m-Terphenyl-modified carbazole host material for highly efficient blue and green PHOLEDS†

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A simple *m*-terphenyl modified carbazole derivative, 9-phenyl-3,6-bis-[1,1′;3′1″]terphenyl-5′-yl-9*H*-carbazole (CzTP) was developed. By using CzTP as a host material, the PHOLEDs showed the maximum power efficiencies ($\eta_{p,\ max}$) of 55 lm W^{-1} for blue and 113 lm W^{-1} for green, respectively.

Since the discovery of phosphorescent iridium complexes, those achieve the internal efficiency of phosphorescent organic light-emitting devices (PHOLED) up to 100%, wide-energy-gap phosphorescent materials have gained considerable attention to realize highly efficient PHOLEDs.[1–3] Generally, for use of phosphorescent emitter, the host materials play a critical role to determine the device performance. The primary roles of phosphorescent host materials are (i) the confinement of the triplet excitons on the emitter, (ii) the suppression of dopant aggregation, and (iii) the adjustment of the carrier balance of holes and electrons in the emissive layer (EML).

To meet these requirements, (a) carbazole-based host materials,[4] (b) tetraphenylsilane-based host materials,[5] (c) phosphine oxide-based host materials,[6] and (d) triphenylamine-based host materials[7] have been reported in FIrpic-based blue PHOLEDs and the devices with the maximum power efficiencies ($\eta_{p,\ max}$) up to 30 lm W^{-1} have been developed. Among them, the carbazole derivatives are one of the most attractive candidates to reduce the driving voltage of PHOLEDs because of (i) the small singlet–triplet exchange energy (ΔE_{ST}), which is attributed to the energy difference between the singlet excited energy (E_{S1}) and the triplet one (E_{T1}),[8] and (ii) the high chemical compatibility with dopants to suppress the aggregation.[9] From this point of view, we have developed phosphorescent host materials and demonstrated highly efficient FIrpic-based PHOLEDs with $\eta_{p,\ max}$ over 60 lm W^{-1}.[10] These results promise that carbazole derivatives provide highly efficient PHOLEDs. In this communication, we report a simple *m*-terphenyl modified carbazole derivative, 9-phenyl-3,6-bis-[1,1′;3′1″]terphenyl-5′-yl-9*H*-carbazole (CzTP) as a host material for highly efficient blue and green PHOLEDs (Fig. 1).

CzTP was designed to possess both high E_{T1} and thermal stability by introduction of two *m*-terphenyl moieties into the 3,6-position on the carbazole moiety. The E_{T1} of *m*-terphenyl is 2.82 eV,[1] which is applicable to blue PHOLED, and the *m*-terphenyl group makes the T_g of carbazole higher, compared with that of well known host materials, such as 3,5-bis(9-carbazolyl)benzene (mCP) and 4,4′-*N*,*N*′-dicarbazolyl-biphenyl (CBP). Therefore, CzTP is supposed to have both high E_{T1} and thermal stability.

First, we conducted the density functional theory (DFT) calculations of CzTP. The optimized structures were calculated at the RB3LYP 6-31G(d) for the ground state, and UB3LYP 6-31G(d) for the excited triplet state, respectively. The single-point energies were calculated at the corresponding 6-311 + G(d,p) levels. The calculated highest occupied molecular orbital (HOMO) energy of CzTP is estimated to be 5.52 eV, and lowest unoccupied molecular orbital (LUMO) energy and HOMO–LUMO energy gap (E_g) are 1.28 eV, and 4.24 eV respectively. Further, to estimate the E_{T1} energy of CzTP, we calculated the E_{T1} energies of CzTP, mCP and CBP by using the previously reported method.[11] The calculated E_{T1} energies were 2.87 eV for CzTP, 3.32 eV for mCP, and 2.66 eV for CBP. Thus, CzTP is expected to have higher E_{T1} than that of CBP from the calculations.

CzTP was prepared *via* a Suzuki–Miyaura coupling reaction of 3,6-dibromo-9-phenylcarbazole **1** with *m*-terphenyl boronic ester **2** in 60% yield (Scheme 1). The characterization of CzTP was established on the basis of mass spectrometry, NMR spectroscopy, and elemental analyses. (see ESI, Fig. S1†)

The compound was purified by train sublimation before device fabrication. The thermal properties of CzTP were estimated by differential scanning calorimetry (DSC). The glass transition temperature (T_g) of CzTP was 135 °C, which is *ca.* 2 times higher than that of mCP (60 °C) and CBP (62 °C),[4e] and formed morphologically stable amorphous films. The HOMO level was observed at 5.91 eV by atmospheric photoelectron spectroscopy (AC-3, Riken Keiki Co.). While the LUMO energy was calculated at 2.48 eV by subtraction of the optical energy gap (E_g) from the HOMO energy.

