

A New Family of Isophorone-Based Dopants for Red Organic Electroluminescent Devices

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A new family of isophorone-based red fluorescent materials (**A**, **B**, **C**, and **D**) with a typical donor- π -acceptor structure was designed and synthesized for use in organic light-emitting devices (OLEDs). The asymmetrical π -conjugation structure of the isophorone skeleton facilitates the formation of highly pure products in comparison with the synthesis of pyran-containing DCM analogues. Saturated red-emitting devices with emission peaks at 640–680 nm were fabricated using these materials as dopants. The current efficiencies were moderately high and remained unchanged, even at high current density in some devices. The CIE coordinates of all the devices were comparable with or better than those of devices using DCM analogues.

Introduction

Organic light-emitting devices (OLEDs) have attracted considerable attention since the initial works by Tang and Vanslyke¹ and Friend and co-workers² 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 2 decades of intensive research, a number of green emitters with high luminous efficiencies, reasonable color purity, and practical lifetime have now been realized in both low-mass molecular and polymer systems.^{5,6} For the case of blue emitters, while there have been significant progresses in recent years,^{7,8} satisfactory blue emitters are still sought for both small molecule and polymer based devices. Lifetime continues to be a problem. By comparison with the other two colors, the situation for red emitters is far behind in terms of both color purity and efficiency. Besides the few red host materials reported recently,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 derivatives,^{13,14} iridium complexes,¹⁵ and rare-earth complexes.^{16,17} Sharp red electroluminescent (EL) emission has been demonstrated using complexes of rare-earth metals such as europium. However, devices based on them yielded poor EL quantum efficiency.^{16–18} Saturated red EL was achieved using phosphorescent porphyrine derivatives and iridium complexes such as TPP, TPC, PtOEP, and Btp₂Ir(acac).^{13–15} The use of phosphorescent emitters increases the theoretical limit of EL quantum efficiency by taking advantage of the higher production ratio of triplet to singlet excitons (3:1). PtOEP-based devices show improved quantum efficiency of 2.2% at 100 A/m². However, these enhanced EL quantum efficiencies decline rapidly with increasing current density due to triplet–triplet exciton annihilation. This disadvantage is especially undesirable when applications require high excitation density (e.g., passive matrix displays). The chromaticity of the PtOEP-based devices at high current density also needs further improvement. The well-known pyran-containing laser dyes, such as DCM, DCM2, DCJT, and DCJT2, have been widely used and are regarded as state-of-the-art red emitters for OLED applications.^{10–12} While many of these molecules do

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have high photoluminescent (PL) quantum yield, their performance in OLEDs typically share a common problem that color purity and efficiency are usually compromised.¹⁹ First, the PL and electroluminescence (EL) of these compounds are in the orange-red region with a broad peak at 590–615 nm and a typical full-width at half-maximum (fwhm) of about 100 nm. The insufficient energy transfer from typical host materials (such as Alq₃) due to insufficient spectral overlap also contributes to the unsaturated and impure red emission. Furthermore, the synthesis and purification of DCM analogues are complicated by the symmetrical nature of the dicyanomethylidenepryan 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 dicyanomethylidenepryan. 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 products, the removal of which requires difficult chromatography or train sublimation isolation. In 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, we report a new family of red-emitting isophorone-based fluorescent dopants for OLED applications. Molecular structures of these compounds are shown in Scheme 1. This series of dopants is characterized by saturated red emission, moderately high fluorescent efficiency, and good chemical and thermal stability. In addition, these compounds can be synthesized by condensation reactions between the donor-containing aldehydes and the electron-withdrawing dicyanomethylideneisophorones with good yields and high products purities. The isophorone skeleton was introduced into the core molecules of the dopants as the electron acceptor because its asymmetrical structure provides only one condensation site and can avoid the double-condensation byproduct formation, which is inevitable in the synthesis of DCM derivatives. Their photophysical properties and electroluminescent behaviors as red emitters were investigated.

