Synthesis and Properties of 3,8-Bis[4-(9*H*-carbazol-9-yl)phenyl]-1,10-phenanthroline for Phosphorescent OLEDs

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 12, 2007; CL-071376; E-mail: mkakimot@o.cc.titech.ac.jp)

A novel bipolar molecule, 3,8-bis[4-(9*H*-carbazol-9-yl)phenyl]-1,10-phenanthroline (CZPT) was synthesized and employed as the host in phosphorescent organic light-emitting devices (OLEDs). A maximum luminance of 7000 cd/m^2 was achieved using *fac*-tris(2-phenylpyridine)iridium (Ir(ppy)₃) as the emitting material.

Considerable progress has been made on phosphorescent organic light-emitting diodes (OLEDs) for their high external quantum efficiency via the intersystem crossing from singlet to triplet excited states followed by relaxing through phosphorescence.^{1,2} Maintaining the charge balance in OLEDs is an important issue for achieving highly efficient devices.³ Bipolar molecules combining both electron-rich and -deficient moieties in the molecular structures, have attracted much interest in OLEDs arising from the fact that a balanced density of charge and high efficiency could be attained by simultaneously supplying the electron and hole to electroluminescent (EL) materials sandwiched between two electrodes.⁴ Further, the bipolar feature bearing both electron- and hole-transporting units enables the simplification of the fabrication for achieving low-cost and large-area devices.

In this study, we report a new bipolar molecule, 3,8-bis[4-(9*H*-carbazol-9-yl)phenyl]-1,10-phenanthroline (CZPT), containing both electron-transporting phenanthroline and holetransporting carbazole units. Phenanthroline and carbazole were chosen as the building blocks in the molecule since the electrondeficient phenanthroline derivatives, such as 2,9-dimethyl-4,7diphenyl-1,10-phenanthroline (BCP), are well known as electron-transporting and hole-blocking materials, while the electron-rich carbazole derivatives have been widely used as holetransporting materials due to their high hole-transport mobility.⁵

CZPT was prepared according to the synthetic procedure as illustrated in Scheme 1. First, 3,8-dibromo-1,10-phenanthroline



Scheme 1. Synthetic procedure of CZPT.

(DBPT)⁶ and BRCZ⁷ were prepared according to the literatures. BRCZ was then converted to 4-(9*H*-carbazol-9-yl)phenylboronic acid (CZBA) treated with *n*-BuLi followed by trimethyl borate.⁸ The Suzuki cross-coupling reaction of DBPT and CZBA led to CZPT. The structure of CZBT was identified by IR and NMR sprectra.⁹

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were employed to investigate the thermal properties of CZPT. As shown in Figure 1, CZPT was thermally stable up to 500 °C with T_d of 530 °C in nitrogen. It has neither obvious T_g nor melting point when heated up to 400 °C and cooled to room temperature by DSC investigation, suggesting it possesses an amorphous state. The excellent thermal stability is attributed to the rigid aromatic structure, which enables preparation of homogeneous and stable morphological thin films by vacuum deposition.



Figure 1. (a) TGA curve, (b) DSC curve.



Figure 2. UV spectrum of CZPT (in THF) and EL spectrum of the device B.

(a)



Figure 3. Characteristics of OLEDs: (a) EL device structure, (b) current–luminance curves.

Figure 2 outlines the UV spectrum, in which the absorption at 375 nm originates from the π - π * transitions from the electron-donating carbazole to the electron-accepting phenanthroline moiety. 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-LUMO energy gap of CZPT was determined to be 3.18 eV. The triplet energy level of CZPT (3.24 eV) is higher than that of Ir(ppy)₃ (2.44 eV), indicating that CZPT is suitable to be used as the host material for Ir(ppy)₃ due to the prevention of back energy transfer from the guest to the host.¹⁰

Phosphorescent OLED devices using CZPT as the host were fabricated by vacuum deposition in two structures as outlined in Figure 3a. As shown in Figure 2, the EL spectra exhibit the typical green luminescence around 520 nm originated from $Ir(ppy)_3$, implying the energy of triplet exitons are well transferred from the host of CZPT to the guest of $Ir(ppy)_3$.

