Solution-Processed Solid Solution of a Novel Carbazole Derivative for High-Performance Blue Phosphorescent Organic Light-Emitting Diodes

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Since Forrest's group advanced the phosphorescent dye to improve light-emission efficiencies,[1] organic light-emitting diodes (OLEDs) have made dramatic progress. Because of the spin-orbit coupling, both the singlet and triplet states can be transferred to the photons, resulting in near 100% internal quantum efficiency, and extremely high efficiencies have been achieved.[2–4] Recently, Kido and coworkers reported a very efficient blue phosphorescent OLED based on an iridium (III) bis[(4,6-difluorophenyl)pyridinato-N,C^{2}picolinate (FIrpic) emitter with recorded efficiencies of 55 and 46 lm W^{-1}, which corresponded to external quantum efficiencies of 26% and 25%, respectively, at a practical luminance of 100 and 1000 cd m^{-2}.[5] In such methodology, the phosphorescent dye is dispersed into a wide energy gap host material to eliminate triplet–triplet annihilation and concentration quenching, and thus to develop suitable host materials is equally important for highly efficient phosphorescent OLEDs. Up to date, the most efficient OLEDs are still being fabricated by vacuum vapor deposition of a multilayer structure based on small molecules, which involves a complex fabrication process. But for low cost general lighting applications or display on large area, a simple solution-based approach is desirable, provided the efficiency of the devices is not compromised.[6] Even though polymer light-emitting diodes can be easily fabricated by solution casting, they are generally difficult to synthesize and purify for electronic devices. Therefore, to develop low-molecular-weight host materials suitable for solution processing will possess both advantages. The largest challenge for small molecules lies in the poor solubility accompanied by the tendency to crystallize and failure to form high quality films. Therefore, it is of significant importance to design and synthesize amorphous small molecules with high purity and that are highly solubility to provide high quality films.[7,8]

Although a large number of new phosphorescent dyes have been demonstrated in the literature, the most efficient one has still proven to be FIrpic. However, FIrpic is a greenish-blue emitter with a typical emission peak around 474 nm and a shoulder at 500 nm, and the corresponding Commission Internationale de L'Eclairage (CIE) coordinates x, y are around (0.15, 0.35), depending on the emission band profile.[9–13] For an efficient host material, it must possess a higher triplet energy level than that of the dopant to ensure effectively exothermic energy transfer. In addition, it must dissolve the dopant well to prevent aggregation or ground-state association to depress spectroscopic broadening.[14] Thirdly, it must have good film-forming and morphological stability as well as thermal and chemical stability. Meeting all the requirements is very demanding.

In this contribution, we report the use of a phenyl-substituted fluorene dimer as a bulky and rigid core functionalized by two carbazole groups to build a high performance amorphous molecule. The newly synthesized compounds is 1,4-bis(9-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-9*H*-fluoren-9-yl)benzene (DTCPFB), whose structure and synthetic route is shown in **Scheme 1**. We choose carbazole and fluorene as building blocks because of their excellent photophysical properties. Due to the non-conjugation linkage mode, the resulting compound possesses high triplet energy (2.85 eV), excellent miscibility to the dopant, and good film-forming and morphological stability as well as thermal and chemical stability, and solution-processed high-performance blue phosphorescent OLEDs with a satisfactory efficiency of 24.0 cd A^{-1} or 8.8 lm W^{-1} were achieved. We also proposed that the host must have low polarity to avoid polarization-induced spectroscopic red-shifts for realizing authentic emission of the dopant in a guest-host emissive system.

