High-luminescence non-doped green OLEDs based on a 9,9-diarylfluorene-terminated 2,1,3-benzothiadiazole derivative†

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We have prepared a highly efficient non-doped green organic light-emitting diode (OLED) incorporating a novel 9,9-diarylfluorene-terminated 2,1,3-benzothiadiazole green emitter (DFBTA), which exhibits an excellent solid state photoluminescence quantum yield (81%), and new triaryldiamines (DPAInT2, DPAInF) with high hole mobility derived from rigid and coplanar cores. The optimal device: ITO/DPAInT2/DPAInF/TCTA/DFBTA/Alq3/LiF/Al displayed impressive device characteristics, including a maximum external quantum efficiency (ηext) of 3.7% (12.9 cd A⁻¹) and a maximum brightness at 168 000 cd m⁻².

Introduction

Since tris(8-hydroxyquinolate) aluminum (Alq3) was first demonstrated for green organic light-emitting diodes (OLEDs) by Tang and Van Slyke,¹ many attempts have been made to improve upon its electroluminescence (EL). The main obstacle for the realization of OLED device applications is the organic material, which should ideally combine a high fluorescence quantum yield (if used as the emitter), suitable energy level alignment, high thermal stability, and good thin-film morphology. Only a limited number of materials meet these requirements for advanced commercial application. Among the functional materials used in multilayer OLEDs, the emitting layer usually comprises a suitable host doped with fluorescent or phosphorescent dyes to achieve high EL quantum efficiency. For example, green OLEDs incorporating host materials doped with fluorescent dyes exhibit promising EL efficiencies and have been studied extensively. The commonly used green dyes, such as coumarin,² quinacridone,³ quinoline,⁴ quinoxaline,⁵ and carbazole derivatives,⁶ all suffer from evident self-quenching fluorescence in their pristine thin films, meaning that these structures can only be exploited as dopants. Successful doping requires precise control over the dopant concentration, which can increase the production cost relative to that of systems employing non-doped organic emitting layers. The other limiting factor is the phase separation encountered in the host–guest mixture, rendering energy transfer ineffective.⁷ To pave the way towards successful commercialization, highly efficient green fluorescent emitters for non-doped OLEDs are in great demand. In this regard, Saitoh et al.* and Antoniadis et al.⁸ have demonstrated efficient non-doped green OLEDs exhibiting external quantum efficiencies (ηext) of 3.4%. However, their current efficiencies (<9 cd A⁻¹) and power efficiencies (5 lm W⁻¹) left some space for further improvement. Recently, Lee and coworkers⁹ demonstrated a non-doped green (EL λmax = 511 nm) OLED device incorporating a dually functional material, phenyl-9-[8-(7,10-diphenylfluoranthenyl)]phenylcarbazole (TDPFPC), that displays an impressive current efficiency of 10.1 cd A⁻¹ and a power efficiency of 12.1 lm W⁻¹. In this paper, we report a molecule that combines the electron-accepting characteristics of 2,1,3-benzothiadiazole with the high photoluminescence of fluorene as a green emitter, and its application in a non-doped green OLED device. Through judicious selection of suitable hole injection (HIL) and hole transporting (HTL) layers, this device exhibited an extremely high luminescence (168 000 cd m⁻²) with a maximum external quantum efficiency (ηext) of 3.7%, a current efficiency of up to 12.9 cd A⁻¹, and a power efficiency of 11 lm W⁻¹.

