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A Highly Efficient Light-Emitting Poly{[5-(diphenylamino)-1,3-phenylenevinylene]-*alt*-(2,5-dihexyloxy-1,4-phenylenevinylene)}: Synthesis and Optical Properties

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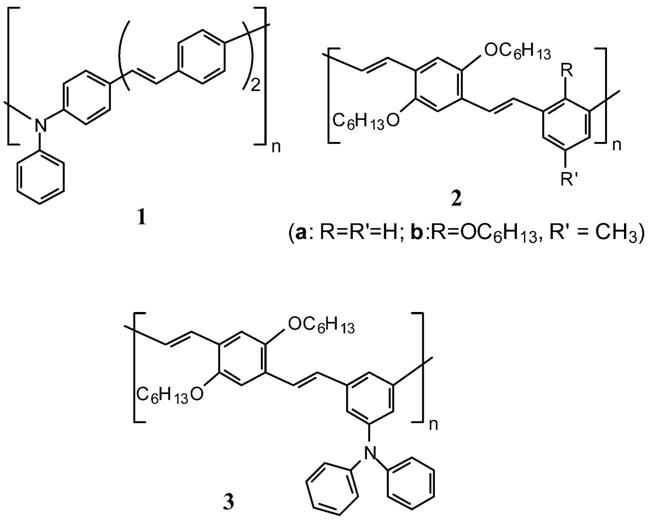
Introduction. Since the discovery of polymeric light-emitting diodes (LEDs)[1] in 1990, considerable progress has been made in the development of π-conjugated polymers and exploration of their application in display technologies.[2,3] The unique combination of their structural, mechanical, photonic, and electronic properties also renders them attractive candidates for use as plastic lasers[4] and chemical sensors.[5]

Light emission from the polymer LED is produced via the recombination of electrons and holes injected through the electrodes. Applying an additional electron injection/transport layer between the emitter and cathode or/and a hole-transporting layer between the emitter and the anode has been successfully used to improve device efficiency and stability.[6−9] Although using blends of polymers with low molecular weight materials with electron/hole-transporting properties[10−13] remains a useful strategy, emissive material with built-in charge-transporting moieties[14−20] proves to be more feasible, since the latter simplifies device fabrication and eliminates problems associated with phase separation of different components. A challenge is to improve the charge-transporting properties while simultaneously preserving or improving the desirable luminescent properties (both fluorescence efficiency and emission color).

Triarylamine- or triphenylamine (TPA)-based derivatives, such as TPD (*N*,*N*-diphenyl-*N*,*N*-di(*m*-tolyl)-*p*-benzidine), have been widely used as the hole-transport layer (HTL) in organic light-emitting diodes (OLEDs).[21] Their applications in polymer light-emitting diodes (PLEDs), however, are restrained intrinsically by their physical properties, such as phase separation, crystallization upon aging,[22] erosion, and spectrum absorption, and by the sophisticated vacuum evaporation procedure required in device fabrication. To circumvent these problems, TPA fragments have been incorporated into the polymer main chain[13,17,18,23] (e.g., **1**[24]), which often alters the emission color due to the presence of nitrogen along the π-conjugated backbone. Pendent-arylamine-based hole-transporting polymers have also been prepared[25,26] and shown to be useful as hole-transporting materials.[27]

Recent studies have shown that poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] derivatives (PmPVpPVs), such as **2**, are highly effective green-emitting materials.[28−31] With a device configuration of ITO/PEDOT/**2a**/Ca, these polymers exhibit promising electroluminescence (EL) (external quantum efficiency ≈ 0.56%).[32] Although the *m*-phenylene linkage helps to confine excitons through π-conjugation interruption, the EL performance of PmPVpPVs has not yet exceeded that of PPVs. A fundamental question remains whether the exciton confinement associated with an *m*-phenylene bridge will eventually lead to materials of superior EL performance. To further improve the EL efficiency of PmPVpPV, we have now synthesized polymer **3**, which includes TPA as a hole-transporting component. The *m*-phenylene in the backbone of **3** belongs to both the emitting chromophore and TPA fragment, thereby creating an intimate contact between them for effective charge injection/migration. In addition, the pendent diphenylamino group attached to the *m*-phenylene ring minimizes its steric impact on the emissive PmPVpPV backbone.

