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A Dithienylbenzothiadiazole Pure Red Molecular Emitter with Electron Transport and Exciton Self-Confinement for Nondoped Organic Red-Light-Emitting Diodes**

By Ju Huang, Xianfeng Qiao, Yangjun Xia, Xuhui Zhu,* Dongge Ma, Yong Cao, and Jean Roncali*

Nondoped red-light-emitting fluorophores are the focus of increasing interest as a possible answer to the technical problems posed by the fabrication of doped red organic light-emitting diodes (LEDs).^[1–4] On the other hand, many red organic emitters of planar structure are subject to aggregation in the solid state, which can result in a dramatic quenching of the photoluminescence.

It has already been shown that some short-chain thiophene-based π -conjugated systems incorporating the 2,1,3-benzothiadiazole unit can present a unique combination of high fluorescence efficiency, high electron affinity, and moderate oxidation potential in solution.^[5] Recently, we showed that symmetrical end-capping of 4,7-di(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole with 3,5-bis(1-naphthyl)phenyl units leads to a solution-processible pure-red electroluminescent molecular glass (**1**) that combines straightforward synthesis and easy purification (Fig. 1).^[6]

In this contribution, we report the fabrication of multilayered organic-LED structures based on compound **1** using vacuum deposition techniques. Analysis of the electrical and optical characteristics of devices with different architectures shows that, in addition to its attractive red-emitting properties, compound **1** exhibits hole-injection and electron-transporting properties that allow for the fabrication of efficient electroluminescent devices without a hole-blocking layer (HBL),

unlike many known red-light-emitting materials based on donor–acceptor structures, in which hole transport is generally predominant in the solid state.^[2,3]

The synthesis of **1** has been described previously.^[6] In a dilute methylene chloride solution, the UV-vis absorption spectrum of **1** presents two absorption bands with maxima at 298 and 486 nm. The fluorescence-emission spectrum shows a maximum at 613 nm, with a photoluminescence quantum yield (Φ_{em}) of 0.58 using rhodamine B in ethanol as a reference. Under excitation with a 488 nm laser light, the fluorescence emission spectrum of thin films cast on quartz from a methylene chloride solution shows an emission maximum at 630 nm, with a full-width at half-maximum (FWHM) of 106 nm and an absolute Φ_{em} of 0.39. The compound is thermally stable, with a decomposition temperature higher than 400 °C, and it exhibits a glass transition at ca. 82 °C in the first heating run, with no crystallization or melting up to 300 °C.^[6] The highest occupied molecular orbital (HOMO, –5.4 eV) and lowest unoccupied molecular orbital (LUMO, –3.2 eV) energy levels were derived respectively from the onset of the oxidation and reduction waves determined by cyclic voltammetry in CH₂Cl₂/CH₃CN (5:1 v/v) in the presence of *n*-Bu₄NPF₆ as electrolyte, using Ag/AgCl as the reference electrode and ferrocene as an internal standard.

The potential of compound **1** as a bulk red emitter in electroluminescent devices has been analyzed for three different multilayered architectures fabricated by sequential vacuum thermal deposition of MoO₃ and organic layers onto indium tin oxide (ITO)-coated glass electrodes. The multilayered device D1 consisted of a 6 nm layer of MoO₃ hole-injection layer, a 70 nm *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) hole-transporting layer (HTL), a 30 nm layer of compound **1**, and a 30 nm tris(8-hydroxyquinoline) aluminium (Alq₃) electron-transporting layer (ETL). The device was completed with the addition of a LiF (1.5 nm) and aluminum (200 nm) bilayer cathode. Device D2 was similar to D1 except for the thickness of the NPB-HTL, which was increased from 70 to 100 nm. In device D3 a 10-nm-thick layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was introduced as hole-blocking layer, while the thickness of the Alq₃ ETL was reduced to 20 nm. The structure of devices D1–(D3 and the corresponding energy-level diagrams are shown in Figure 2.^[7] The luminance (*L*)–(current density (*J*))–(voltage (*V*), and luminous efficiency (*LE*)

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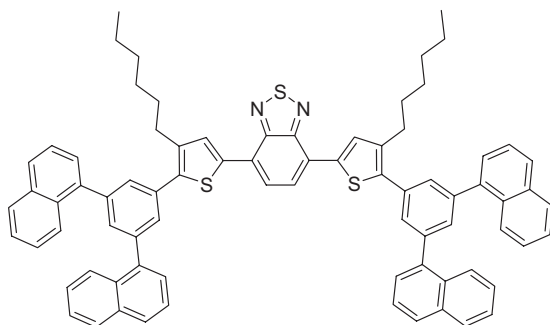


Figure 1. Molecular structure of 1.

versus voltage (V) characteristics of the three devices are shown in Figures 3 and 4, respectively, and the corresponding relevant data are listed in Table 1.

