## Highly efficient red electroluminescent polymers with dopant/host system and molecular dispersion feature: polyfluorene as the host and 2,1,3-benzothiadiazole derivatives as the red dopant<sup>†</sup>

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By selecting polyfluorene as the polymer host, choosing 2,1,3-benzothiadiazole derivative moieties as the red dopant units and covalently attaching 0.3 mol% of the dopant units to the side chain of the polymer host, we developed a novel series of red electroluminescent polymers of dopant/host system with molecular dispersion feature. Their EL spectra exhibited predominant red emission from the dopant units because of the energy transfer and charge trapping from the polymer backbone to the dopant units. The emission wavelength of the polymers could be tuned by modifying the chemical structures of the dopant units. Single-layer devices (device configuration: ITO/PEDOT : PSS/polymer/Ca/Al) of these polymers emitted red light with a peak at 615 nm, a luminous efficiency of 5.04 cd  $A^{-1}$  and an external quantum efficiency of 3.47%, or emitted deep-red light with a peak at 650 nm, a luminous efficiency of 1.70 cd  $A^{-1}$  and an external quantum efficiency of 2.75%. Their high EL efficiencies were due to the energy transfer and charge trapping from the host to the dopant units as well as the molecular dispersion of the dopant units in the host. Increase of the dopant unit content led to increased turn-on voltages and decreased EL efficiencies of the resulting devices.

## Introduction

Since the initial discovery of electroluminescence (EL) from conjugated polymers,<sup>1</sup> electroluminescent polymers have been the subject of intense academic and industrial research because of their potential application in flat-panel displays. For full color displays, blue, green and red light emitting polymers are required. Among them, red light emitting polymers with high EL efficiencies are scarce when compared with the other two colors.

Polyfluorene and its derivatives have recently emerged as the most promising electroluminescent polymers due to their high photoluminescence (PL) and EL efficiencies, good thermal and chemical stability.<sup>2–5</sup> Normally, polyfluorene itself emits blue light with a large bandgap. The common approach to realize red emission from polyfluorene derivatives is to incorporate a narrow bandgap unit into the main chain of polyfluorene.<sup>3–19</sup> For example, 4,7-dithienyl-2,1,3-benzothiadiazole,<sup>8–10</sup> 2,1,3-naphthaselenadiazole,<sup>11,12</sup> 3',4'-dihexyl-2,2';5',2"-terthiophene-1',1'-dioxide,<sup>13</sup> cyanovinyl-containing units,<sup>14,15</sup> 3,4-diphenylmaleimide derivative units,<sup>16</sup> 2-pyran-4-ylidene-malononitrile<sup>17</sup> unit and phenothiazine derivative units<sup>18</sup> all exhibit low-bandgap  $\pi$ -conjugation and the resulting copolymers all show red emission. However, red fluorescent polymers based on low-bandgap-conjugated fluorene copolymers seldom show a luminous efficiency exceeding 1.5 cd A<sup>-1</sup> because red chromophores are prone to aggregation in the solid state and are highly susceptible to concentration quenching. Hence, it remains a challenging task to develop another approach to design efficient and bright red electroluminescent polymers.

Our group has proposed a novel approach to design lightemitting polymers of dopant/host systems with high EL efficiencies and tunable emission colors by covalently attaching a small amount of dopant unit to the side chain of a polymer host (polyfluorene).<sup>20–29</sup> Blue, green and white light emitting polymers have been demonstrated with this strategy. In this article, we further adopt the strategy of the dopant/host system to design a red light emitting polymer by covalently attaching a very small amount of red emissive dopant unit to the side chain of a polymer host. The resulting polymer can be considered as a system with a low content of red dopant unit molecularly dispersed in a polymer host, in which the concentration quenching of the red dopant unit can be effectively suppressed. In the EL process, since the emission comes from the red dopant unit with suppressed concentration quenching, remarkable EL efficiencies can be expected. As the result, single-layer devices of the resulting polymers emit red light with an emission maximum at 615 nm, a luminous efficiency of 5.04 cd  $A^{-1}$  and an external quantum efficiency of 3.47%, or deep-red light with an emission maximum wavelength of 650 nm, a luminous

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efficiency of 1.70 cd  $A^{-1}$  and an external quantum efficiency of 2.75%.

#### **Results and discussion**

#### **Design consideration**

Scheme 1 shows the chemical structures of the target red electroluminescent polymers of the dopant/host system, P-R1, P-R2, P-R3, P-R2-50 and P-R2-100. Polyfluorene was selected as the polymer host because of its large bandgap and good film-forming properties.<sup>2-5</sup> Three red emissive moieties based on the electron-withdrawing 2,1,3-benzothiadiazole unit<sup>30</sup> and the electron-donating triphenylamine unit were designed and selected as the dopant units (their model compounds are MC-R1, MC-R2 and MC-R3, see Scheme 2). One or two thiophene units were inserted between the electron donor and the electron acceptor to tune the emission wavelength of the dopant unit and consequently the emission wavelength of the resulting polymers. All the three model compounds can form dopant/host systems with polyfluorene in terms of spectral overlapping and energy levels. The three dopant units were covalently attached to the side chain of polyfluorene (host) with alkyl spacers in order to realize the molecular dispersion of the dopant units in the host.<sup>31</sup> The contents of the dopant units in P-R1, P-R2 and P-R3 were controlled to be 0.3 mol% to achieve dominant emission from the red dopant units and to avoid their concentration quenching effect. In order to investigate the effect of the dopant unit content on the EL performance of the resulting polymers, the contents of the dopant unit in P-R2, P-R2-50 and P-R2-100 were tuned within the range of 0.3-1.0 mol%.

