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# Substituted Diindenopyrazinediones with Polyalkylcarbazole symmetrically for High-efficiency bluish green Solution-processable OLED

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**ABSTRACT:** Much effort has been devoted to design and synthesize this solution-processable OLEDs, Some significant advances have been achieved with the power efficiencies. However, most of them still lag behind those of evaporated non-doping OLEDs. Two novel peripheral Polyalkyl-carbazole substituted Diindeno-pyrazinediones have been developed for highly-efficient and solution-processable OLEDs. Provide high efficient materials for the solution-processed to reduce costs of OLEDs. By fine-tuning their carriers transfer and injection barriers, solution-processed device based on DTPADIPY-TCz shows highly efficient bluish green

emission with a maximum power efficiency (PE) of 6.88  $\text{Im W}^{-1}$ , which is among the highest reported to date for solution-processable fluorescent OLEDs with a relatively low efficiency roll-off.

**KEYWORDS:** Peripheral substituted; Solution-processable OLEDs; Deep blue emitting; Low turn-on voltage; Low efficiency roll-off

### **TOC GRAPHICS**



# 1. Introduction

As we all know, Organic Light Emitting Diodes (OLEDs) will become the next generation display technology replace liquid crystal. This commercial application has also been put on the agenda, many manufacturers have begun to layout OLED production line, but its manufacturing technique of thermal evaporation process consume huge energy and is complicated. The low energy consumption of solution-processing technology can realize large-area flexible OLED devices, reduced cost, environment-friendly and large-scale. It is one of the important measures to reduce the energy crisis by means of the science. Solution-processable organic light-emitting diodes (OLEDs) have been attracting extensive study due to their simple processes, low costs and large-area fabrication.<sup>[1-3]</sup> Generally, solution-processable OLEDs were constructed with a single or double-layer architectures due to the restriction of intermixing of layers.<sup>[4-6]</sup> For the single-layer non-dopant devices, their performance usually is inferior to their counterparts of evaporated OLEDs.<sup>[7-9]</sup> While these double-layer structure devices, evaporated an electrontransporting or hole-blocking layer behind the solution-processed emitters, show similar efficiencies with vacuum-deposited OLEDs.<sup>[10,11]</sup> Considering these solution-processable devices without hole-transporting layer, it is highly desirable to develop novel emitters with excellent hole transport and low injecting barriers. In the past decades, much effort has been devoted to design and synthesize this kind of materials.<sup>[12]</sup> Some significant advances have been achieved with the maximal power efficiencies of  $\sim 5 \text{ Im W}^{-1}$ .<sup>[13]</sup> However, most of them still lag behind those of evaporated OLEDs. Therefore, the preparation of novel materials with high fluorescent quantum yield, balanced charge injection and transfer properties still remains one of the most active and challenging areas. Peripheral substitution has been demonstrated as one of effective methods to improve transfer and luminescence, some of them exhibited excellent results for solution-processable OLEDs.<sup>[14]</sup> To date, almost of them are mainly concentrated on fluorene and its derivatives,<sup>[15]</sup> which can be substituted easily on the 9,9'-positions of fluorene. However, an undesired green emission would be found in these devices due to the excimer/interchain aggregates and the keto defects.<sup>[16]</sup> In this respect, diindenopyrazinedione (DIPY) and its derivatives, another intermediates having two positions for the substitution of peripheral groups,

have been used as efficient blue emission and n-type organic field-effect transistors (OFET) with excellent performance (efficiencies, 2.01 cd A<sup>-1</sup> and 4.6%; mobility, 0.17 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>).<sup>[17,18]</sup> However, DIPY core possessing rigid and planar structures facilitates to form molecular stacking in their film states,<sup>[19]</sup> quenching the luminescence and limiting their applications for the solution-processable OLEDs. In this regard, the development of novel DIPY derivatives, containing some twisted structures to tune their aggregation<sup>[20]</sup> of intermolecular interaction in film states and twist four carbazole units through alkyl chains attached to the core and peripheral groups four long alkyl chains to improve their solubility<sup>[21]</sup> are critically important for the high-efficient and low-cost OLEDs.

