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Introduction

Organic light-emitting devices (OLEDs) are of current interest from both scientific and practical points of view due to their applications in the next generational full-color flat-panel displays and solid-state lighting sources.1 During the last two decades great progress has been made in the exploitation of OLED materials and the optimization of device structures.^{2,3} Many new emitters with red (R), green (G) or blue (B) emission, hole/electron transporting materials and hosts have been developed for full-color and white OLEDs. To realize highperformance full-color display or white color lighting devices, the R, G and B emission materials together with corresponding hosts, hole- and electron-transporting materials are needed. In other words, 6-8 or more kinds of organic materials are needed to construct a full-color display.4-6 The full-color OLEDs were often established based on a set of complex materials systems and high cost organic syntheses. In this sense, achieving high-performance R, G and B electroluminescence through a simple material system with an aim to reduce the production cost of materials and simplify the manufacturing process is an important issue for OLED applications. Therefore, the design and synthesis of organic

Constructing high-performance blue, yellow and red electroluminescent devices based on a class of multifunctional organic materials[†]

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Two new indolo[3,2-*b*]carbazole derivatives (DPDT-ICZ and DNDT-ICZ) with multifunctionality were designed and synthesized. They were employed as deep-blue emitters, hole-transporting materials and hosts to fabricate organic light-emitting devices (OLEDs). The devices which used them as emitters displayed deep-blue emissions with CIE coordinates of (0.15, 0.08). They have been employed as hole-transporting and host material simultaneously to construct high performance yellow and red phosphorescent OLEDs. High power efficiencies (78.3 Im W⁻¹ for yellow devices and 20.4 Im W⁻¹ for red devices) for phosphorescent OLEDs were achieved. Importantly, these devices displayed the feature of low roll-off of efficiencies. At the luminance of 1000 cd m⁻², roll-off of current efficiencies was 1.3% for the yellow device and 14.6% for the red device.

materials with multifunctionality is still a challenge in the area of organic electroluminescence.

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In this context, we report here two indolo[3,2-*b*]carbazole (ICZ)⁷⁻⁹ analogues DPDT-ICZ and DNDT-ICZ (Scheme 1). The two compounds exhibit high fluorescent quantum efficiencies and intense deep-blue emissions with narrow FWHM (the full width at half maximum). Meanwhile, as candidates for hole-transporting materials, the high HOMO energy levels (about -5.0 eV) are suitable for hole injection. Their hole mobilities are well matched with the electron mobilities of some electron-transporting materials leading to balanced carriers in devices, which is favorable for obtaining high efficiencies and low roll-off of efficiencies. Importantly, the two materials have relatively small singlet-triplet splitting that can reduce the intrinsic energy loss from S₁ to T₁ to improve the power efficiencies of devices. They have been employed as deep-blue emitters, hole-transporting materials and hosts to fabricate high-performance



Scheme 1 Synthetic procedures and structures of compounds.

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[†] Electronic supplementary information (ESI) available: TGA/DSC plots, OLED device data, ¹H NMR, ¹³C NMR, mass spectra. CCDC reference numbers 941266 and 941267. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3tc31271b

OLEDs. A comprehensive investigation that encompasses the crystal structures, photophysical properties, electrochemical properties, charge-transporting properties as well as the detailed electroluminescent (EL) characteristics of the materials will be presented in this contribution.

Experimental section

General information

Instruments. ¹H NMR spectra were measured on a Bruker AVANCE 500 MHz or a Varian Mercury 300 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. UV-Vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer. The absolute fluorescent quantum yields were measured on an Edinburgh FLS920 steady state fluorimeter (excited at 365 nm). Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument at a heating rate of 10 °C min⁻¹ from 20 to 360 °C under a nitrogen atmosphere. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min⁻¹ from 25 to 800 °C under nitrogen. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using Pt as the working electrode, platinum wire as the auxiliary electrode, and a porous glass wick Ag/Ag⁺ as the pseudo-reference electrode with standardization against ferrocene/ferrocenium. The oxidation potentials were measured in CH₂Cl₂ solution containing 0.1 M of *n*-Bu₄NPF₆ as the supporting electrolyte at a scan rate of 100 mV s⁻¹.

Single crystal structures. The single crystals suitable for X-ray structural analysis were obtained by slow evaporation of the solutions of both compounds in dichloromethane. Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromated Mo K α radiation. The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least-squares on F^2 . Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically.