#### Synthesis

The synthetic routes of the model compounds, monomers and polymers are outlined in Scheme 2. The three model compounds, **MC-R1**, **MC-R2** and **MC-R3**, were all synthesized by the two-step Stille coupling of 4,7-dibromo-2,1,3-benzothiadiazole and the corresponding tributylstannyl derivatives with



Scheme 1 Chemical structures of the red light emitting polymers of the dopant/host system.

high yields. The three model compounds were de-methyled by BBr<sub>3</sub> and then reacted with 2,7-dibromo-9-hexyl-9-(6bromohexyl)fluorene (12) to afford the three red-dopantunit-containing monomers, Monomer R1, Monomer R2 and Monomer R3. All five red light emitting polymers were prepared by the Suzuki polycondensation<sup>32</sup> of 2,7dibromo-9,9-dioctyl-fluorene (13), 2,7-bis(trimethyleneborate)-9,9-dioctyl-fluorene (14) and the corresponding red-dopant-unit-containing monomers with corresponding feed ratios. Polyfluorene homopolymer (PF) was also synthesized for comparison. All these polymers are readily soluble in common organic solvents (e.g. toluene, chloroform, tetrahydrofuran) and can form high-quality thin films by spincoating. The number-average molecular weights  $(M_n)$  of **P-R1**, P-R2, P-R3, P-R2-50 and P-R2-100, as determined by gel permeation chromatography (GPC) with polystyrene as standards, range from 21100 to 26300 with polydispersities (PDI) ranging from 2.00 to 2.14. All these polymers exhibit good thermal stability with thermal degradation temperature  $(T_{\rm d})$  higher than 420 °C.

#### **Electrochemical properties**

In order to investigate the LUMO and HOMO energy levels of the three dopant units, we performed cyclic voltammetry measurements of the three model compounds, MC-R1, MC-R2 and MC-R3, in CH<sub>2</sub>Cl<sub>2</sub> solution. The results are shown in Fig. 1a. Their onset oxidation voltages and onset reduction voltages are listed in Table 1. According to the formulae  $E_{\text{HOMO}} = -(E^{\text{ox}} + 4.34) \text{ eV} \text{ and } E_{\text{LUMO}} = -(E^{\text{red}} + 4.34) \text{ eV},^{33}$ the LUMO and HOMO energy levels of the three model compounds were calculated and are listed in Table 1. It is very obvious that the insertion of thiophene units in these model compounds leads to the increase of the HOMO energy levels as well as the decrease of the LUMO energy levels. Despite their difference, the LUMO and HOMO energy levels of all the three model compounds all lie between those of PF (see Fig. 1b), indicating that charge trapping of the red dopant units in the EL process is energetically favorable.<sup>34,35</sup>

The electrochemical properties of the polymers were also investigated by cyclic voltammetry with their thin films on a glassy-carbon working electrode. **P-R1**, **P-R2**, **P-R3**, **P-R2-50** and **P-R2-100** all exhibit the same redox behavior as **PF**. The incorporation of the small amount of red dopant units leads to negligible changes in the electrochemical properties and energy levels of the resulting polymers.

#### **Photophysical properties**

Fig. 2 shows the absorption spectra and photoluminescence (PL) spectra of the three model compounds in toluene. The corresponding absorption and PL maxima are listed in Table 1. It is very interesting that the insertion of each thiophene unit leads to a redshift by 25 nm in the absorption spectra and a redshift by 35 nm in the PL spectra. Table 1 also lists the PL quantum efficiencies ( $\Phi_{PL}$ ) of the three model compounds in toluene.<sup>36</sup> **MC-R1** and **MC-R2** both exhibit high  $\Phi_{PL}$  values of 0.74 and 0.59, respectively. However, the  $\Phi_{PL}$  of **MC-R3** is as low as 0.24. It is obvious that the insertion of thiophene units leads to decreased PL quantum efficiencies. As shown in





Scheme 2 Chemical structures and synthetic routes of the model compounds, monomers and polymers. (*Reagents and conditions*: i) NBS, CCl<sub>4</sub>, 60 °C; ii) a) n-BuLi, THF, -78 °C, b) (n-Bu)<sub>3</sub>SnCl; iii) CuCl, 1,10-phenanthroline monohydrate, KOH, toluene, reflux; iv) Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, 100 °C; v) a) n-BuLi, THF, -78 °C, b) n-C<sub>6</sub>H<sub>13</sub>Br, c) Br<sub>2</sub>, CHCl<sub>3</sub>; vi) Br(CH<sub>2</sub>)<sub>6</sub>Br, NaOH (aq. 50 wt%), toluene, Bu<sub>4</sub>NBr, 80 °C; vii) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -78 °C; viii) K<sub>2</sub>CO<sub>3</sub>, ethanol, reflux; ix) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub> (aq. 2 M), Aliquat 336, toluene, 90 °C.)

Fig. 2a, the absorption spectra of MC-R1, MC-R2 and MC-R3 all overlap with the emission spectrum of PF, favoring Förster energy transfer from the polyfluorene backbone to the red dopant units in the three red polymers. In the case of MC-R3, the spectral overlap is poor and inefficient energy transfer is expected.



