

Isophorone-based Fluorescent Dopant for Red Organic Electroluminescence Device

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Isophorone-based red fluorescent compound 3-(dicyanomethylene)-5,5-dimethyl-1-[2-(*N*-ethyl-3-carbazyl)ethylene]cyclohexene (DCDCC) was synthesized for use in organic light-emitting diodes (OLEDs). DCDCC was characterized by narrow emission in photoluminescence with full-width at half-maximum of only 50 nm in solution and in thin solid film of 70 nm width. Electroluminescence devices with configuration of ITO/NPB/Alq₃:DCDCC/Alq₃/Mg:Ag were fabricated utilizing DCDCC as dopant emitter. An efficient red emission peaked at 612 nm was obtained for the device with 1% (wt. %) DCDCC in Alq₃. The maximum luminance and current efficiency were as high as 3700 cd/m² at 14 V and 1.25 cd/A at 150 mA/cm², respectively.

Keywords OLED, red fluorescence, isophorone, 3-(dicyanomethylene)-5,5-dimethyl-1-[2-(*N*-ethyl-3-carbazyl)ethylene]cyclohexene

Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention since the initial works by Tang *et al.*¹ and Friend *et al.*² due to their potential applications in full-color flat-panel displays.^{3,4} To realize full-color applications, high performance organic materials emitting the three elemental colors of red, green and blue are required. After two decades of intensive research, a number of green and blue emitters with high luminous efficiencies, reasonable color purity and practical lifetime have now been realized in both small molecule and polymer systems.⁵⁻⁷ However, for the red emitters, issues of insufficient efficiency and color purity still remain. Besides the few red host materials reported recently,^{8,9} most of the present red emitters were used as dopants in OLEDs. The typical red dopants include pyran-containing laser dyes,¹⁰⁻¹² phosphorescent porphyrine derivatives¹³⁻¹⁵ and rare-earth complexes.^{16,17} The well-known pyran-containing laser dyes, such as DCM, DCM2, DCJT and DCJTb, have been widely used

and are regarded as the state-of-the-art red emitters for OLEDs applications.¹⁰⁻¹² While many of these molecules do have high photoluminescence (PL) quantum yield, their performance in OLEDs typically shares a common problem that color purity and efficiency are usually compromised¹⁸. Besides, the PL and electroluminescence (EL) peaks of these compounds are broad with a typical full-width at half-maximum (FWHM) of above 100 nm, which mainly contributes to the impure red emission. Furthermore, the synthesis and purification of DCM analogues are complicated by the symmetrical nature of the dicyanomethylidenepyran reactants. All the DCM analogues have electron donor- π -acceptor (D- π -A) structures. They are usually synthesized by condensation reactions between donor-containing aldehydes and acceptor-containing dicyanomethylidenepyrans. Reactions of the two reactants even in a one-to-one stoichiometric ratio is inevitably accompanied by the generation of a considerable portion of the unwanted double-condensed by-products, the removal of which requires difficult chromatography or train sublimation isolation. In the light of the above discussions, it is highly desirable to develop highly efficient red emitters with good color purity that can be synthesized using simple and low cost processes.

In this paper, a red-emitting isophorone-based fluorescent dopant, 3-(dicyanomethylene)-5,5-dimethyl-1-[2-(*N*-ethyl-3-carbazyl)ethylene]cyclohexene (DCDCC), for OLEDs applications, is reported. The molecular structure of DCDCC is shown in Scheme 1. To our best knowledge, it is the first report of DCDCC used in OLEDs although it has been widely used in non-linear optical research. It is characterized by moderately high fluorescent efficiency, and especially sharp photoluminescence with a FWHM of only 50 nm in solution and in thin solid film of 70 nm width. In addition, it can be synthesized by condensation reaction between the electron-donating *N*-ethyl-

