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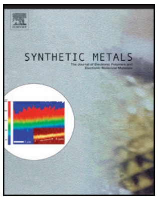

Effective thermally activated delayed fluorescence emitter and its performance in OLED device

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ABSTRACT

Dicyanophenyl derivatives, **DCN1–3**, were rationally synthesized and their thermally activated delayed fluorescence properties were investigated. OLED devices were further fabricated using **DCN1–3**. Particularly **DCN3** (5-{3,6-di(9*H*-carbazole-9-yl)-9*H*-carbazol-9-yl}isophthalonitrile) showed excellent device performances employing TADF mechanism with power efficiency of 15.26Cd/A, luminous efficiency of 8.14 lm/W, the maximum external quantum efficiency of 13.33%, and brightness of 1526 Cd/m^2.

1. Introduction

During the last two decades, organic light-emitting diodes (OLEDs) have received a great deal of attention as a solution for high-resolution and large area flat display panels [1]. Extensive efforts have been devoted to improve their electroluminescence efficiency [2] and a lot of studies have been focused on enhancing the quantum efficiency with appropriate host and phosphorescent materials [3]. Thus, small-molecule based host-dopant systems were most widely used for phosphorescent OLED researches. Up to date, phosphorescent OLEDs with high quantum efficiency close to 20% are reported frequently [4]. And they have become essential materials for high electroluminescence efficiency, although they generally contain expensive rare metals such as Ir or Pt [5].

Very recently it has been proposed that the thermally activated delayed fluorescence (TADF) is the next generation-luminescent system and may provide a solution for the ultimate electroluminescence efficiency. Therefore, it has attracted much interest as alternatives for fluorescence and phosphorescence based OLEDs due to an effective use of not only singlet but triplet excitons for fluorescence using efficient inter-conversion from the triplet excited state (T_1) to the singlet excited state (S_1) through reverse intersystem crossing (RISC) [6]. In order to show TADF phenomenon, the materials should have a small energy gap between singlet and triplet states (ΔE_{st}) [7], which could be attainable from restricted overlap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). With appropriate molecular design, such as a twisted structure between donor and acceptor, the restricted HOMO–LUMO overlap can be achieved [8]. Therefore, with elegant molecular design, efficient charge transfer allows for TADF to yields over 90% of internal quantum efficiency [9]. As such, TADF have been considered one of the most promising alternatives to achieve high efficient emission in wide range of colors.

In this regard, we carefully designed dicyanobenzene derivatives with distorted geometry to induce a small energy difference between S_1 and T_1 in order to obtain effective emitting materials with TADF mechanism. Cyanide, which is well-known strong electron withdrawing group, and carbazole derivatives, which are high triplet moieties, were used to construct a donor-acceptor system. As a result, dicyanobenzene series, **DCN1–3**, were synthesized and evaluated their performances as potential OLED dopants (Fig. 1).

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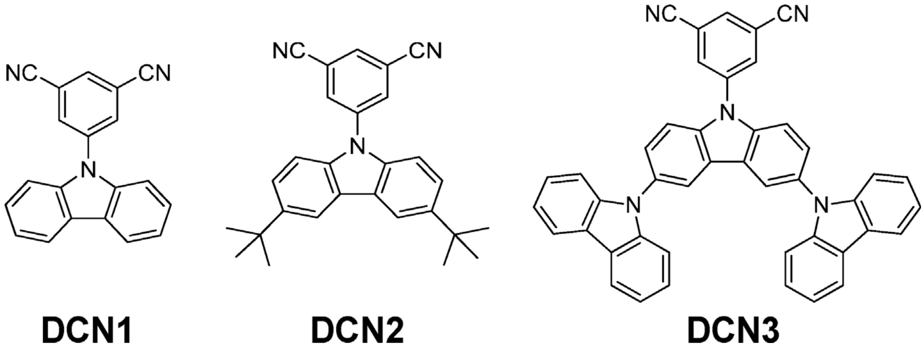

Fig. 1. Chemical structures of **DCN1–3**.

2. Experiment

2.1. Materials

All commercially available starting materials and solvents were purchased from Aldrich, TCI, Luminescence Technology Corp. and Alfa Aesar and used without further purification. All of the reactions and manipulations were carried out under N_2 with standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvents used in inert-atmosphere reactions were dried using standard procedures. Flash column chromatography was carried out with 230–400 mesh silica-gel from Merck using wet-packing method. All deuterated solvents were purchased from Cambridge Isotope Laboratories. The compounds of **1** [10],**2** [11], **4** [12], **5** [13], **6** [14], and **7** [15] were prepared according to the modified literature procedures.

