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A versatile ferrocene-containing material as a p-type charge generation layer for high-performance full color tandem OLEDs⁺

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A novel p-type charge generation material, DPAF, composed of a ferrocene core and a bis(biphenyl)amino group is designed and synthesized for application to tandem OLED devices. This molecular design not only enhances the thermal properties of ferrocene and the hole mobility, but also maintains its electrochemical stability. The red, green, and blue tandem OLEDs all give excellent device performance with low efficiency roll-off by using n-type C_{60} and p-type DPAFs as charge generation layers.

Organic-light-emitting-diodes (OLEDs) possess the advantages of high brightness, long lifetime, and low energy consumption, making them a promising candidate for next-generation solidstate lighting and display.¹⁻³ In recent years, rational molecular design and device engineering have become effective means for achieving high-performance OLEDs.⁴⁻⁶ Among various device manipulations, the tandem devices using a multiple-junction device structure offer a very promising approach to overcome the limitation of efficiency and lifetime in OLEDs.^{7,8} Typically, a tandem OLED is composed of two electroluminescence (EL) diodes, connected head-to-tail via a charge generation layer (CGL).9 Under an applied electric field, the interconnecting layer can directly generate charge carriers and facilitate the injection of the electrons and holes into the adjacent electron- and holetransporting layers of single EL units, respectively.¹⁰ Then, the generated charge carriers recombine with holes injected from the anode and electrons injected from the cathode in the emissive layers of first and second EL units, respectively, resulting in an individual emission from each EL unit. Therefore, the performance of tandem OLEDs linearly increases with the number of EL units.

In tandem devices, the CGL that functions as an internal electrode plays a decisive role in realizing high device performance. An ideal CGL must follow several criteria including efficient charge generation capability for electrons and holes, a small energy barrier for charge injection, high charge carrier mobility, stable electrochemical behaviours, high thermal stability, ease for thermal evaporation, and optical transparency in the visible spectral range. To date, the common CGL structures reported have been transition metal-oxide¹¹ and p-doping/n-doping organic bilayers.¹² However, the former suffers from a high thermal evaporation temperature for the preparation of metal oxide films,¹³ while the latter forms a complex with the migrated n-dopant from the neighbouring electron-transporting layer and thus significantly degrades the device performance and increases the driving voltage.14 In recent years, organic heterojunctions consisting of a p-type and an n-type organic material offer a potential approach in the development of an efficient CGL.¹⁴⁻¹⁶ For example, Kido's group presented the first tandem green OLED connected by a HAT-CN/NPD heterojunction, which shows an extremely high current efficiency of 256 cd A⁻¹.¹⁷ The first example of the white tandem device using a C₆₀/pentacene heterojunction as a CGL was demonstrated by Ma and co-workers.18 The resulting tandem WOLED achieved a power efficiency of 53.8 lm W^{-1} . Although several heterojunction CGLs have been applied in tandem devices, the use of a p-type organic material is still restricted to traditional hole-transporting materials. To date, there is still no report on an efficient organometallic complex that shows high optical transmission as a p-type organic material. Demonstrated in this work is for the first time the use of a newly developed ferrocene derivative, DPAF, as the p-type CGL material to construct highly efficient tandem OLEDs. The ferrocene core is chosen owing to its high HOMO level and reversible electrochemical property. A bis(biphenyl)amino group is introduced to enhance intermolecular interaction and thus increase the hole transport properties and the thermal stability of ferrocene. The resulting DPAF shows good thermal stability, hole mobility and stable electrochemical characteristic. The combination of DPAF with n-type C₆₀ as a CGL results in excellent EL performance with low efficiency roll-off for RGB tandem OLEDs. Moreover, the efficiency and turn-on voltage in all these tandem devices are close to twice the value of a single-unit device, manifesting the feasibility of the ferrocene derivative as a p-type connector.

