

Solution-processible Fluorinated Carbazole Derivative for Phosphorescent Organic Light-emitting Diodes

Ziyi Ge,¹ Teruaki Hayakawa,¹ Shinji Ando,¹ Mitsuru Ueda,¹ Toshiyuki Akiike,² Hidetoshi Miyamoto,²
Toru Kajita,² and Masa-aki Kakimoto*¹

¹Department of Organic & Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552

²Display Research Laboratories, JSR Corporation, 100 Kawajiri-cho, Yokkaichi 510-8552

(Received December 21, 2007; CL-071418; E-mail: mkakimoto@o.cc.titech.ac.jp)

A fluorinated carbazole, 9,9'-[2,2'-bis(trifluoromethyl)-biphenyl-4,4'-diyl]bis(9H-carbazole) (6FCBP) was prepared, which exhibited better solubility compared to the well-known hole-transporting material 4,4'-bis(carbazol-9-yl)biphenyl (CBP). 6FCBP was employed to fabricate OLEDs by spin coating or vacuum deposition with excellent performance.

Considerable progress has been achieved in organic light-emitting diodes (OLEDs) since the promising work by Tang and VanSlyke in 1987.¹ So far, OLEDs have been successfully employed in commercial fields such as full-color displays and solid light sources, whereas they are limited by the low fabrication yield down to 50% resulting from the complicated multi-layer thermal evaporation techniques.² Of the high-performance OLEDs reported to date, most were fabricated by multi-layer vacuum deposition even up to six organic layers.³ Development of solution-processible fabrication such as spin coating or ink-jet printing in OLEDs will offer a promising alternative to vacuum deposition techniques, if high efficiency can also be simultaneously provided.^{4,5} 4,4'-Bis(carbazol-9-yl)biphenyl (CBP) is a well-known hole-transporting material and has been extensively employed in OLED due to its high hole-transporting mobility in addition to the good thermal properties.⁶ However, it can only be fabricated by thermal evaporation due to the low solubility arising from the rigid structure. Further, it exhibits undesirable crystallinity which possibly causes phase separation or aggregation in the layers. Hence, there is a requirement to modify its structure without obviously decreasing its good properties.

In this letter, we reported a hole-transporting molecule, 9,9'-[2,2'-bis(trifluoromethyl)biphenyl-4,4'-diyl]bis(9H-carbazole) (6FCBP), incorporating two trifluoromethyl groups at the biphenyl unit in CBP. Trifluoromethyl group has been widely introduced in molecules to improve the solubility arising from the hydrophobicity and large free volume.⁷

6FCBP was synthesized according to the synthetic procedure as shown in Scheme 1. First, 4,4'-diiodo-2,2'-bis(trifluoro-

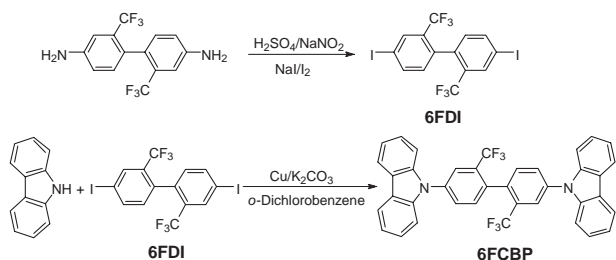
methyl)biphenyl (6FDI) was prepared in diazotation followed by iodination from 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diamine. 6FCBP was synthesized in an Ullmann reaction starting from 6FDI and carbazole catalyzed by copper/K₂CO₃ in *o*-dichlorobenzene. The structures of 6FDI⁸ and 6FCBP⁹ were identified by IR and NMR spectra.

The thermal properties of 6FCBP were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements. As shown in Figure 1, 6FCBP was thermally stable up to 350 °C with the thermal decomposition temperature (*T_d*) of 363 °C in nitrogen. By examination of DSC, 6FCBP exhibits a glass-transition temperature (*T_g*) of 101 °C and a melting point of 232 °C, suggesting it has a good thermal stability.