Preparation of materials. All commercially available reagents were used as received unless otherwise stated. All reactions were carried out using Schlenk techniques under a nitrogen atmosphere.

Synthesis

Scheme 1 outlines the synthetic procedures and structures of compounds. Compounds 1 and 2 were synthesized according to the reported procedures.¹⁰ Then a simple alkylation of 1 and 2 produced compounds DPDT-ICZ and DNDT-ICZ with good yields. After column chromatography, subsequent purification by vacuum sublimation produced the pure samples. Both materials were fully characterized by ¹H NMR, ¹³C NMR, mass spectra (ESI, Fig. S1–S5†) and element analysis. The simple and

cheap synthetic procedures make them promising candidates for practical applications.

Synthesis of DPDT-ICZ. 1 (408 mg) and DMSO (15 ml) were added to a 50 ml two-neck round bottom flask. A solution of 1 g sodium hydroxide in 1 ml distilled water was added to the flask slowly. Then 736 mg of *n*-iodobutane was added to the mixture immediately. The mixture turned yellow and was stirred at room temperature for 20 h. The mixture was poured into 200 ml distilled water and then stirred for 20 min. The resulting solid was isolated by filtration, washed with water and dried to give a vellow solid. The solid was then purified by column chromatography on silica gel using CH_2Cl_2 /petroleum ether (1 : 8 v/v) as the eluent to give an olive-coloured solid. Yield: 62%; ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3, \delta)$: 7.65 (d, 14H; ArH), 6.52 (d, *J* = 1.4 Hz, 4H; ArH), 1.52 (s, 4H; $-CH_2$), 0.94 (s, 6H; $-CH_3$), 0.765 (t, J = 1.1 Hz, 8H; -CH₂). ¹³C NMR (500 MHz, CDCl₃): 13.77, 20.03, 128.16, 128.94. m/z: 520.47 $[M]^+$ (calcd: 520.29). Anal. Calcd for C₃₈H₃₆N₂: C 87.65, H 6.97, N 5.38; found: C 87.80, H 6.98, N 5.44.

Synthesis of 2. A mixture of indole (2.34 g), 1-naphthaldehyde (3.12 g), 0.75 ml of HI solution (45% w/w) and 60 ml of acetonitrile was refluxed for 16 h under a nitrogen atmosphere. After cooling to 0 °C, the mixture was filtered and then the solid was washed with cold acetonitrile. The solid was put into a 100 ml two-neck round bottom flask, which contained 2.0 g iodine and 60 ml of acetonitrile. The mixture was heated at 80 °C for 10 h under a nitrogen atmosphere. After cooling to room temperature, the solvent was removed by rotary evaporation. The solid was added to a solution of sodium thiosulfate, then the mixture was stirred for 20 min. The product was extracted with dichloromethane. After removing the solvent and crystallization in diethyl ether, the slightly yellow solid 2 was obtained. ¹H NMR (300 MHz, CDCl₃, δ): 8.89 (s, 2H; -NH), 6.57– 8.17 (m, 22H; ArH). Yield: 70%. *m/z*: 508.33 [M]⁺ (calcd: 508.19).

Synthesis of DNDT-ICZ. DNDT-ICZ was synthesized and purified by a procedure similar to that for DPDT-ICZ except that CH₂Cl₂/petroleum ether (1 : 10 v/v) was used as the eluent instead of CH₂Cl₂/petroleum ether (1 : 8 v/v). Yield: 50%. ¹H NMR (300 MHz, CDCl₃, δ): 8.16 (d, J = 8.4 Hz, 2H; ArH), 8.05 (d, J = 8.4 Hz, 2H; ArH), 7.85–7.88 (m, 2H; ArH), 7.72–7.78 (m, 2H; ArH), 7.61 (d, J = 8.4 Hz, 2H; ArH), 7.49–7.56 (m, 2H; ArH), 7.19–7.34 (m, 6H; ArH), 6.61 (s, 2H; ArH), 6.22 (d, J = 8.1 Hz, 2H; ArH), 3.53 (s, 4H; –CH₂), 1.15–1.39 (m, 4H; –CH₂), 0.48–0.66 (m, 10H; –CH₂, CH₃). ¹³C NMR (500 MHz, CDCl₃): 13.44, 13.50, 19.79, 19.83, 108.20, 117.89, 122.32, 122.74, 125.17, 125.86, 125.88, 126.39, 126.42, 126.56, 126.67, 126.73, 128.27, 128.32, 128.59, 128.60, 133.41, 133.79, 133.82. *m*/*z*: 620.40 [M]⁺ (calcd: 620.32). Anal. Calcd for C₄₆H₄₀N₂: C 88.99, H 6.49, N 4.51; found: C 89.28, H 6.49, N 4.59.

