# Green light-emitting polyfluorenes with improved color purity incorporated with 4,7-diphenyl-2,1,3-benzothiadiazole moieties

Jun Liu, Laju Bu, Jinpeng Dong, Quanguo Zhou, Yanhou Geng, Dongge Ma, Lixiang Wang,\* Xiabin Jing and Fosong Wang

Received 2nd January 2007, Accepted 18th April 2007 First published as an Advance Article on the web 30th April 2007 DOI: 10.1039/b700004a

By incorporating 4,7-diphenyl-2,1,3-benzothiadiazole instead of 2,1,3-benzothiadiazole into the backbone of polyfluorene, we developed a novel series of green light-emitting polymers with much improved color purity. Compared with the state-of-the-art green light-emitting polymer, poly(fluorene-co-benzothiadiazole) ( $\lambda_{max} = 537$  nm), the resulting polymers ( $\lambda_{max} = 521$  nm) showed 10–20 nm blueshifted electroluminescence (EL) spectra and greatly improved color purity because the insertion of two phenylene units between the 2,1,3-benzothiadiazole unit and the fluorene unit reduced the effective conjugation length in the vicinity of the 2,1,3-benzothiadiazole unit. As a result, the resulting polymers emitted pure green light with CIE coordinates of (0.29, 0.63), which are very close to (0.26, 0.65) of standard green emission demanded by the National Television System Committee (NTSC). Moreover, the insertion of the phenylene unit did not affect the photoluminescence (PL) and EL efficiencies of the resulting polymers. PL quantum efficiency in solid films up to 0.82 was demonstrated. Single-layer devices (ITO/PEDOT/polymer/Ca/Al) of these polymers exhibited a turn-on voltage of 4.2 V, luminous efficiency of 5.96 cd A<sup>-1</sup> and power efficiency of 2.21 lm W<sup>-1</sup>. High EL efficiencies and good color purities made these polymers very promising for display applications.

### Introduction

In the past decade, fluorene-based  $\pi$ -conjugated polymers have emerged as the most promising candidates for use as emitting materials in polymeric light-emitting diodes (PLEDs) because of their high photoluminescence (PL) and electoluminescence (EL) efficiencies, good thermal and spectral stability and color tunability in the full visible range.<sup>1–8</sup> Normally, polyfluorene emits blue light with a large bandgap. By incorporating a narrow bandgap unit into the polyfluorene backbone, the emission colors of polyfluorene derivatives can be tuned over the entire visible range.<sup>9–32</sup> The most commonly used narrow bandgap unit is the electron-deficient 2,1,3-benzothiadiazole. Indeed, poly(fluorene-co-benzothiadiazole) has become the state-of-the-art green light-emitting polymer for PLEDs because of its good thermal and electrical stability, high PL and EL efficiency.<sup>9–18</sup>

High efficiency and long lifetime of green PLEDs have been realized. Thus, the dominant issue for green light-emitting polymers is the color purity. Since the human eye is very sensitive to light in the green–yellow region, pure green emission is difficult to achieve with polymers because EL spectra of polymers usually have large FWHM values (FWHM: full width at half maximum).<sup>14</sup> Therefore, most green emitters appear either bluish-green or yellowish-green. For example, the emission color of poly(fluorene-co-benzothiadiazole) is

green–yellow with CIE coordinates (0.39, 0.57). Hence, it is still a great challenge for the material chemist to improve the color purity of poly(fluorene-co-benzothiadiazole) while maintaining its high PL and EL efficiencies. Covion Corp. has developed a pure green light-emitting polymer with CIE coordinates of (0.34, 0.59).<sup>14,15</sup> Cambridge Display Technology (CDT) has announced a pure green light-emitting polymer with CIE coordinates of (0.31, 0.58), however, their detailed chemical structures and EL performance were undisclosed.<sup>13</sup> Shim and coworkers have reported a pure green light-emitting polyfluorene derivative with CIE coordinates of (0.29, 0.63), however, its EL performance was poor.<sup>26</sup>

