Articles

An Efficient Pyridine- and Oxadiazole-Containing Hole-Blocking Material for Organic Light-Emitting Diodes: Synthesis, Crystal Structure, and Device Performance

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In this paper, we focus on the synthesis and structure of the new bis(1,3,4-oxadiazole) system 2,5-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]pyridine (PDPyDP). We have fabricated light-emitting diodes (LEDs) using poly[2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene] (MEH−PPV) as the emissive material, with and without a thermally evaporated electron-injection/hole-blocking layer of either PDPyDP or its vinylene analogue (E)-1,2-bis-[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]ethene (PDVDP) or its phenylene analogue 1,4-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]benzene (PDPDP). PDPDP is the para isomer of OXD-7, which is a widely used molecular electron-transporting material. Electroluminescence spectra indicate that light is emitted only from the MEH−PPV layer. Using aluminum as the cathode, the bilayer LED with PDPyDP is considerably more efficient than the corresponding single-layer device or devices with PDVDP or PDPDP as the electron-injection layer.

Introduction

Organic light-emitting diodes (LEDs) based on electroluminescence (EL) of conjugated polymers[1] and molecular materials[2] have attracted great attention during the past decade because of their potential applications in a new generation of display and lighting technologies. However, some important and fundamental challenges remain, including maximization of the external quantum efficiency (EQE), design and synthesis of new materials for purer colors, and modes of addressing devices for a full-color display with optimized resolution. A major factor responsible for low device EQEs is that the charge injection and transport in emissive materials are generally unbalanced. This imbalance arises because the energy barrier between the indium tin oxide (ITO) anode and the highest-occupied molecular orbital (HOMO) level of an emissive material is different from that between the metal cathode and its lowest-unoccupied molecular orbital (LUMO) level. In the case of LEDs using poly(*p*-phenylene) (PPV) and PPVs substituted with electron-donating groups, the former is smaller than the latter, and therefore, hole injection is relatively easier than the corresponding electron injection under forward bias. A well-established approach to balanced charge injection is to use an additional layer[3] of a material with a lower LUMO level than the corresponding PPV derivative underneath the cathode to complement the excess hole injection from the opposite electrode.[4] This additional layer consequently becomes an electron-injection layer. In addition, if there is a significant difference in the HOMO levels at the interface between the two organic layers, the layer also functions as a hole-blocking layer.

Molecular and polymeric 1,3,4-oxadiazole (OXD) derivatives are the most widely studied classes of electron-injection and/or hole-blocking materials, mainly because of their electron deficiency, high photoluminescence quantum yield, and good thermal and chemical stabili-

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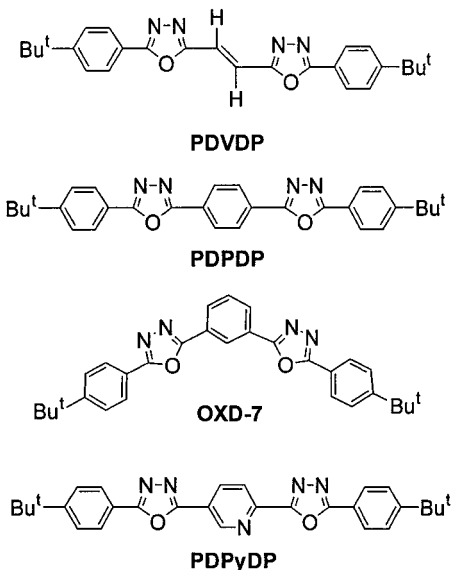§ Tianjin Institute of Technology.

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Scheme 1

ties.[5] In this context, 1,3-bis(2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl)benzene (OXD-7) has been used in LEDs with different emissive materials, and significant improvement in LED performance has been observed by Tsutsui and co-workers.[6] Similarly, as pyridine is a moderately electron-deficient π system, poly(2,5-pyridylene) has also acted as an electron-injection/hole-blocking material for organic LED fabrication.[7] In another report, LEDs using poly(pyridylvinylene) as the emissive material and PPV as the hole-injection material were found to give improved EQEs.[8] Very recently, OXD-7 has been used in an organic–inorganic perovskite LED as an electron-transporting (ET) material.[9] We, therefore, reasoned that a hybrid of pyridine and oxadiazole could lead to increased electron-injection ability.