Device fabrication and measurements

Before device fabrication, the ITO glass substrates were precleaned carefully and treated with plasma for 7 min. Then the sample was transferred to the deposition system. The devices were prepared in vacuum at a pressure of 5×10^{-6} Torr. The holetransporting material NPB (1,4-bis(1-naphthylphenylamino) biphenyl), hole-blocking and electron-transporting material

Bepp₂ (hydroxyphenylpyridine beryllium) were commercially available and thermally evaporated at a rate of 0.2 Å s⁻¹. After the organic film deposition, 1.5 nm of LiF and 100 nm of aluminum were thermally evaporated onto the organic surface. The thicknesses of the organic materials and the cathode layers were controlled using a quartz crystal thickness monitor. All of the used organic materials were purified by a vacuum sublimation approach. The electrical characteristics of the devices were measured with a Keithley 2400 source meter. The EL spectra and luminance of the devices were obtained on a PR650 spectrometer. All the device fabrication and device characterization steps were carried out at room temperature under ambient laboratory conditions. Current-voltage characteristics of singlecarrier devices were measured using the same semiconductor parameter analyzer as for OLED devices. The single-carrier device measurements were performed under dark and ambient conditions.

Results and discussion

Crystal structure

The yellowish crystals of DPDT-ICZ and DNDT-ICZ were obtained by slow evaporation of their dichloromethane solutions and the single crystal structures were examined (Fig. 1). In crystals, the ICZ unit is almost planar with a very small torsion angle of 0.84°, and the side aromatic units are almost perpendicular to the ICZ plane with a dihedral angle of 88.3°. In the solid state, DPDT-ICZ molecules adopt a typical herringbone packing model with a dihedral angle of 49.2°. On each side of the herringbone, benzene units are connected to the ICZ units





Fig. 1 Molecular structures with 50% thermal ellipsoids and packing structures of (a) DPDT-ICZ; (b) DNDT-ICZ.

of neighbour molecules by C-H··· π interactions with a contact distance of 2.97 Å, and the interaction continues on to the next molecules. The two sides of the herringbone have no interactions. Unlike DPDT-ICZ, the DNDT-ICZ molecules adopt a parallel arrangement model with two kinds of molecular rows. Within one molecular row, there is no intermolecular interaction. In the other molecular row, the naphthalene units are connected to the ICZ units by C-H··· π interactions with a contact distance of 2.75 Å. Between the two kinds of molecular rows no contact interaction has been observed. The noncoplanar molecular conformation and weak intermolecular interactions enable the two compounds to have high fluorescent quantum efficiencies in the solid state.

Thermal analysis

Thermal properties were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (see Fig. S6[†] and Table 1). Both compounds have high melting points (298 °C for DPDT-ICZ and 319 °C for DNDT-ICZ) and decomposition temperatures (corresponding to 5% weight loss) (362 °C for DPDT-ICZ and 398 °C for DNDT-ICZ). The glass transition temperature (T_{α}) of DNDT-ICZ is 124 °C, which is much higher than the normal hole-transporting materials NPB and CBP (4,4'-N,N'-dicarbazolylbiphenyl), and should be attributed to the rigid structure of DNDT-ICZ. The good thermal stability is favorable for the formation of uniform thin films upon thermal evaporation and can reduce the possibility of phase separation during operation. This characteristic may suppress the formation of aggregation in films, thus prolonging the device operational lifetime.11 Therefore, DPDT-ICZ and DNDT-ICZ have desirable properties for their application in OLEDs.

