Synthesis and characterization of poly(2,2'-diphenylbiphenyl-4,4'-ylenevinylene-2'',5''-bis(trimethylsilyl)-*para*-phenylenevinylene), a new efficient blue-light emitting polymer

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Abstract

The synthesis and application of poly(2,2'-diphenylbiphenyl-4,4'-ylenevinylene-2'',5''-bistrimethylsilyl-*para*-phenylenevinylene) (DPBP-PPV), a novel blue-light emitting polymer is reported. The EL spectrum of DPBP-PPV is almost identical with its PL spectrum. By blending with PBD, the devices show a high external efficiency of 0.2% with the highest brightness of 300 cd m⁻². © 2001 Elsevier Science B.V. All rights reserved.

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Since the first demonstration of electroluminescence (EL) from poly(*para*-phenylenevinylene) (PPV) by the Cambridge group [1], research concerning EL of π -conjugated polymers has grown rapidly during the last decade. Due to the high intrinsic luminescent efficiency of PPV, many derivatives have therefore been synthesized and investigated in order to control the color of the emission, to facilitate solution processing, and to enhance the external efficiency of EL devices [2–5]. Among these, tuning the color of emission is of particular importance because an array of display requires integration of the red, green, and blue emitting components. To control the emissive properties of PPV solid films, a lot of recent effort has been devoted to the study of substituent effects on the electronic and optical properties. Famous examples are the family of poly[2-methoxy-5-((2'-ethylhexyloxy)-1,4-phenylenevinylene]

(MEHPPV) that carries electron-donating alkoxy groups on the phenylene units and red-shifting the emission wavelength from the parent green-light to the red region [6–9]. Other examples of introducing either electron-deficient aromatic rings or electron-withdrawing groups on the vinylene units have also been reported [10–18]. In addition, blue-light electroluminescent polymers based on oligo-*para*-phenylenevinylene (OPPV) as side-chains or as segments on the backbone have also been developed [19–32].

In this work, we focus our attention on developing a new class of blue light emitting polymers based on the

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PPV skeleton. The desired polymers should have reasonably good solubility in common organic solvents and be able to form high quality thin-films through the spin-coating process. In addition, the ideal emission bandwidth should be narrow and have an emission wavelength within 435–480 nm. In an ideal case, the polymers should have minimal percentage of sp^3 components that may significantly reduce the charge mobility in the matrix [33].

A survey of the previous literature reveals that the EL behavior and the emission bandwidth of OPPV-based polymers are not always consistent with their PL characteristics, and are difficult to predict. For example, polymer **1** emits blue-green light ranging from 450 to 570 nm [23] while polymer **2** emits blue light ranging from 430 to 520 nm [26]. On the other hand, significant greenish tailing was observed in the EL of **3** while blue-light emission was observed in its PL spectrum [24].

1. Results and discussion

In this article we describe the synthesis, characterization, and photophysical behavior of polymers **4** and **5**, and the application of **5** in light emitting diodes. To gain insight into the photophysical properties of OPPV-

Scheme 1. Synthesis of polymer **4**.