The structure and properties relationship was investigated by density functional theory (DFT) calculation (B3LYP; 6-31G*), and the results showed that DTCPFB was a highly twisted non-coplanar tetrahedral molecule, with two active groups of carbazole and the central phenyl-substituted fluorene arranged in a tetrahedral configuration. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were located in the carbazole and fluorenyl ring, respectively (see Supporting Information, Figure S1). The separation between the HOMO and LUMO is preferable

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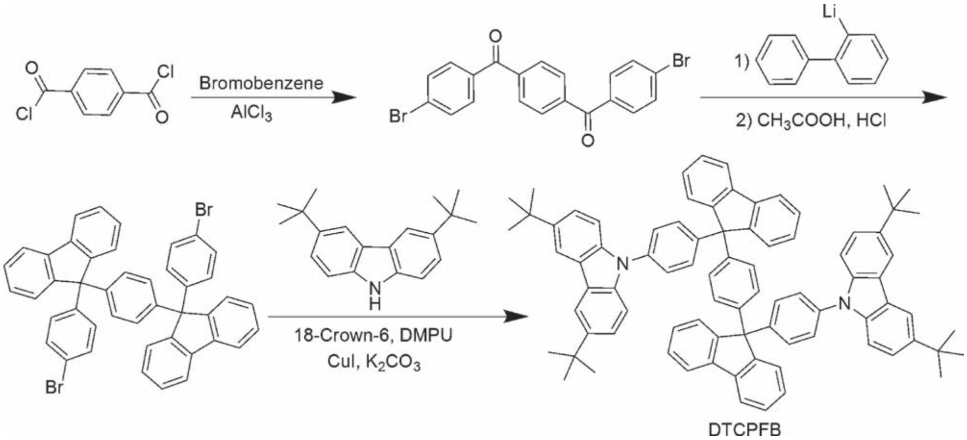
DOI: 10.1002/adma.201001392



Scheme 1. Synthetic route of the resulting compound DTCPFB and intermediates.

for efficient hole- and electron-transfer properties, as demonstrated in the literature.[15] These geometrical characteristics should effectively prevent intermolecular interactions between the π-systems and thus suppress the crystallization of molecules and improve the morphological stability of the thin film. The calculation results also indicate that the fluorenyl skeleton has little effect on the electronic structures of the carbazole moiety combined through the non-conjugated method.

DTCPFB exhibited excellent thermal stability with a 5% weight-loss decomposition temperature (T_d) as high as 442 °C and a high glass transition temperature (T_g) of 242 °C as examined by thermogravimetric analysis and differential scanning calorimetry (DSC) (Figure S2). The T_g was significantly higher than the commonly used materials of bis(carbazol-9-yl) biphenyl (CBP) and *N*,*N*-dicarbazolyl-3,5-benzene (mCP) (62 and 65 °C, respectively).[16,17] Such high T_d and T_g endow our compound with excellent thermal stability, making vacuum deposition a possible method to fabricate homogeneous and amorphous films. To further investigate the thermal and morphological stability as well as miscibility to the dopant as a potential host material, we employed atomic force microscopy (AFM) to explore the surface image of DTCPFB samples doped with variant concentrations of FIrpic dopant. The topographical images revealed that our samples provided smooth and uniform surfaces, free of pinholes, particle aggregation, or phase separation. Importantly, they were thermally stable against heating as witnessed by annealing the films at 110 °C for 12 h (**Figure 1**). This suggested that our compound possesses high thermal and morphological stabilities as well as good miscibility to the dopant, which can be attributed to the bulging tetrahedral configuration of the fluorene framework as well as the high molecular weight.

The singlet and triplet energies were investigated by examining the UV and photoluminescence (PL) spectra, which showed that our compound possesses high singlet and triplet energies (3.46 and 2.85 eV, respectively, corresponding emission of 358 and 435 nm). The higher triplet energy relative to the commonly used host material of CBP (2.56 eV)[17] and the blue phosphorescent emitter of FIrpic (2.65 eV),[18] or that of mCP (2.90 eV),[18] was favorable for efficient energy transfer. In

