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Synthesis of novel coumarin-terminated poly (*p*-phenylene vinylene)s for application in LEDs

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Novel coumarin-terminated poly (*p*-phenylene vinylene)s were synthesized successfully *via* Gilch methodology. The resulting coumarin end-capped poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene (CT-MEH-PPV) film gives yellow photoluminesence with a maximum intensity at 560 nm, which is noticeably blue-shifted about 40 nm from that of MEH-PPV (598 nm). Light-emitting diode based on a double-layer structure (ITO/PEDOT/CT-MEH-PPV/Ba/Al) showed yellow emission with a maximum brightness of 956 cd m^{-2} at 8.8 V and an external quantum efficiency of 0.28% at 49.5 mA cm^{-2}. The coumarin-terminted poly(2,3-diphenyl-5-hexyl -1,4-phenylene vinylene (CT-DPH-PPV), however, has similar emission spectrum with that of DPH-PPV, but its photoluminescence efficiency (0.78) is much more improved than that of DPH-PPV (0.55). The electroluminescent device (ITO/PEDOT/CT-DPH-PPV/Ba/Al) gave green emission peaked at 510 nm with a maximum brightness of 350 cd m^{-2} at 18 V and an external quantum efficiency of 0.04% at 61 mA cm^{-2}. These results suggest that it is a convenient way to modify the structure of conjugated polymers by terminating to tune the emission color and improve photoluminescent and electroluminescent efficiencies as well.

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1. Introduction

Electroluminescent polymers have been attracting much attention over the past ten years [1], and light emitting devices based on them have now achieved performances (efficiency, lifetime and luminance) meet with the requirements for commercialization.

Among the vast kinds of conjugated polymers, poly (phenylene vinylene)s (PPVs) is the most well-studied series due to their excellent luminescent and mechanical properties. Many attempts had been made to increase their quantum efficiency and tune the emission color by chemically modifying the structure of PPVs. However, the introduction of functional moieties into the PPVs' main chain [2–8], which is a common way employed, would alter the electronic properties of the backbone, and may change some essential properties. While the introduction of functional moieties into the PPVs' side chain would lead to a tough synthetic work for those polymers often have too much complicated structures [9–12].

Although introduction of terminator is a normal way to modify the polymer properties in plastic engineering, it is surprisingly that there are few research works focusing on the development of polymer emitters by using terminators. To the best of our knowledge, there was only one literature among so many literatures related to polymer light-emitting materials [13], describing the terminating of the main chain of polyfluorene with hole-transporting moieties, which opens a way to blue LEDs with high efficiency and excellent color stability without altering the electronic properties of the conjugated polymer backbone.

Coumarin derivatives are well-known fluorescence dyes for their high photoluminescence (PL) quantum efficiencies. They have also been emerged as dopants in polymer LEDs due to the concentration quenching [14–18]. However, the doping procedure would lead to the poor performance of LEDs because of the aggregation and crystallization of the dopants. Herein, we incorporated coumarin derivative into the polymer as ending group, which could form better solid solution compared to dopants, and could avoid the crystallization. This is a simple and convenient way to tune the emission color as well as improve the PL and EL efficiencies of the polymer without altering the electronic structures.

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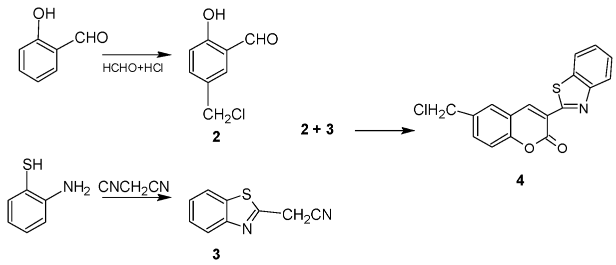


Scheme 1 Synthesis of 3-(2′-benzothiazolyl)-6-chloromethylcoumarin.

2. Experimental

2.1. Chemicals and instrumentals

1,4-Bis(chloromethyl)-2-methoxy-5-(2′-ethylhexyloxy) benzene(**1**) was synthesized according to literature [19]. 5-hexyl-1, 4-Bis(chloromethyl)-2,3-diphenylbenzene(**5**) was synthesized according to literature [19–21].

1H NMR spectra were recorded on a Varian Unity INOVA-400 in $CDCl_3$. Fluorescence quantum yields of the polymers solutions (toluene as solvent) were determined using quinine sulfate ($\Phi_F = 0.55$, excited at 366 nm in 1 M H_2SO4 at 22°C) as reference on fluorescence spectrophotometer (Hitachi 850) and UV-Vis absorption spectrophotomer (Shimadzu UV2100) at 22°C.

