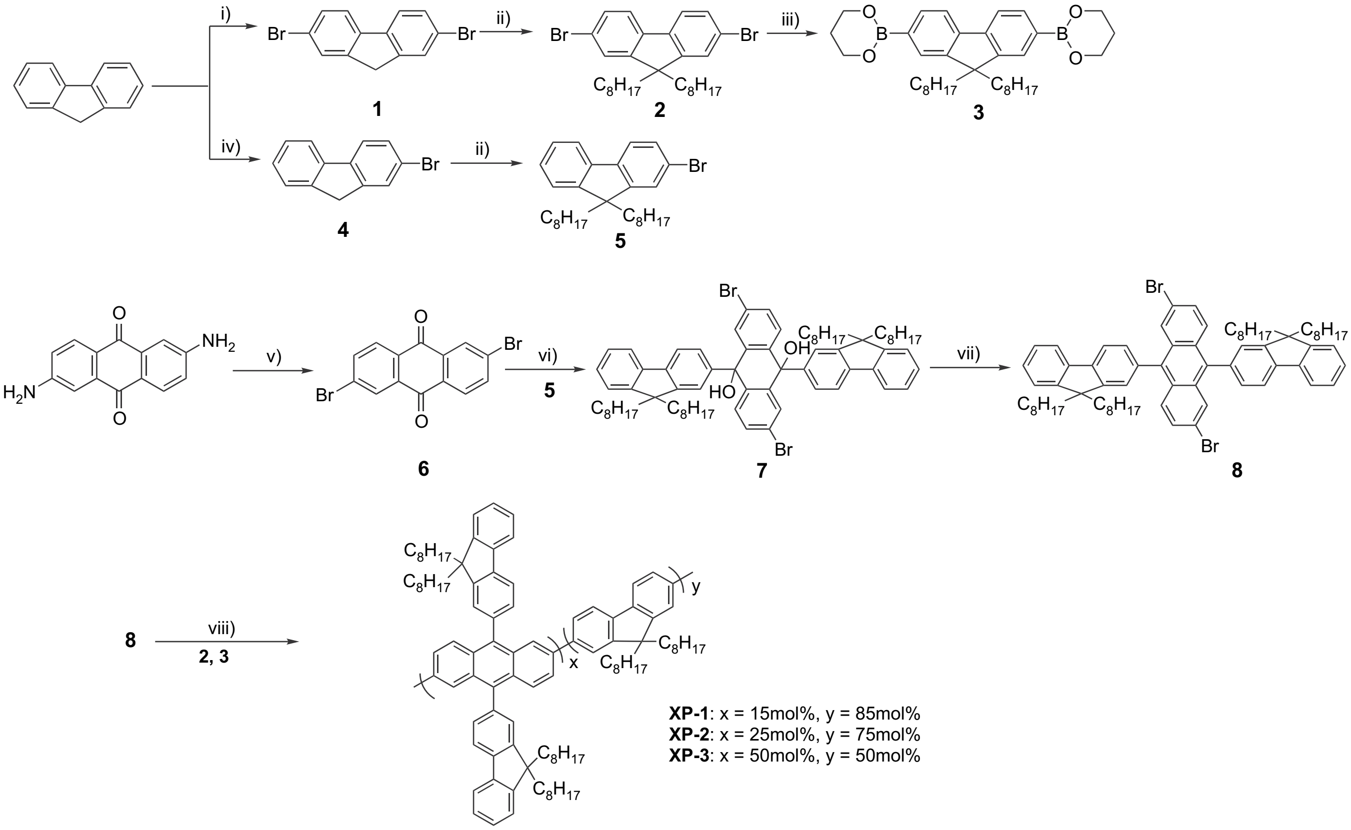
All polymers show essentially the same UV–vis absorption peaks and photoluminescent emission peaks in different solvents, including toluene, CH_2Cl_2, and THF.