In this work, two novel DIPY derivatives, 2,8-bis(7-(9*H*-carbazol-9-yl)-9,9-Dioctyl-9*H*-fluoren-2-yl)-6,6,12,12-Tetrak-is (6-(9*H*-carbazol-9-yl)hexyl)-6,12-Dihydrodiindeno[1,2-b:1',2'-e]pyrazine (DCzDIPY-TCz) and 4,4'-((6,6,12,12-Tetrakis(6-(9*H*-carbazol-9-yl)hexyl)-6,12-Dihydrodiindeno[1,2-b:1',2'-e]pyrazine-2,8-diyl)bis(9,9-Dioctyl-9*H*-fluorene-7,2-diyl))bis(*N*,*N*-Diphenylaniline) (DTPADIPY-TCz) were designed and synthesized by introducing four peripheral carbazole to regulate their energy levels for the charge transfer and injection (**Scheme 1.**). Their absorptive, emissive, thermal and electrochemical properties were investigated and showed ideal performance for electroluminescence emitters. Solution-processed double-layer devices based on these peripheral DIPYs show efficient blue and bluish green emission with a maximum power efficiency (PE) of 6.88 lm W<sup>-1</sup> and a relatively low efficiency roll-off, which is among the highest performance for solution-processable fluorescent OLEDs.



Scheme 1. Synthetic routes for DCzDIPY-TCz and DTPADIPY-TCz

## 2. Experimental section

#### 2.1. Material and method

<sup>1</sup>H NMR spectra were recorded on a Bruker DRX-400 spectrometer at 400 MHz and <sup>13</sup>C NMR were recorded on the same spectrometer at 400 MHz. ESI-MS was measured on a FINNIGAN Trace DSQ mass spectrometer. The elemental analyses were tested on a

PerkineElmer 2400 II elemental analyzer. Absorption and fluorescence spectra were done on a Shimadzu UV-2550 and Shimadzu RF-5301PC spectrophotometers. All the chemicals were purchased from local suppliers or TCI and used as received without further purification. The reactions were sensitive to water or oxygen and performed under argon atmosphere.

#### 2.2. Synthesis

Syntheses of 5-Bromo-2,3-dihydro-2-(hydroxyimino)inden-1-one (1). 5-bromo-indanone (25 g, 118.5 mmol), concentrated hydrochloric acid and toluene (120 mL) were mixed and stirred at room temperature in a 500 mL round flask. Amylnitrite (16.6 g, 142 mmol) was slowly added and the mixture was heated to 40 °C for 5 hours. The reactant was filtered and rinsed with CH<sub>3</sub>OH, Pale power 1 was obtain with the yield of 71% (20.2 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 3.78(s, 2H), 7.67(d, 2H, J=5.25 Hz), 7.89(s, 1H), 12.73(s, 1H).

Synthesis of 2,8-Dibromo-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (2). To a 500 mL round flask, the synthesized 1 (3.1 g, 12.5 mmol) and sodium dithionite (7.24 g, 41.6 mmol) were mixed with EtOH (13 mL). In the nitrogen atmosphere, 28% ammonia solution (26 mL) was added and stirred at 95 °C for 24 h. When the reaction was finished, it was cooled and then more distilled water (100 mL) was added. After stirring, the mixture was filtered and sufficiently rinsed with CH<sub>3</sub>OH, diethyl ether and then 2 was obtained. The yield was 62 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 4.06 (s, 4H) , 7.63-7.67(d, 2H, J=6.01 Hz), 7.8 (s, 2 H), 7.96-8.00(d, 2H, J=6.83 Hz).

**Synthesis of 2,8-Dibromo-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (3).** To a 100 mL round flask, the synthesized 2 (0.84 g, 2 mmol), tetra-n-butyl ammonium bromide (0.12 g, 0.4 mmol) and KOH (0.66 g, 12 mmol) were put in 25 ml DMSO and stirred the mixture for 0.5 h at room temperature. Then, 9-(6-bromohexyl)- 9*H*-carbazole (5.28 g, 16 mmol) was added for three