In this paper, we focus on the synthesis and structure of a new bis-OXD system with one pyridine unit incorporated, namely, PDPyDP (Scheme 1). We thermally evaporated this material to fabricate bilayer LEDs using poly[2-(2-ethylhexoxy)-5-methoxy-1,4-phenylene-vinylene] (MEH–PPV) as the emissive layer. To evaluate the efficiency of this material, the phenylene and *trans*-vinylene analogues, namely, 1,4-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]benzene (PDPDP) and (E)-1,2-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]-

ethene (PDVDP), were synthesized for comparison. PDPDP, first synthesized in 1987,[10] and PDVDP, synthesized in 1988,[11] have not, to our knowledge, been used in OLEDs, although OXD-7 has been extensively explored as an electron-transporting material by Tsutsui and co-workers.[6] In a recent study, we showed that MEH–PPV devices incorporating PDPyDP as an electron-transport layer have improved characteristics over those incorporating OXD-7.[12]

Experimental Section

1. General. Chemicals were purchased from Aldrich and Lancaster and were used without further purification unless otherwise indicated. Solvents were dried according to standard procedures[13] as appropriate. Elemental analyses were performed with a Carlo Erba Strumentazione instrument. Melting points were determined in open-end capillaries using a Stuart Scientific SMP3 melting point apparatus at a ramp rate of 5 °C min^{-1} without calibration. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Unity 300 spectrometer at frequencies of 299.91 and 75.41 MHz, respectively, and chemical shifts are reported in ppm downfield of TMS. Mass spectra were obtained on a VG7070E instrument operating in EI mode at 70 eV. UV–vis absorption spectra were recorded on a Unicam UV2 spectrometer. Photoluminescence spectra of chloroform solutions were measured using a CCD spectrograph following excitation at 350 nm by a monochromated Hg/Xe lamp. The electroluminescence spectra were measured with a CCD spectrograph. Low-angle X-ray scattering experiments were performed with a Bede Scientific GXR1 instrument operating at a wavelength of 1.3926 Å.

2. X-ray Crystallography. X-ray diffraction experiments were carried out at room temperature on a Bruker three-circle diffractometer with a SMART 1 K CCD area detector, using Mo K$_\alpha$ radiation ($\bar{\lambda}$ = 0.71073 Å). Four sets of 0.3° ω scans, each set with different Φ and/or 2θ angles, nominally covered over a hemisphere of reciprocal space. The intensities were integrated using SAINT software.[14] The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data using SHELXTL software.[15] A summary of the experiments is given in Table 1. Full crystallographic data, excluding structure factors, have been filed at the Cambridge Crystallographic Data Centre, CCDC Nos. 139372 (PDPyDP) and 139373 (PDVDP).

3. Device Fabrication. ITO-coated glass was used as the anode. It was first patterned and etched into strips of 2 mm width. Then, it was cleaned by ultrasonication in soap, deionized water, acetone, and dichloromethane sequentially and dried in an argon atmosphere. MEH–PPV, which was used as the active material, was spin-coated onto the ITO-coated glass from its solution in a 1:1 mixture of chloroform and *p*-xylene to form a film with a dry thickness of ca. 80 nm, for both single-layer and double-layer devices. The second layer of electron-injecting/hole-blocking material was deposited by vacuum evaporation[16] at pressures of ca. 6 × 10^{-6} mbar and evaporation rates of ca. 0.1 nm s^{-1} for PDPDP, 0.2 nm s^{-1} for PDVDP, and 0.3 nm s^{-1} for PDPyDP to thicknesses of 74 nm

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Table 1. Crystal Data

compound	PDVDP	PDPyDP
empirical formula	$C_{26}H_{28}N_4O_2$	$C_{29}H_{29}N_5O_2$
crystal system	monoclinic	monoclinic
space group	$C2/c$ (#15)	$P2_1/c$ (#14)
a, Å	23.987(3)	12.993(2)
b, Å	10.493(1)	6.222(2)
c, Å	10.363(1)	15.977(4)
β, °	111.45(1)	99.26(1)
V, Å^3	2427.5(5)	1274.8(6)
Z	4	2
D (calcd), g/cm^3	1.173	1.249
2θ max, °	60.5	50.7
data collected	9296	7436
data unique	3345	2341
data obsd, $I > 2\sigma(I)$	1577	1352
$R(F)$, obsd data	0.061	0.061
w$R(F^2)$, all data	0.167	0.194
largest diff peak, eÅ^{-3}	0.19	0.28

for PDPDP, 55 nm for PDVDP, and 62 nm for PDPyDP. Finally, an Al cathode was evaporated under similar conditions in 1-mm-wide strips normal to the ITO strips. In this work, the relative thicknesses of both the emissive and electron-injection layers were not optimized for maximum brightness and efficiencies. All electrical measurements were made in a vacuum chamber (ca. 10^{-1} mbar). Biases were supplied by a Keithley 2400 source using a linear staircase step of 0.5 V with a 2-s delay between measurements. The EL devices were mounted over a large-area silicon photodiode. Not all of the light from the LED (i.e., scattered light) was collected by the photodiode, and so, the efficiencies quoted in this paper are lower limits. The photocurrents generated were recorded using a Keithley 485 digital picoammeter. For quantum efficiency measurements, the light power was calculated with a typical conversion factor of 0.32 A/W at 590 nm corresponding to the electroluminescence peak of MEH−PPV.