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Scheme 1 depicts the route for the synthesis of DPAF. The target material can be easily synthesized in two steps *via* the coppercatalysed Ullmann reaction of 1-iodoferrocene with ammonium hydroxide, followed by Buchwald–Hartwig coupling with 4-bromobiphenyl using Pd(OAc)₂ as the catalyst. The details of the preparation of DPAF and the full chemical characterization are described in the ESI.† Its thermal characteristics were evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Fig. S1 (ESI†), the new CGL material exhibits a decomposition temperature (T_d) of over 350 °C, defined as the temperature at which the material showed a 5% weight loss. No discernable glass-transition characteristic is found up to 250 °C in the DSC measurement. Compared with the ferrocene derivative reported previously, DPAF exhibits higher thermal stability.^{19,20}

As revealed in Fig. 1, DPAF in the thin film exhibits a strong absorption band at 327 nm in the thin film, ascribed to the electronic transitions involving metal-to-ligand charge transfer and the local excited state, and a weak emission at 420 nm. It is worth noting that there are no obvious optical absorptions in the 400-700 nm range indicating that the DPAF film is transparent in the visible spectral range. This can avoid the excess light absorption in the tandem device and thus is conducive to application in full colour OLEDs. The electrochemical properties of DPAF were characterized by cyclic voltammetry (CV), as shown in Fig. S2 (ESI[†]). DPAF shows a reversible oxidation wave taking place at 0.0 V vs. the ferrocene/ferrocenium (Fc/Fc⁺) couple in the anodic scan. The CV study suggests that the introduction of the bis(biphenyl)amino group does not significantly alter the oxidation potential of ferrocene. Moreover, DPAF exhibits a reproducible CV profile and oxidation potential under repeated CV scans (Fig. S2, ESI[†]), indicative of good electrochemical stability for DPAF. The HOMO level was calculated to be -4.8 eV for DPAF



Fig. 1 Absorption and fluorescence spectra of DPAF in a neat film.

based on the equation HOMO = E_{ox} + 4.8 eV and the LUMO energy level of DPAF was estimated from HOMO – E_{g} to be –1.9 eV.

To understand the hole transporting behaviour of DPAF, the hole-only device was prepared with a structure consisting of ITO/NPB (30 nm)/DPAF (10 nm)/NPB (50 nm)/Al (100 nm), in which NPB was utilised to prevent electron injection from cathode. For comparison, we also fabricated a hole-only device using a well-known p-type CGL material MoO₃ (10 nm) as reference. In the plot of the current density against voltage presented in Fig. S3 (ESI[†]) for these two devices, the DPAF-based hole-only device reveals a very close current density-voltage curve to that of MoO₃, indicative of an excellent p-type material with high hole mobility for DPAF. This result is likely due to the incorporation of the bis(biphenyl)amino group that increases the intermolecular interaction. To gain further insight into the potential of DPAF as a p-type CGL material, the CGL-only device was fabricated with a double-insulating structure of ITO/BPhen (100 nm)/Liq (1 nm)/Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/NPB (100 nm)/Al (100 nm). In the device, C₆₀ is chosen as an n-type CGL material because its low LUMO level is beneficial to the energy level alignment with the HOMO of DPAF, facilitating the electron transfer from DPAF to C60 and thus resulting in charge generation in the DPAF/C60 interface upon a certain electric field. Furthermore, the two reference devices with only DPAF or C₆₀ in the CGL were prepared to confirm the effect of charge generation in the DPAF/C₆₀ CGL. Fig. 2 shows current densityvoltage characteristics of the CGL-only device. Clearly, no current density was observed for the devices with only DPAF or C60 as the CGL or no CGL. In contrast, the CGL-only device composed of DPAF and C₆₀ gives a large current response, suggesting that an efficient charge generation appears at the C_{60} /DPAF interface. This result prompts us to further examine the EL characteristics of tandem OLEDs using C₆₀/DPAF as the CGL.

To probe the new ferrocene-based compound as a promising p-type CGL material for tandem OLEDs, we first fabricated a twounit stacked Ir(ppy)₃-based green device connected by a C₆₀/DPAF CGL (Fig. 3). The green tandem device (device G2) has the configuration of ITO/NPB (30 nm)/TCTA (20 nm)/TCTA:TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm)/TPBi: 6% LiF (5 nm)/Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/MOO₃ (1 nm)/NPB (30 nm)/ TCTA (20 nm)/TCTA:TPBi: 4% Ir(ppy)₃ (30 nm)/TPBi (60 nm).



Fig. 2 Current density versus voltage curves of CGL-only devices.



Fig. 3 Device structures of green, blue, and red phosphorescent tandem OLEDs. The number in the parentheses represents the thickness of the film and its unit is nm.