Photophysical properties

The UV-Vis absorption and photoluminescence (PL) spectra of DPDT-ICZ and DNDT-ICZ in dilute CH_2Cl_2 solutions and neat thin films together with the phosphorescence spectra in CH_2Cl_2 at 77 K are shown in Fig. 2, and the optical data of the two compounds are summarized in Table 1. According to the earlier

Table 1	Physical	properties	of DPDT-ICZ	and DNDT-ICZ
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	DPDT-ICZ	DNDT-ICZ
$T_{\rm g}/T_{\rm m}/T_{\rm d}$ (°C)	^f /298/362	124/319/398
$\lambda_{abs}/nm [sol^{a}/film^{b}]$	286,337,418/	286,339,421/
	286,342421	286,343,423
$\lambda_{\rm PL}/\rm nm [sol^a/film^b]$	442,464/433,454	431,450/439,450
$\Phi_{\rm f} \left[{\rm sol}^a / {\rm film}^b \right]$	0.46/0.51	0.39/0.30
HOMO/LUMO (eV) ^c	4.96/2.10	5.00/2.14
E_{g}^{d} (eV)/ E_{T}^{e} (eV)	2.86/2.45	2.86/2.41
$\Delta E_{\rm ST}$ (eV)	0.36	0.47

^{*a*} Measured in CH₂Cl₂ solution (10⁻⁵ M). ^{*b*} Measured in film. ^{*c*} HOMO was measured from the onset of oxidation potentials, LUMO was deduced from HOMO and E_{g} . ^{*d*} Singlet energy measured from the diluted solution at 298 K. ^{*e*} Triplet energy measured in CH₂Cl₂ at 77 K (10⁻⁵ M). ^{*f*} Not observed.

report,8 the strong absorption peaks around 286 and 337 nm are ascribed to the π - π * transition, peaks around 421 nm are owing to the n- π^* transition of the ICZ unit. Both compounds exhibited intense deep-blue emissions in solutions and films. They have narrow FWHM (22.2 nm for DPDT-ICZ and 33.3 nm for DNDT-ICZ in solution; 40.1 nm for DPDT-ICZ and 39 nm for DNDT-ICZ in films), which is very important for color purity of deep-blue emitters. The PL quantum yields (Φ_f) in solution are 0.46 for DPDT-ICZ and DNDT-ICZ, and these in films are 0.39 for DPDT-ICZ and 0.30 for DNDT-ICZ. These indicate that they are candidates for deep-blue emitters. For DPDT-ICZ, the PL quantum yield in solution is lower than that in film form. Contrarily, for DNDT-ICZ, the PL quantum yield in solution is higher than that in film form. A rational explanation for these phenomena is that in the solid state of DPDT-ICZ the chromophores adopt a J-aggregation state (Fig. 1a) that can enhance the emission efficiency, while in the solid state of DNDT-ICZ the chromophores adopt a H-aggregation state (Fig. 1b) that can induce the emission quenching.12

From the absorption spectra, the energy difference between $S_{0,0}$ and $S_{1,0}$ (E_g) is estimated as 2.86 eV for DPDT-ICZ and DNDT-ICZ. From the phosphorescence spectra, the energy differences between $S_{0,0}$ and $T_{1,0}$ (E_T) are estimated as 2.45 eV for DPDT-ICZ and 2.41 eV for DNDT-ICZ, which are enough for yellow and red phosphorescent emitters. The singlet-triplet



Fig. 2 Room-temperature UV-Vis absorption and PL spectra in CH_2Cl_2 solution (10^{-5} M) and in neat films as well as the phosphorescence spectra in CH_2Cl_2 solution (10^{-5} M) at 77 K of (a) DPDT-ICZ and (b) DNDT-ICZ.

splitting $\Delta E_{\rm ST}$ values are 0.36 eV for DPDT-ICZ and 0.47 eV for DNDT-ICZ that are hardly reached for the commonly used hosts based on carbazole,¹³ silane,¹⁴ phosphine oxide¹⁵ and pyridine.¹⁶ The small $\Delta E_{\rm ST}$ can reduce the intrinsic energy loss from S₁ to T₁, and this is favourable for achieving OLEDs with high power efficiencies.

