Using a double-doping strategy to prepare a bilayer device architecture for high-efficiency red PhOLEDs

Ming-Tzu Kao,^{*a*} Wen-Yi Hung, ^{**b*} Zhen-Han Tsai,^{*b*} Hong-Wei You,^{*b*} Hsiao-Fan Chen,^{*a*} Yun Chi^{*c*} and Ken-Tsung Wong^{**a*}

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A simple, bilayered, red phosphorescent organic light-emitting device featuring a doubly-doped emitting layer comprising of the novel hole-transporting host **DTAF**, the electron-transporting host **27SFBI**, and the emitter Os(bpftz)₂(PPhMe₂)₂ covering the interfacial region provides an unusually high current of *ca*. 1560 mA cm⁻² at 8.5 V, a maximum brightness of 32 700 cd m⁻², external quantum efficiencies as high as 12.3% (10.9% at 1000 cd m⁻²), and a power efficiency of 13.5 lm W⁻¹. This concise device architecture is very cost-effective and competitive for practical applications.

Introduction

Phosphorescent organic light-emitting devices (PhOLEDs) employing transition metal-centered phosphors dispersed in an appropriate host matrix are attracting much attention because both singlet and triplet excitons can be harvested to achieve internal quantum efficiencies of up to 100%.1 Indeed, employing this strategy may pave the way toward the practical commercialization of OLED displays and lighting. In addition to the use of efficient phosphors, the nature of the host material also plays a crucial role affecting the device performance. In most cases, the host material exhibits either hole-transporting (HT) or electrontransporting (ET) characteristics. When using a predominantly HT- or ET-type host, the excitons formed in the device tend to accumulate close to the interface between the emitting layer (EML) and the HT or ET layer (HTL or ETL), respectively. Thus, the inevitable exciton quenching through triplet-triplet annihilation is usually detrimental to the device efficiency. In 2002, Zhou et al. were the first to develop device structures possessing double-emission layers (D-EMLs), prepared by doping both the HT layer and the ET host with a phosphorescent emitter, to increase the size of the exciton formation zone.² The D-EML concept enlarges the exciton recombination zone over the active layers, leading to significantly reduced levels of triplettriplet annihilation relative to those of conventional single emission layer (S-EML) OLEDs.^{2,3} To date, most reported D-EML OLEDs have featured multilayer device structuresa stepped progression of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the HT materials, host materials, and ET materials-to facilitate hole and electron injection into the emissive layer. Such complicated structures require timeconsuming and tedious fabrication processes and usually feature low process yields, adding considerably to the overall production cost.

To overcome this problem, herein we demonstrate an efficient D-EML red PhOLED configured using a simple bilayer device structure that does not feature additional HT or ET layers. This simple device comprises two host materials: a HT-type host having a high HOMO energy level for hole injection and a high LUMO energy level for electron blocking, and an ET-type host having a low LUMO energy level for electron injection and a low HOMO energy level for hole blocking. We doped the interfacial zone of these two host materials with a red-emitting Os-based phosphor to create a wide exciton formation area, resulting in an efficient device exhibiting a maximum external quantum efficiency of 12.3% (13.5 cd A^{-1}), a power efficiency of 16.5 lm W^{-1} , a saturated red emission according to the CIE diagram, and a low driving voltage of 4.5 V to reach a luminance of 1000 cd m^{-2} . Thus, double-doping is a practical means of fabricating highly efficient PhOLEDs having a simple bilayer device structure, potentially reducing the cost of fabrication relative to those of other contemporary display manufacturing processes.

Results and discussion

Design and synthesis

Scheme 1 displays the molecular structures of the host materials, which both feature a fluorene core. Our design of the HT-type host 9,9-di[N,N-di(p-tolyl)aminophenyl-4-yl] fluorene (DTAF) was inspired by the structure of $1,1-bis{4-[N,N-di(p-toly])$ amino]phenyl}cyclohexane (TAPC),4 a widely used HTL material for PhOLEDs that exhibits a high triplet energy ($E_T = 2.87 \text{ eV}$) and a high hole mobility ($\mu_h = ca. \ 10^{-3} \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}$). The low glass transition temperature ($T_g = ca.$ 79 °C) of TAPC, however, limits its long-term use. To enhance the thermal stability of TAPC, we modified its structure by replacing the cyclohexane unit with a fluorene moiety, thereby obtaining DTAF.⁵ For the ET-type host material, we adopted phenylbenzimidazole as the electronaccepting group because we have previously used 2,2'-bis(N-phenylbenzimidazole)-9,9'-spirobifluorene successfully as an ET material.⁶ In this present study, we introduced an additional pphenylene ring between the N-phenylbenzimidazole groups and