For efficient green emission, core chromophores such as coumarin, quinacridone, quinoline, quinoxaline, and carbazole are usually equipped with donor–acceptor (D–A) structural features along the main conjugated backbone. The D–A charge transfer enables the green emission to appear with high quantum yields in dilute solutions. Such intermolecular dipole interactions are, however, detrimental to the photoluminescence efficiency in the solid state, retarding their uses as solid state emitters in OLED devices. One feasible solution toward developing green emitters with strong solid state emissions is to prepare quasi-symmetrical molecules possessing suppressed molecular dipoles. The relatively narrow band gap required for green emission can be achieved through incorporation of a core chromophore having quinoid character. We selected 2,1,3-benzothiadiazole as the core structure for our green emitter because its derivatives possess excellent electro-optical properties, including high
fluorescence quantum yields and high electron affinities. A commonly used strategy to acquire morphological stability without substantially altering the electro-optical properties of a core chromophore is to introduce bulky, rigid, and inert peripheral substituents that effectively suppress the tendency to crystallize. Along this line, we selected 9-biphenyl-9-tolylfluorene units as end-capping groups for the 2,1,3-benzothiadiazole core. In a previous study, we prepared bis(9,9-diarylfluorene) derivatives as efficient and stable UV-emitting materials; the peripheral aryl groups connected to the C9 carbon atom of the fluorene unit contribute significantly to the improved thermal and morphological stability and high photoluminescence quantum yields. The two different aryl C9-substituents of the fluorene moiety, which are isolated from the main conjugation of the chromophore via an sp3-hybridized carbon atom, suppress the tendency to crystallize and maintain the film’s amorphous morphology. Through this design, the terminal bulky 9,9-diarylfluorene units prevent direct π–π stacking interactions of the active benzothiadiazole chromophores, thereby avoiding aggregation/self-quenching problems and maintaining the molecule’s strong fluorescence in the solid state.

Results and discussion

Scheme 1 depicts the synthesis route for the green emitter 4,7-bis(9,9-diarylfluorenyl)-2,1,3-benzothiadiazole (DFBTA). The 9,9-diaryl-substituted 2-bromofluorene 1 was synthesized through the addition of biphenylmagnesium bromide to the corresponding 2-bromofluorenone, followed by a sulﬁric acid-promoted Friedel–Crafts reaction (50% over two steps). The transformation of the bromide 1 into the corresponding pinacolato boronic ester 2 was achieved in good yield (78%) after lithiating compound 1 with an excess amount of n-BuLi at −78 °C and then treating the lithiated complex with 2-isoproxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. Finally, Pd-catalyzed Suzuki coupling of the boronic ester 2 and 4,7-dibromo-benzo[1,2,5]thiadiazole was accomplished by adding a catalytic amount of tri-tert-butylphosphine as a promoter to afford the target DFBTA in moderate yield (60%).

Despite the interesting photoluminescence properties of benzothiadiazole-based molecules, the practical fabrication of high-efficiency OLEDs is seriously limited by the morphological stability and energy levels alignment of neighboring functional layers. Therefore, it was essential for us to develop contiguous materials that are compatible with DFBTA to improve the OLEDs’ performances. Thus, we synthesized new diphenylamino group-terminated hole injection and transport materials. Diphenylamino moieties have been employed previously with fluorene-based oligomers to improve the hole injection and transporting properties of OLEDs, thereby enhancing the device efficiency and stability. We developed our new hole injection and transport materials from rigid and coplanar cores in which p-tolyl substituents occupy the top and bottom faces of the main conjugated backbone. The introduction of aryl substituents prevented undesirable aggregation and improved the thermal and morphological stability, allowing the formation of homogeneous, stable amorphous films through thermal evaporation—a critical issue for the preparation of OLEDs.

We derived the new hole injection material, the diphenylamino-terminated s-indacen[1,2-b:5,6-b’]dithiophene DPAInT2, from an electron-rich coplanar s-indacen[1,2-b:5,6-b’] dithiophene core structure. Scheme 2 depicts our synthesis route for DPAInT2. We have previously reported the synthesis of the coplanar core 349º featuring two fused thiophene rings. Selective bromination of 3 with 2 eq. of NBS afforded the dibromide 4 in 83%. Pd-catalyzed C–N bond cross-coupling of 4 with diphenylamine gave the desired product DPAInT2 in 90% yield. We synthesized the new hole transporter, the diphenylamino-terminated indeno[1,2-b:5,6-b’]dithiophene DPAInF, through the selective bromination of the coplanar indeno[1,2-b:5,6-b’]fluorene derivative 514º with 2.2 eq. of Br2 in the presence of a catalytic amount of FeCl3 (0.05 eq.) to afford the dibromo chromophore 6 in 95% yield. Pd-catalyzed C–N bond cross-coupling of 6 with diphenylamine gave the new hole-transporting material DPAInF in an isolated yield of 68%.