4. Materials. *(E)-1,2-Bis[2-(4-tert-butylphenyl)-1,3,4-oxa-diazol-5-yl]ethene (PDVDP).* The compound was synthesized from fumaric dihydrazide and 4-*tert*-butylbenzoic acid in polyphosphoric acid (PPA), following a reported procedure.[11] The material used for the LEDs was purified first by column chromatography on silica (dichloromethane−methanol) and then crystallized from 1,4-dioxane as white crystals. Large colorless plates suitable for X-ray crystallographic analysis were obtained by slow evaporation of a chloroform solution of the purified solid. Mp: 311.3−313.4 °C. Anal. Calcd for $C_{26}H_{28}N_4O_2$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.47; H, 6.60; N, 12.88. ^{1}H NMR (CDCl$_3$) δ: 1.36 (s, 9H), 7.55 (d, J_{AB} = 8.4 Hz, 2H), 7.58 (s, 1H), 8.04 (d, J_{AB} = 8.7 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ: 31.02, 35.12, 118.97, 120.27, 126.15, 126.99, 156.03, 162.26, 165.07.

1,4-Bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl]benzene (PD-PDP). By analogy with the preparation and purification of PDVDP, this compound was synthesized as a white powder from 1 equiv of terephthalic dihydrazide and 2 equiv of 4-*tert*-butylbenzoic acid in PPA, rather than by the reported method.[10] The purification included filtration of the chloroform solution of the compound through a Celite column and then recrystallization from acetic acid. Mp: 322.2−324.6 °C. Anal. Calcd for $C_{30}H_{30}N_4O_2$: C, 75.29; H, 6.32; N, 11.71. Found: C, 75.12; H, 6.14; N, 11.86. ^{1}H NMR (CDCl$_3$) δ: 1.37 (s, 9H), 7.56 (d, J_{AB} = 8.4 Hz, 2H), 8.08 (d, J_{AB} = 8.1 Hz, 2H), 8.29 (s, 2H). ^{13}C NMR (CDCl$_3$) δ: 31.09, 35.12, 120.72, 126.10, 126.55, 126.85, 127.40, 155.67, 163.45, 165.08.

2,5-Bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl]pyridine (PDPyDP). Pyridine-2,5-dicarboxylic acid dimethyl ester (**2**) was synthesized from the corresponding acid (**1**) as reported.[17] Pyridine-2,5-dicarboxylic acid dihydrazide (**3**) was synthesized by treating the diester **2** with hydrazine hydrate according to