Figure 2 outlines the UV spectra, in which the absorption centered at 291 nm originates from the π - π^* transition. The experimental values of HOMO levels were determined with a Riken AC-2 photoemission spectrometer (PES), and those of LUMO (*S*₁) and the triplet energy levels (*T*₁) were estimated from the UV and phosphorescent spectra, respectively. The HOMO and LUMO levels of 6FCBP were determined to be 5.98 and 2.41 eV, respectively with the energy gap of HOMO-LUMO of 3.57 eV. The triplet energy level of 6FCBP is higher than that of *fac*-tris(2-phenylpyridine)iridium (Ir(ppy)₃) by 2.91 to 2.44 eV, indicating that 6FCBP is suitable to be used as the host material for Ir(ppy)₃ due to the efficient prevention of back energy transfer from the guest to the host.¹⁰

6FCBP can readily dissolve in common organic solvents, such as chloroform, 1,2-dichloroethane, THF, chlorobenzene, and anisole owing to the incorporation of trifluoromethyl groups with large free volume, which enables the preparation of homogeneous thin films by spin coating.

Phosphorescent OLED devices using 6FCBP as the host were fabricated by spin-coating and vacuum deposition with the structure of ITO/PEDOT (20 nm)/6FCBP + 6% mol Ir(ppy)₃ (50 nm)/TPBI (30 nm)/Cs:BCP(1:1) (20 nm)/Al(100



Scheme 1. Synthetic procedure of 6FCBP.

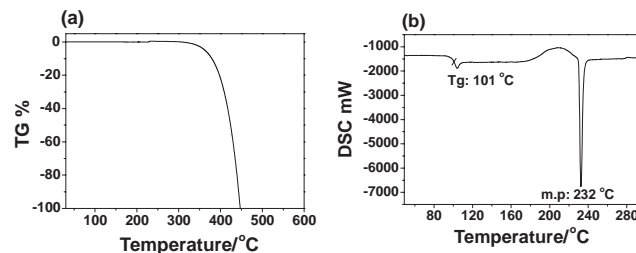


Figure 1. Thermal properties of 6FCBP: (a) TGA curve, (b) DSC curve.

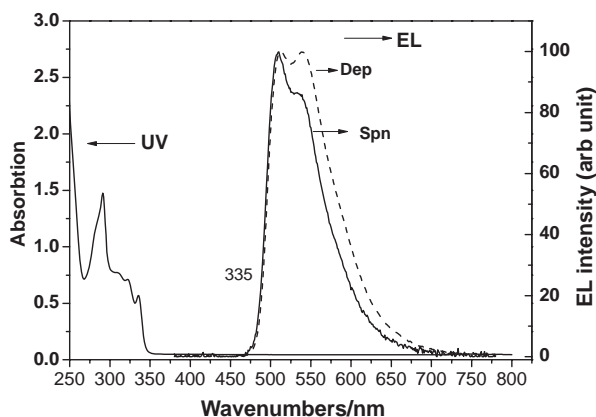


Figure 2. UV absorption spectra of 6FCBP (in THF) and EL spectra of the spin-coated (Spn) and vacuum-deposited (Dep) devices.

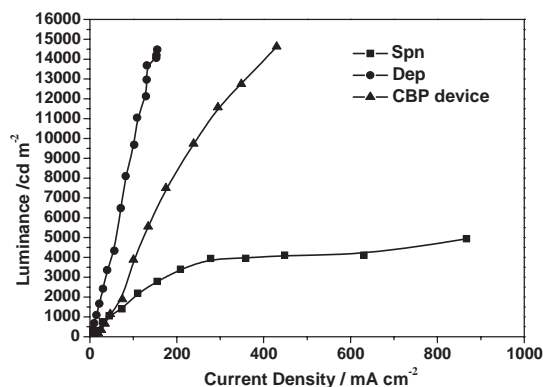


Figure 3. Luminance versus current density characteristics for the devices.

nm). Poly(3,4-ethylenedioxythiophene) (PEDOT) is employed to promote the hole injection and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) serves as the electron-transporting and hole-blocking layer. Cs-doped BCP and Al acts as the composite cathode while ITO served as the anode. 6FCBP doped with 6% mol Ir(ppy)₃ is used as the hole-transporting and emitting layer. As comparison, CBP-based device with the similar structure was also fabricated by vacuum deposition. As shown in Figure 2, the EL spectra of the devices exhibit the typical green luminescence around 520 nm originated from Ir(ppy)₃, implying the energy of triplet excitons are well transferred from the host of 6FCBP to the guest of Ir(ppy)₃.