^aDepartment of Chemistry, National Taiwan University, Taipei, 106, Taiwan. E-mail: kenwong@ntu.edu.tw; Fax: +886 2 33661667; Tel: +886 2 33661665

^bInstitute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, 202. E-mail: wenhung@mail.ntou.edu.tw; Fax: +886 2 24634360; Tel: +886 2 24622192 ext. 6718

^cDepartment of Chemistry, National Tsing Hua University, Hsinchu, 300, Taiwan



Scheme 1 Molecular structures of the materials used in this study and an energy level diagram of the device.

the central spirobifluorene to extend the π -conjugation length and adjust the HOMO and LUMO energy levels, thereby obtaining the new ET-type host 2,2'-bis[4-(1-phenylbenzimidazol-2yl)phenyl]-9,9'-spirobifluorene (**22SFBI**). For comparison, we also synthesized the C2-symmetric 2,7-disubstituted counterpart **27SFBI**. We used the highly efficient red-emitting complex bis[3-(trifluoromethyl)-5-(4-*tert*-butylpyridyl)-1,2,4-triazolate]dimethylphenylphosphine osmium(II) [Os(bpftz)₂(PPhMe₂)₂, **OS1**]⁷ as the red dopant.

We synthesized **DTAF** in one step from 9-fluorenone in 92% yield, as we have described previously.⁵ Scheme 2 displays the synthetic pathways toward **22SFBI** and **27SFBI**. We synthesized the key intermediate for the synthesis of both compounds, *N*-phenylbenzimidazole boronic acid (1), according to literature procedures.⁸ Accordingly, Suzuki couplings of 1 with 2,7-dibromo-9,9'-spirobifluorene (2) and 2,2'-diiodo-9,9'-spirobifluorene (3), in the presence of catalytic amounts of Pd(PPh₃)₄ and P(*t*-Bu)₃, gave good yields of **27SFBI** and **22SFBI**, respectively.

Molecular properties

The rigid molecular structures of **DTAF**, **22SFBI**, and **27SFBI** provide them with high thermal stabilities,⁹ as manifested by their thermal decomposition temperatures (T_d , corresponding to 5% weight loss during thermogravimetric analysis) in the range 358–391 °C (Table 1). For **DTAF**, differential scanning calorimetry (DSC) revealed a glass transition temperature of 124 °C and a melting peak of 320 °C; **22SFBI** and **27SFBI** displayed well-defined glass transition temperatures of 150 and 160 °C,

respectively. We observed no crystallization for **22SFBI** during the second DSC scan. In contrast, the C2-symmetric **27SFBI** exhibited a crystallization peak of 203 °C and a melting peak of 321 °C. We attribute the amorphous behavior of **22SFBI** to its perpendicular configuration, imparted by the orthogonal arrangement of the substituents around the spirobifluorene core,



Scheme 2 The synthesis of 27SFBI and 22SFBI.

Table 1 The physical properties of DTAF, 22SFBI, and 27SFBI

Compound	$T_{\rm g}^{\ a}/T_{\rm c}^{\ b}/T_{\rm m}^{\ c}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$	(λ_{max}) Abs/nm Sol./Film	(λ_{max}) PL/nm Sol./Film	HOMO/eV ^d	LUMO/eV ^d	$\Delta E_{g}^{d}/eV$	$E_{\rm T}/{\rm eV}$	μ^{e} /cm ² V ⁻¹ s ⁻¹
DTAF	124/n.d./360	374	308/311	383/383	-5.22	-1.75	3.47	2.87	(h) 2.5×10^{-3}
22SFBI	150/n.d./273	358	331/337	380, 400/394, 413	-5.77	-2.61	3.16	2.51	(e) 2.8×10^{-6}
27SFBI	160/203/321	391	350/355	401, 421/417, 439	-5.67	-2.67	3.00	2.36	(e) 3.0×10^{-5}

