Tetrahedron 70 (2014) 6328–6336

Contents lists available at ScienceDirect

Tetrahedron

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

New universal bipolar host materials with fluorene as non-conjugated bridge for multi-color electrophosphorescent devices

Ejabul Mondal [a], Wen-Yi Hung [b,*], Hung-Chi Dai [b], Hsiao-Fan Chen [a], Pei-Yu Hung [a], Ken-Tsung Wong [a,c,*]

[a] Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
[b] Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 202, Taiwan
[c] Institute of Atomic and Molecular Science Academia Sinica, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 7 March 2014
Received in revised form 13 April 2014
Accepted 16 April 2014
Available online 25 April 2014

Keywords:
Fluorene
Carbazole
Bipolar host
Phosphorescent OLEDs
White OLEDs

ABSTRACT

Two novel bipolar hosts (**CzFCN2** and **CzDFCN**) comprising a hole-transport carbazole donor and electron-transport cyano-substituted fluorene acceptor have been synthesized, and their thermal, photophysical, and electrochemical properties were characterized. The non-conjugated linkage between the carbazole donor and the cyano-substituted fluorene acceptor provides excellent thermal/morphological properties and high triplet energies (E_T=2.86 eV) for both **CzFCN2** and **CzDFCN**. These bipolar hosts also exhibited reversible redox behavior, which makes them good candidates for the host material in efficient phosphorescent organic light-emitting diode (PhOLED) devices. Multi-color PhOLED devices incorporating **CzFCN**2 and **CzDFCN** as the universal host achieved maximum external quantum efficiencies (η_{ext}) as high as 10.7, 17.0, 17.2, and 17.6% for blue, green, yellow, and red devices, respectively. In addition, three-component white PhOLEDs (WOLEDs) based on **CzFCN2** and **CzDFCN** as host materials exhibited high color stabilities with η_{ext} as high as 10.5 and 12.4% and power efficiencies (η_p) of 20.5 and 26.7 lm W^{-1}, respectively.

1. Introduction

Organic light-emitting devices (OLEDs) have continued to attract the subject of broad research interest in recent years because of their potential applications in full-color, flat-panel displays and solid-state lighting.[1] Among these devices, tremendous efforts have been made in the improvement of phosphorescent organic light-emitting diodes (PhOLEDs) because they can render 100% internal quantum efficiency by harvesting both electro-generated singlet and triplet excitons for emission.[2] To fabricate highly efficient PhOLEDs, a host–guest strategy was employed with triplet emitters (guest) dispersed homogeneously within suitable organic matrix (host) to reduce aggregation quenching and triplet-triplet annihilation.[3] Thus, the design of new host materials has been of great importance for highly efficient PhOLEDs. Efficient host materials should meet the following requirements: (i) the host material should possess high triplet energy (E_T) than that of the emitting phosphor for the confinement of triplet excitons within the emitting layers to prevent detrimental reverse-energy transfer, (ii) the host material typically requires energy-level matching with neighboring layers for effective charge injections.[4], (iii) good and balance carrier-transport properties (ambipolarity) to allow the electron–hole recombination zone spreading over the emitting layer to reduce the efficiency roll-off, and (iv) good thermal and morphological stabilities to reach reasonable device lifetime.

In recent years, the introduction of tailor-made multifunctional bipolar host comprising of hole- and electron-transport components into a single molecule has been a promising strategy to give balanced charges into the emitting layer.[5] However, it is relatively difficult to obtain high triplet energies for bipolar hosts because the presence of electron-donating and -withdrawing moieties in a molecule easily lowers the band gap of the material via intramolecular charge transfer (ICT). This issue can be circumvented by adopting molecular design strategies such as incorporating steric groups,[6] utilizing *ortho* or *meta* linkages,[7] or introducing non-conjugated spacer between two moieties[8] for the interruption of effective π-conjugation between the electron-donating and -withdrawing moieties to suppress the ICT.

Carbazole derivatives have been widely introduced as the hole-transport component in bipolar materials due to its sufficient high triplet energy and good hole-transport ability. To achieve ambipolarity, carbazole-based bipolar host materials have been

* Corresponding authors. Tel.: +886 2 33661665; fax: +886 2 33661667 (K.-T.W.); tel.: +886 2 24622192x6718; fax: +886 2 24634360 (W.-Y.H.); e-mail addresses: wenhung@mail.ntou.edu.tw (W.-Y. Hung), kenwong@ntu.edu.tw (K.-T. Wong).