Fig. 1 Cyclic voltammetry (a) and energy levels (b) of MC-R1, MC-R2, MC-R3 and PF.

 $Table 1 \quad The \ photophysical \ properties, \ electrochemical \ properties and \ energy \ levels \ of \ MC-R1, \ MC-R2 \ and \ MC-R3$ 

	$\lambda_{abs}/$ nm	$\lambda_{\rm PL}/$ nm	$\Phi_{ m PL}$	$E_{ m onset,ox}/V$	HOMO/ eV	$E_{ m onset, red}/V$	LUMO/ eV
MC-R1 MC-R2	464 499	595 620	0.74 0.59	0.83 0.78	-5.17 -5.12	-1.29 -1.17	$-3.05 \\ -3.17$
MC-R3	534	645	0.24	0.75	-5.09	-0.97	-3.37

Fig. 3a and b show the absorption spectra of the polymers in solid films. **P-R1**, **P-R2**, **P-R3**, **P-R2-50** and **P-R2-100** all have similar absorption spectra to that of **PF** with an absorption peak at 393 nm attributed to the  $\pi$ - $\pi$ \* transition of the polymer backbone. The absorption of the three dopant units at 464 nm/499 nm/534 nm cannot be clearly detected. Fig. 3c and d shows the PL spectra of the polymers in solid films with an



Fig. 2 (a) Absorption spectra of MC-R1, MC-R2 and MC-R3 as well as PL spectrum of PF. (b) PL spectra of MC-R1, MC-R2 and MC-R3 in toluene.

excitation wavelength of 380 nm. The PL spectra of **P-R1**, **P-R2** and **P-R3** (see Fig. 3c) all exhibit both blue emission from the polyfluorene backbone and orange/red emission from the three dopant units. Since the absorbance of the excitation light at 380 nm by the red dopant units is negligible, we attribute the strong orange/red emission band to the Förster energy transfer from the polymer backbone to the three dopant units. This is also supported by the aforementioned spectral overlap. The red emission band in the PL spectrum of **P-R3** is relatively weak. This is probably caused by the low  $\Phi_{PL}$  of the red dopant unit as well as the poor energy transfer in the case of **P-R3**. For the PL spectra of **P-R2**, **P-R2-50** and **P-R2-100** (see Fig. 3d), with the increase of the dopant unit content, the relative intensity of the red emission band increases due to the more complete energy transfer.



Fig. 3 Absorption spectra (a, b) and PL spectra (c, d) of P-R1, P-R2, P-R3, P-R2-50 and P-R2-100 in thin films.



Fig. 4 EL spectra of the devices of P-R1, P-R2, P-R3, P-R2-50 and P-R2-100.

## **Electroluminescent properties**

In order to investigate the EL properties of the polymers, we fabricated single-layer devices with the structure of indium-tin oxide (ITO)/poly(styrene sulfonic acid) doped poly(ethylenedioxythiophene) (PEDOT : PSS) (40 nm)/polymer (90 nm)/Ca (10 nm)/Al (100 nm). Fig. 4 shows the EL spectra of these devices at the current densities of about 2 mA  $cm^{-2}$ . The corresponding emission maxima and CIE coordinates are listed in Table 2. The EL spectra of P-R1, P-R2 and P-R3 all exhibit predominant orange/red emission from the dopant units and negligible blue emission from the polyfluorene backbone. The device of P-R1 emits orange light with the emission maximum at 580 nm and CIE coordinates of (0.50, 0.47). P-R2 is a red electroluminescent polymer with the emission maximum at 615 nm and CIE coordinates of (0.59, 0.39). The device of P-R3 emits deep-red light with the emission maximum at 650 nm and CIE coordinates of (0.63, 0.32). Comparison of an EL spectrum with the corresponding PL spectrum shows that the contribution of the blue emission band is much smaller in the EL spectra compared to in the PL spectra. For example, the PL spectrum of P-R3 exhibits dominant blue emission from the polyfluorene backbone and only weak red emission from the dopant unit; in contrast, the EL spectrum of P-R3 exhibits predominant red emission from the dopant unit and negligible blue emission from the polymer



Fig. 5 Voltage-current density-brightness characteristics of the devices based on P-R2 (a) and P-R3 (b).

backbone. This difference in the EL and PL spectra is attributed to the charge trapping effect of the red dopant units.<sup>21,37</sup> In the EL process, both energy transfer and charge trapping contribute to the red dopant unit's emission. However, in the PL process, charge trapping does not occur and only energy transfer is involved. Hence, the relative intensity of the red emission band is much larger in the EL spectra compared to in the PL spectra. As shown in Fig. 4b, the blue emission bands in the EL spectra of **P-R2-50** and **P-R2-100** are more negligible than that in the EL spectrum of **P-R2** because of the more complete energy transfer and charge trapping at higher dopant unit contents.

