

Novel Carbazole/Fluorene Hybrids: Host Materials for Blue Phosphorescent OLEDs

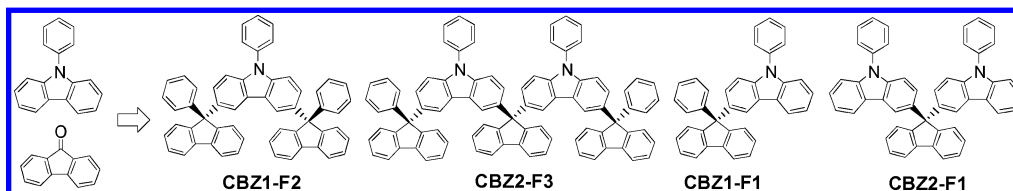
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ABSTRACT



A series of carbazole/fluorene (CBZ*m*-F*n*) hybrids were effectively synthesized through Friedel–Crafts-type substitution of the carbazole rings. These compounds were thermally and morphologically stable host materials for OLED applications. Efficient blue phosphorescent OLEDs were obtained when employing CBZ1-F2 as the host and Irpic as the guest.

Organic light-emitting diodes (OLEDs) remain a subject of intense investigation because of their potential applications in flat-panel displays and solid-state lighting.¹ In these devices, the use of phosphorescent emitters as guests—they increase the efficiency of the light-emitting diodes because they can harvest both singlet and triplet excitons—has stimulated the development of heavy metal-containing electroluminescent guest systems.² To achieve maximum efficiency in these host–guest OLEDs, the triplet energy of the host must be higher than that of the guest. This condition arises because of the preference for exothermic energy to transfer from the host to the guest and, perhaps more

importantly, the demand for effective confinement of the triplet excitons on the guest molecules.³ Such host–guest systems are well-established in green and red organic electrophosphorescent devices; electroluminescence (EL) efficiencies as high as 19% (or 70 lm W⁻¹) for green- and 10% (or 8 lm W⁻¹) for red-light-emitting devices have been reported in the literature.⁴ For triplet-state blue-light emitters, however, the commonly used carbazole-based molecules—including 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP), which has a triplet energy (E_T) of 2.56 eV—simply do not have sufficiently high triplet energies to effectively prevent reverse

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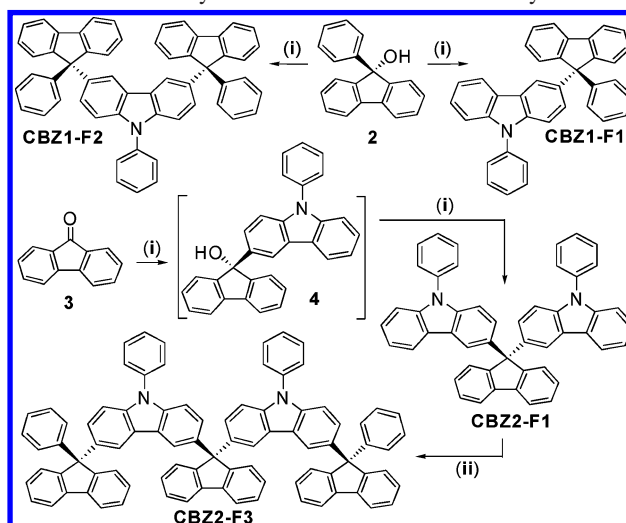
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energy transfer from the guest back to the host.^{3a} A structurally modified host molecule, 1,3-bis(9-carbazolyl)-benzene (mCP), which has a higher value of E_T , has been reported as being better suited for use in phosphorescent blue-light-emitting devices that incorporate bis[(4,6'-difluorophenyl)pyridinato-*N,C2'*]iridium(III) picolinate (FIrpic) as the dopant.^{3b} Although mCP possesses a suitable triplet energy, its relatively low thermal and morphological stability—it has a glass transition temperature (T_g) at 65 °C—may hinder its application as a host material in OLEDs.

In this Letter, we discuss the design and synthesis of novel host materials containing both carbazole and fluorene units for full-color triplet emission in general and blue emission in particular. We chose to use carbazole and fluorene units as building blocks primarily because of their high triplet energies: 3.05 and 2.95 eV, respectively.⁵ We connected the fluorene and carbazole moieties through the sp^3 -hybridized C-9 carbon atom, which serves as a spacer to effectively block conjugation between them;⁶ thus, the individual units' conjugation lengths and triplet energies remained relatively unperturbed. Moreover, the resulting molecules have a sterically bulky 3D cardo structure, which not only hinders their close packing and crystallization but also increases their molecular rigidity, leading to amorphous materials having pronounced morphological stability. Finally, the flexibility of this synthetic strategy allowed us to systematically change the ratio of the carbazole and fluorene units in the hybrids and to fine-tune the charge mobility and thermal properties of the host materials, while preserving the photophysical properties of the building blocks. Coincidentally, during the preparation of this paper, Wong et al.⁷ reported the multistep synthesis of a similar type carbazole/fluorene derivative, which they used as a host material for green and red phosphorescent OLEDs, but not for the more desirable blue phosphorescent OLED devices.