0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.04.051

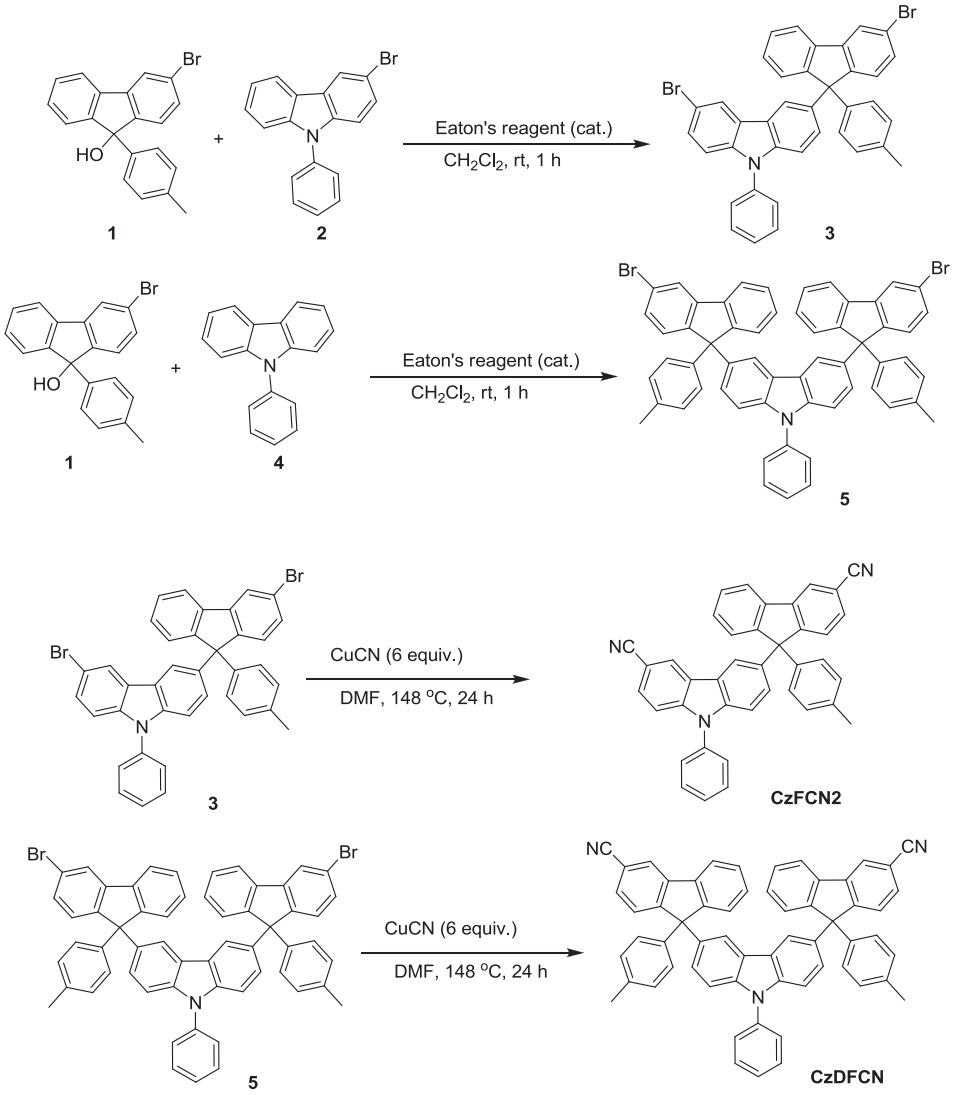
reported by incorporating electron-withdrawing groups such as benzimidazole,[9] triazole,[10] triazine,[11] pyridine,[12] phenanthroline,[13] oxadiazole,[14] phosphine sulfide,[15] and phosphine oxide[8a,16] at its C3, C6, and 9 positions. A carbazole/fluorene hybrid scaffold by connecting fluorene(s)–C9 to the C3 and/or C6 positions of a carbazole has been reported with triplet energies as high as 2.88 eV.[17] Although they exhibited good thermal and morphological properties, poor device efficiencies were obtained resulting from the imbalance charge transport in the emitting layer. To balance the carrier injection and transport in the emitting layer, Hsu et al. reported an efficient blue PhOLED device with external quantum efficiency (η_{ext}) up to 20.6% by appending the electron-withdrawing phosphine oxides at C2 and C7 positions of the fluorene moiety in the carbazole/fluorene-based material.[9d] On the other hand, It has been reported that electron-withdrawing cyano group possesses excellent electron affinity for electron injection.[18] Yet there are only limited reports on cyano acceptor in bipolar host materials for efficient PhOLED devices.[19] Recently, we reported a bipolar host material **CzFCN** composing of carbazole as the hole-transporting (HT) block and CN-substituted fluorene as the electron-transporting (ET) block separated by a saturated carbon bridge, exhibited a high E_T of 2.86 eV and balanced hole/electron mobilities.[20] Under a common device structure, PhOLEDs using **CzFCN** as a host material doped with blue to red emitters can yield η_{ext}>15.1%. In addition, a three-color based white PhOLEDs achieved maximum η_{ext} of 17.3%.

In this report, we have designed, synthesized, and characterized two new bipolar host materials, **CzFCN2** and **CzDFCN**, by incorporating electron-donating carbazole linked to electron-withdrawing 3-cyanofluorene (**CzFCN2**) and 3,6-bis(cyanofluorene) (**CzDFCN**) through an sp^3-hybridized C9 atom of fluorene to effectively impede the effective conjugation between electron-donating and -withdrawing moieties. **CzFCN2** and **CzDFCN** both showed high triplet energies (E_T) of 2.86 eV, good thermal/morphological stabilities, reversible electrochemical properties, and hole- and electron-transport properties. Multi-color PhOLED devices using **CzFCN**2 and **CzDFCN** as universal hosts have been characterized. In addition, three-component white PhOLEDs hosted by **CzFCN2** and **CzDFCN** exhibited high color stability with maximum η_{ext} of 10.5 and 12.4% and η_p of 20.5 and 26.7 lm W^{-1}, respectively.

2. Results and discussion

2.1. Synthesis and characterization

Scheme 1 illustrates the synthetic routes toward bipolar hosts **CzFCN2** and **CzDFCN**. The starting material 3-bromo-9-(*p*-tolyl)-



Scheme 1. Synthetic routes to **CzFCN2** and **CzDFCN**.