We used differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to characterize the morphological and thermal properties, respectively, of the green emitter DFBTA, the hole injector DPAInT2, and the hole transporter DPAInF.
DPAInF; Table 1 summarizes the results. DFBTA, DPAInT2, and DPAInF exhibit distinct glass transition temperatures (T_g) higher than 150 °C; therefore, these materials can form homogeneous and stable amorphous films, an essential property for OLED device applications requiring thermal evaporation. We ascribe the amorphous behavior and high values of T_g to the rigidity of the conjugated backbones and the presence of the peripheral p-tolyl substituents, which effectively suppress intermolecular interactions. The aryl substituents also impart these materials with high tolerance toward thermal degradation, as indicated by their high decomposition temperatures (T_d).

We performed cyclic voltammetry to probe the electrochemical behavior of DFBTA, DPAInT2, and DPAInF (Fig. 1). DPAInT2 and DPAInF feature two consecutive quasi reversible oxidation peaks, with those of the latter occurring at more positive oxidation potentials. We attribute the lower oxidation potentials of DPAInT2 to the electron-donating character of the thiophene moieties embedded in its conjugated backbone. The green emitter DFBTA exhibits two quasi reversible reduction peaks at −1.29 and −1.84 V (vs. Ag/AgCl). We ascribe the first of these reduction peaks to the high electron affinity of the benzo-thiadiazole moiety; the distinct potential difference (550 mV) between the two reductions clearly reveals the excellent charge delocalization along the conjugated backbone of DFBTA upon incorporating the fluorene groups. Ultraviolet photoemission spectroscopy (UPS) was utilized to unambiguously determine the ionization potentials of DFBTA, DPAInT2, and DPAInF in solid films (ESI).† On the basis of the UPS data and the optical band gap, Table 1 summarizes the corresponding HOMO and LUMO energy levels of DFBTA, DPAInT2 and DPAInF. The HOMO energy level of DPAInT2, which we estimated to be −5.20 eV, is close to the work function of ITO, indicating that it might feasibly behave as an effective hole-injection material and potentially serves as an alternative of the most popularly used hole injection layer, poly(3,4-ethylendioxythiophene):poly(styrene sulfonate) (PEDOT:PSS).

Fig. 2 indicates that the absorption and emission maxima of DFBTA in solid films are slightly red-shifted relative to those obtained in dilute solution; Table 1 summarizes the data. More importantly, the photoluminescence quantum yields of DFBTA, measured using a Hamamatsu C9920 integrating sphere, were very high: 81% as a thin film, 100% in solution. These quantum yields are significantly higher than those of the prototypical green emitter Alq3 (filmPL: 5%, thin film: 25%). These results clearly indicate the effectiveness of introducing sterically bulky 9,9-diarylfluorene units as termini of a 2,1,3-benzothiadiazole core—evidently suppressing the detrimental intermolecular interactions and reducing the quenching processes.

We conducted charge-carrier mobility measurements of DFBTA, DPAInT2, and DPAInF using time-of-flight (TOF) techniques at ambient temperature. The devices having the configuration glass/Ag (30 nm)/organic (2–3 μm)/Ag (150 nm) were prepared by vacuum deposition and then placed inside a cryostat and maintained under vacuum. Fig. 3(a) and (b) display typical room-temperature TOF transients of holes for DPAInT2 and DPAInF under an applied electric field. The TOF transients reveal that DPAInT2 exhibits dispersive hole-transporting behavior and DPAInF exhibits non-dispersive hole-transporting characteristics, respectively. In the double-logarithmic representations [insets to Fig. 3(a) and (b)], the carrier-transit time, τ_c, required to determine the carrier mobilities, was extracted from the intersection point of the two asymptotes. The field dependence of the hole mobility, μ, was determined [Fig. 3(c)] from the transit time τ_c according to the equation μ = d^2/VT_c, where d is the sample thickness and V is the