UV–vis absorption spectra of the X-shaped polymers in toluene and in the solid state are shown in Fig. 1. The detailed optical data are summarized in Table 1. For comparison, the UV–vis spectra of poly(9,9-dioctylfluorene) (**PFO**) and monomer **8** are also given. The concentration of all polymer solutions in toluene was fixed at 1×10^{-6} M. Polymer films were prepared on quartz plates from the polymer solutions in toluene (10 mg mL^{-1}) using a spin-coating method (kept at 1000 rpm for 10 s and then at 2000 rpm for 50 s). As shown in Fig. 1(A) and Table 1, the main absorption peaks of the polymers in toluene are in the region 362–374 nm. Those absorption peaks that approach the maximum absorption peak of **PFO** (372 nm) are attributed to the electronic transition (π–π^*) along the main conjugated backbone. With the increase of the molar fraction of X unit in the polymer main chain, the main absorption peak shows a blue-shift from 370 nm to 362 nm. An additional short wavelength absorption peak at 307 nm may be attributed to the X unit ($\lambda_{max} = 307$ nm, see the absorption spectrum of monomer **8**), the intensity of which increases with an increasing content of X unit. Compared with the absorption spectrum of monomer **8**, the absorption peaks at 400–450 nm in Fig. 1(A) are derived from the anthracene unit.

Table 1
Synthesis results and optical data for **XP-1**–**XP-3**

Polymer	Yield (%)	M_n[a]	M_w/M_n	λ_{max} (nm; UV–vis)		λ_{EM}[c] (nm; FL)	
				In toluene	In films[b]	In toluene	In films[b] (ϕ[d])
XP-1	77	18,000	1.68	370	380	468	467 (82%)
XP-2	79	14,000	1.65	364	367	468	467 (77%)
XP-3	73	17,000	1.60	360	340	469	469 (50%)

[a] Determined by GPC (with polystyrene standards).
[b] Cast onto a quartz glass plate at room temperature with toluene as the solvent.
[c] Position of the emission peak from PL data.
[d] Absolute quantum yield of the polymer films, measured by using a calibrated integrating sphere at an exciting wavelength of 325 nm.



Scheme 1. Synthetic procedure of the monomers and the new polymers. Reagents and conditions: (i) $Br_2/FeCl_3$, $CHCl_3$, 0 °C to room temperature; (ii) DMSO, aq. NaOH (50 wt%), 1-bromooctane, tetrabutylammonium bromide (TBAB), room temperature; (iii) (1) *n*-BuLi, THF, −78 °C; (2) $(i\text{-PrO})_3B$, −78 °C to room temperature; (3) 1,3-propanediol, toluene, 110 °C; (iv) NBS, propylene carbonate, 65 °C to room temperature; (v) *t*-BuONO, $CuBr_2$, CH_3CN, 65 °C; (vi) (1) *n*-BuLi, THF, **5**, −78 °C; (2) **6**, THF; (vii) KI, $NaH_2PO_2 \cdot H_2O$, AcOH, 120 °C; (viii) $Pd(PPh_3)_4$, 2 M aq. Na_2CO_3, toluene, 80 °C.

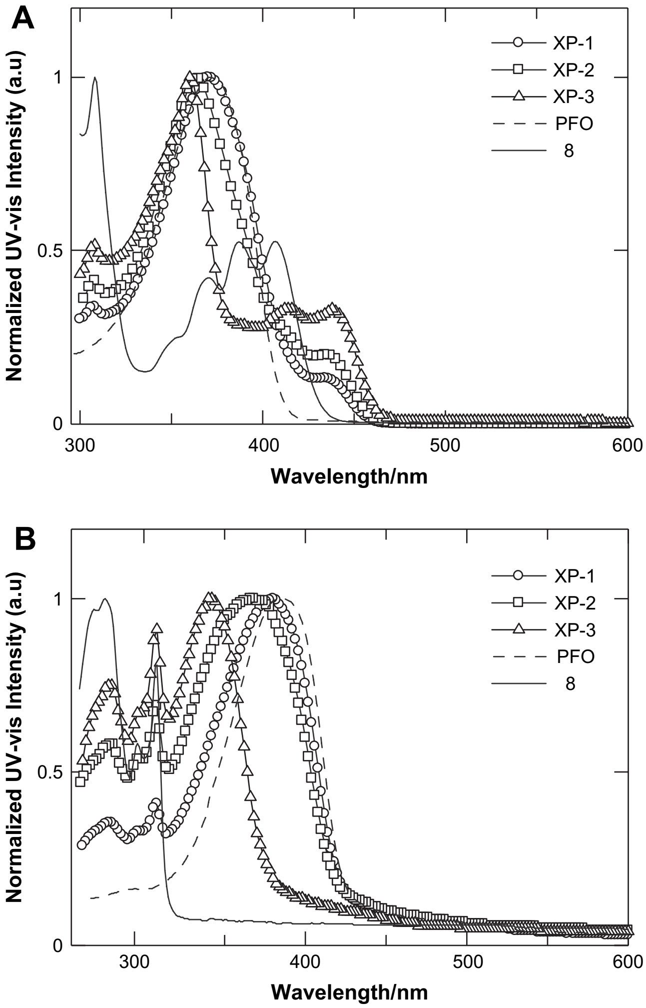


Fig. 1. UV–vis absorption spectra of polymers and monomer **8** in toluene (A) and in films (B).