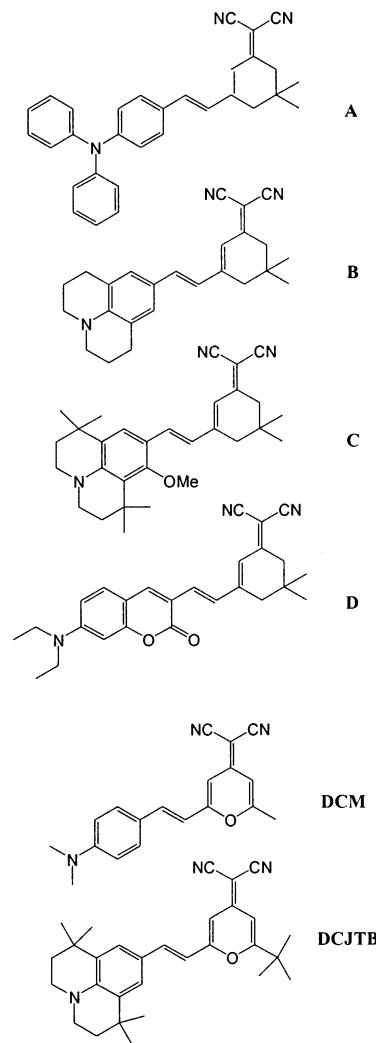
Experimental Section

Materials and Instruments. All the reagents and solvents used for the synthesis of the red emitters were purchased from Aldrich and Across companies and used without further purification. Tris(8-hydroxyquinolinato)aluminum (Alq₃) and 1,4-bis(1-naphthylphenylamino)biphenyl (NPB) used for EL devices fabrication were synthesized in our laboratory and purified by train sublimation.

¹H NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz). The infrared (IR) spectra were measured as KBr pellets on a BIO-RAD FTS-165 FT-IR spectrometer. Elemental analyses (EA) were performed by a Flash EA 1112 method. The photoluminescence and absorption spectra of red emitters in solution and in films were recorded with a Perkin-Elmer LS50 fluorescence spectrometer and a Perkin-Elmer Lambda 2S UV-visible spectrophotometer, respectively.

Preparation of the Red Dopant Materials. The synthetic procedures of the red dopant materials are shown in

Scheme 1. Molecular Structures of the Present Isophorone-Based Red Dopants and DCM and DCJT_B



Scheme 2. The dicyanomethylideneisophorone intermediate was synthesized according to the literature method with a high yield of 95%.²⁰ An acetonitrile solution containing equimolecular dicyanomethylideneisophorone and donor-containing aldehyde as well as piperidine (10 mol % of the aldehyde) was refluxed for 10 h and a precipitate was formed upon cooling the solution to room temperature. The precipitate filtered from the solution was very pure as indicated by thin-layer chromatography with a high yield over 85%. The product was further recrystallized in acetonitrile to achieve high purity required for OLED applications. The molecular structures of all the products were confirmed by spectral data.

A: ¹H NMR (CDCl₃, δ): 1.09 (s, 6H), 2.47 (s, 2H), 2.65 (s, 2H), 6.78 (s, 1H), 6.88 (s, 1H), 6.96–7.40 (m, 15H). FT-IR (KBr pellets, cm⁻¹): 3030, 2948, 2863, 2208 (–CN), 1590, 1553, 1493, 1325, 1172, 758. Anal. Calcd for C₃₁H₂₇N₃: C, 84.32%; H, 6.16%; N, 9.52%. Found: C, 84.28%; H, 6.35%; N, 9.48%.

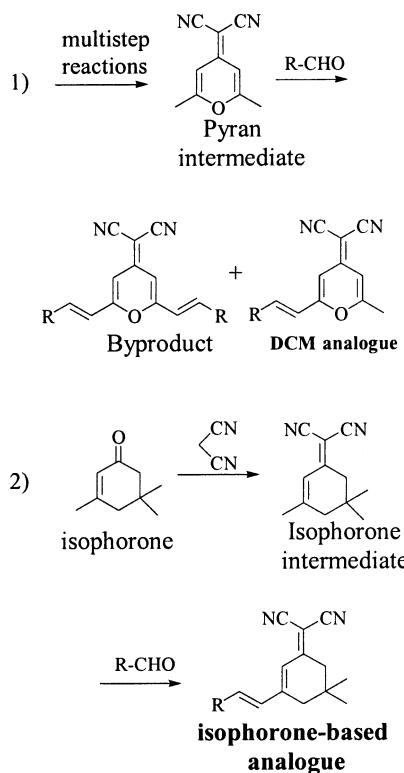
B: ¹H NMR (CDCl₃, δ): 1.05 (s, 6H), 1.98 (t, 4H), 2.41 (s, 2H), 2.56 (s, 2H), 2.78 (t, 4H), 3.25 (t, 4H), 6.71 (s, 1H), 6.78 (s, 1H), 6.92 (s, 1H), 6.98 (s, 2H). FT-IR (KBr pellets, cm⁻¹): 3016, 2928, 2831, 2213 (–CN), 1618, 1586, 1489, 1389, 1300, 1139, 742. Anal. Calcd for C₂₅H₂₇N₃: C, 81.3%; H, 7.3%; N, 11.38%. Found: C, 81.25%; H, 7.45%; N, 11.24%.