**Table 1** Physical properties of the green emitter DFBTA, the hole injector DPAInT2, and the hole transporter DPAInF

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_g/°C</th>
<th>T_d/°C</th>
<th>T_a/°C</th>
<th>E_1/2^{ox}/V</th>
<th>E_1/2^{red}/V</th>
<th>ΔE/mV</th>
<th>HOMO/ΔE</th>
<th>LUMO/ΔE</th>
<th>Abs l_{max,sol.}/nm</th>
<th>PL l_{max,sol.}/nm</th>
</tr>
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<tbody>
<tr>
<td>DFBTA</td>
<td>180</td>
<td>459</td>
<td>418</td>
<td>0.47±0.60</td>
<td>−1.29,−1.84</td>
<td>193,186</td>
<td>6.40</td>
<td>−3.82</td>
<td>310,415; 315,421</td>
<td>525,544</td>
</tr>
<tr>
<td>DPAInT2</td>
<td>176</td>
<td>418</td>
<td>420</td>
<td>0.50±0.95</td>
<td>−1.00,−1.50</td>
<td>100,94</td>
<td>5.20</td>
<td>−2.58</td>
<td>412,420; 467,495</td>
<td>470,503</td>
</tr>
<tr>
<td>DPAInF</td>
<td>183</td>
<td>390</td>
<td>420</td>
<td>0.50±0.95</td>
<td>−1.00,−1.50</td>
<td>100,100</td>
<td>5.60</td>
<td>−2.68</td>
<td>405,407; 423,448</td>
<td>427,452</td>
</tr>
</tbody>
</table>

For each individual redox couple, ΔE = E_{ox} − E_{red}. a Determined by valence-band ultraviolet photoemission spectra (UPS) measurements. b LUMO = HOMO + ΔE_g, where ΔE_g was calculated from the absorption onset of solid film.

**Fig. 1** Cyclic voltammograms of DFBTA, DPAInT2, and DPAInF.

**Fig. 2** UV–Vis absorption and photoluminescence (PL) spectra of DFBTA in dilute dichloromethane solution and as a solid film, and the electroluminescence (EL) spectrum of a device incorporating DFBTA as an emitter.
applied voltage. The hole mobilities exist in the range $3 \times 10^{-3}$ to $1 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ for fields varying from 1.0 to 5.3 $\times$ 10$^5$ V cm$^{-1}$. The observed hole mobility in DPAInT2 ($\mu_h = ca. 3 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) is lower by approximately two orders of magnitude relative to that of its pure hydrocarbon counterpart, DPAInF ($\mu_h = ca. 1 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) under the same electric field ($E = 2.8 \times 10^5$ V cm$^{-1}$). We ascribe the low mobility of DPAInT2 mainly to the relatively nonlinear molecular backbone that originates from the intrinsic molecular geometry of the thiophene ring. This deviation from linearity for DPAInT2 increases the complexity of its molecular ordering in solid films, rendering carrier transport more difficult. For DFBTA, the transient photocurrent signal was too weak to evaluate its mobility using the TOF technique.

To achieve high-efficiency OLEDs, it is necessary to feature an emitter having a high photoluminescence quantum efficiency ($\Phi_{PL}$) in devices of sophisticated construction with judicious selections of compatible functional materials. Of primary importance in the device architecture are a small hole/electron injection barrier from the hole/electron transport layer to the emitting layer and a balanced current density of electrons and holes in the emitting layer, which will favor a low driving voltage and a high device efficiency. To evaluate the feasibility of using DFBTA as an emitting material, DPAInT2 as a hole-injection material, and DPAInF as a hole-transporting material, we fabricated four different non-doped green-emitting devices (I–IV) having the structure ITO/HIL (20 nm)/HTL (20 nm)/TCTA (10 nm)/DFBTA (30 nm)/ETL (30 nm)/LiF (0.5 nm)/Al (150 nm) (Scheme 3). Here, PEDOT:PSS and DPAInT2 were used as the HIL; 4,4’-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) and DPAInF were used as the HTL. Insertion of a hole-transporting material 4,4’,4”-tris(N-carbazolyl)triphenylamine (TCTA) with the required energy levels between HTL and DFBTA, can reduce the hole-injection barrier to DFBTA. Alq3 was used in devices II and IV as the electron-transporting/hole-blocking layer. Lithium fluoride (LiF) was used as the electron-injection layer; aluminum (Al) was the cathode. Fig. 2 reveals that the electroluminescence (EL) spectra of these devices display no emissions from other materials (ESI†)—only the green-light emission from DFBTA with CIEx,y 1931 (Commission Internationale de L’Eclairage) coordinates of (0.38, 0.58).

