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Red emissive AIE luminogens with high hole-transporting properties for efficient non-doped OLEDs†

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Two bifunctional red AIE luminogens with efficient solid-state emission and good hole-transporting characteristics are reported. Efficient non-doped OLEDs are fabricated with high external quantum efficiencies of up to 3.9%. Bilayer EL devices using them as both EMLs and HTLs are fabricated with good performances.

Red is one of the primary colors for full-color organic light-emitting diodes (OLEDs) and organic white light-emitting diodes. However, organic materials with efficient red emission and good thermal properties are rare.¹ Unlike their blue and green counterparts, conventional red chromophores are usually constructed from nearly planar macrocyclic units with extended π -conjugation, such as 6,13-diphenylpentacene and porphyrins,² or strong electron-donating (D) and -accepting (A) units, such as pyran-containing compounds.³ An example of such chromophores is Nile red,⁴ which is a classical commercial dye with high fluorescence quantum yield (67%) in 1,4-dioxane but almost no light emission in the solid state. This is due to strong intermolecular interactions, which promote the formation of species such as excimers that are detrimental to light emission. Such an aggregation-caused quenching (ACQ) effect⁵ has significantly hampered and complicated the practical applications of conventional

red emitters. Because of this, in electroluminescent (EL) devices, they are typically utilized as dopants with careful control of their concentration to prevent unsaturated red emission resulting from insufficient energy transfer.⁶ On the other hand, these guest–host systems inevitably exhibit performance degradation due to the phase separation upon temperature elevation while the device is working.⁷ Thus, it is desirable to have red-emitting materials that are free from the ACQ effect for non-doped OLEDs.

In 2001, our group observed a phenomenon of aggregation-induced emission (AIE) in silole molecules.⁸ These luminogens are non-emissive in dilute solutions but are induced to emit intensely by aggregate formation.⁹ Thus, such a phenomenon is exactly opposite of the ACQ effect. Since then, many research groups around the world have worked on the AIE phenomenon. Thanks to the enthusiastic efforts by scientists, many AIE molecules with high fluorescence quantum yields (Φ_{FS}) of up to unity in the solid state have been prepared and found to be promising materials for OLED applications.¹⁰ Most of the AIE luminogens developed so far emit at shorter wavelength regions with emission maximum normally less than 600 nm. Few of them, however, show emission in the red region, possibly due to involved synthetic difficulties. Nowadays, conventional blue¹¹ or green¹² emitters with non-planar structures and hence weak π – π interactions perform as good as AIE luminogens do in non-doped OLEDs. The EL performances of the red-emissive ones are still far from satisfactory, with typical maximum external quantum efficiencies ($\eta_{\text{ext,max}}$) ranging from 0.2% to 1.5%.¹ As a result, the development of red AIE luminogens has become the main choice or the only option for the fabrication of efficient red non-doped OLEDs. Indeed, a few red AIE luminogens have been prepared and show promising device efficiency.¹³

Emitters with both efficient solid-state emission and good charge-transporting properties are in high demand because they allow simpler device fabrication, an overall higher stability and a lower production cost.¹⁴ Arylamines, such as *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB)¹⁵ are well-known hole-transporting materials and have been widely utilized in OLED studies due to their outstanding

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† Electronic supplementary information (ESI) available: Emission spectra of TTB and TNB in different solvents; tables summarizing their optical, electronic and thermal properties; time-resolved fluorescence decay curves; cyclic voltammograms; TGA and DSC thermograms; EL spectra, curves and performances; and energy level diagrams. See DOI: 10.1039/c5cc01690h