Scheme 1. Structures of Polymers 1−3



Results and Discussion. a. Synthesis of Monomers and Polymer. As shown in Scheme 2, the monomer 5-(*N*,*N*-diphenylamino)benzene-1,3-dicarbaldehyde (**8**) was synthesized from 5-aminoisophthalic acid (**4**) in four steps. Condensation polymerization between dialdehyde **8** and diphosphonate **9** was carried out at 110 °C in toluene using potassium *tert*-butoxide as a base, which afforded polymer **3** as a pale yellow resin in 58% yield. ^{1}H NMR of the polymer in $CDCl_3$ detected no aldehyde groups, indicating that polymerization was complete. Polymer **3** was readily soluble in common organic solvents such as chloroform, methylene chloride, and tetrahydrofuran. Uniform thin films could be cast from its solutions. On the basis of size exclusion chromatography (SEC) analysis, the weight-average molecular weight of **3** was estimated to be 4.6×10^4 (polydispersity index ≈ 2.3). Thermogravimetric analysis (TGA) in air showed that the polymer was thermally stable up to about 300 °C.

b. Photoabsorption and Photoluminescence of Solutions. The absorption spectrum of polymer **3** in THF solution exhibited two bands with $\lambda_{max} = 308$ and 406 nm (Figure 1). The longer wavelength (or lower energy) absorption band of **3** ($\lambda_{max} = 406$ nm) was very similar to that of the parent polymer **2a** ($\lambda_{max} = 408$ nm),[33] indicating a small substitution effect from the diphenylamino group to the electronic band-gap of the material. Fluorescence of **3** in THF displayed two

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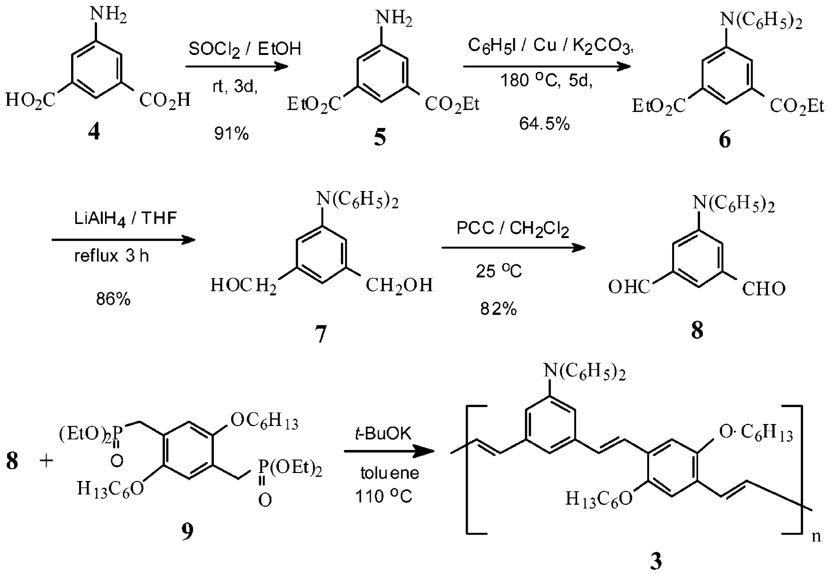
Scheme 2. Synthesis of Monomers and Polymer 3



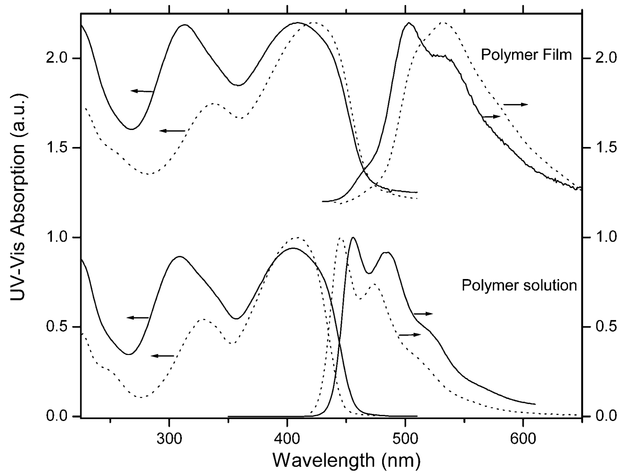


Figure 1. UV–vis and photoluminescence of polymer **3** (solid line) and its parent polymer **2a** (dotted line) in THF solution (bottom) and film (top) states.