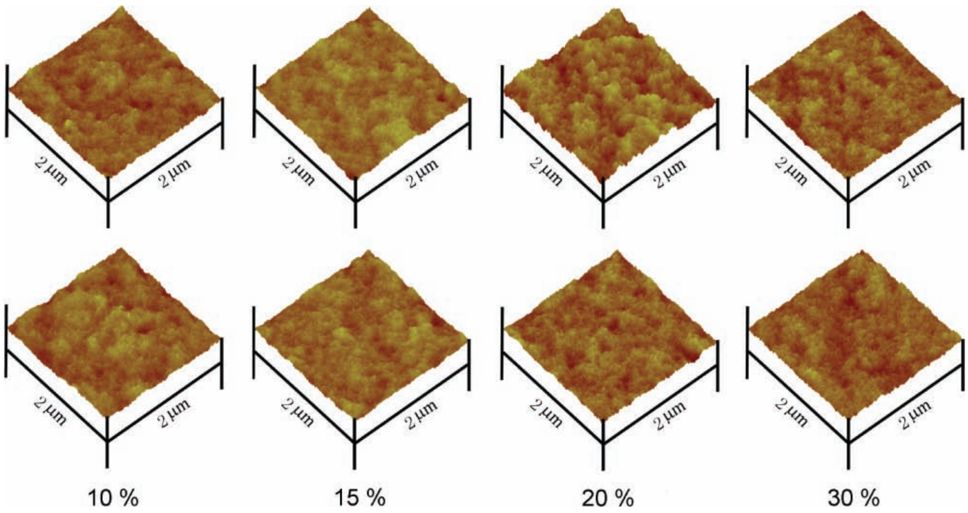


Figure 1. AFM imagine of the DTCPFB films doped with 10%, 15%, 20%, and 30% of FIrpic, top, before heating, bottom, after heating at 110 °C for 12 h under nitrogen atmosphere.

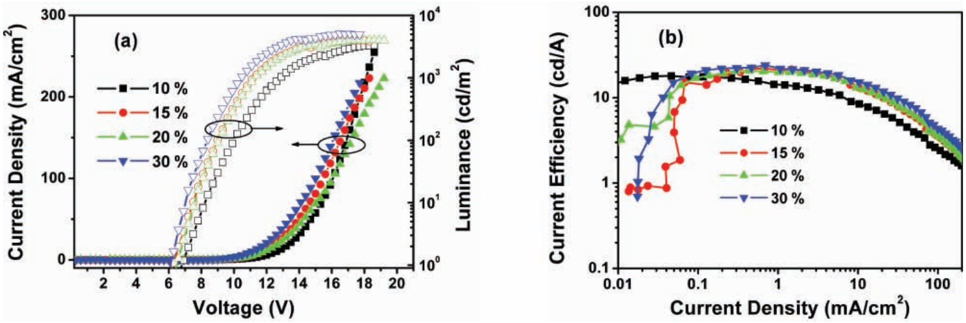


Figure 2. a) Current density –voltage–luminance curves and b) luminance efficiency as a function of current density of devices with variant doping concentrations of FIrpic.

the UV spectra two distinct groups of peaks at 286, 297, and 310 nm, and 334 and 348 nm, attributed to the fluorene and carbazole, respectively, were observed (Figure S3). Moreover, the negligible bathochromic shift (within 1 nm) in the peak positions of the UV and PL spectra indicated negligible intermolecular interactions between DTCPFB molecules in the solid packing state, which was consistent with the molecular structure, a high twisted tetrahedral configuration, which effectively prevented intermolecular interactions.

Moreover, our compounds possessed excellent electrochemical reversibility as proved by cyclic voltammetry (CV) analysis (Figure S4), which is sharply contrasting to mCP which showed irreversible redox behavior.[19] This can be attributed to the introduction of two *tert*-butyl groups at the C3 and C6 positions of carbazole. Excellent reversible redox properties suggested that our compound underwent reversible electrochemical doping and dedoping processes during potential sweeps, which is desirable for charge transporting materials. The HOMO and LUMO energy levels were calculated to be −5.63 and −2.16 eV, respectively. Compared with mCP (HOMO = −5.9 eV, LUMO = −2.4 eV)[20] our compound showed improved HOMO and LUMO energy levels, which means a greater match with the indium tin oxide (ITO) anode. On the other hand, a higher LUMO energy level was better for obstructing electrons to overflow the emissive layer and encounter the anode, which leads to more efficient recombination. High thermal and chemical stability, excellent miscibility to the dopant, and a high triplet energy level (2.85 eV), plus good film forming properties and morphological stability were achieved simultaneously in our compound, as mentioned above, and thus an ideal host material was expected.