Table 2 summarizes the EL performance of the single-layer devices of **P-R1**, **P-R2** and **P-R3**. All these devices exhibit very high EL efficiencies. For example, the device of **P-R2** emits red light with the CIE coordinates of (0.59, 0.39), turn-on voltage of 5.0 V and maximum brightness of 12170 cd m<sup>2</sup>. At a current density of 8.12 mA cm<sup>-2</sup>, it exhibits the maximum luminance efficiency of 5.04 cd A<sup>-1</sup>, power efficiency of 1.76 lm W<sup>-1</sup> and external quantum efficiency of 3.47%. Fig. 5a shows its voltage-current density-brightness curve. The device of **P-R3** emits deep red light with the CIE coordinates of (0.63, 0.32), turn-on voltage of 5.0 V and maximum brightness of 3240 cd m<sup>-2</sup>. At a current density of 10.68 mA cm<sup>-2</sup>, it shows the maximum luminance efficiency of 1.70 cd A<sup>-1</sup>, power efficiency of 0.68 lm W<sup>-1</sup> and external quantum efficiency of 2.75%. The voltage-current density-brightness characteristics of this device are shown in

Table 2EL performance of the devices of P-R1, P-R2, P-R3, P-R2-50 and P-R2-100

	Turn-on voltage/V	Luminous efficiency/cd A <sup>-1</sup>	Power efficiency/lm W <sup>-1</sup>	External quantum efficiency (%)	Maximum brightness/cd m <sup>-2</sup>	$\lambda_{\rm max}/{\rm nm}$	CIE coordinates $(x, y)$
P-R1	5.0	10.46	5.30	3.96	14570	580	$\begin{array}{c} (0.50, \ 0.47) \\ (0.59, \ 0.39) \\ (0.63, \ 0.32) \\ (0.60, \ 0.39) \\ (0.61, \ 0.38) \end{array}$
P-R2	5.0	5.04	1.76	3.47	12170	615	
P-R3	5.0	1.70	0.73	2.75	3240	650	
P-R2-50	5.5	4.13	1.73	2.86	9197	615	
P-R2-100	6.0	2.40	0.78	1.69	7810	617	



Fig. 6 Dependence of the external quantum efficiencies on the current densities of the devices of P-R1, P-R2, P-R3, P-R2-50 and P-R2-100.

Fig. 5b. The dependence of the external quantum efficiencies on the current densities of the three devices is shown in Fig. 6a. The high EL efficiencies of the red electroluminescent polymers of the dopant/host system are attributed to the energy transfer and charge trapping from the polyfluorene backbone to the three dopant units.<sup>21,37</sup>

Table 2 also lists the EL performances of the devices of **P-R2**, **P-R2-50** and **P-R2-100**. It can be seen that the increase of the dopant unit contents leads to the decrease of the EL efficiencies (see Fig. 6b) and the increase of the turn-on voltages of the resulting devices. The former is attributed to the exciton quenching of the dopant unit at high content and the latter is due to the charge trapping effect of the dopant unit. At low driving voltage, the electrons/holes injected from the cathode/anode are trapped by the dopant units near the cathode/anode are trapped by the dopant units of the doposite charge carriers. Therefore, high turn-on voltage is required for the device to emit light. The higher the dopant unit content, the more charge carrier traps, the higher the turn-on voltage.

In comparison, we fabricated a control device with a blend of **PF** and 0.3 mol% **MC-R3** as the emissive layer. Its EL spectrum shows dominant red emission from **MC-R3** and negligible blue emission from **PF**. This device emits deep red light with the maximum luminous efficiency of 1.25 cd  $A^{-1}$ and power efficiency of 0.64 lm  $W^{-1}$ . This performance is somewhat inferior to that of the device based on **P-R3**, indicating that covalently attaching the dopant to the host and molecular dispersion of the dopant in the host are favorable for the excellent EL performance of the resulting polymers.

## Conclusion

In summary, we have developed a series of red electroluminescent polymers of dopant/host systems by covalently attaching very small amounts of red emissive dopant units (2,1,3-benzothiadiazole derivative units) to the side chain of a polymer host (polyfluorene). Their EL spectra exhibit predominant red emission from the dopant units due to the energy transfer and charge trapping from the polymer host to the dopant units. Single-layer devices (ITO/PEDOT/polymer/Ca/ Al) of these polymers emit red light with a maximum at 615 nm and an external quantum efficiency of 3.47%, or with a maximum at 650 nm and an external quantum efficiency of 2.75%. The remarkable EL performance is attributed to the energy transfer and charge trapping from the host to the red dopant unit as well as the molecular dispersion of the small amount of red dopant units in the host. Our results indicate that intramolecular dopant/host systems are an efficient strategy to develop light emitting polymers with very high EL efficiencies and different emission colors (blue, green, red and white). Further investigation of deep red electroluminescent polymers of dopant/host systems with enhanced PL quantum efficiency of deep-red dopant unit is in progress in our laboratory.

## **Experimental**

The synthesis of 4-diphenylamino-1-bromobenzene (1), <sup>27</sup> tributyl(4-(diphenylamino)phenyl)stanne (2), <sup>27</sup> 2-(4-(diphenyl-amino)phenyl)thiophene (8), <sup>27</sup> tributyl(5-(4-(diphenylamino) phenyl)thienyl-2)stannane (9) <sup>27</sup>, 4,7-dibromo-2,1,3-benzothia-diazole, <sup>38</sup> 9,9-dioctyl-2,7-dibromofluorene (13)<sup>39</sup> and 9,9-dioctyl-2,7-bis(trimethyleneborate)fluorene (14)<sup>39</sup> have been reported previously.