The performance and characteristics are shown in Table 1, Fig. 4, and Fig. S5 (ESI[†]). Both single-unit and tandem devices emit green light from Ir(ppy)₃ and no additional emission from the host or other materials is observed in their EL spectra. Notably, the emission peak of tandem OLEDs is found to have a broader full width at half maximum than that for single unit devices. The variation in the emission peak is likely the result of the disparity in the distance between the emitting layer and the Al cathode for each device.²¹ The fabricated green tandem OLED turns on at a low voltage of 5.1 V and shows an excellent performance with a maximum external quantum efficiency (EQE) of 59.5%, a current efficiency (CE) of 234.8 cd A^{-1} , and a power efficiency (PE) of 135.9 lm W⁻¹. Relative to the EL performance of the single unit device (EQE = 27.6%, CE = 104.0 cd A^{-1} , and PE = 108.4 lm W^{-1} with a turn-on voltage of 2.5 V), the EQE and CE of the tandem device are two-fold superior to those found in the single unit device, while a twice increase in the driving voltage was observed for the tandem OLED. To explore the influence of the MoO₃ layer on the tandem device performance in device G2, we fabricated tandem device G3 with a device configuration the same as that of device G2, except that there was no MoO₃ adjacent to the C₆₀/DPAF bilayer. As revealed in Fig. S6 (ESI[†]), device G3 shows an EQE of 39.7%, significantly lower than that of device G2 with a MoO₃ layer. This is because

Table 1 Summary of EL performance for RGB devices V_{on}^{a} EQE _{max} (cd A ⁻¹) PE _{max} (lm W ⁻¹) EQE ₃₀₀₀ ^b (%) λ_{max}^{c} CIE ^c } (nm) (x, y) $G1^{d}$ 2.5 27.6 104.0 108.4 26.3 514 (0.27, 0.4) $G2^{e}$ 5.1 59.5 238.4 135.9 56.3 518 (0.28, 0.4) $R1^{d}$ 2.5 26.9 26.8 28.0 24.6 627 (0.66, 0.4) $R2^{e}$ 5.1 48.9 51.4 26.0 44.6 628 (0.67, 0.4) $B1^{d}$ 3.4 26.0 70.4 48.1 24.7 473 (0.13, 0.4)	Table 1Summary of EL performance V_{on}^{a} EQEmaxCEmaxDevice ^a (V)(%)(cd A ⁻¹)	ance for Re PE _{max} (lm W ⁻¹)	GB devices EQE ₃₀₀₀ ^b (%)	λ_{\max}^{c} (nm)	$CIE^c \\ (x, y)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c} V_{\mathrm{on}}{}^{a} & \mathrm{EQE}_{\mathrm{max}} & \mathrm{CE}_{\mathrm{max}} & \mathrm{I} \\ \mathrm{Device}{}^{a} & (\mathrm{V}) & (\%) & (\mathrm{cd} \ \mathrm{A}^{-1}) & (\mathrm{cd} \ \mathrm{Ce}^{-1}) & (\%) \end{array}$	PE _{max} (lm W ⁻¹)	EQE ₃₀₀₀ ^b (%)	$\begin{array}{c} \lambda_{\max}{}^{c} \\ (nm) \end{array}$	$CIE^c \\ (x, y)$
$ \begin{array}{ccccccccccccccccccccccccccccccc$					
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	108.4 135.9 28.0 26.0 48.1	26.3 56.3 24.6 44.6 24.7	514 518 627 628 473	(0.27, 0.65) (0.28, 0.64) (0.66, 0.33) (0.67, 0.32) (0.13, 0.39)

 a Turn-on voltage at 1 cd m $^{-2}.\ ^b$ EQE at 3000 cd m $^{-2}.\ ^c$ Recorded at 8 V. d Single unit device. e Tandem OLED.