C: ¹H NMR (CDCl₃, δ): 1.08 (s, 6H), 1.34 (s, 6H), 1.42 (s, 6H), 1.76 (t, 4H), 2.47 (s, 2H), 2.58 (s, 2H), 3.18–3.26 (m, 4H), 3.78 (s, 3H), 6.77 (s, 1H), 6.82 (s, 1H), 7.32 (s, 1H), 7.35 (s,

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Scheme 2. Comparison of the Synthetic Procedures for Isophorone-Based Dopants and for DCM Analogues



1H). FT-IR (KBr pellets, cm^{-1}): 3052, 3024, 2952, 2932, 2209 (−CN), 1586, 1533, 1457, 1324, 1216, 1148, 894, 746. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_3$: C, 79.12%; H, 8.13%; N, 9.23%. Found: C, 79.28%; H, 8.23%; N, 9.12%.

D: ^1H NMR (CDCl_3 , δ): 1.08 (s, 6H), 1.25 (t, 6H), 2.45 (s, 2H), 2.58 (s, 2H), 3.44 (q, 4H), 6.50 (s, 1H), 6.62 (d, 1H), 6.86 (s, 1H), 7.16 (s, 1H), 7.22 (s, 1H), 7.32 (d, 1H), 7.80 (s, 1H). FT-IR (KBr pellets, cm^{-1}): 2960, 2932, 2217 (−CN), 1702, 1622, 1586, 1553, 1521, 1413, 1196, 1128, 963. Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{N}_3\text{O}_2$: C, 75.54%; H, 6.54%; N, 10.17%. Found: C, 75.23%; H, 6.62%; N, 10.04%.

Fabrication and Testing of OLED Devices. Devices with a configuration of indium tin oxide (ITO, $100 \Omega/\square$)/NPB (60 nm)/Alq₃:red dopant (40 nm)/Alq₃ (20 nm)/Mg:Ag were fabricated by vacuum deposition. Before deposition, the ITO substrates were 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 substrates were then loaded into a deposition chamber with a base pressure better than 1×10^{-6} mbar. The devices were fabricated by evaporating organic layers onto the ITO substrate sequentially at a pressure below 5×10^{-6} mbar. The doped layer of red dopant in Alq₃ 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 Alq₃ layer. The EL spectra and current–voltage–luminescence characteristics were measured with a Spectrascan PR 650 photometer and a computer-controlled dc power supply under ambient conditions. The emission area of the devices is 0.1 cm^2 as determined by the overlap area of the anode and the cathode.

Results and Discussions

Design, Synthesis, and Photophysics of Isophorone-Based Compounds. As illustrated in Scheme 2, the isophorone-based red analogues can be easily synthesized by a two-step process, which is easier than that used to synthesize the DCM analogues.¹¹ Furthermore,

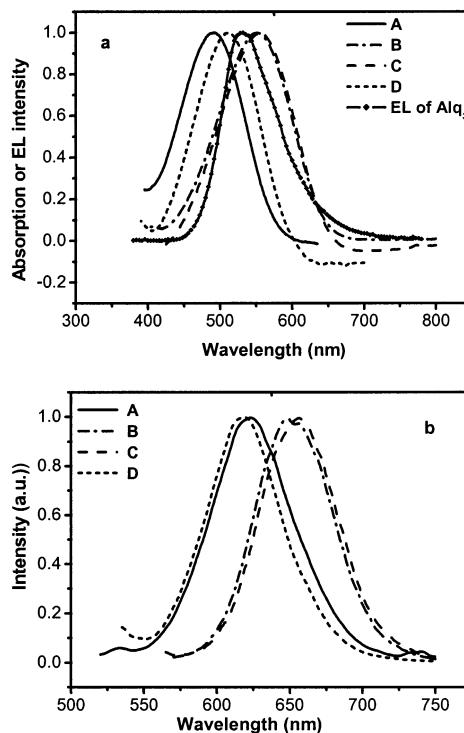


Figure 1. Absorption (a) and fluorescent (b) spectra of the present red-emitting compounds.

the dicyanomethylideneisophorone has only one π -electron conjugation path and consequently only one methyl is active for participation in the next condensation reaction with a donor-containing aldehyde. Therefore, the final isophorone-based products is pure enough, even without further purification. This is a significant advantage for large-scale commercial applications where saving in production cost is of prime importance. On the other hand, the dicyanomethylidenepyran has two π -electron conjugation routes symmetrically and two methyl groups have equal possibility to react with the donor-containing aldehyde. So the desired DCM product is inevitably contaminated by the double-condensed byproduct, which demands tedious separation by chromatography or train sublimation.