In poly(fluorene-co-benzothiadiazole), light is emitted from the vicinity of the benzothiadiazole unit (see Scheme 1) because of energy transfer from the wide bandgap fluorene unit to the narrow bandgap benzothiadiazole vicinity unit.<sup>16</sup> Therefore, its emission color can be fine tuned by modifying the chemical structure of the benzothiadiazole vicinity unit. In this article, we report a series of pure green light-emitting copolymers based on fluorene and 4,7-diphenyl-2,1,3-benzothiadiazole, aimed at improving the color purity of the state-of-the-art green light-emitting poly(fluorene-co-benzothiadiazole). As shown in Scheme 1, in the new polymers, the insertion of the two phenylene moieties in the vicinity of the benzothiadiazole unit makes the vicinity of the benzothiadiazole unit a little more twisted than before. Therefore, the emission spectra in the vicinity of the benzothiadiazole unit and consequently of the resulting polymers are slightly blueshifted and pure green emission is expected. As a result, the resulting polymers emit pure green light with the emission maximum at 521 nm and CIE coordinates of (0.29, 0.63), which are very close to the

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry and Graduate School of Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: lixiang@ciac.jl.cn; Fax: +86-431-85685653



Scheme 1 Schematic illustration of the reason for the slight spectral blueshift resulting from incorporating 4,7-diphenyl-2,1,3-benzothiadiazole instead of 2,1,3-benzothiadiazole into polyfluorene.

(0.26, 0.65) of standard green emission demanded by the National Television System Committee (NTSC). Moreover, the insertion of the two phenylene units does not affect the EL efficiency of the resulting polymers. Their single-layer devices (ITO/PEDOT/polymer/Ca/Al) exhibit a luminous efficiency of 8.25 cd  $A^{-1}$  and a power efficiency of 4.45 lm  $W^{-1}$ .

#### Experimental

#### Materials

All the reagents and solvents used for the syntheses were purchased from Aldrich or Acros companies and used without further purification. 4,7-Dibromo-2,1,3-benzothiadiazole (1),<sup>33</sup> 9,9-dioctyl-2,7-dibromofluorene (4)<sup>34</sup> and 9,9-dioctyl-2,7-bis-(trimethyleneborate)fluorene (5)<sup>34</sup> were prepared following already published procedures. All reactions were performed under a dry argon atmosphere.

#### 4,7-Diphenyl-2,1,3-benzothiadiazole (2)<sup>35</sup>

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (2.94 g, 10 mmol), phenylboric acid (2.56 g, 21 mmol), potassium carbonate (5.52 g, 40 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.094 g, 0.08 mmol), H<sub>2</sub>O (20 mL) and toluene (50 mL) was heated at 90 °C for 5 h. After cooling, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the solvent was evaporated, the crude product was recrystallized from ethanol to afford the title compound as a yellow solid. Yield: 2.39 g (83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.96 (d, 4H), 7.80 (s, 2H), 7.56 (t, 4H), 7.47 (d, 2H).

#### 4,7-Bis(4-bromophenyl)-2,1,3-benzothiadiazole (3)

A solution of bromine (10 mL, 194 mmol) in chloroform (10 mL) was added dropwise to a mixture of 4,7-diphenyl-2,1,3-benzothiadiazole (2.39 g, 8.3 mmol), iodine (0.12 g, 0.47 mmol) and chloroform (30 mL). The resulting mixture was stirred at room temperature for 12 h. After workup, the solid was filtered off and washed sequentially with aqueous NaHSO<sub>3</sub>, water and methanol to afford the crude product. Recrystallization in toluene gave the title compound as yellow needles. Yield: 2.88 g (78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.86 (d, 4H), 7.77 (s, 2H), 7.68 (d, 4H). Anal. calcd for

C<sub>18</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>S: C, 48.46; H, 2.26; N, 6.28. Found: C, 48.09; H, 2.53; N, 6.14.