Electrochemical properties

The electrochemical properties were investigated by cyclic voltammetry (CV) (Fig. 3). Both compounds showed reversible oxidation behaviors suggesting the potential of possessing good hole transporting abilities. The HOMO energy levels are determined to be 4.96 eV for DPDT-ICZ and 5.00 eV for DNDT-ICZ, respectively. The high HOMO energy levels may be favored for hole injection. No reduction waves were observed for the two compounds, and the LUMO energy levels (2.1 eV for DPDT-ICZ and 2.14 eV for DNDT-ICZ) were deduced from HOMO and $E_{\rm g}$. The high LUMO energy levels can effectively prevent the electron injection. The HOMO and LUMO energy levels indicate that DPDT-ICZ and DNDT-ICZ may be good hole-transporting materials.

Single-carrier devices

The hole-only and electron-only devices with structures of [ITO/ DPDT-ICZ or DNDT-ICZ or NPB (70 nm)/MoO₃ (10 nm)/Al] for hole-only and [ITO/TPBi (20 nm)/DPDT-ICZ or DNDT-ICZ (60 nm)/LiF (1.5 nm)/Al] for electron-only devices (Fig. 4) were fabricated. Because the LUMO of MoO₃ (-2.3 eV) is much higher than that of Al (-4.3 eV), the electron cannot be injected into the device, so we can get the pure hole current. By using TPBi (1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene) thin film as hole-blocking layer, we can also get the pure electron current in electron-only devices. The mobility was estimated from the single carrier devices based on the space charge limited current (SCLC) method and *I*-*V* characteristics (Fig. 4a and b) of singlecarrier devices.¹⁷ For both compounds, the hole mobilities (3.26 × 10⁻⁵ cm² V⁻¹ S⁻¹ for DPDT-ICZ and 1.02×10^{-5} cm² V⁻¹



Fig. 3 Cyclic voltammograms of DPDT-ICZ and DNDT-ICZ in CH₂Cl₂.



Fig. 4 Current density *versus* voltage characteristics of the hole-only and electron-only devices of (a) DPDT-ICZ and (b) DNDT-ICZ, and the hole-only devices of (c) NPB, DPDT-ICZ and DNDT-ICZ.

 S^{-1} for DNDT-ICZ) are much higher than their electron mobilities (2.38 × 10⁻⁸ cm² V⁻¹ S⁻¹ for DPDT-ICZ and 1.83 × 10⁻⁹ cm² V⁻¹ S⁻¹ for DNDT-ICZ). It is worth noting that the hole mobilities of the compounds are slightly lower than that of NPB within the driving voltage range from 2.4 to 7.5 V (Fig. 4c), which is the voltage range of device operation. This characteristic may be favourable for the carrier balance in devices because the electron mobilities of many electron-transporting materials are much lower than the hole mobilities of hole-transporting materials. Therefore, constructing OLEDs with high efficiencies and low roll-off of efficiencies based on the two compounds can be expected.

Electroluminescent properties

To check the electroluminescent properties of DPDT-ICZ and DNDT-ICZ deep-blue-emitting devices with the structures of [ITO/NPB (45 nm)/DPDT-ICZ or DNDT-ICZ (20 nm)/Bepp₂ (35 nm)/LiF (1.5 nm)/Al] were fabricated. Undoped thin films of DPDT-ICZ (device B1) and DNDT-ICZ (device B2) were employed as the emitting layer in devices B1 and B2, respectively. NPB was used as the hole-transporting layer, Bepp₂ (Fig. 5)¹⁸ served as the electron-transporting layer and LiF was utilized as the electroninjecting layer. The electroluminescent performances of devices B1 and B2 are shown in Fig. 6, 8, S7[†] and Table 2. Devices B1 and B2 displayed deep-blue emissions with Commission International de l'Eclairage (CIE) coordinates of (0.15, 0.08), which are very close to the National Television Standards Committee (NTSC) standard (0.15, 0.07). Meanwhile, both devices exhibited good EL color stabilities with the variation of driving voltages. This characteristic is important for high performance displays and lighting sources.

Devices **B1** and **B2** had low turn-on voltages (2.6 V), which can be ascribed to their easy hole injection because of the high HOMO energy levels (-5.0 eV) of DPDT-ICZ and DNDT-ICZ. The maximum brightness (L_{max}), maximum external quantum efficiencies ($\eta_{\text{ext.max}}$), current ($\eta_{\text{c.max}}$) and power ($\eta_{\text{p.max}}$) efficiencies of device **B1** are 4117 cd m⁻², 0.96%, 1.31 cd A⁻¹ and 1.58 lm W⁻¹, respectively.

