Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 9658

PAPER

Spiro-configured bipolar hosts incorporating 4,5-diazafluroene as the electron transport moiety for highly efficient red and green phosphorescent OLEDs

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Received 8th February 2012, Accepted 15th March 2012 DOI: 10.1039/c2jm30749a

We designed and synthesized a series of spiro-configured bipolar hosts (CSC, DSD, TST, and NSN) comprising electron-transporting 4,5-diazafluorene and hole-transporting carbazole or diarylamine with thorough characterizations of their thermal, photophysical, electrochemical properties, and carrier mobilities. Time-of-flight (TOF) measurements and single-carrier devices revealed these compounds had good hole and electron mobilities $(10^{-5} - 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ together with promising physical properties, rendering them good host materials for efficient electrophosphorescence. The green PhOLED with (PPy)₂Ir(acac) as the emitter incorporating CSC as the host exhibited a remarkable high brightness of 260 000 cd m⁻² at 2400 mA cm⁻² (11 V) with the maximum external quantum efficiency (η_{ext}) of 17.1%, the η_{ext} remained as high as 15.4% under a high brightness of 10 000 cd m⁻² at a low operating voltage of 5.1 V even without *p*-*i*-*n* device configuration. The NSN-based PhOLED with the red dopant Os(bpftz)₂(PPhMe₂)₂ has a maximum brightness of 77 900 cd m⁻² at 1100 mA cm⁻² (10 V) with the maximum η_{ext} of 19.5%. The η_{ext} remained as high as 19.1% under a practical brightness of 10000 cd m⁻² (4.6 V). These results suggest that the spiro-configured D–A hosts are well-suited for achieving highly efficient PhOLED with limited efficiencies roll-off.

Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have attracted much attention because they effectively harvest electrogenerated singlet and triplet excitons to accomplish internal quantum efficiency close to 100% [external quantum efficiency $(\eta_{\text{ext}}) = ca. 20\% \text{ (ph/el)}]^{1}$ A massive amount of research effort has been devoted to the development of novel materials and sophisticated device architectures for the prospective uses of PhOLEDs in display and lighting technologies. To realize highly efficient PhOLEDs, a suitable host material is usually employed to suppress the intrinsic detrimental effects, such as aggregation quenching and/or triplet-triplet annihilation, of transition metalcentered phosphors.² The molecular design of such host material is rather challenging as it requires optimized physical properties including (i) appropriate HOMO-LUMO levels to effectively allow smooth charge carriers (hole and electron) injection from the neighboring active layers into the emitting layer for achieving low operating voltages; (ii) balanced charge carrier mobilities to give maximum charge recombination within the emitting layer;

and (iii) high triplet energy for ensuring exothermic host-to-guest energy transfer and preventing reverse energy transfer to confine phosphorescence emission from the metal-centered phosphor.

Recently, PhOLED-related research has significantly drifted to the development of host materials possessing bipolar properties. The incorporation of hole- and electron-transporting moieties into the host material provides more balanced charge fluxes and better charge transport properties in the emitting layer, potentially simplifying the device structure (i.e., free of using an HTL and/or ETL). In this regard, developing host materials with efficient holeand electron-transporting properties (ambipolarity) is highly demanded to achieve highly efficient and cost-effective PhOLEDs. Our recent review classified some representative bipolar host materials into several categories according to their structural features as well as the molecular design strategies. The structureproperty-performance relationships of various classes of bipolar host materials were also highlighted.3 In general, carbazole or arylamine derivatives are usually adopted as the hole-transport moieties in bipolar materials, whereas various electron-deficient moieties such as nitrogen-heterocycles, 1,10-phenanthroline, 1,3,4oxadiazole, benzimidazole, phosphine oxide, and phenylsulfonyl are suitable for incorporating as electron-transport moieties. For example, Tao et al. reported an ortho-linked oxadiazole/aminebased bipolar compound as the host for green and red dopants, giving maximum η_{ext} as high as 20.2% for green and 18.5% for deep red electrophosphorescence.⁴ Hsu *et al.* achieved peak η_{ext} of 20.6% with a phosphine-oxide/amine-based bipolar host for blue