#### General procedure of Suzuki polymerization<sup>36</sup>

To a mixture of 2,7-dibromo-9,9-dioctylfluorene (4), 2,7-dibromo-9,9-bis(trimethyleneborate)fluorene (5), 4,7-dibromo-2,1,3-benzothiadiazole (1) or 4,7-bis(4-bromophenyl)-2,1,3benzothiadiazole (3) with a corresponding feed ratio, Aliquat 336 (0.10 g, 0.25 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (11.0 mg, 0.01 mmol) under argon was added 2 M aqueous K<sub>2</sub>CO<sub>3</sub> (2.5 mL) and toluene (7 mL). The mixture was heated to 90 °C and stirred in the dark for 48 h, followed by being poured into methanol. The precipitate was collected by filtration and dried and then dissolved in dichloromethane. The solution was then washed with water and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of most of the solvent, the residue was poured into methanol to give polymer fibre. The polymer was purified by a Soxhlet extraction in acetone for 24 h. The reprecipitation procedure in dichloromethane/methanol was then repeated several times. The final product, a vellowish-green fibre, was obtained after drying in vacuum with a yield of 45-60%.

**PFG5:** 4 (0.2468 g, 0.45 mmol), **5** (0.2792 g, 0.5 mmol) and **3** (0.0223 g, 0.05 mmol) were used in the polymerization. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.11 (br, 0.26H), 7.88 (br, 2.26H), 7.69 (d, 4H), 7.47 (br, 0.21H), 2.11 (br, 3.87H), 1.36 (br, 22.30H), 0.82 (t, 10.73H). Anal. calcd: C, 89.16; H, 10.05; N, 0.366. Found: C, 88.12; H, 10.07; N, 0.60.

**PFG10**: **4** (0.2193 g, 0.40 mmol), **5** (0.2792 g, 0.50 mmol) and **3** (0.0446 g, 0.10 mmol) were used in the polymerization. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.11 (br, 0.48H), 7.83 (br, 2.63H), 7.68 (d, 4H), 7.47 (br, 0.39H), 2.11 (br, 3.88H), 1.36 (br, 22.06H), 0.82 (t, 10.47H). Anal. calcd: C, 88.62; H, 9.79; N, 0.74. Found: C, 88.14; H, 10.01; N, 0.69.

**PFG20: 4** (0.1645 g, 0.30 mmol), **5** (0.2792 g, 0.50 mmol) and **3** (0.0892 g, 0.20 mmol) were used in the polymerization. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.11 (br, 1.08H), 7.88 (br, 3.52H), 7.69 (d, 4H), 7.47 (br, 0.88H), 2.11 (br, 3.62H), 1.36 (br, 22.28H), 0.82 (t, 10.63H). Anal. calcd: C, 87.49; H, 9.25; N, 1.52. Found: C, 86.37; H, 8.23; N, 1.63.

**PFY10**: **4** (0.2193 g, 0.40 mmol), **5** (0.2792 g, 0.5 mmol) and **1** (0.0294 g, 0.10 mmol) were used in the polymerization. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.09 (br, 0.32H), 8.01 (br, 0.43H), 7.93 (br, 0.52H), 7.85 (d, 0.98H), 7.68 (d, 4H), 7.49 (br,

View Article Online

0.52H), 2.11 (br, 3.75H), 1.36 (br, 22.28H), 0.82 (t, 10.87H). Anal. calcd: C, 88.36; H, 9.98; N, 0.77. Found: C, 88.17; H 10.23; N, 0.61.

#### Instrument

<sup>1</sup>H NMR spectra were recorded with a Bruke Avance 300 NMR spectrometer. Elemental analysis was carried out using a Bio-Rad elemental analysis system. The number- and weightaverage molecular weights ( $M_n$  and  $M_w$ , respectively) of the polymers were determined by gel permeation chromotagraphy (GPC) with a Waters 410 instrument with polystyrene as the standard and THF as the eluent. UV-Vis absorption spectra were measured by a Perkin-Elmer Lambda 35 UV-Vis spectrometer. PL and EL spectra were recorded with a Perkin-Elmer LS50B spectrofluorometer. Cyclic voltammograms of polymer films on a glassy carbon electrode were recorded on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system at room temperature in a solution of  $nBu_4NClO_4$  (0.10 M) in 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. The current-voltage and brightness-voltage curves of the devices were measured using a Keithley 2400/2000 current/ voltage source unit calibrated with a silicon photodiode.