^{*a*} Glass transition temperature. ^{*b*} Crystallization temperature. ^{*c*} Melting temperature. ^{*d*} HOMO determined using photoelectron yield spectroscopy (AC-2). LUMO = HOMO + E_g , where E_g was calculated from the absorption onset of the solid film. ^{*e*} The value of μ was determined from the TOF measurement at $E = 5.7 \times 10^5$ V cm⁻¹, (h) for hole, (e) for electron.

disrupting intermolecular interactions and suppressing its tendency to crystallize. Thus, upon thermal evaporation, we would expect these host materials to form homogeneous and stable amorphous films—an essential property for OLED device applications.

The ability of the host materials to conduct electrons or holes is important for maintaining charge balance within the emissive layer. To evaluate the carrier mobilities of DTAF, 22SFBI, and 27SFBI, we performed time-of-flight (TOF) measurements.¹⁰ Fig. 1(a)-(c) displays typical room temperature TOF transients for these materials under an applied electric field: we observe a non-dispersive hole transient photocurrent for DTAF and dispersive electron transient photocurrents for both 22SFBI and **27SFBI.** We determined the transit times (t_T) from the cusps of the double-logarithmic plots of the transient photocurrents [insets to Fig. 1(a)-(c)]; we then calculated the mobility using the formula, $d^2/Vt_{\rm T}$, where d is the sample thickness and V is the applied voltage. The hole mobility of DTAF (up to 2×10^{-3} cm² $V^{-1} s^{-1}$) is similar to that of TAPC ($\mu_{\rm h} = ca. 10^{-3} {\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}$), suggesting that the structural modification from TAPC to DTAF had a limited effect on the hole transport behavior. The observed electron mobility ($\mu_e = ca. 3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) of **27SFBI** was greater than that of **22SFBI** ($\mu_e = ca. 2.8 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Under the same electric field ($E = 5.7 \times 10^5 \text{ V cm}^{-1}$), the observed electron mobility of 22SFBI was significantly less than

that of **27SFBI**, presumably because of the perpendicular arrangement of the two active sites for electron migration in **22SFBI**. The orthogonal configuration leads to greater spatial hindrance between neighboring **22SFBI** molecules and, subsequently, increases the carrier hopping distance.¹¹

We measured the UV-vis absorption and photoluminescence (PL) spectra of DTAF, 22SFBI, and 27SFBI in solution (CH₂Cl₂) and in the form of solid films on quartz slides (Fig. 2, Table 1). DTAF exhibits similar absorption (ca. 310 nm) and emission (ca. 383 nm) maxima in solution and in its solid state film; in the latter, an additional shoulder emission (>420 nm), which is also observed for TAPC,12 is due to aggregation of ditolylamino subunits. The structure of 27SFBI differs from that of 22SFBI by the presence of two diphenylbenzimidazole groups attached to the same biphenyl branch of the spirobifluorene core. The extended π - conjugation length of **27SFBI** results in slightly redshifted (by ca. 20 nm) absorption, PL, and phosphorescence spectra relative to those of its 2,2'-disubstituted counterpart **22SFBI**. The triplet energies (E_T) of **DTAF**, **22SFBI**, and **27SFBI** were 2.87, 2.51 and 2.36 eV, respectively, estimated from the peaks of the shortest wavelength of the phosphorescence spectra recorded in EtOH at 77 K. The HOMO energy levels of DTAF,



Fig. 1 Representative TOF transients: (a) **DTAF** ($d = 1.6 \ \mu\text{m}$) at $E = 1.9 \times 10^5 \ \text{V cm}^{-1}$; (b) **22SFBI** ($d = 1.9 \ \mu\text{m}$) at $E = 7.5 \times 10^5 \ \text{V cm}^{-1}$; (c) **27SFBI** ($d = 2.1 \ \mu\text{m}$) at $E = 4.8 \times 10^5 \ \text{V cm}^{-1}$. Insets: Double-logarithmic plots of (a)–(c). (d) Carrier mobilities plotted with respect to $E^{1/2}$ at ambient temperature.