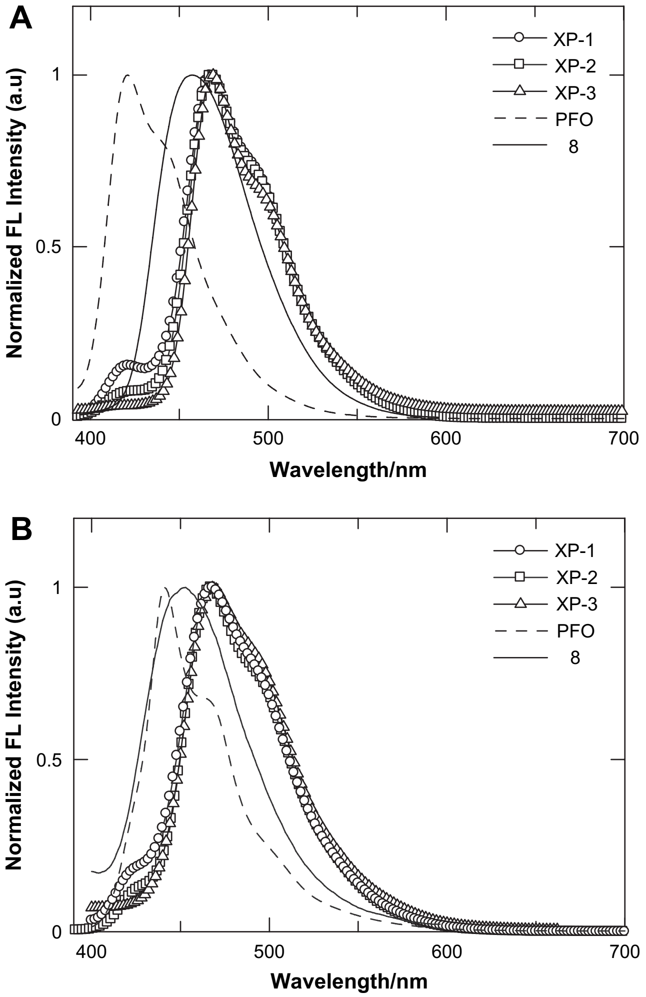


Fig. 2. PL emission spectra of polymers and monomer **8** in toluene (A) and in films (B). In all cases, the excitation wavelengths were UV–vis peaks of polymers and monomer **8**.

Fig. 1(B) depicts the absorption spectra of the polymers in the solid state. The shorter wavelength absorption peaks at 307 nm and 276 nm are derived from the X units (see the absorption spectrum of monomer **8**, which displays two peaks at 308 nm and 276 nm in the solid state). The absorption peaks of X unit are in the same positions in the solid state, relative to the UV–vis spectra in the solution. The similar phenomenon was found for the monomer **8**. It is attributed to the huge steric structure of X unit. The longer wavelength absorption peaks of polymers are in the region 340–380 nm. The main absorption peaks of polymers show a tendency that they change from the low energy to high energy with the increasing X unit content in the polymers. For instance, the main absorption peak of **XP-1** has a red-shift of 10 nm relative to that in the solution, whereas **XP-3** shows a blue-shift of 20 nm from solution to film. Such tendency is probably caused by the different conjugation degree of the polymer backbones in the solution and thin films, e.g., in the solution the large X units less influenced the coplane between the conjugated units in the polymers, whereas in the solid state the X units restricted the rotation of C–C bond and resulted in weak coplanarity.

PL emission spectra of **XP-1**–**XP-3**, **PFO** and monomer **8** in toluene and in the solid state are shown in Fig. 2. PL spectra of **XP-1**–**XP-3** in toluene display two emission peaks at about 420 nm and 467–469 nm, respectively, in Fig. 2(A). The first peak is attributed to the emission of the fluorene chromophoric segments (see PL spectrum of **PFO**, $\lambda_{EM} = 421$ nm), and its intensity reduces with the decrease of the molar fraction of fluorene unit in the polymer main chain. The second peak derives from the emission of X unit (see PL spectrum of monomer **8**, $\lambda_{EM} = 457$ nm). As shown in Fig. 2(B), the maximum emission peaks of **XP-1** and **XP-2** show a slight blue-shift of 1 nm from solution to film, **XP-3** shows the same PL spectra both in solution and in solid state, whereas **PFO** indicates a big red-shift. These phenomena may be caused by the steric hindrance of X unit that restrains the intermolecular aggregation [21]. The absolute PL quantum yields (ϕ) of **XP-1**–**XP-3** in the solid state, measured by using a calibrated integrating sphere, are exceptionally high (50–82%). Such yields exhibit a decreasing tendency with the increasing molar fraction of anthracene unit as the reported work [17a,c]. The high absolute PL quantum yields of polymers suggest that the polymers with novel structures display high PL efficiencies due to the introducing of X units.