#### **Device fabrication**

The indium-tin oxide (ITO) glass plates were degreased in an ultrasonic solvent bath and then dried in a heating chamber at a temperature of 120  $^{\circ}$ C. The poly(styrene sulfonic acid) doped

poly(ethylenedioxythiophene) (PEDOT) was spin-coated on the treated 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 at ambient atmosphere with their solution in chloroform (10 mg ml<sup>-1</sup>). Finally, a thin layer of calcium (10 nm) followed by a layer of aluminum (100 nm) was deposited in a vacuum thermal evaporator through a shadow mask at a pressure of 3 ×  $10^{-3}$  Pa. The active area of the diodes was 16 mm<sup>2</sup>.

#### **Result and discussion**

#### Synthesis and characterization

As shown in Scheme 2, the key monomer, 4,7-bis(4-bromophenyl)-2,1,3-benzothiadiazole (3), was synthesized by the bromination of 4,7-diphenyl-2,1,3-benzothiadiazole (2), which was prepared by the Suzuki coupling of 4,7-dibromo-2,1,3benzothiadiazole and phenyl boric acid. The copolymers were prepared by Suzuki polycondensation of 2,7-dibromo-9,9dioctylfluorene (4), 2,7-bis(trimethyleneborate)-9,9-dioctylfluorene (5) and 4,7-di(4-bromophenyl)-2,1,3-benzothiadiazole (3). The feed ratios of the three comonomers were 45:50:5, 40:50:10 and 30:50:20. The corresponding polymers are named as PFG5, PFG10 and PFG20, respectively. The actual 4,7-diphenyl-2,1,3-benzothiadiazole unit (DPBT) content in the copolymers, calculated from their <sup>1</sup>H NMR, is very close to the feed ratios of **3** as shown in Table 1. For comparison, we also used 4,7-dibromo-2,1,3-benzothiazole instead of 4,7-di(4-bromophenyl)-2,1,3-benzothiadiazole to carry out



Scheme 2 Chemical structures and synthetic routes of the monomer and copolymers.

 Table 1
 Molecular weight and composition of PFG5, PFG10, PFG20

 and PFY10

Polymer	Feed ratio <sup>a</sup>	Content <sup>b</sup>	$M_{\rm n}$	$M_{ m w}$	PDI <sup>c</sup>
PFG5	0.05	0.060	15 000	35 000	2.33
PFG10	0.10	0.107	17 500	43 100	2.47
PFG20	0.20	0.215	18 100	46 300	2.56
PFY10	0.10	0.113	20 300	49 100	2.42
<sup><i>a</i></sup> Feed rat	io of the come	onomer 3 or ${}^{1}$ H NMR	1. <sup>b</sup> Actua	l benzothia	adiazole

the polymerization and obtained the polymer **PFY10** with the actual 2,1,3-benzothiadiazole unit (BT) content of 11.3 mol%. The number-average molecular weights of the polymers, as measured with GPC using polystyrene as standards, vary from 15 000 to 20 300 with the polydispersity index ranging from 2.33 to 2.47 (see Table 1). All these polymers are soluble in common organic solvents, such as toluene, chloroform and tetrahydrofuran.

### Photophysical properties

The UV-Vis absorption spectra and PL spectra of the polymers were measured both in solution and in thin films. As shown in Fig. 1(a) and Fig. 1(b), the band at 379 nm in the absorption spectra of **PFG5**, **PFG10**, and **PFG20** is attributed to the  $\pi$ - $\pi$ \* transition of the fluorene segments and the small shoulder at about 420 nm is attributed to the narrow bandgap in the vicinity of the benzothiadiazole unit. In comparison, the shoulder in the absorption spectrum of **PFY10**, which originates from the vicinity of the benzothiadiazole unit, is located at about 430 nm. It is obvious that the vicinity of the benzothiadiazole unit in **PFG5**, **PFG10**, and **PFG20** shows a more blueshifted absorption maximum than that in **PFY10**,



Fig. 1 Absorption spectra of PFG5, PFG10, PFG20 and PFY10 in dilute solution (a) and in solid film (b).



