Hexaphenylbenzene Derivatives for Blue Organic Light-emitting Devices

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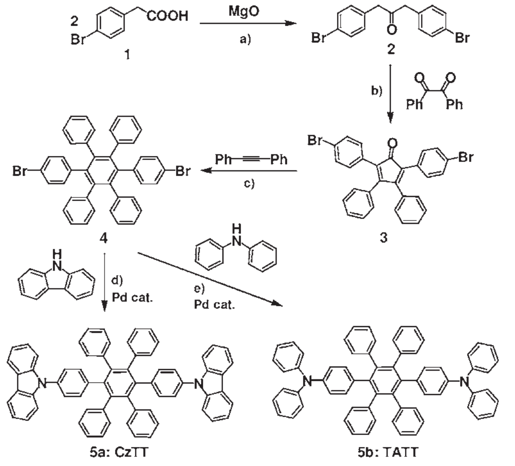
Novel hexaphenylbenzene derivatives having high triplet energy levels were synthesized and used in blue organic electrophosphorescent devices. The device with a blue phosphorescent emitter, iridium(III) bis[(4,6-difluorophenyl)pyridinato-*N*,$C^{2'}$]-picolinate, exhibited a high external quantum efficiency of 11% (24 cd/A) and a high power efficiency of 12 lm/W at 100 cd/m^2.

Organic light-emitting devices (OLEDs) have been expected to be the next generation flat panel displays and solid-state lighting devices.[1–3] Recently, extremely high efficiencies have been observed by using phosphorescent metal complexes as emitting centers. This is due to the fact that both singlet and triplet excited states are involved in the luminescence process at room temperature. Thus, internal quantum efficiencies could reach 100%.[4]



a) MgO 1.1 equiv., 340 °C, 2–4 Torr, 30 min.
b) Benzyl 1.2 equiv., 1.5 M KOH in EtOH, 70 °C, 15 min.
c) Diphenylacetylene 2.0 equiv., Benzophenone, 300 °C 20 min.
d) *N*-Carbazole 2.2 equiv., Pd(OAc)$_2$, P(*t*-Bu)$_3$, NaO^{t}Bu 6 equiv., Toluene, reflux, 24 h
e) Diphenylamine 2.2 equiv., Pd(OAc)$_2$, P(*t*-Bu)$_3$, NaO^{t}Bu 6 equiv., Toluene, reflux, 24 h

Scheme 1. Syntheses of CzTT and TATT.

Phosphorescent metal complexes require properly chosen wide-energy-gap host materials and carrier transporting materials so that the triplet excited energy at the metal complex can be confined. For instance, a blue OLED, with phosphrescent iridium(III) bis[(4,6-difluorophenyl)pyridinato-*N*,$C^{2'}$]-picolinate (FIrpic) as a guest emitter and 4,4′-*N*,*N*′-carbazolylbiphenyl (CBP) as a host, exhibits rather low efficiencies such as an EQE of 6.0%.[5] This is due to the fact that the host material, CBP, does not have sufficiently high triplet energy level to confine the triplet excited energy of the emitting center.[5,6] In this study, we designed and synthesized novel hexaphenylbenzene derivatives having high triplet excited energy (T_1) levels for the blue phosphorescent complex-based OLEDs.

The structures of the hexaphenylbenzene derivatives and the synthetic scheme are shown in Scheme 1.[7] A mixture of (*p*-bromophenyl)acetic acid (**1**) and magnesium oxide as a heating medium were heated to 340 °C in reduced pressure 2–4 Torr for 30 min. After cooling at room temperature, 1,3-bis(*p*-bromophenyl)-2-propanone (**2**) was extracted with EtOH in 14% yield. 2,5-Bis(*p*-bromophenyl)-3,4-diphenylcyclopentadion (**3**) was prepared by a condensation reaction of **2** with benzyl and potassium hydroxide in EtOH at 70 °C for 15 min in 92% yield. 4,4″-Dibromophenyl-2′,3′,5′,6′-tetraphenyl-*p*-terphenyl was prepared by the Diels–Alder reaction of **3** with diphenylacetylene in 77% yield. Finally, 5a: CzTT and 5b: TATT were synthesized by the palladium-catalyzed coupling reaction[8] in 96 and 86% yield, respectively. Each of the crude materials was purified by silica-gel column chromatography and further purified by thermal gradient sublimation under N_2 gas stream. The structures of **1**–**5** were characterized by ^{1}H NMR and MS spectroscopy.[9] Hexaphenylbenzene derivatives show no glass-transition temperature (T_g) up to 300 °C by differential scanning calorimetry analysis.

