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## 1. Introduction

Organic light-emitting diodes (OLEDs) have become of significant commercialization interest for their potential applications in full color flat-panel displays and solid state lightings.<sup>1,2</sup> Compared to the 25% of internal quantum efficiency (IQE) of conventional fluorescent OLEDs, phosphorescent OLEDs based on heavy metal complexes which can utilize both singlet and triplet excitons through intersystem crossing to theoretically approach 100% IQE have drawn much attention from both academia and industry.<sup>3</sup> To reduce concentration quenching and triplet-triplet annihilation,

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# A low-cost phenylbenzoimidazole containing electron transport material for efficient green phosphorescent and thermally activated delayed fluorescent OLEDs

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A new phenylbenzoimidazole-based electron-transport material (ETM), 2,4,6-tris(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)benzonitrile (*i*TPBI-CN), is designed and synthesized through a simple low-cost one-step C–N coupling reaction by using 2,4,6,-trifluorobenzonitrile and 2-phenyl-1*H*-benzo[*d*]imidazole as the starting materials. In comparison with the four step synthesis of commercial ETM of 2,2,2-(1,3,5phenylene)-tris(1-phenyl-1*H*-benzimidazole) (TBPI), the introduction of a cyano moiety into *i*TPBI-CN greatly simplifies the synthetic procedure and allows for an isomerized linkage of phenylbenzoimidazole. The glass transition temperature increases from 124 °C of TPBI to 139 °C of *i*TPBI-CN. Both compounds show similar HOMO levels of ~5.9 eV and a triplet energy of ~2.6 eV. The deeper LUMO level of *i*TPBI-CN (2.79 eV) than TPBI (2.38 eV) allows for more efficient electron-injection and a much higher device efficiency. Solution-processed green phosphorescent OLEDs with the structure of ITO/PEDOT:PSS/ host:lr(mppy)<sub>3</sub>/*i*TPBI-CN *versus* TPBI/LiF/Al show maximum current and power efficiencies of 37.7 cd A<sup>-1</sup> and 29.0 lm W<sup>-1</sup> *versus* 26.1 cd A<sup>-1</sup>, 12.2 lm W<sup>-1</sup> in the CBP host and 31.3 cd A<sup>-1</sup> and 23.9 lm W<sup>-1</sup> *versus* 20.6 cd A<sup>-1</sup>, 7.4 lm W<sup>-1</sup> in the mCP host. Furthermore, the superior device performance of *i*TPBI-CN over TPBI is also found in both CBP and mCP hosted green thermally activated delayed fluorescence (TADF) devices by using 2,3,5,6-tetracarbazole-4-cyano-pyridine (4CzCNPy) as a dopant.

phosphorescent triplet emitters are normally doped into suitable organic host materials.<sup>4</sup>

The basic structure of an OLED is multilayered, typically consisting of a transparent metal oxide anode, a hole-transport layer (HTL), an emissive layer (EML), an electron-transport layer (ETL), and a metal cathode. A high hole mobility of up to almost  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has already been achieved in most widely reported hole-transport materials, such as 1-bis[4-[*N*,*N*-di(4-tolyl)-amino]phenyl]-cyclohexane (TAPC) and *N*,*N*-dinaphthyl-*N*,*N'*-diphenylbenzidine (NPB).<sup>5</sup> On the other hand, the electron mobility of excellent electron-transport materials is at least 10-fold lower than that of hole mobility of a HTL in devices.<sup>4a</sup> As charge transport properties of electron- and hole-transport materials are imbalanced, the electron feeding from the cathode into the emissive layer dominates the device characteristics of OLEDs.<sup>6</sup> Therefore, the development of efficient organic electron-transport materials is a challenge of high priority.<sup>7</sup>

An appropriate electron-transport material should possess low-cost synthesis, high electron mobility, decent chemical and thermal stability, low-lying highest occupied molecular orbital (HOMO) energy levels to block hole leakages from the emissive layer and low-lying lowest unoccupied molecular orbital (LUMO)