For all devices, the electroluminescence emission originates *solely* from the red emissive layer. The EL spectrum of D2 shows an emission peak at 630 nm with a FWHM of 95 nm quite similar to the photoluminescence emission spectrum of compound 1 in the solid state (Fig. 5). Excitons are perfectly confined over a wide voltage range with practically no variation of the Commission Internationale de L'Eclairage (CIE) coordinates, which is remarkable in the absence of a hole blocker.

Device D2 showed the highest luminous efficiency at a working voltage below ca. 9.5 V (Fig. 4 and Table 1). At a current density of 22 mA cm^{-2} , $V = 7.1 \text{ V}$ and $L = 462 \text{ cd m}^{-2}$, thus $LE = 2.1 \text{ cd A}^{-1}$, corresponding to an external quantum efficiency (η^{ext}) of 2.8%. A maximum luminous efficiency of 3.0 cd A^{-1} was observed at a low current density of 0.10 mA cm^{-2} , corresponding to a η^{ext} of 3.8%. Even at a luminance of 1000 cd m^{-2} , luminous efficiency still remained 1.7 cd A^{-1} at 8.3 V. Therefore, the pure saturated red EL performances shown by device D2 appear to compare favorably to those recently reported for devices based on red-light-emitting structures involving strong electron-donor

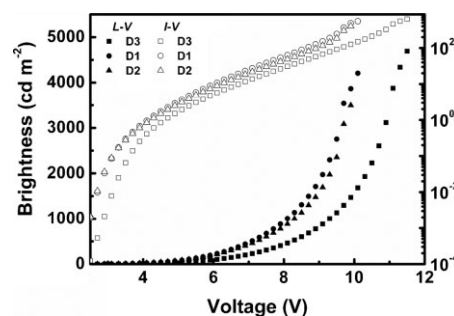


Figure 3. Luminance–current density–voltage characteristics of devices D1–D3.

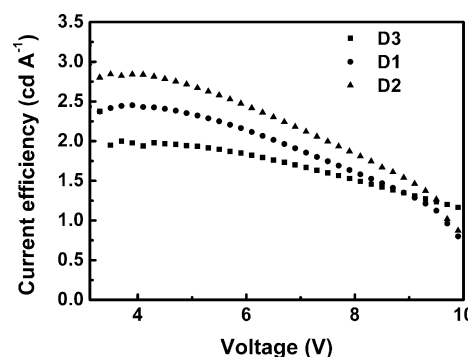


Figure 4. Luminous efficiency vs voltage characteristics of devices D1–D3.

aryl amines, for which a hole blocker was needed to obtain similar CIE coordinates.^[2,3]

It is well known that electrons are the minority charge carriers in NPB/Alq₃ devices. Acknowledging this, one could expect an excess of holes to be injected into the emissive layer of compound 1. In device D2, the HTL is 30 nm thicker than in D1, with all other device parameters kept constant. The thicker HTL could possibly limit excessive hole injection under a given applied voltage, yielding more balanced charge recombination and thus a higher light-emission efficiency. A thicker HTL is often preferable to prevent short circuits and dielectric breakdown in “thin film” electroluminescent devices, as long as the driving voltage is not significantly affected.^[8,9] On the other hand, however, any time the layer thickness is changed, the device efficiency may be affected due to the cavity effect.

Generally, when hole transport is pre-dominant in the emissive layer, the addition

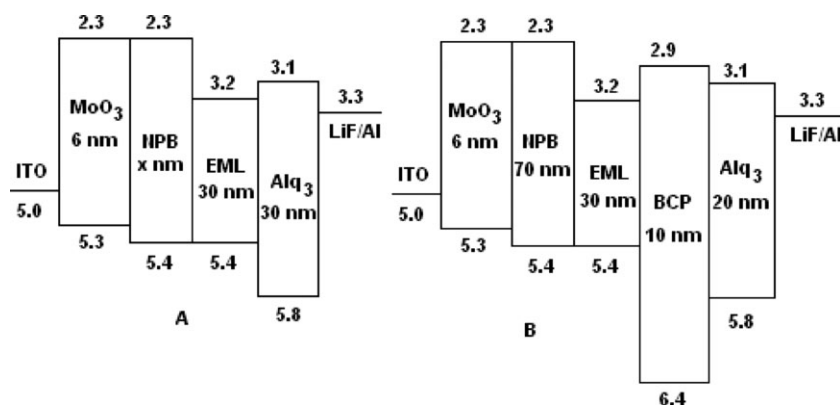


Figure 2. Structure of devices 1–3 and schematic illustration of energy-level Diagrams[7]. A) $x = 70 \text{ nm}$ for device D1 and $x = 100 \text{ nm}$ for D2; B) device D3.

Table 1. Summary of device characteristics.

Device	V _{onset}	LE _{max}	~19 mA cm ⁻²			~100 mA cm ⁻²	
	[V] ^[a]	[cd A ⁻¹]	V	LE [cd A ⁻¹]	L [cd m ⁻²]	V	LE [cd A ⁻¹]
D1	3.0	2.4	6.7	2.0	379	8.7	1.4
D2	2.9	3.0	6.9	2.2	402	9.0	1.5
D3	3.5	2.0	7.5	1.6	309	9.6	1.2

^[a] ~1 cd m⁻².

