Organic Electronics 52 (2018) 22–31

Contents lists available at ScienceDirect

Organic Electronics

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

Systematically tuning of optoelectronic properties from electron donating to accepting substituents on bicarbazole/cyanobenzene hybrids: Host to dopant materials for phosphorescent and delayed fluorescence OLEDs

Xudong Cao[a,1], Xianping Zhang[a,1], Menghan Wang[a], Dengke Shi[a], Qingjing Wu[a], Youtian Tao[a,*], Wei Huang[a,b]

[a] Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing, 211816, PR China

[b] Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, PR China

ARTICLE INFO

Keywords:
Delayed fluorescence
Phosphorescence
Bicarbazole
Host
Dopant

ABSTRACT

Six bicarbazole/cyanobenzene hybrid compounds are designed and synthesized by changing the substituents from electron-donating phenylcarbazole (PCzCNBCz, **1**), phenoxy (OPCNBCz, **2**) and methyl (MCNBCz, **3**), neutral hydrogen (HCNBCz, **4**) to electron-accepting trifluomethyl (CF_3CNBCz, **5**) and cyano (DCNBCz, **6**) moieties, respectively at the same *meta*-position of cyanobenzene (refer to carbazole). The substituted units are judiciously designed with both conjugated (phenylcarbazole and cyano) and non-conjugated (phenoxy, methyl and trifluomethyl) units. Their HOMO and LUMO energy levels are rationally adjusted from 5.17 to 5.46 eV and 2.13–2.50 eV, respectively. Compared to bare hydrogen-attached **4** with triplet energy (T_1) of 2.7 eV, the conjugated moiety based **1** and **6** lowered T_1 to $\leq$2.50 eV, while other compounds bearing either non-conjugated donating or accepting units unexpectedly maintain T_1 as high as ~2.70 eV. Moreover, the singlet-triplet bandgaps (ΔE_{ST}) can also be tailored from 0.01 to 0.32 eV, therefore, delayed fluorescence characteristics are observed in the electron-accepting trifluomethyl and cyano substituted **5** and **6**. The high triplet **2**, **3** and **4** are served as host materials for blue phosphorescent OLEDs, with maximum external quantum efficiency (EQE) up to 20.5%, while **5** and **6** are used as sky-blue and greenish-blue emitters in delayed fluorescence OLEDs, with maximum EQE of 4.9 and 10.0%, respectively.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted massive attention from both the academic and industry communities due to their great potential applications in full color flat-panel displays and solid-state lightings [1–3]. Generally, according to spin statistics, the ratio for singlet to triplet excitons formed under the electrical excitation exhibits an approximate proportion of 1:3 [4a]. Therefore, due to the limited utilization of only singlet excitons, the internal quantum efficiency (IQE) of conventional fluorescent OLEDs [4b-4d] is limited to 25%. In addition, in the triplet heavy metal complexes-based phosphorescent OLEDs, a maximum IQE of 100% can be achieved by simultaneously harvesting both singlet and triplet excitons through intersystem crossing (ISC) [2]. Recently, tremendous efforts have been made on low-cost pure organic materials of thermally activated delayed fluorescence (TADF) which can also obtain 100% of IQE by up-converting triplet excitons to singlet excitons through reverse ISC [3,5–10].

In phosphorescent and TADF OLEDs, donor-acceptor (D-A) structured organic materials which comprise both electron-donating and electron-withdrawing moieties have been extensively investigated in emissive layers either as bipolar transport organic hosts or as efficient delayed fluorescence dopant emitters [11–17]. Molecular engineering on D-A type organic materials were mostly designed by the tailoring the relative position or the variation on the conjugated or non-conjugated bridge between the electron-donating and accepting moieties or the change on the number of donor and accepter moieties [18]. For example, Tao et al. reported a series of bipolar transport host materials with *ortho*-, *meta*- and *para*-linkage between various donors such as carbazole, triphenylamine or 9,9′-spirobifluorene and the electron-accepting oxadiazole units [19–24]. It is found that the triplet energy followed the sequence of *meta*- > *ortho*- > *para*-linkage, while the best performance was achieved in the twisted *ortho*-positioned

* Corresponding author.
E-mail address: iamyttao@njtech.edu.cn (Y. Tao).