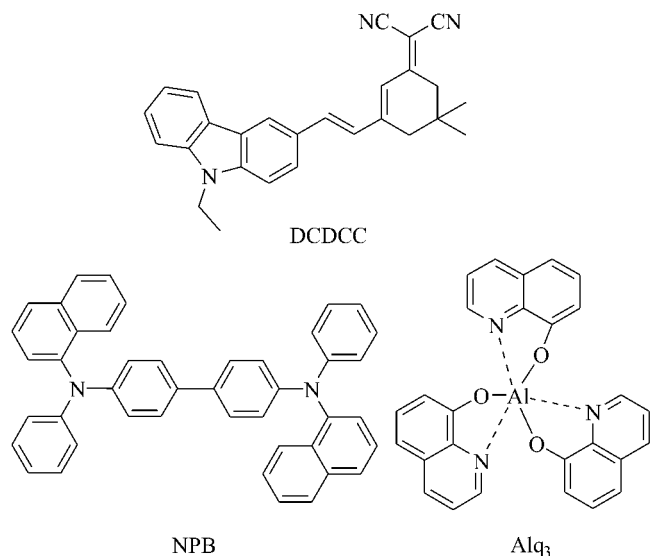
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3-carbazolecarbox-aldehyde and the electron-withdrawing dicyanomethylideneisophorone with good yield and high product purity. Isophorone skeleton was introduced into the core molecule of DCDCC as the electron acceptor because its asymmetrical structure provides only one condensation site and can avoid the double-condensation byproduct formation. The photophysical properties and electroluminescent behaviors of DCDCC as red emitter were investigated.

Scheme 1 Molecular structures of DCDCC and other materials used in the device fabrication



Experimental

Materials and instruments

All the reagents and solvents used in the synthesis were purchased from Aldrich and Acros companies and used without further purification. Tris(8-hydroxyquinolino)aluminum (Alq_3) and 1,4-bis(1-naphthylphenylamino) biphenyl (NPB) used for OLEDs fabrication were synthesized in our laboratory and purified by column chromatography several times. DCDCC was synthesized according to the reported method with a high yield of 85%.¹⁹ The molecular structure was confirmed by spectral data which were identical with those in literature.

The photoluminescence and absorption spectra of DCDCC in solution and in film were recorded with a Perkin-Elmer LS50 fluorescence spectrometer and a Perkin-Elmer Lambda 2S UV-visible spectrophotometer, respectively.

Fabrication and testing of OLED devices

Devices with a configuration of ITO/NPB (60 nm)/ Alq_3 :DCDCC ($x\%$, 20 nm)/ Alq_3 (30 nm)/Mg:Ag were fabricated by vacuum deposition. ITO stands for indium tin oxide. Before deposition, the ITO substrate was cleaned with detergents and deionized water, dried in an oven for

about 2 h, and finally treated with UV-ozone for about 25 min. The ITO substrate was then loaded into a deposition chamber with a base pressure of 1×10^{-7} kPa. The devices were fabricated by evaporating organic layers onto the ITO substrate sequentially at a pressure below 5×10^{-7} kPa. The doped layer of DCDCC in Alq_3 was prepared by coevaporation with the dopant concentration controlled by carefully adjusting the evaporating rates of the dopant and the host. A cathode layer of Mg:Ag (mass ratio of 9:1) was evaporated onto the Alq_3 layer. The EL spectra and current-voltage-luminescence characteristics were measured with a Photo Research PR650 Spectra and an Advantest R6145 DC Voltage Current Source, Keithley 2000 Multimeter, as well as Minolta LS-110 Luminance Meter connected with a computer sampling system under ambient conditions. The emission area of the device is 0.2×0.2 cm^2 as determined by the overlap area of the anode and the cathode.