2.2. Synthesis of-(2′-benzothiazolyl)-6-chloro-methylcoumarin (4)

Intermediates **2** and **3** were synthesized according to literatures (Scheme 1) [21, 22]. 2 mL of 4% sodium hydroxide water solution was added to a mixture of **2** (3.4 g, 20 mmol), **3** (3.5 g, 20 mmol) and dried 1, 4-dioxane (30 mL) under stirring at 35°. After 5 min, 30 mL of 18% hydrochloric acid was added. The resulting mixture was refluxed for 0.5 h and cooled down, and then 100 mL of water was added with continuous stirring. The precipitate was connected by filtration, washed with water, then purified by column chromatography on silica gel ($CHCl_3$ as eluent) to give yellow needle crystals (2.2 g, 33.5%). m.p. 239–240°C; ^{1}HNMR($CDCl_3$) δ (ppm): 9.18 (1H, s,—CH=),8.15-7.45 (7H, m, 7Ph-H), 4.67 (2H, s, ClCH2); MS: $m/z = 328$ (M+); Elemental analysis for $C_{17}H_{10}ClNO_2S$: (%): Calcd: C, 62.29; H, 3.07. Cl, 10.82; N, 4.27; S, 9.78; Found: C, 62.24; H, 3.10; Cl, 10.89; N, 4.31; S, 9.73.

2.3. Synthesis of polymer CT-MEH-PPV

To a stirred solution of **1** (0.5 g, 1.5 mmol) and **4** (25 mg, 0.076 mmol) in THF (20 mL), was added into *t*-BuOK solution (1.0 M in THF, 60 mL). The resulting mixture was stirred for 24 h at r.t. before it was poured into methanol (200 mL). The orange solid was collected by filtration and washed by acetone and methanol. After purified by two times of additional precipitations, from THF into hexane and from THF into methanol, the resulting polymer CT-MEH-PPV was obtained as orange powders with a yield of 63% after drying under vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.6–6.5 (br, m, 4 H); 4.2–3.6 (br, m, 5 H); 2.0–0.6 (br, m, 15 H); FT-IR (KBr pellet, cm^{-1}), $\nu_{\max}$: 2924, 2854, 1502, 1452, 1410, 1383, 1206, 1093, 1042, 977.

2.4. Synthesis of polymer CT-DPH-PPV

Polymer CT-DPH-PPV was obtained as pale yellow powders with a yield of 58% from the reaction of **4** with **5** according to the procedure described for the synthesis of polymer CT-MEH-PPV.^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.5–7.0 (br m, 11 H); 6.9–5.8 (br m, 2 H); 2.4 (br s, 2 H) 1.6–0.86(br m, 11H); FTIR (KBr pellet, cm^{-1}), $\nu_{\max}$: 2925, 2875, 1684, 1560, 1458, 1393, 1087, 987, 924, 860,758, 698.

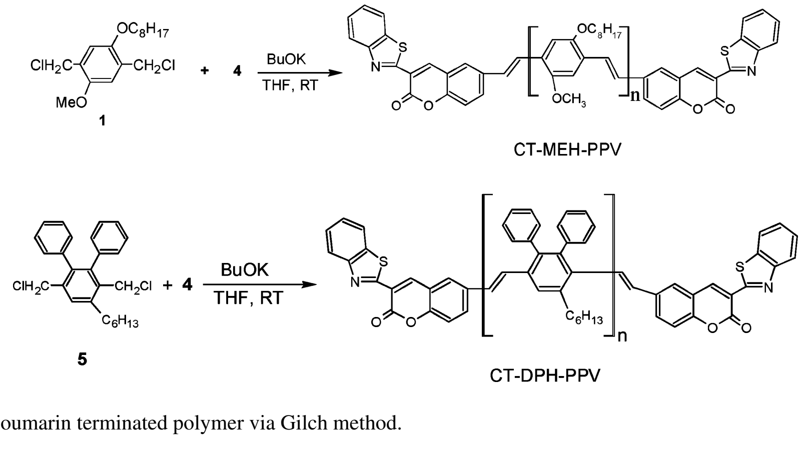
2.5. Fabrication of LEDs

For the fabrication of the devices, glass substrates coated with indium-tin oxide (ITO) with a sheet resistance of 100 Ω□$^{-1}$ (CSG Co. Ltd.) were cleaned subsequently in ultrasonic baths of ionic detergent water, acetone, and anhydrous molecules. A thin film layer of PEDOT (Batron-P 4083) (100 nm) [(PEDOT is poly(ethylenedioxythiophene) doped with poly(styrenesulfonic acid)) and the polymers (70 nm) (from a 10 mg/mL of the polymers in toluene solution) were spin-coated on ITO at 1500 rpm for 30 s in turn; after that a thin layer of Ba (4 nm)/Al (200 nm) was deposited onto the polymer film by thermal evaporation under a vacuum of 10^{-6}Torr.