Fig. 4 and Table 2 provide the current–voltage–brightness ($I–V–L$) characteristics and EL efficiencies of the four devices. In device I we used conventional PEDOT:PSS and NPB as the HIL
and HTL, respectively; this device exhibited a maximum external quantum efficiency of 2.6% (8.6 cd A^{-1}). For comparison and optimization purposes, in device III we replaced the PEDOT:PSS and NPB with DPAInT2 and DPAInF, respectively. The new HIL and HTL possess higher thermal stability and provide more-balanced carrier recombination in DFBTA. Accordingly, device III displayed enhanced EL performance relative to that of device I; the maximum external quantum efficiency of device III reached 3.3% (11.4 cd A^{-1}). In addition, the introduction of DPAInT2 as the HIL offers a significant advantage over conventional PEDOT:PSS in that the pure organic HIL material does not produce acidity to etch ITO or introduce contamination into the HTL.\(^{18}\) In devices II and IV, the insertion of Alq3 as the electron-transport layer between DFBTA and the cathode was crucial to block holes and to confine excitons within the emissive zone. As a consequence, devices II and IV exhibited lower driving voltages and higher performance relative to those of devices I and III (Table 2). The decreased driving voltage can be attributed to the low electron-injection barrier for Alq3 to enhance the current density of the device; for example, \(J = 6600\) mA cm\(^{-2}\) in device IV. Among these four devices, device IV exhibited the highest efficiency: a turn-on voltage of 2.5 V (defined as the voltage at which the EL is rapidly enhanced), a maximum external quantum efficiency of 3.7% (12.9 cd A^{-1}) at 100 cd m\(^{-2}\), and a low driving voltage of 4.6 V. As far as we are aware, this is the best performance reported to date for a non-doped green-light-emitting OLED. In addition, device IV possesses good durability, a high value of \(\eta_{\text{ext}}\) of 2.25% at 100 mA cm\(^{-2}\), and a maximum luminance of 168 000 cd m\(^{-2}\) at 6600 mA cm\(^{-2}\) (14 V). Furthermore, we replaced the electron-transporting material in device IV from Alq3 to 3-(biphenyl-4-yl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ) only to device with lower maximum \(\eta_{\text{ext}}\) (3.13 %) as compared to that of the parent device (ESI).\(^{1}\)

### Conclusions

In summary, we have synthesized and characterized (i) a highly efficient green emitter (DFBTA) based on a 2,1,3-benzothiadiazole core terminated with bulky 9,9-diarylfluorene and (ii) two triaryldiamines (DPAInT2, DPAInF) derived from rigid and coplanar cores. The peripheral aryl substituents of these novel materials provide sufficient steric hindrance to mitigate intermolecular interactions, rendering these novel materials with high morphological and thermal stability, and high PL quantum yields for DFBTA in solid films (up to 81%). Combining the high PL efficiency of DFBTA (emitter), the high HOMO energy of DPAInT2 (hole injection layer), and the high hole mobility of DPAInF (hole transport layer), we fabricated an optimal device having the configuration ITO/DPAInT2/DPAInF/TCTA/DFBTA/Alq3/LiF/Al that featured improved carrier injection and transport and good exciton confinement in the emissive layer. This device exhibited a maximum external quantum efficiency (\(\eta_{\text{ext}}\)) of 3.7% (12.9 cd A^{-1}), a brightness of 168 000 cd m\(^{-2}\), and good durability, as well as a high value of \(\eta_{\text{ext}}\) of 2.25% at a luminance of 8000 cd m\(^{-2}\) and a current density of 100 mA cm\(^{-2}\).