times with the time interval of 20 min. After that, the mixture was heated to 55 °C for 20 h. When the reaction was finished, the mixture was washed with water. The organic solution was dried with MgSO<sub>4</sub>, purified with chromatography on silica gel. The white power was obtained with the yield of 0.34 g, 12%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 0.5-0.8(m, 8H), 0.98-1.15(m, 16 H), 1.60-1.67 (m, 8 H), 1.89 (t, 4 H, *J*=11.36 Hz), 2.17 (t, 4 H, *J*=11.50 Hz), 4.10 (t, 8 H, *J*=6.48 Hz), 7.15-7.27 (m, 16 H), 7.36-7.42(m, 8 H), 7.54-7.61(m, 4H), 7.93(d, 2H, *J*=3.90 Hz), 8.06(d, 2H, *J*=3.80Hz). ESI-MS (m/z): 1410.3, 1411.2. (M<sup>+</sup>+1). Anal. Calcd for C<sub>90</sub>H<sub>86</sub>Br<sub>2</sub>N<sub>6</sub>: C, 76.58; H, 6.14; N, 5.95; Found: C, 76.51; H, 6.07; N, 6.01.

Synthesis of 9-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-9H-carbazole (4). Carbazole (5 g, 30 mmol), 2,7-dibromo-9,9-dioctyl-9H-fluorene (22 g, 40 mmol), CuI (1 g, 5.2 mmol), K<sub>2</sub>CO<sub>3</sub> (6.2 g, 45 mmol), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU, 2 ml), 18-crown-6 (0.32 g, 1.2 mmol) were put in 100 mL flask with 50 mmol dichlorobenzene. The mixture was heated to 170 °C for 24 h on the nitrogen atmosphere. After reaction, the solvent was removed and purified by chromatography on silica gel. Yield, 38%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 0.74-0.90 (m, 10H), 1.1-1.3(m, 20H), 1.97-2.06 (m, 4H), 7.32-7.39 (m, 2H), 7.43-7.50 (m, 4H), 7.53-7.61 (m, 4H), 7.64-7.70 (m, 1H), 7.89-7.94 (m, 1H), 8.21(d, 2H, *J*=3.6 Hz); ESI-MS (m/z): 633.1, 635.3 (M<sup>+</sup>+1).

Synthesis of 4-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-N,N-diphenylaniline (5). 2,7dibromo-9,9-dioctyl-9H-fluorene (8.2 g, 15 mmol), (4-(diphenylamino)phenyl)- boronic acid (2.9 g, 10 mmol) and  $PdCl_2(PPh_3)2$  (100 mg, 0.14 mmol) was added to a 250 ml flask. The toluene (50 ml) and 2M K<sub>2</sub>CO<sub>3</sub> (aq, 20 ml) were added under argon atmosphere. The mixture was stirred at 100 °C for 24 h. After cooling, extraction with DCM, the organic layer was collected and dried with MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was absorbed onto silica. Chromatography on silica gel with gradient elution (PE/DCM) and a white solid was gotten (3.5 g, yield, 49%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  [ppm]: 10.1 (s, 1H), 7.91 (d, 2H, *J*=8.14 Hz), 7.71 (d, 2H, *J*=8.40 Hz), 7.50 (d, 2H, *J*=8.67 Hz), 7.30-7.24 (m, 4H), 7.13 (d, 6H, *J*=7.36 Hz), 7.06 (t, 2H, J=7.35 Hz). ESI-MS (m/z): 350.1 (M<sup>+</sup>+H<sup>+</sup>); ESI-MS (m/z): 711.2, 713.1 (M<sup>+</sup>+1).

Synthesis of 9-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H- fluoren-2yl)-9H-carbazole (6). 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (3.15 g, 9 mmol), PdCl<sub>2</sub>(dppf) (0.22 g, 0.27 mmol) and Potassium acetate (2.52 g, 27 mmol) were put into a two-neck round-bottom flask equipped with a stirrer and reflux condenser. 1,4-dioxane (40 mL) was added and the mixture was stirred under nitrogen for 10 min. After that compound 4 (3.2 g, 5.0 mmol) was added and the mixture was kept at 85 °C for 10 h. After cooling to room temperature, the mixture was extracted with ethyl acetate followed by purification by column chromatography on silica gel with ethyl acetate/hexane (v/v, 1:3) as the eluent to offer a white solid. Yield: 3.3 g, 97%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 0.69-0.87 (m, 10H), 1.05-1.25(m, 20H), 1.44 (s, 12H), 1.96-2.14 (m, 4H), 7.33 (t, 2H, *J*= 6.84 Hz), 7.42-7.50 (m, 4H), 7.53-7.59 (m, 2H), 7.78-7.86 (m, 2H), 7.87-8.0 (m, 2H), 8.20 (d, 2H, *J*= 3.6 Hz); ESI-MS (m/z): 682.2 (M<sup>+</sup>+1).