TGA shows that 1 wt% loss temperatures of **XP-1**–**XP-3** are more than 217 °C, suggesting that the polymers have good thermal stability.

3.3. Electrochemical properties

The electrochemical properties of the new polymers were measured by cyclic voltammetry (CV) of their cast films on platinum plates, and the results are shown in Fig. 3 and Table 2. All polymers exhibited quasi-reversible oxidative cycles. Electrochemical

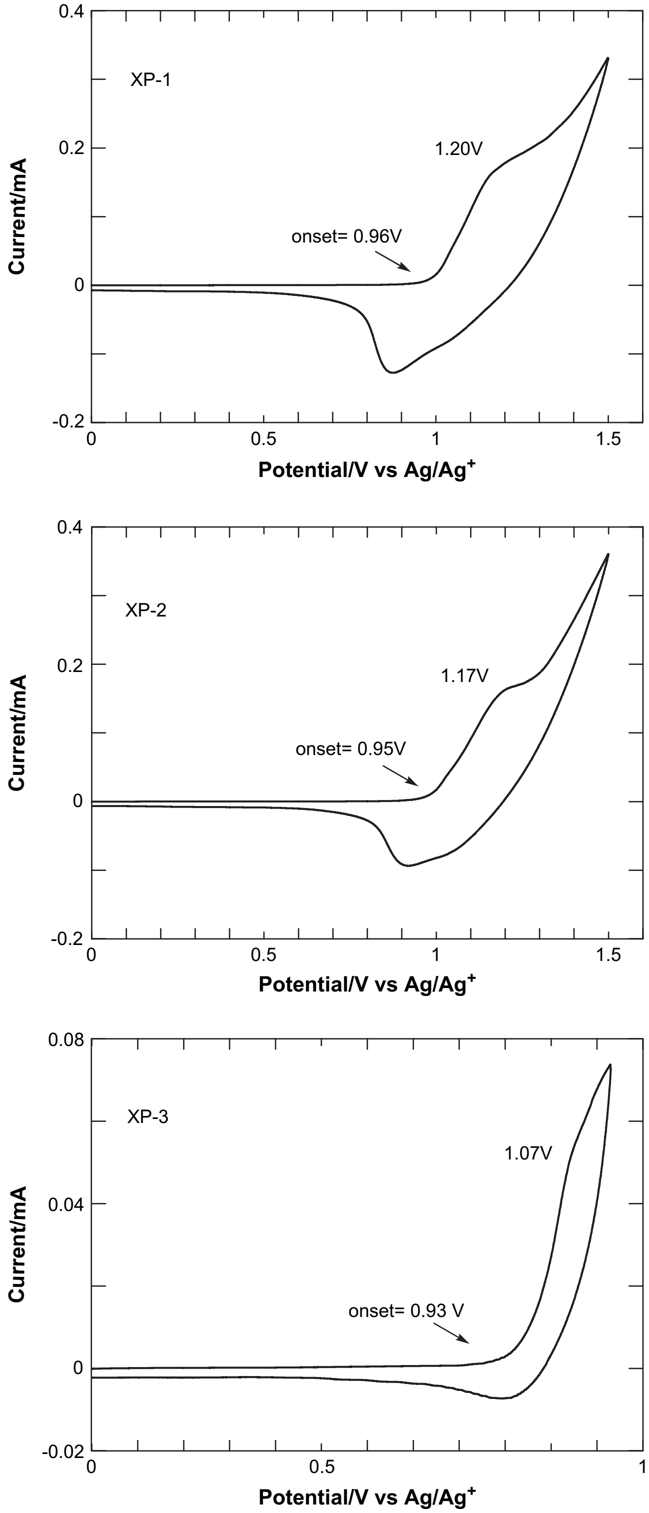


Fig. 3. CV curves of cast films of **XP-1**–**XP-3** on Pt electrodes (wires) with a sweep rate of 100 mV s^{-1} in acetonitrile solutions of 0.10 M [Bu$_4$N]ClO$_4$ (Bu = butyl).