Fig. 2 Room-temperature absorption and emission (PL) spectra of (a) **DTAF**, (b) **22SFBI**, and (c) **27SFBI** in CH₂Cl₂ solutions (Solu.) and as neat films (Film), and corresponding phosphorescence (Phos.) spectra recorded from their EtOH solutions at 77 K.

22SFBI, and 27SFBI were -5.22, -5.77 and -5.67 eV, respectively, determined from the photoemission spectra recorded in air (AC-2); we deduced the LUMO energy levels from the difference between the HOMO energy levels and the optical band gaps. Scheme 1 depicts the energy levels of DTAF, 22SFBI, 27SFBI, and the red emitter Os(bpftz)₂(PPhMe₂)₂, OS1. The HT-type host (DTAF) possesses an appropriate HOMO energy level (-5.22 eV) to provide a low hole injection barrier and a highlying LUMO energy level (-1.75 eV) to block electrons from the ETL. In contrast, the ET-type hosts (27SFBI, 22SFBI) possess appropriate LUMO energy levels (-2.67 and -2.61 eV, respectively) to provide low electron injection barriers and low-lying HOMO energy levels (-5.67 and -5.77 eV, respectively) to block holes from the HTL. In addition, we expected the relatively high hole and electron mobilities of these materials to lead to effective hole and electron transport in the corresponding devices. Accordingly, for bilayer devices featuring DTAF/27SFBI or DTAF/22SFBI, we would expect the charge carriers to be significantly accumulated at the interface. With judicious selection of a doping phosphor with suitable HOMO/LUMO energy levels to cover the interfacial zone between the HT-host and the ET-host, the accumulated holes and electrons would be smoothly injected into the guest emitter from HT-host and ET-host. respectively. The triplet energies of these materials allow excellent triplet energy confinement within the emissive layers. The wide emissive zone could reduce the possibility of triplet-triplet annihilation and, thereby, improve the device efficiency with reduced performance roll-off.

Device performance

In our design of the bilayer device, we employed **DTAF** as the HT-type host together with 27SFBI or 22SFBI as the ET-type host. Individually doping the HT-type host or ET-type host with the Os-based red emitter provided single emitting layer (S-EML) reference devices for comparison with the devices having a D-EML. To smooth the ITO electrode surface and improve the quality of hole injection from the anode, we spun poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid) (PEDOT:PSS) onto the pre-cleaned (by UV-ozone) substrate to form a 30 nmthick polymer buffer layer. We fabricated two reference devices featuring an S-EML [(I) ITO/PEDOT:PSS/DTAF (15 nm)/ DTAF:6 wt% Os1 (30 nm)/27SFBI (55 nm)/LiF/Al; (II) ITO/ PEDOT:PSS/DTAF (15 nm)/27SFBI:6 wt% Os1 (25 nm)/27SFBI (55 nm)/LiF/Al] and one double-doped device [(III) ITO/ PEDOT:PSS/DTAF (15 nm)/DTAF:6 wt% Os1 (5 nm)/27SFBI:6 wt% Os1 (20 nm)/27SFBI (55 nm)/LiF/Al]. For comparison, we also employed 22SFBI as an ET-type host to fabricate the D-EML device IV: ITO/PEDOT:PSS/DTAF (15 nm)/DTAF:6 wt% Os1 (5 nm)/22SFBI:6 wt% Os1 (25 nm)/22SFBI (55 nm)/ LiF/Al]. Fig. 3 presents the current density-luminance-voltage (I-L-V) curves and key characteristics of these devices; Table 2 summarizes the data.

The *I*–*L*–*V* characteristics of devices **I**–**IV** reveal that holes and electrons were both readily injected from the anode and cathode, respectively, to the organic layers; as a result, the operating voltages were low for both the S-EML and D-EML devices. All of the *L*–*V* curves of these devices feature a steep increase after the turn-on voltage reached 2 V. The maximum luminance of the



Fig. 3 (a) The current density–voltage–luminance (I-V-L) characteristics. (b) External quantum (η_{ext}) and power efficiencies (η_P) as a function of brightness. (c) The EL spectra of devices.