2.2. Instrumentation

^{1}H NMR spectra were recorded on a Varian AS400 (399.937 MHz for ^{1}H and 100.573 MHz for ^{13}C) spectrometer. ^{1}H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ^{13}C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Absorbance and emission spectra were obtained using an Agilent UV–vis–NIR spectrophotometer and Hitachi F-7000 fluorescence spectrophotometer. HOMO–LUMO geometries in the ground state and electronic properties were calculated by Gaussian09 software using DFT calculation at the B3LYP/6-31G* level. Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min under a N_2 flow (50 ml/min) using Scinco TGA N-1000 instrument. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821 instrument and the measurements were performed at a heating (cooling) scan rate of 10 (−10) °C/min under nitrogen. Transient photoluminescence decay profiles were measured by a fluorescence lifetime measurement system that consists of a He-Cd nanosecond pulse laser (Spectra Physics INDI-40-10), a spectrograph (Princeton Instrument, SP2150) equipped with a PMT (Hamamatsu, H107231-20) and a 500 MHz digital oscilloscope (Agilent, DSO-X 3054A). The EL spectra and CIE color coordinates were obtained using a Spectrascan PR650 photometer, and the current–voltage–luminescence (*J*–*V*–*L*) characteristics were measured using a Keithley 2400 source unit.

2.3. Synthesis

*5. -(9*H*-Carbazol-9-yl) isophthalonitrile (**DCN1**)*

A mixture of 9-(3,5-dibromop-henyl)-9*H*-carbazole (**1**) (440 mg, 1.1 mmol) and copper(I) cyanide (246 mg, 2.7 mmol) in *N*-methyl-2-pyrrolidone (5.6 ml) was refluxed under nitrogen atmosphere for 72 h. The reaction mixture was quenched by adding aqueous sodium hydroxide (10%) at room temperature. The crude was extracted by dichloromethane (DCM) and the collected organic was dried over $MgSO_4$. After filtration, the collected solution was concentrated and the crude solid was purified with silica-gel column chromatography using DCM/hexane (1/1 v/v) to afford pure **DCN1** in 82.1% yield (265 mg). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.16–8.10 (m, 4H), 7.98 (s, 1H), 7.48 (t, $^3J_{H-H}$ = 7.83 Hz, 2H), 7.40–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$): δ (ppm) 140.5, 139.7, 134.0, 133.2, 127.0, 124.4, 122.0, 121.1, 116.2, 116.1, 109.1.

*3. ,6-Di-*tert*-butyl-9-(3,5-dibromophenyl)-9*H*-carbazole (**3**)*

A mixture of 3,6-di-*tert*-butyl-9*H*-carbazole (**2**) (980 mg, 3.5 mmol), 1,3,5-tribromobenzene (480 mg, 1.5 mmol), copper(I) iodide (14.5 mg, 0.08 mmol), 1,10-phenanthroline (27.5 mg, 0.15 mmol) and K_2CO_3 (843 mg, 6.1 mmol) in DMF (4.8 ml) was refluxed under nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was filtered, and the filtrate was extracted with ethyl acetate and dried over $MgSO_4$. After filtration, the collected solution was concentrated and the crude solid was purified with silica-gel column chromatography using DCM/hexane (1/30 v/v) to afford pure **3** in 57% yield (439 mg). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.12 (s, 2H), 7.71 (s, 1H), 7.69 (s, 2H), 7.49 (d, $^3J_{H-H}$ = 8.24 Hz, 2H), 7.36 (d, $^3J_{H-H}$ = 8.24 Hz, 2H), 1.46 (s, 18H).

*5. -(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)isophthalonitrile (**DCN2**).*

A mixture of **3** (1.75 g, 3.4 mmol) and copper(I) cyanide (763 mg, 8.5 mmol) in *N*-Methyl-2-pyrrolidone (17 ml) was refluxed under nitrogen atmosphere for 72 h. The reaction mixture was quenched by adding aqueous sodium hydroxide (10%) at room temperature. The mixture was filtered and the filtrate was extracted by DCM and washed with water. After drying over $MgSO_4$, organic was collected by filtration and concentrated. The crude solid was purified with silica-gel column chromatography using DCM/hexane (1/1 v/v) to afford **DCN2** in 74% yield (1.02 g). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.16 (s, 2H), 8.15 (s, 2H), 7.92 (s, 1H), 7.53 (d, $^3J_{H-H}$ = 8.61 Hz, 2H), 7.36 (d, $^3J_{H-H}$ = 8.61 Hz, 2H), 1.49 (s, 18H). ^{13}C NMR ($CDCl_3$): δ (ppm) 145.2, 141.0, 138.0, 133.3, 132.5, 124.6, 124.5, 117.1, 116.3, 116.0, 108.6, 35.1, 32.1.

*9. -(3,5-Dibromophenyl)-3,6-di(9*H*-carbazol-9-yl)-9*H*-carbazole (**8**)*

A reaction mixture of 3,6-di(9*H*-carbazol-9-yl)-9*H*-carbazole (**7**) (2.94 g, 5.9 mmol), 1,3,5-tribromobenzene (2.6 g, 8.3 mmol), copper(I) iodide (50.6 mg, 0.27 mmol), 1,10-phenanthroline (100 mg, 0.55 mmol) and K_2CO_3 (3 g, 21.7 mmol) in DMF (13 ml) was refluxed under nitrogen atmosphere for 13 h. After cooling to room temperature, the crude was filtered at room temperature and the filtrate was extracted with ethyl acetate, followed by column chromatography on silica gel with toluene/hexane (1/2 v/v) to