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#### Paper

energy levels to facilitate electron injection to the emissive layer, as well as high enough triplet energy levels to confine triplet excitons within the emissive layer.8 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and tris(8-hydroxyquinoline)aluminum (Alq3) which are the most widely used relatively cheaper electrontransport materials were normally combined together as the hole blocking and electron transporting materials in green to red phosphorescent OLEDs due to their rather low triplet energy of 2.09 and 2.5 eV,10 respectively. 2,2,2-(1,3,5-phenylene)-tris(1phenyl-1H-benzimidazole) (TBPI)<sup>11</sup> is another widely used electron transporting material in blue to red phosphorescent OLEDs due to its relatively higher triplet energy levels (2.6-2.74 eV) and electron mobility  $(3.3-8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at an electric field of 4.7–7  $\times$ 10<sup>5</sup> V cm<sup>-1</sup>).<sup>12</sup> In our previous work, because of one order higher of electron mobility, higher triplet energy and better matched LUMO energy levels, TPBI was used instead of BCP/Alq3 to simplify the device architectures and improve electron injection and transport, as well as confine triplet excitons in the emissive layer, and thus to significantly enhance the device performances in green phosphorescent OLEDs.13 Besides, oxadiazole containing 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD)<sup>14</sup> and 1,3-bis[(4-tertbutylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7)15 are mostly employed as ETLs in solution-processable phosphorescent polymer light-emitting devices, other electron-withdrawing 1,2,4-triazole, pyridne and phosphine oxide derivatives such as 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (Tm3PyPB),<sup>16</sup> 3-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole  $(t-Bu-TAZ)^{17}$  and dibenzo[b,d]thiophene-2.8-divlbis(diphenylphosphine oxide) (PO15)<sup>18</sup> have also been widely used as HBLs/ETLs in blue PhOLEDs due to their high triplet energies and favorable energy levels. However, their design and synthesis rely mainly on a multi-step strategy, which involves in noble metal catalyzed Ullman and Suzuki cross coupling reactions, or rigorous conditions and/or the use of harsh reagents such as thionyl chloride, sulfuric acid and phosphorus (oxy) chloride. Therefore, in order to reduce the cost for the commercialization of OLEDs, from the materials point of view, it is highly desirable to develop organic materials exhibiting an encouraging device performance with the simplest synthetic chemistry by directly using commercially available inexpensive starting materials.<sup>19</sup>

Based on this concept, in this study, a novel phenylbenzimidazole-derivative is designed as an electron transport material in comparison with TPBI. By introducing the electron-withdrawing cyano moiety into the central phenyl ring, the new material 2,4,6-tris(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)benzonitrile (*i*TPBI-CN) can be readily synthesized through a simple low-cost one-step C-N coupling reaction by using 2,4,6-trifluoro-benzonitrile and 2-phenyl-1H-benzo[d]imidazole as the starting materials. It should be noted that the synthesis of iTPBI-CN shows significant advantage of general four steps of 1-phenyl-1H-benzo[d]imidazol-2-yl based TPBI or its derivatives with TPBI as a core central structure. Moreover, the structure-property relationships between TPBI and *i*TPBI-CN are systematically investigated both through experimental and theoretical methods. Solution processible green phosphorescent and thermally activated delayed fluorescent devices by using the new *i*TPBI-CN instead of TPBI as an ETL, both CBP and mCP as hosts, exhibited much better device performances.

### 2. Experimental

### 2.1 General information

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a MECUYR-VX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. Mass spectra were measured on a Bruker autoflex matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF). UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min<sup>-1</sup> from -40 °C to 300 °C under argon. The glass transition temperature  $(T_{o})$  was determined from the second heating scan. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20 °C min<sup>-1</sup> from 25 to 600 °C. Cyclic voltammetry (CV) was measured in nitrogen-purged dichloromethane for oxidation scan and tetrahydrofuran for reduction scan, using a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (0.1 M) was used as a supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc<sup>+</sup>/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s<sup>-1</sup>. Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

**Computational details.** The geometrical and electronic properties of both compounds were performed using the Gaussian 09 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee–Yang–Perdew correlation functionals) with the 6-31G(d) atomic basis sets The triplet states  $\Delta E$  (T<sub>1</sub> – S<sub>0</sub>) were calculated using time dependent density functional theory (TD-DFT) calculations with B3LYP/ 6-311+g(d). Molecular orbitals were visualized using Gauss view.

### 2.2 Synthesis of 2,4,6-tris(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)benzonitrile (*i*TPBI-CN)

A mixture of 2-phenylbenzimidazole (1.02 g, 5.2 mmol), 2,4,6-trifluorobenzonitrile (0.25 g, 1.6 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.99 g, 7.2 mmol) in dimethyl sulfoxide (DMSO) (8 mL) was stirred at 150 °C for 12 h under an argon atmosphere. After cooling to room temperature, the mixture was poured into water, filtered, and then purified by column chromatography over silica gel with CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (10:1) as an eluent to afford a white solid (0.95 g, 88%). <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  ppm 8.34 (s, 2H), 7.91–7.88 (m, 3H), 7.72–7.61 (m, 12H), 7.48–7.38 (m, 9H), 7.29–7.27 (d, 3H, *J* = 6 Hz); <sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>SO,):  $\delta$  ppm 155.2, 155.1, 145.8, 145.7, 145.6, 144.3, 138.8, 133.3, 133.1, 132.9, 132.6, 132.3, 132.2, 132.0, 126.9, 126.6, 122.8, 122.7, 115.2, 114.9, 114.1, 113.5, 113.4, 113.3; MALDI-TOF (*m*/*z*): 679.637 [M<sup>+</sup>];