3. Results and discussion

3.1. Synthesis and characterization

The coumarin-terminated PPVs (CT-MEH-PPV and CT-DPH-PPV) were synthesized via Gilch methodology (Scheme 2). Their molecular weights were



Scheme 2 preparation of coumarin terminated polymer via Gilch method.

TABLE I Molecular weights of the polymers

Polymer	Monomer/terminator feed ratio (mol/mol)	Mn (g/mol)	Mn/Mw
CT-MEH-PPV	95:5	2.08×10^5	1.18
CT-DPH-PPV	95:5	1.53×10^5	3.37

TABLE II The PL efficiency of terminated polymers to unterminated polymers

Polymer	MEH-PPV	CT-MEH-PPV	DPH-PPV	CT-DPH-PPV
Φ_F	0.28	0.30	0.55	0.78

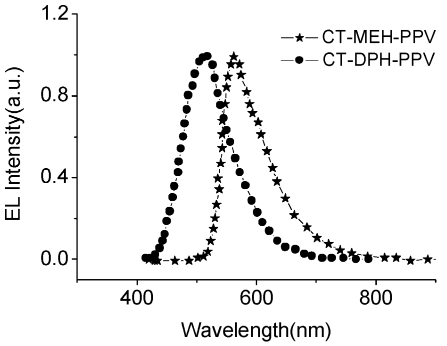


Figure 2 EL spectra of the devices with the configuration.

determined by gel permeation chromatography (GPC) using polystyrene as the standard. The results are listed in Table I. Comparing the ^{1}HNMR spectra of polymers CT-MEH-PPV and MEH-PPV, these ^{1}H NMR signals show a similar shape, but in varying intensities [24].

The ^{1}HNMR spectra of polymer CT-DPH-PPV is also similar with DPH-PPV. Both CT-DPH-PPV and DPH-PPV contained *cis*(Z) and *trans*(E) vinylene groups, as revealed by ^{1}HNMR(with the signal for the Z form at 6.06 ppm and that for the E form at 6.46 ppm) and IR(with *trans*-vinylene out-of-plane bending at 987 cm^{-1} and the *cis* form at 860 cm^{-1}).

3.2. Optical properties

The thin films for PL measurements were prepared by spin-coating from toluene solutions (5 mg/mL, 1500 rpm) on quartz plates followed by drying under vacuum for 2 h at room temperature. The main features of PL spectra of the polymers are summarized in Fig. 1 and Table II. As shown in Fig. 1, the CT-MEH-PPV film emits yellow light with a maximum at 560 nm, noticeably blue-shifted about 40 nm from that of MEH-PPV (598 nm) prepared under the same condition. In general, the PL emission spectrum of MEH-PPV has three peaks, which come from a single electronic state and represent vibronic structure (the 0-0, 0-1, 0-2 emission bands). The relative heights of three emission peaks will alter with different spin speed, solvent, and the solution concentration [25–31]. Thus, the PL spectrum of MEH-PPV films may be significantly different (yellow, or orange-red) by different way of manufacture. To the best of our knowledge, the yellow emission (575 nm) is the bluest emission of MEH-PPV among all the literatures [25–31]. Other than the blue shift, the PL spectra of CT-MEH-PPV and MEH-PPV have the same general shape, which indicated that it is an efficient way to tune the fluorescent color by employing coumarin derivative as a terminator to PPVs.

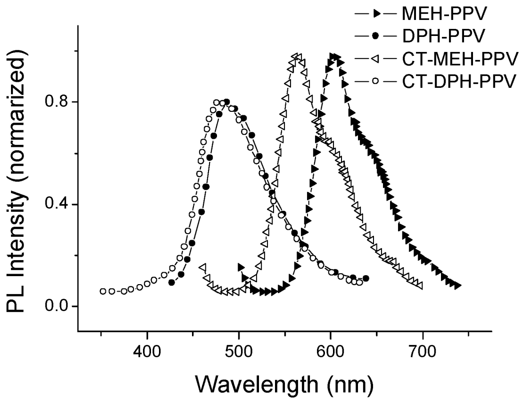


Figure 1 PL spectrum of terminated polymers and unterminated polymers.