Fig. 2 PL spectra of PFG5, PFG10, PFG20 and PFY10 in dilute solution (a) and in the solid film (b).

indicating that the vicinity of the benzothiadiazole unit in **PFG5**, **PFG10**, and **PFG20** has a larger bandgap and less effective conjugation length than **PFY10**. The insertion of the two phenylene moieties makes the vicinity of the benzothiadiazole unit a little more twisted and reduces its effective conjugation length (see Scheme 1).

Fig. 2 shows the PL spectra of the polymers in dilute toluene solution and in thin solid films with the excitation at 380 nm. The PL spectra of these polymers in toluene [Fig. 2(a)] show two emission bands. The band in blue region (400-460 nm) is attributed to the fluorene segments and the other band in the green-yellow region (470-600nm) is due to emission from the vicinity of the benzothiadiazole unit. Considering the weak absorption band and the strong emission band from the vicinty of the benzothiadiazole unit, we attribute the emission band from the vicnity of the benzothiadiazole unit to the Förster energy transfer from the fluorene segments to the vicinity of the benzothiadiazole unit.<sup>37</sup> The vicinity of the benzothiadiazole unit serves as exciton trap, confining the excitons and giveing rise to green light emission. The PL spectra of these polymers in solid film (Fig. 2b) show only a green emission band with no blue emission band. This is due to the more complete energy transfer from the fluorene segments to the vicinity of the benzothiadiazole unit in the solid film compared to in dilute solution. In the former case, polymer chains are packed together, enabling both intramolecular energy transfer and intermolecular energy transfer. In contrast, in the latter one, polymer chains are separated by solvent molecules and only intramolecular energy transfer is involved.<sup>19</sup> The PL spectrum of **PFG10** is blueshifted by 16 nm compared to that of PFY10 because the insertion of the phenylene units reduces the effective conjugation length in the vicinity of the



Fig. 3 Cyclic voltagramms of PFG5, PFG10, PFG20 and PFY10.

benzothiadiazole unit in **PFG10**. In the PL spectra of **PFG5**, **PFG10**, and **PFG20**, with the increase in the DPBT unit content, the green emission band is slightly redshifted due to the interaction (possibly aggregates, excimers or polaron pairs)<sup>38</sup> in the vicinity of the benzothiadiazole unit.

The PL quantum efficiencies ( $\Phi_{PL}$ ) of these polymer films were measured with an integrated sphere with the excitation at 409 nm according to the literature.<sup>39</sup> **PFG5**, **PFG10**, **PFG20** and **PFY10** all exhibit  $\Phi_{PL}$  of 0.80 or so. The insertion of phenylene units does not affect the PL quantum efficiencies of the resulting polymers.

#### **Electrochemical properties**

The electrochemical properties of the polymers in the solid films were investigated by cyclic voltammetry in degassed acetonitrile with  $nBu_4NClO_4$  (0.10 M) as the electrolyte. Fig. 3 shows the cyclic voltagramms of **PFG5**, **PFG10**, **PFG20** and **PFY10**. The onset potential of the oxidation process and the reduction process are listed in Table 2. Based on the onset potential and the formulae<sup>40</sup> [ $E_{HOMO} = -(E^{ox} + 4.34)$  eV and  $E_{LUMO} = -(E^{red} + 4.34)$  eV], we estimate the HOMO and LUMO energy levels of the polymers (see Table 2). All four polymers show similar energy levels with HOMO of about



Fig. 4 EL spectra of the devices of PFG5, PFG10, PFG20 and PFY10.