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Scheme 2
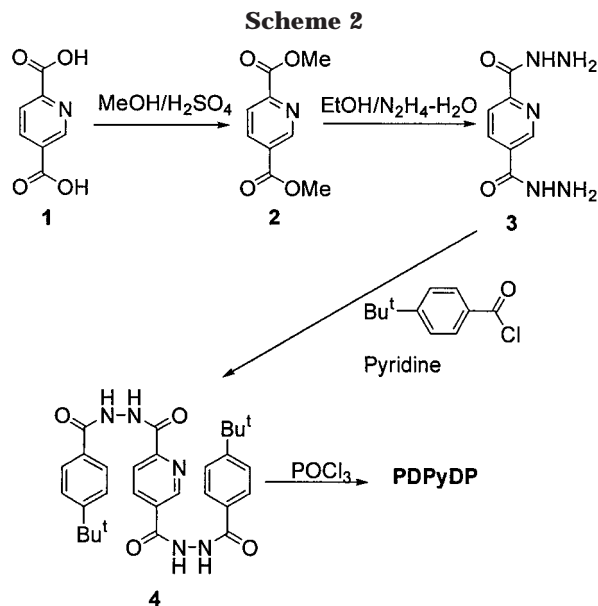
published reports.[18] The dihydrazide **3** (0.98 g, 5 mmol) was suspended in dry pyridine (10 mL) cooled with an ice bath. 4-*tert*-Butylbenzoyl chloride (2.0 mL, 11 mmol) was added dropwise through a syringe with stirring. The cooling bath was removed after the addition, and the mixture was stirred at 20 °C for 20 min and then warmed to 50 °C for an additional 20 min. The mixture was poured into ice−H$_2$O (150 mL). A light yellow solid obtained by suction filtration was washed with a large volume of water and then dried under high vacuum. The solid was carefully mixed with POCl$_3$ (20 mL), and the mixture was stirred and refluxed for 2 h, before being cooled to room temperature. The mixture was carefully hydrolyzed by being poured, in portions, onto crushed ice (ca. 200 g) and was then neutralized with concentrated NaOH solution. Suction filtration of the mixture and washing of the filtrate with water and methanol yielded a light yellow solid, which was dissolved in dichloromethane and then column chromatographed on silica (with dichloromethane as the eluent) to yield pure PDPyDP (1.27 g, 53%) as pale-yellow crystals, mp: 313.7−314.5 °C. A light yellow single crystal suitable for X-ray structural analysis was obtained by recrystallization from chloroform. Anal. Calcd for $C_{29}H_{29}N_5O_2$: C, 72.63; H, 6.10; N, 14.60. Found: C, 72.52; H, 6.08; N, 14.58. ^{1}H NMR (CDCl$_3$) δ: 1.38 (s, 9H), 1.39 (s, 9H), 7.57 (m, 4H), 8.10 (m, 2H), 8.15 (m, 2H), 8.49 (dd, J_1 = 8.4 Hz, J_2 = 0.6 Hz, 1H), 8.62 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H), 9.53 (dd, J_1 = 2.1 Hz, J_2 = 0.7 Hz, 1H). ^{13}C NMR (CDCl$_3$) δ: 31.06, 35.13, 35.14, 120.34, 120.42, 121.88, 123.36, 126.07, 126.19, 126.95, 127.17, 135.26, 155.95, 155.99, 161.54, 163.00, 165.47, 166.01.

Results and Discussion

1. Synthesis of Materials. PDVDP was synthesized as reported[11] by the reaction of fumaric dihydrazide with 4-*tert*-butylbenzoic acid in PPA. The compound was further purified by column chromatography and then by recrystallization for improved LED performance. The structure of the compound was unambiguously established by high-field NMR spectroscopy and X-ray structural analysis, which have not been reported previously. Similarly, PDPDP was synthesized from terephthalic dihydrazide (1 equiv) and 4-*tert*-butylbenzoic acid (2 equiv) in PPA using a procedure different from that reported earlier,[10] and its structure was determined by

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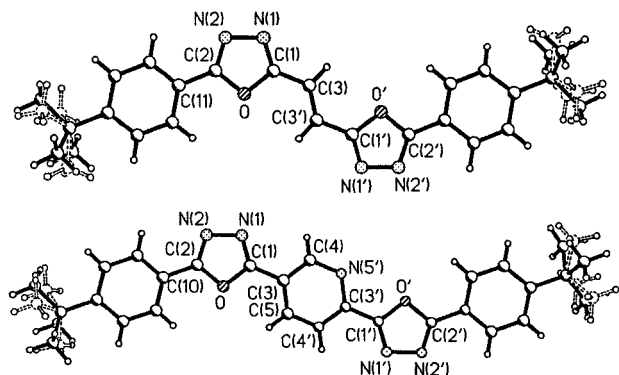
Figure 1. X-ray molecular structures of PDVDP (upper) and PDPyDP (lower), showing the disorder of the *tert*-butyl groups. Primed atoms are generated by inversion centers. The pyridine N atom in PDPyDP is disordered between positions 4, 4′, 5, and 5′.

high-field NMR spectroscopy and CHN analysis. Because monopyridinecarboxylic acids do not condense efficiently with hydrazine in strong acids,[19] we chose the route via bis(dihydrazide) (**4**, Scheme 2) to prepare the pyridine analogue PDPyDP. 2,5-Pyridinedicarboxylic acid **1** was esterified to the diester **2** by being refluxed in methanol with H_2SO_4 in 86% yield. The diester was then treated with hydrazine hydrate to give the dihydrazide **3** in almost quantitative yield (99%). Condensation of dihydrazide **3** with 4-*tert*-butylbenzoyl chloride yielded the bis(dihydrazide) **4**. This compound was soluble in a range of solvents including methanol, ethanol, and 1,4-dioxane but did not crystallize well out of these solvents. We treated the raw material directly with $POCl_3$ to obtain the cyclized product PDPyDP, which could be purified easily by both column chromatography and recrystallization. Because of its increased solubility in organic solvents (and hence the ease of purification of intermediates), OXD-7 was prepared using a method analogous to that of PDPyDP.

