Dyes and Pigments 132 (2016) 94–102

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Solution-processable, single-layer, blue organic light-emitting diodes employing dual emitting cores of hybridized local and charge-transfer units

Yongqi Bai [a, b], Ling Hong [a], Tao Lei [a], Lei Zhang [a], Xinhua Ouyang [a, **], Zhiyang Liu [a], Yali Chen [b], Weishi Li [c, ***], Ziyi Ge [a, *]

[a] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China
[b] Department of Chemistry, Shanghai University, Shanghai 200444, PR China
[c] Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

ARTICLE INFO

Article history:
Received 3 March 2016
Received in revised form
12 April 2016
Accepted 26 April 2016
Available online 27 April 2016

Keywords:
Blue OLEDs
Dual emitting cores of hybridized local and charge-transfer
Solution-processability
Single-layer structure

ABSTRACT

Two novel dual emitting core hybridized local and charge-transfer emitters of 4′,4‴-(1,1′-((9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(4,1-phenylene))bis(1H-p-henanthro[9,10-d]imidazole-2,1-diyl))bis(N,N-diphenyl-[1,1′-biphenyl]-4-amine) and 4′,4‴-(1,1′-((9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(3,1-phenylene))bis(1H-phenanthro[9,10-d]imidazole-2,1-diyl))bis(N,N-diphenyl-[1,1′-biphenyl]-4-amine) were designed and synthesized by introducing two hybridized local and charge-transfer units for single-layer, solution-processable, and blue organic light-emitting diodes (OLEDs). Their absorption, photoluminescence, hybridized local and charge-transfer characteristics, thermal stability and electrochemistry were systematically studied. The single-layered devices by using them as emitters showed efficient blue emission with a maximum brightness 5521 cd/m^2 for 4′,4‴-(1,1′-((9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(4,1-phenylene))bis(1H-p-henanthro[9,10-d]imidazole-2,1-diyl))bis(N,N-diphenyl-[1,1′-biphenyl]-4-amine) and 4403 cd/m^2 for 4′,4‴-(1,1′-((9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(3,1-phenylene))bis(1H-phenanthro[9,10-d]imidazole-2,1-diyl))bis(N,N-diphenyl-[1,1′-biphenyl]-4-amine). The maximal efficiencies of the former were up to 3.71 cd/A, 2.33 lm/W, and 2.88%. Furthermore, at the high luminescence, the device still indicated good performance with relative low efficiency roll-off. The relationships of structures and properties were also discussed. Most importantly, we provided a new method to construct solution processable small molecules for highly efficient single-layer OLEDs.

Hybridized local and charge-transfer (HLCT) materials have been given widespread attention because the high efficiency can be achieved by simultaneously utilizing the large overlap of local excited (LE) and the broad orbital dipole of charge transfer (CT) states [1–3]. For HLCT materials, LE states produce the high fraction of single excitons and CT states lead to highly-efficient fluorescence radiative decay [4]. In this regard, the exciton utilizing efficiency (EUE) would have abilities to obtain nearly 100% internal quantum efficiency. To achieve compatible and combined of LE and CT excitons, the HLCT materials should be contained at least a twisted angle with donor-acceptor structures, which can manage effectively the mixtures of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well as the LE and CT interaction between donor and acceptor. Based on the strategy of molecular design, many HLCT materials have been demonstrated and showed good performance [5,6]. For example, N,N-diphenyl-4′-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)-[1,1′-biphenyl]-4-amine is one of the most well-known donor–acceptor type HLCT materials with electron-donating tirphenylamine and electron-withdrawing phenanthro[9,10-d]imidazole moieties. Obviously, a twisted angle (~20–55°) located on biphenyl linker were found to be the origin of the CT and LE intercross. More importantly, its HOMO and LUMO partially delocalize to the whole molecule, instead of there being a fully

---

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: ouyangxh@nimte.ac.cn (X. Ouyang), liws@mail.sioc.ac.cn (W. Li), geziyi@nimte.ac.cn (Z. Ge).