To demonstrate the possibility that the two compounds may be used as hole-transport materials and hosts of phosphors simultaneously in devices, the phosphorescent OLEDs were fabricated. The device structures, materials used in devices and their energy level diagram are summarized in Fig. 5. Phosphorescent (ppy)₂Ir(tipg)¹⁹ and (bt)₂Ir(dipba)²⁰ were used as yellow and red emitters, respectively, in the OLEDs. The current density–voltage–luminance (*J–V–L*) characteristics, efficiencies



Fig. 5 The materials used in devices, their energy level diagram and device structures.



Fig. 6 (a) Current density–voltage–luminance (*J–V–L*) characteristics, current efficiency and power efficiency *versus* luminance curves of devices **B2**, **Y2**, **R2** based on DNDT-ICZ; (b) EL spectra and CIE 1931 coordinates of devices **B2**, **Y2**, **R2** based on DNDT-ICZ; (c) PL spectra of the emitting layers of devices **Y1**, **Y2**, **R1**, **R2**.

versus luminance curves, EL spectra as well as external quantum efficiencies (EQE) are shown in Fig. 6, 8 and S7.[†] These devices have low turn-on voltages (about 2.5 V) and rapidly increased luminance feature. To achieve high luminance at low driving voltage and current density is very beneficial for prolonging device lifetimes. The devices display high efficiencies of 58.9 cd A^{-1} and 73.8 lm W^{-1} for **Y1**, 64.8 cd A^{-1} and 78.3 lm W^{-1} for **Y2**, 15.6 cd A^{-1} and 19.6 lm W^{-1} for **R1**, 17.8 cd A^{-1} and 20.4 lm W^{-1} for **R2**. Their high efficiencies can be ascribed to good carrier injection, balanced carriers, and small singlet–triplet splitting of hosts. From tens to thousands of luminance units, the efficiencies of these devices decrease slowly. At the luminance of 1000 cd m⁻², roll-off of current efficiencies are 1.3% for **Y1**,

1.7% for Y2, 22% for R1, 14.6% for R2. The low roll-off of efficiencies may be attributed to the well matched hole- and electron-transporting ability between the host and electrontransporting material.¹⁹ Although DPDT-ICZ and DNDT-ICZ are typical hole-transporting materials with poor electron-transporting ability, the bipolar carrier transporting properties of (ppy)₂Ir(tipg) and (bt)₂Ir(dipba) have been confirmed in our previous studies.^{20,21} This characteristic ensures that electrons



Fig. 7 (a) Current density–voltage–luminance (*J–V–L*) characteristics; (b) current efficiency and power efficiency *versus* luminance curves of devices **Y1f**, **Y2f**, **R1f**, **R2f**.

Lectroluminescent properties of the devices										
	Dopant	$V_{\mathrm{on}}\left[\mathrm{V}\right]$	$L_{ m max} \left[m cd \ m^{-2} ight]$	$\eta_{\rm c}{}^b \left[{\rm cd} \; {\rm A}^{-1} ight]$	$\eta_{ m p}^{~b} [{ m lm} { m W}^{-1}]$	$\eta_{\mathrm{ext}}^{\ \ b}$ [%]	CIE $(x,y)^c$			
B1	_	2.6	4117	1.31, 1.02, 0.56	1.58, 0.82, 0.28	0.96, 0.71, 0.40	0.15, 0.08			
B2	—	2.6	6010	1.36, 1.29, 0.88	1.64, 1.13, 0.49	1.35, 1.25, 0.85	0.15, 0.08			
Y1	(ppy) ₂ Ir(tipg)	2.4	49 340	58.9, 58.9, 58.1	73.8, 70.8, 61.5	18.1, 15, 14.7	0.43, 0.56			
Y1f	(ppy) ₂ Ir(tipg)	2.4	47 930	61.2, 60.6, 57.8	70.0, 69.4, 63.0	17.3, 16.8, 17.3	0.43, 0.56			
Y2	(ppy) ₂ Ir(tipg)	2.5	52 670	64.8, 64.8, 63.7	78.3, 73.6, 59.9	18.1, 18.0, 17.7	0.43, 0.56			
Y2f	(ppy) ₂ Ir(tipg)	2.5	48 060	66.2, 64.3, 63.6	80.5, 74.4, 58.6	18.6, 18.3, 18.0	0.43, 0.56			
R1	(bt) ₂ Ir(dipda)	2.5	21 170	15.6, 14.8, 12.1	19.6, 15.7, 12.3	10.3, 9.8, 8	0.63, 0.37			
R1f	(bt) ₂ Ir(dipda)	2.5	31 460	16.3, 15.2, 14.6	20.1, 15.6, 10.2	10.3, 10.2, 9.3	0.63, 0.37			
R2	(bt) ₂ Ir(dipda)	2.5	29 590	17.8, 17, 15.2	20.4, 17.9, 17.1	11.8, 11.2, 10.1	0.63, 0.37			
R2f	(bt) ₂ Ir(dipda)	2.5	37 730	18.5, 17.9, 16.7	22.1, 17.9, 16.5	12, 11.7, 10.6	0.63, 0.37			