### Experimental

**Synthesis of bromide 1**

Under reflux, a suspension of the yellow solid 2-bromo-fluorenone (6.4 g, 25.0 mmol) in THF (100 mL) was added into a flask containing biphenylnitromagnesium bromide, which had been prepared in advance from 4-bromobiphenyl (8.7 g, 37.5 mmol) and magnesium (0.9 g, 37.5 mmol) in THF (100 mL). The mixture was heated under reflux for another 6 h and then cooled to room temperature, quenched with water, and extracted twice with EtOAc. The combined organic extracts were dried (MgSO\(_4\)) and concentrated by rotary evaporation. Recrystallization (CH\(_2\)Cl\(_2\)--hexane) afforded a crude product that was dissolved in toluene and added slowly into a mixture of tolune and concentrated H\(_2\)SO\(_4\) (1 mL) under reflux; the resulting mixture was then heated under reflux with stirring for 6 h. The cooled solution was quenched with saturated aqueous NaHCO\(_3\) and extracted twice with CH\(_2\)Cl\(_2\). The combined organic extracts were dried (MgSO\(_4\)) and concentrated under vacuum to yield 1 (6.1 g, 50%) as a white solid, which was purified by column chromatography (EtOAc--hexane, 1 : 3). M.p. 141–143 °C; \(\nu_{\text{max}}(\text{film})/\text{cm}^{-1}\) 3435, 3067, 3027, 2916, 2390, 1608, 1562, 1512, 1411, 1267, 1162, 1008, 813, 770, 731 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.73 (1H, d, \(J = 7.6\), Ar–H), 7.63 (1H, d, \(J = 8.0\), Ar–H), 7.56–7.54 (2H, m, Ar–H), 7.53–7.46 (3H, m, Ar–H), 7.46–7.38 (6H, m, Ar–H), 7.34–7.28 (3H, d, \(J = 7.6\), Ar–H), 7.31–7.26 (3H, m, Ar–H), 7.26–7.30 (3H, m, Ar–H), 7.11 (2H, d, \(J = 8.0\), Ar–H), 7.07 (2H, d, \(J = 8.0\), Ar–H), 2.32 (3H, s, Ar–CH\(_3\)); \(^{11}\)B NMR (CDCl\(_3\), 100 MHz) \(\delta\) 152.8, 150.5, 143.8, 141.6, 140.1, 139.2, 138.7, 138.5, 136.2, 130.3, 129.0, 128.7, 128.3, 128.0, 127.8, 127.6, 127.3, 126.8, 126.7, 126.6, 125.8, 121.2, 112.1, 119.9, 65.1, 21.4; MS (m/z, FAB\(^{+}\)) 488 (100), 486 (95); HRMS Calcd for C\(_{32}\)H\(_{23}\)Br\(^{79}\).

**Synthesis of boronic ester 2**

N-Butyllithium (1.6 M, 1.9 mL, 3.0 mmol) was added slowly into a flask containing compound I (974 mg, 2 mmol) in THF.
The mixture was partitioned between CH$_2$Cl$_2$ and water and extracted twice with CH$_2$Cl$_2$. The combined organic phases were dried (MgSO$_4$) and concentrated in vacuo. The residue was purified by recrystallization (CH$_2$Cl$_2$/pentane) to yield 2 (833 mg, 78%) as a white solid. M.p. 137–140 °C; $\nu_{\text{max}}$(film)/cm$^{-1}$ 2970, 1593, 1490, 1352, 1175, 843, 732 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.00 (1H, s, Ar–H), 7.95 (1H, d, J 7.6, Ar–H), 7.89–7.86 (2H, m, Ar–H), 7.62–7.60 (2H, m, Ar–H), 7.53–7.48 (3H, m, Ar–H), 7.46–7.41 (3H, m, Ar–H), 7.39–7.34 (4H, m, Ar–H), 7.34–7.23 (2H, m, Ar–H), 7.13 (1H, d, J 8.4, Ar–H), 2.37 (3H s, Ar–CH$_3$), 1.39 (12H, s, 4$x$CH$_2$). $^1$C NMR (CDCl$_3$, 100 MHz) $\delta$ 151.4, 150.7, 150.0, 144.5, 142.5, 142.1, 140.2, 139.3, 138.7, 135.6, 133.8, 131.7, 128.5, 128.2, 128.1, 127.7, 127.6, 126.6, 126.5, 124.8, 125.7, 120.2, 119.8, 119.1, 83.6, 64.9, 25.2, 21.3; MS (m/z, FAB$^+$) 534.2 (100); HRMS Calcd for C$_{68}$H$_{52}$N$_2$S$_2$ 534.2730, found 534.2755.