The electroluminescent properties were investigated using the same samples by capping an electron-transporting and hole-blocking layer, 1,3,5-tris(1-phenyl-1*H*-benzo[d]imidazol-2-yl)benzene (TPBI), on which the cathode was deposited. The current density–voltage–luminance (*J*–*V*–*L*) characteristics are depicted in **Figure 2**. The current density increases as the doping concentration increases, with the 30% doped device showing the maximum current density among the four devices at a given voltage. Accordingly, the turn-on voltage (V_{on}, recorded at 1 cd m^{-2}) decreased as the doping concentration increased from 6.8 V for the 10% doped device to 6.0 V for the 30% device. The maximum efficiency was achieved in the 30% doped device with a luminance efficiency of 24.0 cd A^{-1} or 8.8 lm W^{-1} at 8.7 V, with a corresponding brightness of 165 cd m^{-2}, while the other devices showed moderate efficiencies with device a having the lowest of 18.0 cd A^{-1} or 7.2 lm W^{-1}. Despite this, its efficiency was still higher than the literature value reported by Qiu's group (12.7 cd A^{-1})[12] and even comparable to the vacuum deposited multilayer devices. For example, Wong et al. reported a triphenylsilylcarbazole device with an efficiency of 24 cd A^{-1} or 16 lm W^{-1} at a practical brightness of 100 cd m^{-2};[19] Yang et al. reported a triphenylamine device with a maximum efficiency of 25 cd A^{-1} or 17 lm W^{-1};[21] Forrest et al. reported a mCP device with a maximum efficiency of 8.9 lm W^{-1} and a CBP device of 6.3 lm W^{-1}.[18,22] Another thing worth mentioning is that the maximum efficiency was achieved at practical luminance of 100–1000 cd m^{-2}, which indicates a greater use for commercial applications.[23] For instance, device d has a luminance efficiency of 22.5 cd A^{-1} at 100 cd m^{-2}, and 19.3 cd A^{-1} at 1000 cd m^{-2}.

The obvious advantages of our devices over the large majority of other devices lie in the electroluminesence (EL) spectra, as shown in **Figure 3**. Our devices displayed bluer emission with an emission peak at 467.9–470.4 nm and a vibrational peak at 489.3–491.3 nm with a narrow full-width at half maximum (FWHM) of 47–53 nm for devices a–d. For example, device a showed the bluest emission with a FWHM of 47 nm with CIE coordinate *x*, *y* values of (0.141, 0.229), which is the bluest emission based on a FIrpic emitter.

We probed this phenomenon and found that the dopant FIrpic was a polar molecule whose emission was affected by the polarity of the matrix, with a bluer emission in a low or non-polar solvent (Figure 3 and Table S1). Secondly, our host material is a low polarity material which was proved by comparing the PL spectra of the doped samples with the PL spectra of FIrpic in dilute solutions of variant polarities. Thirdly, our host material and FIrpic can form a solid solution, not just a simple blend as proved by thermal measurement and phase contrast optical microscopy (Figure S5 and 6). The obvious advantage of a solid solution lies in the pure emission of the dopant molecule, similar to the PL spectrum in dilute liquid solution, as demonstrated in the literature.[24] In analogy to the solvatochromism of a normal liquid solution, the emission of the solid solution was also affected by the host polarity arising from the difference between the chromophore–chromophore

