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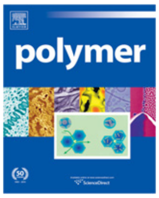

Synthesis and electroluminescence properties of fluorene-*co*-diketopyrrolopyrrole-*co*-phenothiazine polymers

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ABSTRACT

A series of fluorene-*co*-diketopyrrolopyrrole(DPP)-*co*-phenothiazine polymers, named as Flu-DPP-Phen, were synthesized by a palladium-catalyzed Suzuki coupling reaction with different feed ratios among 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), 2,5-dioctyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione, and 3,7-dibromo-10-octylphenothiazine. Their chemical structures and compositions were confirmed by ^{1}H NMR and elemental analysis. These terpolymers were found to be thermally stable and readily soluble in common organic solvents. Absorption and photoluminescence (PL) properties of Flu-DPP-Phen exhibit regular change with increasing of DPP contents in the terpolymers. Electroluminescence (EL) properties of all the terpolymers were characterized with the device configurations of ITO/PEDOT/terpolymer/Ba/Al and ITO/PEDOT/PVK/terpolymer/Ba/Al. Owing to exciton confinement on the narrow band gap DPP unit, the emission of fluorene segments is quenched completely with very low content of DPP (0.2 mol%). The EL spectra of all the terpolymers show exclusive long-wavelength emission originating from DPP units, which implied that the energy transfer in the terpolymer is very efficient. EL colors of the terpolymers vary from orange to red, the maximum emission is gradually red-shifted from 582 nm to 600 nm. The best EL performance was achieved by Flu-DPP-Phen(50:30:20) with maximum external quantum efficiency (EQE) of 0.25% and maximum brightness of 259 cd/m^2 in the device configuration of ITO/PEDOT/PVK/terpolymer/Ba/Al. The preliminary EL results proved that DPP units could effectively improve the electron affinity, and phenothiazine units could significantly enhance the hole injection ability, which resulted in the remarkable improvement of EQE.

1. Introduction

Since the initial polymeric light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) were reported by the Cambridge group [1], these new apparatus have received considerable attention due to their potential application in flat-panel displays and lighting applications [2–4]. PLEDs are promising devices for use in full-color displays because they have a number of advantages over conventional devices such as a low driving voltage, wide view angle, self-emitting property, full-color capability, low weight, potentially large area color displays and flexibility [5–7]. PLEDs are expected to become dominant displays in the future [8].

Because of their high photoluminescence and electroluminescence efficiencies as well as good thermal properties, polyfluorene and their derivatives (PFs) have been extensively studied during the past few years [9–12]. Moreover, the emission color of PFs can be easily tuned in the entire visible region by introducing narrow band gap comonomers into the polyfluorene backbone [13]. Nevertheless, there are some drawbacks that continue to hamper their potential applicability. Firstly, undesired green emission that appears upon thermal annealing or device operation. This low-energy emission band has been attributed to the formation of excimers or aggregates in the solid state [12]. Secondly, there is high ionization potential (5.8 eV) for PFs in PLEDs, i.e., a high energy barrier exists when holes travel into PFs from the indium tin oxide (ITO)/poly (3,4-ethylenedioxythiophene) (PEDOT) layer (5.0–5.2 eV), which results in higher driving voltages [14]. Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Because of unique electrooptical properties, polymers containing phenothiazine and its derivatives were potential candidate materials for PLEDs [15]. Obviously, phenothiazine and its derivatives which were incorporated into PFs should

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improve the injection and transport of holes. And what's more, the nonplanar structure of the phenothiazine ring should impede stacking aggregation and intermolecular excimer formation in the polymer main chain [16].

Another notable problem for PFs in PLEDs applications is that most of the fluorene-containing copolymers synthesized to date have low electron affinity and are typically p-type or hole-transport-dominated polymers [17]. Because electroluminescence in a PLED arises from the recombination of holes and electrons in an active polymer layer, any unipolar characteristics in the polymer layer may result in an unbalance in hole and electron injection and/or transport, leading to lower efficiency of the devices [12,18,19]. It is important to develop efficient PFs with high electron affinity to achieve a more balanced injection and transport of carriers (holes and electrons).

Despite many attempts to tune the color of blue-emitting PFs, appropriate red-emitting materials that meet the requirements of display applications have yet to be obtained [16]. If two chromophores with different energy band gaps are mixed together, then the emission will predominately or exclusively come from the chromophore with the narrower energy band gap because of energy transfer [15,16,20]. Hence, comonomers with narrow energy band gap can be introduced into PFs for color tuning. To date, those aromatic heterocycles such as thiophene, bithiophene, benzothiazole, and benzodithiazole derivatives are the most widely used as narrow energy band gap comonomers [12,16]. However, only a limited number of fluorene-based copolymers are known for red electroluminescence [21]. The exploration of novel classes is still needed for further improvements.

In recent years, DPP derivatives with the pyrrolo[3,4-c]pyrrole-1,4-dione unit as the new electroluminescent materials have drawn broad attention due to their unique structure and properties [22,23]. DPP derivatives possess brilliant red, high photoluminescence quantum yields and excellent chemical and thermal stability as well as photostability. They are potential materials applied in luminescent field as a kind of new electroluminescent materials [24–27]. Additionally, DPP derivatives are convenient obtained from commercial resources or simple synthetic procedures and easy optimization of the structure through variations of aryls on 3- and 6-positions. It will be very attractive to incorporate DPP derivatives into PFs back bone for red emission. According to our former study [28,29], DPP derivatives exhibit high electron affinity because of their two lactam units.

