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Toward Highly Photoluminescent and Bipolar Charge-Transporting Conjugated Polymers

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SUMMARY: DBPP (2,5-di-(2-biphenyl)-1,4-phenylene) units were embedded into a PPV (poly(p-phenylenevinylene)) backbone, resulting in a dramatic improvement in the solid-state photoluminescence quantum efficiency of the polymer. Oxadiazole units were introduced as PPV main-chain substitutents, imparting the resulting polymer with bipolar charge-transporting properties. A carefully-designed conjugated polymer combining both DBPP and oxadiazole units showed both high PL efficiency and bipolar charge transport ability, making it a promising candidate for the fabrication of efficient single-layer LED devices.

Introduction

Polymer light-emitting diodes (LEDs) have drawn significant attention in the last decade and significant progress has been made in terms of both device efficiency and stability$^{1-4)}$. While a wide variety of polymers have been developed for LED applications, very few, if any, can be fabricated as efficient single-layer LED devices with air-stable cathodes. Two chief reasons are that most conjugated polymers do not have high photoluminescence (PL) quantum efficiency in the solid state and they do not transport electrons and holes with comparable efficiency. While several approaches have been taken to tackle either one of these two problems, designing a polymer which possesses both high solid-state PL efficiency and bipolar charge-transport ability is still a challenge. Here, we report our efforts in developing highly luminescent and bipolar charge transporting conjugated polymers.

Results and Discussion

Solid-State Photoluminescence Enhancement: One chief reason for the low PL efficiency of conjugated polymers is that conjugated backbones tend to stack

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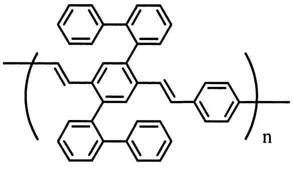
cofacially with each other due to the favorable interchain π–π interactions: this leads to a self-quenching process of excitons[5,6)]. Introducing appropriate substituents into the PPV backbone to prevent its close packing should therefore increase its PL efficiency[7)]. We have found that a 2,5-di-(2-biphenyl)-1,4-phenylene (DBPP) unit was a good pack-blocking unit[8)]. The DBPP unit adopts a three-dimensional geometry (one pendant phenyl ring points out, another down from the conjugated plane) due to the steric interactions. Thus, if this unit is incorporated into a PPV backbone, it should prevent the PPV backbone from stacking in any dimension.



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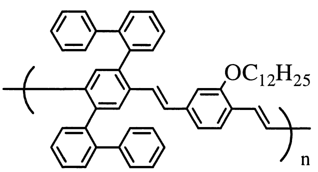

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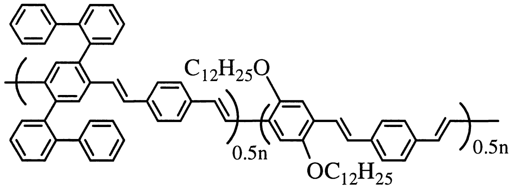

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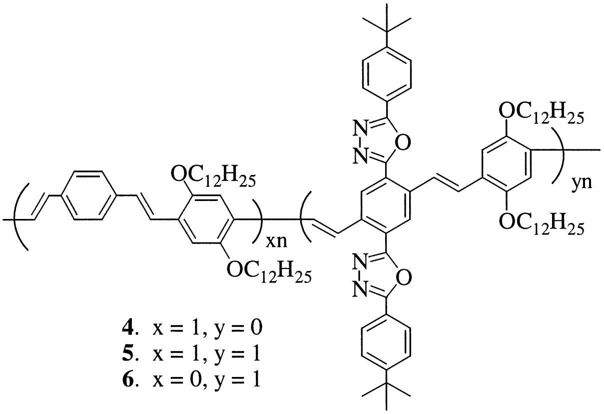
A DBPP-type monomer with dialdehyde functional groups, 2,5-di-(2-biphenyl)-1,4-benzenedicarboxaldehyde, was synthesized by the Suzuki Coupling reaction[9)] of 2,5-dibromo-1,4-benzenedicarboxaldehyde and 2-biphenylboronic acid, both synthesized in one step from commercially-available starting materials[10)]. Three polymers (Polymers 1-3) have been synthesized by the Horner-Wittig-Emmons (HWE) reaction[11)]. As shown in Table 1, Polymers **2** and **3** exhibit high molecular weights and significantly improved solid-state PL quantum efficiencies. For comparison, the PL efficiencies of a PPV polymer (Poly(2,5-dioctyloxy-1,4-phenylene vinylene)(DO-PPV) were measured under the same conditions. Its PL efficiencies in dilute solution and as solid film are both significantly lower than that of Polymers **1-3**. Compared to solutions, PL spectra of films are slightly red-shifted by less than 20 nm for Polymers **1~3**, in contrast to a nearly 40 nm red-shift for DO-PPV. These results indicate that the DBPP unit can indeed significantly block the interchain interactions, thus limiting the exciplex formations.