^{*a*} Abbreviations: V_{on} : turn-on voltage; L_{max} : maximum luminance; η_c : the maximum current efficiency; η_p : the maximum power efficiency; η_{ext} : the maximum external quantum efficiency. ^{*b*} In the order of maximum, then values at 100 and 1000 cd m⁻². ^{*c*} Measured at 100 cd m⁻².

can be injected into the emitting layer efficiently. Close comparison of the EL data (Table 2) revealed that the DNDT-ICZ based devices (**B2**, **Y2** and **R2**) showed slightly higher performance than those of DPDT-ICZ based devices (**B1**, **Y1** and **R1**). It is worth noting that the EL data summarized in Table 2 were recorded within the driving voltage range of 2.4 to 4.0 V. The better EL performance of DNDT-ICZ may be attributed to the slightly higher hole transport ability of DNDT-ICZ compared with DPDT-ICZ within the driving voltage range of 2.4 to 4.0 V (Fig. 4). On the other hand, DNDT-ICZ possesses slightly lower LUMO energy level compared with DPDT-ICZ (Table 1), which may enhance the electron injection from the electron transport layer to the emitting layer and improve the EL performance.

The electroluminescent (EL) spectra of devices are shown in Fig. 6 and S7.† There are only peaks of guests, which means complete energy transfer from hosts to guests. We examined the PL spectra of doped films, which were identical to those of the emitting layers (Fig. 6c). Energy had been efficiently transferred to guests at the doping concentrations used in the devices. We conclude that energy transfer plays an important role in the emitting mechanism and the two compounds are good hosts for yellow and red PhOLEDs.

Phosphorescent OLEDs with structures of [ITO/NPB (30 nm)/ DPDT-ICZ or DNDT-ICZ : 5% (ppy)₂Ir(tipg) (20 nm)/Bepp₂



Fig. 8 EQE *versus* luminance curves of devices (a) B1, B2, Y1, Y2, R1, R2; (b) Y1f, Y2f, R1f, R2f.

(50 nm)/LiF/Al] for DPDT-ICZ in Y1f and DNDT-ICZ in Y2f, [ITO/ NPB (30 nm)/DPDT-ICZ or DNDT-ICZ : 10% (bt)₂Ir(dipba) (10 nm)/Bepp₂ (60 nm)/LiF (1.5 nm)/Al] for DPDT-ICZ in **R1f** and DNDT-ICZ in **R2f** were fabricated for comparison. The current density–voltage–luminance (*J*–*V*–*L*) characteristics, efficiencies *versus* luminance curves are shown in Fig. 7 and 8, and the device performances are listed in Table 2. The performances of the four reference devices are comparable to those devices which use DPDT-ICZ or DNDT-ICZ as hole-transporting materials, suggesting that the two compounds are good hole-transporting materials.

Conclusions

In summary, two ICZ derivatives (DPDT-ICZ and DNDT-ICZ) have been synthesized and employed as emitters, hole-transporting materials and hosts to fabricate high performance OLEDs. Deep blue OLEDs and highly efficient phosphorescent OLEDs (yellow and red colors) were achieved based on the two compounds. The multifunctional characteristics enable DPDT-ICZ and DNDT-ICZ to successfully carry out dual roles (hole-transporting materials and hosts of phosphors) in highly efficient OLEDs. Our study presents a strategy for the construction of high performance OLEDs based on simple material systems.

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