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phosphorescent emission.⁵ Most recently, a blue-emitting PhOLED reported by Jeon et al. incorporating the bipolar host comprising of hole-transporting carbazole and electron-transporting diphenylphosphoryl oxide achieved the highest η_{ext} of 25.1%.6 These bipolar host materials explicitly manifested their importance and competence for realizing highly efficient PhOLEDs. The introduction of twisted conformation and/or saturated system of designing bipolar hosts efficiently diminishes the electronic communication between the donor and the acceptor, which therefore leads to high triplet energies.5b,7 Accordingly, in line with the molecular design strategy, the non-conjugated spirobridged donor (D)-acceptor (A) molecular scaffold can effectively impede π -orbital interactions between the individual chromophore branches and thus afford the flexibility of independent fine-tuning of the electronic properties of donor and acceptor. Moreover, the orthogonal molecular configuration is beneficial to the thermal and emission stability due to suppressed intermolecular interaction in the solid state. Our previous report revealed the successful application of bipolar hosts comprising of a 9,9'-spirobifluorene core, achieving the highest η_{ext} of 20.4% for red-emitting PhOLEDs.8 However, these hosts are generally engaged with low triplet energies which substantially limit their compatibility with various shorter wavelength-emitting phosphors. This shortcoming can be circumvented by replacing the 2,7-dicyanofluorene (acceptor) with a less-conjugated 4,5-diazafluorene as the electron-transport moiety of a spiro-bridged bipolar host system.

The heterocyclic 4,5-diazafluorene was demonstrated in our previous work as an efficient electron-transport moiety in a spiro-configured D-A bipolar host material, 4,5-diaza-2',7'-bis(carbazol-9-yl)-9,9'-spirobifluorene (CSC), for highly efficient single-layer green PhOLEDs with an external quantum efficiency and a power efficiency of 8.3% and 12.3 lm W⁻¹, respectively, at a practical brightness of 1000 cd m⁻² (8.0 V).⁹ The bipolar characteristic of CSC is imparted by the electron-transporting 4,5-diazafluorene¹⁰ and the hole-transporting carbazoles. Facile synthetic modification on the donor branch is readily provided by the reactive 2' and 7' positions of 4,5-diazaspirobifluorene. As a result, we adopted the advantages of spiro-bridged D-A system and substantially extended our previous work on bipolar host materials by introducing various arylamine donors with different electron-donating ability such as diphenylamine, di-p-tolylamine, and 1-naphthylphenylamine. We anticipate that the triplet energies, energy levels, and carrier-transport properties of these bipolar materials can be tailored via judicious molecular design on the donor branch. As a consequence, the structural-property-performance relationships in the corresponding PhOLEDs will be systematically established after detailed characterizations of the bipolar hosts. On the other hand, in the consideration of device structure, the single-layer devices generally attract much attention due to their cost-effectiveness and simple fabrication process. However, the extraordinary high demand in their molecular design imposes significant difficulties on the development of single-layer device. Comparatively, several important merits of multiple-layer device architecture such as energy-barrier reduction, carrier balance, and exciton confinement ensure a maximum device performance, rendering this type of device structure suitable for characterizing the properties of new materials.

Results and discussion

Synthesis

Herein, we designed and synthesized a series of bipolar materials with a spiro-bridged D-A configuration, 4,5-diaza-2',7'-bis(carbazol-N-yl)spirobifluorene (CSC), 4,5-diaza-2',7'-bis(diphenylamino)spirobifluorene (DSD), 4,5-diaza-2',7'-bis(di-p-tolylamino) spirobifluorene (TST), and 4,5-diaza-2',7'-bis(1-naphthylphenylamino)spirobifluorene (NSN) (Chart 1). It has been mentioned that the 4,5-diazafluorene derivatives possess high electron affinity, so are capable of being electron injecting/transporting moieties. The different donors on 2',7'-position of fluorene moiety have considerable effect on the photo-induced electron transfer (PET) process which results in different energy levels, triplet energies, and hole injecting/transporting properties.¹¹ The perpendicular spiro-linkage minimizes the π -orbital interactions between the individual D and A chromophore branches, which retains the electron-transport behavior in each bipolar material. The synthesis of CSC and DSD was previously reported by our group.¹⁰ TST and NSN were synthesized according to the synthetic procedure of DSD with the use of di(p-tolyl)amine and 2-naphthylphenylamine, respectively (Scheme 1).