We have briefly reported that a novel polyfluorene derivative which contained DPP and phenothiazine units had remarkable improvement of EQE [30]. In order to get a full understanding of their role in the conjugated PFs, we report the systematically study on the synthesis of a series of three component copolymers with different ratios of fluorene, phenothiazine, diketopyrrolopyrrole units and the structure–property relationships of DPP-fluorene-phenothiazine polymers here. PLEDs based on the terpolymers are expected to emit a red light, and exhibit better hole-injection/transport in polymer electronic devices.

2. Experimental section

2.1. Measurement and characterization

^{1}H NMR spectra were collected on a Bruker DRX 400 spectrometer in $CDCl_3$ with tetramethylsilane as inner reference. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 515-410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. Thermogravimetric analysis (TGA) was conducted on a Pyris 1 TGA under a heating rate of 10 °C/min and a N_2 flow rate of 100 ml/min. Elemental analysis was performed using a Vario EL *III* instrument. UV–vis absorption spectra were recorded on an HP 4803 Instrument. PL and EL spectra were recorded on an Instaspec IV CCD spectrophotometer. The absolute PL quantum yields were determined in an Integrating sphere IS080 (Labsphere) with 325 nm excitation of He–Cd laser (Mells Griod), as the percent of the total output photons in all directions *vs* the total input photons. The luminance-voltage curves (L–V) were measured using a Keithley 236 source measurement unit and a calibrated silicon photodiode. The luminance was calibrated using a PR-705 SpectraScan spectrophotometer (Photo research). The external quantum efficiency (EQE) was collected by measuring the total light output in all directions in an integrating sphere. It was determined as the percent of the total output photons *vs* the total input electrons from each electrode.

2.2. Materials

2,5-Dioctyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**1**) was synthesized as described before [27]. 9,9-Dihexylfluorene-2,7-bis(trimethylene boronate) (**2**) and tetrakis (triphenylphosphine) palladium ($Pd(PPh_3)_4$) were purchased from Sigma Aldrich and Alfa Aesar, respectively, and were used without any further purification. 3,7-Dibromo-10-octylphenothiazine (**3**) was synthesized according to the procedures in the literature [31]. 2-Bromo-9,9-di-*n*-octyl-fluorene was synthesized from fluorene as a starting material according to the literature [32].

2.3. General procedure of polymerization

Monomer **1**, K_2CO_3 (17 equiv), monomer **2**, Pd $(PPh_3)_4$ (2 mol%), and monomer **3** were dissolved in a mixture of THF and water (50/50, v/v) under N_2. The mixture was heated to 80 °C and stirred vigorously for 48 h. Additional **2** (6 mol%) was added, and the mixture was refluxed under N_2 for 6 h; then 2-bromo-9,9-di-*n*-octyl-fluorene (12 mol%) was added, and the mixture was refluxed for another 6 h. The reaction mixture was cooled, and the solid was precipitated in methanol. The solid was filtered off, washed with dilute HCl, dissolved in chloroform, and precipitated in acetone. After being extracted with acetone in a Soxhlet apparatus for 24 h, terpolymers were obtained as pale brown to dark red solid with yields of 73–81%.

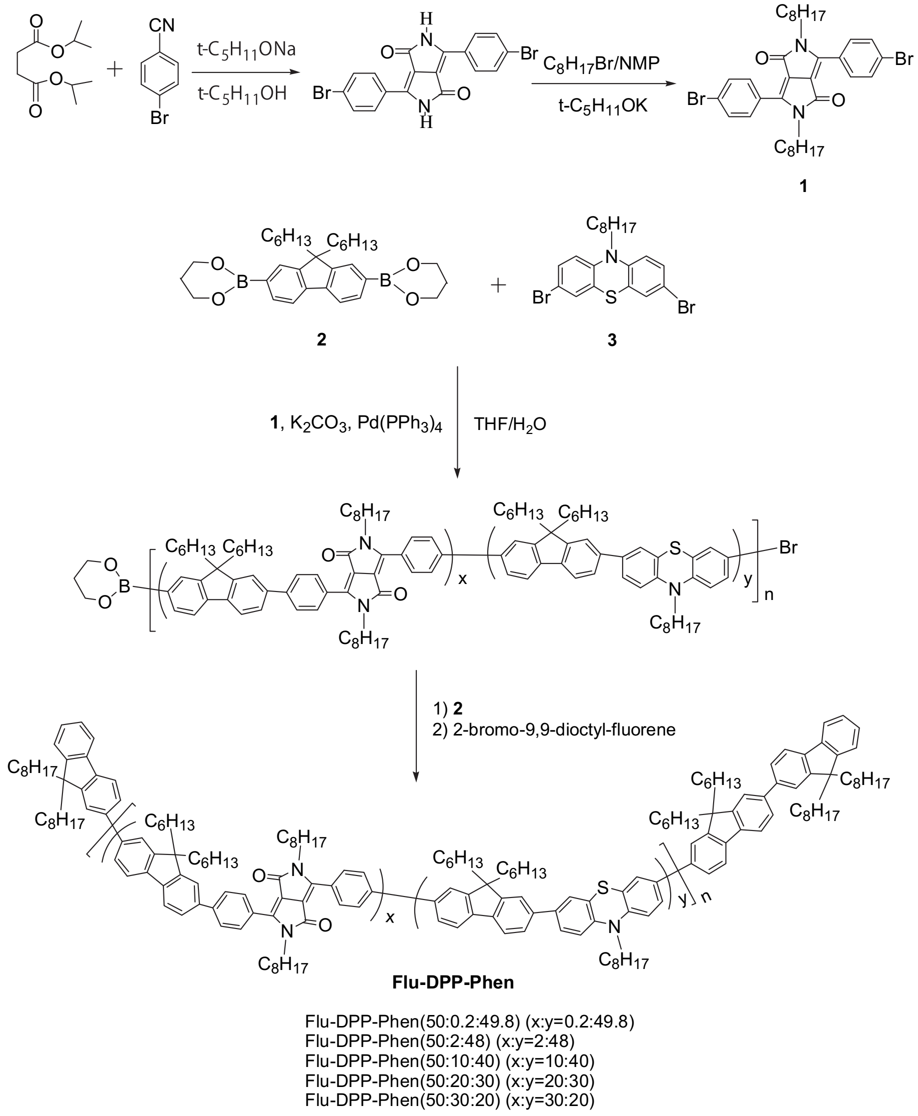
2.4. EL devices fabrication and characterization