2. X-ray Crystallography. The structures of PDVDP and PDPyDP (Figure 1) were determined by single-crystal X-ray diffraction. In both cases, the molecules are located at crystallographic inversion centers, and the *tert*-butyl groups are rotationally disordered. The disorder was described as two sets of positions of the methyl groups, with occupancies of 63 and 37% in PDVDP and 79 and 21% in PDPyDP. In the pyridine ring of PDPyDP, the nitrogen atom is distributed randomly between all four unsubstituted positions. Except for the methyl groups, both molecules are approximately planar, especially PDPyDP. The oxadiazole rings in PDVDP form dihedral angles of 3° with the olefin moiety and 12° with the benzene ring; in PDPyDP, they form angles of 3° with the pyridine ring and 5° with the benzene ring. The crystal packing of PDPyDP (Figure 2) is intermediate between layered and herringbone motifs; the mean plane of a molecule is inclined by 14° to the layer plane and by ca. 30° to the molecular planes of the adjacent layers. It is noteworthy that the "long axes" (defined as the vector between the quaternary carbon atoms) of all of the molecules in the structure are parallel within 9°.
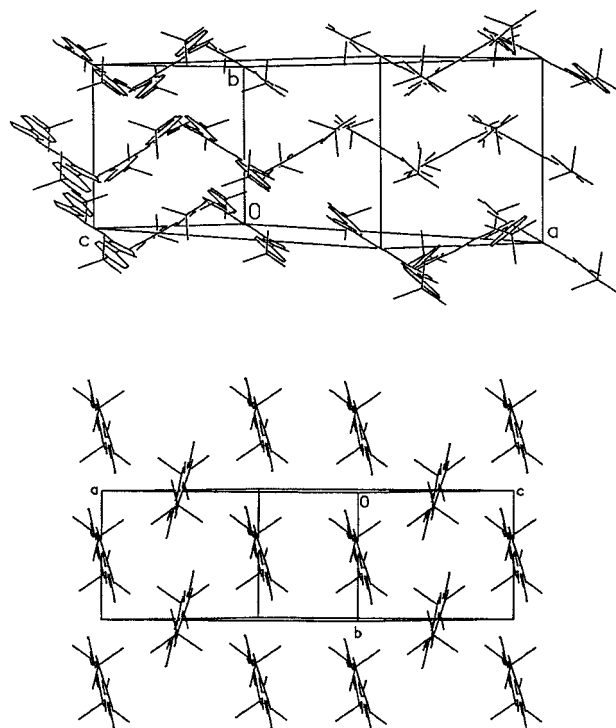

Figure 2. Packing diagrams of PDVDP (upper) and PDPyDP (lower) viewed along the long axes of the molecules.

Molecules of PDVDP (Figure 2) are packed in a peculiar "interwoven" motif. Mean planes of contacting molecules form dihedral angles of 61°, but the long axes of the molecules diverge by no more than 16°. The differences between the two kinds of packing style would be expected to result in a difference of charge mobility within the material.

Studies of oligothiophenes[20] have revealed that the crystal structures of the compounds most effective for charge transport in thin films have the following features: (i) the molecules are arranged in discrete layers; (ii) long axes, and preferably planes of molecules in a layer, are parallel to each other; and (iii) the "tilt angle" between the long molecular axis and the normal to the maximum-density plane of the layer is minimal. The latter condition implies that the parallel slip between adjacent molecules is minimal. Such an arrangement, observed in bulk crystals, can be preserved down to a thickness of several micrometers, making the film a two-dimensional medium in which charge mobility is favored in the direction parallel to the film, i.e., perpendicular to the long axis of the molecule. However, some mixed-ring systems do not conform to condition iii.[21]

As shown in Figure 2, separate layers are much more in evidence in the structure of PDPyDP, whereas PDVDP displays a peculiar interwoven motif. In both structures, the long axes of all of the molecules are approximately parallel, to within 9° in PDPyDP and 16° in PDVDP. The packing of PDPyDP within a layer is intermediate between parallel and herringbone (T-

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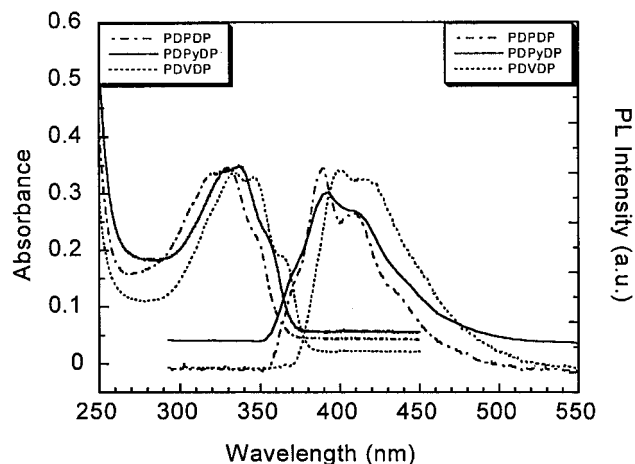
Figure 3. Solution UV–vis absorption and photoluminescence (excited at 350 nm) spectra of PDPDP, PDPyDP, and PDVDP in chloroform.