#### 4-(N-Phenyl-N-(4-methoxy)phenylamino)-1-bromobenzene (3)

A mixture of 4-bromo-diphenylamine (4.50 g, 20.0 mmol), 4-methoxy-1-iodobenzene (5.76 g, 24.5 mmol), CuCl (0.20 g, 2.0 mmol), 1,10-phenanthroline monohydrate (0.40 g, 2.0 mmol), KOH (11.2 g, 200 mmol) and toluene (45 mL) was heated to reflux and stirred for 36 hours. After workup, the reaction mixture was poured into brine and extracted with  $CH_2Cl_2$ . The organic layer was washed with brine and then dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography on silica gel to afford the title compound as a white solid. Yield: 4.75 g (67%).

## Tributyl(4-(*N*-phenyl-*N*-(4-methoxy)phenylamino)phenyl)stannane (4)

To a solution of 3 (1.77 g, 5.0 mmol) in THF (20 mL) at -78 °C was added n-BuLi (1.6 M solution in hexane, 3.2 mL, 5.2 mmol). After stirring for 1 hour, the mixture was added to (n-Bu)<sub>3</sub>SnCl (1.5 mL, 5.5 mmol). The resulting mixture was slowly warmed to room temperature and stirred overnight. After workup, the mixture was poured into aqueous NaHCO<sub>3</sub> and extracted with hexane. The organic layer was washed with water and then dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent afforded the title compound as a light-yellow liquid. Yield: 2.83 g (100%).

# 4-(4-(Diphenylamino)phenyl)-7-bromo-2,1,3-benzothiadiazole (5)

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (2.95 g, 10.0 mmol), **2** (1.60 g, 3.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.034 g,

0.3 mmol) and toluene (50 mL) was heated to 100 °C and stirred in the dark for 24 hours. After workup, the mixture was poured into aqueous KF and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and then dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography on silica gel to afford the title compound as an orange-yellow solid. Yield: 0.92 g (67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.88 (d, 1H), 7.80 (dd, 2H), 7.53 (d, 1H), 7.21–7.16 (m, 4H), 7.32–7.25 (m, 6H), 7.06 (t, 2H).

## 4-(4-(Diphenylamino)phenyl)-7-(4-(*N*-phenyl-*N*-(4-methoxy)-phenylamino)phenyl)-2,1,3-benzothiadiazole (MC-R1)

A mixture of **5** (0.91 g, 2.0 mmol), **4** (1.70 g, 3.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.034 g, 0.3 mmol) and toluene (30 mL) was heated to 100 °C and stirred in the dark for 24 hours. After workup, the mixture was poured into aqueous KF and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and then dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography on silica gel to afford the title compound as an orange-red solid. Yield: 1.11 g (84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.90 (dd, 3H), 7.77 (s, 2H), 7.38–7.18 (m, 19H), 7.12–7.02 (m, 3H), 6.91 (dd, 2H), 3.86 (s, 3H). Anal. calcd: C, 79.11; H, 4.94; N, 8.58. Found: C, 79.01; H, 4.46; N, 8.67%.

# 2-(4-(*N*-Phenyl-*N*-(4-methoxy)phenylamino)phenyl)thiophene (6)

Compound **6** was synthesized following the same procedure for **MC-R1** using **3** and tributyl(thienyl-2)stannane instead of **5** and **4**. Yield: 56%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.48 (d, 2H), 7.27 (m, 4H), 7.12–7.04 (m, 8H), 6.89 (d, 2H), 3.85 (s, 3H).

## Tributyl(5-(4-(*N*-phenyl-*N*-(4-methoxy)phenylamino)phenyl)thienyl-2)stannane (7)

Compound 7 was synthesized following the same procedure for 4 using 6 instead of 3. Yield: 99%.

## 4-(5-(4-(*N*-Phenyl-*N*-(4-methoxy)phenylamino)phenyl)thienyl-2)-7-bromo-2,1,3-benzothiadiazole (10)

Compound **10** was synthesized following the same procedure for **5** using **7** instead of **2**. Yield: 37%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.12 (d, 1H), 7.88 (d, 1H), 7.73 (d, 1H), 7.56 (d, 4h), 7.29 (m, 4H), 7.15–7.05 (m, 7H), 6.93 (d, 2H), 3.86 (s, 3H).

## 4-(5-(4-(*N*-Phenyl-*N*-(4-methoxy)phenylamino)phenyl)thienyl-2)-7-(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole (MC-R2)

Compound **MC-R2** was synthesized following the same procedure for **MC-R1** using **2** and **10** instead of **5** and **4**. Yield: 78%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.15 (d, 1H), 7.91 (d, 2H), 7.74 (d, 1H), 7.58 (d, 2H), 7.36–7.08 (m, 23H), 6.91 (d, 2H), 3.86 (s, 3H). Anal. calcd: C, 76.81; H, 4.66; N, 7.62. Found: C, 77.34; H, 4.26; N, 7.09%.

## 4-(5-(4-(*N*-Phenyl-*N*-(4-methoxy)phenylamino)phenyl)thienyl-2)-7-(5-(4-(diphenylamino)phenyl)thienyl-2)-2,1,3benzothiadiazole (MC-R3)

Compound **MC-R3** was synthesized following the same procedure for **MC-R1** using **9** and **10** instead of **5** and **4**. Yield: 86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.11 (d, 2H), 7.87 (s, 2H), 7.56 (t, 4H), 7.32–7.25 (m, 8H), 7.16–7.03 (m, 15H), 6.87 (d, 2H), 3.82 (s, 3H). Anal. calcd: C, 74.97; H, 4.44; N, 6.86. Found: C, 74.63; H, 5.08; N, 6.23%.