The solid state phosphorescent spectrum is often observed as a broad spectrum with no clear peaks.[10b] Therefore, we calculated the highest phosphorescent energy (E_{T1}) of all the materials from the onset of the phosphorescent spectrum.

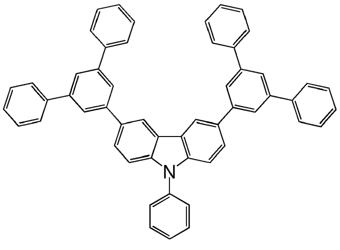

Fig. 1 Chemical structure of CzTP.

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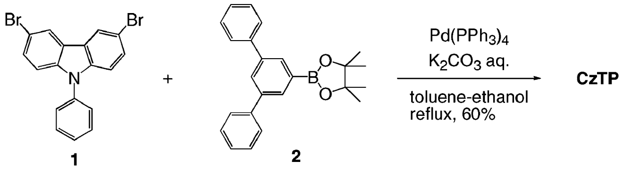

Scheme 1 Synthesis of CzTP.

The E_{T1} energies of CzTP, mCP and CBP were observed at 2.70, 3.00 and 2.60 eV, respectively (see ESI, Fig. S1 and S2†). On an average of these three E_{T1} energies, the experimental values are 0.18 eV lower than the calculated values. The singlet excited energy (E_{S1}) of the materials were estimated from the E_g, and the ΔE_{ST} is calculated from the E_{S1} and E_{T1} values. The E_{T1} of CzTP is 0.07 eV smaller than that of FIrpic,[10b] and 0.17 eV higher than that of Ir(ppy)$_3$.[12] The expanded π-conjugation of the 3,6-position on the carbazole moiety reduces the E_{T1} of CzTP compared with that of mCP.

In OLEDs, the electrical carrier injection into the host material takes place on its HOMO and LUMO, that is, holes are injected into the HOMO, while electrons are injected into the LUMO. Therefore, the host material with a smaller E_g, which approximately corresponds to E_{S1}, can make the driving voltage of OLEDs lower.[13] In addition, for the confinement of the exciton on a blue phosphorescent emitter FIrpic, the host material with high E_{T1} energy over 2.77 eV is also desirable. To reduce the driving voltage of blue PHOLEDs, it is necessary to adjust the E_{S1} energy as low as possible maintaining a high E_{T1} energy. In other words, both small ΔE_{ST} and high E_{T1} energies are essentially required to design an effective host material. In case of CzTP (ΔE_{ST} = 0.73 eV), the ΔE_{ST} is 0.11 eV smaller than that of CBP (ΔE_{ST} = 0.84 eV), and 0.24 eV larger than that of mCP (ΔE_{ST} = 0.49 eV). Compared with the non-carbazole materials such as TmPyPB (ΔE_{ST} = 1.17 eV)[10c] and B3PyPB (ΔE_{ST} = 1.28 eV),[10g] the ΔE_{ST} is 0.34–0.58 eV small (Fig. 2, see also ESI, Table S1†). Thus, the driving voltage of PHOLED is expected to be reduced using CzTP as a host.

