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An α-Carboline-containing Host Material for High-efficiency Blue and Green Phosphorescent OLEDs

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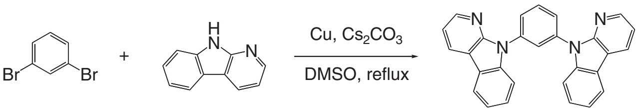
An α-carboline derivative, 9,9′-*m*-phenylenedi-α-carboline (mCaP) was designed and synthesized as a host material for phosphorescent OLEDs. By using a combination with phosphorescent emitters such as FIrpic and $Ir(ppy)_3$, we have successfully developed high-performance OLEDs with a power efficiency ($\eta_{p,100}$) at 100 cd m^{-2} of 37 lm W^{-1} for blue, and 94 lm W^{-1} for green, respectively.

Phosphorescent organic light-emitting devices (OLEDs) have received considerable attention for next-generation lighting and flat-panel display applications.[1–7] In phosphorescent OLEDs, the host material plays a critical role in determining the OLED performance. The primary requirements of host materials are 3-fold: (1) the confinement of triplet excitons on the emitter; (2) the suppression of emitter aggregation; (3) the adjustment of the carrier balance of holes and electrons in the emissive layer (EML).[4,6–8] To meet these requirements, we have already reported a pyridine-containing host material 2,6-bis-[3-(carbazol-9-yl)phenyl]pyridine (DCzPPy). DCzPPy-based OLEDs showed outstanding performance in blue and white OLEDs.[9] Most recently, Fukagawa and co-workers have reported high-efficiency blue OLEDs based on 2,2-bis[4-(pyridoindol-9-yl)phenyl]adamantane (Ad-Pd).[10] These two hosts have electron-deficient C=N double bond(s), and the weak electron-accepting nature of C=N double bonds promotes electron-injection as well as electron-transport creating superior carrier balance of holes and electrons in EML.

In this communication, we introduce an α-carboline derivative 9,9′-*m*-phenylenedi-α-carboline (mCaP) as a host material for phosphorescent OLEDs. Similar to DCzPPy and Ad-Pd, mCaP has two electron-deficient C=N double-bonds, and can be regarded as an aza analog of a conventional host material 9,9′-*m*-phenylenedicarbazole (mCP).

First, we conducted density functional theory (DFT) calculations of mCaP. The optimized structures were calculated at the RB3LYP 6-31G(d) for the ground state. The single-point energies were calculated at the corresponding RB3LYP 6-311+G(d,p) levels. The calculated highest occupied molecular orbital (HOMO) energy of mCaP was estimated to be 5.91 eV, and lowest unoccupied molecular orbital (LUMO) energy was 1.46 eV. On the other hand, the corresponding HOMO/LUMO energies of mCP were estimated to be 5.80 and 1.26 eV, respectively. In this calculation, the LUMO energy of mCaP was evaluated to be 0.20 eV deeper than that of mCP, probably because of the electron-accepting nature of C=N double bonds.

The starting material α-carboline was prepared according to the literature.[11] mCaP was synthesized via an Ullmann coupling of α-carboline with 1,3-dibromobenzene in 34% yield (Scheme 1). The characterization of mCaP was established on the basis of ^{1}H NMR, mass spectrometry, and elemental analyses.[12] The product was purified by train sublimation before device fabrication.



Scheme 1. Synthetic route of mCaP.

Table 1. Physical properties of mCaP and mCP

Compd	T_g/°C[a]	T_m/°C[a]	I_p/eV[b]	E_g/eV[c]	E_a/eV[d]
mCaP	85	223	6.00	3.39	2.61
mCP	60[e]	187	6.09	3.49	2.60

[a]Determined by DSC measurement. [b]Measured by AC-3 UV photoelectron yield spectrometer. [c]Taken as the point of intersection of the normalized absorption spectra. [d]Calculated using I_p and E_g values. [e]Data from ref. 13.