Synthesis of 4-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H- fluoren-2-yl)-N,N-diphenylaniline (7). The synthetic process of compound 7 is the same with the way of compound 6. Yield: 6.22 g, 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 0.65-0.74 (m, 4H), 0.81-0.88 (m, 6H), 1.04-1.26 (m, 20H), 1.45 (s, 12H), 2.0-2.12 (m, 4H), 7.08 (t, 2H, *J*=7.11Hz), 7.18-

7.24 (m, 6H), 7.29-7.35 (m, 4H), 7.57-7.64 (m, 4H), 7.73-7.90 (m, 4H); ESI-MS (m/z): 759.2 (M<sup>+</sup>+1).

Synthesisof2,8-bis(7-(9H-carbazol-9-yl)-9,9-dioctyl-9H-fluoren-2-yl)-6,6,12,12-tetrakis(6-(9H-carbazol-9-yl)hexyl)-6,12-dihydrodiindeno[1,2-b:1',2'-e]pyrazine

(**DCzDIPY-TCz**). The synthetic process of DCzDIPY-TCz is the same with the way of compound 5. Yield: 0.363 g, 46%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ [ppm] 0.68-0.91 (m, 28H), 1.10-1.23 (m, 56H), 1.60-1.68 (m, 8H), 2.05-2.18 (m, 12H), 2.33-2.45 (m, 4H), 4.04-4.14 (m, 8H), 7.16 (t, 8H, *J*= 7.33 Hz), 7.21-7.26 (m, 8H), 7.36 (t, 12H, *J*= 7.47 Hz), 7.45-7.54 (m, 10 H), 7.60-7.65 (m, 4H), 7.73-7.80 (m, 6H), 7.84 (d, 2H, *J*= 4.01 Hz), 7.92 (d, 2H, *J*= 3.89Hz), 7.99-8.09 (m, 10H), 8.23 (d, 2H, *J*=4.01Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ [ppm] 152.9, 152.0, 150.9, 142.8, 141.1, 140.4, 140.3, 139.9, 137.8, 136.6, 126.6, 125.9, 125.5, 123.4, 122.7, 121.9, 121.5, 121.0, 120.2, 119.9, 118.6, 109.8, 108.5, 55.6, 53.0, 42.7, 40.3, 38.4, 31.8, 30.0, 29.5, 29.3, 29.2, 28.7, 26.6, 24.0, 22.6, 14.1; ESI-MS (m/z): 2361.3 (M<sup>+</sup>+1); Anal. Calcd for C<sub>172</sub>H<sub>182</sub>N<sub>8</sub>: C, 87.49; H, 7.77; N, 4.75; Found: C, 87.51; H, 7.71; N, 4.78.

Synthesis of 4,4'-((6,6,12,12-tetrakis(6-(9H-carbazol-9-yl)hexyl)-6,12-dihydrodi- indeno[1,2b:1',2'-e]pyrazine-2,8-diyl)bis(9,9-dioctyl-9H-fluorene-7,2-diyl))bis(N,N-diphenylaniline) ( DTPADIPY-TCz). The synthetic process of DTPADIPY-TCz is the same with the way of compound 5. Yield: 0.454 g, 52%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 0.58-0.88 (m, 28H), 1.04-1.24 (m, 56H), 1.60-1.68 (m, 8H), 1.09-2.20 (m, 12H), 2.30-2.44 (m, 4H), 4.04-4.14 (m, 8H), 7.11-7.26 (m, 28H), 7.29-7.37 (m, 18H), 7.59-7.64 (m, 8H), 7.67-7.88 (m, 14H), 8.01-8.08 (m, 8H), 8.19-8.25 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm] 151.9, 151.7, 150.8, 150.7, 147.7, 147.1, 142.9, 140.6, 140.2, 139.7, 139.5, 135.5, 129.3, 127.8, 126.3, 125.5, 124.4, 124.0, 122.7, 121.5, 121.0, 120.2, 118.6, 108.5, 55.4, 53.0, 42.8, 40.4, 38.4, 31.8, 30.0, 29.7, 29.5, 29.2, 28.6, 26.6, 23.9, 22.6, 14.2; ESI-MS (m/z): 2517.2 (M<sup>+</sup>+1); Anal. Calcd for C<sub>184</sub>H<sub>194</sub>N<sub>8</sub>: C, 87.78; H, 7.77; N, 4.45; Found: C, 87.72; H, 7.75; N, 4.53.