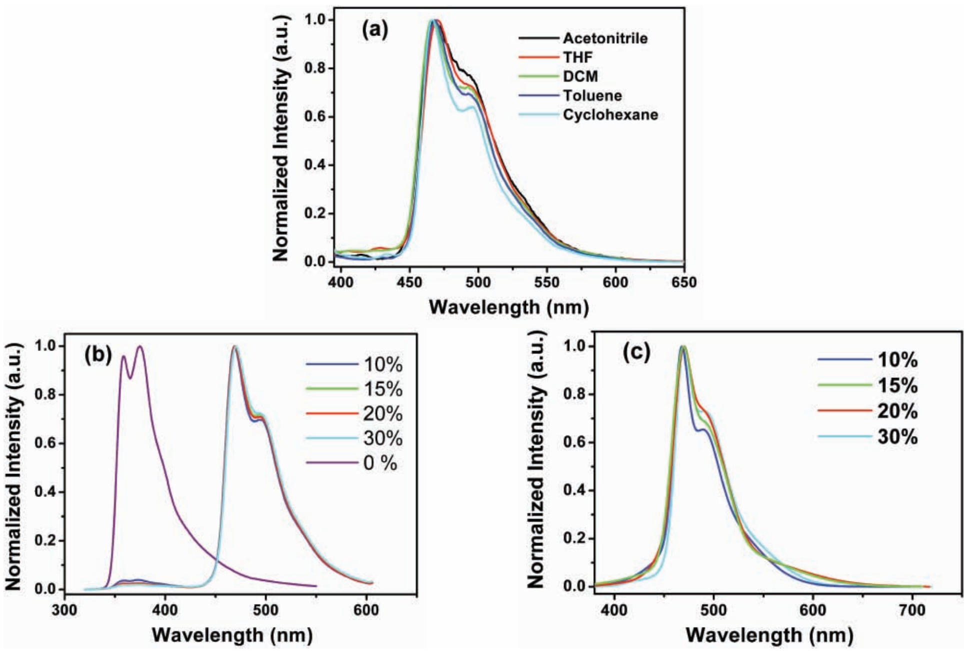


Figure 3. a) PL spectra of FIrpic in dilute solutions (1.1×10^{-5} mol L^{-1}). b) PL and c) EL spectra of DTCPFB films doped with varying concentrations of FIrpic at 9 V.

interactions and chromophore–matrix interactions.[25,26] Thus the more blue emission was attributed to the lower polarity, excellent miscibility, and morphological stability of our host material, as discussed above, which effectively separated and clamped the dopant, and depressed the ground-state association, leaving a similar single molecule emission of the dopant in the solid solution.

In summary, a novel solution processable carbazole and fluorene-based amorphous molecule has been designed and synthesized. Utilizing this compound as a host material and FIrpic as a dopant of a solid solution, high-performance blue phosphorescent OLEDs have been achieved arising from the excellent morphological stability, miscibility, low polarity, and high triplet energy of the host material. We believe this work will provide a guide to blue phosphorescent emission in molecular design and device fabrication.

Experimental Section

General information: All starting materials were obtained from commercial suppliers and used without further purification; solvents were purified according to the standard procedure. 1,3,5-Tris(1-phenyl-1*H*-benzo[d]imidazol-2-yl)benzene was purified by gradient sublimation three times.

1,4-Bis(9-(4-bromophenyl)-9H-fluoren-9-yl)benzene (DBPFB): 2-Bromobiphenyl (3.495 g, 15 mmol) and tetrahydrofuran (THF, 50 mL) were mixed and cooled to −78 °C and then *n*-BuLi (2.5 M in hexane, 6 mL, 15 mmol) was added dropwise. The whole solution was stirred at this temperature for 45 min followed by the dropwise addition of a solution of 1,4-bis(4-bromobenzoyl)benzene (4.441 g, 10 mmol) in THF (50 mL). The resulting mixture was gradually warmed to ambient temperature and kept stirring for 12 h, after which 50 mL of saturated aqueous $NaHCO_3$ was added to quench the reaction. The mixture was exacted with CH_2Cl_2 (3 × 60 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude residue was dissolved in acetic acid (100 mL) and a catalytic amount of aqueous HCl (12 N) was added, and then the whole mixture was heated to reflux for 10 h. After cooling to room temperature, the mixture was condensed under reduced pressure. The crude residue was purified by re-crystallization from toluene to afford 6.87 g of pure DBPFB, yield 96%. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.73 (d, J = 7.6 Hz, 4H), 7.36–7.22 (m, 16H), 6.99 (d, J = 7.6 Hz, 8H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 150.6, 145.0, 143.7, 140.1, 131.3, 129.9, 128.0, 127.8, 127.7, 126.1, 120.7, 120.2, 64.7. EIMS (m/z (%)): calcd for $C_{44}H_{28}Br_2$, 716.5; found, 716.3 (100).