D-EML device III ($L = 32\ 700\ \text{cd}\ \text{m}^{-2}$) was significantly higher than those of the S-EML devices I (L = 14400 cd m⁻²) and II $(L = 18 400 \text{ cd m}^{-2})$ in the applied voltage range from 8.5 to 9 V. Meanwhile, D-EML device III exhibited a significantly higher current density ($I = 1560 \text{ mA cm}^{-2}$) than those of the S-EML devices I ($I = 1000 \text{ mA cm}^{-2}$) and II ($I = 930 \text{ mA cm}^{-2}$). For the S-EML device I, based on the observed carrier-transport behavior and the HOMO/LUMO energy levels of DTAF and 27SFBI, it is likely that the electrons that accumulated at the DTAF-27SFBI interface were injected directly into Os1, which was present only in the DTAF layer, followed by recombination with holes within the DTAF layer. A similar mechanism might have operated in the S-EML device II, in which direct hole injection from DTAF into Os1 was possible because the difference in HOMO energy levels between DTAF and Os1 is much smaller than the difference between DTAF and 27SFBI. Therefore, the S-EML devices I and II displayed similar properties. In contrast, we would expect the carrier recombination zone of the D-EML device III to cover the interfacial area between the two active layers, mainly due to the mismatched HOMO/LUMO energy levels. The carriers that reached the interface would have been preferably trapped by the dopant, suppressing the loss of luminance efficiency during prolonged device operation. For these reasons, it would be reasonable to expect a higher luminance and current density for the D-EML device III, relative to those of the S-EML devices I and II. As a result, Fig. 3(b) reveals that the two S-EML devices possessed lower efficiencies relative

	Host	$V_{\rm on}{}^a/{\rm V}$	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$I_{ m max}/M{ m mA~cm^{-2}}$	max. η_{ext} [%]	max. $\eta_{\rm l}$ /cd A ⁻¹	max. $\eta_{\rm p}$ [lm W ⁻¹]	<i>L</i> = 1000 nit [V; %]	CIE coordinates $[x, y]$
I	DTAF	2	14 400 (9 V)	1000	7.3	8.8	9.5	5.7; 5.5	0.65, 0.34
Π	27SFBI	2	18 400 (8.5 V)	930	9.9	10.5	10.6	5.2; 7.7	0.66, 0.34
Ш	DTAF/27SFBI	2	32 700 (8.5 V)	1560	12.3	13.5	16.5	4.5; 10.9	0.66, 0.34
IV	DTAF/22SFBI	2	25 700 (10.5 V)	1760	12.4	12.9	11.6	5.9; 8.2	0.66, 0.34
^a Def	ined as the voltage a	at which the	EL is rapidly enhanc	ed.					

Table 2 The electroluminescence data of the devices prepared at various host material

to that of the D-EML device III. The S-EML device I exhibited maximum values of η_{ext} and η_{P} of 7.3% (8.8 cd A⁻¹) and 9.5 lm W^{-1} , respectively, with the S-EML device II providing corresponding values of 9.9% (10.5 cd A⁻¹) and 10.6 lm W⁻¹, respectively; both these sets of values are far from those provided by the D-EML device III [12.3% (13.5 cd A^{-1}) and 16.5 lm W^{-1} , respectively]. The lower current efficiencies of the S-EML devices are an indication of unbalanced charge recombination, due to the unipolar characteristics of the active layers used. The improved efficiency in the D-EML device can be rationalized by considering that the wide triplet-exciton generation region across the interfacial area significantly reduced the number of possible quenching pathways and avoided charge carrier loss. As a consequence, the D-EML OLED exhibited higher efficiency and stability relative to those of the conventional S-EML OLEDs.

Next, we compared the behavior of the D-EML structures employing either 27SFBI or 22SFBI as the ET-type host. The I-V-L characteristics revealed that the D-EML III incorporating 27SFBI as the ET-type host exhibited a higher luminance and current density at the same applied voltage than those of the D-EML device IV incorporating 22SFBI as the ET-type host. At a luminance of 1000 cd m⁻², device III provided values of η_{ext} and $\eta_{\rm P}$ of 10.9% and 8.3 lm W⁻¹ at 4.5 V, respectively, considerably better than those of device IV (8.2% and 4.5 lm W^{-1} at 5.9 V, respectively). These values clearly indicate that the electron mobilities (Table 1) of 27SFBI and 22SFBI have pronounced effects on the corresponding device performances. We ascribe the superior performance of the D-EML device III over that of device IV to the more balanced charge recombination of the former. The normalized EL spectra of all four of these devices (I-IV) displayed [Fig. 3(c)] the deep-red emissions of the dopant Os(bpftz)₂(PPhMe₂)₂, each with CIE coordinates (CIE1931) of (0.66, 0.34). No other detectable peaks appeared in the EL spectra upon increasing the applied voltage.

