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Molecular Evolution of Host Materials by Regular Tuning N/P Ratio for High-Performance Phosphorescence Organic Light-Emitting Diodes

Di Liu,*[a] Fang Wang,[b] Ruijuan Yao[a]

[a] State Key Laboratory of Fine Chemicals, College of Chemistry, Dalian University of Technology, Dalian 116024, China. *E-mail: liudi@dlut.edu.cn

[b] College of Chemical Engineering, Dalian University of Technology, Dalian 116024, China.

Abstract

By linking pyridine and 1,2,4-triazole as electron-deficient group, two "dual n-type unit" bipolar host materials, named 2-(3,5-Di(9*H*-carbazol-9-yl)-phenyl)-5-(1*H*-triazol-1-yl)pyridine (PyTzDCz) and 2-(3-(9*H*-carbazol-9-yl)-phenyl)-5-(1*H*-triazol-1-yl)pyridine (PyTzSCz), and one bipolar reference compound 2-(3,5-di(9*H*-carbazol-9-yl)-phenyl)-pyridine (PyDCz) were designed and synthesized for use in phosphorescence organic light-emitting diodes (PhOLEDs). From the parent 1,3-bis(9*H*-carbazol-9-yl)benzene (mCP) via PyDCz and PyTzDCz to PyTzSCz, the molar ratio of n-type pyridine/triazole to p-type carbazole was regularly tuned as 0:2, 1:2, 2:2, and 2:1. With regular increase of n/p ratio from 0:2 gradually to 2:1, the LUMO levels of these hosts are regularly deepened to enhance electron injection, and the turn-on voltages of their blue and

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green PhOLEDs are regularly decreased. Particularly the PyTzSCz-hosted blue PhOLED turned on at 2.6 V with high power efficiency of 48.1 lm W^{-1} (corresponding to an external quantum efficiency of 26.4% and a current efficiency of 45.9 cd A^{-1}), which are the lowest turn-on voltage so far and one of the highest power efficiencies reported for FIrpic PhOLEDs containing a single host. The PyTzSCz-hosted green device also exhibited low turn-on voltage of 2.4 V and high external quantum efficiency of 28.0%. This study manifests the molecular evolution trend of host materials from hole-transporting via bipolar to "dual n-type unit bipolar" for performance optimization.

Keywords: Phosphorescence OLEDs, bipolar host materials, pyridine, 1,2,4-triazole, n/p molar ratio

Introduction

Phosphorescent Organic light-emitting diodes (PhOLEDs), which incorporate a phosphorescent emitter can convert both singlet and triplet excitons into photons to realize internal quantum efficiency as high as 100%, have progressed rapidly in energy-saving flat-panel displays and eco-friendly solid-state lighting.[1-4] To suppress the severe triplet-triplet annihilation (TTA) and aggregation-caused quenching (ACQ), phosphorescent emitters should be dispersed in a suitable host material generally.[5,6] In principle, an ideal host should have sufficient high triplet energy (E_T) to prevent reverse energy transfer and confine triplet excitons on guest emitters, appropriate frontier molecular orbital level to match will the adjacent function layers, high

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morphological and thermal stability to maintain device reliability at high luminance level.[7-9] Carbazole derivatives are widely used as host materials due to its high E_T (over 3.0 eV)[10] and excellent hole-transporting property of cabazole, e.g. 1,3-bis(9*H*-carbazol-9-yl)benzene (mCP)[8] is one of the most classical carbazole-based host materials having a simple molecular structure and a triplet energy of >2.9 eV. However high driving voltages were often observed for the devices due to its unipolar (hole) carrier-transport property. For industrialized application of OLEDs, low driving voltage and high power efficiency are primary requirements, thus the practical application of mCP in high-performance OLEDs is restricted.[11] In order to improve the positive and negative charge balancing state in OLEDs, bipolar host materials containing both hole-transporting p-type group and electron-transporting n-type group have been invented. It has been established that the bipolar materials have better charge carrier balancing abilities than the traditional unipolar hosts and can shift the charge recombination zone away from the emitting layer/hole or electron transporting layer interface and hence improve the device performance. Large amount of bipolar host materials have been developed by using pyridine, pyrazine, pyrimidine, imidazole, triazole, oxadiazole, diphenylphosphine oxide, cyanobenzene as n-type unit for application in OLEDs and good performance were achieved in their PhOLEDs.[3,4,12,13] For example, 4,4′-Bis[(9H-carbazol-9-yl)-3,30-dicyano]biphenyl (CBP-CN)[5],9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole-3-carbonitrile (mCPCN)[12], 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy)[4] and bis-4-(*N*-carbazolyl)phenyl)phenylphosphine oxide (BCPO)[13] were developed on the

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basis of their unipolar parent molecules and exhibited better device performance than the parents due to improved charge balancing abilities.

In recent years, a new type of bipolar host materials, i.e. “dual n-type unit” bipolar host materials were invented by our research team,[14-16] which are characterized by the presence of two n-type units that are directly linked to each other and away from the p-type group. As the electron-injection and -transportation are further improved by these two n-type units, the positive and negative charge balancing ability of these “dual n-type unit” bipolar hosts are further improved in comparison with the common bipolar hosts and finally lead to increased emission efficiency and reduced efficiency roll-off.[16] However, some important issues still remain unclear, for example, whether the dual n-type units strategy has universal applicability, whether the dual n-type units strategy match all kinds of p-type groups, and so on. In this work, we combined pyridine and 1,2,4-triazole as a novel dual n-type unit 5-(1*H*-triazol-1-yl)pyridine (PyTz), and incorporated it in unipolar host mCP to construct bipolar host 2-(3,5-Di(9*H*-carbazol-9-yl)-phenyl)-5-(1*H*-triazol-1-yl)pyridine (PyTzDCz). Since the electron mobility of most organic n-type groups are lower by orders of magnitude than the hole mobility of most p-type units[14], we removed one carbazole unit from PyTzDCz to increase the molar ratio of n-type unit and designed another analogue, named 2-(3-(9*H*-carbazol-9-yl)-phenyl)-5-(1*H*-triazol-1-yl)pyridine (PyTzSCz). Different from the reported 1,3,5-trissubstituted or 3,4,5-trissubstituted 1,2,4-triazole based host materials that use the 1,2,4-triazole ring as the linking bridge for other