#### 2.3 Device fabrication and measurements

The patterned indium tin oxide (ITO) glass substrates were ultrasonically cleaned with detergent, alcohol and acetone, deionized water and then dried at 120 °C in a vacuum oven for more than one hour. After ultraviolet (UV)-ozone treating for 4 min, a 40 nm PEDOT:PSS was spin-coated on the ITO substrate and dried at 120 °C in a vacuum oven for 15 min to remove the residual solvent. Afterward, the emissive layers (EMLs) were spin-coated on top of PEDOT:PSS from chlorobenzene and then annealed using a hot plate at 80 °C for 20 min to extract the residual solvent. The thickness of the emissive layer is about 40–45 nm. Following that, the samples were transferred into a thermal evaporator chamber. Then ETLs (60 nm), LiF (0.5 or 0.8 nm), and Al (100 nm) were deposited by thermal evaporation under a pressure of  $5 \times 10^{-4}$  Pa, respectively. The active area of the device is 13.5 mm<sup>2</sup>.

The luminance-current-voltage characteristics of the devices were recorded using a combination of a Keithley source-meter (model 2602) and a calibrated luminance meter. Electroluminescence (EL) spectra and Commission international de l'eclairage (CIE) coordinates were obtained using a spectra-scan PR655 spectrophotometer. The thickness of the organic films was measured using a spectroscopic ellipsometer ( $\alpha$ -SE, J. A. Wollam Co. Inc.). All the measurements were carried out at room temperature under ambient conditions.

### 3. Results and discussion

Scheme 1 illustrates the chemical structure and synthetic routes for TPBI and the new compound *i*TPBI-CN studied in this work. As shown, superior advantage for the synthesis of *i*TPBI-CN is demonstrated. The preparation of TPBI follows a four-step literature method.<sup>12b,20</sup> Firstly, the reaction of 1-fluoro-2nitrobenzene and aniline in the presence of potassium fluoride at 170-180 °C for 72 h gave 2-nitro-N-phenylaniline, followed by the reduction of the nitro group with stannous chloride dihydrate, then the resulting diamine derivative reacted with 1,3,5-benzenetricarbonyl trichloride to produce the corresponding triamide, after the final condensation reaction at 250 °C for 3 h, TPBI was obtained with a total yield of  $\sim 40\%$ .<sup>20</sup> On the other hand, *i*TPBI-CN can be facilely synthesized through a one-step aromatic nucleophilic substitution reaction by using 2-phenyl-1*H*-benzo[*d*]imidazole as a nitrogen nucleophile and electron-withdrawing cyano activated trifluorobenzene as an electrophile under the conditions of K<sub>2</sub>CO<sub>3</sub> base and DMSO solvent. A high yield of 88% was obtained. More importantly, all the starting materials are cheap and easily accessible from commercial resources. Different from our previous work on this simple one-step catalyst free C-N coupling reaction employing the electron-donation 9H-carbazole or its alkyl substituted derivatives,<sup>21</sup> in this work, we expanded to the electronwithdrawing 2-phenyl-1H-benzo[d]imidazole as a nitrogen nucleophile. In the synthesis of *i*TPBI-CN, phenyl-benzo[*d*]imidazole



Scheme 1 Synthetic routes for literature reported commercial TPBI (ref. 20) and the new compound *i*TPBI-CN.

functions as a nitrogen source in the C-N coupling reaction, thus the nitrogen atom in benzoimidazole (2-phenyl-1H-benzo-[d]imidazol-1-yl) is linked to the C atom at the central phenyl ring. However, in TPBI, the carbon atom in benzoimidazole (1-phenyl-1*H*-benzo[*d*]imidazol-2-yl) is linked to the central phenyl. Therefore, the phenyl-benzo[d]imidazole unit exhibited an isomerized structure between TPBI and *i*TPBI-CN. The new compound *i*TPBI-CN was fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, mass and elemental analysis. The optimized geometries are shown in Fig. 1. The dihedral angles involving the C-N linkage between phenyl and benzoimidazole rings are much larger than the C-C linkage in both compounds. Therefore, at the same position, the dihedral angles between the central phenyl and benzoimidazole ring for *i*TPBI-CN (62.7–74.2°) are  $\sim 30^{\circ}$  larger than those in TPBI (37.1°), suggesting a more twisted structure of *i*TPBI-CN due to the isomerized linkage for phenyl-1Hbenzo[d]imidazole as well as the substitution of cyano moieties to the central phenyl core.