Conclusions

We have demonstrated a new strategy—using a simple bilayer device architecture with double-doped emissive layers—for the fabrication of highly efficient deep-red PhOLEDs. The success of this approach is based on the use of tailor-made host materials and careful selection of the red dopant. The different charge transport properties and the mismatched HOMO/LUMO energy levels of the HT-type host **DTAF** and the ET-type hosts **22SFBI** and **27SFBI** allow the charge carriers to accumulate at the HT– ET interfacial region. The red emitter Os(bpftz)₂(PPhMe₂)₂, which possesses appropriate HOMO/LUMO energy levels, was

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double-doped to cover the HT–ET interfacial zone, rendering direct charge injection and trapping on the triplet emitter possible. This design prevents the accumulation of charge carriers at the interface, with the wide emission zone reducing the degree of triplet–triplet annihilation, leading to improved device efficiency. Optimally, we obtained a red device (CIE coordinates: x = 0.66, y = 0.34) exhibiting a high external quantum efficiency of 12.3% (10.9% at 1000 cd m⁻²) and a power efficiency of 13.5 lm W⁻¹. Our simple bilayer device design provides a practical means of using the double-doping strategy to fabricate highly efficient PhOLEDs possessing high device efficiency and operating at a low operation voltage; therefore, it is potentially cost-competitive with other contemporary display manufacturing processes.

Experimental

Synthesis

2,7-Bis[4-(1-phenylbenzimidazol-2-yl)phenyl]-9,9'-spirobifluorene (27SFBI). Tri-tert-butylphosphine (6.4 mL) and Na₂CO_{3(a0)} (2 M, 20 mL) were added to a solution of 2,7-dibromo-9,9'-spirobifluorene (2) (1.0 g, 2.1 mmol), 4-(1-phenylbenzimidazol-2-yl)phenylboronic acid (1) (1.66 g, 5.28 mmol), and Pd(PPh₃)₄ (100 mg, 0.086 mmol) in toluene (50 mL) under Ar and then the mixture was heated under reflux for 48 h. After cooling to room temperature, the reaction mixture was partitioned between CH₂Cl₂ and brine. The organic layer was dried (MgSO₄) and concentrated. The crude product was washed with hexane to afford pure 27SFBI (1.51 g, 84%) as a white solid. Mp 321 °C (DSC); ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta 7.91 \text{ (d, } J = 8.0 \text{ Hz}, 4\text{H}), 7.86 \text{ (d, } J = 6.0 \text{ Hz},$ 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 4H), 7.48 (d, J = 8.0 Hz, 4H), 7.46–7.35 (m, 8H), 7.32 (d, J = 8.0 Hz, 4H), 7.29 (d, J = 6.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 2H), 6.91 (s, 2H), 6.79 (d, J = 8.0 Hz, 2H);¹³C NMR(CDCl₃, 100 MHz) δ 151.4, 149.4, 147.9, 142.3, 141.3, 141.2, 140.5, 139.4, 136.8, 136.5, 129.5, 129.2, 128.2, 128.1, 127.6, 127.5, 127.0, 126.6, 126.4, 123.8, 123.0, 122.7, 122.0, 120.2, 119.8, 119.4, 110.1, 66.1; HRMS (m/z, FAB⁺) Calcd. for C₆₃H₄₀N₄ 852.3253, found 852.3245.