## 9-Hexyl-2,7-dibromofluorene (11)

To a solution of fluorene (8.30 g, 50.0 mmol) in dry THF (150 mL) at -78 °C was added n-C<sub>4</sub>H<sub>9</sub>Li (1.6 M solution in hexane, 31.2 mL, 49.9 mmol). After stirring for one hour, the mixture was added to n-C<sub>6</sub>H<sub>13</sub>Br (8.3 mL, 58.4 mmol). The resulting mixture was slowly warmed to room temperature and stirred overnight, followed by pouring into water and extraction with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and then dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent afforded a colorless liquid. The liquid was mixed with CHCl<sub>3</sub> (100 mL) and anhydrous FeCl<sub>3</sub> (0.51 g, 0.31 mmol). Bromine (5.7 mL, 110 mmol) was added dropwise to the mixture in the dark and the resulting mixture was stirred at room temperature in the dark for 24 hours. After workup, the mixture was washed subsequently with aqueous NaHSO3 and water, followed by drying with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent afforded the crude product, which was further purified by recrystallization in ethanol to give the title compound as a white solid. Yield: 13.68 g (67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.65 (s, 2H), 7.60 (d, 2H), 7.52 (d, 2H), 4.00–3.97 (m, 1H), 2.04–1.96 (m, 2H), 1.25–1.15 (m, 8H), 0.88 (t, 3H).

## 9-Hexyl-9-(6-bromohexyl)-2,7-dibromofluorene (12)

A mixture of **11** (8.1 g, 20 mmol),  $(n-C_4H_9)_4$ NBr (0.32 g, 1.0 mmol), 1,6-dibromohexane (15.0 mL, 100 mmol), toluene (30 mL) and aqueous NaOH (50 wt%, 50 mL) was stirred at 80 °C for 18 hours. After workup, the organic layer was separated and washed subsequently with dilute chloric acid, aqueous NaHCO<sub>3</sub> and water, followed by drying with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent and the excessive 1,6-dibromohexane at reduced pressure afforded the crude product, which was further purified by column chromatography to give the title compound as a white solid. Yield: 9.80 g (86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.54 (d, 2H), 7.46 (m, 4H), 3.31 (t, 2H), 1.97–1.90 (m, 4H), 1.70 (m, 2H), 1.22–1.07 (m, 12H), 0.80 (t, 3H), 0.62 (br, 4H).

## Synthesis of Monomer R1

To a solution of **MC-R1** (0.33 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) at -78 °C was added dropwise BBr<sub>3</sub> (1.0 M solution in CH<sub>2</sub>Cl<sub>2</sub>, 4.0 mL, 4.0 mmol) and the mixture was stirred at this temperature for 2 hours. The reaction mixture was slowly warmed to room temperature and stirred for 24 hours, followed by the addition of several drops of water. After removal of the solvent with reduced pressure at room temperature, the residual was mixed with K<sub>2</sub>CO<sub>3</sub> (2.07 g, 15 mmol), 2,7-dibromo-9-hexyl-9-(6-bromohexyl)fluorene (0.40 g, 0.7 mmol) and ethanol

(15 mL) and then was heated to reflux for 24 hours. After workup, the mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and then dried with Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by silica column chromatography to give the title compound as an orange-red solid. Yield: 0.085 g (15%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.90 (t, 4H), 7.67 (s, 2H), 7.56 (d, 2H), 7.51–7.48 (m, 4H), 7.36–7.04 (m, 21H), 6.86 (d, 2H), 3.88 (t, 2H), 2.01–1.93 (m, 4H), 1.64 (m, 2H), 1.29–1.07 (m, 10H), 0.82 (t, 3H), 0.65 (br, 4H). Anal. calcd: C, 71.27; H, 5.36; N, 4.96. Found: C, 72.34; H, 4.78; N, 4.46%.

#### Synthesis of Monomer R2

**Monomer R2** was synthesized following the same procedure for **Monomer R1** using **MC-R2** instead of **MC-R1**. Yield: 17%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.10 (d, 1H), 7.87 (d, 2H), 7.70 (d, 1H), 7.55–7.50 (m, 4H), 7.47–7.44 (m, 4H), 7.36– 7.08 (m, 23H), 6.80 (d, 2H), 3.84 (br, 2H), 1.95–1.89 (m, 4H), 1.60 (m, 2H), 1.25–1.05 (m, 10H), 0.78 (t, 3H), 0.61 (br, 4H). Anal. calcd: C, 70.41; H, 5.16; N, 4.63. Found: C, 71.63; H, 4.98; N, 4.71%.

#### Synthesis of Monomer R3

**Monomer R3** was synthesized following the same procedure for **Monomer R1** using **MC-R3** instead of **MC-R1**. Yield: 14%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.10 (br, 2H), 7.16 (br, 2H), 7.61–7.51 (m, 6H), 7.46–7.44 (m, 4H), 7.32–7.05 (m, 23H), 6.81 (t, 2H), 3.84 (br, 2H), 1.95–1.89 (m, 4H), 1.61 (m, 2H), 1.26–1.05 (m, 10H), 0.79 (t, 3H), 0.62 (br, 4H). Anal. calcd: C, 69.65; H, 4.99; N, 4.33. Found: C, 70.03; H, 5.26; N, 4.56%.