based materials, 1,4-distyrylbenzene **4** was used as a probe to investigate the excitation and emission characteristics of OPPVs [4]. The Wadsworth–Emmons synthetic approach [34,35] for **4** is summarized in Scheme 1. A three-step synthetic sequence transforms the commercially available precursor **6** to the aldehyde **7**. Wadsworth–Emmons coupling of **7** with **8** led to **4** in moderate yields. OPPV **4** was further purified twice by sublimation at $180^\circ C$ under vacuum (5×10^{-5} torr). The concentration-dependent steady-state fluorescence spectra for **4**, shown in Fig. 1(b–d), in toluene were collected from a typical right-angle detection fluorescence spectrometer equipped with a 1×1 cm quartz cuvette. The spectrum for a highly diluted solution (10^{-6} M) of **4** shows a maximum centered at 440 nm with the electronic-vibrational (vibronic) couplings ranging from 400 to 480 nm. Gradually increasing the concentration of **4** from 10^{-6} to 10^{-2} M alters the pattern of the emission spectra as well as their emission intensity. The first vibronic emission band peaking at 415 nm gradually disappears while the second and third vibronic emission bands peaking at 440 and 470 nm remain [36]. Examination of its absorption spectrum as well as the excitation spectrum reveals that **4** has a strong absorption peaking at 370 nm with a tail extending to 430 nm. At high concentrations, self-absorption may occur that reduces the emission below 430 nm [37]. In extreme cases, emissions below 430 nm would probably be significantly suppressed under the typical experimental conditions. This possibility was supported by the frontal-surface fluorescence-spectrometric experiment [37] which gives rise to a shoulder at 420 nm. To obtain further support for the self-absorption mechanism, a liquid thin-film of a 10^{-2} M solution of **4** was employed in the fluorescent experiment in order to minimize the path-length for the self-absorption process [38]. Under these conditions, a normal emission spectrum was obtained (Fig. 1, spectrum a).

Fig. 1. Curves (a)–(f) are photoluminescence spectra of **4** under various conditions: (a) conc. 10^{-2} M in toluene, liquid film; (b), (c) and (d) are obtained in toluene under typical experimental conditions with conc. 10^{-6} , 10^{-4} and 10^{-2} M, respectively; (e) thin film prepared by vapor deposition under vacuum; (f) single crystals.

Vacuum deposition of **4** on a quartz plate would lead to an amorphous solid film. The photoluminescence spectrum (Fig. 1, spectrum e) shows only one major emission at 450 nm with a shoulder appearing at 490 nm. Although the energy-transfer mechanism may be more complicated in aggregated or solid state [39,40], similar to that in highly concentrated solution, the first vibronic band at 415 nm disappears. The appearance of the emission shoulder at 490 nm may due to either an emission arising from the low-energy $0 \rightarrow n$ vibronic transition or from the partial crystallization areas of the solid-film, in comparison to the identical emission wavelength of the single crystals of **4** (Fig. 1, spectrum f) [41–43].

All these results indicate that the complicated vibronic emission spectrum of OPPV could be simplified through the self-absorption or energy transfer mechanism in the solid film, leading to a single major emission with narrow bandwidth. The higher energy vibronic emission may be re-absorbed and channelled to the desired lower energy blue light emission. In addition, the emission spectrum may become narrower if the crystallinity or formation of highly ordered aggregation [41–43] could be suppressed.

On the basis of the above conclusions, polymer **5** was rationally designed and synthesized (Scheme 2). The key dialdehyde **9** was prepared from Suzuki coupling of phenylboronic acid [44] with the corresponding diiodoesters **11** [45–47]. Due to the non-planar conformation of the biphenyl units [48], each of the OPPV units will be confined as an independent unit and non-conjugated with each other. More importantly, the phenyl substituents on the biphenyl units would hinder the rotation of the biphenyl backbone, prohibiting the biphenyl unit from coplanarization in the excited state

Scheme 2. Synthesis of polymer **5**.

and maintaining the OPPV fluorophore as an independent blue light emitting unit. In addition, the presence of the phenyl side chain would increase the solubility of **5** as well as reduce its tendency towards crystallization [49–51].

Polymer **5** is reasonably soluble in CHCl_3 and highly soluble in 1,2-dichlorobenzene. The soluble portion of polymer **5** in CHCl_3 prepared accordingly has a weight-average molecular weight $M_w = 2400$ relative to the polystyrene standard in gel permeation chromatography (GPC) measurements with $M_w/M_n = 1.7$. No obvious glassy transition temperature was observed on the basis of differential scanning calorimetry (DSC) analysis scanning from 50 to 300°C . Polymer **5** has extremely good thermal stability. The thermogravimetric analysis (TGA) trace indicated decomposition at 400°C (5% weight loss) under N_2 . No elimination of small molecules was observed below this temperature, indicating that a high degree of conjugation had been formed during the polymerization reaction.