Although DPH-PPV and CT-DPH-PPV have almost the same PL emission spectra (see Fig. 1), the PL efficiency of CT-DPH-PPV is significantly higher than that of DPH-PPV. Note that efficient energy transfer, of the Förster type [32], ideally requires a large spectral overlap between the emission of the "donor" and the absorption of the "acceptor" species. The courmarin derivative **4** shows a very strong blue emission (450 nm) in toluene solution, while the photo induced adsorption (PIA) of DPH-PPV is from 350 to 470 nm. Thus there must be efficient energy transfer between courmarin **4** and DPH-PPV. The PL efficiencies of CT-DPH-PPV and DPH-PPV solution (toluene as solvent) are 0.78 and 0.55 respectively, which reflects that the existence of terminator coumarin 4 could improve the PL efficiency of DPH-PPV.

3.3. Electroluminescent properties of LEDs

The electroluminescence spectra of the two LEDs fabricated are shown in Fig. 2, indicating that CT-MEH-PPV and CT-DPH-PPV follow the same traces of their PL spectra, with peaks at 561 and 510 nm, respectively. The similarity of the PL and EL spectra suggests that same excitations are involved in both cases. Fig. 3 compares the I-V-L curves of the LEDs. Both the two devices show good rectification behaviors. The yellow emission from device ITO/PEDOT/CT-MEH-PPV/Ba/Al starts at about 5.2 V and reaches a maximum brightness of 956 cd m^{-2}at a bias of 8.8 V, and an EL external quantum efficiency of 0.28% was obtained at a bias voltage of 6.2 V at a current density of 49.5 mA cm^{-2}. As for device ITO/PEDOT/CT-DPH-PPV/Ba/Al, green emission could be observed with turn-on voltage of 10.6 V, and a maximum brightness of 350 cd m^{-2}at a voltage of 18V, while its EL external quantum efficiency is about 0.04% (at 16.7 V with a current density of 61 mA cm^{-2}). What should be emphasized is that all these results are obtained basing on unoptimized LEDs, thus much

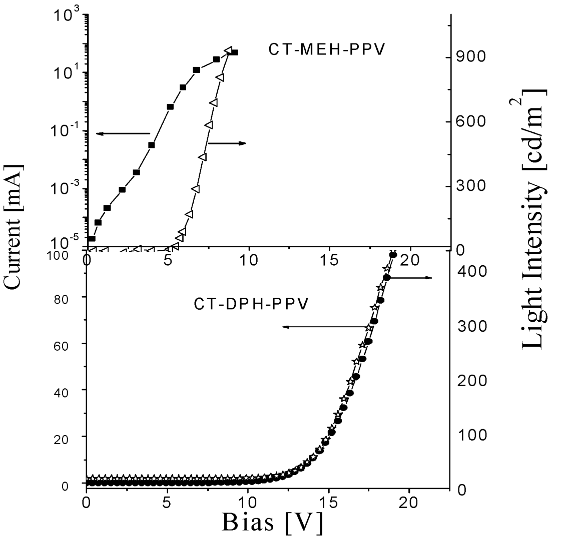


Figure 3 Current-voltage (I-V) and luminance-voltage (L-V) curves of an ITO/PEDOT/polymer/Ba/Al.

better performances may be achieved after optimization of devices.

4. Conclusions

Two kinds of light-emitting PPV derivatives were synthesized employing coumarin derivative as a terminator. Device fabricated with CT-MEH-PPV film as emitter gave yellow electroluminescence peaked at 560 nm, noticeably blue-shifted about 40 nm from that of MEH-PPV (598 nm), and a maximum brightness of 956 cd m^{-2} at 8.8 V. CT-DPH-PPV shows very similar PL emission spectrum with that of DPH-PPV, but an improved PL efficiency (0.78 vs. 0.55). LED fabricated with CT-DPH-PPV (ITO/PEDOT/CT-DPH-PPV/Ba/Al) showed EL emission at 510 nm, a maximum brightness of 350 cd m^{-2} at 18 V. From these results, we believe that these two kinds of coumarin-terminated polymers are promising candidates for EL materials, and furthermore, it is a very convenient way to modify the structure of conjugated polymers, without altering their electronic properties, by terminating to tune the fluorescent color and improve PL and EL efficiency as well.

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