Thermal properties

The morphological properties and thermal stabilities of spirobridged bipolar hosts CSC, DSD, TST, and NSN were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 1), respectively. We observed distinct glass transition temperature (T_{a}) for CSC (179 °C), DSD (137 °C), TST (148 °C), and NSN (190 °C) followed by crystallization peaks of CSC (255 °C), DSD (226 °C), and TST (238 °C), no crystallization of NSN during the DSC scan. Compounds CSC, DSD, TST, and NSN exhibited good thermal stabilities with decomposition temperatures (T_{d} , corresponding to 5% weight loss) ranging from 348 to 416 °C. A high glass transition temperature is desirable for host material in PhOLEDs because it suppresses the formation of aggregates and prevents morphological changes upon heating. Such an orthogonal molecular configuration of spiro-configured bipolar host material is very beneficial to the thermal stability and thin film homogeneity, which are critical criteria for PhOLED devices.



Chart 1 Chemical structures of the bipolar hosts.



Scheme 1 Synthesis of TST and NSN.

Photophysical properties

Fig. 1 depicts the UV-visible absorption and photoluminescence (PL) spectra of spiro-bridged bipolar molecules CSC, DSD, TST, and NSN in solution (CH₂Cl₂) and solid thin films. The photophysical data are summarized in Table 1. All molecules exhibit two sets of absorption peaks which are assigned to the electronic transitions of 4,5-diazafluorene (shorter wavelength) and the donor branch (longer wavelength). The pronounced red-shifted emission maxima with Stokes shift of ca. 140 nm of DSD, TST, and NSN which are due to a mechanism involving rapid photoinduced electron transfer (PET).12 The emission generated from the chargeseparated excited state is highly sensitive to the dielectric environment because of its high polarity. Therefore, the longer emission wavelengths in solution than that in thin films are expected due to higher dielectric environment of CH2Cl2 and suppressed intermolecular interaction. In contrast, with less electron-donating carbazoles for CSC, the PET process becomes less efficient as observed for the smaller Stokes shift. The phosphorescence spectra of CSC, DSD, TST, and NSN in EtOH at 77 K show the highest-energy 0-0 phosphorescence emission at 468, 515, 519, and 521 nm corresponding to the triplet energy (E_T) of 2.65, 2.41, 2.39, and 2.38 eV, respectively. The higher $E_{\rm T}$ of CSC is consistent with the shorter emission wavelength in solution and film, attributed to the less donating ability of carbazole moieties. The triplet energy of CSC is sufficiently high for hosting green emitter whereas the others are appropriate for red phosphorescent emitters as a result of efficient prevention of reverse triplet energy transfer.

Cyclic voltammetry

We used cyclic voltammetry (CV) to probe the electrochemical properties of the bipolar compounds CSC, DSD, TST, and NSN

Table 1Physical properties of CSC, DSD, TST, and NSN



Fig. 1 Room-temperature absorption and emission (PL) spectra of CSC, DSD, TST, and NSN in CH_2Cl_2 solutions and in neat films and corresponding phosphorescence (Phos) spectra recorded from their EtOH solutions at 77 K.



Fig. 2 Cyclic voltammograms of CSC, DSD, TST, and NSN; 0.1 M TBAP (reduction) in THF and 0.1 M TBAPF₆ (oxidation) in CH₂Cl₂ were used as supporting electrolytes. A glassy carbon electrode was used as the working electrode; scan rate 100 mV s⁻¹.

(Fig. 2). The irreversible oxidation during the first CV scan of **CSC** is due to electropolymerization of carbazoles occurring at the C3 and C6 positions. Two reversible oxidations in a range

	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm c}/^{\circ}{\rm C}$	$T_{\rm m}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$	$E_{1/2}^{\text{ox}}/\text{V}^a$	$E_{1/2}^{\text{red}}/\mathrm{V}^b$	(HOMO ^c /LUMO/E _g ^d)/eV	λ_{abs}/nm , sol./film	λ _{PL} /nm, sol./film	E _T /eV
CSC	179	255	>400	416	Irr.	-1.93	-5.63/-2.36/3.27	293, 344/297, 347	377/413	2.65
DSD	137	226	291	348	0.70, 0.99	-2.01	-5.20/-2.20/3.00	307, 380/320, 382	518/470	2.41
TST NSN	148 190	238 n.d.	285 308	360 397	0.60, 0.91 0.71, 1.02	$-2.12 \\ -2.01$	-5.00/-2.00/3.00 -5.07/-2.07/3.00	308, 385/320, 389 320, 382/322, 385	538/478 503/460	2.39 2.38

^{*a*} Oxidation potential. ^{*b*} Reduction potential. ^{*c*} HOMO energy level determined using photoelectron yield spectroscopy (AC-2). LUMO = HOMO + E_{g} . ^{*d*} Calculated from the absorption onset of the solid film.