2,2'-Bis[4-(1-phenylbenzimidazol-2-yl)phenyl]-9,9'-spirobifluorene (**22SFBI**). Tri-*tert*-butylphosphine (5.3 mL) and Na₂CO_{3(aq)} (2 M, 15 mL) were added to a solution of 2,2'-diiodo-9,9'-spirobifluorene (**3**) (1.00 g, 1.76 mmol), 4-(1-phenylbenzimidazol-2-yl)phenylboronic acid (**1**) (1.40 g, 4.46 mmol), and Pd(PPh₃)₄ (100 mg, 0.086 mmol) in toluene (50 mL) under Ar and then the mixture was heated under reflux for 48 h. After cooling to room temperature, the reaction mixture was partitioned between CH₂Cl₂ and brine. The organic layer was dried (MgSO₄) and concentrated. The crude product was washed with hexane to afford pure **22SFBI** (1.53 g, 85%) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ 7.90 (d, J = 8 Hz, 2H), 7.86 (d, J = 8 Hz, 4H), 7.63 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 4H), 7.47 (d, J = 6.0 Hz, 4H), 7.45–7.35 (m, 8H), 7.32 (d, J = 8.0 Hz, 4H), 7.31 (d, J = 8.0 Hz, 2H), 7.24–7.14 (m, 4H), 7.10 (t, J = 7.2 Hz, 2H), 6.96 (s, 2H), 6.74 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.7, 140.1, 148.8, 142.7, 141.4, 141.4, 141.0, 139.6, 137.1, 136.8, 131.8, 131.7, 129.7, 129.5, 129.0, 128.6, 128.4, 128.2, 128.2, 127.9, 127.7, 127.2, 126.8, 126.6, 126.5, 123.9, 123.2, 122.9, 122.3, 120.3, 120.1, 119.6, 110.3, 66.0; HRMS (m/z, FAB⁺) Calcd. for C₆₃H₄₀N₄ 852.3253, found 852.3253.

Photophysical measurements

Steady state spectroscopic measurements were conducted both in solution and solid films prepared by vacuum (2×10^{-6} torr) deposition on a quartz plate (1.6×1.0 cm). Absorption spectra were recorded with a U2800A spectrophotometer (Hitachi). Fluorescence spectra at 300 K and phosphorescent spectra at 77 K were measured on a Hitachi F-4500 spectrophotometer upon exciting at the absorption maxima. Quantum efficiency measurements were recorded with an integration sphere coupled with a photonic multi-channel analyzer (Hamamatsu C9920), which gave anthracene a quantum yield of 23%. The experimental values of HOMO levels were determined with a Riken AC-2 photoemission spectrometer (PES), and those of LUMO levels were estimated by subtracting the optical energy gap from the measured HOMO.

Time-of-flight (TOF) mobility measurements

The samples for the TOF measurements were prepared through vacuum deposition in the configuration glass/Ag (30 nm)/organic $(2-3 \mu m)/A1(150 nm)$; they were then placed inside a cryostat and maintained under vacuum. The thickness of organic film was monitored in situ with a quartz crystal sensor and calibrated by a thin film thickness measurement (K-MAC ST2000). A pulsed nitrogen laser was used as the excitation light source through the transparent electrode (ITO) 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 transit time of t_T . 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 $\mu = D/(t_T E) = D^2/(V t_T)$, in which the carrier transit time, t_T , can be extracted from the intersection point of two asymptotes to the plateau and the tail sections in double-logarithmic plots.

OLED device fabrications

All chemicals were purified through vacuum sublimation prior to use. The OLEDs were fabricated through vacuum deposition of the materials at 10^{-6} torr onto ITO-coated glass substrates having a sheet resistance of 15 Ω sqr⁻¹. The ITO surface was cleaned ultrasonically—sequentially with acetone, methanol, and deionized water—and then it was treated with UV-ozone. A hole-injection layer of poly(3,4-ethylenedioxythiophene)-poly-(4-stylenesurfonate) (PEDOT:PSS) was spin-coated onto the substrates and dried at 130 °C for 30 min to remove residual water. Organic layers were then vacuum deposited at a deposition rate of *ca.* 1-2 Å s⁻¹. Subsequently, LiF was deposited at 0.1 Å s⁻¹ and then capped with Al (*ca.* 5 Å s⁻¹) through shadow masking without breaking the vacuum. The *I–V–L* characteristics of the devices were measured simultaneously using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si-photodiode in a glovebox system. EL spectra were measured using a photodiode array (OTO SD1000) with a spectral range from 200 to 850 nm and a resolution of 2 nm.

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