Bipolar Host Materials for Green Triplet Emitter in Organic Light-emitting Diodes

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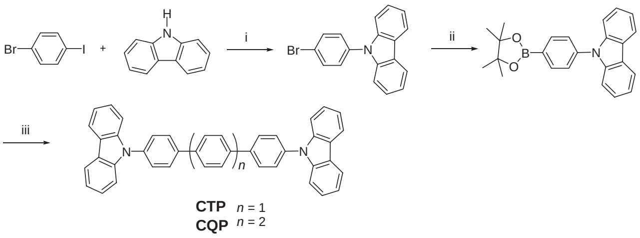
We have developed novel bipolar host materials for high efficiency green phosphorescent OLEDs (PHOLEDs). Phenyl moieties were inserted in a 9,9′-(biphenyl-4,4′-diyl)dicarbazole (CBP) compound to provide much easier electron injection and to increase electron mobility. The efficiency increase and voltage reduction by this modification were observed in green PHOLEDs. At a given constant luminance of 1000 cd/m^2, the power efficiency was enhanced about twenty percent in the general green PHOLED devices.

The efficiencies of organic light-emitting diodes (OLEDs) have advanced rapidly in recent year due to development of phosphorescent guest molecules containing transition metals that can harvest both singlet and triplet excitons generated by electron injection.[1–5] For efficient PHOLEDs, the transition-metal guest materials are doped into charge-transporting host materials. Tremendous researches on phosphorescent guest materials are on going but no intensive effort has been made to develop host materials. One of important properties of host materials for PHOLEDs is well-balanced carrier transportability. As this capable material, a CBP material was mainly used because of bipolar carrier transporting characteristics.[6] However, CBP has very good hole-transporting capability rather than that of electron because of the carbazole chemical unit. Novel host materials having similar carrier-transporting capabilities of hole and electron are required for highly efficient PHOLEDs. Usually, holes and electrons in OLEDs are transferred through the HOMO and LUMO level of used materials, respectively. A host with a wide HOMO–LUMO energy gap (E_g) causes the increase in the driving voltage and lowering efficiency of OLEDs. The CBP host material has a wide band gap due to the large exchange energy between singlet and triplet excited states, which makes deep HOMO and high LUMO states. Therefore, hole injection into host and electron injection into host become energetically unfavorable in red and green PHOLEDs and then the quest becomes a deep trap for hole and/or electron transport in emitting layer.[7,8] Recently, we have designed novel host materials for red and green PHOLEDs based on several molecular design concepts. Another phenyl ring was inserted to enhanced electron-transporting capability. The wide band gap was reduced in order to minimize charge trapping by the quest molecule for red or green PHOLEDs. The LUMO energy level of host was adjusted to be matched to electron-transporting materials or hole-blocking materials such as Alq_3 and Balq.

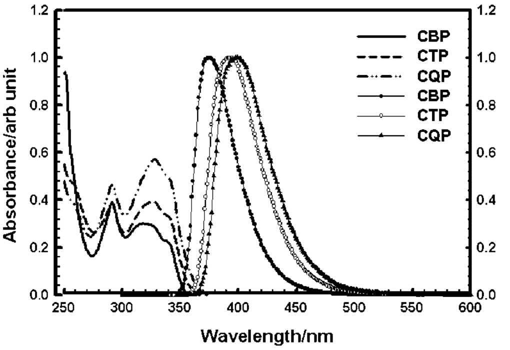
Novel host materials were synthesized as shown in Scheme 1. Three or four benzene rings were inserted between two carbazole groups via the Suzuki cross-coupling reaction based on CBP structure. 9,9′-(1,1′:4′,1″-terphenyl-4,4″-diyl)dicarbazole (CTP) and 9,9′-(1,1′:4′,1″:4″,1‴-quaterphenyl-4,4‴-diyl)dicarbazole (CQP) were synthesized with 57 and 51% yields, respectively at the final step.[9]