1,4-Bis(9-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-9H-fluoren-9-yl) benzene (DTCPFB): A mixture of DBPFB (1 mmol, 0.716 g), 3,6-di-*tert*-butyl-9*H*-carbazole (0.573 g, 2.05 mmol), CuI (0.019 g, 0.010 mmol), and K_2CO_3 (0.580 g, 4.2 mmol) in 2 mL of 1,2-dichlorobenzene, 0.05 mL of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), and 0.010 g of 18-crown-6 was stirred at 170 °C for 8 h under a nitrogen atmosphere. After cooling to room temperature the mixture was added to 20 mL of water and 60 mL of CH_2Cl_2, and the organic phase was separated and concentrated under reduced pressure to give a gray solid, which was subjected to column chromatography (CH_2Cl_2 and petroleum ether as eluant, 1:2, v/v, R = 0.3) to yield 0.835 g of the pure target product of DTCPFB; yield 75%. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.09 (d, J = 1.1 Hz, 4H), 7.80 (d, J = 7.5 Hz, 4H), 7.48 (d, J = 7.6 Hz, 4H), 7.41–7.35 (m, 16H), 7.32 (t, J = 7.9 Hz, 8H), 7.17 (s, 4H), 1.44 (s, 36H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 151.1, 144.4, 144.0, 142.7, 140.2, 139.1, 136.7, 129.5, 128.1, 127.8, 127.7, 126.4, 126.2, 123.5, 123.3, 120.3, 116.1, 109.3, 65.0, 34.7, 32.0. MALDI-TOF MS (m/z (%)): calcd for $C_{84}H_{76}N_2$, 1113.5 ; found, 1113.1 (100). Anal. calcd for $C_{84}H_{76}N_2$: C 90.60, H 6.88, N 2.52; found: C 90.58, H 6.89, N 2.51.

1,4-Bis(4-bromobenzoyl)benzene[27] and 3,6-di-*tert*-butyl-9*H*-carbazole were prepared according to the literature procedure.[28]

Device Fabrication and Measurements: In a general procedure, ITO-coated glass substrates were etched, patterned, and washed with detergent, deionized water, acetone, and ethanol in turn. Polyethylenedioxythiophene: polystyrene sulfonate was spin-coated to smooth the ITO surface and promote hole injection, and then the emissive layer was spin-coated from chlorobenzene solution, on which an electron-transporting/hole-blocking layer was deposited by vacuum deposition at a pressure of 8×10^{-5} Pa. In all devices, a thin (8 Å) Cs_2CO_3 layer served as the electron-injecting layer at the Ag electrode interface and a 100-nm-thick Ag capping layer were deposited through a shadow mask. The active area of the device was 6 mm^2. EL spectra were collected using a Hitachi F-4500 spectrophotometer and chromaticity coordinates were measured with a SpectraScan PR650 photometer. *J–V–L* measurements were recorded simultaneously using a Keithley 4200 semiconductor parameter analyzer and a Newport multifunction 2835-C optical meter, with luminance measured in the forward direction. All device characterizations were carried out under ambient laboratory air at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (20825208, 60736004, 20721061), the National Major State Basic Research Development Program (2006CB806203, 2006CB932103, 2009CB623603), and the Chinese Academy of Sciences.

Received: April 18, 2010
Revised: May 9, 2010
Published online: June 10, 2010

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