The thermal properties of the new compound were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 2). The thermal decomposition temperature ( $T_d$ , corresponding to 5% weight loss) determined from TGA



**Fig. 1** Optimized geometries and corresponding dihedral angles for TPBI and *i*TPBI-CN.



Fig. 2 TGA (a) and DSC (b) curves of *i*TPBI-CN.



**Fig. 3** Normalized UV-Vis absorption and PL spectra of TPBI and *i*TPBI-CN in CHCl<sub>3</sub> and the film state at room temperature.

for *i*TPBI-CN was as high as 410 °C, and the glass transition temperatures ( $T_{\rm g}$ ) observed from DSC curves was 139 °C. Under a similar star-shaped molecular skeleton, the introduction of one cyano unit into *i*TPBI-CN makes its  $T_{\rm g}$  15 °C higher than literature record of 124 °C for TPBI.<sup>22</sup> The high thermal stability of the compound could be attributed to the rigid and bulky configuration.

The UV-Vis absorption and photoluminescence (PL) spectra at room temperature for both benzoimidazole-based compounds are shown in Fig. 3, and the peak maxima are summarized in Table 1. The absorption peak for *i*TPBI-CN was observed at 278 and 282 nm in chloroform and the film state, respectively, which can be attributed to  $\pi - \pi^*$  transitions of the molecule, these data were red-shifted to 304 and 314 nm for TPBI. The blue-shifted higher energy absorption of *i*TPBI-CN is clearly a consequence of steric interactions that prevents effective conjugation between the phenylbenzimidazole groups and the central cyanobenzene core.23 However, iTPBI-CN exhibited significantly red-shifted emission than TPBI at room temperature, with photoluminescence peaks at 455 and 432 nm in chloroform and the film state respectively, compared to 364 and 381 nm for TPBI, which might be induced by the introduction of a strong electron-withdrawing cyano-moiety. The singlet  $(E_S)$  and triplet energy  $(E_{\rm T})$  determined by the highest-energy vibronic sub-band of the 77 K fluorescence and phosphorescence spectra (Fig. 4) is TPBI 3.55 and 2.63 eV, respectively, which is in accordance with previous report.<sup>12b</sup> Due to the red-shifted emission, the singlet energy of *i*TPBI-CN is greatly lowered to 2.99 eV, however, the triplet energy only slightly reduced to 2.60 eV, indicating that the introduction of an electron-withdrawing cyano moiety and the



Fig. 4 Solid-state fluorescence and phosphorescence spectra of TPBI and *i*TPBI-CN at 77 K.

Table 1 Ph	1 Physical properties of TPBI and <i>i</i> TPBI-CN												
	$T_{\rm g}/T_{\rm d}{}^{g} \left[^{\circ} { m C}\right]$	$\lambda_{\rm abs}{}^a$ [nm]	$\lambda_{\mathrm{abs}}{}^{b} [\mathrm{nm}]$	$\lambda_{\rm em}{}^a$ [nm]	$\lambda_{\rm em}{}^{b} [{\rm nm}]$	$E_{\rm S}^{\ c} \left[ {\rm eV} \right]$	$E_{\mathrm{T}}^{d} [\mathrm{eV}]$	$E_{\mathrm{T}}^{e} [\mathrm{eV}]$	HOMO/LUMO <sup>f</sup> [eV]				
TPBI iTPBI-CN	124/— 139/410	304 278	314 282	364 455	381 432	3.55 2.99	2.63 2.60	2.84 2.95	-5.89/-2.38 -5.90/-2.79				

<sup>*a*</sup> Measured in CHCl<sub>3</sub> solution at room temperature. <sup>*b*</sup> Measured in the film state at room temperature. <sup>*c*</sup> Singlet energy was calculated from low temperature (77 K) fluorescence spectra. <sup>*d*</sup> Triplet energy was calculated from low temperature (77 K) phosphorescence spectra. <sup>*e*</sup> Triplet energy was obtained from DFT calculation. <sup>*f*</sup> Measured from the on-set of oxidation and reduction curves of CV. <sup>*g*</sup>  $T_{g}$  of TPBI was recorded from ref. 22.





Fig. 5 HOMO–1, HOMO, LUMO and LUMO+1 distribution, highest occupied and lowest unoccupied natural transition orbitals (HONTO and LUNTO, respectively) of lowest singlet (S1) and triplet excited (T1) states for compounds TPBI and *i*TPBI-CN.

isomerization structure of phenylbenzoimidazole to the central phenyl core show little influence on triplet energy.  $E_{\rm T}$  of the new low-cost *i*TPBI-CN is much higher than that of the green phosphorescent emitter (~2.4 eV), implying that it may act as an appropriate electron transport material to confine triplet excitons in the emissive layer for green to red phosphorescent OLEDs.<sup>24</sup>