CTP $n = 1$
CQP $n = 2$

Scheme 1. The synthetic method of CTP and CQP. Reagents and conditions: (i) K_3PO_4, CuI, *trans*-1,2-diaminocyclohexane, toluene, reflux (condition A) or KOH, $CuCl_2$, 1,10-phenanthroline, *o*-xylene, reflux (condition B); (ii) 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, *n*-BuLi, THF, −78 °C (condition A) or bis(pinacolato)diboron, $PdCl_2(dppf)$, KOAc, DMSO, 80 °C (condition B); (iii) $Pd(PPh_3)_4$, K_2CO_3, THF, H_2O, toluene, 100 °C, 1,4-dibromobenzene for compound CTP or 4,4′-diiodobiphenyl for compound CQP.

The absorption and emission characteristics of CTP and CQP are summarized in Figure 1. Their UV–vis absorption spectra in tetrahydrofuran (THF) show that all of them have multiple absorptions ranging from 250 to 360 nm with a tail extending to about 370 nm. The CBP absorbs at 291 and 318 nm, CTP absorbs at 290 and 325 nm, and CQP absorbs at 290 and 328 nm. The last absorption peak by inserting benzene ring slightly shifted to longer wavelength as expected. The maximum emission



	λ_{ab}/nm	λ_{em}/nm	HOMO/eV	LUMO/eV
CBP	318, 291	375	5.86	2.37
CTP	325, 290	393	5.86	2.44
CQP	328, 290	399	5.83	2.47

Figure 1. Absorption, emission and energy band characteristics of CTP and CQP.

peaks were located 375, 393, and 399 nm for CBP, CTP, and CQP, respectively, implying that the energy level of the singlet state is lowed along with the enlargement of the conjugated systems. The HOMO energy levels were measured by surface analyzer (Riken-Keiki AC2), while the LUMO energy levels were estimated based on the HOMO energy levels and the optical band gaps obtained from the absorption spectra. The HOMO energy levels are 5.86 and 5.83 eV for CTP and CQP, respectively. Although the conjugated systems are structurally different, the HOMO energy levels of the three compounds were almost the same, suggesting that hole injection ability is similar. However, a LUMO energy level was decreased by adding phenyl rings. The CTP and CQP were expected that the electron is easily injected from an electron-transporting layer compared to CBP. Therefore, the driving voltage reduction of red and green PHOLEDs was expected by applying these CTP and CQP host materials. Ability of triplet exciton confinement by these host materials was compared by using Ir(ppy)$_3$ 8%-doped films (40 nm) on glass. Relative phosphorescent quantum efficiencies compared with CBP film were 2.0 for CTP and 0.9 for CQP, indicating that these materials play a good triplet hosts in PHOLEDs. The decomposition temperature (T_d), glass-transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) for three host materials were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements. Onset decomposition tem perature (T_d) of CTP and CQP were determined to be 498 and 535 °C, respectively, which are all higher than that of CBP (458 °C). In addition, excellent film forming qualities, good evaporation without decomposition, and less crystalline properties were observed. The crystallization temperatures of CTP and CQP were observed to be 295 and 335 °C, respectively, which is a significant improvement compared to 187 °C of CBP. CBP has serious crystallization issues on shadow masks for making full color devices in mass production. However, these materials show a significant improvement against such issues. The T_m of CTP and CQP were 319 and 378 °C, respectively.