Results and discussion

Photophysical properties of DCDCC

DCDCC is an intramolecular charge transfer compound with typical D- π -A structure. It reveals solvatochromism behavior both in absorption and emission in solvents with varying polarity. DCDCC is strongly fluorescent both in dichloromethane solution and in solid film on quartz substrate. The fluorescence spectra of DCDCC in solution and in film are shown in Fig. 1. The emission of DCDCC is in the red region (596 nm in CH_2Cl_2 and 616 nm in solid film) and characterized by sharp emission peak with a FWHM of only 50 nm in dichloromethane solution and 70 nm even in solid state film. Such an excellent color purity is definitely a very important merit of using DCDCC as red emitter for OLEDs application. Its photoluminescence quantum yield in dichloromethane is estimated as 0.27 related to Rhodamine B standard in water (0.71).²⁰

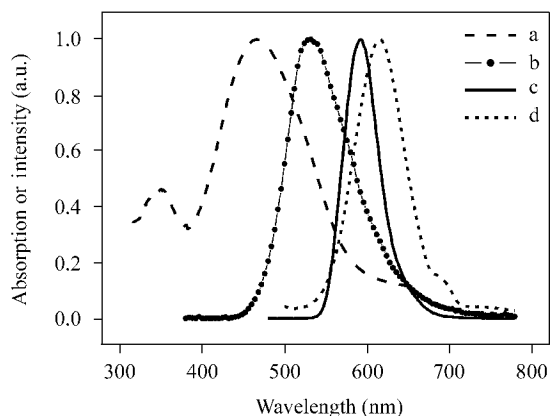


Fig. 1 Absorption (a: in thin solid film) and fluorescence (c: in dichloromethane; d: in thin solid film) spectra of DCDCC. The EL spectrum of Alq_3 (b) is also included.

The absorption spectrum of DCDCC in film and the

electroluminescence (EL) spectrum of Alq₃ are also shown in Fig. 1. It can be seen that there is significant overlap between the EL spectrum of Alq₃ and the absorption spectrum of DCDCC. This suggests that efficient Förster energy transfer from the Alq₃ host to the DCDCC dopant can be expected in EL devices.

All properties DCDCC displays, including its saturated red fluorescence emission, the moderately high fluorescence quantum yield, the good overlap of its absorption with Alq₃ emission, and the easiness of preparation and purification, imply that DCDCC may be a promising red emitter in OLEDs application.

EL performance of DCDCC-based devices

EL devices using DCDCC as dopant in Alq₃ host layer were fabricated. The EL spectrum of the device with 1% (wt. %) DCDCC is shown in Fig. 2. It can be inferred, by comparing the PL spectrum of DCDCC in solution and in its thin solid film, that the red EL emission of the device with emission maximum of 612 nm originates from the fluorescence of DCDCC, which in turn is the result of the efficient energy transfer between host Alq₃ and dopant DCDCC. The emission color and the EL spectra of the device almost remained unchanged with increasing current density. While there is still a trace of Alq₃ emission at 520 nm due to incomplete energy transfer from the host to the dopant molecules, and the Alq₃ emission can be suppressed by increasing the dopant concentration to 2% (wt. %) or higher to improve the color purity but at the expense of luminescence and efficiency.

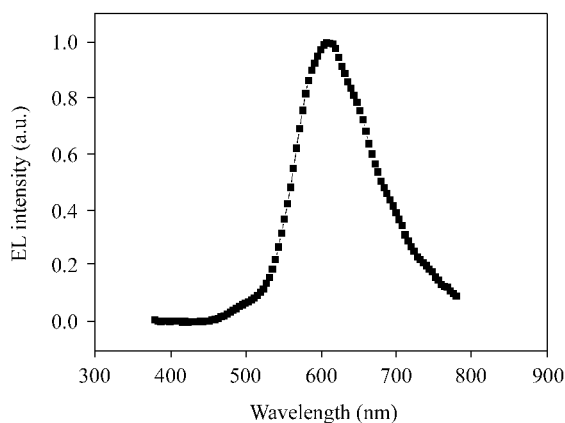


Fig. 2 EL spectrum of red emitting device with ITO/NPB (60 nm)/Alq₃:DCDCC (1%, 20 nm)/Alq₃ (30 nm)/Mg:Ag structure.