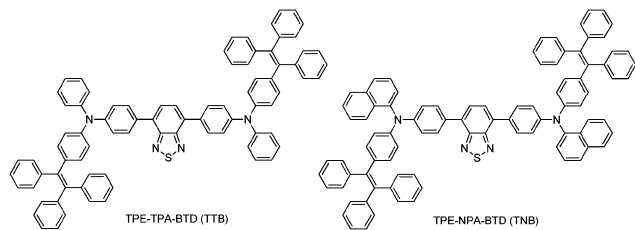


Fig. 1 Chemical structures of TPE-TPA-BTD (TTB) and TPE-NPA-BTD (TNB).

hole-transporting capability. Introduction of arylamines into AIE luminogens is anticipated to create new emitters with bifunctional properties of high hole transportation and strong solid-state light emission.¹⁶ Indeed, many such bifunctional materials with AIE features have been prepared, although most of them show blue or green emission.¹⁷ To enrich the family of bifunctional red AIE luminogens for fabricating OLEDs with simple configurations and further raising the present device performances, in this work, two red emissive AIE luminogens, abbreviated as TPE-TPA-BTD (TTB) and TPE-NPA-BTD (TNB) with good hole-transporting properties are designed and synthesized using tetraphenylethene (TPE), a typical AIE luminogen, and arylamines as building blocks (Fig. 1). Their EL properties are systematically studied. The results show that non-doped EL devices based on these luminogens exhibit good performances. An even more encouraging result is that the bilayer EL device using TTB as both the hole-transporting layer (HTL) and the emitting layer (EML) shows good performance comparable to that of the device using NPB as the HTL, with $\eta_{\text{ext,max}}$ higher than the previous reported value of 2.5%.^{13a} The above good results should shed some light on the development of efficient bifunctional red luminogenic materials for non-doped OLED applications.

TTB and TNB are prepared according to previously published procedures.¹⁸ Both compounds are soluble in common organic solvents, such as toluene (Tol), tetrahydrofuran (THF), dichloromethane (DCM), chloroform, ethyl acetate (EA) and *N,N*-dimethylformamide (DMF), but are insoluble in water. The absorption spectra of TTB and TNB in THF peak at 471 and 470 nm, respectively, which change slightly by varying the solvent polarity (Table S1, in the ESI[†]). The photoluminescence (PL) spectra of TTB and TNB measured in different solvents are shown in Fig. S1 (ESI[†]). When the solvent is changed from Tol to DMF or with an increase in the solvent polarity, the emission of TTB and TNB shifts from 598 nm (orange) to 659 nm (red), and 595 nm (orange) to 649 nm (red), respectively. This suggests that both molecules show the intramolecular charge transfer (ICT) effect due to the electron donation from the arylamine unit to the electron-accepting benzothiadiazole.¹⁹ The ICT effect facilitates good electronic communication functionality and contributes to the red emission of TTB and TNB.

TTB and TNB are AIE-active with high $\Phi_{\text{p,s}}$ of 48.8% and 63.0% in the solid state, respectively (Table S2, ESI[†]). Their solid-state fluorescence decays can be well fitted by single exponential decay functions, from which lifetimes of 4.93 and 3.19 ns, respectively, are calculated (Fig. S2, ESI[†]).

To get a further insight into the photophysical properties of TTB and TNB at the molecular level, density functional theory calculations are carried out using a suite of Gaussian 03 programs.¹⁸ The optimized molecular geometries suggest that both TTB and TNB adopt non-planar conformations as they are constructed from the propeller-shaped TPE unit and the twisted arylamine functionality. Such molecular structures should effectively prevent intermolecular close packing in the aggregated state, thus endowing TTB and TNB with high Φ_{F} in the solid state.

To evaluate the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of both luminogens, their electrochemical properties are investigated by cyclic voltammetry (Fig. S3, ESI[†]). The HOMOs of TTB and TNB are calculated to be -5.23 and -5.21 eV, respectively, from the onset of their oxidation peaks. Such values are close to that of NPB, which is indicative of their good hole-transporting properties. The energy gaps (E_{g}) of TTB and TNB estimated from the onset wavelengths of their UV spectra are found to be 2.26 and 2.27 eV, respectively. Their LUMOs can be obtained using the equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$ and are equal to -2.97 and -2.94 eV, respectively. Since the two compounds have very close energy levels, this explains the high similarity between their absorption and emission behaviors.