To gain insight into the electronic properties of the compounds, DFT calculations on the frontier molecular orbitals are performed. Fig. 5 shows the ground state highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO), the next highest occupied molecular orbitals (HOMO-1) and the next lowest unoccupied molecular orbitals (LUMO+1), as well as the highest occupied natural transition orbitals (HONTO) and lowest unoccupied natural transition orbitals (LUNTO) of singlet and triplet excited states for both TPBI and *i*TPBI-CN. The two occupied orbitals, HOMO and HOMO-1 for *i*TPBI-CN are mainly located on the 1-phenyl-1Hbenzo[d]imidazol-2-yl side group, and the lowest unoccupied orbital is mainly located on the electron-deficient cyanophenenyl core, while the LUMO+1 only on the central phenyl core with negligible contribution from phenylbenzoimidazolyl side group but no contribution from the cyano group. The results for the star-shaped TPBI show that all the HOMO and LUMO orbitals are distributed partly over the phenylbenzoimidazolyl side groups and the central phenenyl group. Similar distributions with the ground state HOMO and LUMO distributions can also be found in their HONTO and LUNTO singlet excited states for both compounds. Both the HONTO and LUNTO tripletexcited states for TPBI and *i*TPBI-CN are well controlled and located at the 1-phenyl-1*H*-benzo[*d*]imidazol-2-yl moiety. As the maximum conjugation length is the prior impact factor determining the triplet energy levels, it is at the same scale of phenylbenzoimidazolyl for these two molecules. Therefore, similar  $E_{\rm T}$  values are obtained which is consistent with the experimental results.

The electrochemical properties of the compounds were probed by cyclic voltammetry (Fig. 6). Under the same conditions, TPBI and *i*TPBI-CN showed quasi-reversible oxidation and reduction behavior. Their HOMO and LUMO energy levels were determined from the onsets of the oxidation and reduction potentials (relative to the vacuum level), respectively (Table 1). In response to their ground state HOMO level distributions which are mainly delocalized through the phenylbenzoimidazolyl skeleton, both compounds exhibited similar HOMO levels of  $\sim 5.9$  eV. However, the LUMO



**Fig. 6** Cyclic voltammetry for TPBI and *i*TPBI-CN in CH<sub>2</sub>Cl<sub>2</sub> (oxidation) and THF (reduction).

levels are greatly lowered from 2.38 eV of TPBI to 2.79 eV of *i*TPBI-CN, due to the introduction of a strong electron-withdrawing cyano group stabilizing the molecular orbitals.

In order to investigate the electron transporting ability of the two phenylbenzoimidazolyl containing electron-transport materials, electron-only devices based on an ETL thickness of 60 nm with the structure of ITO/LiF (0.8 nm)/TPBI or *i*TPBI-CN (60 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated. Data were obtained in 4 batches of experiments with an average of 16 devices. From their current density-voltage (J-V) characteristics (Fig. 7), it is observed that the new compound *i*TPBI-CN exhibited significant higher current and lower voltage than TPBI based devices, indicating the more efficient electroninjection from the cathode to the ETL in the *i*TPBI-CN device. As the LUMO energy levels of *i*TPBI-CN (2.8 eV) are much lower than TPBI (2.4 eV), the electron injection barrier from cathode LiF/Al  $(2.9 \text{ eV})^{25}$  to the ETL of *i*TPBI-CN is 0.1 eV, lower than 0.5 eV in TPBI. On the other hand, the higher current at the same voltage of *i*TPBI-CN might suggest better electron transport properties of *i*TPBI-CN.

To evaluate the performance of the low cost *i*TPBI-CN as an electron transport material, solution processed green phosphorescent organic light-emitting devices A–D with the structure of ITO/PEDOT:PSS (40 nm)/EML (40–45 nm)/ETL (60 nm)/LiF (0.5 nm)/Al were fabricated. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and LiF were used as the hole- and electron-injecting materials, respectively, CBP or mCP hosts doped with 6 wt% of tris[2-(*p*-tolyl)pyridine]iridium(m) [Ir(mppy)<sub>3</sub>] were spin-coated as the emissive layers, and the newly designed *i*TPBI-CN was vacuum deposited as the electron



Fig. 7 Current density–voltage curves of electron-only devices for TPBI and *i*TPBI-CN with the structure of ITO/LiF (0.8 nm)/TPBI or *i*TPBI-CN (60 nm)/LiF (0.8 nm)/Al (100 nm), data are obtained from an average of 16 devices.

transporting layer. Simultaneously, the widely used commercial electron transport material TPBI based devices were also demonstrated for comparison. The luminance–voltage–current density (L-V-J) characteristics, current and power efficiency *versus* luminance curves and the EL spectra of the devices are shown in Fig. 8(a–d), and the key device data are summarized in Table 2. As shown, *i*TPBI-CN exhibited significantly higher device efficiencies than TPBI in both CBP and mCP hosted devices. In CBP hosted devices A and B, a relatively lower turn-on voltage ( $V_{on}$ ) of