Fig. 3 Typical transient photocurrent signals for holes: (a) **DSD** (1.55 μ m thick) at $E = 5.8 \times 10^{-5}$ V cm⁻¹, (b) **TST** (1.8 μ m thick) at $E = 5.0 \times 10^{-5}$ V cm⁻¹, (c) **NSN** (1.55 μ m thick) at $E = 7.0 \times 10^{-5}$ V cm⁻¹. Insets are the double logarithmic plots of (a)–(c). (d) Electron and hole mobilities of **CSC**, **DSD**, **TST**, and **NSN** plotted with respect to $E^{1/2}$.



Fig. 4 Current–voltage (I-V) characteristics of electron-only devices. Inset: the relative energy level diagram of the electron-only devices.



Scheme 2 Structures of the heavy metal complexes used in this study.

between 1.2 and 0.5 V for **DSD**, **TST**, and **NSN** are assigned to the oxidations of arylamine moieties. The lowest oxidation potential is observed for **TST** (0.60 V), as expected for the strongest electron-donating capability of di-*p*-tolylamine among the four donors. The pronounced potential difference ($\Delta E \sim 0.3$ V) between the first and second oxidations of **DSD**, **TST**, and NSN indicates that the efficient resonance delocalization of the radical cation occurs on the donor branch. Four bipolar compounds underwent one reversible reduction at a reduction potential close to that of 4,5-diaza-9,9'-spirobifluorene. Therefore, we unambiguously assign the reduction site as being located on the acceptor branch, 4,5-diazafluorene. In line with the trend of electron-donating capability, the largest reduction potential (-2.12 V) was found for **TST**. For the determination of HOMO energy levels, we used photoelectron yield spectroscopy (Riken AC-2), and then estimated the LUMO energy levels from the HOMO values and the optical band gaps (E_g) by using the equation of LUMO = HOMO + E_g . The measured redox potentials and calculated HOMO/LUMO energies are summarized in Table 1.

Charge carrier mobility and electron only devices

The charge-transport characteristics of the bipolar compounds can be investigated by their charge carrier mobility using the conventional time-of-flight (TOF) technique.13 The typical transient photocurrent signals (holes for DSD, TST, and NSN) revealed their dispersive transport behaviors and presented the charge mobilities plotted as a function of the square root of the electric field in Fig. 3. For electric field strengths ranging from 3.6×10^5 to 6×10^5 V cm⁻¹, the electron and hole mobilities of CSC are within the range from 5×10^{-6} to 8×10^{-6} cm² V⁻¹ s⁻¹ and from 4.1×10^{-6} to 5.2×10^{-6} cm² V⁻¹ s⁻¹, respectively. The same order of magnitude of the hole and electron mobilities suggests an effective ambipolarity and balanced carrier transport behavior of CSC.8 The hole mobilities of bipolar compounds with amino-type donors (DSD, TST, and NSN) recorded by TOF are less than that of CSC, in the range of $5 \times$ 10^{-7} and 6 \times $10^{-6}~\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}.$ The hole mobilities follow the trend of CSC > DSD > NSN > TST, which does not correlate to their electron-donating capability estimated from HOMO energy levels (TST > NSN > DSD > CSC). Since charge carrier mobility is related to the intermolecular interaction such as the mode of molecular aggregation in the solid state, electron rich structure moiety does not necessary to enhance the hole mobility.

For DSD, TST, and NSN, no photocurrents were observed for electrons. Therefore, we fabricated electron-only devices with a device structure of ITO/BCP (300 nm)/bipolar host (500 nm)/TPBI (200 nm)/LiF/Al to evaluate the electron transport behavior. Fig. 4 depicts the current vs. voltage characteristics of electron-only devices. The introduction of BCP with contact of ITO is for limiting the injection of hole carrier, as shown in the inset of Fig. 4. The magnitude of current follows the order of NSN > TST > DSD > CSC. Although the assessment of the electron mobility via the current density of the electron-only device does not reflect the same trend of electron mobility obtained from TOF measurement due to low electron mobilities of BCP and TPBI which serve as the limiting factor of the current density in electron-only devices,¹⁴ the higher currents obtained from NSN, TST, and DSD compared with that of CSC still imply comparable electron mobilities, which should lie in the region of 10^5 – 10^6 cm² V⁻¹ s⁻¹ (the electron mobility of CSC is in the range of 5 \times 10⁻⁶ to 8 \times $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