Synthesis of green emitter DFBTA

Pd(PPh$_3$)$_4$ (115 mg, 0.1 mmol), 4,7-dibromobenz[d1,2,5]thiadiazole (293 mg, 1.0 mmol), and 2-(9-biphenyl-9-tyrilylfluorenone)pinacol boronate (1175 mg, 2.0 mmol) were placed into a 250 mL two-neck flask equipped with a septum. The flask was evacuated and back-filled with argon. Toluene (50 mL), K$_2$CO$_3$ (20 mL). The mixture was extracted twice with CHCl$_3$. A solution of Br$_2$ (1.41 g, 8.8 mmol, 2.2 eq.) in CHCl$_3$ (15 mL) was added dropwise to a stirred solution of 5 (2.46 g, 4 mmol, 1 eq.) and FeCl$_3$ (32 mg, 0.2 mmol, 0.05 eq.) in CHCl$_3$ (15 mL) at 0 °C. After stirring for 5 h, the solution was quenched with 2 M K$_2$CO$_3$ (20 mL). The mixture was extracted twice with CHCl$_3$. The combined organic phases were washed with brine, dried (MgSO$_4$), and then concentrated through rotary evaporation. After washing with hexane, the product was obtained as a white solid (2.74 g, 95%). M.p. >400 °C; $\nu_{\text{max}}$(film)/cm$^{-1}$ 3065, 3032, 1600, 1487, 1449, 1016, 751 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.06 (2H, d, J 8.8, Ar–H), 7.97 (2H, s, Ar–H), 7.92 (2H, d, J 8.0, Ar–H), 7.83 (2H, d, J 7.2, Ar–H), 7.69 (2H, s, Ar–H), 7.52 (4H, d, J 7.2, Ar–H), 7.84–7.27 (20H, m, Ar–H), 7.21 (4H, d, J 8.4, Ar–H), 7.06 (4H, d, J 8.4, Ar–H), 2.29 (6H, s, 2$x$Ar–CH$_3$). $^1$C NMR (CDCl$_3$, 100 MHz) $\delta$ 153.9, 151.4, 148.8, 142.5, 140.5, 140.2, 139.5, 139.2, 136.6, 136.1, 133.1, 128.8, 125.8, 128.0, 127.8, 127.7, 127.4, 126.9, 126.8, 126.1, 120.3, 120.0, 65.1, 21.0; MS (m/z, FAB$^+$) 949.5 (60), 391.3 (80), 307.0 (100); HRMS Calcd for C$_{78}$H$_{70}$N$_2$S$_2$ 948.3538, found 948.3953; Anal. Calcd for C$_{78}$H$_{70}$N$_2$S$_2$ C, 85.75, H 4.90, found C, 85.65, H, 4.24.
12 mmol, 6 eq.), tBu3P (0.05 M in toluene, 4 mL, 0.15 mmol), and toluene (30 mL) was heated under reflux for 2 d. After cooling to room temperature, the mixture was extracted twice with CH2Cl2. The combined organic phases were washed with brine and dried (MgSO4); the product was isolated as white crystals after recrystallization (CH2Cl2–hexanes, 1 : 1) to afford DPAnInF (1.29 g, 68%). M.p. 390–391 °C (DSC); \( \nu \) 3054, 2987, 1422, 1266, 896, 735, 705 cm\(^{-1}\); \(^1\)H NMR (CDCl3, 400 MHz) \( \delta \) 7.58 (2H, s, Ar–H), 7.46 (2H, d, Ar–CH3); 13C NMR (C 2D2Cl4, 100 MHz) \( \delta \) 152.4, 150.1, 146.6, 146.4, 142.1, 138.1, 135.5, 133.9, 128.6, 128.3, 127.6, 123.4, 122.6, 122.2, 121.2, 119.8, 116.7, 64.2, 21.3; MS \( (m/z, \text{ FAB}) \) 949 (0.3); HRMS \( (m/z, \text{ FAB}) \) Calcd for C13H26N2: 948.4443, found 948.4444; Anal. Calcd. C, 91.10%; H, 5.95%; N, 2.95. Found C, 90.93%; H, 6.08%; N, 2.64.