#### General procedure of the polymers

A mixture of 2,7-dibromo-9,9-dioctylfluorene (13), 2,7-bis-(trimethyleneborate)-9,9-dioctylfluorene (14), corresponding red-unit-containing comonomer, Aliquat 336 (0.10 g. 0.25 mmol), tetrakis(triphenylphosphine)palladium (11.0 mg, 0.01 mmol) under argon was added 2.5 mL degassed 2 M aqueous potassium carbonate and 6 mL degassed toluene. The resulting mixture was stirred in the dark at 90 °C for 48 hours and then poured into methanol. The precipitate was collected by filtration, dried and then dissolved in dichloromethane. The solution was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After most of the solvent had been removed, the residue was poured into stirred methanol to give a fiber-like solid. The polymer was further purified by extraction with acetone for 24 hours. The reprecipitation procedure in dichloromethane-methanol was then repeated several times. The final product was obtained after drying in vacuum with a yield of 45-60%.

**PF**: light yellow fibre. **13** (0.2742 g, 0.500 mmol) and **14** (0.2742 g, 0.500 mmol) were used in the polymerization. GPC:  $M_n = 2.47 \times 10^4$ , PDI = 2.09. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.87 (d, 2H), 7.72 (br, 4H), 2.10 (br, 4H), 1.14 (br, 24H), 0.81 (t, 6H). Anal. Calcd: C, 89.69; H, 10.31. Found: C, 89.08; H, 10.02%. **P-R1**: orange-red fibre. **13** (0.2726g,

0.497 mmol), 14 (0.2792 g, 0.500 mmol) and Monomer R1 (0.0033 g, 0.003 mmol) were used in the polymerization. GPC:  $M_{\rm n} = 2.16 \times 10^4$ , PDI = 2.07. **P-R2**: red fibre. **13** (0.2726g, 0.497 mmol), 14 (0.2792 g, 0.500 mmol) and Monomer R2 (0.0036 g, 0.003 mmol) were used in the polymerization. GPC:  $M_{\rm n} = 2.63 \times 10^4$ , PDI = 2.03. **P-R3**: violet-red fibre. **13** (0.2726 g, 0.497 mmol), 14 (0.2792 g, 0.500 mmol) and Monomer R3 (0.0040 g, 0.003 mmol) were used in the polymerization. GPC:  $M_{\rm n} = 2.24 \times 10^4$ , PDI = 2.09. P-R2-50: red fibre. 13 (0.2713 g, 0.495 mmol), 14 (0.2792 g, 0.500 mmol) and Monomer R2 (0.0060 g, 0.005 mmol) were used in the polymerization. GPC:  $M_{\rm p} = 2.43 \times 10^4$ , PDI = 2.14. P-R2-100: red fibre. 13 (0.2687 g, 0.490 mmol), 14 (0.2792 g, 0.500 mmol) and Monomer R2 (0.0123 g, 0.010 mmol) were used in the polymerization. GPC:  $M_{\rm p}$  =  $2.11 \times 10^4$ , PDI = 2.00. P-R1, P-R2, P-R3, P-R2-50 and P-R2-100 all exhibited similar <sup>1</sup>H NMR and elemental analysis results as those of PF.

#### Instruments

<sup>1</sup>H NMR spectra were recorded with a Bruker Avance 300 NMR spectrometer. The elemental analyses were performed using a Bio-Rad elemental analysis system. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Waters 410 instrument with polystyrene as standard and THF as eluent. UV-Vis absorption spectra were measured by a Perkin-Elmer Lambda 35 UV/Vis spectrometer. Photoluminescence spectra were recorded by a Perkin-Elmer LS50B spectrofluorometer. Cyclic voltammograms of polymer films on glassy carbon electrodes were recorded on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system at room temperature in a solution of n-Bu<sub>4</sub>NClO<sub>4</sub> (0.10 M) in fresh acetonitrile at a scan rate of 100 mV s<sup>-1</sup>. A Pt wire and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. Cyclic voltammograms of small organic molecules were carried out with their solution in fresh dichloromethane. Other conditions were the same as for polymer films except that a Pt disc was used as the working electrode. The EL spectra and currentvoltage and brightness-voltage characteristics of devices were measured with a Spectrascan PR650 spectrophotometer in the forward direction and a computer-controlled Keithley 2400 instrument under ambient conditions.

#### **Device fabrication**

ITO glass plates were degreased in an ultrasonic solvent bath and then dried in a heating chamber at 120 °C. The PEDOT : PSS was spin-coated on the cleaned ITO at 3000 rpm for 60 s and then baked for 15 min at 120 °C to give an approximate thickness of 40 nm. The polymer layer (approximately 90 nm) was then spin-coated onto the PEDOT/ITO coated glass substrate in fresh toluene solution (15 mg ml<sup>-1</sup>) under ambient atmosphere. Finally, a thin layer of calcium (10 nm) followed by a layer of aluminium (100 nm) was deposited in a vacuum thermal evaporator through a shadow mask at a pressure of  $3 \times 10^{-3}$ -5  $\times 10^{-3}$  Pa. The active area of the diodes was 10 mm<sup>2</sup>.