Figure 3 illustrates the current–luminance (*I*–*L*) characteristics of the devices and the results are summarized in Table 1. Spin-coated 6FCBP device exhibits good performance with the maximum luminance of 4900 cd/m² and current efficiency of 2.6 cd/A. The corresponding vacuum-deposited device shows an improved performance with the maximum luminance and current efficiency of 14000 cd/m² and current efficiency of 10.4 cd/A, which may be attributed to the better film formation resulting from the thermal evaporation relative to spin coating. The performance of vacuum-deposited 6FCBP-based device is comparable with that of CBP-based one (14500 cd/m² and 12.9 cd/A) in a similar structure.

Table 1. EL performance of the devices

Device	Fabrication	V_{on}^a /V	L_{max}^b /cd m ⁻²	$\eta_{c,max}^c$ /cd A ⁻¹
6FCBP	Spn	5.1	4900	2.6
6FCBP	Dep	9.9	14000	10.4
CBP	Dep	5.3	14500	12.9

^aTurn-on voltage. ^bMaximum luminance. ^cMaximum current efficiency.

In summary, we have successfully optimized the solubility of CBP by incorporating two trifluoromethyl groups at the biphenyl unit and developed a fluorinated carbazole molecule of 6FCBP, which exhibits desirable solubility in common solvents allowing a solution-processed fabrication. The spin-coated 6FCBP device doped with Ir(ppy)₃ as the guest exhibits a good performance, while the vacuum-deposited one shows an enhanced maximum luminescence and current efficiency up to 14000 cd/m² and 10.4 cd/A, respectively, which is comparable with the similar CBP-based device.

References and Notes

- 1 C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
- 2 C.-L. Ho, W.-Y. Wong, G.-J. Zhou, B. Yao, Z. Xie, L. Wang, *Adv. Funct. Mater.* **2007**, *17*, 2925.
- 3 Y. Agata, H. Shimizu, J. Kido, *Chem. Lett.* **2007**, *36*, 316.
- 4 J.-A. Cheng, C. H. Chin, C. H. Liao, *Chem. Mater.* **2004**, *16*, 2862.
- 5 M. C. Gather, A. Köhnen, A. Falcou, H. Becker, K. Meerholz, *Adv. Funct. Mater.* **2007**, *17*, 191.
- 6 M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4.
- 7 Z. Ge, S. Yang, Z. Tao, J. Liu, L. Fan, *Polymer* **2004**, *45*, 3627.
- 8 Characterization of 6FDI: ¹H NMR (CDCl₃, 300 MHz, δ): 8.05 (s, 2H), 7.89–7.85 (d, 2H), 6.99–6.96 (d, 2H). ¹³C NMR (CDCl₃, 75 MHz, δ): 139.8, 135.8, 135.0, 132.8, 130.9, 130.5, 130.1, 129.6, 128.0, 124.4, 120.7, 117.0, 93.5. IR (KBr, cm⁻¹): 1612, 1504, 1449, 1302, 1232, 1178, 1129, 749.
- 9 Synthesis and characterization of 6FCBP: The mixture of carbazole (4.013 g, 24 mmol), 6FDI (5.420 g, 10 mmol), Cu (1.398 g, 22 mmol), K₂CO₃ (5.528 g, 40 mmol), 18-crown-6 ether (0.260 g, 1 mmol), and *o*-dichlorobenzene (50 mL) was heated at reflux for 24 h, followed by diluted with THF and filtered through celite. The solvents were removed in vacuum and the residue was purified by column chromatography on silica gel with hexane as the eluent followed by recrystallization from hexane/THF to offer a white solid of 6FCBP. Yield: 2.81 g (45%). ¹H NMR (CDCl₃, 300 MHz, δ): 8.20–8.16 (d, 4H), 8.06 (s, 2H), 7.89–7.84 (d, 2H), 7.71–7.67 (d, 2H), 7.53–7.45 (m, 8H), 7.39–7.32 (t, 4H). ¹³C NMR (CDCl₃, 75 MHz, δ): 140.3, 138.2, 135.3, 133.3, 131.4, 130.9, 130.6, 129.1, 126.4, 125.3, 124.6, 123.7, 121.6, 120.7, 120.5, 109.5. IR (KBr, cm⁻¹): 1927, 1590, 1471, 1395, 1302, 1248, 1151, 1054, 1000, 994, 885, 831, 684, 549. Anal. Calc for C₃₈H₂₂F₆N₂: C, 73.54; H, 3.57; N, 4.51%. Found: C, 73.61; H, 3.51; N, 4.53%.
- 10 K.-T. Wong, Y.-M. Chen, Y.-T. Lin, H.-C. Su, C.-C. Wu, *Org. Lett.* **2005**, *7*, 5361.