shaped): the mean planes of adjacent molecules form a dihedral angle of ca. 30°. The corresponding interplanar angle in PDVDP is 61°. Thus, PDPyDP satisfies conditions i and ii much better than PDVDP. However, the parallel slip between adjacent molecules of PDPyDP in a layer is approximately one-quarter of the total length of the molecule, and the long molecular axis is tilted by ca. 60° from the perpendicular to the layer, in poor agreement with condition iii.

Structural studies of such systems are sparse. A survey of the Cambridge Structural Database[22] (April 2000 release, 215403 structures) revealed only four structures (excluding transition metal complexes), that contain a linear chain of three or more aromatic rings, one of them an oxadiazole ring. Of these, three isostructural compounds, diphenyl-, difuryl-, and dithienyl-oxadiazole,[23] adopt planar conformations but a packing motif with adjacent molecules having perpendicular planes and perpendicular long axes. The only compound with parallel packing is 2,5-bis[(tetrahydrobenzothi-enyl)thienyl]oxadiazole,[21] a potential LED material with a relatively good fluorescence quantum yield. The latter molecule adopts a slight (ca. 9°) U bend; the packing motif is one of face-to-face pseudo-dimers, arranged into a lamellar structure with a parallel slip of one-half the molecular length between adjacent dimers. To our knowledge, no linear system with more than one oxadiazole ring has been structurally characterized so far, nor has a molecule with an olefinic moiety directly bonded to an oxadiazole ring.

3. UV–Vis Absorption and Photoluminescence (PL) Spectroscopy.
The UV–vis absorption and photoluminescence spectra of PDVDP, PDPDP, and PD-PyDP in chloroform solution are presented in Figure 3. Because of the structural similarity, the absorption and emission spectra of all three compounds are very similar in shape. The highest absorption peak wavelengths (the central peak) of both PDPyDP and PDVDP are red-shifted by 8 and 17 nm, respectively, compared with that of PDPDP (330 nm). This could be explained by the reduced LUMO–HOMO band gaps resulting from the
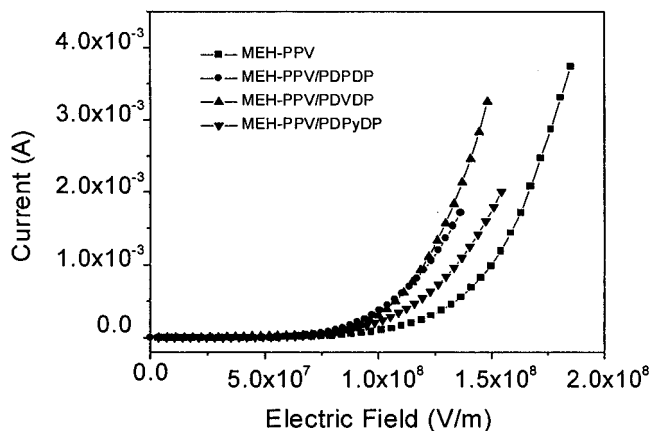
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Figure 4. Current versus electric field for both single-layer and bilayer LEDs. In each case, ITO was used as the anode, and aluminum was the cathode.
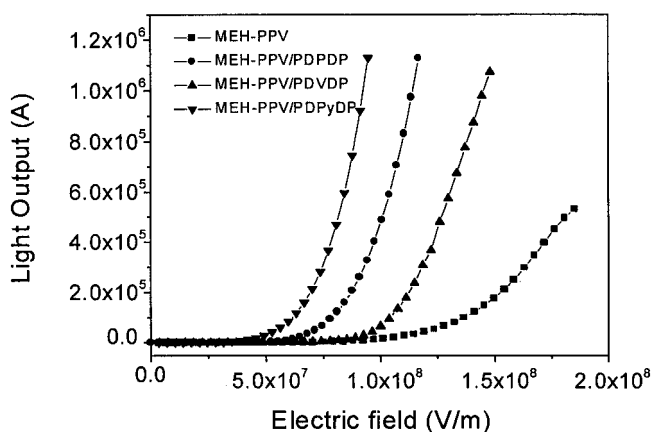