The thermal properties of TTB and TNB are investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. As shown in Fig. S4 (ESI[†]), TTB and TNB are thermally very stable, losing merely 5% of their weight at high temperatures of 456 and 535 °C, respectively. Such an outstanding thermal stability is impressive and rare among the AIE luminogens reported previously.²⁰ The glass transition temperature (T_{g}) of TNB is detected to be 169 °C, which is significantly higher than those of DCJTb ($T_{\text{g}} = 98$ °C),²¹ a commercial red-doped material, and NPB ($T_{\text{g}} = 98$ °C). No exothermic peak associated with crystallization is detected in the DSC thermogram of TTB during the heating scan, suggesting that the luminogen remains non-crystalline during the whole measurement.

The efficient solid-state emission and high thermal stability of TTB and TNB make them promising materials for fabricating non-doped EL devices. We first studied their EL by constructing trilayer non-doped EL devices I and II with a configuration of ITO/NPB (80 nm)/TTB or TNB (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm), where NPB functions as the HTL, TTB or TNB is utilized as the EML, 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi) serves as both electron-transporting and hole-blocking material, and LiF serves to enhance electron injection. As shown in Fig. 2 and Fig. S5 (ESI[†]), the EL maximum of both devices is located at 604 nm, which is slightly blue-shifted from the PL peak of their solid films (617 nm) but far from the EL peaks of NPB (440 nm)²² and TPBi (400 nm).²³ This confirms that EL is indeed from the EML. Device I using TTB as the EML turns on at a low bias of 3.2 V, emitting brilliantly with a maximum luminance (L_{max}) of 15 584 cd m⁻² and a maximum current efficiency ($\eta_{\text{C,max}}$), a power efficiency ($\eta_{\text{P,max}}$) and a $\eta_{\text{ext,max}}$ of 6.4 cd A⁻¹, 6.3 lm W⁻¹ and 3.5%, respectively (Fig. 2). Driven at 1000 cd m⁻², the device also

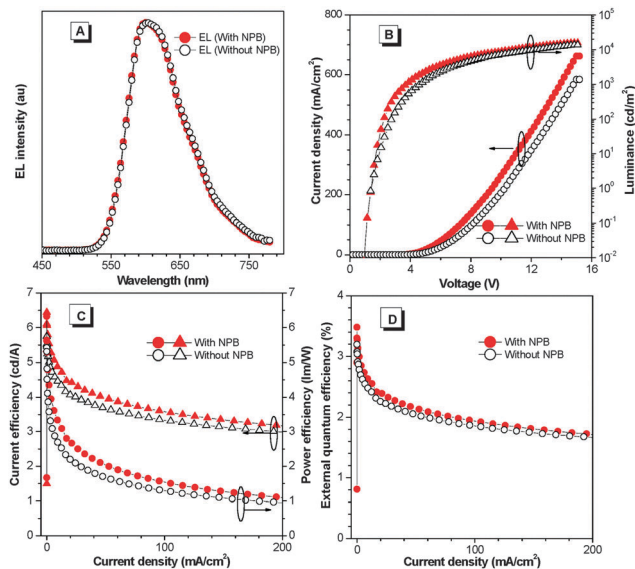


Fig. 2 (A) EL spectra of TTB. (B) Current density–voltage–luminance characteristics of multilayer EL devices using TTB. Changes in (C) power and current and (D) external quantum efficiencies with the applied current density in multilayer EL devices using TTB. Device configuration: ITO/(NPB)/TTB/TPBi/LiF/Al.