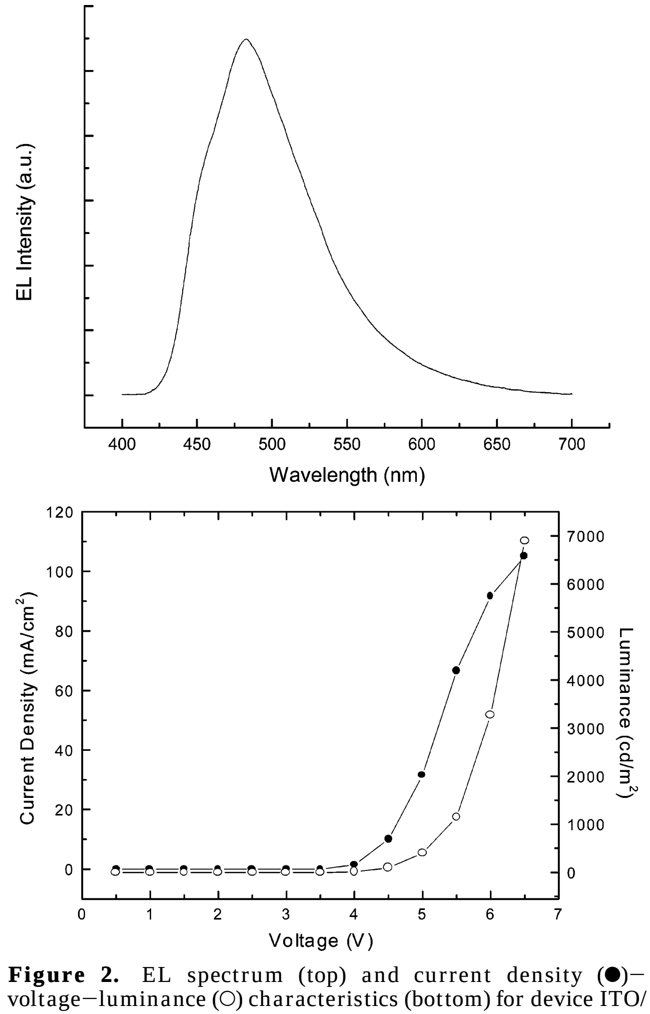


Figure 2. EL spectrum (top) and current density (●)–voltage–luminance (○) characteristics (bottom) for device ITO/PEDOT/polymer **3**/Ca.

emission bands with $\lambda_{max} = 456$ and 483 nm, which are about 10 nm red-shifted from the fluorescence peaks of **2a** (λ_{max} = 445 and 473 nm). The observed slight bathochromic shift in the emission of **3** is in agreement with the anticipated substitution effect. The fluorescence quantum efficiency of **3** was measured to be $\phi_{fl} \approx$ 63%, which is about the same as that of **2a** ($\phi_{fl} \approx$ 64%).[33] In summary, the solution PL characteristics of PmPVp-PV backbone were essentially unaffected by the attachment of diphenylamino group to the *m*-phenylene ring.

c. Thin Film Optical Properties. Polymer films were prepared by spin-casting from THF solutions onto quartz plates. Films of **3** exhibited two absorption bands ($\lambda_{max} \approx$ 313 and 408 nm), slightly red-shifted from its respective solution absorption bands. Although the low-energy absorption band of **3** in solution was slightly red-shifted from that of **2a**, the absorption of film **3** was blue-shifted from that of film **2a**. The opposite trends observed from the absorption of the solution and film states indicated that the chromophore–chromophore interaction in the ground state of film **3** was weaker than that in the film **2a**, attributed to the bulky diphenylamino substituent in the former. Fluorescence of film **3** exhibited a major peak and a shoulder ($\lambda_{max} \approx$ 503 and 530 nm, respectively). Consistent with the trend observed in the absorption, the emission of film **3** was also blue-shifted from that of film **2a** (by ~11 nm) but remained in the green region. Since a minor emission shoulder at ~465 nm was observed, the major emission band at 503 nm from **3** was assigned to the 0–1 transition. In contrast to the solution spectrum in which the fluorescence of **3** was red-shifted from that of **2a**, the film fluorescence of the former was blue-shifted from that of the latter. The opposite trend observed in the fluorescence of **3** and **2a** in the solution and film states suggested that the film of the former had less aggregation because of the steric bulkiness of the diphenylamino substituent on the *m*-phenylene ring.

d. EL Properties. A double-layer device ITO/PEDOT/**3**/Ca displayed bright green-blue light ($\lambda_{max} = 483$ nm) with a peak full width at half-maximum (fwhm) of ~83 nm (Figure 2). The EL of **3** was notably blue-shifted by ~20 nm from the film PL,[34] which is in contrast to that observed from its parent polymer (the EL of **2a** agrees well with its film PL).[33] Charge injection into the triphenylamine fragment is probably responsible for the observed blue shift, as the hole-containing triphenylamine may require a different molecular conformation to accommodate the positive charge, thereby causing slight PPV backbone twisting. Sample heating in the device[35] may also be partially responsible for the blue shift. The current density−voltage−luminance characteristics of the device are shown in Figure 2. The device had a turn-on voltage at around 4 V. The luminance of the device reached as high as 6895 cd/m^2, attributing to improved hole injection into the PmPVpPV polymer. The maximum external EL quantum efficiency of **3** reached up to 2.66%, which is much higher than that of its parent polymer **2a**. Since charge injection in **3** was not perfectly balanced, we feel that the device efficiency and brightness can be further raised. These results indicate that the EL performance of PmPVpPV materials could compete or even exceed those of conventional PPV materials.

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Supporting Information Available: Synthesis and characterization of monomers and polymer, device fabrication, and TGA curve. This material is available free of charge via the Internet at http://pubs.acs.org.

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