

Bis(thiophenyl)benzothiadiazole Derivatives as Hole-Transporting Red Emitters for Efficient Solution-Processed Pure Red Electroluminescent Devices

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Abstract

A series of bis(thiophenyl)benzothiadiazole derivatives, **TnTB**, were synthesized and characterized. They showed an outstanding red emission with high T_g amorphous and good film-forming properties and excellent OLED performance ($\eta_{\max} = 4.22 \text{ cd A}^{-1}$, PE = 3.16 lm W^{-1} , $\lambda_{\text{EL}} = 662 \text{ nm}$, CIE = 0.66, 0.33).

1. Introduction

In recent years, organic light-emitting diodes (OLEDs) have emerged as a potential candidate for next-generation display and solid-state lighting due to their low driving voltage, high brightness and high efficiency.¹ An important focus of current OLED research is on improving both device structures and new efficient emitting materials. In term of device fabrication, it is well-established that the solution processing is the most favorable fabrication method of OLEDs for low cost and large-area applications. Using small molecule emitters also have great advantages, because the materials used are easy to synthesize and to purify. Among the three primary color light-emitting materials and devices, the red one still lag behind in terms of luminescent efficiency and good color fidelity. So far, most of the reported small-molecule red emitters are the dopants,² while the non-doped one is rare especially the non-doped pure red emitters are very rare.³ In this work, we therefore design new solution processed non-doped red emitters based on the emissive bis(thiophenyl)benzothiadiazole core aiming to improve the performance of the material. The design involves multiple substitutions of this core with a bulky electron donating triphenylamine (TPA) unit which could suppress of aggregation-induced fluorescence quenching of the planar conjugated core as well as increase the hole transporting capability, thermal stability and solubility of the molecule. With this strategy, we notice a significant enhancement in the performance of red OLED compared to the parent compound. Herein, we report a synthesis, physical properties, and a study on OLED fabrication and performance of **TnTB** (Fig. 1).

2. Results and Discussion

A series of bis(thiophenyl)benzothiadiazole derivatives, **TnTB**, was synthesized using a combination of selective bromination and Suzuki cross-coupling reactions, and ob-

tained as purple solids in good yields. These materials show good solubility in most organic solvents allowing their thin films to be fabricated by solution casting processes, which are required for low-cost processing for device manufacturing.

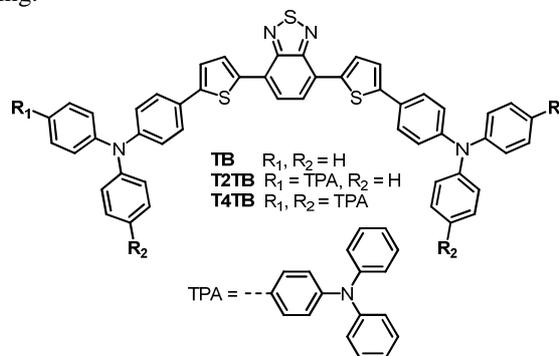


Fig. 1 Molecular structures of **TnTB**.

Quantum chemical calculations of **TnTB** performed using TD-CAM-B3LYP/6-31G(d,p) method reveal that the terminal TPA units in **TB** adopt a planar conformation to the plane of bis(thiophenyl)benzothiadiazole core forming a long π -conjugated backbone, while extra TPA substituents in **T2TB** and **T4TB** assume a non-planar geometry round this planar π -conjugated core, which could help to impede the close π - π contact between the molecules and effect on the optical, morphological and thermal properties of the material.

In solution, the absorption spectra of **TnTB** show characteristic absorption peaks ascribing to the π - π^* transition of the TPA and diphenylaminophenyl thiophene moieties at 309 and 358-372 nm, respectively, while the one at longer wavelengths (528-540 nm) admiring the presence of a donor to acceptor intermolecular charge transfer transition (ICT) in the molecule. Their solution photoluminescence (PL) spectra display featureless emission peaks in the red region (641-650 nm). The absorption peaks and edges of the ICT bands and PL peaks of **TnTB** are slowly red shifted from **TB** to **T2TB** and **T4TB**, suggesting that the extra electron donating TPA peripheries in **T2TB** and **T4TB** have some electronic effects to the backbone of the molecule by adding more electrons to the donor moiety as shown in the DFT results (HOMO orbitals). The thin film PL spectra also show featureless emission peaks in the red

region. A large red-shift (29 nm) is observed the thin film emission maxima of **TB** relative to its solution spectrum, while minor shifts (1-4 nm) are noticed in the cases of **T2TB** and **T4TB**. This indicates that tiny intermolecular π - π interactions in the solid state of **T2TB** and **T4TB**, due to bulkiness effects of the extra TPA substituents.