#### 3. Results and discussion

#### 3.1 Synthesis

The synthetic routes of DCzDIPY-TCz and DTPADIPY-TCz are shown in Scheme 1. The synthesis process consists of three steps and two steps of precursor preparation process, then the target molecules were prepared with a Suzuki coupling of 6,6,12,12-Tetrakis(6-(9*H*-carbazol-9-yl)hex-yl)-2,8-Dibromo-6,12-Dihydrodiindeno[1,2-b:1',2'-e]pyrazine (**3**) and 9-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-2-yl)-9*H*-carbazole (**6**), 4-(9,9-dioctyl-7-(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-yl)-9*H*-fluoren-2-yl)-*N*,*N*-Diphenylaniline (**7**).All of the compounds were identified with <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectrometry, spectroscopy, and elemental analysis.

#### 3.2 Theoretical calculations

To see clearly their geometrical structures and electron density distributions, density functional theory (DFT) calculations were performed with the B3LYP/6-31G(d, p) basis set by using the Gaussian 03 program. Their ground geometries and electron densities of HOMOs and LUMOs are shown in Figure 1. Obviously, both of them have two large torsion angles in the optimized geometries, one is between the DIPY core and the fluorene planes, another locates on the fluorene plane and carbazole/triphenylamine. There large angles are beneficial for suppressing their fluorescent quenching induced by the aggregation in the solid states.<sup>[22]</sup> The calculated HOMOs and LUMOs of DCzDIPY-TCz and DTPA DIPY-TCz are separately distributed on the triphenylamine fluorene/carbazole fluorene and the DIPY units, respectively. The separation of the HOMO and LUMO is efficient for carrier transfer and balance in the emitter layers of OLEDs.<sup>[23]</sup>



HOMO(677)/-4.91 eV

LUMO(678)/-2.03 eV

**Figure 1.** The HOMO and LUMO electron cloud spatial distributions of DCzDIPY-TCz and DTPADIPY-TCz using Gaussian 03 program calculations.

#### 3.3 Thermal properties

Figure 2a plots the cures of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in the profiles of TGA, DCzDIPY-TCz and DTPADIPY-TCz exhibit suitable thermal stability with 5% weight loss at a temperature of ~373 °C. The results suggest both of them are stable for fabricating electroluminescent devices. As shown in the insert Figure 2a, it can be seen that both of them have an endothermic peak at ~104 °C corresponding to glass transition, implying the formation of amorphous film at temperatures below 104 °C with spin-coating method.

#### 3.4 Electrochemical properties

Electrochemical properties of DCzDIPY-TCz and DTPADIPY-TCz were tested by cyclic voltammetry (CV) and their voltammogram was presented in Figure 2b. Both of them displayed similarly reversible oxidation behaviors owing to the homologous oxidation of triphenyl-amine and carbazole units. Their HOMO levels are estimated from the onset of oxidation potentials ( $E^{ox}$  vs. saturated calomel electrode) with the values of -5.45 eV (DTPADIPY-TCz) and -5.55 eV (DCzDIPY-TCz). Their LUMO levels are calculated from the absorption onsets (film absorption) and HOMOs. The values are -2.82 eV for DTPADIPY-TCz and -2.88 eV for DCzDIPY-TCz, respectively.



**Figure 2.** a) TGA and DSC (insert) profiles of DCzDIPY-TCz and DTPADIPY-TCz; b) Cyclic voltammogram of DCzDIPY-TCz and DTPADIPY-TCz vs SEC.