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groups or as the molecular geometrical core[17,18], the 1,2,4-triazole units in PyTzDCz and PyTzSCz were placed at the pyridine units by grafting it from its 1-site N atom, which is more favorable for controlling π-conjugation length, and this strategy endows each of them with high E_T value of 2.74 eV, which are high enough to guarantee their capability to act as hosts for RGB emitters. To evaluate the dual n-type unit PyTz, a bipolar reference compound 2-(3,5-di(9*H*-carbazol-9-yl)-phenyl)-pyridine (PyDCz) which contains only one pyridine unit was prepared for comparison. In this way, along the order of mCP, PyDCz, PyTzDCz and PyTzSCz, the n/p molar ratio was regularly tuned as 0:2, 1:2, 2:2, and 2:1. In addition to develop novel high-performance host materials, this work is emphasized to systematically study the influence of n/p ratio to the optoelectronic parameters and device performance and finally to disclose the molecular evolution trend of host materials for PhOLEDs from the traditional unipolar host via bipolar host to “dual n-type unit” bipolar hosts.

Results and Discussion

Synthesis and thermal properties

The chemical structures and synthetic routes of PyTzDCz and PyTzSCz are shown in Scheme 1. Two target compounds were prepared in 71-76% yields by a tetrakis-(triphenylphosphine)palladium(0) mediated typical Suzuki cross-coupling between brominated n-type unit and carbazole-containing boronic acid.[19] The key intermediate 2-bromo-5-(1*H*-triazol-1-yl)pyridine (A1) was prepared through a CuI

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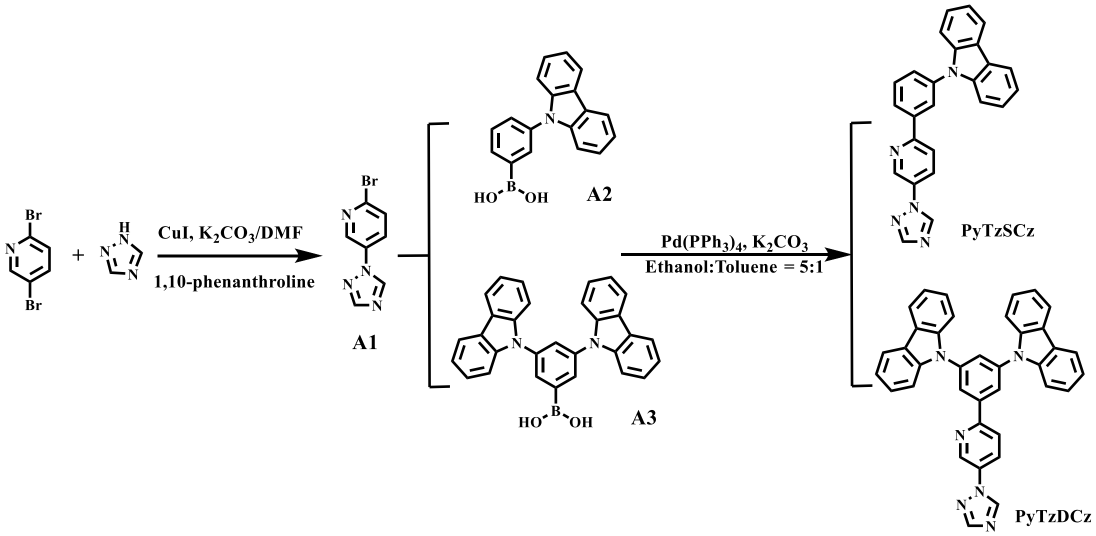
catalyzed Ullmann reaction between 2,5-dibromopyridine and 1,2,4-triazole according to the literature procedure[16], and all other chemicals were commercial available and used without further purification. Since they have good solubility in common organic solvents, PyTzDCz and PyTzSCz were thoroughly purified by silica gel column chromatography and repeated recrystallization in methanol/chloroform to reach a high purity for OLEDs application. The detailed synthetic procedures and structure characterization are provided in Electronic Supporting Information (ESI†). The synthesis of the reference compound PyDCz is described in the ESI†.



Scheme 1 Chemical structures and synthetic routes of PyTzDCz and PyTzSCz.

PyTzDCz and PyTzSCz exhibited good thermal stability and amorphous stability as verified by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) study, and all the pertinent dates are summarized in Table 1. PyTzDCz and PyTzSCz showed thermal decomposition temperatures (T_d) at 408.0 and 330.6 ℃ (corresponding to 5% weight loss), respectively, as depicted by the TGA thermograms in Fig. S1 (ESI†). The glass transition temperatures (T_gs) of these two compounds were detected by DSC traces in Fig. 1 at 132.7 ℃ for PyTzDCz and 69.4 ℃ for

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PyTzSCz. The remarkable higher T_d and T_g of PyTzDCz than PyTzSCz should be caused by the higher molecular weight of PyTzDCz and the special contribution from one additional carbazole group since it is a famous chemically and morphologically stable building block.[16] Both PyTzDCz and PyTzSCz exhibit higher glass transition temperatures than the widely used host material mCP (T_g = 60.0 ℃)[8], implying that improved device stability can be expected for these novel host materials. The melting point of PyTzSCz was observed at 176 ℃.