Flu-DPP-Phen were dissolved in toluene or p-xylene and filtered through a 0.45 μm filter. Patterned indium tin oxide (ITO)-coated glass substrates were cleaned with acetone, detergent, distilled water, and 2-propanol, subsequently in an ultrasonic bath. After treatment with oxygen plasma, 50–60 nm of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-P 4083, Bayer AG) was spin-coated onto the ITO substrate followed by drying in a vacuum oven. Poly(-vinylcarbazole) (PVK) from 1,1,2,2-tetrachloroethane solution was coated on top of a dried PEDOT:PSS layer subsequently. A thin film of Flu-DPP-Phen was coated onto the anode by spin-casting inside a drybox. The film thickness of the active layer was 70–80 nm, as measured with an Alfa Step 500 surface profiler (Tencor). For EL devices with Ba as cathodes, a thin layer of Ba (4–5 nm) and subsequently 150 nm layers of Al were vacuum-evaporated subsequently on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa.

3. Results and discussion

3.1. Synthesis and characterizations

The conjugated terpolymers derived from monomers **1**, **2** and **3** were prepared by palladium(0)-catalyzed Suzuki coupling reactions with an equivalent molar ratio of the diboronic ester monomer to the dibromo monomers (Scheme 1). The molar ratio of **2** to **1** and **3** was always kept as **2**: (**1** + **3**) = 1:1, the molar feed ratios of **1**–**3** were 0.2:49.8, 2.0:48.0, 10.0:40.0, 20.0:30.0, 30.0:20.0, and the corresponding terpolymers were named as Flu-DPP-Phen(50:0.2:49.8), Flu-DPP-Phen(50:2:48), Flu-DPP-Phen(50:10:40), Flu-DPP-Phen(50:20:30), Flu-DPP-Phen(50:30:20), respectively. Their chemical structures and compositions were verified by ^{1}H NMR and elemental analysis. For these terpolymers, *n*-octyl substituents in the 2,5-positions of DPP and 10-position of phenothiazine were employed to improve the solubility of the resulting terpolymers. At the end of polymerization, 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) was added to remove bromine end groups and 2-bromo-9,9-di-*n*-octyl-fluorene was added to remove boronic ester end groups, because boron and bromine units could quench emission and contribute to excimer formation in PLED applications [33]. All the terpolymers were found to be soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, and THF. Molecular weights and polydispersity indices (PDI) are listed in Table 1. M_n and M_w ranged from 5605 to 30,454 (M_n) and from 10,320 to 70,487 (M_w), respectively, with PDI ranging from 1.84 to 2.79. The actual contents of monomers **1** and **3** in the terpolymer were calculated according to elemental analysis, and the results were very close to the feed compositions. The chemical structures of the terpolymers were confirmed by ^{1}H NMR, as shown in Fig. 1. As expected, the intensity of signals corresponding to protons of DPP moieties (protons a, b, c, and d), relative to protons of phenothiazine moieties (protons f and g), increase gradually along with DPP contents increasing in the terpolymers. The thermal properties of the terpolymers are shown in Table 1. TGA revealed that onset decomposition temperatures (based on 5% weight loss, T_d) were in range of 198–357 °C. Flu-DPP-Phen(50:0.2:49.8) and Flu-DPP-Phen(50:30:20) exhibited very good thermal stability, losing less than 5% weight on heating to ~350 °C in TGA runs under nitrogen.



Scheme 1. Synthetic route of the terpolymers.

Table 1
Yields, molecular weights, and thermal properties of the terpolymers.

Polymers	Yield (%)	M_w	M_n	PDI	1 (mol%)[a]	3 (mol%)[a]	Td (°C)[b]
Flu-DPP-Phen (50:0.2:49.8)	73	45,316	16,232	2.79			342
Flu-DPP-Phen (50:2:48)	76	25,842	13,137	1.97	2.1	47.9	220
Flu-DPP-Phen (50:10:40)	71	10,320	5605	1.84	11.2	38.8	307
Flu-DPP-Phen (50:20:30)	79	36,299	18,305	1.98	21.1	28.9	198
Flu-DPP-Phen (50:30:20)	81	70,487	30,454	2.32	28.2	21.8	357

[a] Calculated from the results of elemental analysis.
[b] Based on 5% weight loss.