#### 3.5 Photophysical properties

UV-vis absorption, photoluminescence (PL) spectra in solution and film of DCzDIPY-TCz and DTPADIPY-TCz are shown in Figure 3. Both of them have two similar absorption located at ~420 nm and ~350 nm, indicating the same electronic transitions. Compared with their absorption in solution and film, a red-shift about 20 nm is observed due to the molecular aggregation in their film states. In accordance with the onset of their film absorptions, their optical band gaps are 2.67 eV for DCzDIPY-TCz and 2.63 eV for DTPADIPY-TCz. The

maximum film PL peaks of DCzDIPY-TCz and DTPADIPY-TCz are in the range of 450–480 nm. DTPADIPY-TCz shows a bathochromic emission about 20 nm in comparison with its counterpart DCzDIPY-TCz, which can be attributed to the strong electron-donating property of triphenylamine. Additionally, their solution emission appears obvious solvatochromic shift with the changes of solvent polarity (Figure 3b and Figure S1), suggesting the occurrence of charge transfer on photoexcitation.<sup>[24]</sup> In particular, we can see that the FWHM of DTPADIPY-TCz in dichloromethane broadens while redshifts by 20 nm relative to THF, possibly due to the different dynamic processes in dichloromethane. The phosphor is excited to produce a dipole moment, causing the dichloromethane molecules to be disturbed and reassembled into a particular solvent cage. It is possible that the special solvent cage of this phosphor in dichloromethane make the PL spectrum different.



**Figure 3.** a) UV-vis absorption in solution and film, PL spectra in film; b) PL spectra of T DTPADIPY-TCz in different solvents.

#### 3.6 Electroluminescence

The electroluminescent properties were investigated by fabricating the solution-processed double-layer devices with the structure of ITO/PEDOT:PSS(40 nm)/DCzDIPY-TCz or DTPADIPY-TCz (40 nm)/TPBi (50 nm)/LiF (1 nm)Al (120 nm), in which ITO, PEDOT:PSS and TPBI are abbreviations of indium tin oxide, poly(3,4-ethyl-enedioxythiophene): polystyrene sulfonate, and 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene, respectively. The current density-voltage-luminance, efficiencies-brightness, and electroluminescent (EL) characteristics are shown in Figure 4 and Figure S2. Their EL spectra shows typical emissions from DCzDIPY-TCz and DTPADIPY-TCz compared with their PL ones, suggesting that carriers recombination is effectively restricted in DCzDIPY-TCz and DTPADIPY-TCz. The device using DCzDIPY-TCz as emitter exhibits blue electroluminescence with CIE coordinates of (0.24, 0.14) and a maximum power efficiency (PE) of 0.35 lm W<sup>-1</sup>. While the device based on DTPADIPY-TCz shows better device efficiencies with a maximum PE of 2.20  $\text{Im W}^{-1}$ , which is a higher level among the reported to date for solution-processable fluorescent OLEDs.<sup>[25,26]</sup> As we can see in Figure 4 e), the maximum external quantum efficiency (EQE) of DCzDIPY-TCz and DTPADIPY-TCz are 0.53 and 1.15%, respectively. They all exhibited a low efficiency roll-off blow 1000 cd m<sup>-2</sup>, TPA efficiency roll-off smaller, especially. As the strong interaction between triphenylamine with DIPY, the EL of DTPADIPY-TCz shifts to be a bluish green emission with CIE coordinates of (0.21, 0.35). In comparison with their PEs, DTPADIPY-TCz-based device is twice higher than that of DCzDIPY-TCz by only replacing carbazole to triphenylamine. This may be attributed to the difference of hole injection barriers (the interface of PEDOT:PSS/emitting-layer) and carriers transfer. Due to the different hole injection barriers, their turn-on voltages alter largely with 3.8 V for DTPADIPY-TCz and 5.5 V for DCzDIPY-



TCz. Carriers transfer properties were also important to the high power efficiency. To find hole and electron transfer characteristics of

**Figure 4.** a) Current density–voltage–luminance characteristics; b) Current efficiency and power efficiency versus brightness curves; c) Electroluminescent spectra of DCzDIPY-TCz and DTPADIPY-TCz; d) Current density–voltage profiles of hole-only and electron-only devices of DTPADIPY-TCz; e) V-EQE characteristics of DCzDIPY-TCz and DTPADIPY-TCz-based single-layer OLEDs.