3.6 V was achieved for both devices, with a maximum luminance  $(L_{\rm max})$  of 36 315 and 26 250 cd m<sup>-2</sup>, respectively. The maximum current  $(\eta_{\rm c,max})$  and power efficiency  $(\eta_{\rm p,max})$  for TPBI based device A was 26.1 cd A<sup>-1</sup> and 12.2 lm W<sup>-1</sup>, which greatly increased to 37.7 cd A<sup>-1</sup> and 29.0 lm W<sup>-1</sup> in device B by using *i*TPBI-CN as an electron transport material, with an  $\eta_{\rm c,max}$  improvement of 44% and  $\eta_{\rm p,max}$  of 134%. Similar trends can be observed in mCP hosted devices C and D with an ETL. And maximum current and power efficiency of 20.6 cd A<sup>-1</sup> and 23.9 lm W<sup>-1</sup> for TPBI based on device D were obtained.

In order to further verify the superior performance of *i*TPBI-CN over commercial TPBI, devices E-H by using our recently developed thermally activated delayed fluorescence (TADF) dye 2,3,5,6-tetracarbazole-4-cyano-pyridine (4CzCNPy) were also investigated.<sup>21d</sup> The device configuration was slightly changed as ITO/PEDOT:PSS (40 nm)/host:4CzCNPy (8 wt%, 40-45 nm)/ ETL (60 nm)/LiF (0.8 nm)/Al. The key device data and L-V-I, efficiency vs. Luminance curves as well as the EL spectra can be found in Table 2 and Fig. 9(a–d) respectively. As shown, similar results with phosphorescent devices were observed. Both CBP and mCP hosted devices with the new iTPBI-CN as an ETL exhibited obvious lower turn-on voltages and higher device efficiencies. Devices E (CBP host) and G (mCP host) based on TPBI showed turn-on voltages of 5.1 and 5.6 V, respectively, which were reduced to 3.6 and 4.1 V in *i*TPBI-CN based devices F and H. The current efficiency in TPBI based devices E and G



Fig. 8 Current density-voltage-luminance (a), current efficiency-luminance (b), power efficiency-luminance curves (c) and EL spectra at 9 V (d) for green phosphorescent devices A–D.

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Table 2 Electroluminescent properties of the green phosphorescent devices

	Host/Dopant	ETL	$V_{\rm on}^{\ a}$ (V)	$L_{\max}^{b}$ (cd m <sup>-2</sup> )	$\eta_{\mathrm{c,max}}^{c} \left( \mathrm{cd} \ \mathrm{A}^{-1} \right)$	$\eta_{\mathrm{p,max}}^{d} (\mathrm{Im} \mathrm{W}^{-1})$	CIE $(x,y)$ at 9 V
A	CBP/Ir(mppy) <sub>3</sub>	TPBI	3.6	36 315	26.1	12.2	(0.32,0.62)
В	$CBP/Ir(mppy)_3$	<i>i</i> TPBI-CN	3.6	26 250	37.7	29.0	(0.29, 0.62)
С	$mCP/Ir(mppy)_3$	TPBI	5.2	13 954	20.6	7.4	(0.31,0.61)
D	$mCP/Ir(mppy)_3$	<i>i</i> TPBI-CN	4.1	9545	31.3	23.9	(0.28,0.61)
Е	CBP:4CzCNPy	TPBI	5.1	11 166	9.3	3.5	(0.35,0.59)
F	CBP:4CzCNPy	<i>i</i> TPBI-CN	3.6	26 590	23.4	10.0	(0.36,0.60)
G	mCP:4CzCNPy	TPBI	5.6	21 911	15.7	5.7	(0.34,0.59)
Η	mCP:4CzCNPy	<i>i</i> TPBI-CN	4.1	22 830	20.2	6.9	(0.34,0.61)

<sup>a</sup> Turn-on voltage. <sup>b</sup> Maximum luminance. <sup>c</sup> Maximum current efficiency. <sup>d</sup> Maximum power efficiency.



Fig. 9 Current density-voltage-luminance (a), current efficiency-luminance (b), power efficiency-luminance curves (c) and EL spectra at 9 V (d) for green TADF devices E-H.

was 9.3 and 15.7 cd  $A^{-1}$ , respectively, these values for *i*TPBI-CN containing F and H were increased to 23.4 and 20.2 cd  $A^{-1}$  respectively.

Due to their similar HOMO energy levels to block holes, the much better device performances for *i*TPBI-CN based devices may be attributed to the more efficient electron-injection behavior and electron transport properties than in TPBI based devices, as discussed in the electron only devices.

