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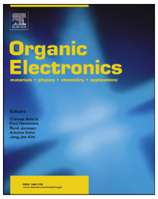

Simultaneously enhancement of quantum efficiency and color purity by molecular design in star-shaped solution-processed blue emitters

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ABSTRACT

A series of fluorene-free bipolar star-shaped molecules, **Sn-Cz-OXD** (n = 1–5), with increasing conjugated length in branches were synthesized as high efficient blue emitters for OLEDs. With the extension of conjugated branches, the solid PL quantum efficiency and external quantum efficiency of **Sn-Cz-OXD** significantly increased with longer spacer, while the emission spectrum of these materials exhibited a blue-shift with enhanced color purity due to the unique molecular design. All materials maintained exceptionally high thermal stability after prolonged heat treatment at 150 °C in air. The photophysical, electrochemical, thermal properties of these emitters were studied in relation to the molecular structure. Nondoped device based on **S4-Cz-OXD** with structure ITO/PEDOT:PSS/EML/TPBI/LiF/Al emitted stable pure blue light with CIE coordinates of (0.157, 0.146). It exhibited high current efficiency and external quantum efficiency of 4.96 cd A^{-1} and 4.20%, respectively. These values are among the best results for solution-processed non-doped blue device based on fluorene-free materials, indicating its potential for commercial applications.

1. Introduction

Solution-processed organic light-emitting diodes (OLEDs) have received tremendous attention in both academic research and potential commercial applications as low cost, flexible, large area full-color displays [1,2]. To realize full-visible-spectra display, blue emitters play an very important role because they not only supply blue emission as one of the three-primary colors, but also generate other colors by energy cascade to lower energy fluorescent or phosphorescent dopants [3]. However, efficient blue emitters are difficult to achieve due to their intrinsic wide band gap, which also causes the difficulty in injection of electron. As a result, blue OLEDs usually show inferior device performance compared with that of green and red OLEDs [4].

Recently, star-shaped blue emitters have attracted much research interest in the development of OLEDs since they can combine the advantages of both small molecules and polymers [5–8]. Compared with polymers, which are actually a mixture of different molecules, star-shaped oligomers have precise structures and are easy to purify and reproduce. On the other hand, they possess excellent solubility in organic solvents, which pave the way for solution-processing and fabrication of device. Besides, star-shaped molecules usually have high photoluminescent (PL) quantum efficiency than its linear counterparts [9] because their star-branched structure could suppress the intermolecular interaction, prevent aggregation and close packing, and reduce concentration quenching. Besides, star-shaped structure also facilitates the formation of amorphous film.

So far, most reported star-shaped blue emitters were oligofluorenes [8–12]. Yang et al. designed a series of starburst fluorene oligomers with a planar triphenylamine core to achieve a maximum CE of 3.83 cd A^{-1} and a maximum EQE of 4.19% [11]. Zou et al. synthesized a series of starburst oligofluorenes using phenyl as the core with a maximum EQE of 6.8% and CE of 5.4 cd A^{-1} [8]. Subsequently, they fine-tuned the turn-on voltage of 3.6 V by

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introducing electron donor diphenylamine end-caps to raise the HOMO level although this may reduce the spectral stability [12]. Improved device performance was also reported in star-like branched polyfluorene [13,14].

Although these star-shaped oligofluorenes were found to have good device efficiency, their practical application is hindered due to some remaining issues. Fluorene unit intrinsically has unstable EL spectrum so that an additional green emission could be observed during long time operation or thermal treatment in air due to the generation of ketonic defects [15–18]. Besides, fluorene is a strong p-type hole conductors, which might lead to an unbalanced charge injection and transportation. In order to develop better blue emitting material, recently we designed a fluorene-free star-shaped D-π-A blue emitter **S1-Cz-OXD** with excellent thermal stability. It showed much higher solid PL quantum efficiency compared with a linear counterpart of it and had great potential to be a good blue emitting material for OLEDs. This indicates to a new direction to develop star-shaped blue emitters with high stability and efficiency. D-π-A design was also introduced in emitter **S1-Cz-OXD**, endowing it with bipolar properties, to improve the charge transportation balance in the device [19].

To further optimization, extending of the conjugated branches of the star-shaped emitters is employed to enhance the solid PL quantum efficiency (Φ_f), since it would suppress the intermolecular interaction more effectively, as observed in many star-shaped oligofluorenes molecules [8,12,20]. Additionally, this was supposed to improve the color purity of the emission blue light. For the unipolar oligofluorene emitters, more fluorene repeat units would reduce the energy bandgap and cause red shift of the emission spectra due to extent π-conjugation [21–24]. For example, starburst oligofluorenes with a phenyl core exhibited red-shift of 43 nm when the amount of fluorene unit in branches increased from 1 to 4 [8]. However, in D-π-A molecules, when the conjugated spacer between donor and acceptor increased, there would be less overlap of electron orbit between donor and acceptor moiety. This would reduce the charge transfer ability from donor to acceptor and leading to blue-shift in PL spectrum [25]. Thus the undesired red-shift could be prevented.