Figure 5. Light output versus electric field data for the LEDs whose current/electric field curves are shown in Figure 4.

different degrees of coplanarity of the three molecules. In PDPyDP, a nitrogen atom with a lone pair of electrons replaces one of the four central C–H groups of PDPDP and, consequently, reduces the steric repulsion between the central chromophore and the neighboring oxadiazole rings. In contrast, for PDVDP, a *trans*-vinylene moiety replaces the six-membered rings of the other two compounds, so this molecule is the most planar. The solution PL spectra of all three compounds are almost mirror images of their UV–vis absorption spectra. A similar red-shift trend was observed in the PL spectra, in which the PDPyDP peak was shifted by 2 nm and the PDVDP peak by 9 nm relative to that of PDPDP. These data suggest that the geometric relationship of these compounds in their ground states is retained in their excited states.

4. Bilayer LEDs using PDPDP, PDVDP, and PDPyDP.
Tsutsui and co-workers have used OXD-7 as an electron-transporting/hole-blocking material in efficient polymeric LEDs.[6] In our studies, we compared four types of device: a single-layer LED using MEH–PPV as the emissive material, ITO as the anode, and aluminum as the cathode; and three bilayer LEDs with the structure ITO/MEH–PPV/PDXDP/Al, where the PDXDP layer was PDPDP, PDVDP, or PDPyDP. The current versus applied electric field characteristics of these devices are compared in Figure 4, while Figure 5 displays the light output versus electric field behavior
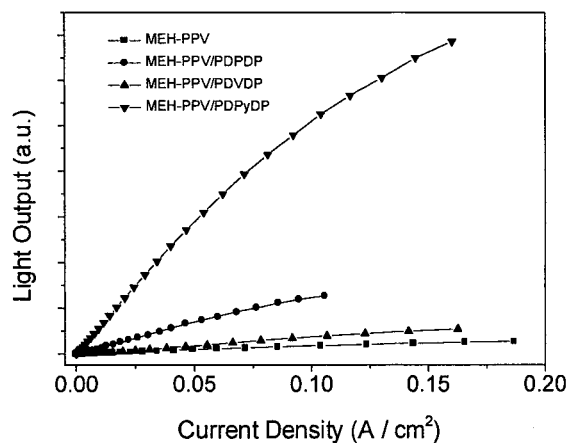
Figure 6. Light output versus current density for the single-layer and bilayer LED devices whose electrooptical characteristics are provided in Figures 4 and 5.

Figure 7. Normalized electroluminescence spectra for the single-layer and bilayer LED devices whose electrooptical characteristics are provided in Figures 4 and 5.

for the same devices. The three bilayer structures yield almost identical current versus electric field data, suggesting similar electrical transport processes in the three devices. The turn-on electric field for EL is lower for the bilayer structures than for the single MEH−PPV layer device, the lowest value being observed for the LED incorporating PDPyDP.

Figure 6 shows the light output versus current density curves for the four LEDs. Approximately linear behavior was measured for all of the device structures. At a current density of 50 mA cm^{-2}, the values of external quantum efficiency were (5.9×10^{-3})% for the MEH−PPV single-layer device, (1.1×10^{-2})%, for the bilayer device using PDVDP, (4.2×10^{-2})% for the PDPDP-containing structure, and 0.24% for the LED incorporating PDPyDP. The EQE of the MEH−PPV single-layer device was therefore approximately doubled by using PDVDP, increased by about 6 times with PDPDP, and increased by about 30 times with PDPyDP. It is worth noting that further improvement in the efficiency figures is possible through optimization of the relative thickness of the different layers and the use of dopants.[24]

The electroluminescent spectra of the LEDs with and without the electron-transporting layers are presented in Figure 7. The peak EL emissions of the three bilayer devices are characteristic of MEH−PPV emission and independent of the structure of PDXDP, indicating that the light originates from the MEH−PPV layer.