The isophorone-based red emitters are strong intramolecular charge-transfer compounds with D- π -A structures. They reveal solvatochromism behavior both in absorption and emission in different solvents with varying polarity. Figure 1 shows the absorption and emission spectra of all the red emitters in dichloromethane. The EL spectrum of Alq₃ is also shown for reference. It can be seen that there is good overlap between the EL spectrum of Alq₃ and the absorption spectra of all the red emitters. This suggests that efficient Förster energy transfer from the Alq₃ host to the red dopants can be expected in EL devices. The luminescent wavelength and intensities of these intramolecular charge transfer compounds are susceptible to the medium polarity. They give moderately strong luminescence in dichloromethane with emission peaks ranging from 620 to 650 nm. The emission wavelengths for **B** and **C** are 30 nm longer than those for **A** and **D**, which can be explained by the fact that the rigid Julolidine group has stronger electron-donating ability than the triphenylamine and the diethylaminocoumarin

Table 1. Comparison of Photophysical Data in Dilute Dichloromethane Solution and Energy Levels of the New Dopants and DCM and DCJTB

| dyes | UV (nm) λ_{max} | PL (nm) λ_{max} | Q_y (%) | HOMO (eV) | LUMO (eV) | E_g (eV) |
|--------------------|-----------------------------------|-----------------------------------|--------------|--------------|--------------|---------------|
| A | 492 | 623 | 21 | 5.49 | 3.46 | 2.03 |
| B | 552 | 648 | 10 | 5.56 | 3.81 | 1.75 |
| C | 553 | 656 | 13 | 5.46 | 3.65 | 1.81 |
| D | 510 | 620 | 14 | 5.45 | 3.58 | 1.87 |
| DCM ^a | 467 | 576 | — | — | — | — |
| DCJTB ^a | 512 | 615 | 78 | — | — | — |

^a From refs 12–14, in 1,2-dichloroethane.

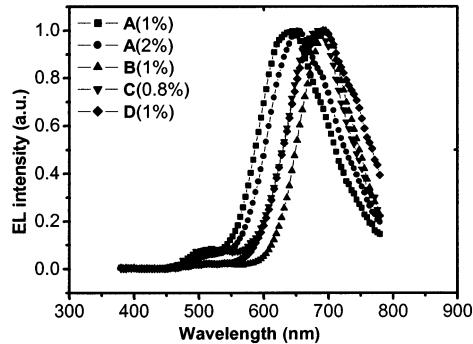


Figure 2. EL spectra of red-emitting devices with the structure ITO/NPB (60 nm)/Alq₃:dopant (40 nm, x%)/Alq₃ (20 nm)/Mg:Ag.

groups. Correspondingly, the charge transfer within the **B** and the **C** molecules is much stronger and the band gaps are smaller. The PL quantum yields (Q_y) of these compounds in dichloromethane were measured using quinine sulfate as the standard ($Q_y = 0.66$).²¹ In general, the PL quantum yield for most red-emitting materials is not very high. This is probably because their relatively small energy gap between the ground state and the lowest excited state allows more routes of nonirradiative decay. The highest occupied molecular orbital (HOMO) energy levels of all these compounds were measured by ultraviolet photoelectron spectra (UPS). The energy gap (E_g) was determined by the absorption cutoff of the absorption spectra of the sample films on a quartz substrate. The HOMO energy level along with the energy gap data were used to calculate the lowest unoccupied molecular orbital (LUMO) energy level. The spectral and energy data for these red emitters are summarized in Table 1.

EL Performance of Isophorone-Based Dopants. EL devices using isophorone-based compounds as dopants in an Alq₃ host layer were fabricated. The EL spectra for these devices at different doping concentrations of 0.8 wt % (**C(0.8%)**), 1 wt % (**A(1%)**, **B(1%)**, and **D(1%)**) and 2 wt % (**A(2%)**) were shown in Figure 2. It is clear that saturated red EL emission was obtained in all devices. For device **A(1%)**, the EL spectrum is peaked at 640 nm and has CIE coordinates at (0.61, 0.36). It was found that the color coordinates of this device remained almost 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, the Alq₃ emission can be suppressed by increasing the dopant concentration to 2 wt % to improve the color purity. For devices **B(1%)**,

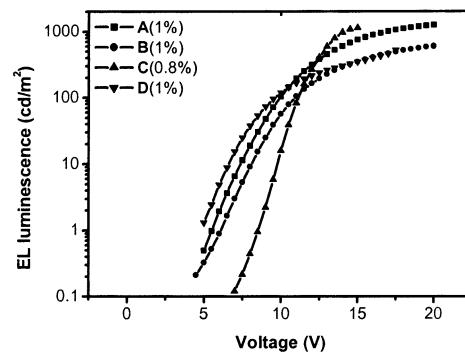


Figure 3. Luminescence–voltage characteristics of the present red-emitting devices.