Table 2 EL Performance of devices as a function of the host and emitter

Device	Host: 8 wt% dopant ^a	$V_{\rm on}{}^b/{\rm V}$	<i>L</i> at 1000 nit ^{<i>c</i>} /V (%)	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$I_{\rm max}/{\rm mA~cm^{-2}}$	$\eta_{\rm ext\ max}$ /%, cd A ⁻¹	$\eta_{\rm pmax}/{\rm lm}~{\rm W}^{-1}$	CIE1931 (<i>x</i> , <i>y</i>)
A1	CSC : (PPy) ₂ Ir(acac)	2	3.7, 16.9	260,000 (11V)	2410	17.1, 64	65.4	0.36, 0.61
A2	CSC : $Ir(PPy)_3$	2	4.1, 15	208,000 (10.5V)	2600	15.5, 56	58.4	0.33, 0.62
A3	CSC: (PBi) ₂ Ir(acac)	2	3.8, 17.2	241,400 (10.5V)	2500	17.4, 60.5	58.7	0.39, 0.58
A4	CSC : (TPm) ₂ Ir(acac)	2	4.7, 17.1	268,200 (12V)	2200	17.1, 64	60.6	0.40, 0.58
B1	DSD: OS1	2	5.0, 19	47,700 (11V)	1160	19.4, 20.6	22.2	0.65, 0.35
B2	DSD: OS2	2	4.6, 17.2	63,700 (11V)	1710	17.3, 28.5	27.3	0.62, 0.38
C1	TST: OS1	2	4.9, 19.2	41,800 (11V)	1020	19.4, 20.3	20.2	0.66, 0.34
C2	TST: OS2	2	4.7, 15.6	42,500 (10.5V)	1200	16.0, 26	24.1	0.62, 0.38
D1	NSN: OS1	2	4.6, 19.1	61,300 (10.5V)	1310	19.5, 21.5	22	0.65, 0.35
D2	NSN: OS2	2	4.3, 17.8	77,900 (10V)	1110	18.0, 30.2	30	0.62, 0.38

^{*a*} Device configuration: ITO/PEDOT:PSS (30 nm)/NPB (20 nm)/TCTA (5 nm)/host:dopant (25 nm)/TPBI (50 nm)/LiF (0.5 nm)/Al (100 nm). ^{*b*} Turn-on voltage at which emission became detectable. ^{*c*} The values of driving voltage and η_{ext} of device at 1000 cd m⁻².



Fig. 5 (a) J-V-L characteristics, (b) plots of EL efficiency versus brightness and (c) EL spectra for devices incorporating **CSC** doped with different green dopants.

Electroluminescence

To study the device performance, we fabricated multi-layer devices using those spiro-bridged D–A bipolar hosts doped with green or red dopant as emitter in the structure: ITO/PEDOT:PSS (30 nm)/NPB (20 nm)/TCTA (5 nm)/emitter (25 nm)/TPBI (50 nm)/LiF (0.5 nm)/Al (100 nm). Here, we used **CSC** as the host material with



Fig. 6 (a) J-V-L characteristics and (b) plots of EL efficiency versus brightness for red devices.

a series of common Ir-based green dopants, bis(2-phenylpyridinato)iridium(III) acetylacetonate (PPy)₂Ir(acac),¹² tris(2-phenylpyridinato)iridium(III) Ir(PPy)₃,¹⁵ bis(2,N-diphenylbenzimidazolito)iridium(III) acetylacetonate (PBi)₂Ir(acac),¹⁶ and bis(2-*o*-tolylpyrimidine)iridium(III) acetylacetonate (TPm)₂Ir(acac)⁹ for device