## 4. Conclusion

In conclusion, we have demonstrated a new phenylbenzoimidazolyl containing electron transport material *i*TPBI-CN. The introduction of an electron-withdrawing CN unit has spurred *i*TPBI-CN to be synthesized directly through a one-step low-cost catalyst free C–N coupling reaction by using cheap starting materials. Compared to the four step synthesis of the widely reported commercially available electron transporting TPBI, *i*TPBI-CN exhibited red-shifted emission, similar HOMO levels and triplet energies, deeper LUMO and efficient electron injection. By using *i*TPBI-CN as an electron transporting layer, maximum current and power efficiencies of 37.7 cd A<sup>-1</sup> and 29.0 lm W<sup>-1</sup> have been achieved for CBP and 31.3 cd A<sup>-1</sup> and 23.9 lm W<sup>-1</sup> for mCP hosted solution processed green phosphorescent OLEDs. These values in TPBI based devices lower to 26.1 cd A<sup>-1</sup>, 12.2 lm W<sup>-1</sup> and 20.6 cd A<sup>-1</sup>, 7.4 lm W<sup>-1</sup>. And a superior device performance of the new electron-transport *i*TPBI-CN over TPBI has also been achieved in green TADF devices. Further work on vacuumed deposited devices as well as

lifetime for the comparison of *i*TPBI-CN and TPBI is underway. The much easier low-cost synthesis and higher device efficiency suggest great potential of the new electron-transport *i*TPBI-CN material for commercial applications.

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## Notes and references

- 1 C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett., 1987, 51, 913.
- 2 C. Adachi, M. A. Baldo, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, 2000, 77, 904.
- 3 (a) S. R. Forrest, M. A. Baldo, D. F. O. Brien, Y. You, A. Shoustikov, S. Sibley and M. E. Thompson, *Nature*, 1998, 395, 151; (b) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 1999, 75, 4; (c) Y. Tao, Q. Wang, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Funct. Mater.*, 2010, 20, 2923; (d) L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong and J. Kido, *Adv. Mater.*, 2011, 23, 926; (e) Y. Chi and P. T. Chou, *Chem. Soc. Rev.*, 2010, 39, 638; (f) W. Y. Wong and C. L. Ho, *Coord. Chem. Rev.*, 2009, 253, 1709; (g) H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH, Weinheim, 2008.
- 4 (a) Y. Tao, C. Yang and J. Qin, *Chem. Soc. Rev.*, 2011, 40, 2943;
  (b) F. Wang, Y. Tao and W. Huang, *Acta Chim. Sin.*, 2015, 73, 9.
- 5 (a) J. Lee, N. Chopra, S. H. Eom, Y. Zheng, J. Xue, F. So and J. Shi, *Appl. Phys. Lett.*, 2008, 93, 123306; (b) D.-H. Lee, Y.-P. Liu, K.-H. Lee, H. Chae and S. M. Cho, *Org. Electron.*, 2010, 11, 427; (c) H. Sasabe, E. Gonmori, T. Chiba, Y.-J. Li, D. Tanaka, S.-J. Su, T. Takeda, Y.-J. Pu, K. Nakayama and J. Kido, *Chem. Mater.*, 2008, 20, 5951.
- 6 (a) M. Ichikawa, K. Wakabayashi, S. Hayashi, N. Yokoyama, T. Koyama and Y. Taniguchi, *Org. Electron.*, 2010, 11, 1966;
  (b) M. Ichikawa, S. Fujimoto, Y. Miyazawa, T. Koyama, N. Yokoyama, T. Miki and Y. Taniguchi, *Org. Electron.*, 2008, 9, 77.
- 7 (a) C.-H. Shih, P. Rajamalli, C.-A. Wu, M.-J. Chiu, L.-K. Chu and C.-H. Cheng, J. Mater. Chem. C, 2015, 3, 1491; (b) S.-J. Yoo, H.-J. Yun, II. Kang, K. Thangaraju, S.-K. Kwon and Y.-H. Kim, J. Mater. Chem. C, 2013, 1, 2217.
- 8 (a) S.-J. Su, H. Sasabe, Y.-J. Pu, K-i. Nakayama and J. Kido, *Adv. Mater.*, 2010, 22, 3311; (b) A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, 16, 4556; (c) Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, 107, 953.
- 9 M. A. Baldo and S. R. Forrest, Phys. Rev. B: Condens. Matter Mater. Phys., 2000, 62, 10958.