Scheme 1 illustrates our synthetic route. Eaton's reagent (7.7 wt % P_2O_5 in CH_3SO_3H) was used as the catalyst and condensing agent.⁸ The reaction of 9-phenylcarbazole (**1**, 1.0 equiv) with 9-phenyl-9-fluoreneol (**2**, 2.0 equiv) in CH_2Cl_2 at 25 °C gave CBZ1-F2 in excellent yield (92%). When we used an excess of **1** (2.0 equiv vs 1.0 equiv of **2**), we obtained CBZ1-F1 (66%) along with a lesser quantity of CBZ1-F2 (29%). These reactions proceeded smoothly through protonation of 9-phenyl-9-fluoreneol, followed by formation of the transitory carbocation, which in turn underwent Friedel–Crafts-type electrophilic substitution very efficiently at the electron-rich carbon atom(s) of the carbazole ring(s).⁹ A similar acid-catalyzed condensation reaction of **1** with 9-fluorenone (**3**) at 100 °C afforded CBZ2-F1 (73%). In this case, 9-fluorenone was probably initially converted to the

Scheme 1. Synthesis of Carbazole-Fluorene Hybrids^a



^a Reagents: (i) 9-phenylcarbazole (**1**), Eaton's reagent/ CH_2Cl_2 ; (ii) 9-phenyl-9-fluoreneol (**2**), Eaton's reagent/ CH_2Cl_2 .

intermediate 9-(9-phenylcarbazol-3-yl)-9-fluoreneol (**4**), which then reacted with **1** in a manner similar to that described above for 9-phenyl-9-fluoreneol. Again, the electron-rich positions of the carbazole rings in CBZ2-F1 reacted efficiently with **2** to give CBZ2-F3 in high yield (92%). Our approach toward synthesizing nonconjugated carbazole/fluorene hybrids is simpler and more direct than the multistep synthetic route reported recently for the preparation of a CBZ1-F2 analogue.⁷ Moreover, our synthetic strategy provides the ability to fine-tune the composition of the hybrid.

We used differential scanning calorimetry (DSC) to investigate the thermal properties of these carbazole/fluorene hybrids (Table 1). During the first heating cycle, CBZ1-F2 and CBZ2-F1 melted at 328 and 360 °C, respectively; CBZ1-F1 exhibited a glass transition at 108 °C, followed by crystallization at 181 °C and melting at 209 °C; CBZ2-F3 exhibited only a glass transition at 231 °C. Upon cooling from the melts, all of the hybrid compounds formed glassy states. In subsequent heating cycles, each hybrid exhibited a distinct glass transition within the temperature range of 108–231 °C, but did not undergo recrystallization or melting. In comparison, 9-phenylcarbazole has a melting point (T_m) as low as 97 °C, and mCP has a relatively low value of T_g of 65 °C.¹⁰ Consequently, these CBZ*m*-F*n* hybrids form amorphous glasses that are more stable than that of mCP, and therefore, they are more promising—in terms of their thermal stability—for application into OLEDs. We attribute the enhanced morphological stability of these hybrid compounds to their rigid 3D cardo structures hindering the crystallization process.¹¹ Additionally, the higher molecular weights of these hybrids, relative to that of mCP, may also

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Table 1. Thermal, Optical, and Electrochemical Properties of Carbazole Derivatives

compound	T_g (°C)	TGA (°C) ^a	Abs (nm) (ϵ) ^b	PL (nm) ^b	HOMO (eV)	LUMO (eV)	E_T (eV)
CBZ1-F1	108	361	334, 348 (5000)	358, 373	5.54	2.10	2.88
CBZ2-F1	162	429	334, 348 (9900)	359, 374	5.55	2.11	2.88
CBZ1-F2	171	429	339, 353 (4900)	365, 380	5.52	2.14	2.88
CBZ2-F3	231	533	340, 354 (10300)	366, 381	5.52	2.15	2.87
1			329, 342 (4700)	350, 365			

^a 5% weight loss temperatures. ^b Recorded in chloroform at room temperature; units for ϵ : $M^{-1} cm^{-1}$.

play a role in raising their glass transition temperatures. These CBZ*m*-F*n* hybrids also exhibit satisfactory thermochemical stability; for example, thermogravimetric analyses performed under a nitrogen atmosphere provided 5% weight loss temperatures that were as high as 361–533 °C. Because of their excellent thermal and morphological stabilities, we were able to prepare homogeneous and stable amorphous thin films of these hybrids through vacuum deposition.