The photophysical properties of FIrpic and Ir(ppy)$_3$-doped CzTP films were evaluated. The PL quantum efficiency (η_{PL}) of 11 wt% FIrpic-doped CzTP film was measured under N_2 flow using a integrating sphere excited at 331 nm with a multichannel spectrometer as the optical detector. The doped film showed high η_{PL} values of 71 ± 1%, that is smaller than that of mCP/FIrpic film (85 ± 1%).[3b] Although CzTP has the smaller E_{T1} than that of FIrpic, the transient PL decay curve of 11 wt% FIrpic-doped CzTP film exhibited almost single-exponential decay (98%) with the phosphorescence lifetime (τ_p) of 1.34 μs at room temperature, indicating the effective suppression of the FIrpic exciton quenching in the host (see ESI, Fig. S3†). The triplet emission energy of CzTP (2.70 eV), which is corresponding to the E_{T1}, is 0.07 eV smaller than that of FIrpic (2.77 eV). However, the triplet absorption energy of CzTP is considered to be larger than the E_{T1} of FIrpic. This may be attributed to the large structural relaxation energy of CzTP. From η_{PL} and τ_p, the radiative decay rate (k_r) of FIrpic in CzTP is evaluated to be 5.3 × 10^5 s^{-1}, which is slightly smaller than the k_r in mCP. Similarly, η_{PL} of 8 wt% Ir(ppy)$_3$-doped CzTP film showed 80 ± 1%, that is 10% smaller than that of CBP/Ir(ppy)$_3$ film (90 ± 2%).[3b] The transient PL decay curve of 8 wt% Ir(ppy)$_3$-doped film exhibited almost single-exponential decay (96%) with τ_p of 1.27 μs (see ESI, Fig. S3†). The k_r of Ir(ppy)$_3$ in CzTP is also estimated to be 6.3 × 10^5 s^{-1}, which is good agreement with the k_r in CBP. Thus, the superior performances of blue and green PHOLED can be realized using CzTP as a host material.

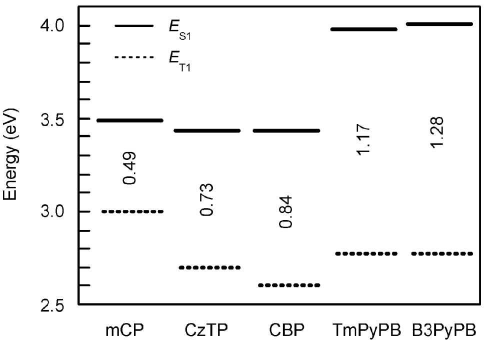

Fig. 2 Singlet (E_{S1}), triplet (E_{T1}) and ΔE_{ST} (inset) energies of materials.

To investigate the function of CzTP as a host material, a blue PHOLED with a structure of [ITO (110 nm)/poly(arylene ether sulfone)-containing tetraphenylbenzidine (TPDPES) doped with 10 wt% tris(4-bromophenyl)aminium hexachloroantimonate (TBPAH) layer[14] (20 nm)/2,2′-bis[3″-(*N*,*N*′-ditolylamino)phenyl]biphenyl (3DTAPBP)[10a] (20 nm)/FIrpic 11 wt% doped CzTP (10 nm)/3,5,3″,5″-tetra-3-pyridyl-[1,1′;3′,1″]terphenyl (B3PyPB)[10g] (50 nm)/LiF (0.5 nm)/Al (100 nm)] were fabricated. The E_{T1} of 3DTAPBP and B3PyPB are reported to be 2.82 and 2.77 eV, respectively. Therefore, the triplet exciton quenching of FIrpic at the EML/hole-transport layer interface and/or the EML/electron-transport layer interface can be minimized in this blue PHOLED. The EL spectrum is illustrated as the inset in Fig. 3(b). The emission was only from FIrpic with no emission from neighboring materials. The current density–voltage–luminance (*J*–*V*–*L*) characteristics are shown in Fig. 3(a). The turn-on voltage at 1 cd m^{-2} was 3.0 V, and the applied voltages at 100 cd m^{-2} and 1000 cd m^{-2} were 3.4 V and 4.1 V for, respectively, those are lower than the other FIrpic-based PHOLEDs. The power efficiency–luminance and current efficiency–luminance characteristics are shown in Fig. 3(b). The superior device performances were recorded to be 55 lm W^{-1} (52 cd A^{-1}) at 1 cd m^{-2}, 43 lm W^{-1} (46 cd A^{-1}) at 100 cd m^{-2} and 29 lm W^{-1} (38 cd A^{-1}) at 1000 cd m^{-2}, respectively.

On the other hand, the mCP/FIrpic device showed slightly lower device performances than that of the CzTP/FIrpic device, though the mCP/FIrpic film showed *ca.* 15% higher η_{PL} than that of CzTP/FIrpic film. This probably results from the better carrier balance in the CzTP/FIrpic device.

