Substituted Diindenopyrazinediones with symmetrical Polyalkyl-carbazole for high-efficiency blueish green solution-processable OLED

Lei Zhang [a, c, 1], Yongqi Bai [a, 1], Zhiyang Liu [a], Weigang Jiang [a], Tao Lei [a], Rongjuan Yang [a],
Amjad Islam [a], Yumei Zhang [b], Xinhua Ouyang [a], Ziyi Ge [a, *]

[a] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[b] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, China
[c] Nano Science and Technology Institute, University of Science and Technology of China, Suzhou 215123, China

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 lm W^{-1}, which is among the highest reported to date for solution-processable fluorescent OLEDs with a relatively low efficiency roll-off.

© 2017 Elsevier Ltd. All rights reserved.

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 [1–3]. Generally, solution-processable OLEDs were constructed with a single or double-layer architectures due to the restriction of intermixing of layers [4–6]. For the single-layer non-dopant devices, their performance usually is inferior to their counterparts of evaporated OLEDs [7–9]. While these double-layer structure

devices, evaporated an electron-transporting or hole-blocking layer behind the solution-processed emitters, show similar efficiencies with vacuum-deposited OLEDs [10,11]. 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 [12]. Some significant advances have been achieved with the maximal power efficiencies of ~5 lm W^{-1} [13]. 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 [14]. To date, almost of them are mainly concentrated on fluorene and its derivatives [15], 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 [16]. 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^{-1} and 4.6%; mobility, 0.17 cm^{2}V^{-1}s^{-1}) [17,18]. However, DIPY core possessing rigid and planar structures facilitates to form molecular stacking in their film states [19], 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 [20] 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 [21] 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^{-1} and a relatively low efficiency roll-off, which is among the highest performance for solution-processable fluorescent OLEDs.

2. Experimental section

2.1. Material and method

^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer at 400 MHz and ^{13}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

2.2.1. 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 h. The reactant was filtered and rinsed with CH$_3$OH, Pale power 1 was obtain with the yield of 71% (20.2 g). ^{1}H NMR (400 MHz, CDCl$_3$) δ [ppm] 3.78 (s, 2H), 7.67 (d, 2H, *J* = 5.25 Hz), 7.89 (s, 1H), 12.73 (s, 1H).

2.2.2. 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$_3$OH, diethyl ether and then 2 was obtained. The yield was 62%. ^{1}H NMR (400 MHz, CDCl$_3$) δ [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).

2.2.3. 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$_4$, purified with chromatography on silica gel. The white power was obtained with the yield of 0.34 g, 12%. ^{1}H NMR (400 MHz, CDCl$_3$) δ [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* = 3.80 Hz). ESI-MS (*m/z*): 1410.3, 1411.2. (M$^+$+1). Anal. Calcd for C$_{90}$H$_{86}$Br$_2$N$_6$: C, 76.58; H, 6.14; N, 5.95; Found: C, 76.51; H, 6.07; N, 6.01.

2.2.4. 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-9*H*-fluorene (22 g, 40 mmol), CuI (1 g, 5.2 mmol), K$_2$CO$_3$ (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%. ^{1}H NMR (400 MHz, CDCl$_3$) δ [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$^+$+1).

2.2.5. Synthesis of 4-(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)-N,N-diphenylaniline (5)

2,7-dibromo-9,9-dioctyl-9*H*-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 2 M K$_2$CO$_3$ (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$_4$. 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%). ^{1}H NMR (400 MHz, CDCl$_3$), δ [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$^+$+H$^+$); ESI-MS (*m/z*): 711.2, 713.1 (M$^+$+1).

2.2.6. Synthesis of 9-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H- fluoren-2-yl)-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$_2$(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