Figure 3b outlines the representative current–luminance (*I–L*) characteristics of CZPT devices and the results are summarized in Table 1. In device A, poly(3,4-ethylenedioxythiophene (PEDOT) is employed to promote the hole injection, and CZPT doped with 6% mol of $Ir(ppy)_3$ served as the emitting layer. Device A exhibits good performance with the maximum luminance of 4100 cd/m² and current efficiency at 100 cd/m² of 2.5 cd/A, individually. When a layer of 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) was employed as the hole

Table 1. EL performance of the devices

Device	Turn on voltage/V	Maximum luminance/cd m ⁻²	Luminance efficiency at $100 \text{ cd m}^{-2}/\text{cd A}^{-1}$
А	8.1	4100	2.5
В	10.5	7000	3.0

and exciton blocker, the performance of device B increased to 7000 cd/m^2 and 3.0 cd/A, respectively. The HOMO level of TPBI (6.20 eV as determined) is higher than that of CZBP (5.76 eV) by 0.44 eV, which increased the HOMO energy level barrier between the cathode and the emitting layer. Thus, the holes were blocked and the charge recombination was efficiently confined in the emitting layer consequently, suggesting that TPBI is an effective hole-blocking layer to improve the device performance.

In summary, a novel bipolar host, CZPT was prepared and employed as the host in phosphorescent OLEDs. CZPT exhibited excellent thermal stability and desirable amorphous state. Two Ir(ppy)₃-based devices, with CZPT as the hosts possessed high performance. The device exhibited improved efficiency when a hole-blocking layer of TPBI was used.

References and Notes

- J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Funct. Mater.* **2006**, *16*, 575.
- 2 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* 1998, 395, 151.
- 3 Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto, T. Ohara, J. Am. Chem. Soc. 2000, 122, 11021.
- 4 T. H. Huang, J. T. Liu, L. Y. Chen, Y. T. Lin, C. C. Wu, *Adv. Mater.* **2006**, *18*, 602.
- 5 Y. Agata, H. Shimizu, J. Kido, Chem. Lett. 2007, 36, 316.
- 6 D. Tzalis, Y. Tor, S. Failla, J. S. Siegel, *Tetrahedron Lett.* 1995, 36, 3489.
- 7 Q. Zhang, J. Chen, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, J. Mater. Chem. 2004, 14, 895.
- CZBA: ¹H NMR (DMSO-*d*₆, ppm) 8.26 (s, 2H), 8.24–8.22 (d, 2H), 8.10–8.07 (d, 2H), 7.60–7.58 (d, 2H), 7.42–7.38 (m, 4H), 7.28–7.24 (t, 2H). ¹³C NMR (DMSO-*d*₆, ppm) 139.9, 138.4, 135.9, 126.3, 125.3, 122.8, 120.5, 120.1, 109.7.
- 9 The mixture of CZBA (1.03 g, 3.6 mmol), DBPT (1.01 g, 3 mmol), Pd(PPh₃)₄ (0.10 g, 0.09 mmol), K₂CO₃ (2 M, 15 mL), and THF (60 mL) was degassed and refluxed for 48 h. The precipitation was filtered and washed with THF, then recrystallized in DMF to give a yellow solid of CZPT. Yield: 0.83 g (42%). ¹H NMR (DMSO-*d*₆, ppm) 9.70 (s, 2H), 9.07–9.06 (d, 2H), 8.41–8.37 (m, 8H), 8.28 (s, 2H), 7.99–7.96 (d, 4H), 7.64–7.56 (m, 8H), 7.46–7.41 (t, 4H). ¹³C NMR (DMSO-*d*₆, ppm) 151.4, 149.6, 140.6, 137.5, 136.2, 135.3, 133.4, 129.0, 128.4, 128.0, 126.1, 126.0, 123.5, 120.4, 120.2, 109.7. IR (KBr, cm⁻¹): 3438, 1602, 1525, 1449, 1335, 1229.
- 10 K.-T. Wong, Y.-M. Chen, Y.-T. Lin, H.-C. Su, C.-C. Wu, Org. Lett. 2005, 7, 5361.