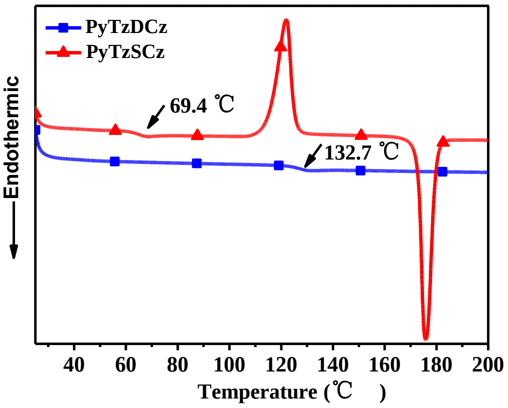

Fig. 1 DSC traces (at the second heating cycle) of PyTzDCz and PyTzSCz recorded at a heating rate of 10 ℃ min^{-1}.

Table 1. Physical data of PyTzDCz, PyTzSCz, PyDCz and mCP.

Compound	λ_{abs} [a] [nm]	λ^{em}_{max} [a] [nm]	E_S [b] (eV)	E_T [b] (eV)	E_g [c] (eV)	HOMO/LUMO (eV) [d]	T_d [e] (℃)	T_g (℃)
PyTzDCz	297,334,345	391	3.51	2.74	3.08	-5.64/-2.56	408.0	132.7
PyTzSCz	296,334,340	400	3.41	2.75	2.91	-5.54/-2.63	330.6	69.4
PyDCz				2.84		-5.58/-2.43		
mCP [f]				3.03		-5.65/-2.09		

[a] Absorption and fluorescence wavelengths in neat film. [b] Measured in 2-MeTHF at 77 K. [c] The electrochemical band gap determined as the potential

difference between oxidation onset and reduction onset multiplied by the electron charge (e). [d] Determined using electrochemical potentials. [e] T_d is the thermal decomposition temperature corresponding to a 5% weight loss. [f] E_T and HOMO/LUMO of mCP are cited from literature[8].

Photophysical Properties

The UV-vis absorption and photoluminescence (PL) spectra of PyTzDCz and PyTzSCz were measured in thin films on quartz substrates at room temperature (Fig. 2a), and all photophysical data are summarized in Table 1. Owing to the same molecular skeletons of PyTzDCz and PyTzSCz, they exhibited similar absorption spectra position and profiles, and the absorption peak at 296 nm could be assigned to the π-π∗ transition of carbazoles and the long-wavelength peaks around 340 nm can be attributed to n-π* transitions of the conjugated structure surrounding the carbazole unit.[20] Upon optical excitation at 296 nm, PyTzDCz and PyTzSCz have shown bluish violet emission with peaks at 391 and 400 nm, respectively. Meanwhile, the optical bandgaps of PyTzDCz and PyTzSCz are 3.40 eV, which were estimated from the absorption threshold wavelengths of neat films by absorption edge technique.[15] In order to investigate their excited states and solvatochromic behavior, both absorption and fluorescence spectra were measured in various solvents with different polarities (n-hexane, toluene, dichloromethane (DCM), acetonitrile and ethanol). As shown in Fig. S2 (ESI†), the absorption spectra of PyTzDCz and PyTzSCz are almost independent of the solvent polarity, indicating that solvent polarity has a negligible effect on the dipole moments of the ground states of these compounds.[21] However,

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with gradually increasing solvent polarity, the fluorescence spectra of PyTzDCz and PyTzSCz exhibited regular bathochromic-shift, confirming the photoinduced intramolecular charge transfer excited states of these hosts resulted from their donor-acceptor bipolar feature.[16]

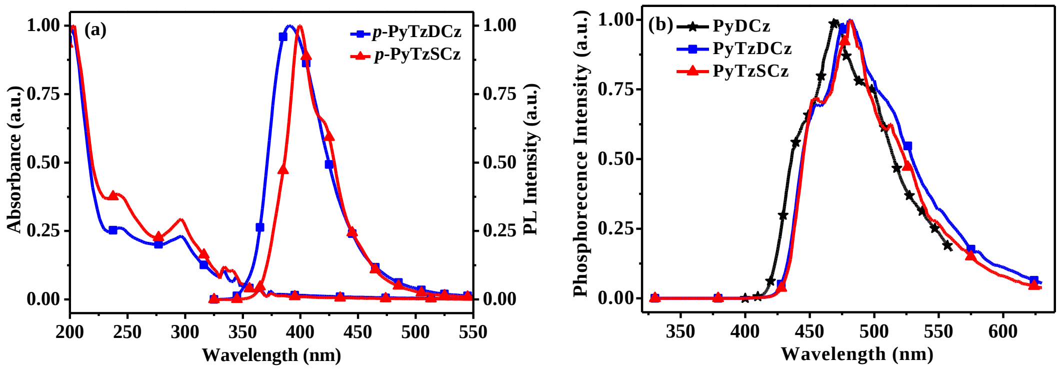

Fig. 2 UV-vis absorption and PL spectra of (a) PyTzDCz and PyTzSCz in thin films on quartz substrates at room temperature, and phosphorescence spectra of (b) PyTzDCz, PyTzSCz and PyDCz in frozen 2-MeTHF matrix at 77 K.