A. The DSD, TST, and NSN hosts doped with osmium(II) bis(3-(trifluoromethyl)-5-(4-tert-butylpyridyl)-1,2,4-triazolate)dimethylphenylphosphine Os(bpftz)₂(PPhMe₂)₂ (OS1)¹⁷ and osmiubis(3-(trifluoromethyl)-5-(4-tert-butylpyridyl)-1,2,4-trim(II) azolate)diphenylmethylphosphine Os(bpftz)₂(PPh₂Me)₂ (OS2)¹⁸ as red phosphors for devices **B**, **C**, and **D**, respectively. The conducting polymer polyethylene dioxythiophene:polystyrene sulfonate (PEDOT:PSS) is used as a hole injection layer (HIL). A thin layer of 4,4',4"-tri(N-carbazolyl)triphenylamine (TCTA) with a high triplet energy ($E_{\rm T} \sim 2.76 \text{ eV}$) as an exciton-blocking layer¹⁹ is inserted at 4,4'-bis(N-(1-naphthyl)-N-phenyl)biphenyldiamine (NPB)/emitter interface, which can prevent the exciton diffusion, giving higher device efficiency. The low energy HOMO/LUMO levels of 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBI) are beneficial for blocking holes and facilitating electron injection/transport.20 LiF and Al served as the electron-injection layer and cathode, respectively. Such multi-layer structure possesses efficient confinement of holes and electrons in the emitting layer and prevents the exciton diffusion, resulting in higher device efficiency. Scheme 2 shows chemical structures of the heavy metal complexes used in this study; Table 2 summarizes the electroluminescence data of the devices.

Fig. 5 presents the current density-voltage-luminance (J-V-L) characteristics, device efficiencies and EL spectra of the devices with CSC host and different green dopants (device A1-A4). The device A1 incorporating (PPy)₂Ir(acac) as the dopant exhibited the best performance - a relatively low turn-on voltage of 2 V (defined as the voltage at which the EL increased rapidly) and its driving voltage was merely 5.1 V at a practical brightness of 10000 cd m⁻². The turn-on voltage is much lower than that of the signal-layer device (1000 cd m⁻² at 8 V).9 We ascribe the reduced driving voltage of the multi-layer structure to facile hole/electron-injections. Fig. 5b presents the external quantum and power efficiency profiles plotted with respect to the brightness. The device exhibited maximum efficiencies of 17.1%, 64 cd A^{-1} and 65.4 ml W^{-1} greater than that of its signal-layer counterpart (8.3%, 31.4 cd A^{-1} and 16.1 ml W^{-1}). Even as the brightness reaches 10 000 cd m⁻², η_{ext} is still as high as 15.4% and shows a slow quantum efficiency roll-off. We attribute this large enhancement in CSC-based device performance to the wellmatched energy levels, charge balance and triplet exciton confinement provided by suitable hole- and electron-transport layers.

Fig. 6 presents the *J*–*V*–*L* characteristics and EL efficiencies of devices incorporating **DSD**, **TST**, and **NSN** as host materials doped with **OS1** and **OS2** as red phosphors. Table 2 summarizes the electroluminescence characteristics of the resulting devices. All *J*–*V* curves exhibited almost the same profiles due to similar energy levels (HOMO/LUMO), triplet energies (E_T), and carrier mobilities (see Table 1). The devices exhibited significantly lower operating voltages, presumably because of the smaller energy barriers when using **DSD**, **TST**, and **NSN** as the host materials. As a result, these devices turned on sharply at low voltages of 2 V and exhibited a maximum brightness of 63 700 cd m⁻² at 1710 mA cm⁻² (device **B2**). Fig. 6b shows these devices exhibited high η_{ext} (16–19.5%) and a slow quantum efficiency roll-off, when the brightness reaches 1000 cd m⁻², η_{ext} is still as high as 15.6–19.2%. Among these devices, the highest η_{ext} of 19.5% (21.5 cd A⁻¹) with saturated red emission of CIE1931 coordinates (0.65, 0.35) were obtained in device **D1** when using **NSN** as host and **OS1** as dopant. Even at a practical brightness of 1000 cd m⁻², the operating voltage was only 4.6 V and the efficiency remained high at 19.1%. The EL spectra revealed pure dopant emissions without any other emission originating from the adjacent organic layer, indicating the excellent confinement of carriers within the emitting layer (Fig. 6c).