Table 1. Optical Properties of Polymers 1-3

polymer	Mw (kDa)	PDI	fluorescence			
			THF solution		film	
			λ_{max} (nm)	Φ_{pl}	λ_{max} (nm)	Φ_{pl}
1	4.5	1.5	488	0.77	504	0.82
2	151	2.5	503	0.73	520	0.61
3	235	2.8	510	0.53	522	0.77

Oxadiazole-Substituted PPVs Exhibiting Bipolar Charge-Transport Properties: Most conjugated polymers transport electrons much less efficiently than they transport holes. One approach to improving the electron-transporting properties of a conjugated polymer is to introduce electron-withdrawing substituents into the polymer backbone. CN-substituted PPV is one example[12-13]. The electron-withdrawing substituents lower the LUMO of the backbone, thus decreasing the electron injection barrier. We have recently utilized oxadiazole rings as main-chain substituents[14]. The structures of these polymers are shown as Polymers **4-6**.



4. x = 1, y = 0
5. x = 1, y = 1
6. x = 0, y = 1

The UV/Vis spectra of Polymers **5** and **6** show two strong absorption peaks: one at ca. 465 nm is the absorption peak of the PPV backbone, while the other absorption peak at 320 nm can be assigned to the orthogonal conjugated oxadiazole unit. When polymer films are excited at 460 nm, both Polymer **5** and Polymer **6** show one broad emission peak at 640 nm. In dilute THF solutions, both polymers show an emission maximum of 550 nm. Emissions from the oxadiazole unit at 395 nm are not observed even when polymers are excited at 320 nm-where oxadiazole units absorb strongly, indicating the existence of efficient energy transfer from the oxadiazole moiety to the PPV backbone.

Single-layer LED devices were made by spin-coating a polymer solution(20 mg of polymer in 1 ml of tetrachloroethane, spin rate: 1000 rpm) onto ITO-coated glass substrates (sheet resistance of ITO is about 20 Ω). A 1000 Å thick layer of aluminum or 1000 Å of calcium covered with 500 Å of Al was then deposited under vacuum (2×10^{-6} torr, 5-10 Å/s deposition rate). An HP 4155A Semiconductor Parameter Analyzer with a calibrated silicon photodiode detector was used to measure the LED performance (I-V and EL-V curves) under ambient conditions. The external quantum efficiency was calculated based on the EL intensity and electric current running through the device without any correction. Devices of all three polymers were fabricated under the same conditions. The external efficiencies and turn-on voltages of these polymer devices are listed in Table 2.

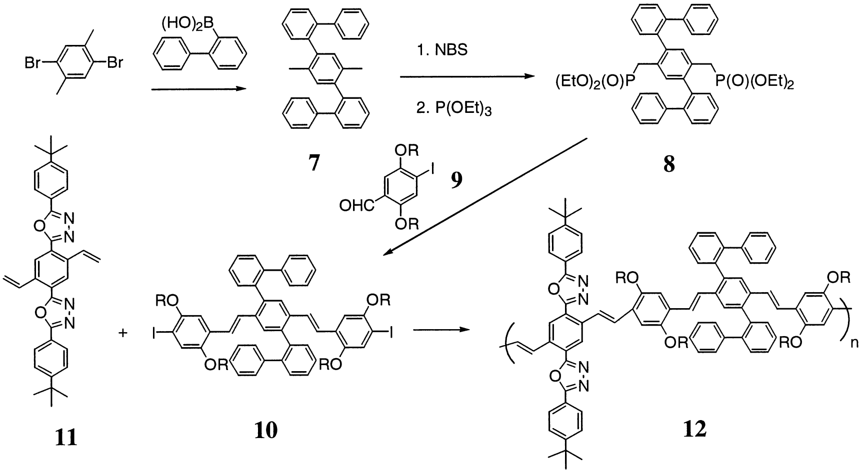
Table 2. External Efficiencies of Single-Layer Polymer LEDs

	ITO/Polymer/Al		ITO/Polymer/Ca	
Polymer	η%	V_{on} /V) (V_{on}'/V)[a]	η%	V_{on} /V
1	0.002	15 (10)	0.01	10
2	0.018	10 (8.5)	0.068	7.5
3	0.041	8 (8)	0.066	7.5

[a] V_{on} is the turn-on voltage of light with V_{on}' the turn-on voltage of current.