Fig. 2b shows the phosphorescence spectra of PyTzDCz, PyTzSCz and the reference PyDCz measured in a frozen 2-methyltetrahydrofuran (2-MeTHF) matrix at 77 K. Since the 1,2,4-triazole unit was grafted onto pyridine from its saturated 1-site N atom and does not extend the π-conjugation, PyTzDCz, PyTzSCz and PyDCz have similar phosphorescence spectra position, and the triplet energies (E_Ts) of PyTzDCz and PyTzSCz determined to be 2.74 eV from the highest energy vibronic band of phosphorescence spectra (452 nm) are close to that of PyDCz (2.84 eV). Evidently to incorporate 1,2,4-triazole unit from its 1-site N atom onto pyridine as the second n-type unit is an effective strategy to adjust the n/p molar ratio without at the expense of the triplet energy. Both PyTzDCz and PyTzSCz have sufficiently high E_Ts to act as

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the hosts for the typical blue phosphor iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C$^{2'}$]picolinate (FIrpic, E_T=2.63 eV)[22] and green phosphor tris[2-phenylpyridinato-C^2,N] iridium(III) (Ir(ppy)$_3$, E_T=2.40 eV).[23] The singlet-triplet energy differences (ΔE_{ST}) were estimated from the low-temperature photoluminescence (LT PL) spectra (Fig. S3 in ESI†) that simultaneously gave both singlet energies (E_Ss) and triplet energies (E_Ts) as 0.77 eV for PyTzDCz and 0.67 eV for PyTzSCz, which are similar to those for the majority of reported host materials (0.5-1 eV).[8,11,24]

Electrochemical properties and theoretical calculations

The electrochemical properties of PyTzDCz and PyTzSCz were probed by cyclic voltammetry (CV) measurements in deoxygenated dilute DCM (for anodic scan) and *N*,*N*-dimethylformamide (DMF) solutions (for cathodic scan) containing 0.1 M tetra(n-butyl)ammonium hexafluorophosphate (n-Bu_4NPF_6) as the supporting electrolyte at a scan rate of 100 mV s^{-1},[14] and their cyclic voltammograms are shown in Fig. 3. These two compounds showed reversible oxidation and irreversible reduction waves with quite similar profiles due to their same electron-donating and -withdrawing units. The onset potential of the first oxidation wave (E_{ox}^{onset}) were used to calculated the HOMO levels according to the equation of $E_{HOMO} = -e(E_{ox}^{onset} + 4.4)$[3], while the LUMO levels were calculated from the onset potential of the reduction wave (E_{red}^{onset}) using equation of $E_{LUMO} = -e(E_{red}^{onset} + 4.4)$[3]. The HOMO/LUMO were determined as ca. −5.64 eV/−2.56 eV for PyTzDCz and −5.54 eV/−2.63 eV for PyTzSCz. The relatively shallow HOMO levels indicate a small hole-injection barrier

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from a widely used hole transporting material 1,1-bis(4-(*N*,*N*-di(p-tolyl)-amino)phenyl)-cyclohexane (TAPC, HOMO = −5.50 eV)[3] to these hosts in the emitting layer of OLEDs. Under identical measuring conditions, the reference compound PyDCz exhibited a similar HOMO level (−5.58 eV) and a higher LUMO level (−2.43 eV) than these two new hosts. It is clear that, with host going from mCP via PyDCz to PyTzDCz and further to PyTzSCz, the n/p ratio is gradually increased from 0:2 via 1:2 to 2:2 and further to 2:1, the LUMO levels are regularly deepened in the order of -2.40[8] < -2.43 < -2.56 < -2.63 eV, reflecting the stepwise improvement of electron injection from unipolar hole-transporting host, to bipolar host and further to "dual n-type unit" bipolar hosts. Hence, it can be expected that combining pyridine and 1,2,4-triazole as dual n-type unit should be an effective strategy to enhance the electron injection into the emitting layer and reduce the driving voltage of PhOLEDs. The electrochemical bandgaps (E_gs) of these hosts were calculated from the potential difference between E_{ox}^{onset} and E_{red}^{onset} multiplied by the electron charge as 3.08 eV for PyTzDCz and 2.91 eV for PyTzSCz.

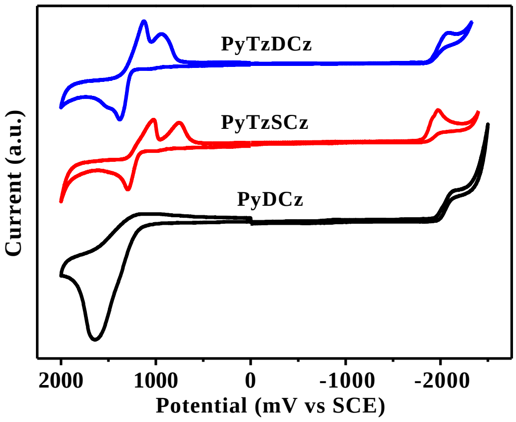

Fig. 3 Cyclic voltammograms of PyTzDCz, PyTzSCz and PyDCz measured in dilute DCM (anodic) and DMF (cathodic) solutions at a scan rate of 100 mV s^{-1}.

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The geometrical and electronic properties of PyTzDCz and PyTzSCz were calculated by density functional theory (DFT) calculations using B3LYP hybrid functional theory with Gaussian 09[25], and their optimized steric structures and HOMO/LUMO distribution are given in Fig. 4. HOMO orbitals are mainly located on the electron-donating carbazoles with a small contribution from the adjacent phenyl ring, and LUMO orbitals are mainly distributed in dual n-type unit PyTz and the adjacent phenyl. In comparison with the reference PyDCz whose LUMO is localized on pyridine-phenyl part, the LUMOs of PyTzDCz and PyTzSCz spread onto the triazole ring, confirming that the terminal triazole ring contributes to determine the LUMO of these molecules in combination with pyridine-phenyl part. This provides a solid evidence for the “dual n-type unit” strategy in the molecular design of these new host materials. The sufficient spatial separation of HOMO and LUMO further confirmed the bipolar charge transporting feature of these compounds. From the optimized steric molecular structures of PyTzDCz and PyTzSCz, the dihedral angles between carbazole and adjacent phenyl ring are greater than 50°, which helps to guarantee the distorted molecular configuration and high triplet energy.