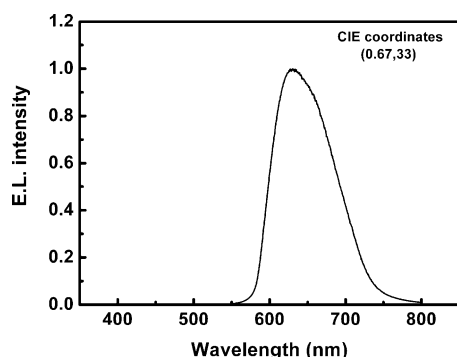


Figure 5. EL spectrum of device D2 at 5 V.

of a hole-blocking layer contributes to confining exciton formation at the EML/HBL interface, thus increasing external quantum efficiency. However, as shown in Figure 4 and in Table 1, the introduction of a HBL in D3 produces a decrease in luminous efficiency (Fig. 4). This result can be attributed to a decreased electron injection into **1**. On the other hand, the lower current observed in device D3 (Fig. 1) suggests that BCP could be a less effective electron transporter than Alq₃.^[10] Apparently, a certain injection energy barrier exists at both the EML/BCP and BCP/Alq₃ interfaces (Fig. 2B).

In the case of a red emitter based on 4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole end-capped with a 2-(carbazoyl-9-yl)-9,9-dioctylfluorenyl moiety,^[6] a two-layer EL device exhibited an almost twofold increase in η^{ext} in the presence of a HBL. This result indicates that hole transport dominates in the emitter, as expected from the presence of the carbazoyl block in the structure, and in agreement with previous observations.^[2,3] The absence of NPB and Alq₃ emissions in devices D1 and D2 strongly supports the idea that holes and electrons are effectively injected and confined in the 30-nm-thick emissive layer (Fig. 5). Based on the energy-level diagram in Figure 2A,^[6,7] there seems to be practically no energy barrier for injection of holes from the HOMO of NPB and of electrons from the LUMO of Alq₃. This is consistent with the more efficient transport of electrons than holes in **1**. Thus, the exciton-formation zone resides near the HTL.

Another advantage in achieving highly efficient nondoped red-light-emitting devices without a HBL lies in the difficulty to find electron-transporting/hole-blocking materials showing high durability under operation.^[11]

Finally, we removed the Alq₃ layer and fabricated the device ITO/MoO₃(6 nm)/NPB(70 nm)/EML(60 nm)/LiF(1.5 nm)/

Al(200 nm) with an emissive layer 30 nm thicker. The device showed pure red electroemission, with a luminous efficiency of 1.7 cd A⁻¹ at a current density of 19 mA cm⁻² and a voltage of 7.2 V, again confirming the electron-transporting nature of **1**. The lower efficiency with respect to device D2 is consistent with more efficient electron injection from a combination of Alq₃/LiF/Al layers.^[12]

To summarize, efficient nondoped red-light-emitting devices have been fabricated using a novel dithienylbenzothiadiazole emitter. The characterization of devices with different architectures provides a coherent picture, consistent with preferential electron transport in the red-emitting compound and with exciton self-confinement, leading to efficient charge recombination within the neat emissive layer. Based on their synthetic accessibility, electroluminescent performance, and the lack of need for a hole blocker, this class of molecular red emitters can thus open interesting perspectives for future research in the area of organic red-light-emitting materials.

Experimental

1 was synthesized according to our recently published procedure [6]. The devices were fabricated by vacuum thermal deposition of MoO₃ and organic materials onto an ITO-coated glass slide at a deposition rate of 0.2 nm s⁻¹ under pressure of less than 5 × 10⁻⁴ Pa. The evaporation rates were monitored by a frequency counter and calibrated by a Dektak 6M Profiler (Veeco). The multilayered device structure was: ITO/MoO₃(6 nm)/NPB(*x* nm)/1(30 nm)/Alq₃(30 nm)/LiF(1.5 nm)/Al(200 nm), where MoO₃ acts as the hole-injection layer, NPB is the hole-transporting layer (*x* = 70 nm for D1 and 100 nm for D2), and Alq₃ is the electron-transporting layer (ETL). ITO and LiF/Al are the anode and bilayer cathode, respectively. The metallic cathode was evaporated at a higher rate of ~0.8–1 nm s⁻¹. A device with a hole blocker and a yet thinner Alq₃ layer ITO/MoO₃(6 nm)/NPB(70 nm)/1(30 nm)/BCP(10 nm)/Alq₃(20 nm)/LiF(1.5 nm)/Al(200 nm) was denoted D3. Current–brightness–voltage characteristics were measured using Keithley source measurement units (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured using a JY SPEX CCD3000 spectrometer. The active area of each device is 0.16 cm². All the measurements were carried out in ambient atmosphere at room temperature.

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