**Cyclic voltammetry**

The oxidation potentials were determined by cyclic voltammetry (CV) in CH2Cl2 solution (1.0 mM) containing 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF6) as a supporting electrolyte at a scan rate of 100 mV s\(^{-1}\). The redox potentials were determined by CV in THF solution (1.0 mM) containing 0.1 M tetra-n-butylammonium perchlorate (TBAP). A glassy carbon electrode and a platinum wire were used as the working and counter electrodes, respectively. The ferrocene/ferrocenium redox couples occur at values of +0.61 V and +0.45 V in CH2Cl2/TBAPF6, respectively, vs. Ag/AgCl (saturated). All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode.

**Photophysical properties measurements**

Steady state spectroscopic measurements were conducted both in solution (1.0 \( \times \) 10\(^{-4}\) M in dichloromethane) and solid films prepared by vacuum deposition (2 \( \times \) 10\(^{-6}\) torr) deposition on a quartz plate (1.6 \( \times \) 1.0 cm). Absorption spectra were recorded with a U2800A spectrophotometer (Hitachi) and fluorescence spectra were acquired on a F4500 fluorescence spectrophotometer (Hitachi) upon exciting at the absorption maxima (416 nm for solution; 422 nm for solid film). Quantum efficiency measurements were recorded with an integration sphere coupled with a photonic diode array (Ocean Optics S2000) with a spectral range from 200 to 850 nm and a resolution of 2 nm.

**Ultraviolet photoemission spectroscopy (UPS) measurement**

The valence-band ultraviolet photoemission spectra were carried out with He I (21.2 eV) and He II (40.8 eV) as excitation sources. The Fermi level of the system was measured on the gold substrate before the organic deposition. The energy levels of the HOMOs of organic samples were determined by extrapolating the edges of the HOMO peak down to the background of the UPS spectra. The vacuum levels of the films were deduced from the onset of lowest binding energy in the spectra and the photon energy of excitation sources.

**Time-of-flight (TOF) mobility measurements**

The samples for the TOF measurement were prepared by vacuum deposition using the structure: glass/Ag(30 nm)/ organic (2–3 nm)/Al(150 nm), and then placed inside a cryostat and kept under vacuum. All organic materials were purified by vacuum sublimation before use. The thicknesses of the organic films were monitored in situ with a quartz crystal sensor and calibrated by a profilometer (Tencor Alpha-step 500). A pulsed nitrogen tunable dye laser was used as the excitation light source (to match the absorption of organic films) through the semitransparent electrode (Ag) induced photogeneration of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Al), and then recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) are swept across the sample with a transient time of \( t_f \). With the applied bias \( V \) and the sample thickness \( D \), the applied electric field \( E \) is \( V/D \), and the carrier mobility is then given by \( \mu = D(t_fE) = D(t_fV)/t_f \), in which the carrier transit time, \( t_f \), can be extracted from the intersection point of two asymptotes to the plateau and the tail sections in double-logarithmic plots.

**OLED device fabrications**

ITO substrates were cleaned in an ultrasonic detergent bath, followed by acetone and methanol. The substrates were subsequently treated in an UV-ozone cleaner to remove any residual organic contaminants. A hole-injection layer of poly(3,4-ethylendioxythiophene)-poly(4-styrenesulfonate) (PEDOT:PSS) was spin coated first onto the ITO substrate followed by drying at 120 °C for 30 min to remove residual solvent. Organic layers were then vacuum deposited at a deposition rate of 2–3 Å s\(^{-1}\). Finally, 0.5 nm of LiF and a 100 nm thick Al cathode were deposited through a shadow mask with an area of 0.10 cm\(^2\). OLED device characterization was carried out with a computer-controlled Keithley 6430 source meter and Keithley 6487 picoammeter equipped with a calibrated silicon photodetector at 25 °C under nitrogen atmosphere. EL spectra were measured using a photodiode array (Ocean Optics S2000) with a spectral range from 200 to 850 nm and a resolution of 2 nm.

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**References**