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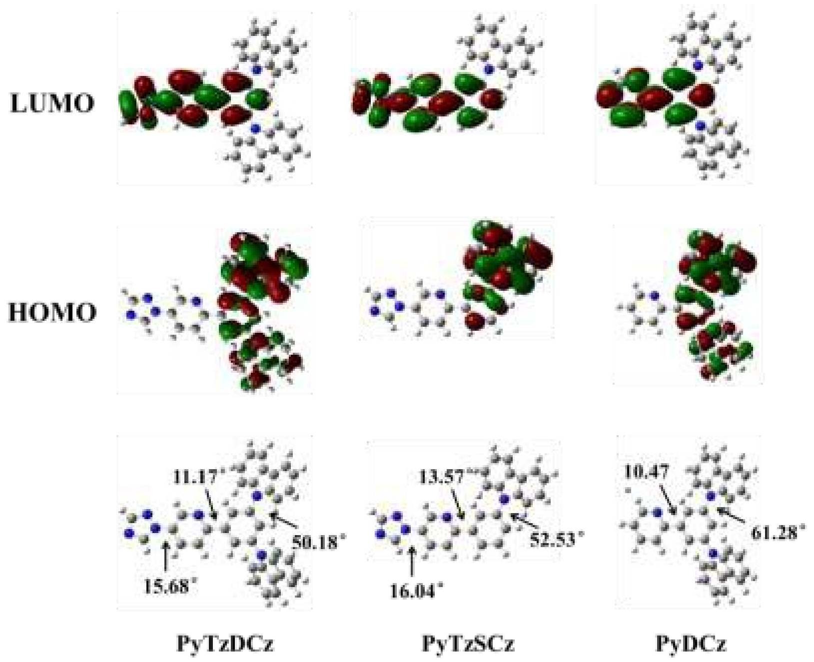

Fig. 4 Geometry optimized steric molecular structures and HOMOs/LUMOs distribution of PyTzDCz, PyTzSCz and PyDCz.

Single-carrier devices and charge-transporting properties

To further verify the function of PyTz, single-carrier devices were fabricated with the structure of ITO/PEDOT:PSS (40 nm)/TAPC (7 nm)/host (100 nm)/TAPC (7 nm)/Al (200 nm) for hole-only devices, and ITO/TmPyPB (7 nm)/host (100 nm)/TmPyPB (7 nm)/LiF (1 nm)/Al (200 nm) for electron-only devices. The unipolar host mCP and the reference bipolar molecule PyDCz were also studied in the same way for comparison. The thickness of the host layer is set deliberately to be tremendously larger than adjacent ancillary layers to reveal the intrinsic charge transporting nature of these host materials. The chemical structure of relevant materials and the energy level diagram of single carrier devices are illustrated in Fig. S4 in ESI†. TAPC/Al and ITO/TmPyPB interfaces were used to prevent electron and

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hole injection due to their large barrier of 2.3 eV and 1.88 eV, respectively. As shown in Fig. 5a and 5b, mCP devices only got hole current, but almost zero electron current, consistent with its unipolar hole-transporting nature. All other single-carrier devices exhibited significantly high current densities in the typical voltage range of OLEDs, suggesting that all other three compounds possess bipolar charge-transporting features with sufficient hole- and electron-transporting abilities.[26] Obviously, the hole currents of the hole-only devices are directly correlated with the p-group number in each host molecule, rather than with the p/n ratior. It is reasonable that the PyTzDCz, PyDCz based hole-only devices have similar hole current with mCP devicesince they have same carbazole number in each molecule, which are all higher than that of PyTzSCz device possessing only one carbazole unit. By incorporating PyTz as dual n-type unit, PyTzDCz and PyTzSCz exhibited much higher electron currents than PyDCz, clearly confirming the function of the second n-type unit 1,2,4-triazol. The regular increase of electron current in the order of mCP, PyDCz, PyTzDCz and PyTzSCz should benefit from the stepwise improvement in both electron injection and transportation caused by the corresponding evolution of the n-type unit in these host materials. The improved electron injection can be verified by the ascending of the current density-voltage curves at reduced voltage with n-type unit going from pyridine to PyTz. The improved electron transportation can get evidence from the more oblique current density-voltage curves with n/p ratio changing from 1:2, via 2:2 to 2:1.

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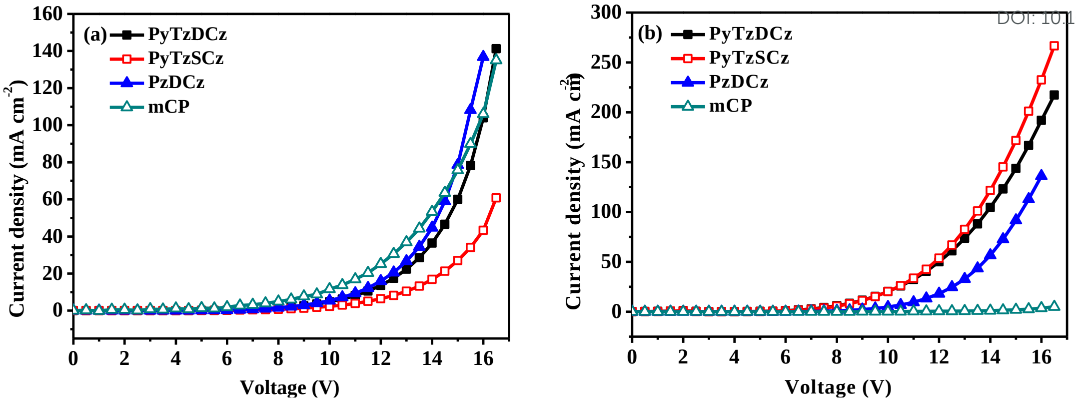

Fig. 5 The current density versus voltage curves of the (a) hole-only and (b) electron-only devices for PyTzDCz, PyTzSCz, PyDCz and mCP.