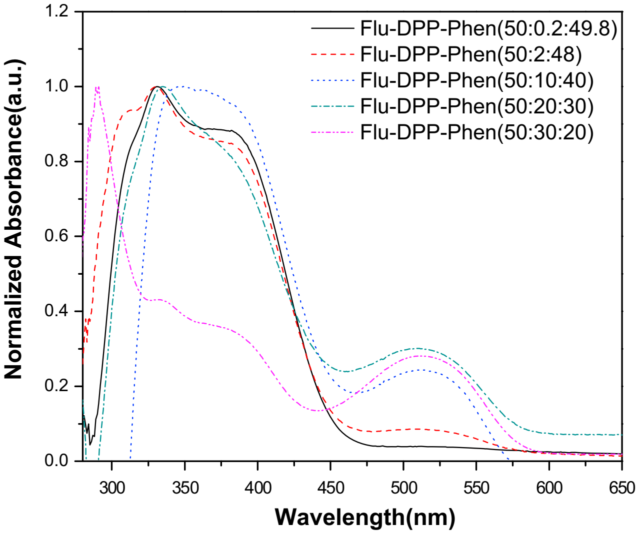


Fig. 2. UV–vis absorption spectra of the terpolymers in thin films.

3.2. *Optical and photoluminescence properties*

The UV–vis absorption spectra of the terpolymers in thin films are shown in Fig. 2. Flu-DPP-Phen(50:0.2:49.8) and Flu-DPP-Phen(50:2:48) in thin films possess very similar absorption spectra with maximum peaks at 331 nm, attributed to π–π* transition of the terpolymers. In addition, a weak absorption peak at 382 nm is attributed to the fluorene unit. However, Flu-DPP-Phen(50:10:40), Flu-DPP-Phen(50:20:30) and Flu-DPP-Phen (50:30:20) show different absorption spectra. The additional long-wavelength absorption peak at 513 nm is attributed to the DPP segments. Moreover, the absorption intensity at 513 nm increased gradually with DPP content increasing in the terpolymer backbone. In the case of Flu-DPP-Phen(50:0.2:49.8) and Flu-DPP-Phen(50:2:48) containing 0.2% and 2% of DPP in the terpolymers, respectively, the absorption peak of the DPP unit is not apparent in the solid film. In one word, the two distinguishable absorption features of all terpolymers demonstrate that the electronic configurations of three components (fluorene, DPP and phenothiazine) in the terpolymers are not well mixed.

Photoluminescence spectra in $CHCl_3$ solutions and in thin solid films are shown in Figs. 3 and 4, respectively. All characteristic data of absorption and photoluminescence are summarized in Table 2. As shown in Fig. 3, PL spectra of the terpolymers in $CHCl_3$ solutions at a concentration of 1×10^{-5} M also change regularly with the variation of DPP contents. The PL emission spectra of dilute solutions of Flu-DPP-Phen(50:0.2:49.8) and Flu-DPP-Phen(50:2:48) reveal that they are nearly identical with maximum emission peaks at 486 nm. No typical emission from fluorene (at about 450 nm) was observed, which implied that the emission of fluorene was quenched. There is no signature of DPP emission. Increasing the DPP contents to 10% for Flu-DPP-Phen(50:10:40), the DPP emission emerges with maximum at 560 nm, but the intensity is weak relatively. Once the DPP units increase to 20%, the intensity of the DPP emission peak at 574 nm of Flu-DPP-Phen(50:20:30) is enhanced dramatically and become stronger than the short-wavelength emission (482 nm). Moreover, the emission in short-wavelength region nearly disappears with DPP content up to 30% for Flu-DPP-Phen(50:30:20). This can be attributed to strong intramolecular energy transfer. Compared with the maximum PL emission peak (578 nm) of alternating fluorene-DPP copolymer **P1** in the previous work [28], all the maximum PL emission peaks (486–574 nm) of the terpolymers in solutions are regularly blue-shifted; and what's more, the emission peak in short-wavelength

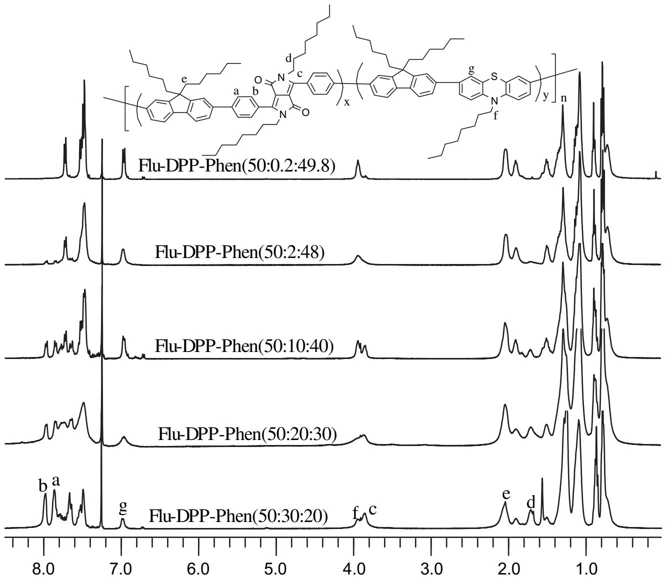


Fig. 1. ^1H NMR spectra of the terpolymers in $CDCl_3$.