We attribute this behaviour to the relatively balanced bipolar transport of these spiro-bridged D–A host materials, thereby increasing the opportunities for carrier recombination. The suitable values of $E_{\rm T}$ of 2.38–2.41 eV effectively suppress the reverse energy transfer from the red triplet dopant to the host.²¹ Furthermore, it is worth mentioning that the roll-off characteristic of the quantum efficiency was suppressed at higher brightness. The performance of these devices was outstanding as compared to those of previously reported results for deep-red OLEDs.^{5b,22}

Conclusions

In summary, we have realized highly efficient red- and green electrophosphorescent devices incorporating new spiro-configured bipolar host CSC, DSD, TST, and NSN, in which 4,5diazafluorene was introduced as electron-transporting moiety. The promising physical properties of these bipolar hosts such as high morphological and thermal stabilities, suitable energy levels, and balanced electron/hole mobilities make them compatible with various Ir-green and Os-red phosphors. In order to confine triplet excitons within the emitting layer, we adopted corresponding dopant having triplet energy less than that of host, a series of devices with CSC:green dopant and (DSD or TST or NSN):red dopant were fabricated. The green-phosphorescent device doped with (PBi)₂Ir(acac) achieved an external quantum efficiency, maximal luminance, and power efficiency of 17.4%, 241400 cd m⁻², and 58.7 lm W⁻¹, respectively. Particularly, the device A1 incorporating (PPy)₂Ir(acac) as the dopant exhibited maximum efficiencies of 17.1%, 64 cd A⁻¹ and 65.4 ml W⁻¹, and showed a slow quantum efficiency roll-off as the brightness reaches to 10 000 cd m⁻², η_{ext} is still as high as 15.4%. Among the red PhOLEDs, the one employing bipolar host material NSN doped with Os(bpftz)₂(PPhMe₂)₂ (device D1) achieved an external quantum efficiency, a maximal luminance, and a power efficiency of 19.5%, 61 300 cd m⁻², and 22 lm W⁻¹, respectively. More importantly, these highly efficient PhOLEDs showed limited efficiencies roll-off due to the balanced charge carriers flux within the emitting layer. Our results indicate that spiro-configured bipolar hosts with electron/hole transport moiety and spiro-configured architecture are promising molecular scaffold for achieving highly efficient electrophosphorescent devices.

Acknowledgements

We greatly appreciate the financial support from National Science Council of Taiwan (NSC 98-2119-M-002-007-MY3 and 100-2112-M-019-002-MY3) and Ministry of Economic Affairs (100-EC-17-A-08-S1-042).

References

- (a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151; (b) A. Köhler, J. S. Wilson and R. H. Friend, *Adv. Mater.*, 2002, **14**, 701; (c) W. S. Huang, J. T. Lin, C. H. Chien, Y. T. Tao, S. S. Sun and Y. S. Wen, *Chem. Mater.*, 2004, **16**, 2480; (d) J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2006, **16**, 575; (e) T. Tsuzuki and S. Tokito, *Adv. Mater.*, 2007, **19**, 276; (f) E. Orselli, R. Q. Albuquerque, P. M. Fransen, R. Fröhlich, H. M. Janssen and L. D. Cola, *J. Mater. Chem.*, 2008, **18**, 4579.
- 2 (a) M. A. Baldo, C. Adachi and S. R. Forrest, *Phys. Rev. B: Condens. Matter*, 2000, **62**, 10967; (b) S.-J. Su, H. Sasabe, T. I. Takeda and J. Kido, *Chem. Mater.*, 2008, **20**, 1691.
- 3 A. Chaskar, H.-F. Chen and K.-T. Wong, *Adv. Mater.*, 2011, 23, 3876.
- 4 Y. Tao, Q. Wang, C. Yang, Q. Wang, Z. Zhang, T. Zou, J. Qin and D. Ma, *Angew. Chem., Int. Ed.*, 2008, **47**, 8104.
- 5 (a) F.-M. Hsu, C.-H. Chien, C.-F. Shu, C.-H. Lai, C.-C. Hsieh, K.-W. Wang and P.-T. Chou, *Adv. Funct. Mater.*, 2009, **19**, 2834; (b) F.-M. Hsu, C.-H. Chien, Y.-J. Hsieh, C.-H. Wu, C.-F. Shu, S.-W. Liu and C.-T. Chen, *J. Mater. Chem.*, 2009, **19**, 8002.
- 6 S. O. Jeon, S. E. Jang, H. S. Son and J. Y. Lee, *Adv. Mater.*, 2011, 23, 1436.
- 7 (a) L. Zeng, T. Y.-H. Lee, P. B. Merkel and S. H. Chen, J. Mater. Chem., 2009, 19, 8772; (b) M. K. Kim, J. Kwon, T.-H. Kwon and J.-I. Hong, New J. Chem., 2010, 34, 1317; (c) Y. Tao, Q. Wang, Y. Shang, C. Yang, L. Ao, J. Qin, D. Ma and Z. Shuai, Chem. Commun., 2009, 77; (d) Y. Tao, Q. Wang, C. Yang, C. Zhong, J. Qin and D. Ma, Adv. Funct. Mater., 2010, 20, 2923; (e) F.-M. Hsu, C.-H. Chien, P.-I. Shih and C.-F. Shu, Chem. Mater., 2009, 21, 1017; (f) W.-Y. Hung, T.-C. Tsai, S.-Y. Ku, L.-C. Chi and K.-T. Wong, Phys. Chem. Chem. Phys., 2008, 10, 5822.
- 8 S.-Y. Ku, W.-Y. Hung, C.-W. Chen, S.-W. Yang, E. Mondal, Y. Chi and K.-T. Wong, *Chem.-Asian J.*, 2012, **7**, 133.

