

A highly efficient wide-band-gap host material for blue electrophosphorescent light-emitting devices

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We report on an efficient wide-band-gap host material for blue electrophosphorescence devices, namely, 1,2-*trans*-di-9-carbazolylcyclobutane (DCz). Photophysical studies show that lower-energy excimer formation between the carbazole units can be efficiently suppressed in a DCz film, thus maintaining its high triplet-state energy and inducing an exothermic energy transfer from DCz to iridium(III)bis[(4,6-difluorophenyl)-pyridinato-*N*,*C*^{2'}]picolate (FIrpic). Electrophosphorescent devices comprising a FIrpic:DCz emitting layer exhibit a superior performance with a maximum external quantum efficiency of 9.8%, a maximum luminance efficiency of 21.5 cd/A, and a maximum power efficiency of 15.0 lm/W at 0.01 mA/cm². © 2007 American Institute of Physics. [DOI: 10.1063/1.2821116]

Phosphorescent emitters, such as Ir(III), Pt(II), or Eu(III) complexes, are appropriate for obtaining highly efficient organic light-emitting devices (OLEDs) because they enable an effective use of both triplet and singlet excitons, thus providing a 100% internal quantum efficiency for light emission.¹⁻⁴ In designing phosphorescent OLEDs, the use of a host material with a higher triplet-excited-state (¹*T*) energy than that of a phosphorescent dopant is essential to ensure exothermic energy transfer. However, until now it has been very difficult to synthesize a suitable host material for blue phosphorescent dopants, because achieving a ¹*T* energy higher than that of the blue phosphors is not a simple task. The reason for this is that aromatic structures are inevitably required for the host material (to ensure a good charge-carrier mobility and thermal stability), but they unfavorably lower the ¹*T* energy.⁵

Carbazole is known to be a potential host material for blue electrophosphorescence because of its wide-band-gap energy, high ¹*T* energy, and good charge-transporting ability.⁶⁻⁹ Particularly, arylamine-type host materials containing two carbazole groups have shown appropriately high ¹*T* levels; for example, *N,N'*-dicarbazolyl-3,5-benzene (mCP) exhibits a ¹*T* energy of 2.90 eV (Ref. 6) and 4,4'-bis(9-carbazolyl)-2,2'-dimethyl-biphenyl shows a ¹*T* energy of 3.0 eV.⁷ However, the planar and rigid arrangement of the carbazole units in these compounds leads to the formation of excimers in the concentrated film state,¹⁰⁻¹² which results in detrimental charge trapping and the appearance of low-¹*T*-energy sites, thus eventually limiting the device efficiency and long-term operation stability.⁵ Here, we propose a host material comprising a 1,2-*trans*-configuration of carbazoles locked in a cyclobutane ring for the suppressed excimer formation. This *trans* configuration prevents the in-

tramolecular formation of excimers between adjacent carbazoles. Furthermore, its sterically bulky nature also prevents intermolecular excimer formation—a fact that has been thoroughly investigated for photoconductors.¹³ From this host material, we expect a reduced concentration of excimer-forming sites, thus giving a higher ¹*T* energy and a better OLED performance. In this letter, we demonstrate the occurrence of efficient blue electrophosphorescence provided by effective exothermic energy transfer from the 1,2-*trans*-di-9-carbazolylcyclobutane (DCz) host to the blue phosphorescent iridium complex, iridium(III)bis[(4,6-difluorophenyl)-pyridinato-*N*,*C*^{2'}]picolate (FIrpic). The obtained host material exhibited effective suppression of excimer formation, thereby providing a higher ¹*T* level (as identified by transient photoluminescence). The OLED performance of the FIrpic:DCz device was also found to be superior to that of a reference device fabricated using mCP as the host material.

Figure 1(a) shows the molecular structure of DCz, which was readily synthesized via the photochemical cyclodimerization of *N*-vinylcarbazole [acetone solution (~0.1 g/ml) under irradiation at 365 nm (4 W)],¹⁴⁻¹⁶ with a high conversion (80% after workup).