Electroluminescent devices

In order to evaluate PyTzDCz and PyTzSCz as potential host materials, FIrpic-doped sky-blue PhOLEDs B1 and B2 were fabricated with the typical sandwiched structure of ITO/PEDOT:PSS (40 mn)/TAPC (20 nm)/TCTA (5 nm)/host:FIrpic (4wt%, 30 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (200 nm). mCP- and PyDCz-hosted blue device B3 and B4 were also fabricated with the same structures for comparison. PEDOT:PSS and TAPC were used as the hole-injecting and -transporting layers (HIL, HTL), TmPyPB as electron-transporting layer. Particularly, a thin layer of TCTA was used as the second HTL[15,27] to facilitate charge balance in emitting layer by slowing down hole transportation due to its relatively lower hole mobility than TAPC. The energy level diagrams of these devices are shown in Fig. S4 in ESI†. The current density-voltage-brightness (*J*-*V*-*B*) characteristics and efficiency curves of these devices are shown in Fig. 6 and Fig. S5 and the electroluminescence (EL) data are summarized in Table 2. The turn-on voltage (V_{on}, to deliver a brightness of 1 cd m^{-2}) of devices B1 and B2 were lower than devices B3 and B4 by about 1.0 V,

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which should be attributed to the deeper LUMO levels caused by the dual n-type unit PyTz and thus the improved electron injection and transportation. A regular trend can be observed in these four blue devices: the turn-on voltage is gradually reduced from 3.6, 3.5, 2.7 to 2.6 V with the n/p ratio is increased from 0:2, 1:2, via 2:2 to 2:1 in the corresponding hosts mCP, PyDCz, PyTzDCz and PyTzSCz, once again manifesting the special function of the dual n-type unit strategy. As shown in Fig. 6a, the PyTzDCz and PyTzSCz hosted devices B1 and B2 exhibited much higher current densities and brightness than PyDCz based device B3, furthermore, the brightness increased much rapidly than the current density in these two devices, as a result, devices B1 and B2 achieved much higher efficiencies than B3. The PyTzDCz hosted device B1 achieved a maximum power efficiency (η_p) of 43.9 lm W^{-1} (corresponding to a maximum external efficiency (η_{ext}) of 21.9% and a current efficiency (η_c) of 37.8 cd A^{-1}). PyTzSCz-hosted B2 exhibited the best performance among all these blue devices with 48.1 lm W^{-1} (26.4%, 45.9 cd A^{-1}). PyDCz-hosted B3 exhibited mild performance of 17.8% (36.1 cd A^{-1}, 28.3 lm W^{-1}). While device B4 with the widely-used unipolar host mCP exhibited efficiency of 14.7% (32.5 cd A^{-1}, 25.5 lm W^{-1}). It is obvious that the device efficiencies including η_c, η_p, and η_{ext} were enhanced constantly with the n/p ratio is increased from 0:2, 1:2, via 2:2 to 2:1 in the corresponding hosts mCP, PyDCz, PyTzDCz and PyTzSCz. Evidently the superior performance in PyTzDCz and PyTzSCz hosted devices should benefit from the improved electron injection and transportation and thus the better charge balancing abilities of these dual n-type unit bipolar hosts. As indicated by FIrpic device data

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within the recent 10 years in Table S1, a turn-on voltage of 2.6 V and a power efficiency of 48.1 lm W^{-1} in present PyTzSCz hosted device B2 should be the lowest turn-on voltage and one of the highest power efficiencies reported for FIrpic PhOLEDs containing a single host so far.[14,16,18,26,28-30] The turn-on voltage of 2.6 V is even lower than the theoretical limit of FIrpic, i.e. the band gap voltage of 2.64 V that is determined as the emitted photo energy *hν* (1240/469=2.64 eV) at the EL peak wavelength (469 nm, Fig. S5) divided by the electron charge (e). The similar case was previously observed in Ir(ppy)$_3$ based green OLEDs.[31-33] In addition to the appropriate selection of dual n-type unit host materials in present work, it is generally believed that the extra lower turn-on voltage than the theoretical limit is caused, at least partially, by the thermal energy *kT* carried by the electrons and holes. The extra thermal energy would make these high-energy carriers more readily diffuse over to the side of opposite type where they recombine than those low-energy ones.[31-33]

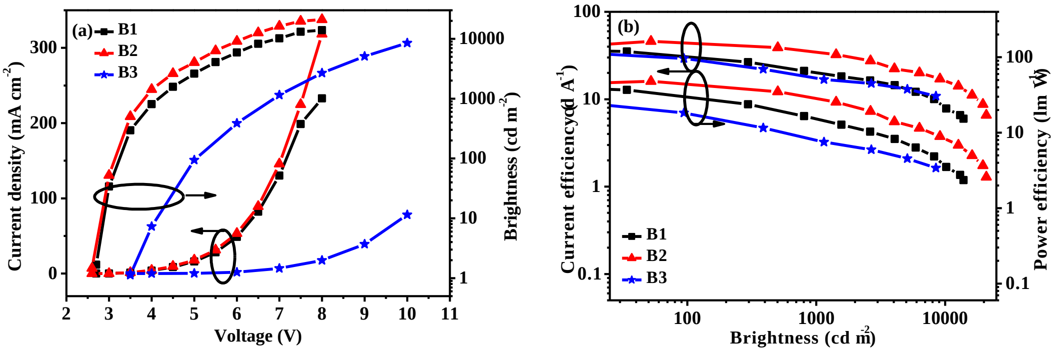

Fig. 6 (a) The current density-voltage-brightness characteristics and (b) the efficiency curves for PyTzDCz, PyTzSCz and PyDCz-hosted blue PhOLEDs B1 to B3.