Fig. 4 (a) EL spectra and (b) external quantum efficiency (solid) and power efficiency (open) vs. luminance characteristics for the RGB single-unit and tandem OLEDs.

the larger barrier between DPAF and NPB makes hole injection difficult. Thus, MoO₃ plays the role of smoothly injecting charges into the adjacent EL units in tandem device G2. From this viewpoint, 22 MoO₃ is a layer of the intermediate connector C_{60} /DPAF/MoO₃ of tandem device G2. In the intermediate connector, the C60/DPAF can easily generate charges at its interface and the resulting charges can be successfully injected into the two-unit devices,²³ leading to a twice increase in efficiency. In addition, both devices exhibit very low efficiency roll-off due to the bipolar property of the co-host system. The tandem device gives an EQE of 56.3% with an EQE roll-off of 5.4% at the luminance of 3000 cd m⁻², similar to that obtained from the single unit cell. To further verify the merit of this newly designed p-type CGL material, we prepared a green tandem device using C_{60}/MoO_3 as the CGL material (device G4). In this tandem OLED, the device structure is the same as device G2 except that MoO₃ was used instead of DPAF as the CGL material. Its EL property is displayed in Fig. S6 (ESI[†]). It is found that the tandem device connected by C60/DPAF achieves higher EL performance compared with that using C_{60}/MoO_3 as the connector (EQE = 50.2%, CE = 197.8 cd A^{-1} , and PE = 89.2 lm W^{-1}). This is because the larger energy difference between the HOMO of MoO₃ and the LUMO of C_{60} make charge generation process at the C_{60} /MoO₃ interface difficult, leading to a decrease of EL efficiency (Fig. S7, ESI[†]).²³ This finding demonstrates that the C₆₀/DPAF CGL can generate charge carriers efficiently. Thus, the use of DPAF as a p-type CGL material is superior to the conventional MoO₃.

To demonstrate that the C₆₀/DPAF CGL can be applied in full colour tandem devices, tandem OLEDs based on FIrpic and Ir(piq)₂(acac) as emitters are next examined. The blue and red two-unit stacked devices were fabricated using the respective structures of ITO/NPB (30 nm)/mCP (10 nm)/mCP:TmPyPB: 5% FIrpic (30 nm)/TmPyPB (60 nm)/TmPyPB: 6% LiF (5 nm)/ Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/MoO₃ (1 nm)/NPB (30 nm)/ mCP (10 nm)/mCP:TmPyPB: 5% FIrpic (30 nm)/TmPyPB (60 nm)/LiF (1 nm)/Al (100 nm) and ITO/NPB (30 nm)/TCTA (20 nm)/TCTA:Bebq₂: 4% Ir(piq)₂(acac) (30 nm)/Bebq₂ (50 nm)/ Bebq₂: 6% LiF (5 nm)/Al (1 nm)/C₆₀ (4 nm)/DPAF (1 nm)/MoO₃ (1 nm)/NPB (30 nm)/TCTA (20 nm)/TCTA:Bebq₂: 4% Ir(piq)₂(acac) (30 nm)/Bebq₂ (60 nm)/LiF (1 nm)/Al (100 nm). The representative performance parameters and device characteristics of these tandem devices and the corresponding single unit OLEDs are also summarized in Table 1, Fig. 4, and Fig. S5 (ESI⁺). Tandem blue device B2 and red device R2 afforded outstanding EQEs of 59.4 and 48.9% with turn-on voltages of 6.8 and 5.1 V, CE values of 115.9 and 51.4 cd A^{-1} and PE values of 43.8 and 26.0 lm W^{-1} , respectively. At a high brightness of 3000 cd m⁻², the EQEs remain at 53.6 and 44.6% with low roll-off values of 9.8 and 8.8% for blue and red tandem OLEDs, respectively. The turn-on voltages and device efficiencies increase by about two times compared with the corresponding single unit devices, proving that the C₆₀/DPAF CGL works very well in blue and red tandem devices also. Overall, the blue, green, and red tandem OLEDs connected by C₆₀/DPAF CGLs reveal excellent performance with low efficiency roll-off and appear among the best results reported for RGB tandem OLEDs. These encouraging results demonstrate that the DPAF is a promising p-type CGL material for developing highly efficient tandem OLEDs.

In summary, we have successfully developed a ferrocenebased p-CGL material by incorporating the bis(biphenyl)amino group into the ferrocene core. The new p-CGL material possesses improved thermal behaviour, stable redox potential, and good hole mobility. By using the organic heterojunction composed of n-type C_{60} and p-type DPAF as CGLs, the RGB tandem OLEDs achieve EQEs of 48.9, 59.5, and 59.4% with low efficiency roll-off at high luminance. To the best of our knowledge, DPAF is the first example using a ferrocene-based organometallic compound as a p-type CGL in tandem OLEDs.

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