http://dx.doi.org/10.1016/j.dyepig.2016.04.042
0143-7208/

separation. By using it as emitter for electroluminescence (EL), the device exhibited a maximum current efficiency (CE) of 5.66 cd/A and external quantum efficiency of 5.02% [6]. Subsequently, several derivatives of the imidazole and tirphenylamine moieties were synthesized and the different emission spectrum of the HLCT materials was obtained [7]. In addition, some of other structures derived from the donor–acceptor compound were also reported, including carbazole [8–10], triphenylamine [11–13], and phenoxazine [14] moieties as the donor units, and phenanthrene [15], anthracene [16], quinazoline [17], acridine [18], benzo[c][1,2,5] thiadiazole and naphtha[2,3-c][1,2,5]- thiadiazole [19] moieties as the acceptor units. By analyzing these HLCT materials, all of them should have a strong electron-donating moieties with high-lying HOMO level, while the corresponding electron-withdrawing abilities of acceptors were low with the twisted linkers. Although these materials showed high-efficient EL with maximum external quantum efficiency (EQE) > 5.0%, corresponding to the $\chi_S > 25\%$, all of these devices are constructed with complicated multiply structures and deposed by thermal vacuum technology, which is cost-consumption as well as low qualified rate. In order to solve the problem, the development of solution-processability and single-layer HLCT-based devices will provide an effective alternative if the high efficiency can also be simultaneously kept. Therefore, it is highly desirable to develop novel HLCT materials for the solution-processable, single-emission layer OLEDs. However, it is still a challenge to researchers.

In this work, two novel HLCT materials with dual emitting cores of hybridized local and charge-transfer units, 4′,4‴-(((9-(heptadecan-9-yl)-9H-carbazole- 2,7-diyl)bis(4,1-phenylene))bis(1H-phenanthro[9,10-d]imidazole-1,2-diyl))bis(N,N-diphenyl-[1,1′-biphenyl]-4-amine (p-DPABI-Cz) and 4′,4‴-(((9-(heptadecan-9-yl)-9H- carbazole-2,7-diyl) bis(3,1-phenylene))bis(1H-phenanthro [9,10-d]imidazole-1,2-diyl)) bis(N,N-diphenyl-[1,1′-biphenyl]-4-amine) (m-DPABI-Cz), were designed and synthesized as shown in Scheme 1. Both of them showed suitable thermal stabilities, ideal fluorescence, high fluorescent quantum yield, appropriate energy levels, and a HLCT exited state with intercrossed LE and CT characteristics. Furthermore, the solution processable single-layer OLEDs were fabricated and exhibited a blue emission with CIEs of (0.16, 0.17) and (0.16, 0.16) for p-DPABI-Cz and m-DPABI-Cz, respectively. The devices based on p-DPABI-Cz as the emitting layer achieved an external quantum efficiency (EQE) of 2.88%, current efficiency (CE) of 3.71 cd A^{-1}, and power efficiency (PE) of 2.32 lm W^{-1}, which is among the best efficiencies of solution-processable single-layer blue devices. Furthermore, the relationship between the linked position and electroluminescent performance, their ground-states geometries, photophysical properties and device analyses were studied.

1. Experimental

1.1. General information

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. NMR spectra (^{1}H NMR & ^{13}C NMR) was recorded on a Bruker DRX-400 spectrometer. ESI-MS was measured on a FINNIGAN Trace DSQ mass spectrometer. The elemental analyses were tested on a PerkineElmer 2400 II elemental analyzer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Netzsch DSC204 instrument and a TA Q500 instrument, respectively. UV–Vis and fluorescent emission were done on a Shimadzu UV-2550 and Shimadzu RF-5301PC spectrophotometers.

*1.1.1. Synthesis of 4′-(diphenylamino)-[1,1′-biphenyl]-4-carbaldehyde (**1**)*

A mixture of 4-bromobenzaldehyde (3.7 g, 20 mmol), (4-(diphenylamino)phenyl)boronic acid (5.32 g, 18.4 mmol) and $PdCl_2(PPh_3)_2$ (100 mg, 0.14 mmol) was added to a 250 ml flask. The THF (70 ml), 2 M K_2CO_3 (aq, 20 ml) and ethanol (20 ml) was added under argon atmosphere. The mixture was stirred at 78 °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 from 7:1 to 3:1, v/v) and a yellowish solid was gotten (4.62 g, yield, 72%). ^{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^+).