Table 2: Electroluminescence characteristics of the sky-blue and green PhOLEDs.[a]

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Device	Host	Dopant	V_{on} (V)	L_{max} (cd m^{-2})	η_c [b] (cd A^{-1})	$\eta_{p,max}$ (lm W^{-1})	η_{ext} [b] (%)	CIE (x, y) [c]
B1	PyTzDCz	FIrpic	2.7	13924 (8V)	37.8, 19.5, 13.3	43.9	21.9, 11.4, 7.6	0.14, 0.27
B2	PyTzSCz		2.6	20920 (8V)	45.9, 35.6, 21.2	48.1	26.4, 20.4, 12.2	0.14, 0.27
B3	PyDCz		3.5	8483 (10V)	36.1, 19.2, 14.0	28.3	17.8, 9.5, 6.9	0.14,0.35
B4	mCP		3.6	15627 (9V)	32.5, 27.5, 22.9	25.5	14.7, 11.3, 10.5	0.15, 0.33
G1	PyTzDCz	Ir(ppy)$_3$	2.4	112860 (9V)	85.0, 79.3, 75.4	106.7	25.8, 23.7, 22.4	0.27, 0.62
G2	PyTzSCz		2.4	102640 (8V)	92.9, 88.6, 82.5	97.2	28.0, 26.3, 25.0	0.27, 0.62
G3	PyDCz		3.2	58330 (10V)	66.4, 63.3, 53.2	40.0	18.8, 17.9, 15.1	0.30,0.63
G4	mCP		3.1	64276 (9V)	51.0, 48.9, 42.5	35.6	15.0, 14.4, 12.5	0.28, 0.63

[a] Abbreviations: V_{on}, turn-on voltage. L_{max}, maximum luminance. η_{ext}, external quantum efficiency. η_c, current efficiency. η_p, power efficiency. CIE (x, y), Commission International de I'Eclairage coordinates. [b] Order of measured values: maximum, then at 1000 and 5000 cd m^{-2}. [c] Measured at 6 V.

Enlightened by the excellent performance of these dual n-type unit bipolar host materials in above sky-blue phosphorescent OLEDs, we further explored the versatility of these hosts for green emitter Ir(ppy)$_3$. The green devices G1 to G4 have the same configuration as the above blue ones but with 7 wt% Ir(ppy)$_3$ doped in these hosts as the emitting layers. The *J-V-B* characteristics and efficiency curves are shown in Fig. 7 and the EL data are summarized in Table 2. G1 and G2 displayed typical green emission from Ir(ppy)$_3$ (EL spectra shown in Fig. S5) with CIE coordinates of around (0.27, 0.62), and there were no residue emission from the host or adjacent layers. A similar trend in device performance was observed in these green devices: as

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the n/p ratio is increased from 0:2, 1:2, via 2:2 to 2:1 in the corresponding hosts mCP, PyDCz, PyTzDCz and PyTzSCz, the green emission efficiencies are regularly increased, and the turn-on voltage of G1 and G2 are also lower than G3 and G4 by about 0.7 V. Among these green devices, the PyTzSCz-hosted G2 achieved the best performance with 97.2 lm W^{-1} (28.0%, 92.9 cd A^{-1}). The G1 also demonstrated a good device performance with 106.7 lm W^{-1} (25.8%, 85.0 cd A^{-1}), and both G1 and G2 turned on at low voltage of 2.4 V, which is close to the theoretical limit of the band gap voltage (2.37 V) of $Ir(ppy)_3$.[15] In recent years, Kido[34,35] and Li[14,16] reported high efficiencies for $Ir(ppy)_3$ PhOLEDs containing single bipolar host, such as 24% (128 lm W^{-1}), 28% (105 lm W^{-1}), 27.3% (96.1 lm W^{-1}), and 28.2% (102.8 lm W^{-1}), which stand for the typical data for single host based green PhOLEDs so far. It is obvious that the efficiencies 28.0% (97.2 lm W^{-1}) of G2 and 25.8% (106.7 lm W^{-1}) of G1 are among the best data ever reported for $Ir(ppy)_3$ PhOLEDs containing a single host material. Evidently the superior performance of G1 and G2 should be attributed to the more balanced carrier in emitting layer caused by the appropriate n/p ratio in hosts PyTzDCz and PyTzSCz. Furthermore, the efficiencies of green devices G1 and G2 are quite stable with very low efficiency roll-offs. For example, at a practical brightness of 1000 cd m^{-2}, the efficiency roll-offs of G1 and G2 are 8.1% and 6.1% respectively, and even at an extremely high brightness of 5000 cd m^{-2}, G1 and G2 still maintained high external quantum efficiency of 22.4% and 25.0%. Evidently the “dual n-type unit” designing strategy and the consequent excellent charge balancing abilities and optimized HOMO/LUMO levels and triplet energies of these bipolar

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hosts, especially PyTzSCz that possesses a n/p ratio of 2:1, should be the essential factors accounting for their excellent performance in both sky-blue and green PhOLEDs.