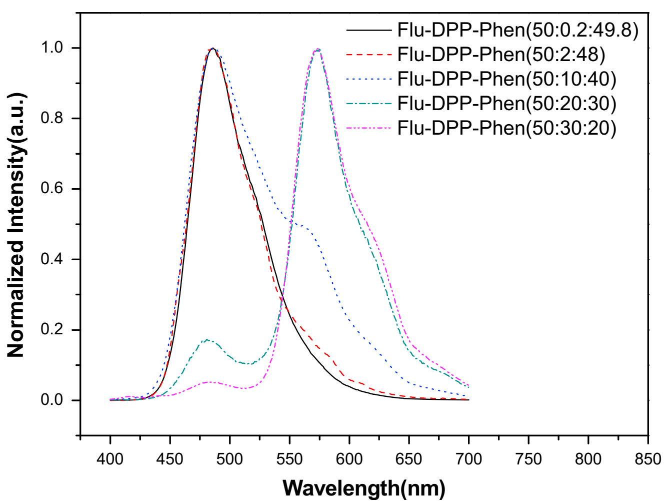


Fig. 3. Photoluminescent spectra of the terpolymers in $CHCl_3$ solutions (1×10^{-5} M, excitation wavelength 325 nm).

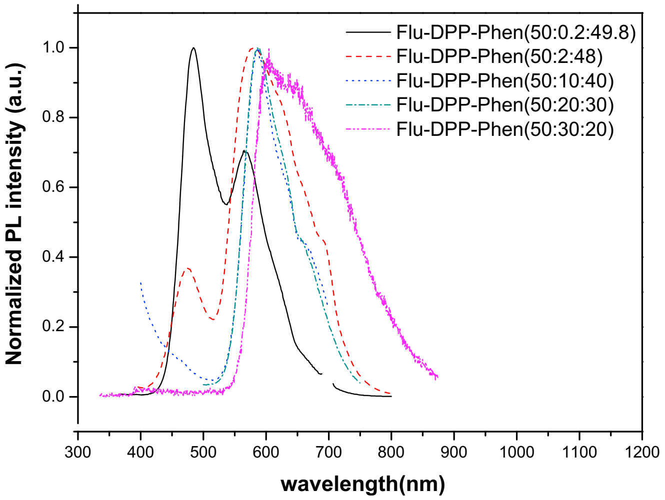


Fig. 4. Photoluminescent spectra of the terpolymers in thin films (excitation wavelength 325 nm).

region around 480 nm disappears completely when DPP content increases to 50 mol% regard to the alternating fluorene-DPP copolymer **P1**.

PL spectra of the terpolymers in thin films closely resemble spectra in chloroform solution, as shown in Fig. 4. However, some differences should be noticed: first, the threshold of DPP content for complete quenching of emission from fluorene and phenothiazine segments is lowered to 10%; second, the maximum emission of PL is some red-shifted for the terpolymers, compared with those in chloroform solution. These facts can be attributed to more intramolecular or intermolecular interactions in the film than in the solution [34].

Interestingly, as the fraction of DPP increased, the PL emission maximum for all terpolymers in thin films in the longer wavelength region gradually is red-shifted (566–604 nm), and this phenomenon is identical with the fluorene-DPP alternating copolymers [29]. Two interpretations are possible to explain the phenomenon: increase in the π-conjugation length with increase in the fraction of DPP, and aggregate formation between the moieties of DPP.

The absolute PL efficiencies of the terpolymers in thin films were measured in the integrating sphere using a HeCd laser line of 325 nm as the excitation source, and the results are listed in Table 2. The PL efficiencies decrease quickly with increasing DPP content in the terpolymers from 10.95% for Flu-DPP-Phen(50:0.2:49.8) to 4.54% for Flu-DPP-Phen(50:10:40), which is probably due to quenching effect of the carbonyl groups in DPP unit. Carbonyl groups which facilitate intersystem crossing of singlet to triplet with their n–π* transition, and possible intramolecular charge transfer is responsible for the loss of PL efficiency. However, the PL efficiencies do not change dramatically when DPP content increases to 10% or more. The PL quantum yield of Flu-DPP-Phen(50:0.2:49.8) is the highest among the five terpolymers, which implies that nonplanar phenothiazine ring can effectively restrain the fluorescent quenching effect caused by carbonyl groups. The most interesting insight from these photophysics results is that the phenothiazine ring is an excellent building block for impeding π-stacking aggregation and intermolecular excimer formation, because phenothiazine ring is nonplanar [16].

Table 2
Photophysical properties of the terpolymers.