At room temperature, the DCz film—evaporated on a quartz substrate—showed a characteristic carbazole monomeric emission ($\lambda_{\text{max}}=353$ nm) with a significantly suppressed excimer fluorescence [which commonly appears at $\lambda > 420$ nm, see Fig. 1(a)]. In addition, the fluorescence spectrum of DCz overlaps very well with the metal-to-ligand charge-transfer absorption band of FIrpic so that an efficient Förster energy transfer is expected to take place from DCz to FIrpic. We observed a high-energy ¹*T* emission band in the low-temperature (12 K) time-resolved photoluminescence spectra [see Fig. 1(a)], which suggests a facile ¹*T*-¹*T* energy transfer. Two sharp emission peaks (at 371 and 389 nm), which were assigned to a delayed fluorescence, decayed rapidly, whereas a broad emission signal (at around 421 nm,

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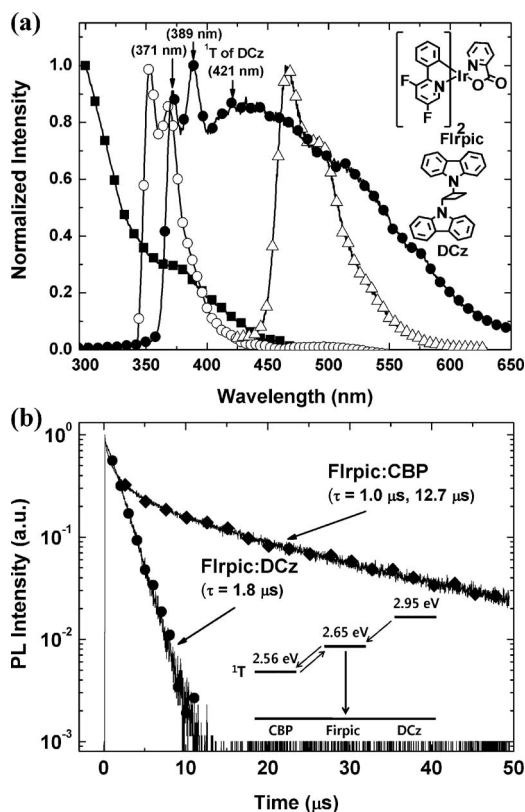


FIG. 1. Photophysical properties of emissive materials. (a) Molecular structures of Flrpic and DCz. Absorption (closed squares) and emission (open triangles) spectra of a 3 wt% Flrpic-doped polymethylmethacrylate (PMMA) film on a glass substrate, and fluorescence (open circles) and phosphorescence (closed circles) spectra of a DCz film (100 nm). (b) Phosphorescence decay of 6 wt% Flrpic-doped CBP (diamonds) and DCz (circles) films.

2.95 eV) was assigned to a triplet emission of DCz. Hence, considering the 1T energy of Flrpic (2.65 eV), an exothermic energy transfer can be expected from DCz to Flrpic. To investigate this energy transfer, we measured the transient photoluminescence by means of the direct excitation of a thermally evaporated DCz film (50 nm) doped with 6 wt% Flrpic. 4,4'-*N,N'*-dicarbazole-biphenyl (CBP) and mCP films doped with Flrpic (6 wt%) were also prepared and used as controls. As shown in Fig. 1(b), the phosphorescence-decay profile of Flrpic in a CBP host can be deconvoluted into two components, namely, a fast-decay component (of 1.0 μ s) and a slow-decay one (of 12.7 μ s). The observation of a long-lived phosphorescence indicates a thermally activated back energy transfer from Flrpic to CBP, which results from the low-lying 1T level of the latter compound.⁵ In contrast, the phosphorescence decay of Flrpic in DCz consists of a single component with a time constant of 1.8 μ s. No longer-lived phosphorescence was observed, which indicates that the triplet excitons in the Flrpic:DCz film are efficiently trapped within Flrpic. This phosphorescence behavior is almost identical to that observed for Flrpic in the well-known high- 1T -energy (2.90 eV) (Ref. 6) host mCP (which shows a monoexponential decay with a time constant of 1.7 μ s). This result can be explained by an efficient exothermic energy transfer from DCz to Flrpic and is also consistent with a high-energy triplet emission [see Fig. 1(a)] of DCz.