In this paper, we present the strategy toward novel star-shaped blue emitters **Sn-Cz-OXD** (n = 2–5) with a tris(1,3,4-*oxadiazole*) phenylene as core, 3,6-di-*tert*-butyl-9H-carbazolas as terminal groups, and benzene units as the spacers. We also report on their high solid PL quantum efficiency, high thermal and electrochemical stability. Moreover, **S4-Cz-OXD** showed best performance and was selected as emitting material for the solution-processed non-doped OLED device. Compared with the control device based on **S1-Cz-OXD** (459 nm, 3.13%, 3.64 cd A^{-1}, 1.58 lm W^{-1}), **S4-Cz-OXD** based non-doped device exhibited a blue-shift emission at 452 nm, enhanced external quantum efficiency (EQE) of 4.20%, current efficiency (CE) of 4.96 cd A^{-1} and power efficiency (PE) of 2.08 lm W^{-1}.

2. Results and discussions

2.1. Molecular design and synthesis

Chemical structures of target molecules are shown in Scheme 2. These four star-shaped molecules were designed based on a radial donor-π-acceptor architecture, whereby the molecules can possess a bipolar characteristic favorable for more balanced charge injection/transport as well as higher carrier recombination efficiency [26]. The electron-rich carbazole and electron-deficient oxadiazole units were selected to serve as donor/acceptor units because of their excellent charge transport properties and good chemical stability.

Among these molecules, **S1-Cz-OXD** has been studied earlier [19]. It was found to have superior high solid PL efficiency and excellent thermal stability due to its molecular design. And the performance of its non-doped device was comparable with other solution processed blue OLEDs. Based on this molecule, **S2-Cz-OXD** and **S3-Cz-OXD** with increased arm length were designed to further suppress the molecular aggregation in order to achieve higher quantum efficiency in solid state. Considering the potential poor solubility of **S3-Cz-OXD** due to its rigid construction, **S4-Cz-OXD** with alkoxy chains in the arms were also designed to improve the solubility, and facilitate the solution processing in device fabrication.

The synthesis route is shown in Scheme 1. The synthesis of the core (**15**) and **S1-Cz-OXD** was described in an earlier paper [19]. 1,4-Hydroquinone (compound **1**) was reacted with bromohexane in DMF at 80 °C in the presence of K_2CO_3 to give compound **2** with 51% yield. Then compound **3** was obtained by reaction of compound **2** with bromine at a yield of 82% [27]. Subsequent treatment of the above bromides **3** with n-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave the corresponding boronic esters **4** [28]. Then compound **4** underwent a Suzuki reaction to produce compound **5** in a yield of 60%. An Ullmann reaction [29] was used to attach the phenyl bridge onto the nitrogen atom of 3,6-Di-*tert*-butyl-9H-carbazole (**6**) to give the *N*-phenylcarbazole derivatives **7** and **9** with 61% and 64% yields. The corresponding boronic esters **8** or **10** were again obtained by the similar procedure to that used for the synthesis of compound **4**. Boronic esters **8** react with bromides **3** and **5** through Suzuki reaction to produce bromides **11** and **13** with yields of 45% and 42%, which produce boronic ester **12** and **14** by the same esterification for the synthesis of compound **4.** A classic Suzuki reaction was used to coupling the bromides core (**15**) and different boronic esters **8**, **10**, **12** and **14,** and to give the corresponding target molecules **S2-Cz-OXD**, **S3-Cz-OXD**, **S4-Cz-OXD** and **S5-Cz-OXD**, respectively. The identity and purity of these compounds were confirmed by ^{1}H NMR, ^{13}C NMR spectra, MS (MALDI-TOF), and elemental analysis, as presented in the experimental part.

S1-Cz-OXD was tested to have good solubility. Its solubility was found to be around 25 mg mL^{-1} in $CHCl_3$ and 18 mg mL^{-1} in mixed solution of toluene: chlorobenzene (1:1). The solubility of **S2-Cz-OXD** in $CHCl_3$ reduced to 15 mg mL^{-1} and 12 mg mL^{-1}. And, for **S3-Cz-OXD**, the solubility fell to less than 3 mg mL^{-1} and less than 1 mg mL^{-1} in $CHCl_3$ as expected. **S4-Cz-OXD** and **S5-Cz-OXD**, with the solubilization function of six alkoxy chains, showed increased solubility of 20 mg mL^{-1} and 15 mg mL^{-1} in $CHCl_3$ as well as 10 mg mL^{-1} and 8 mg mL^{-1} in mixed toluene: chlorobenzene (1:1), respectively.

2.2. Properties and characterizations

2.2.1. Photophysical properties

Fig. 1a and **b** show the UV–visible absorption and PL spectra of the four molecules in diluted toluene solution. Their peak absorption and emission wavelengths as well as Φ_f are listed in Table 1. In dilute solution of toluene, the main absorption peaks are located at 369 nm, 356 nm, 348 nm, 350 nm and 349 nm for **S1-Cz-OXD**, **S2-Cz-OXD**, **S3-Cz-OXD**, **S4-Cz-OXD** and **S5-Cz-OXD**. And the peaks of their PL emission wavelengths (excited at 350 nm) are 422 nm, 420 nm, 418 nm, 428 nm and 425 nm, respectively. Both values showed slight blue-shift from **S1-Cz-OXD** to **S3-Cz-OXD** with the increase of arm length. This is because for D-π-A type molecules, the light absorption and emission are determined by the energy of intramolecular charge transfer from donor unit to acceptor unit. In this case, with the increasing arm length, the distance between donor and acceptor unit was also increased, this will weaken the