Polymers	UV, λ_{max} (nm)	PL, λ_{max} (nm)		η_{PL} (%)
	Thin film	Solution	Thin film	Thin film
Flu-DPP-Phen(50:0.2:49.8)	331,382	486	483,566	10.95
Flu-DPP-Phen(50:2:48)	331,382	486	476,579	6.93
Flu-DPP-Phen(50:10:40)	346,513	486,560	587	4.51
Flu-DPP-Phen(50:20:30)	335,513	482,574	587	4.24
Flu-DPP-Phen(50:30:20)	289,513	482,574	604	4.72

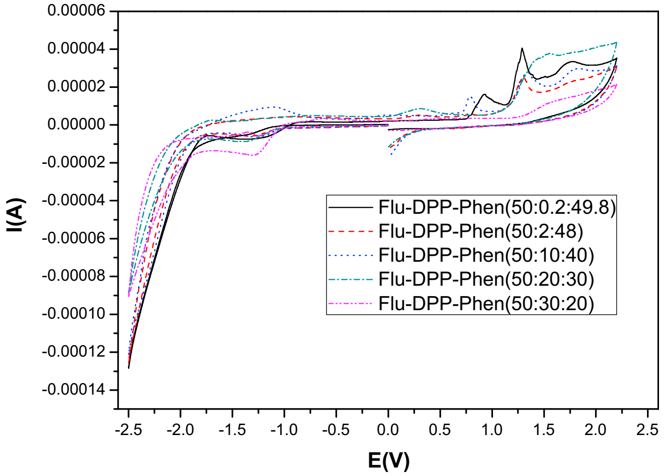


Fig. 5. Cyclic voltammograms of the terpolymers on a Pt electrode at a scanning rate of 50 mV/s.

It should be noted that all the PL efficiencies of these terpolymers are lower than the fluorene-DPP alternating copolymers reported previously [29]. The low PL efficiencies of the terpolymers might be due to the presence of the phenothiazine unit, which is more effective as a quencher than the carbonyl group of DPP unit. In addition, the fluorene content in the terpolymer (50 mol%) is less than the fluorene content (50–99 mol%) in the DPP-fluorene alternating copolymers in ref. 29, which might result lower PL efficiencies than the DPP-fluorene alternating copolymer because fluorene segments usually exhibit high photoluminescence efficiencies. Another possible reason may be attributed to the disordered main chain structure of these random terpolymers.

3.3. *Electrochemical properties of the terpolymers*

The electrochemical properties of the terpolymers were investigated by cyclic voltammetry (CV). The oxidation and reduction potentials are closely related to the HOMO and LUMO levels of the copolymers. The terpolymer films deposited on a platinum wire electrode were scanned both positively and negatively (scan rate of 50 mV/s) in 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile by using calomel as reference electrode. As shown in Fig. 5, in the anodic scans, the onset oxidation potentials of the terpolymers ranged from 0.99 to 1.16 V. HOMO energy levels of the terpolymers were between −5.39 eV and −5.56 eV calculated according to the empirical formula $E_{HOMO} = -(E_{ox} + 4.4)$ eV. Compared with the alternating fluorene-DPP copolymer **P1** [28], HOMO energy levels of the terpolymers were higher than the energy level of P1 (−5.6 eV), implying that the energy barriers between the work function of PEDOT/PSS (−5.0 eV)

Table 3
Electrochemical properties of the terpolymers.

Polymers	E_{ox} (V)	E_{red} (V)	HOMO(eV)	LUMO(eV)	E_g(eV)
Flu-DPP-Phen(50:0.2:49.8)	1.16	−1.07	−5.56	−3.33	2.23
Flu-DPP-Phen(50:2:48)	1.15	−1.03	−5.55	−3.37	2.18
Flu-DPP-Phen(50:10:40)	1.15	−1.02	−5.55	−3.38	2.17
Flu-DPP-Phen(50:20:30)	1.14	−1.01	−5.54	−3.39	2.15
Flu-DPP-Phen(50:30:20)	0.99	−1.02	−5.39	−3.38	2.01

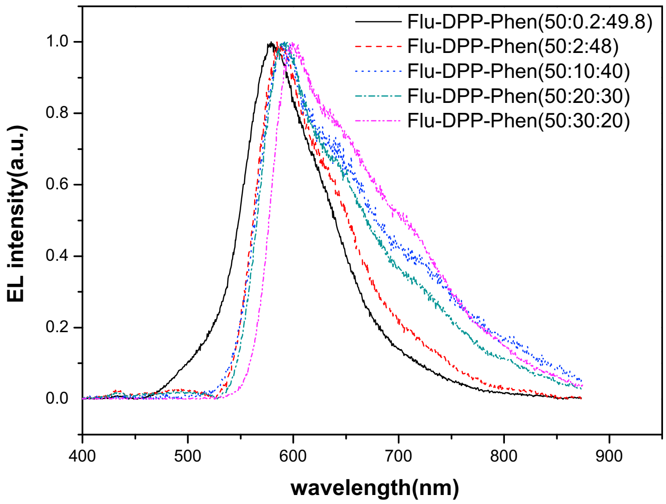


Fig. 6. Electroluminescent spectra of the terpolymers in the devices with the configuration of ITO/PEDOT/terpolymer/Ba/Al.

and HOMO energy levels of the terpolymers reduced due to the incorporation of phenothiazine units into polymer main chains. During the cathodic scans, the onset reduction potentials of the terpolymers were between −1.01 V and −1.07 V, and LUMO energy levels were estimated to be ranged from −3.33 to −3.39 eV according to the empirical formula $E_{\mathrm{LUMO}} = -(E_{\mathrm{red}} + 4.4)$ eV. The electrochemical band gaps were calculated from HOMO and LUMO levels, and the results are summarized in Table 3. It can be seen that the energy band gaps of the terpolymers gradually decrease from 2.23 to 2.01 eV with increasing DPP contents in the terpolymers.