Good quality thin-films of **5** with a thickness of 650–800 Å could easily be obtained through spin-coating from a chloroform solution (13 mg ml^{-1}). The thickness of the thin-film was evaluated using ellipsometry. Fig. 2 shows the electronic absorption spectrum as well as the photoluminescent spectrum of polymer **5**. An absorption maximum at 375 nm and an emission at 450 nm are characteristics for distyrylbenzenes [4], indicating that the distyrylbenzene units are more or less non-conjugated with each other. The emission spectrum shows a blue color peaking at 450 nm with a narrow full width at half-maximum (FWHM) of 55 nm, ranging from 440 to 495 nm. A relatively small Stokes-shift of 75 nm for **5**, in comparison to a large

Fig. 2. (a) Absorption (ABS), (b) photoluminescence (PL, excitation wavelength at 380 nm) spectrum of DPBP-PPV, and (c) electroluminescence (EL) spectrum of PDB (28.5 wt.%) doped DPBP-PPV.

value of about 170 nm for **12** in solution (Fig. 3), suggests that the rotation and coplanarization of the biphenyl unit in the excited state is retarded.

The indium–tin oxide (ITO) coated glass electrodes used for the preparation of EL devices were pretreated with poly(styrenesulfonic acid)/poly(3,4-ethylenedioxythiophene) (PEDOT) as a hole-injection layer. The polymer films were spin-coated at 5000 rev. min⁻¹ from CHCl₃ solution with a concentration of 13 mg ml⁻¹, giving films of 800 Å thickness. A layer of Mg/Ag (10:1) contacts was then deposited on top of the polymer under vacuum at pressures below 1×10^{-6} torr.

The typical current–voltage and brightness–voltage curves of LED devices fabricated from pure or 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) blended polymer **5** are shown in Fig. 4 for comparison. LEDs fabricated with polymer **5** show bright emission easily observable under normal room

Fig. 3. Absorption and photoluminescence (excitation wavelength at 238 nm) spectra of **12** in MeOH. A large Stokes shift of 170 nm was observed.

Fig. 4. (a) Brightness–voltage and (b) current–voltage profiles of the EL devices fabricated from ITO/PEDOT/DPBP-PPV/Mg: (●) with 28.5 wt.% of PDB; (■) without PDB.

illumination. The turn-on voltage of 13 V is close to the 15 V for the PPV polymer, using Al as the electrode. Significant reduction of the turn-on voltage and enhancement of the external quantum efficiency by doping with PBD indicates an imbalanced injection of opposite charges in the original polymer matrix (Table 1). We believe that the electron injection is less efficient than the hole injection, and therefore requiring PBD, a good electron-transport material, to balance the electron injection and optimize the performance of the device. Other factors such as the change of interface

Table 1
Performance of the ITO/PEDOT/DPBP-PPV, PBD, TPB/Mg devices

	DPBP-PPV/PBD/TPB (weight ratios)		
	(100:0:0)	(100:40:0)	(100:40:40)
External quantum efficiency (%)	<0.1	0.2	0.015
Brightness (cd m ⁻²)	80	300	200

properties or morphology of the polymer matrix may also significantly affect the performance of LED devices. Similar to the PPV series, polymer **5** should have a good hole-transport behavior. Doping with hole-transport compounds such as *N,N,N',N'*-tetraphenyl-1,1'-biphenyl-4,4'-diamine (TPB) only enhances the background current without increasing the brightness of the device, and therefore retarding the quantum efficiency of the EL.

2. Conclusions

In summary, we have synthesized a novel blue-light emitting polymer DPBP-PPV. The EL spectrum of DPBP-PPV is almost identical to its PL spectrum (Fig. 2). By doping with PBD, the devices show a high external efficiency of 0.2% with the highest brightness of 300 cd m⁻², indicating that DPBP-PPV is a good hole-transport but poor electron-transport electroluminesive polymer. Optimization of the device performance and life-time, mechanistic studies for the energy transfer process of **4** and **5** in solid state, and the feasibility of using derivatives of **4** as the emissive layer in EL applications are under investigation.

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