Figure 1 displays the absorption and photoluminescence (PL) spectra of the hybrids and their parent compound **1** in chloroform solutions; Table 1 summarizes this spectral data. We believe that the lowest-energy absorption of the hybrids at ca. 340 nm, which was already present in **1**, derives from carbazole-centered transitions; the absorption band due to π - π^* transitions centered in the fluorene subunit occurs at higher energies.⁷ This hypothesis is further supported by the values of the molar extinction coefficients (ϵ)—ca. $5.0 \times 10^3 M^{-1} cm^{-1}$ for CBZ1-F2 and CBZ1-F1 and ca. $9.9 \times 10^3 M^{-1} cm^{-1}$ for CBZ2-F1 and CBZ2-F3—reflecting the number of carbazole units within these hybrids (Table 1). Similar phenomena have been noted in a 9-phenylcarbazole-based dendrimer series.¹² The features of the lowest absorption and PL of the hybrids resemble those of carbazole **1**, except for slight red shifts (of 5 and 8 nm in the absorption and emission maxima, respectively) upon introducing 9-fluorenyl units

at the 3- and/or 6-positions of the carbazole ring. This result indicates that the quaternary C-9 carbon atom of a fluorene moiety serves as a spacer to effectively interrupt any extended π -conjugation of the carbazole units.

We examined the electrochemical behavior of these hybrids through cyclic voltammetry using ferrocene as the internal standard. Both of the monosubstituted 9-phenylcarbazoles, CBZ1-F1 and CBZ2-F1, exhibited irreversible oxidation processes with onset potentials of 0.74 and 0.75 V, respectively. In contrast, the disubstituted compounds, CBZ1-F2 and CBZ2-F3, in which the 3- and 6-positions of the 9-phenylcarbazoles were substituted, were electrochemically reversible. These results are in consonance with previous reports that protection of the 3- and 6-positions (through substitution) effectively prevents C–C couplings at these positions, that is, the chemical reactions that are responsible for irreversibility toward oxidation.¹³ Such electrochemical reversibility of disubstituted CBZ1-F2 and CBZ2-F3 should improve the stability of their EL devices. For CBZ1-F2, we observed only one reversible oxidation occurring on the central carbazole unit, with formal oxidation (E°) and onset potentials of 0.72 and 0.81 V, respectively. In the case of CBZ2-F3, we detected two poorly resolved, reversible oxidations with the onset potential at 0.72 V. Differential pulse voltammetry (DPV) of CBZ2-F3 clearly demonstrated the appearance of two distinguishable oxidations at 0.77 and 0.88 V (E°). The relatively small potential difference in the oxidation indicates that the monocationic species generated during the first oxidation does not delocalize its charge efficiently over the two carbazole moieties, which are connected through an sp^3 -hybridized carbon atom. On the basis of the onset potential for the oxidation and the band gap determined from the optical absorption threshold, we estimated the HOMO and LUMO energy levels of the hybrids (Table 1) with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level).¹⁴

To evaluate the potential of the CBZ*m*-F*n* hybrids for use as host materials in blue phosphorescent OLEDs, we measured the PL spectra of the hybrids at 77 K in 2-MeTHF glasses. A well-structured emission from the triplet in the region of 425–500 nm is clearly evident (Figure 1c). The measured lifetimes of these states (ca. 120 μs) are consistent

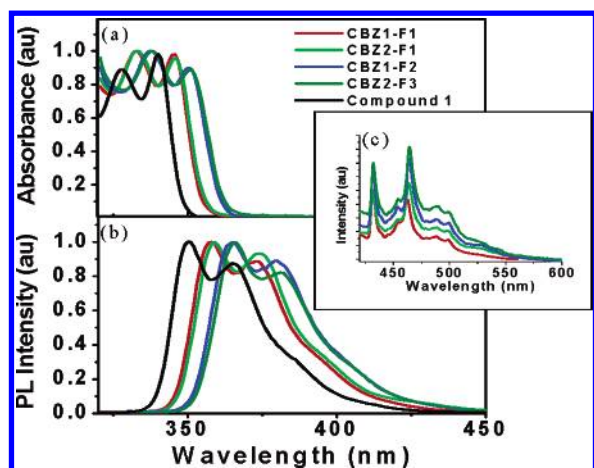


Figure 1. (a) Absorption and (b) photoluminescence (PL) spectra of the CBZ*m*-F*n* hybrids and compound **1** in chloroform. (c) Normalized phosphorescence (77 K) spectra of the CBZ*m*-F*n* hybrids in 2-methyltetrahydrofuran (2-MeTHF).