Compared with the conventional host and carrier transport materials, such as CBP, the extension of the π conjugation of CzTT and TATT is reduced owing to the twisted structure of the bulky hexaphenylbenzene unit. Thus, wide HOMO–LUMO energy gaps and high T_1 levels are expected for hexaphenylbenzene derivatives. The optical energy gaps or HOMO–LUMO energy gaps, of CzTT and TATT were determined from UV–vis absorption edges using a Shimadzu UV-2200A spectrophotometer to be 3.49 and 3.33 eV, respectively.

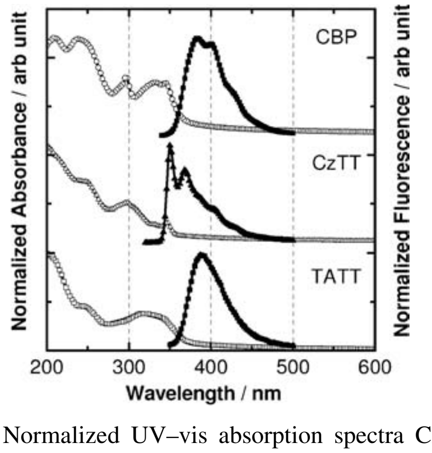


Figure 1. Normalized UV–vis absorption spectra CBP (open circle), CzTT (open triangle), and TATT (open square). Normalized fluorescent spectra CBP with Ex. = 331 nm (closed circle) CzTT with Ex. = 297 nm (closed triangle) and TATT with Ex. = 331 nm (closed square).

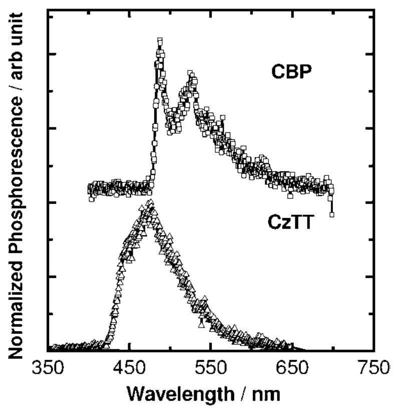


Figure 2. Normalized phosphorescent spectra vacuum-deposited CBP (open circle) and CzTT (open triangle) films at 4.2 K, measured by streak camera with a N_2 gas leaser (337 nm) as an excitation light.

The ionization potentials (I_p) of CzTT and TATT were determined, using Riken Keiki AC-1 under ambient atmosphere, to be 6.20 and 5.82 eV, respectively.

Figure 1 shows UV–vis absorption spectra and fluorescence spectra of vacuum-deposited CBP, CzTT, and TATT films. CzTT has wider gap energy than conventional material CBP, and blue-shifted fluorescence. Figure 2 displays phosphorescent spectra of vacuum-deposited CBP and CzTT at 4.2 K. CzTT shows blue-shifted phosphorescence compared with CBP. These results confirm that a hexaphenylbenzene unit is effective to control the extension of the π conjugation.

We measured the absolute photoluminescence quantum efficiencies (PLQEs) for Firpic (1 wt %)-doped CzTT and CBP films using a calibrated integrating sphere purged with N_2 (C9920 from Hamamatsu Photonics K. K.). The PLQEs of CzTT and CBP are 72 ± 1 and $62 \pm 1\%$, respectively. The higher PLQE of Firpic-doped CzTT indicate that the triplet excited energy of FIrpic was effectively confined by CzTT because of its higher triplet excited energy level.