Device	V <sub>on</sub> <sup>a</sup> (V)	CE <sub>max</sub> (cd A <sup>-1</sup> )	x PE <sub>max</sub> (lm W <sup>-1</sup> )	EQE <sub>max</sub> (%)	CIE <sup>b</sup> (x, y)	at 100 cd m <sup>-2</sup>			Č	at 1000 cd m <sup>-2</sup>			
						V (V)	CE (cd A <sup>-1</sup> )	PE (lm W <sup>-1</sup> )	EQE (%)	V (V)	CE (cd A <sup>-1</sup> )	PE (lm W <sup>-1</sup> )	EQE (%)
Cz	5.49	0.83	0.35	0.53	0.243,0.142	6.65	0.56	0.35	0.35	7.67	0.83	0.34	0.53
TPA	3.84	2.49	2.20	1.15	0.207,0.349	5.18	2.36	1.43	1.09	6.74	1.90	0.89	0.91

a: at the luminance of 1 cd  $m^{-2}$ ; b: at the current density of 10 mA cm<sup>-2</sup>.

**Table 1.** Electroluminescent characteristics of the devices with DCzDIPY-TCz and DTPADIPY-TCz-based.

DTPADIPY-TCz, we also fabricated the hole-only and electron-only devices with configurations of ITO/PEDOT:PSS (40 nm)/DTPADIPY-TCz (40 nm)/MnO<sub>3</sub> (10 nm)/Al (100 nm) and ITO/Al(100 nm)/DTPADIPY-TCz (40 nm)/TPBi (50 nm)/LiF (1 nm)/Al (100nm) (see the Figure. 4d). Because the environment of the device is low electric field conditions, the device structure containing only hole or electron transport material is prepared, and the hole or electron transport capacity is measured by steady current current-voltage method. In other words, it is examined whether their carrier mobility is matched and the carrier mobility follows the following formula:  $J = \frac{9}{8} \varepsilon_r \varepsilon_0 L \frac{V^2}{d^3}$ . The *L* is the carrier mobility,  $\varepsilon_r$  and  $\varepsilon_0$  are dielectric constants, *J* is current density, *V* is applied voltage, and *d* is device thickness. Then we use the Origin software according to Figure 4 d) to calculate the electron and hole mobility. The electron mobility is  $4.98 \times 10^{-4}$  cm<sup>-2</sup>/V•S, and the hole mobility is  $1.68 \times 10^{-4}$  cm<sup>-2</sup>/V•S. Thus, their carrier mobility is very similar, indicating that DTPADIPY-TCz-based devices exhibit balanced holes and electrons transport. Therefore, the balanced carriers transfer and suitable hole injection barrier collectively contribute to the improvement of power efficiency. Notably, at high brightness of 100 and 1000 cd m<sup>-2</sup>, the power efficiencies of DTPADIPY-TCz still keep as 1.43 lm W<sup>-1</sup> and 0.89 lm W<sup>-1</sup>, DCzDIPY-TCz still keep as 0.35 lm W<sup>-1</sup> and 0.34 lm W<sup>-1</sup>, respectively, implying a relatively low efficiency roll-off.

#### 4. Conclusions

In conclusion, two novel peripheral carbazole substituted Diindenopyrazinediones have been demonstrated for high-efficient and solution-processable OLEDs. By fine-tuning their carriers transfer and hole injection barriers, double-layer solution-processed device based on DTPADIPY-TCz shows highly efficient bluish green emission with a maximum power efficiency (PE) of 2.30 lm  $W^{-1}$  and a relatively low efficiency roll-off. Our results show that peripheral carbazole substituted Diindenopyrazinediones could be used as a promising unit for constructing efficient emitters of solution-processed OLEDs to reduce the cost of industrialization.

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# Highlights

1. We have designed and synthesized two kinds of solution-processable Substituted Diindenopyrazinediones with Polyalkyl-carbazole symmetrically blue fluorescent OLED materials with novel structure and improved carrier transport and luminescence properties.

2. Solution-processed device based on DTPADIPY-TCz shows highly efficient bluish green emission with a maximum power efficiency (PE) and current efficiency (CE) of 2.20 lm W<sup>-1</sup> and 2.49 cd A<sup>-1</sup>, which is still the initial 40% and 76% of power efficiency and current efficiency even at 1000 cd/m<sup>2</sup>. Means that the two molecules with very low efficiency roll-off.

3. By fine-tuning their carries transfer and injection barriers, solution-processed device based on DTPADIPY-TCz shows highly efficient blue emission and a relatively low efficiency roll-off of external quantum efficiency(EQE).