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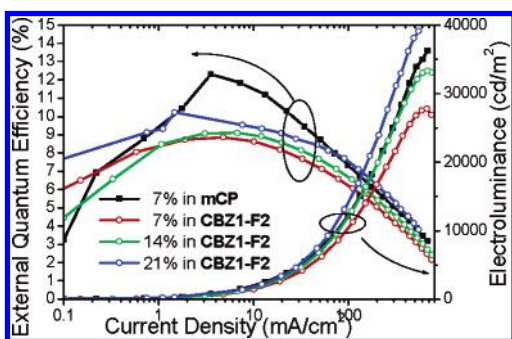


Figure 2. External quantum efficiency–current density–electroluminescence characteristics of devices I–IV.

with their assignment as organic triplet states. We estimated the triplet energies of the four CBZ*m*-*Fn* hybrids to be ca. 2.88 eV, suggesting that these hybrids can be used as host materials for triplet blue emitters, such as FIrpic ($E_T = 2.65$ eV). To test our assumption, we fabricated a series of prototypical FIrpic OLEDs (devices I–IV) containing either CBZ1-F2 or mCP as the host material for the dopant FIrpic. Devices I–III were OLEDs incorporating CBZ1-F2 as the host material; they had the structures in the form ITO/NPB (30 nm)/CBZ1-F2:FIrpic (*x*%, 30 nm)/TPBI (30 nm)/LiF (1 nm)/Al (150 nm), where *x* was 7, 14, and 21% for devices I–III, respectively. For comparison, device IV had the same device structure, but with mCP as the host material: ITO/NPB (30 nm)/mCP:FIrpic (7%, 30 nm)/TPBI (30 nm)/LiF (1 nm)/Al (150 nm); in this case, we doped the device at 7%, the optimal doping concentration for the FIrpic phosphorophore.^{3b}

We observed that the performance of the CBZ1-F2 host devices (devices I–III) was improved upon increasing the dopant concentration. Nevertheless, regardless of the FIrpic dopant concentration (Figure 2), within the practical current density range (ca. 1–20 mA/cm²), the EL efficiencies of the CBZ1-F2-based OLEDs (devices I–III) were all slightly inferior to that of the mCP-based OLED (device IV). We attribute this finding to the difference between the triplet-state excitation energies of CBZ1-F2 and FIrpic (2.88–2.65 = 0.23 eV) being smaller than that between mCP and FIrpic (3.02–2.65 = 0.37 eV).¹⁰ On the other hand, upon increasing the doping concentration of FIrpic from 7 to 14 to 21%,

devices I–III displayed the increasing maximum electroluminescence: from 27 800 to 33 300 to 39 100 cd/m² (Figure 2). We observed similar trends for the electroluminescence at practical current densities of 10 and 20 mA/cm². In terms of their EL efficiency, devices I–III also exhibited (Figure 2) increasing external quantum efficiencies (from 8.9 to 9.1 to 10.2%) and current efficiencies (from 14.8 to 16.5 to 19.2 cd/A). It is interesting to observe that the tolerant doping concentration of FIrpic was higher for CBZ1-F2 than for the mCP host matrix. Consequently, the maximum electroluminescence of device III (39 100 cd/m²) was higher than that of device IV (36 300 cd/m²). Such results imply that CBZ1-F2 is a more effective host material for isolating the FIrpic molecules from one another. A greater separation of FIrpic molecules means a lower degree of T_1 – T_1 annihilation when the device is operated under a high current density. This result is consistent with the higher degree of efficiency roll-off for device IV than for devices I–III at elevated current density; for example, device IV had an efficiency roll-off of 52% at 200 mA/cm², whereas devices I–III were 39–43% off from their peak efficiencies. Such results were anticipated because of the bulkier molecular structure and much higher value of T_g of CBZ1-F2 relative to those of mCP.

In summary, electron-rich 9-phenylcarbazole reacted efficiently with 9-phenyl-9-fluorenone (**2**) and 9-fluorenone (**3**) to furnish a series of well-characterized carbazole/fluorene (CBZ*m*-*Fn*) hybrids in high yields. The incorporation of a rigid linkage between the carbazole and fluorene moieties (at the C-9 position of the fluorene derivative) enhanced these materials' thermal and morphological stabilities; in addition, the tetrahedral nature of the C-9 connection preserved the electrical and optical properties of the carbazole unit. Initial results indicated that efficient blue phosphorescent OLED devices could be prepared when using CBZ1-F2 as the host material and FIrpic as the dopant. We are currently investigating devices based on other CBZ*m*-*Fn*'s and exploring their structure–performance correlation.

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Supporting Information Available: Synthetic details, structural characterizations, and DSC thermograms of the carbazole/fluorene hybrids. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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