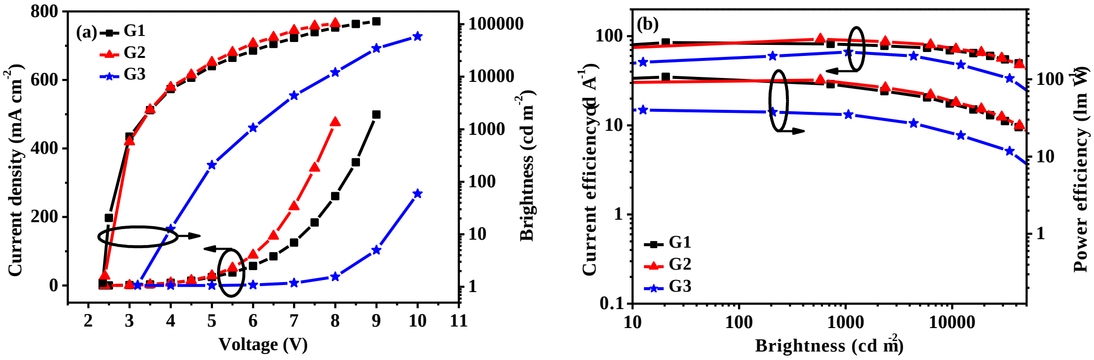

Fig. 7 (a) The *J*-*V*-*B* characteristics and (b) efficiency curves for PyTzDCz, PyTzSCz and PyDCz-hosted green PhOLEDs G1 to G3.

Conclusion

Two novel "dual n-type unit" bipolar host materials PyTzDCz and PyTzSCz have been developed by using 1,2,4-triazole-pyridine as the dual n-type unit. From the traditional unipolar mCP to the bipolar reference compound PyDCz and further to PyTzDCz and PyTzSCz, the n/p ratio shows a regular change from 0:2 to 1:2 further to 2:2 to 2:1. By means of both experimental study and theoretical calculations, it has been demonstrated that with regular increase of the n/p ratio in each host, the LUMO level was pulled down and the electron injection barrier was reduced to certain extent, and the positive and negative charge balancing ability of the host is stepwisely improved. As a result, the driving voltage of the sky-blue and green PhOLED with these host materials is gradually reduced and the emission efficiency is regularly increased. Particularly for the host PyTzSCz with n/p ratio of 2:1, the sky-blue

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PhOLED turn-on at rather low voltage of 2.6 V with high power efficiency of 48.1 lm W^{-1} (EQE of 26.4%), which are the lowest turn-on voltage so far and one of the highest power efficiencies reported for FIrpic PhOLEDs containing a single host. The systematic study of these simple host materials has confirmed the charge balancing ability of the host materials, rather than its amorphous stability, dominates to determine the overall performance of PhOLEDs, and further demonstrated that the "dual n-type unit" bipolar hosts may be the ideal type of host materials favorable for best PhOLEDs performance owing to the excellent charge balancing ability.

Experimental Section

General information

A 500 and 126 MHz Varian Unity Inova spectrophotometer was used to record the ^{1}H NMR and ^{13}C NMR spectra, and the mass spectra were taken on HP1100LC/MSD MS spectrometer. The fluorescence and UV-vis absorption spectra measurements were performed on a Hitachi F-7000 spectrometer and a PerkinElmer Lambda 750s spectrophotometer, respectively. The phosphorescence spectra were measured on a Hitachi F-7000 spectrometer at 77 K in 2-MeTHF. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were carried out using Perkin-Elmer thermogravimeter (Model TGA7) and a Netzsch DSC 201, at a heating rate of 10 ℃ min^{-1} under a nitrogen atmosphere, respectively. The cyclic voltammetry properties were studied on an electrochemical workstation (BAS100B, USA) and using a conventional three electrode configuration at a scan

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rate of 100 mV s^{-1}. A glass carbon working electrode, a Pt-wire counter electrode, and a saturated calomel electrode (SCE) reference electrode were used. All the measurements were made at room temperature on samples dissolved in dichloromethane or *N*,*N*-dimethylformamide, deoxygenated with argon, and with 0.1 M $[Bu_4N]PF_6$ as the electrolyte. Density functional theory (DFT) calculations using B3LYP functional were performed. The basis set used for the C, H, N atoms was 6-31G. There are no imaginary frequencies for both the optimized structures. All these calculations were performed with Gaussian 09.

OLED fabrication and measurements

The pre-cleaned ITO glass substrates, with a sheet resistance of 15 Ω per square, were treated by UV-ozone for 20 min. A 40 nm thick PEDOT:PSS film was first deposited on the ITO glass substrate and baked at 120 ℃ for 30 min in air. Subsequently, the substrate was transferred into a vacuum chamber to deposit the organic layers with a base pressure less than 10^{-6} Torr (1 Torr = 133.32 Pa). Finally, the device fabrication was completed through the thermal deposition of LiF (1 nm) and then capping with Al metal (200 nm) as a cathode. The emitting area of each pixel was determined by overlapping of two electrodes as 9 mm^2. The EL spectra, CIE coordinates and *J-V-B* curves of the devices were measured with a PR705 photometer and a source-measure-unit Keithley 236, under ambient conditions at room temperature. The forwarding viewing external quantum efficiency (η_{ext}) was calculated by using the current efficiency, EL spectra and human photopic sensitivity.

The details of compound synthesis and characterization are provided in

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Electronic Supporting Information.

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TOC Graphic Abstract

By gradually increasing the molar ratio of n-type to p-type groups from the unipolar to bipolar and further to dual n-type unit bipolar host materials, the overall performance of the phosphorescence organic light-emitting diodes is constantly and regularly improved. The novel dual n-type unit bipolar host with n/p ratio of 2:1 exhibits a turn-on voltage of 2.6 V and an efficiency of 48.1 lm W^{-1}, which are the lowest turn-on voltage and one of the highest power efficiencies reported so far for FIrpic devices containing a single host.