As shown in Table 2, when the number of oxadiazole substituents increases, the EL efficiency increases and the operating voltage decreases, especially for the LED device with Al as the cathode. The difference between the turn-on voltage of light and that of current also decreases from **4** to **5** and to **6**. These results indicate that the electron-transporting properties are indeed improved by introducing oxadiazole substituents.

Towards Polymers with Both High PL Efficiency and Bipolar Charge Transport Properties: It is noted that the LED efficiency of Polymer **6** is significantly lower than that of our previously reported main-chain oxadiazole PPVs$^{15)}$. One of the chief reasons, as we found during photoluminescence studies of polymers in solutions and as solid films, is that this polymer exhibits, contrary to our expectations, very strong cofacial packing. The emission wavelengths of polymer films red-shifted by nearly 100 nm compared to that of polymer solutions. The strong interchain interaction may result from the alternating electron-withdrawing and electron-donating substitutions on the PPV phenyl rings. Such strong interchain interactions significantly decrease the solid state PL quantum efficiency.



Scheme 1: Synthesis of a PPV polymer containing both DBPP and oxadiazole units.

To improve the PL quantum efficiency and at the same time maintain its bipolar charge-transport properties, we synthesized Polymer **12** which contains both DBPP and oxadiazole units. The synthetic approach to Polymer **12** is shown in Scheme 1.

The synthesis of Compound **11** was previously reported14). To synthesize Compound **10**, Compound **7** was first synthesized by the Suzuki coupling reaction of 2,5-dibromo-*p*-xylene with 2-biphenylboronic acid in 78% yield. Compound **7** was then converted to **8** by bromination with NBS (85% yield), followed by the reaction with triethylphosphite (68% yield). HWE reaction of **8** with **9** gave the desired Monomer **10** in 55% yield. Polymer **12** was synthesized by the Heck coupling reaction.

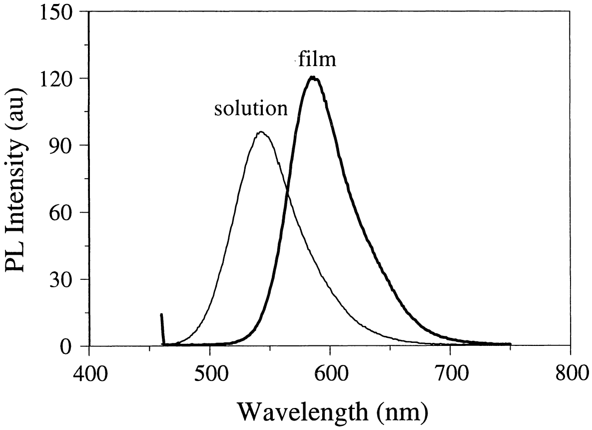


Fig. 1: Fluorescence spectra of Polymer **12** in THF solution and as a solid film.

As shown in Figure 1, The fluorescence spectra of Polymer **12** show a maximum at 544 nm in dilute THF solution and 585 nm in the solid state. A red shift of around 40 nm is observed, in sharp contrast to the nearly 100 nm red-shift observed for Polymer **6**. The quantum efficiency of Polymer **12** in the solid state was found to be at least five times greater than that of Polymer **6**. This result indicates again that the DBPP unit can indeed block the interchain interactions. Device evaluations using Polymer **12** as the emissive polymer is currently under way.

Conclusion

It has been shown that incorporating DBPP units into the backbone of a PPV backbone results in a significant enhancement in PL efficiency. It has also been found that introducing oxadiazole units as main-chain substitutents imparts bipolar charge-transporting properties. Combing both DBPP and oxadiazole units into a single conjugated polymer results in a polymer exhibiting both high PL quantum efficiency and bipolar charge-transporting properties, making such a polymer a promising candidate for single-layer LED applications.

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