- 10 V. I. Adamovich, S. R. Cordero, P. I. Djurovich, A. Tamayo, M. E. Thompson, B. W. D'Andrade and S. R. Forrest, *Org. Electron.*, 2003, 4, 77.
- 11 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.
- (a) M. E. Kondakova, T. D. Pawlik, R. H. Young, D. J. Giesen, D. Y. Kondakov, C. T. Brown, J. C. Deaton, J. R. Lenhard and K. P. Klubek, *J. Appl. Phys.*, 2008, **104**, 094501; (b) S.-y. Takizawa, V. A. Montes and P. Anzenbacher Jr, *Chem. Mater.*, 2009, **21**, 2452; (c) J. Y. Shen, C. Y. Lee, T.-H. Huang, J. T. Lin, Y.-T. Tao, C.-H. Chien and C. T. Tsai, *J. Mater. Chem.*, 2005, **15**, 2455; (d) H. Kim, Y. Byun, R. R. Das, B.-K. Choi and P.-S. Ahn, *Appl. Phys. Lett.*, 2007, **91**, 093512; (e) W.-Y. Hung, T.-H. Ke, Y.-T. Lin, C.-C. Wu, T.-H. Hung, T.-C. Chao, K.-T. Wong and C.-I. Wu, *Appl. Phys. Lett.*, 2006, **88**, 064102.
- 13 (a) Y. Tao, Q. Wang, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Funct. Mater.*, 2010, 20, 2923; (b) Y. Tao, Q. Wang, C. Yang, J. Qin and D. Ma, *ACS Appl. Mater. Interfaces*, 2010, 2, 2813.
- 14 H. Xia, M. Li, D. Lu, C. Zhang, W. Xie, X. Liu, B. Yang and Y. Ma, *Adv. Funct. Mater.*, 2007, 17, 1757.
- 15 J. Lee, N. Chopra, S.-H. Eom, Y. Zheng, J. Xue, F. So and J. Shi, *Appl. Phys. Lett.*, 2008, **93**, 123306.
- 16 S.-J. Su, Y. Takahashi, T. Chiba, T. Takeda and J. Kido, *Adv. Funct. Mater.*, 2009, **19**, 1260.
- 17 Q. Wang, J. Ding, D. Ma, Y. Cheng, L. Wang, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2009, **19**, 84.
- (a) X. Cai, A. B. Padmaperuma, L. S. Sapochak, P. A. Vecchi and P. E. Burrows, *Appl. Phys. Lett.*, 2008, **92**, 083308; (b) L. S. Sapochak, A. B. Padmaperuma, P. A. Vecchi, X. Cai and P. E. Burrows, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2007, **6655**, 665506; (c) M.-H. Wu, J.-H. Lee, M.-K. Leung, C.-C. Liao and Y. Chang, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2004, **5519**, 263.
- 19 (a) E. Ahmed, T. Earmme and S. A. Jenekhe, Adv. Funct. Mater., 2011, 21, 3889; (b) T. Earmme, E. Ahmed and S. A. Jenekhe, Adv. Mater., 2010, 22, 4744.
- 20 J. Shi, C. W. Tang and C. T. Chen, U. S. Pat., 5,646,948, 1997.
- 21 (a) C. Tang, R. Bi, Y. Tao, F. Wang, X. Cao, S. Wang, T. Jiang, C. Zhong, H. Zhang and W. Huang, *Chem. Commun.*, 2015, 51, 1650; (b) Y. Tao, Q. Wang, C. Yang, Q. Wang, Z. Zhang, T. Zou, J. Qin and D. Ma, *Angew. Chem., Int. Ed.*, 2008, 47, 8104; (c) Y. Tao, S. Gong, Q. Wang, C. Zhong, C. Yang, J. Qin and D. Ma, *Phys. Chem. Chem. Phys.*, 2010, 12, 2438; (d) C. Tang, T. Yang, X. Cao, Y. Tao, F. Wang, C. Zhong, Y. Qian, X. Zhang and W. Huang, *Adv. Opt. Mater.*, 2015, DOI: 10.1002/adom.201500016.
- 22 Z.-Y. Liu, S.-R. Tseng, Y.-C. Chao, C.-Y. Chen, H.-F. Meng, S.-F. Horng, Y.-H. Wu and S.-H. Chen, *Synth. Met.*, 2011, 161, 426.
- 23 C.-H. Chen, L.-C. Hsu, P. Rajamalli, Y.-W. Chang, F.-I. Wu, C.-Y. Liao, M.-J. Chiu, P.-Y. Chou, M.-J. Huang, L.-K. Chu and C.-H. Cheng, *Dalton Trans.*, 2010, **39**, 892.
- 24 Y.-C. Chen, G.-S. Huang, C.-C. Hsiao and S.-A. Chen, J. Am. Chem. Soc., 2006, **128**, 8549.
- 25 T.-F. Guo, F.-S. Yang, Z.-J. Tsai, T.-C. Wen, S.-N. Hsieh and Y.-S. Fu, *Appl. Phys. Lett.*, 2005, **8**7, 013504.