Dyes and Pigments 134 (2016) 285–290

Contents lists available at ScienceDirect

Dyes and Pigments

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

Pyridoindole based intramolecular charge transfer type host material for blue phosphorescent organic light-emitting diodes

Sung Yong Byeon, Jeong Min Choi, Jun Yeob Lee*

School of Chemical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 446-740, South Korea

ARTICLE INFO

Article history:
Received 24 April 2016
Received in revised form
5 July 2016
Accepted 14 July 2016
Available online 15 July 2016

Keywords:
Diphenylether linkage
High triplet energy
Pyridoindole
Blue device
Driving voltage

ABSTRACT

A *meta*-linked diphenylether based host material, 9-(3-(3-(9H-carbazol-9-yl)phenoxy)phenyl)-9H-pyrido[2,3-*b*]indole (CzDPEPI), was investigated as an intramolecular charge transfer type host material to harvest triplet excitons of phenylimidazole type blue Ir triplet emitters. A host with two carbazole units was a reference material to confirm the role of the pyridoindole moiety. The CzDPEPI host behaved as a high triplet energy and driving voltage reducing host due to the pyridoindole moiety assisting electron injection and improved power efficiency of blue phosphorescent device.

1. Introduction

The development of blue phosphorescent organic light-emitting diodes (PHOLEDs) has been a great challenge among researchers for the last decade due to difficulty of designing high triplet energy organic materials compatible with high triplet energy phosphorescent emitters [1–5]. As the triplet energy of deep blue phosphorescent emitters is as high as 2.75 eV, the triplet energy of organic materials such as host, hole transport layer and electron transport layer should reach at least 2.80 eV to circumvent exciton quenching of the phosphorescent emitters by host or adjacent charge transport materials [6–8]. Especially, the host materials are in direct contact with the phosphorescent emitters, which stresses the importance of triplet energy of the host materials.

In order to match the triplet energy of the host materials with that of phosphorescent emitters, various design approaches were tried [9–13]. Detailed design process is different, but general background concept common in each molecular design approach is to shorten the conjugation length of aromatic moieties comprising the molecular structure. For example, conjugation shortening design methods such as distortion of core structure and sp^3 hybridized linker successfully increased the triplet energy of the host materials above 2.80 eV [14–17]. The conjugation shortening moieties were commonly modified with a carbazole moiety or carbazole derivatives. However, only limited number of host materials are available to cover the triplet energy of blue triplet emitters and more designs to adjust the triplet energy, photophysical properties, electrochemical properties and thermal properties are essential.

In this work, a molecular design combining conjugation shortening diphenylether linkage, hole carrying carbazole unit and electron carrying pyridoindole unit was reported [18–20]. The carbazole and pyridoindole units were also included as donor and acceptor units to form intramolecular charge transfer complexes. The effectiveness of the molecular design was judged by comparing material and device characteristics of 9-(3-(3-(9H-carbazol-9-yl)phenoxy)phenyl)-9H-pyrido[2,3-*b*]indole (CzDPEPI) with those of 9,9′-(oxybis(3,1-phenylene))bis(9H-carbazole) (CzDPECz), which substantiated the merit of the new molecular design in terms of quantum efficiency (QE) and driving voltage.

2. Experimental section

2.1. General information

The reactants, 9*H*-carbazole, copper iodide (CuI) and (±)-*trans*-1,2-diaminocyclohexane, picolinic acid (Aldrich Chem. Co.), 1,3-diiodobenzene, sodium *tert*-butoxide and 3-chlorophenol (Alfa

---

* Corresponding author.
E-mail address: leej17@skku.edu (J.Y. Lee).

http://dx.doi.org/10.1016/j.dyepig.2016.07.021
0143-7208/© 2016 Elsevier Ltd. All rights reserved.

Aesar, Thermo Fisher Scientific Inc.), 9*H*-pyrido[2,3-*b*]indole, palladium(II) acetate (Pd(OAc)$_2$ and tri-*tert*-butylphosphine (P&H tech Co.), potassium phosphate tribasic, dimethyl sulfoxide (DMSO, Duksan Sci. Co.) were used without any further purifications.

Electrochemical analysis was conducted using Iviumstat equipped with an electrolyte consisted of acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration, Ag reference electrode, and Pt counter electrode was Pt. Ferrocene was an internal standard material of the measurement. The photoluminescence spectra was obtained using PerkinElmer LS-55 fluorescence spectrophotometer using *n*-hexane, tetrahydrofuran, and acetonitrile.