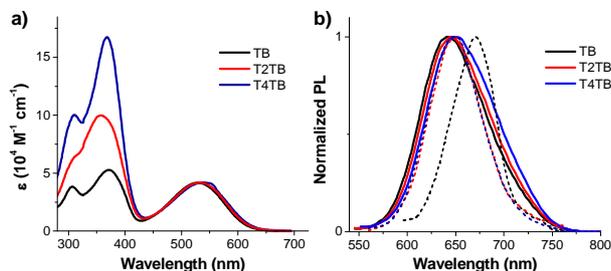


Fig. 2. Plots of a) UV-vis absorption spectra in CH_2Cl_2 and b) normalized PL spectra in CH_2Cl_2 (solid line) and thin films (dot line) spin-coated on quartz substrates.

The results by TGA reveal that all compounds retain thermally stable materials ($T_{5d} > 350\text{ }^\circ\text{C}$). DSC analysis of **TB** show sharp endothermic melting peak of a crystalline phase at $251\text{ }^\circ\text{C}$, while DSC traces of **T2TB** and **T4TB** display only endothermic baseline shifts due to the glass transition (T_g) at 153 and $176\text{ }^\circ\text{C}$, respectively, with no crystallization or melting being observed at higher temperatures, indicating amorphous characteristics.

A double-layer OLED using **T4TB** and **T2TB** as an EML with the device structure of ITO/PEDOT:PSS/EML (spin coating) (30-40nm)/PCB (40 nm)/LiF (0.5 nm)-Al (150 nm) were fabricated and compared with the device fabricated with **TB** (Fig. 3 and Table I). A double-layer OLED using **T4TB**-based diode exhibits a high L_{max} of 17716 cd m^{-2} at 14.4 V , a η_{max} of 4.22 cd A^{-1} at 2.9 mA cm^{-2} and a V_{on} of 3.2 V . The **T2TB**-based double-layer device shows a substantial lower device performance with a L_{max} of 7376 cd m^{-2} , a η_{max} of 1.99 cd A^{-1} at

28.7 mA cm^{-2} and a V_{on} of 3.2 V , while **TB**-based diode shows a low performance (η_{max} of 1.79 cd A^{-1} at 5.0 mA cm^{-2}). The higher EL efficiency of the **T4TB**- and **T2TB**-based devices than **TB**-based device might derive from a combination of a better thin film-forming quality and a higher Φ_F of **T4TB** and **T2TB**. All devices emit a bright red luminescence. The EL spectra of the diodes exhibit a featureless emission peak and match with the PL spectra of the EML and also its single-layer device, indicating that the EL purely originates from their corresponding emitters. The emission peaks and FWHM values of the EL spectra are in the range of 662 - 675 nm and 104 - 114 nm , respectively. The **T4TB**-based diode exhibits an excellent red color quality with CIE coordinates of $(0.661, 0.327)$, which are nearly identical to the NTSC standard. Also, no emission shoulder resulting from the excimer and exciplex species formed at the EML/BCP interface, which often occurs in devices fabricated from EMLs with planar molecular emitter, is detected. Moreover, stable emission is obtained from all devices, and the EL spectra did not change over the entire applied voltages. Even though the overall performance of these red light-emitting devices is not competitive with recently reported red light-emitting phosphorescence devices, the simplicity of device structure in the study is surely an advantage.

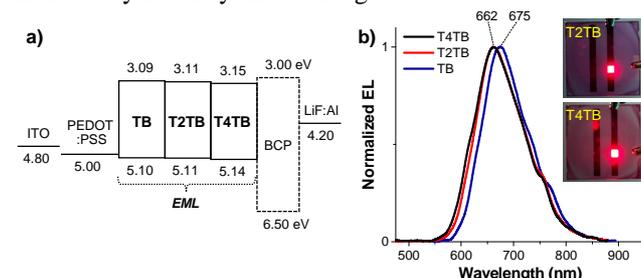


Fig. 3 (a) Schematic energy diagram of the fabricated OLEDs. (b) EL spectra of the OLEDs and their emission colors.

Table I Performance parameters of the OLEDs: ITO/PEDOT:PSS/EML (spin coating)/PCB/LiF-Al

EML	$\lambda_{\text{max}}^{\text{EL}}$ (FWHM) (nm)	V_{on}/V_{100} (V)	L_{max} (cd m^{-2}) at voltage (V)	J_{max} (mA cm^{-2})	η_{max} at J/η at L_{100}/L_{1000} (cd A^{-1} , mA cm^{-2})	PE (lm W^{-1})	CIE (x, y)
T4TB	662 (114)	3.2/4.6	17716 (14.4)	995	4.22 (2.9)/4.19/3.39	3.16	0.661, 0.327
T2TB	662 (108)	3.2/6.2	7376 (14.0)	872	1.99 (28.7)/1.65/1.89	1.83	0.672, 0.318
TB	675 (104)	3.3/6.4	6552 (14.2)	935	1.79 (5.0)/1.50/1.14	1.60	0.693, 0.305

3. Conclusions

In summary, we have demonstrated the simple design of an efficient non-doped red emitter for solution processed OLED. A simple structured OLED using **T4TB** as an EML gives a high luminance efficiency and a pure red emission.

Acknowledgements

This work was financially supported by the TRF (DBG 5580001) and RAIST Foundation. We acknowledge the scholarship support for A Thangthong from the RGJ PhD scholarship.

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Appendix

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