Fig. 3 shows the luminescence-current density-voltage characteristic of the device with 1% (wt. %) of DCDCC. Although the device structure and other experimental conditions were not optimized, the maximum luminescence of the present device can reach up to 3700 cd/m² at the driving voltage of 14 V.

The current efficiency versus current density characteristics for the device is illustrated in Fig. 4. The current

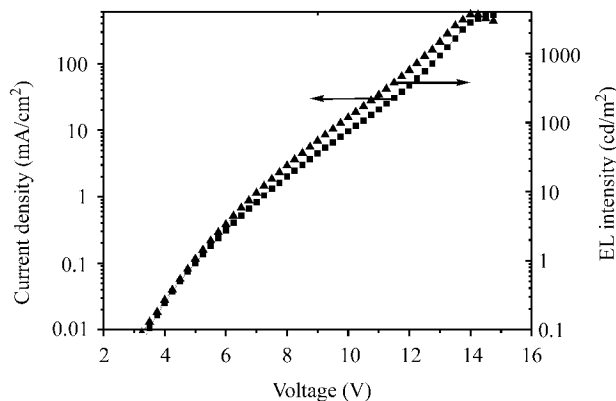


Fig. 3 Luminescence-current-voltage characteristic of the red-emitting device.

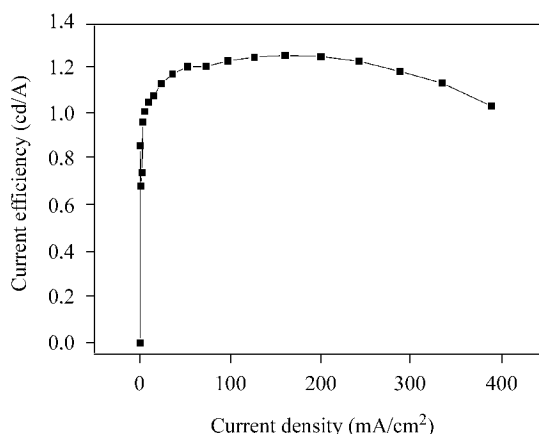


Fig. 4 Current efficiency versus current density characteristics of the device with the structure of ITO/NPB (60 nm)/Alq₃:DCDCC (1%, 20 nm)/Alq₃ (30 nm)/Mg:Ag.

efficiency is 1.1 cd/A at the current density of 20 mA/cm² and has the maximum of 1.25 cd/A when the current density reaches to 150 mA/cm². It decreased very slowly with increasing the current density even up to 400 mA/cm² as shown by the curve. Efficiency decay at high current density for red OLEDs is common due to the emission quenching by charged or triplet species that are electrogenerated in the OLEDs.²¹ It is expected that the luminescence, efficiency, especially the EL emission spectra and consequently the color purity of the present device can be further improved by optimizing the device structure and other conditions such as doping concentration, thickness of each functional layer *etc.*

Conclusion

An isophorone-based red-emitting fluorescent compound 3-(dicyanomethylene)-5,5-dimethyl-1-[2-(*N*-ethyl-3-carbazyl)ethylene]cyclohexene (DCDCC) was used for the first time in OLEDs. Its synthesis and, particularly, its purification are much easier compared with the pyran-based DCM analogues due to the asymmetrical nature of isophorone skeleton reactant. DCDCC is strongly fluorescent and, more importantly, is characterized by

sharp emission band. EL devices utilizing DCDCC as doping emitter were fabricated and an efficient red emission with peak at 612 nm was obtained at 1% (wt.%) dopant concentration. The maximum luminance and current efficiency of the device were as high as 3700 cd/m² and 1.25 cd/A respectively even without optimization. All the merits such as easy synthesis, good color purity and high EL efficiencies of DCDCC make it possible as a potential candidate of red emitter in OLEDs.

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