-5.78 eV and LUMO of about -2.17 eV. Their HOMO and LUMO energy levels are very close to the data reported for the polyfluorene homopolymer,<sup>41</sup> indicating that their oxidation and reduction processes both originate from the fluorene segments. The signals for the redox behavior of the benzothia-diazole unit are too weak to be recorded. From the obtained onset oxidation and reduction potential, we estimate the polymers' electrochemical bandgaps to be about 3.56 eV (see Table 2), which is much larger than the corresponding optical bandgaps estimated from the onset of optical absorption in solid film.

#### **Electroluminescence properties**

To investigate the EL properties of the polymers, single-layer devices based on these polymers were fabricated with the configuration ITO/PEDOT (40 nm)/polymer (90 nm)/Ca (10 nm)/Al (100 nm). Their EL spectra are presented in Fig. 4 and the corresponding CIE coordinates are listed in Table 3. The polymers' EL spectra are blueshifted by 20 nm in comparison with the corresponding PL spectra. For **PFY10**, the EL spectrum exhibits a maximum at 537 nm with CIE coordinates of (0.36, 0.57). In comprarison, the EL spectrum of **PFG10** exhibits a maximum at 525 nm with CIE coordinates

Table 2 Photophysical and electrochemical properties of PFG5, PFG10, PFG20 and PFY5

Polymer	In solution		In solid film			Oxidation		Reduction			
	$\lambda_{\rm abs}/\rm nm$	$\lambda_{\rm PL}/\rm nm$	$\lambda_{abs}/nm$	λ/nm	$\phi_{ m PL}$	$E_{\rm g}{}^{a}/{\rm eV}$	$E_{\text{onset}}/V$	E <sub>HOMO</sub> /eV	$E_{\text{onset}}/V$	E <sub>LUMO</sub> /eV	$E_{g}^{b}/eV$
PFG5	379	429, 525	379	535	0.81	2.56	1.40	-5.74	-2.18	-2.16	3.58
PFG10	379	429, 525	379	535	0.83	2.55	1.44	-5.78	-2.15	-2.19	3.59
PFG20	379	525	379	545	0.78	2.55	1.46	-5.80	-2.12	-2.22	3.58
PFY10	373	429, 544	367	558	0.84	2.49	1.40	-5.74	-2.19	-2.15	3.59
<sup>a</sup> Bandgap	estimated	from the ons	set waveleng	th of opt	ical abso	orption in	solid film. <sup>b</sup>	Bandgap estin	nated from t	the onset oxid	ation and

reduction potential.

Table 3 EL performance of the devices of the polymers

Polymer	Onset voltage/V	Maximum brightness/cd m <sup>-2</sup>	Luminous efficiency/cd A <sup>-1</sup>	Power efficiency/lm $W^{-1}$ $\lambda_{max}/nm$		CIE coordinates $(x, y)$	
PFG5	4.2	10 260	5.96	2.21	521	(0.29, 0.63)	
PFG10	4.1	22 650	8.25	4.45	525	(0.31, 0.58)	
PFG20	4.3	13 680	5.78	2.34	528	(0.33, 0.59)	
PFY10	4.6	19 025	4.99	1.90	537	(0.36, 0.57)	

of (0.31, 0.58). The insertion of the phenylene units leads to a blueshift by 12 nm in the EL spectra and changes the emisson color from green-yellow to saturated green. The insertion of the phenylene units greatly improves the color purity of the resulting polymers. In particular, the CIE coordinates of **PFG5**, (0.29, 0.63), are very close to (0.26, 0.65) of the standard green emission demanded by the NTSC.