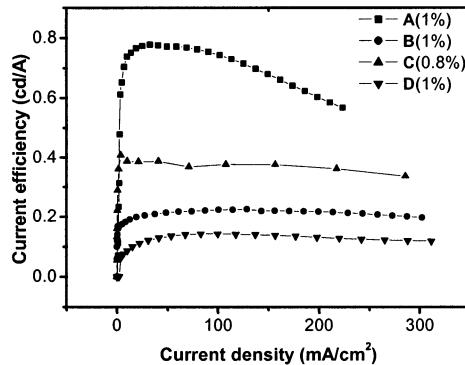


Figure 4. Current efficiency illustration of the red-emitting devices.

C(0.8%), and **D(1%)**, the EL emissions are peaked at 668–680 nm, which give more saturated red light.

Figure 3 shows the luminescence–voltage characteristics of the devices. Obviously, device **A(1%)** has the highest luminescence among all the devices. This is mainly because **A** has the highest PL quantum yield among all the dopants. The maximum luminescence for **A(1%)** is as high as 1266 cd/m² at a driving voltage of 20 V. Device **C(0.8%)** also achieves a high luminescence of 1126 cd/m² at 15 V.

The current efficiency versus current density characteristics for these devices are illustrated in Figure 4. Compared to other typical red-emitting devices,^{22,23} the present devices show little decrease in current efficiency as the current density increases. This characteristic is highly beneficial for applications that require high excitation density such as in passive dot matrix devices. It is expected that the luminescence and efficiency of the present devices can be further improved by optimizing the device structure and other conditions such as doping concentration. The EL performances for all the present devices and the reported DCM and DCJTB devices are summarized in Table 2. Evidently, the CIEs of the present devices are comparable with or better than those of DCM and DCJTB devices. The DCM device can only achieve a CIE of (0.62, 0.36) at a very high doping concentration of 10% at the expense of luminescence and efficiency.

In summary, a family of isophorone-based fluorescent materials was synthesized for use in OLEDs. The

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Table 2. Comparison of Electroluminescence Performance between the Present Devices and the Reported DCM and DCJTB Devices

| dopant (concentration) | L_{\max} (cd/m ²) | $J, V(L_{\max})$ mA/cm ² , V | η_{\max} (cd/A) | η_{\max} (lm/W) | CIE (x, y) |
|---------------------------|------------------------------------|--|-------------------------|-------------------------|-------------------|
| A(1%) | 1266 | 223, 20 | 0.78 | 0.25 | 0.61, 0.36 |
| B(1%) | 595 | 302, 20 | 0.24 | 0.08 | 0.64, 0.33 |
| C(0.8%) | 1126 | 420, 15 | 0.41 | 0.13 | 0.60, 0.36 |
| D(1%) | 523 | 406, 17.5 | 0.16 | 0.05 | 0.64, 0.34 |
| DCM(10%) ^a | 150 | –, 10 | – | – | 0.62, 0.36 |
| DCJTB(1%) ^a | – | –, – | – | 0.65 ^b | 0.62, 0.37 |

^a From refs 12–14. ^b Efficiency at 20 mA/cm².

asymmetrical nature of the isophorone reactant facilitates the synthesis of a high-purity product compared with the synthesis of DCM analogues. These isophorone-based red emitters are moderately luminescent. EL devices using these compounds as dopants achieved saturated red emission with EL peaks at 640–680 nm. The luminescence and current efficiency can reach 1266

cd/m² and 0.78 cd/A respectively for a dopant **A**-based device, although no optimization has yet been performed. The CIE coordinates of all the present devices are comparable with or better than those of DCM and DCJTB devices. While performance of the present red OLEDs is still not ideal, the present device and the isophorone-based red emitters can be potentially useful in OLED applications. This kind of compounds definitely warrant further exploration. On the other hand, the present approach of using an asymmetric reagent to improve the product purity and yield clearly offers an advantage for synthesis of similar organic emitters.

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