The device structures of ITO/NPB(40 nm)/CBP(or CTP or CQP):Ir(ppy)$_3$(8%, 30 nm)/Balq(5 nm)/Alq$_3$(20 nm)/LiF/Al were employed. Figure 2 shows the current–voltage (a) and voltage–luminescence (b) characteristics of green PHOLEDs with CBP, CTP, and CQP as host materials. Three devices were measured until 10,000 cd/m^2 brightness value. At a given constant voltage of 5 V, the current density of CBP, CTP and CQP was found to be 0.02, 0.38, and 0.15 mA/cm^2, respectively. As expected, the current flow with novel host materials was significantly improved because of the lower electron injection barrier and reduction of carrier trapping by the dopant material. The operation driving voltage to reach 1000 cd/m^2 was 9.1 V for CBP, 6.5 V for CTP, and 8.9 V for CQP, respectively. About 2.6 V driving voltage reduction was observed when the CTP was used as a green host. This result suggests that the CTP has proper triplet energy level to transfer triplet energy to Ir(ppy)$_3$ in green PHOLEDs. Figure 2 shows power efficiency characteristics of the green PHOLEDs with CBP, CTP, and CQP host materials. The maximum power efficiency of CBP, CTP, and CQP was 13.15, 16.28, and 8.80 lm/W, respectively. The green PHOLEDs with CTP as the host material exhibited the best power efficiency characteristics among these three green devices. The CQP device showed the lowest efficiency value, which indicate that the triplet level is not proper in Ir(ppy)$_3$-based PHOLEDs. The triplet energy level of CBP and Ir(ppy)$_3$ is known to be 3.0–3.4 and 2.8–3.0 eV, respectively.[6,10,11] The energy gap between singlet and triplet state in CBP is about 0.5 eV. Based on this assumption, the triplet energy of CTP and CQP may be around 2.8–3.0 eV. Therefore, it is found that CTP is a good host and CQP is not proper material in green PHOLEDs. We are under research a CQP material as a red host in PHOLEDs.

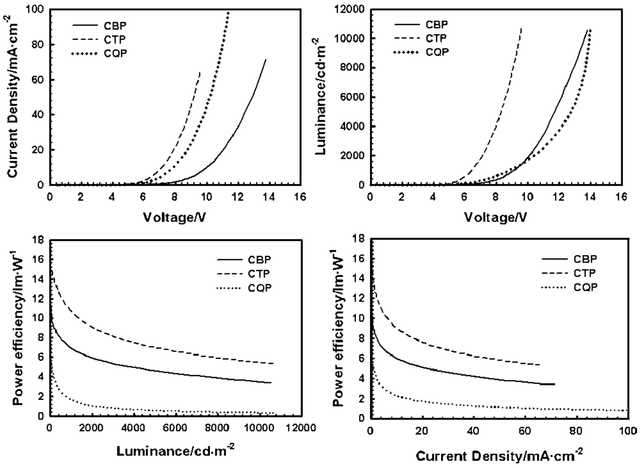


Figure 2. (a) *I–V*, (b) *L–V*, and (c) efficiency–brightness characteristics with CBP, CTP, and CQP host materials in green PHOLEDs.

In summary, a new host material, CTP, has been developed for high efficiency green PHOLEDs. This host has very small electron injection barrier. The electron trapping by the dopant was also minimized owing to lower LUMO energy level. As the results, the driving voltage was reduced about 2.6 V and power efficiency was enhanced about twenty percent compared to that of CBP based PHOLED.

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9 Spectral data: **CTP**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19–8.17 (d, 4H), 7.92–7.89 (d, 4H), 7.84 (s, 4H), 7.79–7.67 (d, 4H), 7.52–7.50 (d, 4H), 7.48–7.42 (t, 4H), 7.33–7.29 (t, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.9, 139.6, 139.5, 137.1, 128.41, 127.7, 126.07, 123.5, 120.4, 120.0, 109.9; MS (FAB) m/z: 561.6 $[M + H]^+$. **CQP**: ^{1}H NMR (400 MHz, CDCl$_3$ + DMSO-d_6) δ 8.18–8.16 (d, 4H), 7.93–7.90 (d, 4H), 7.84 (s, 4H), 7.70–7.68 (d, 4H), 7.52–7.50 (d, 4H), 7.45–7.41 (t, 4H), 7.33–7.31 (d, 4H); MS (FAB) m/z: 637.6 $[M + H]^+$.
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