The EL performance data for the devices are summarized in Table 3. The device based on PFY10 exhibits a turn-on voltage of 4.6 V, luminous efficiency of 4.99 cd  $A^{-1}$ , power efficiency of 1.90 lm  $W^{-1}$  and maximum brightness of 19 025 cd  $m^{-2}$ . In contrast, the device based on PFG10 shows a turn-on voltage of 4.1 V, luminous efficiency of 8.25 cd A<sup>-1</sup>, power efficiency of 4.45 lm  $W^{-1}$  and maximum brightness of 22 650 cd  $m^{-2}$ with CIE coordinates of (0.31, 0.58). The insertion of the phenylene unit leads to no decrease in the EL efficiencies of the resulting polymers. Fig. 5(a) shows the voltage-current density-brightness characteristics of the device based on PFG10. Fig. 5(b) shows the dependence of the luminous efficiency and power efficiency on the current density of this device. The device based on PFG5 emits pure green light with a turn-on voltage of 4.2 V, luminous efficiency of 5.96 cd  $A^{-1}$ , power efficiency of 2.21 lm W<sup>-1</sup> and maximum brightness of 10 260 cd  $m^{-2}$  with CIE coordinates of (0.29, 0.63). This performance is among the best reported for green electroluminescent polymers.9-18,24-27 Further improvement of EL performance can be expected after device optimization.

#### Conclusion



In conclusion, by incorporating 4,7-diphenyl-2,1,3-benzothiadiazole instead of 2,1,3-benzothiadiazole into the backbone of

**Fig. 5** Voltage–current density–brightness curve (a) and dependence of the luminous efficiency and power efficiency on the current density (b) of the device based on **PFG10**.

polyfluorene, we have developed a novel series of green lightemitting polymers. The insertion of the two phenylene moieties between the benzothiadiazole unit and the fluorene unit reduced the effective conjugation length in the vicinity of the benzothiadiazole unit and consequently led to a slight blueshift by 10-20 nm in the EL spectra of the resulting polymers. As a result, the color purity was greatly improved. CIE coordinates of (0.29, 0.63), which are very close to the (0.26, 0.65) of standard green emission required by the NTSC, were achieved. Furthermore, the insertion of the phenylene units led to no decrease of the PL and EL efficiencies of the resulting polymers. Non-optimized single-layer devices of these polymers emitted pure green light with a luminous efficiency of 5.96 cd  $A^{-1}$  and a power efficiency of 2.21 lm  $W^{-1}$ . High EL efficiencies and good color purities indicated these polymers to be promising candidates for green light-emitting polymers for display applications.

#### Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 20574067 and No. 50633040), Science Fund for Creative Research Groups (No. 20621401) and 973 Project (No. 2002CB613402).

#### References

- 1 U. Scherf and E. J. W. List, Adv. Mater., 2002, 14, 477.
- 2 M. T. Bernius, M. Inbasekaran, J. O'Brien and W. S. Wu, Adv. Mater., 2000, 12, 1737.
- 3 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
- 4 D. Neher, Macromol. Rapid Commun., 2001, 22, 1365.
- 5 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.
- 6 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.
- 7 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.
- 8 T. Miteva, A. Meisel, W. Knoll, H.-G. Nothofer, U. Scherf, D. C. Müller, K. Meerholz, A. Yasuda and D. Neher, *Adv. Mater.*, 2001, **13**, 565.
- 9 M. Bernius, M. Inbasekaran, E. P. Woo, W. S. Wu and L. Wujkoski, *Thin Solid Films*, 2000, 363, 55.
- 10 W. S. Wu, M. Inbasekaran, M. Hudack, D. Welsh, W. Yu, Y. Cheng, C. Wang, S. Kram, M. Tacey, M. Bernius, R. Fletcher, K. Kiszka, S. Munger and J. O'Brien, *Microelectron. J.*, 2004, 35, 343.
- 11 M. Inbasekaran, W. S. Wu and E. P. Woo, U. S. Pat., 5 777 070, 1998.
- 12 M. Inbasekaran, E. P. Woo, W. S. Wu and M. T. Bernius, PCT application W0046321A1, 2000.
- 13 I. S. Millard, Synth. Met., 2000, 111-112, 119.
- 14 H. Spreitzer, H. Becker, E. Breuning, A. Falcou, K. Treacher, A. Büsing, A. Parham, P. Stöβel, S. Heun and J. Steiger, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2003, 4800, 16.
- 15 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.
- 16 P. Herguth, X. Jiang, M. S. Liu and A. K.-Y. Jen, *Macromolecules*, 2002, **35**, 6094.
- 17 Q. F. Xu, J. Y. Ouyang, Y. Yang, T. Ito and J. Kido, *Appl. Phys. Lett.*, 2003, 83, 4695.
- 18 Y. He, S. Gong, R. Hattori and J. Kanicki, *Appl. Phys. Lett.*, 1999, 74, 2265.
- 19 J. Luo, J. B. Peng, Y. Cao and Q. Hou, Appl. Phys. Lett., 2005, 87, 261103.