*1.1.2. Synthesis of 4′-(1-(4-bromophenyl)-1H-phenanthro[9,10-d] imidazol-2-yl)-N,N- diphenyl-[1,1′-biphenyl]-4-amine (**2**)*

Phenanthrene-9,10-dione (1.56 g, 7.5 mmol), ammonium acetate (1 g, 13 mmol), and compound **1** (1.75 g, 5 mmol) were dissolved in 60 ml acetic acid under argon at room temperature. After 30 min, 4-bromoaniline (2.24 g, 13 mmol) was added and stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was diluted with 300 ml water, filtered and then the residue was washed with ethanol. The solid was dissolved in 70 ml DCM, washed with aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel with gradient elution (from PE:DCM = 2:1 to DCM:EA = 10:1, v/v) and a yellowish solid was obtained (2.84 g, yield, 82%). ^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 8.88 (d, 1H, J = 8.06 Hz), 8.78 (d, 1H, J = 8.38 Hz), 8.71 (d, 1H, J = 8.28 Hz), 7.74 (d, 3H, J = 8.37 Hz), 7.66 (t, 1H, J = 7.28 Hz), 7.59 (d, 2H, J = 7.64 Hz), 7.55–7.53 (m, 3H), 7.48 (d, 2H, J = 8.22 Hz), 7.42 (d, 2H, J = 8.56 Hz), 7.35–7.22 (m, 6H), 7.12 (d, 6H, J = 7.70 Hz), 7.02 (t, 2H, J = 7.27 Hz). ESI-MS (*m*/*z*): 691.3, 693.2 (M^+). Anal. Calcd for $C_{45}H_{30}BrN$: C, 78.03; H, 4.37; N, 6.07; Found: C, 78.11; H, 4.41; N, 6.09.

*1.1.3. Synthesis of 4′-(1-(3-bromophenyl)-1H-phenanthro[9,10-d] imidazol-2-yl)-N,N- diphenyl-[1,1′-biphenyl]-4-amine (**3**)*

The synthesis of compounds **3** was followed the procedure of compound 2. A white solid was obtained with the yield of 1.18 g and 85.3%. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 8.95 (d, 1H, J = 7.03 Hz), 8.79 (d, 1H, J = 7.38 Hz), 8.71 (d, 1H, J = 7.38 Hz), 7.82–7.76 (m, 3H), 7.71–7.64 (m, 3H), 7.57–7.49 (m, 7H), 7.37–7.28 (m, 6H), 7.21 (d, 1H, J = 8.08 Hz), 7.16–7.14 (m, 5H), 7.07 (t, 2H, J = 7.20 Hz). ESI-MS (*m*/*z*): 692.1, 694.3 (M^++H^+). Anal. Calcd for $C_{45}H_{30}BrN$: C, 78.03; H, 4.37; N, 6.07; Found: C, 78.09; H, 4.39; N, 6.11.

1.1.4. Synthesis of 4′,4‴-(1,1′-((9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(4,1- phenylene))bis(1H-phenanthro[9,10-d]imidazole-2,1-diyl))bis(N,N-diphenyl-[1,1′-biphenyl]-4-amine) (p-DTPABI-Cz)

9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl- 1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.66 g, 1 mmol), compound **3** (1.73 g, 2.5 mmol) and Pd $(PPh_3)_4$ (100 mg, 0.14 mmol) were added to a 250 mL flask with 30 mL THF, 2 M K_2CO_3 (aq, 10 ml) and ethanol (10 ml) under argon atmosphere. The mixture was stirred at 78 °C for 24 h. After reaction, the mixture was extracted with DCM and organic layer was collected, dried with $MgSO_4$. The solvent was removed and the crude product was separated with chromatography, a yellowish solid was obtained (0.98 g, yield, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 8.99 (d, 2H, J = 7.43 Hz), 8.81 (d, 2H, J = 8.42 Hz), 8.75 (d, 2H, J = 8.18 Hz), 8.30 (t, 2H, J = 8.64 Hz), 8.03 (d, 5H, J = 7.57 Hz), 7.84–7.76 (m, 7H), 7.71 (d, 8H, J = 7.36 Hz), 7.58 (d, 6H, J = 8.27 Hz), 7.51 (d, 4H, J = 8.27 Hz), 7.45 (d, 2H, J = 8.39 Hz),