3.4. Electroluminescence properties

A double-layer device with a configuration of ITO/PEDOT/terpolymer/Ba/Al was fabricated, where PEDOT doped with poly(styrenesulfonic acid) (PSS) functions as a buffer layer and a hole-injection/transport layer. The EL spectra of the terpolymers are shown in Fig. 6. The emission maxima and chromaticity coordinates for the terpolymers are summarized in Table 4. In contrast to PL spectra, EL emission consists exclusively of orange or red emission peaked around 582–600 nm originating from DPP units for the terpolymers. The emission from fluorene and phenothiazine segments is completely quenched. The differences in the PL and EL spectra at low doping concentrations were attributed to the differences in the recombination zone for photo- and electric excitations. It is important to note that the short-wavelength emission is completely quenched even at 0.2% DPP loading in the feed, indicating intramolecular and intermolecular energy transfer is a very quick and efficient process. As a result, the generated excitons are efficiently confined to DPP sites. The DPP moiety even at the low content can serve as an efficient trap for all of generated excitons, and the terpolymer emits exclusively from the narrow energy band gap component. With increasing DPP contents, the EL emission maxima for the terpolymers are gradually red-shifted from 582 nm for Flu-DPP-Phen(50:0.2:49.8) to 600 nm for Flu-DPP-Phen(50:30:20), and this change pattern coincides with the trend of the red shift of PL emission maximum. Compared with the EL emission spectrum of alternating fluorene-DPP copolymer **P1** [28], all the maximum EL emission peaks (582–600 nm) of the terpolymers are regularly blue-shifted. As summarized in Table 4, CIE coordinates change from (0.51, 0.48) for Flu-DPP-Phen(50:0.2:49.8) to (0.62, 0.38) for Flu-DPP-Phen(50:30:20), and the emission color of the devices changes from orange to red, which indicate that the more DPP contents in the terpolymers, the more saturated red emission can be achieved. In particular, the chromaticity value of Flu-DPP-Phen(50:30:20) is (0.62, 0.38) which is very close to the standard red emission (0.66, 0.34) demanded by NTSC [17].

Fig. 7 shows brightness-voltage curves of the terpolymers in the devices with the configuration of ITO/PEDOT/terpolymer/Ba/Al. The maximum EQE, maximum brightness, and turn-on voltages of the devices are also listed in Table 4. The turn-on voltages of the devices range from about 5.1 to 10.2 V. Furthermore, the PLED device based on Flu-DPP-Phen(50:30:20) exhibits the lowest turn-on voltage among all the devices. It is worthy to note that the turn-on voltage (5.1 V) of Flu-DPP-Phen(50:30:20) is lower obviously than the turn-on voltage (8 V) of the alternating fluorene-DPP copolymer **P1**. This fact can also be attributed to easier hole injection and enhanced hole transport, which is mainly contributed by the introduction of phenothiazine segments into copolymers. The maximum brightness of all the devices are in the range of 37–195 cd/m^2, and the maximum EQEs change from 0.01% to 0.11%. With increasing the DPP content, maximum brightness and maximum EQEs of light-emitting devices first decrease, and then gradually increase. The best device performance of the terpolymers is observed for Flu-DPP-Phen(50:30:20) with the maximum brightness of 195 cd/m^2 and maximum EQE of 0.11%. Furthermore, the maximum brightness (195 cd/m^2) of Flu-DPP-Phen(50:30:20) is increased by 27% compared with the maximum brightness (153 cd/m^2) of the alternating fluorene-DPP copolymer **P1**. Terpolymers exhibit good EL performances with low DPP contents (0.2%) and high DPP contents (30%), while EL performances are very poor of terpolymers with medium DPP contents (2–20%). These results are consistent with fluorene-DPP copolymers [29]. Even for Flu-DPP-Phen(50:10:40) with DPP content of 10% in the feed, both the brightness–voltage plot and the EQE–voltage plot of the light-emitting device (LED) could not be detected because of too low luminance and efficiency. Flu-DPP-Phen(50:0.2:49.8) might be superior to other terpolymers in consideration of conjugation that is responsible for carrier mobility, which is critical for efficient EL. In addition, the phenothiazine units can impede π-stacking aggregation and intermolecular excimer formation due to nonplanar ring. However, when DPP content increases to 30% in the feed for Flu-DPP-Phen(50:30:20), it exhibits best EL performance, which partially attributes to more efficient energy transfer from wide band gap fluorene segments to narrow band gap DPP segments. Moreover, more DPP units will largely improve electron affinity and achieve more balanceable mobility of carriers (holes and electrons).

Table 4
EL performances of the devices with the configuration of ITO/PEDOT/terpolymer/Ba/Al.

Polymers	EL Emission $\lambda_{\max}$(nm)	CIE Coordinate (x,y)	Turn-on Voltage (V)[a]	Maximum Brightness (cd/m^2)	Maximum EQE (%)
Flu-DPP-Phen(50:0.2:49.8)	582	(0.51,0.48)	7.6	178	0.049
Flu-DPP-Phen(50:2:48)	589	(0.56,0.42)	10.2	80	0.021
Flu-DPP-Phen(50:10:40)	590	(0.57,0.42)			
Flu-DPP-Phen(50:20:30)	592	(0.58,0.47)	6.4	37	0.018
Flu-DPP-Phen(50:30:20)	600	(0.62,0.38)	5.1	195	0.110

[a] Turn-on voltage corresponds to luminance of about 1.5 cd/m^2.

