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The facile synthesis and high efficiency of the red electroluminescent dopant DCINB: A promising alternative to DCJTB

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ABSTRACT

The cost of manufacturing 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) is prohibitively high because the synthesis of one of the key intermediates, 1,1,7,7-tetramethyljulolidine, is costly, produces by-products and is of low yield. As an alternative low-cost process, a novel red dopant 4-(dicyanomethylene)-2-*tert*-butyl-6-(8-(4-methyl)phenyl-2,3-dihydro-1*H*-cyclopenta [3*a*,8*a*]indolin-5-enyl)-4*H*-pyran (DCINB) bearing an indoline unit instead of 1,1,7,7-tetramethyljulolidine as electron donor has been conveniently synthesized in high yield. The dopant exhibited very similar absorption and emission behaviour to DCJTB, but displayed superior fluorescence quantum yield and electroluminescence efficiency, which was attributed to high recombination ratio of excitons imparted by the introduced indoline unit. The synthesis and purification stages are simple and can be scaled-up, thereby offering a possible alternative to the commercial DCJTB.

1. Introduction

Organic light-emitting devices (OLEDs) have attracted considerable attention because of their potential applications in flat-panel displays. During the past decade, the study on high efficient organic electroluminescent (EL) materials has become one of the foremost topics in chemistry and physics [1–4], and much progress has been made [5,6]. For full color displays, it is necessary to have a set of primary green, blue and red emitters with sufficiently high luminous efficiency and proper chromaticity. At present, organic materials for green and blue OLEDs with high efficiency, saturated emission and practical lifetime have been developed rapidly [7,8]. However, the development of organic materials for red electroluminescence is far behind in terms of both color purity and efficiency, and the performance of red OLEDs is still not satisfactory [9]. Most of red fluorophores with narrow band gap are highly susceptible to concentration quenching, and become either weak or even not emissive at all in solid state [9,10]. In order to prevent the concentration quenching, doping a red emitter with strong fluorescence into a suitable host as the emitting layer is a common method to obtain high-performance red OLEDs [10–12]. There has been intensive study in developing organic red dopants, such as pyran-containing compounds [13–16], europium chelate complexes [17–19], and porphyrin compounds [20–22]. The pyran-containing compounds, such as 4-(dicyanomethylene)-2-methyl-6-(4-(dimethylaminostyryl)-4*H*-pyran) (DCM) analogues, typically consisting of two parts of an electron donor unit and an electron acceptor unit, are regarded as one of the most important red dopants for OLED applications. Up to date, 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) with solution PL $\lambda_{max} \sim 630$ nm and a quantum efficiency >90% is still one of the most efficient red dopants of tris(8-hydroxyquinolinato) aluminum (Alq3) hosted OLEDs [10,23,24]. However, the cost of manufacturing DCJTB is prohibitively high owing to the synthetic complication of one of the key intermediates, 1,1,7,7-tetramethyljulolidine (TMJ), which is tedious to synthesize with too many by-products and a low yield [25–27]. Accordingly, it is very desirable to develop high efficient red alternative to DCJTB with convenient and low-cost synthetic processes. Presently, many structural modifications have been attempted on their electron-accepting or electron-donating groups of dicyanomethylene-pyran derivatives. For example, Lee et al. reported a family of red dopants with a longer conjugation moiety benzopyran (4-dicyanomethylene-chromene) as electron acceptor to explore a better red chromaticity (longer wavelength) than

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(4-(dicyanomethylene)-2-methyl-6-(2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizin-9-yl)ethenyl)-4*H*-pyran) (DCM2) and DCJTB [14]. Huang et al. introduced a (diethylamino)-2-alkoxy segment as electron donor in the red dopant materials with the advantages of high yield, convenient synthesis and narrow FWHM [16]. However, EL performances and efficiencies are still not yet comparable to DCJTB.

Herein we reported the facile synthesis and high EL performance of a red EL emitter, 4-(dicyanomethylene)-2-*tert*-butyl-6-(8-(4-methyl)phenyl-2,3-dihydro-1*H*-cyclopenta[3*a*,8*a*]indolin-5-enyl)-4*H*-pyran (DCINB; Fig. 1). The 4-(dicyanomethylene)-2-*tert*-butyl-6-methyl-4*H*-pyran unit in DCJTB was retained as electron acceptor and an indoline unit instead of introducing TMJ as electron donor. With respect to the traditional red dopant DCJTB, the synthesis and purification of DCINB were simple and amenable to scale-up. Specifically, the luminance and the current efficiency of an EL device fabricated with DCINB were 1.8 and 4.6 times, respectively, greater than that of DCJTB with almost the same EL peak, indicative of a promising alternative to DCJTB.

2. Experimental

2.1. General procedure

Both 4-(dicyanomethylene)-2-*tert*-butyl-6-methyl-4*H*-pyran (**3**) and 8-(4-methyl)phenyl-2,3-dihydro-1*H*-cyclopenta[3*a*,8*a*]indoline (**1**) were prepared as reported in the literature [28–30]. All reagents and solvents were analytical grade chemicals. ^{1}H NMR and ^{13}C NMR measurements were recorded on a Bruker AV-400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Mass spectra measurements were carried out on Micromass LCT. UV–vis absorption and fluorescence spectra were measured using a Varian Cary 100 UV–vis spectrophotometer and Varian Cary Eclipse fluorescence spectrophotometer, respectively. Cyclic voltammograms were recorded with VersaStat II at a constant scan rate of 100 mV/s. Measurements were performed in a conventional three-electrode cell. The working electrode was platinum electrode coated with a thin film of DCINB; the counter electrode was platinum wire and the reference electrode was Ag/AgCl with a solution containing 0.1 M (n-Bu)$_4$NPF$_6$ in acetonitrile as the supporting electrolyte.