- 20 Q. Hou, Y. S. Xu, W. Yang, M. Yuan, J. B. Peng and Y. Cao, J. Mater. Chem., 2002, 12, 2887.
- 21 J. Yang, C. Jiang, Y. Zhang, R. Yang, W. Yang, Q. Hou and Y. Cao, *Macromolecules*, 2004, **37**, 1211.
- 22 R. Yang, R. Tian, Q. Hou, W. Yang and Y. Cao, *Macromolecules*, 2003, **36**, 7453.
- 23 Q. Peng, Z. Y. Lu, Y. Huang, M. G. Xie, S. H. Han, J. B. Peng, Y. Cao and W. Huang, *Macromolecules*, 2004, 37, 260.
- 24 M. S. Liu, J. D. Luo and A. K.-Y. Jen, Chem. Mater., 2003, 15, 3496.
- 25 Q. Peng, Z. Y. Lu, Y. Huang, M. G. Xie, D. Xiao and D. C. Zou, J. Mater. Chem., 2003, 13, 1570.
- 26 E. Lim, B.-J. Jung and H.-K. Shim, Macromolecules, 2003, 36, 4288.
- 27 J. Pei, W.-L. Yu, W. Huang and A. J. Heeger, *Chem. Commun.*, 2000, 1631.
- 28 S. Beaupré and M. Leclerc, Adv. Funct. Mater., 2002, 12, 192.
- 29 N. S. Cho, D.-H. Hwang, B.-J. Jung, E. Lim, J. Lee and

Chem. Soc., 2003, 125, 437.

H.-K. Shim, *Macromolecules*, 2004, 37, 5265.
C. Ego, D. Marsitzky, S. Becker, J. Zhang, A. C. Grimsdale, K. Müllen, J. D. MacKenzie, C. Silva and R. H. Friend, *J. Am.*

- 31 G. Kläner, J.-I. Lee, M. H. Davey and R. D. Miller, Adv. Mater., 1999, 11, 115.
- 32 G. Kläner, M. H. Davey, W. D. Chen, J. C. Scott and R. D. Miller, *Adv. Mater.*, 1998, **10**, 993.
- 33 K. Pilgram, M. Zupan and R. Skiles, *J. Heterocycl. Chem.*, 1970, 7, 629.
- 34 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.
- 35 J. M. Raimundo, P. Blanchard, H. Brisset, S. Akoudand and J. Roncali, *Chem. Commun.*, 2000, 939.
- 36 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457.
- 37 T. Förster, Discuss. Faraday Soc., 1959, 7, 27.
- 38 T.-O. Nguyen, B. J. Schwartz, R. D. Schaller, J. C. Johnson, L. F. Lee, L. H. Haber and R. J. Saykally, *J. Phys. Chem. B*, 2001, **105**, 5153.
- 39 M. S. Wrighton, D. S. Ginley and D. L. Morse, J. Phys. Chem., 1974, 78, 2229.
- 40 A. J. Bard and L. A. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 1984.
- 41 S. Janietz, D. D. C. Bradley, M. Grell, C. Giebeler, M. Inbasekaran and E. P. Woo, *Appl. Phys. Lett.*, 1998, **73**, 2453.

# Looking for that **Special** chemical biology research paper?

TRY this free news service:

# **Chemical Biology**

- highlights of newsworthy and significant advances in chemical biology from across RSC journals
- free online access
- updated daily
- free access to the original research paper from every online article
- also available as a free print supplement in selected RSC journals.\*

\*A separately issued print subscription is also available.

Registered Charity Number: 207890

## 220306

# www.rsc.org/chembiology

**RSCPublishing**