Further, we fabricated a green PHOLED with a structure of [ITO (110 nm)/TPDPES: 10 wt% TBPAH (20 nm)/1,1-bis[4-[*N*, *N*-di(*p*-tolyl)amino]phenyl]cyclohexane (TAPC) (30 nm)/CzTP: 8 wt% Ir(ppy)$_3$ (10 nm)/B3PyPB (50 nm)/LiF (0.5 nm)/Al (100 nm)]. All the materials, TAPC, CzTP and B3PyPB, have higher E_{T1} than that of Ir(ppy)$_3$, thus the triplet exciton quenching of Ir(ppy)$_3$ can be completely suppressed in this green PHOLED. The *J*–*V*–*L* characteristics and the EL spectrum are shown in Fig. 4. The turn-on voltage at 1 cd m^{-2} is 2.8 V,

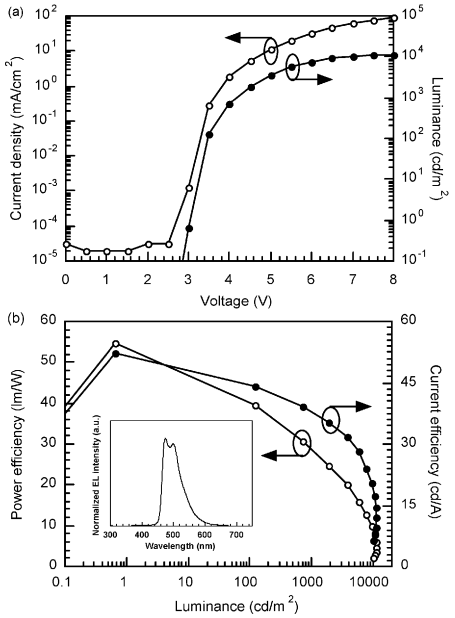

Fig. 3 (a) Current density–voltage and luminance–voltage characteristics for CzTP/FIrpic-based blue PHOLED. (b) Power efficiency-luminance and current efficiency-luminance characteristics. Inset: EL spectrum of the device.

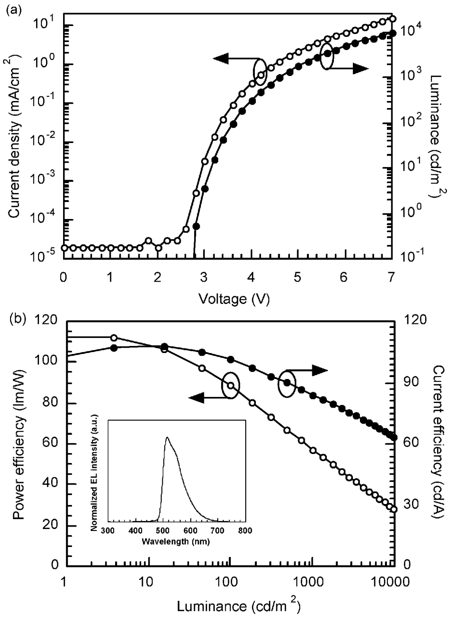

Fig. 4 (a) Current density–voltage and luminance–voltage characteristics for CzTP/Ir(ppy)$_3$-based green PHOLED. (b) Power efficiency-luminance and current efficiency-luminance characteristics. Inset: EL spectrum of the device.

and the applied voltages at 100 cd m^{-2} and 1000 cd m^{-2} are 3.6 V and 4.6 V, respectively. The green device perfomances were observed to be 113 lm W^{-1} (102 cd A^{-1}) at 1 cd m^{-2}, 89 lm W^{-1} (102 cd A^{-1}) at 100 cd m^{-2} and 57 lm W^{-1} (84 cd A^{-1}) at 1000 cd m^{-2}, respectively. The CzTP/Ir(ppy)$_3$ device showed comparable performances with the CBP/Ir(ppy)$_3$ device, which showed $\eta_{\mathrm{p,\ max}}$ of 118 lm W^{-1} (105 cd A^{-1}), though CzTP/Ir(ppy)$_3$ film showed *ca.* 10% lower η_{PL} than that of CBP/Ir(ppy)$_3$ film. These blue and green PHOLED efficiencies clearly indicate that CzTP functions as an effective host for PHOLEDs.

In summary, we developed a simple *m*-terphenyl modified carbazole phosphorescent host material, CzTP with high T_g of 135 °C and E_{T1} of 2.70 eV. By using CzTP as a host material for PHOLEDs, the devices showed the $\eta_{\mathrm{p,\ max}}$ of 55 lm W^{-1} for blue and 113 lm W^{-1} for green without light outcoupling enhancement, respectively.

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