2.2. Synthesis

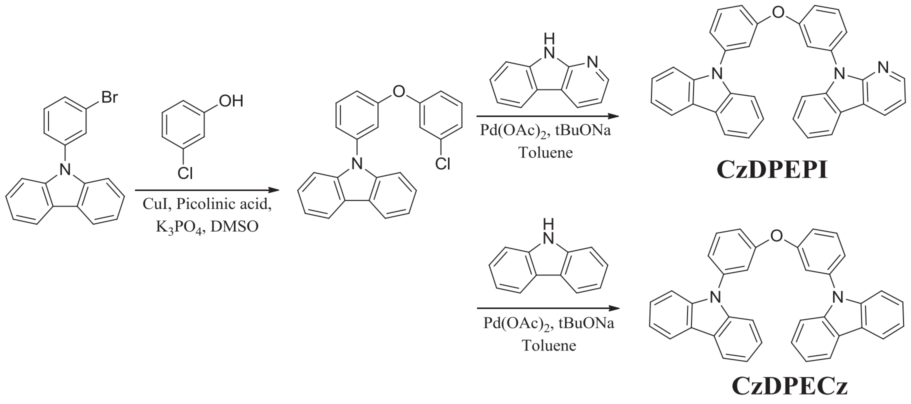
2.2.1. 9-(3-(3-chlorophenoxy)phenyl)-9H-carbazole

9-(3-Bromoophenyl)-9*H*-carbazole (1.00 g, 3.10 mmol), 3-chlorophenol (0.60 g, 4.66 mmol), copper iodide (0.30 g, 1.55 mmol), picolinic acid (0.19 g, 1.55 mmol) and potassium phosphate tribasic (1.97 g, 9.30 mmol) were added into round-bottomed flask and dissolved in DMSO (20 ml). 3-Chlorophenol (3.28 g, 11.43 mmol) was added into the solution and then the solution was refluxed. After 18 h, the reaction mixture was extracted with ethyl acetate and deionized water, and dehydrated using MgSO$_4$. A viscid liquid was obtained after further purification by column chromatography using ethyl acetate and hexane mixed solvent.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.62 (d, 1H, J = 7.5 $\mathrm{H_Z}$), 8.44 (d, 1H, J = 6.5 $\mathrm{H_Z}$), 8.28 (d, 1H, J = 8.0 $\mathrm{H_Z}$), 7.67 (t, 1H, J = 8.0 $\mathrm{H_Z}$), 7.55–7.49 (m, 3H), 7.44 (t, 1H, J = 8.3 $\mathrm{H_Z}$), 7.40–7.33 (m, 4H), 7.26–7.11 (m, 4H), 7.15–7.12 (m, 4H). MS (APCI) *m/z* 370.2 [(M + H)$^+$].

2.2.2. 9-(3-(3-(9H-carbazol-9-yl)phenoxy)phenyl)-9H-pyrido[2,3-b]indole (CzDPEPI)

9-(3-(3-chlorophenoxy)phenyl)-9H-carbazole (1.00 g, 2.70 mmol), 9H-pyrido[2,3-*b*]indole (0.54 g, 3.24 mmol), sodium *tert*-butoxide (0.77 g, 8.11 mmol), and Pd(OAc)$_2$ (0.3 g, 1.35 mmol) were put into a round-bottomed flask and then were dissolved in toluene (50 ml). Tri-*tert*-butylphosphine (0.27 g, 1.35 mmol) was added into the solution and then the solution was heated to reflux temperature followed by reaction for 24 h. Work-up procedure of CzDPEPI was the same as that of 9-(3-(3-chlorophenoxy)phenyl)-



Scheme 1. Detailed synthetic scheme of CzDPEPI and CzDPECz.

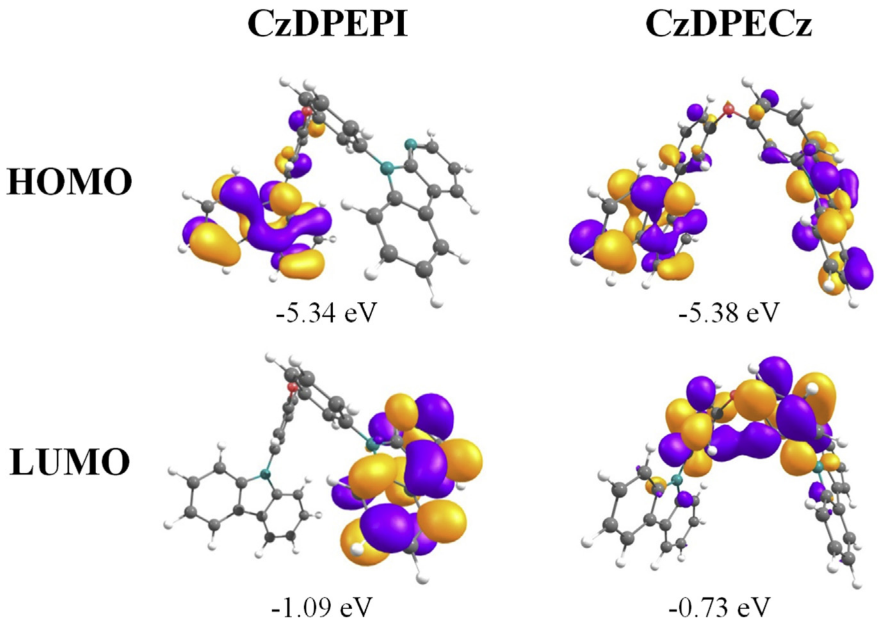


Fig. 1. Calculated HOMO/LUMO distribution and energy levels of CzDPEPI and CzDPECz. B3LYP 6-31G* basis set was used for the calculation.