Blue electrophosphorescent OLEDs have been fabricated using Flrpic:DCz and Flrpic:mCP as the emitting

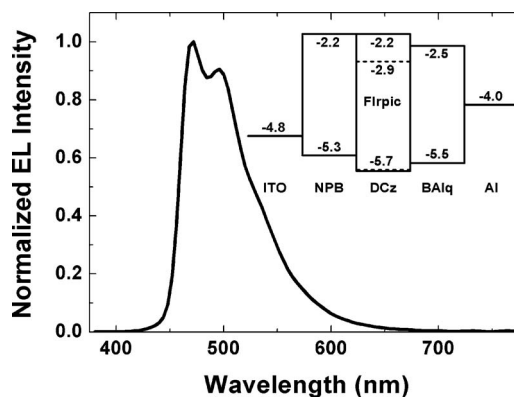


FIG. 2. EL spectra of an Flrpic:DCz device. Inset: energy diagrams of the device (in eV).

layers; the devices have the configurations indium tin oxide/NPB (400 Å)/8% Flrpic:DCz or mCP (300 Å)/BAQ (400 Å)/LiF (10 Å)/Al (where NPB=4,4-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl and BAQ=4-biphenyloxolatoaluminum (III) bis (2-methyl-8-quinolato) 4-phenylphenolate). The electroluminescence (EL) spectrum of an Flrpic:DCz device (Fig. 2, measured at a current density of 1 mA/cm²) exhibits a characteristic Flrpic emission (λ_{\max} =472 and 496 nm) with a total absence of host emission. Figure 3 shows the current-voltage-luminance (*J-V-L*) characteristics of Flrpic:DCz and Flrpic:mCP devices. As can be seen, the Flrpic:DCz unit maintains a higher luminance and a higher current density than its Flrpic:mCP counterpart throughout the studied voltage range (namely, 0–11 V). It is worth noting that the Flrpic:DCz device is better than the Flrpic:mCP one, although both of them are exothermic-energy-transfer systems (which are quite different to the endothermic Flrpic:CBP system). The luminance of the Flrpic:DCz device reached a value of 12 320 cd/m² at an applied voltage of 11 V. This good *J-V-L* characteristics are most likely originated from a good charge injection into the emitting layer and an efficient charge trapping within Flrpic, as shown in the energy-level diagram in the inset of Fig. 2. A maximum external quantum efficiency of 9.8%, a maximum luminance efficiency of 21.5 cd/A, and a maximum power efficiency of 15.0 lm/W were obtained (at a current density of 0.01 mA/cm²) for our Flrpic:DCz device. All these characteristics are superior to those of Flrpic:mCP (which exhibits a maximum external quantum efficiency of 9.3%, a maximum luminance efficiency of 20.4 cd/A, and a

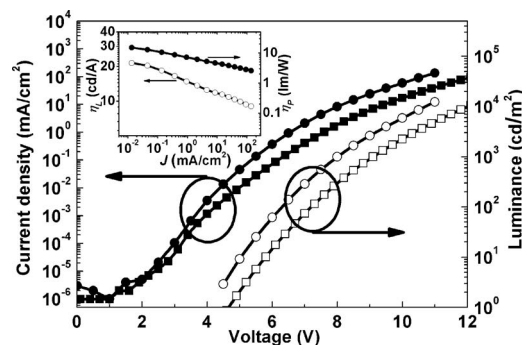


FIG. 3. *J-V-L* characteristics of Flrpic:DCz (circles) and Flrpic:mCP (squares) devices. Inset: efficiency of the Flrpic:DCz device.

maximum power efficiency of 13.2 lm/W), thus indicating an efficient exciton trapping within FIrpic.

In conclusion, we have fabricated a highly efficient blue electrophosphorescent OLED by using a carbazole-based host material DCz. Excimer formation of the carbazole units is efficiently suppressed in DCz, which makes it possible to achieve a high 1T level of the host layer and thus exothermic energy transfer from DCz to FIrpic. As a consequence of this suppressed excimer formation, the performance of the FIrpic:DCz device was superior to that of a FIrpic:mCP device.

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