[1] The two authors contributed equally to this work.

http://dx.doi.org/10.1016/j.orgel.2017.09.041
Received 11 August 2017; Received in revised form 18 September 2017; Accepted 22 September 2017
Available online 07 October 2017

compounds. In order to maintain high triplet energy of the bipolar hosts, various methodologies based on the reduce or break of the π-conjugation between electron-donating and electron-withdrawing groups by the introduction of a fluorene spacer [25], methyl steric group [26,27], non-conjugated σ-bonds linkage or the sp^3-hybridized Si bridge [28,29] have been presented. Besides, by increasing the number of acceptor group from one to two in carbazole/phosphine oxide containing bipolar hosts, the maximum EQE was improved from 17.1 to 19.2% in deep blue phosphorescent OLEDs [30,31]. Similar to the bipolar host materials mentioned above, several TADF materials were designed by changing the position and number of donor or acceptor moieties. For example, Adachi group reported a series of carbazole/dicyanobenzene based D-A compounds, the two carbazole-containing 2CzPN emits sky-blue light, while four carbazole based 4CzIPN, 4CzPN and 4CzTPN with the two accepting cyano units located at the *meta*-, *ortho*- and *para*-position of benzene ring, respectively exhibits green to greenish-yellow emission, further end-capping the 3,6-position of carbazole by methyl or phenyl, the emission color tuned to orange or orange-red [3]. To the best of our knowledge, simple and systematic modifications on D-A type organic materials by various electron-donating and accepting substituted units have been seldom reported.

Herein, we reported six bicarbazole/cyanobenzene hybrid compounds by introducing substituted groups from electron-donor, neutral hydrogen to accepter moieties to systematically tune the optoelectronic properties of the organic D-A type materials. The HOMO/LUMO energy levels, singlet and triplet energies could be rationally adjusted, and the function as either host for blue electro-phosphorescence or dopant emitter for delayed fluorescence OLEDs were also managed. The three high-triplet materials of OPCNBCz and MCNBCz or HCNBCz with non-conjugated phenoxy and methyl electron-donating substituents or neutral hydrogen were applied as hosts in blue phosphorescent OLEDs, and the best EQE of 20.5% was achieved in the most simple structure of HCNBCz based device, while the electron-withdrawing CF_3 and CN substituted narrow ΔE_{ST} of CF_3CNBCz and DCNBCz were served as delayed fluorescence dopant in sky-blue and greenish-blue OLEDs, exhibiting maximum EQE of 4.9 and 10.0%, respectively.

2. Experimental section

2.1. General information

^{1}H NMR and ^{13}C NMR spectra were measured on a MECUYRVX300 spectrometer. Mass spectra were carried out on a Bruker autoflex matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF). Elemental analyses of carbon, hydrogen and nitrogen were performed on a Vario EL III microanalyzer. Infra-red (IR) spectra were conducted on Nicolet 6700. UV–Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescence (PL) spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer. The transient lifetime was measured in PMMA neat film using the Edinburgh FLS-920 Instruments. The photoluminescence quantum yield (PLQY) was measured in toluene under air or N_2 using the Edinburgh FLS-920 Instruments. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 449C instrument. The thermal stability of the samples under the nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20 °C min^{-1} from 25 to 500–600 °C. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min^{-1} from 40 to 200–300 °C under the nitrogen atmosphere. The glass transition temperature (T_g) was determined from the second heating scan. Cyclic voltammetry (CV) was measured in the nitrogen-purged dichloromethane for oxidation scan using a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) was used as a supporting electrolyte. The conventional three-electrode configuration is employed, which consists of a platinum working electrode, a platinum wire auxiliary electrode and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s^{-1}. The onset potential of the new compounds was determined from the intersection of two tangents drawn at rising and background current of the cyclic voltammongram at first circle. The half-wave potential ($E_{1/2}$) value for Fc^+/Fc are calculated as the average of cyclic voltammetric anodic and cathodic peaks. The HOMO energy levels were calculated from the oxidation curves according to the formula: [4.8 eV + (E_{onset} - $E_{1/2(Fc/Fc)^+}$)]. And LUMO energy level was deduced from the energy band gap (E_g) and HOMO level.