Table 2
Electrochemical properties of **XP-1**–**XP-3**

Polymer	E_{ox}^{onset} (eV)	E_g^{opt} [a]	HOMO (eV)	LUMO (eV)
XP-1	0.96	2.91	−5.36	−2.45
XP-2	0.95	2.94	−5.35	−2.41
XP-3	0.93	3.35	−5.33	−1.98

[a] Optical band gap was estimated from the onset wavelength of optical absorption in films.

oxidation (or p-doping) of **XP-1**–**XP-3** started at 0.96 V, 0.95 V, 0.93 V versus Ag$^+$/Ag, and gave p-doping peaks at 1.20 V, 1.17 V, 1.07 V, respectively. According to the relationship between the oxidation onset potential (E_{ox}^{onset}) and HOMO energy [22], the HOMO level values of three polymers were estimated as $-(E_{ox}^{onset} + 4.4)$. The detailed data are listed in Table 2. The HOMO levels of the polymers slightly decrease from 5.36 eV for **XP-1** to 5.33 eV for **XP-3** with increasing fraction of X unit. The LUMO level values of them were estimated by subtraction of the optical band gap E^{opt} (eV) from the HOMO values. As shown in Table 2, the LUMO levels also decreased with increasing X unit content.

3.4. Electroluminescence properties

In order to investigate the electroluminescence properties of the new polymers, the non-optimizing devices based on the polymers with a configuration of ITO/PEDOT:PSS/polymer/LiF/Ca/Al were fabricated. The detailed data are listed in Table 3. As shown in Fig. 4, all the devices exhibited blue-light emission with the maximum EL emission peaks at around 466 nm, which were slightly blue-shifted, compared with the PL spectra of the corresponding polymer films. The devices displayed low turn-on voltages, which decreased from 4.5 V to 3.5 V with increasing X unit content. The highest luminescence reached 387 cd m^{-2} for **XP-1** at a current density of 253 mA cm^{-2} and 524 cd m^{-2} for **XP-2** at a current density of 341 mA cm^{-2}. The highest luminescence of 885 cd m^{-2} with a current density of 429 mA cm^{-2} was obtained for the device configured from **XP-3**. Further improvement on the EL performance can be expected by optimization in the fabrication, configuration and encapsulation.

Table 3
Properties of the devices of **XP-1**–**XP-3**

Polymer	Bias1[a] (V)	Bias2[b] (V)	Current density[c] (mA cm^{-2})	Luminance[d] (cd m^{-2})
XP-1	4.5	12	253	387
XP-2	4	10	341	524
XP-3	3.5	11	429	885

[a] Turn-on voltage.
[b] Voltage at the highest luminance.
[c] Current density at the highest luminance.
[d] The highest luminance.

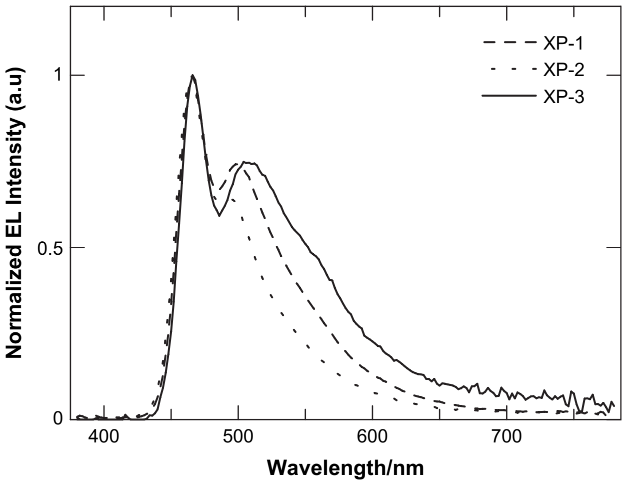


Fig. 4. EL spectra of the devices of **XP-1**–**XP-3**.

4. Conclusion

We have synthesized three new π-conjugated polymers containing X unit comprising fluorene blocks and anthracene blocks. The polymers show the special optical properties due to X unit, which are different from that of **PFO**. All polymers display high solid PL efficiency and good solubility. The HOMO and LUMO levels of the polymers decrease with increasing X unit content. The Electroluminescent devices based on the polymers emit blue light with low turn-on voltage and high brightness.

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