- 9 W.-Y. Hung, T.-C. Wang, H.-C. Chiu, H.-F. Chen and K.-T. Wong, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10685.
- 10 K.-T. Wong, R.-T. Chen, F.-C. Fang, C.-C. Wu and Y.-T. Lin, Org. Lett., 2005, 7, 1979.
- 11 K.-T. Wong, H.-F. Chen and F.-C. Fang, Org. Lett., 2006, 8, 3501.
- 12 C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, J. Appl. Phys., 2001, 90, 5048.
- 13 P. M. Borsenberger and D. S. Weiss, Organic Photoreceptors for Imaging Systems, Marcel Dekker, New York, 1993.
- 14 (a) Z.-Y. Xie, T.-C. Wong, L.-S. Hung and S.-T. Lee, *Appl. Phys. Lett.*, 2002, **80**, 1477; (b) Y. Li, M. K. Fung, Z. Xie, S.-T. Lee, L.-S. Hung and J. Shi, *Adv. Mater.*, 2002, **14**, 1317.
- 15 (a) H. Inomata, K. Goushi, T. Masuko, T. Konno, T. Imai, H. Sasabe, J. J. Brown and C. Adachi, *Chem. Mater.*, 2004, 16, 1285; (b) X. Ren, J. Li, R. J. Holmes, P. I. Djurovich, S. R. Forrest and M. E. Thompson, *Chem. Mater.*, 2004, 16, 4743.
- 16 (a) W.-S. Huang, J. T. Lin, C.-H. Chien, Y.-T. Tao, S.-S. Sun and T.-S. Wen, *Chem. Mater.*, 2004, 16, 2480; (b) W.-S. Huang, J. T. Lin and H.-C. Lin, *Org. Electron.*, 2008, 9, 557.
- 17 Y.-L. Tung, S.-W. Lee, Y. Chi, Y.-T. Tao, C.-H. Chien, Y.-M. Cheng, P.-T. Chou, S.-M. Peng and C.-S. Liu, J. Mater. Chem., 2005, 15, 460.
- 18 P.-I. Shih, C.-F. Shu, Y.-L. Tung and Y. Chi, *Appl. Phys. Lett.*, 2006, 88, 251110.
- 19 S.-J. Su, E. Gonmori, H. Sasabe and J. Kido, Adv. Mater., 2008, 20, 4189.
- 20 S.-J. Yeh, M.-F. Wu, C.-T. Chen, Y.-H. Song, Y. Chi, M.-H. Ho, S.-F. Hsu and C. H. Chen, *Adv. Mater.*, 2005, **17**, 285.
- 21 G. Zhou, W. Y. Wong, B. Yao, Z. Xie and L. Wang, Angew. Chem., Int. Ed., 2007, 46, 1149.
- 22 (a) Y.-Y. Lyu, J. Kwak, W. S. Jeon, Y. Byun, H. S. Lee, D. Kim, C. Lee and K. Char, Adv. Funct. Mater., 2009, 19, 420; (b) Y.-L. Tung, S.-W. Lee, Y. Chi, Y.-T. Tao, C.-H. Chien, Y.-M. Cheng, P.-T. Chou, S.-M. Peng and C.-S. Liu, J. Mater. Chem., 2005, 15, 460; (c) C.-H. Wu, P.-I. Shih, C.-F. Shu and Y. Chi, Appl. Phys. Lett., 2008, 92, 233303; (d) C.-H. Chien, F.-M. Hsu, C.-F. Shu and Y. Chi, Org. Electron., 2009, 10, 871.