2.2. Computational details

The geometrical and electronic properties of the six compounds were performed using the Gaussian 09 program package [32]. The calculation was optimized by means of the B3LYP [33,34] (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functional) with the 6-31G(d) [35] atomic basis sets. Molecular orbitals were visualized using Gauss view.

2.3. Device fabrication and measurements

Phosphorescent and TADF OLED devices were fabricated by vacuum thermal evaporation technology. All layers were grown on pre-cleaned ITO substrates with a sheet resistance of 10 Ω sq^{-1}. ITO surface was treated by oxygen plasma for 15 min. All the layers was deposited in a chamber without breaking vacuum (≈5 × 10^{-4} Pa) for sequential deposition of 10 nm of MoO_3, 40 nm of 4,4′-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)aniline] (TAPC), 20 nm of emitting layer (EML), 40 nm of 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB), 0.8 nm of LiF, and 200 nm of Al. The phosphorescent devices were investigated by the structure of ITO/MoO_3 (10 nm)/TAPC (40 nm)/1,3-Bis(*N*-carbazolyl)benzene (mCP) (5 nm)/**2–4**: bis[(4′,6′-difluorophenyl)-pyridinato-*N*,$C^{2'}$]iridium(III) picolinate (FIrpic) (20 nm, 10%)/TmPyPB (40 nm)/LiF (0.8 nm)/Al (200 nm) and the TADF devices were prepared with the configuration of ITO/MoO_3 (10 nm)/TAPC (40 nm)/mCP:**5** or **6** (20 nm, 10%)/TmPyPB (40 nm)/LiF (0.8 nm)/Al (200 nm). The active area was 16 mm^2.

All the measurements were carried out in ambient atmosphere. Current density-Voltage-Luminance (*J-V-L*) characteristics were measured by a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. Electroluminescent (EL) spectra were measured by a Spectrascan PR650 spectrophotometer. EQEs were calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution.

2.4. Synthesis

All the starting materials were commercially available from Energy Chemical. Synthesis of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9*H*-carbazole (BPCz) was followed by literature procedures [36]. All the ^{1}H NMR,^{13}C NMR and IR spectra have been listed in the supporting information.

2.4.1. PCzCNBCz (1)

Synthesis of C040: A mixture of 9*H*,9′*H*-3,3′-bicarbazole (500 mg, 1.50 mmol), 2-bromo-6-fluorobenzonitrile (661.9 mg, 3.31 mmol) and K_2CO_3 (0.99 g, 7.2 mmol) in dimethyl sulfoxide (DMSO) (6 mL) was stirred at 140 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water, filtered and then purified by column chromatography over silica gel with CH_2Cl_2/petroleum ether (1: 1) as eluent to afford a white solid (937 mg, 90%). ^{1}H NMR (300 MHz, $(CD_3)_2SO$, δ ppm): 8.74 (s, 2H), 8.44 (d, J = 3.0 Hz, 2H), 8.18 (d, J = 3.0 Hz, 2H), 8.01–7.92 (m, 6H), 7.53–7.32 (m, 8H); MALDI-TOF (m/z): 692.3 [M^+].

Synthesis of **PCzCNBCz**: A mixture of C040 (500 mg, 0.72 mmol),