The increased electron-transporting ability of PDPyDP over the two analogues could be the result of two possible effects. First, the electron-deficient pyridine ring decreases the LUMO level of the PDPyDP molecule more than a C=C or a benzene ring would;consequently, the energy barrier to electron-injection is decreased. The other possibility is that the electron mobility is higher in crystalline PDPyDP than in the other two materials. Molecules of PDPyDP pack in a different way from PDVDP molecules in the solid state (Figure 2). The former is in a kind of layered motif and molecules within the layers are parallel to each other; therefore, the overlap of the molecular orbitals of PDPyDP molecules in the solid state should be more significant. In contrast,
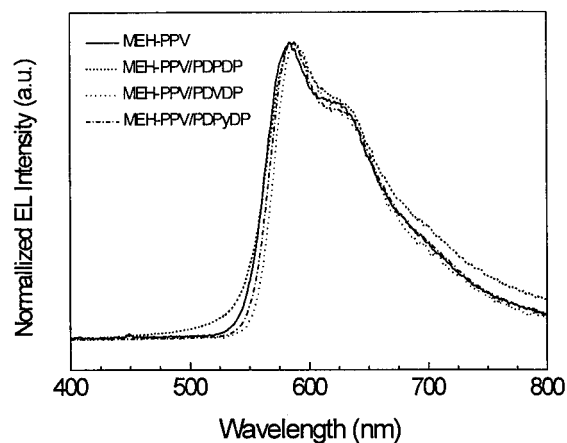
molecules of PDVDP interweave with each other, forming dihedral angles of 61° between the mean planes of the contacting molecules. In this kind of packing, valence orbitals are less likely to overlap to form conducting bands. Low-angle X-ray diffraction experiments revealed a single weak Bragg peak at 3.1° (assuming this was the first-order peak, the corresponding d spacing was 1.29 nm) for a PDPyDP film thermally evaporated under the same conditions as those used in the LED fabrication, indicating that the PDPyDP film was, at least partially, crystalline. In contrast, no such structure was seen in the X-ray data for films of PDPDP and PDVDP. However, AFM images of PDPyDP evaporated onto spun MEH−PPV film revealed a uniform film, but no structural features could be discerned.

The PDPyDP bilayer devices were found to be not particularly stable initially. Following storage in a low vacuum after the EL measurements (ca. 0.1 mbar for 12−24 h), dark regions were observed in the emissive area. Recharacterization of the stored device led to a reduced light output, proportional to a decrease of the sample current (but the EQE retained its initial value of ca. 0.2%). However, preliminary experiments showed that the inclusion of additional buffer layers of copper phthalocyanine and tris(8-hydroxyquinoline)aluminum between the anode and the MEH−PPV layer and between the PDPyDP layer and the Al electrode, respectively, could be used to enhance the device lifetime considerably. Full details of this work are provided elsewhere.[12] In another type of double-layer configuration in which the MEH−PPV was doped with ~15% rubrene, we found that annealing the degraded device could fully restore, and then improve, the characteristics of the device, and also the stability to a significant extent. Figure 8 shows the time dependence of the light output of one these devices. Extrapolated plots of these curves indicate that the device annealed at 175 °C had a half-life of ca. 150 h. Full details concerning the stablization of devices using MEH−PPV and PDPyDP will be published elsewhere.[24]

Conclusions

PDPyDP and its vinylene (PDVDP) and phenylene (PDPDP) analogues have been synthesized, and the

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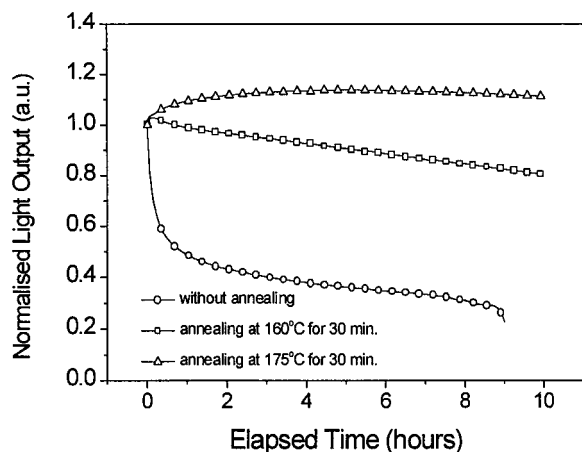
Figure 8. Normalized light output versus time for ITO/MEH−PPV (ca. 15% Ru)/PDPyDP/Al devices operated at constant current (10 mA/cm^2) under low vacuum (10^{-1} mbar).

X-ray single-crystal structures of the former two compounds have been determined. LEDs using MEH−PPV as the emissive material, with and without an electron-injection/hole-blocking layer (PDXDP), have been fabricated. EL spectra indicate that light was emitted only from MEH−PPV at the unoptimized thickness (ca. 80 nm) for both of the organic layers. Using Al as the anode, the bilayer LED with the PDPyDP electron-injection layer was about 30 times more efficient than the corresponding single-layer system. However, PD-PyDP accelerated the degradation of the corresponding bilayer devices. Preliminary experiments indicate that additional buffer layers could improve the stability of the device. This work further demonstrates the merits of incorporating pyridine units into LED materials.[25]

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