Blue OLEDs using the hexaphenylbenzene derivatives, as the carrier transport layers, and FIrpic, as the emitting center, were fabricated. In order to enhance the hole injection from the anode to the organic layer, poly(arylene ether sulfone)-containing tetraphenylbendizine (PTPDES) doped with tris(4-bromophenyl) aminium hexachloroantimonate (TBPAH) was used as the anode buffer layer, which was spin-coated on a patterned and cleaned indium–tin oxide (ITO)-coated glass substrate. Then, organic layers were successively vacuum-deposited onto the polymer layer at 2–4×10^{-6} Torr. The cathode consists of 0.5 nm of lithium fluoride (LiF) as the electron injection layer and 100 nm of aluminum.

A device with a structure of ITO/TBPAH (10 wt %)-doped PTPDES (20 nm)/TATT (30 nm)/FIrpic (8 wt %)-doped CzTT (30 nm)/3-(4′-*tert*-butylphenyl)-4-phenyl-5-(4″-biphenyl)-1,2,4-triazole (TAZ) (30 nm)/LiF (0.5 nm)/Al (100 nm) exhibited blue emission from FIrpic with a peak wavelength of 472 nm. As seen in Figure 3, a high EQE of 11% (24 cd/A) and a power efficiency of 12 lm/W at 100 cd/m^2 were obtained. A maximum luminance of 12,500 cd/m^2 was achieved at a voltage of 12.5 V. On the other hand, a device using conventional materials with a structure of ITO/TBPAH (10 wt %)-doped PTPDES (20 nm)/*N*,*N*′-bis-(1-naphthyl)-*N*,*N*′-diphenyl-4,4′-diamine) (NPD) (30 nm)/FIrpic (8 wt %)-doped CBP (30 nm)/TAZ (30 nm)/LiF (0.5 nm)/Al (100 nm) exhibited a low EQE of 4.8% at 100 cd/m^2. These results reflect that the triplet excited energy of Firpic can be confined well by CzTT and TATT, while the conventional materials, CBP and NPD, serve as the triplet quenching sites owing to their low T_1 levels.

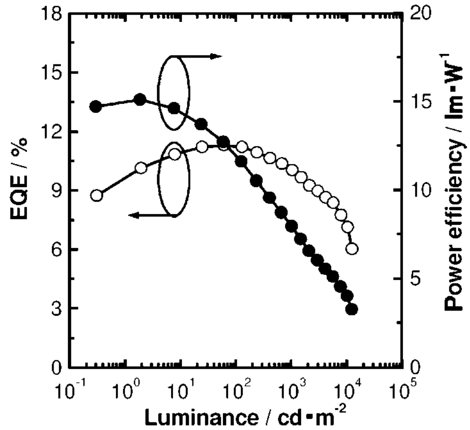


Figure 3. External quantum efficiency (open circles) and power efficiency (closed circles) as a function of luminance for the device ITO/10 wt % TBPAH doped PTPDES (20 nm)/TATT (30 nm)/FIrpic 8 wt % doped CzTT (30 nm)/TAZ (30 nm)/LiF (0.5 nm)/Al (100 nm).

In conclusion, we successfully synthesized novel hexaphenylbenzene derivatives having wide energy gap and high T_1 levels and fabricated a blue OLED with high efficiencies.

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9 **CzTT**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.95–7.10 (m, 28H), 7.15–7.50 (m, 12H), 8.05–8.15 (d, $J = 8.1$ Hz, 4H); FAB-MS: m/z Calcd MW, 864.4; $m/z = 865$ (M^+), 861, 700, 613, 460, 307. **TATT**: (270 MHz, $CDCl_3$) δ 6.58–6.72 (m, 6H), 6.80–6.86 (m, 6H), 6.88–7.00 (m, 28H), 7.12–7.20 (m, 8H); FAB-MS: m/z Calcd MW, 869.1; $m/z = 869$ (M^+), 767, 702, 613, 482, 460.