performs well with η_C , η_P and η_{ext} of 4.4 cd A^{-1} , 2.6 lm W^{-1} and 2.3%, respectively. Even better results are achieved in device II fabricated from TNB. The device starts to emit at 3.2 V, showing high L_{max} , $\eta_{C,max}$, $\eta_{P,max}$, and $\eta_{ext,max}$ of 16396 cd m^{-2} , 7.5 cd A^{-1} , 7.3 lm W^{-1} and 3.9%, respectively (Fig. S5, ESI†). These values are pretty high for red emitters reported so far. At 1000 cd m^{-2} , high η_C , η_P and η_{ext} values of 4.6 cd A^{-1} , 2.6 lm W^{-1} and 2.4%, respectively, are also achieved (Table S3, ESI†). Such high EL performances are impressive and outperform the previous literature results.²⁴

To decipher the unique EL properties of TTB and TNB, the associated energy level diagrams and device configurations are analyzed. As shown in Fig. 3 and Fig. S6 (ESI†), the LUMO of TPBi is higher than those of TTB and TNB, while the HOMO of NPB is lower than those of TTB and TNB. Thus, no injection barrier exists in TPBi/emitter and NPB/emitter junctions. This enables efficient injection of both holes and electrons to the EML at low bias. Moreover, the much lower HOMO level of TPBi than TTB or TNB (*ca.* 1 eV) effectively blocks the leakage of holes to the cathode,²⁵ while the leakage of electrons to the anode is also hampered to a certain extent by the large energy

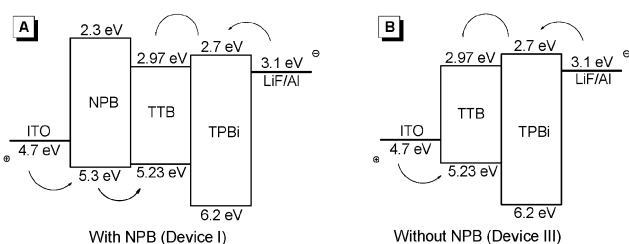


Fig. 3 Energy level diagrams and device configurations of (A) device I and (B) device III.

barrier of 0.7 eV existing between the EML and the HTL. The excitons are thus likely to be confined in the EML, resulting in enhanced EL efficiency.

Since TTB and TNB possess hole-transporting arylamino moieties and have high HOMO levels, they may also function as HTLs besides functioning as emitters. From the energy level diagrams shown in Fig. 3 and Fig. S6 (ESI†), it is possible to remove the NPB layer because the HOMO of the luminogens (*ca.* -5.2 eV) are close to that of NPB (-5.3 eV). To verify this, devices III and IV containing no NPB as the HTL are fabricated. Device III containing TTB as both the EML and the HTL turns on at a low voltage of 3.5 V and emits intense red light with an L_{max} of 13459 cd m^{-2} . Its $\eta_{C,max}$, $\eta_{P,max}$ and $\eta_{ext,max}$ are 5.7 cd A^{-1} , 5.4 lm W^{-1} and 3.2%, respectively, which are very close to those of device I containing NPB as the HTL (Table S3, ESI†). Device IV constructed from TNB also emits intensely with $\eta_{C,max}$, $\eta_{P,max}$ and $\eta_{ext,max}$ comparable to those of device II. These results indicate that both luminogens, especially TTB, can serve as both hole-transporting and light-emitting materials in simplified bilayer EL devices with good performances. It is noteworthy that all the EL curves are smooth, which is suggestive of high stability of the EL devices.

In this communication, the optical, thermal and EL properties of two red AIE luminogens (TTB and TNB) are investigated. Both luminogens exhibit high hole-transporting properties and good thermal stability in the solid state. Efficient non-doped OLEDs are fabricated, which exhibit good device performances with maximum external quantum efficiencies of up to 3.9%. Bilayer EL devices using TTB and TNB as both hole-transporting and emitting materials also show comparable performances to those of devices using NPB as the HTL. The above results demonstrate that both TTB and TNB are promising bifunctional materials for non-doped red OLED applications.

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