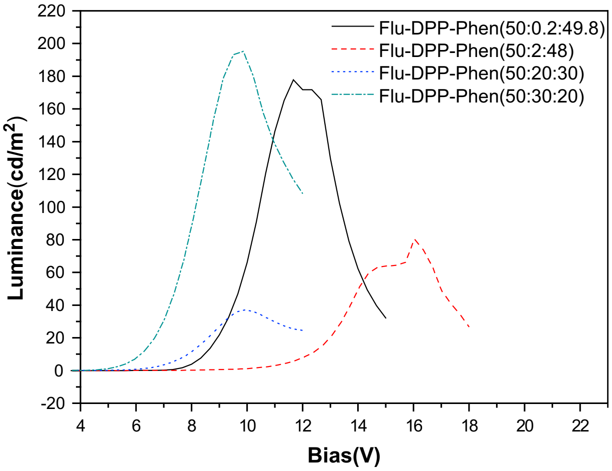


Fig. 7. Brightness-voltage curves of the terpolymers in the devices with the configuration of ITO/PEDOT/terpolymer/Ba/Al.

To further investigate the expected enhancement of hole injection arising from the electron-rich sulfur and nitrogen heteroatoms of phenothiazine units, we fabricated another kind of device with a configuration of ITO/PEDOT(50 nm)/PVK(30 nm)/terpolymer (80 nm)/Ba/Al, and PVK was introduced as the hole injection anode [35]. Responding EL spectra (not shown) are almost identical to those of the EL devices without a PVK layer. Other parameters are summarized in Table 5. EL properties of the terpolymers with medium DPP contents are still poor. We found that turn-on voltages obviously increased when PVK was introduced. Compared with those of the EL devices without a PVK layer, maximum EQEs of the devices based on the terpolymers with more phenothiazine units or low DPP units, Flu-DPP-Phen(50:0.2:49.8) and Flu-DPP-Phen (50:2:48), dramatically decreased, indicating that hole mobility was higher than electron mobility for Flu-DPP-Phen(50:0.2:49.8) and Flu-DPP-Phen(50:2:48) due to more electron-rich phenothiazine units were incorporated into the main chain of the terpolymers, which resulted in unbalance in hole and electron injection and transporting. Therefore superfluous holes led fluorescent quenching and thereby led significant falling of EQE. With phenothiazine contents decreasing or DPP contents increasing, the maximum EQEs of the devices using Flu-DPP-Phen(50:10:40), Flu-DPP-Phen(50:20:30) and Flu-DPP-Phen (50:30:20) as active layers were evidently improved compared with the corresponding EL devices without PVK layer. This might be attributed to enhancement of electron affinity by DPP units. It is worthy to note that the maximum brightness of the devices with the configuration of ITO/PEDOT/PVK/terpolymer/Ba/Al exhibit the nearly variational trend compared with the devices with the configuration of ITO/PEDOT/terpolymer/Ba/Al. The EL device with Flu-DPP-Phen(50:30:20) as the emissive layer shows the highest EQE (0.25%) and the maximal brightness (259 cd/m^2). From these results, we can conclude that the holes injection and transport ability are improved with the phenothiazine units incorporated into the backbone of copolymers. Similar results have been reported in the literature [36]. Moreover, these results also support the other fact that incorporation of DPP units into polymer main chain can effectively improve electron affinity.

Table 5
EL performances of the devices with the configuration of ITO/PEDOT/PVK/terpolymer/Ba/Al.

Polymers	Turn-on voltage (V)[a]	Maximum brightness (cd/m^2)	Maximum EQE (%)
Flu-DPP-Phen(50:0.2:49.8)	12.6	159	0.029
Flu-DPP-Phen(50:2:48)	15.8	90	0.017
Flu-DPP-Phen(50:10:40)	5.6	10	0.003
Flu-DPP-Phen(50:20:30)	9.8	15	0.026
Flu-DPP-Phen(50:30:20)	9.4	259	0.250

[a] Turn-on voltage corresponds to the luminance of about 1.5 cd/m^2.

4. Conclusions

In conclusion, a series of soluble conjugated random terpolymers Flu-DPP-Phen contained fluorene, DPP and phenothiazine units were successfully synthesized by palladium(0)-catalyzed Suzuki coupling reactions with various molar ratios of the electron-rich phenothiazine and the narrow energy band gap DPP contents. ^{1}H NMR and elemental analysis show that these polymers possess well-defined chemical structures. The actual contents of DPP units and phenothiazine units are close to feed ratios. TGA measurements display excellent thermal stabilities of most terpolymers. Absorption spectra and PL spectra of the terpolymers vary regularly with increase of DPP contents. Only very few DPP units (0.2%) are needed to completely quench emission from fluorene segments in the terpolymers, implying that energy transfer is very efficient due to exciton trapping on the narrow band gap DPP sites. Emission colors of EL devices change from orange to red, and the EL peaks are gradually red-shifted from 582 nm to 600 nm with increasing DPP content in polymer chains, corresponding CIE coordinates from (0.51, 0.48) to (0.62, 0.38). Parameters of the devices with structures of ITO/PEDOT/PVK/terpolymer/Ba/Al support the conclusion that incorporation of DPP units into polymer main chain can effectively improve electron affinity, and incorporation of phenothiazine units can obviously enhance the holes injection and transport ability, which would result in balance in carriers injection and transport, and therefore can significantly improve the EL performances.

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