#### References

- J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
- 2 M. T. Bernius, M. Inbasekaran, J. O'Brien and W. S. Wu, Adv. Mater., 2000, 12, 1737.
- 3 D. Neher, Macromol. Rapid Commun., 2001, 22, 1365.
- 4 U. Scherf and E. J. W. List, Adv. Mater., 2002, 14, 477.
- 5 T. Miteva, A. Meisel, W. Knoll, H. G. Nothofer, U. Scherf, D. C. Muller, K. Meerholz, A. Yasuda and D. Neher, *Adv. Mater.*, 2001, **13**, 565.
- 6 M. Bernius, M. Inbasekaran, E. P. Woo, W. S. Wu and L. Wujkoski, J. Mater. Sci.: Mater. Electron., 2000, 11, 111.
- 7 C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker and K. Meerholz, *Nature*, 2003, **421**, 829.
- 8 Q. Hou, Q. M. Zhou, Y. Zhang, W. Yang, R. Q. Yang and Y. Cao, *Macromolecules*, 2004, 37, 6299.
- 9 Q. Hou, Y. S. Xu, W. Yang, M. Yuan, J. B. Peng and Y. Cao, J. Mater. Chem., 2002, 12, 2887.
- 10 J. Luo, J. B. Peng, Y. Cao and Q. Hou, Appl. Phys. Lett., 2005, 87, 261103.
- 11 R. Q. Yang, R. Y. Tian, Q. Hou, W. Yang and Y. Cao, *Macromolecules*, 2003, 36, 7453.
- 12 J. Yang, C. Y. Jiang, Y. Zhang, R. Q. Yang, W. Yang, Q. Hou and Y. Cao, *Macromolecules*, 2004, 37, 1211.
- 13 S. Beaupre and M. Leclerc, Adv. Funct. Mater., 2002, 12, 192.
- 14 N. S. Cho, D. H. Hwang, B. J. Jung, E. Lim, J. Lee and H. K. Shim, *Macromolecules*, 2004, 37, 5265.
- 15 N. S. Cho, D. H. Hwang, J. I. Lee, B. J. Jung and H. K. Shim, *Macromolecules*, 2002, 35, 1224.
- 16 L.-H. Chan, Y.-D. Lee and C.-T. Chen, *Macromolecules*, 2006, **39**, 3262.
- 17 Q. Peng, Z. Y. Lu, Y. Huang, M. G. Xie, S. H. Han, J. B. Peng and Y. Cao, *Macromolecules*, 2004, 37, 260.
- 18 N. S. Cho, J.-H. Park, S.-K. Lee, J. Lee, H.-K. Shim, M.-J. Park, D.-H. Hwang and B.-J. Jung, *Macromolecules*, 2006, **39**, 177.
- 19 I. S. Millard, Synth. Met., 2000, 111-112, 119.
- 20 J. Liu, C. C. Min, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *Appl. Phys. Lett.*, 2006, 88, 083505.

- 21 J. Liu, G. L. Tu, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *J. Mater. Chem.*, 2006, 16, 1431.
- 22 G. L. Tu, Q. G. Zhou, Y. X. Cheng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *Appl. Phys. Lett.*, 2004, 85, 2172.
- 23 G. L. Tu, C. Y. Mei, Q. G. Zhou, Y. X. Cheng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *Adv. Funct. Mater.*, 2006, 16, 101.
- 24 J. Liu, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *Adv. Funct. Mater.*, 2006, 16, 957.
- 25 J. Liu, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *Adv. Mater.*, 2005, **17**, 2974.
- 26 J. Liu, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Mater.*, 2007, **19**, 531.
- 27 J. Liu, X. Guo, L. J. Bu, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Funct. Mater*, DOI: 10.1002/adfm.200600988, in press.
- 28 J. Liu, S. Y. Shao, L. Chen, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Mater.*, 2007, **19**, 1859.
- 29 J. Liu, L. Chen, S. Y. Shao, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Mater.*, DOI: 10.1002/adma.200701104, in press.
- 30 K. R. J. Thomas, J. T. Lin, M. Velusamy, Y.-T. Tao and C.-H. Cheun, Adv. Funct. Mater., 2004, 14, 83.
- 31 C. Ego, D. Marsitzky, S. Becker, J. Zhang, A. C. Grimsdale, K. Müllen, J. D. MacKenzie, C. Silva and R. H. Friend, J. Am. Chem. Soc., 2003, 125, 437.
- 32 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457.
- 33 A. J. Bard and L. A. Faulkner, Electrochemical Methods— Fundamentals and Applications, Wiley, New York, 1984.
- 34 K. Utsugi and S. Takano, J. Electrochem. Soc., 1992, 139, 3610.
- 35 H. Suzuki and S. Hoshino, J. Appl. Phys., 1996, 79, 8816.
- 36 M. S. Wrighton, D. S. Ginley and D. L. Morse, J. Phys. Chem., 1974, 78, 2229.
- 37 S. E. Shaheen, B. Lippelen, N. Peyghambarian, J.-F. Wang, J. D. Anderson, E. A. Mash, P. A. Lee, N. R. Armstrong and Y. Kawabe, *J. Appl. Phys.*, 1999, **85**, 7939.
- 38 K. Pilgram, M. Zupan and R. Skiles, J. Heterocycl. Chem., 1970, 7, 629.
- 39 X. W. Chen, J. L. Liao, Y. M. Liang, M. O. Ahmed, H. E. Tseng and S.-A. Chen, J. Am. Chem. Soc., 2003, 125, 636.