2.2. 5-Formyl-8-(4-methyl)phenyl-2,3-dihydro-1H-cyclopenta[3a,8a]indoline (2)

Phosphorus oxychloride (ed note; reacts violently with water; incompatible with many metals, alcohols, amines, bases and solvents; toxis; corrosive; 20 mL, 200 mmol) was added to *N*,*N*-dimethylformamide (35 mL, 443 mmol) at 0 °C, and the ensuing solution was stirred at room temperature for 15 min. A solution of 8-(4-methyl)phenyl-2,3-dihydro-1*H*-cyclopenta[3*a*,8*a*] indoline (11.6 g, 46.5 mmol) in dichloromethane (120 mL) was added to the reaction solution. After stirring at 95 °C for 5 h, the solution was poured into ice water, neutralized with aqueous NaOH (10 wt%) and then the mixture was extracted with dichloromethane. The organic layer was washed with water and brine, successively, and dried over anhydrous $MgSO_4$. After removing solvents, the resulting intermediate **2** was obtained from recrystallization with ethanol. Yield: 78% (10.0 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.69 (s, 1H, –CHO), 7.63 (s, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.16–7.23 (m, 4H), 6.73 (d, $J = 8.8$ Hz, 1H), 4.91 (t × d, $J = 8.4$, 1.6 Hz, 1H), 3.84 (t × d, $J = 7.8$, 1.6 Hz, 1H), 2.37 (s, 3H), 1.49–2.12 (m, 6H).

2.3. DCINB

A mixture of **2** (1.0 g, 3.6 mmol), **3** (0.77 g, 3.6 mmol), piperidine (2 mL), acetic acid (1 mL) and toluene (40 mL) was refluxed under argon for 5 h. Then the reaction mixture was cooled to room temperature, and the solid was filtered. Solid DCINB was obtained after recrystallization with toluene. Yield: 86% (1.44 g). m.p. 255–257 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.36–7.32 (d, $J = 16.0$ Hz, 1H, –CH═), 7.33 (s, 1H, phenyl-H), 7.21–7.19 (dd, $J = 8.4$, 1.6 Hz, 1H, phenyl-H), 7.20–7.17 (m, 4H, phenyl-H), 6.79 (d, $J = 8.4$ Hz, 1H, phenyl-H), 6.60 (d, $J = 2.0$ Hz, 1H, pyran-H), 6.52 (d, $J = 2.0$ Hz, 1H, pyran-H), 6.51 (d, $J = 6.0$ Hz, 1H, –CH═), 4.87–4.90 (m, 1H, –CH–), 3.82–3.86 (m, 1H, –CH–), 2.36 (s, 3H, –CH_3), 1.68–2.09 (m, 6H, –CH_2–), 1.38 (s, 9H, –C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 171.79, 160.33, 156.74, 150.92, 138.96, 138.54, 136.03, 133.19, 129.99, 124.65, 123.70, 121.46, 115.78, 115.76, 112.51, 106.95, 105.34, 102.34, 69.70, 57.64, 44.96, 36.62, 35.30, 33.36, 28.13, 24.31, 20.89. IR (KBr pellet): 3025.4, 2975.6, 2934.1, 2855.3, 2195.8 (–C≡N), 2187.6 (–C≡N), 1638.2, 1596.4, 1552.4, 1513.3, 1491.6, 1383.8, 1327.4, 1195.7, 1125.7, 1101.4, 966.1, 928.5, 852.8, 838.6,

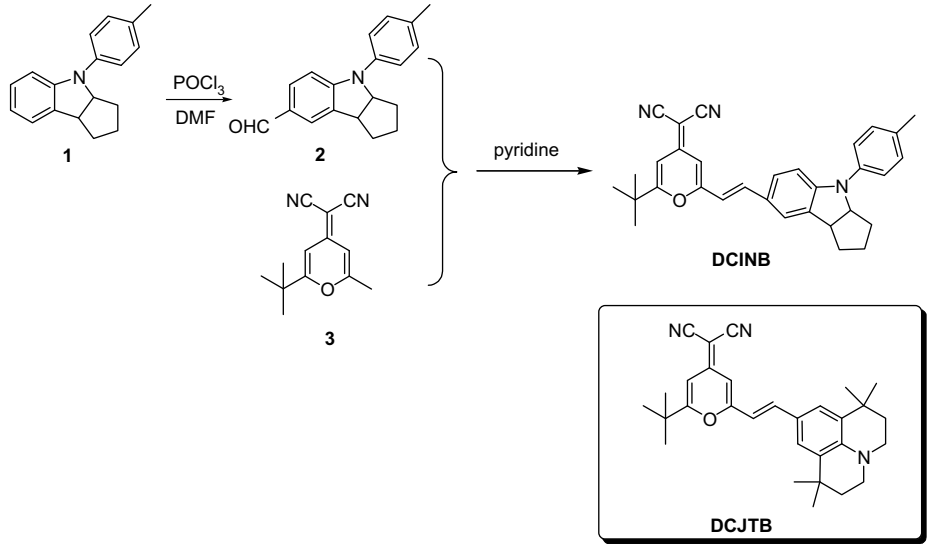

Fig. 1. Synthetic route of red dopant DCINB and the chemical structure of DCJTB as reference.