The thermal properties were measured by differential scanning calorimetry (DSC). The glass-transition temperature (T_g) was observed to be 85 °C, which is 25 °C higher than that of mCP (60 °C).[13] The melting point (T_m) was 223 °C, which is about 30 °C higher than that of mCP (187 °C). These better thermal properties can be attributed to a week intra- and/or intermolecular CH–N hydrogen-bond interaction in solid state.[14] The ionization potential (I_p) was observed at 6.00 eV by atmospheric-photoelectron-yield spectroscopy (AC-3, RIKEN Keiki Co.). The electron affinity (E_a) was calculated to be 2.61 eV by subtraction of the optical energy gap (E_g) from the I_p. On the other hand, the corresponding I_p and E_a of mCP were estimated at 6.09 and 2.60 eV, respectively. Unlike the calculations, rather similar E_a's were obtained from mCaP and mCP by means of the conventional method using E_g. The phosphorescence spectra were measured with a streak camera at 4.2 K. The onset phosphorescence was observed at 2.81 eV for mCaP and 3.00 eV for mCP, respectively (see Supporting Information (SI) in detail[17]). Therefore, mCaP is considered to be applicable for a blue phosphorescent OLED. All the physical properties are summarized in Table 1.

Prior to blue OLED fabrication using a common blue phosphorescent emitter iridium(III) bis[(4,6-difluorophenyl)pyridinate-*N*,$C^{2'}$]picolinate (FIrpic), the photophysical properties of a 10 wt% FIrpic-doped mCaP film were evaluated. The PL quantum efficiency (η_{PL}) was measured under N_2 flow using an integrating sphere excited at 331 nm with a multichannel spectrometer as the optical detector. The mCaP/FIrpic film showed a high η_{PL} value of 78 ± 1%, that is similar to that of mCP/FIrpic film (80 ± 1%). The transient PL decay curve of mCaP/FIrpic film exhibited almost single-exponential decay (98%) with the phosphorescence lifetime (τ_p) of 1.50 µs at room

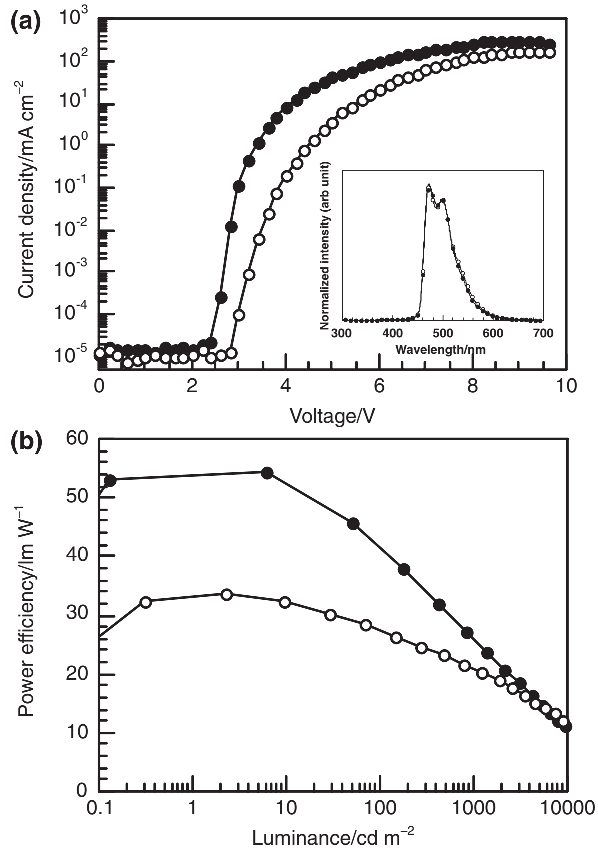


Figure 1. (a) *J–V* characteristics and (b) *PE–L* characteristics of blue PHOLEDs using mCaP (closed circle) and mCP (open circle) as a host material. Inset: EL spectra of the devices.

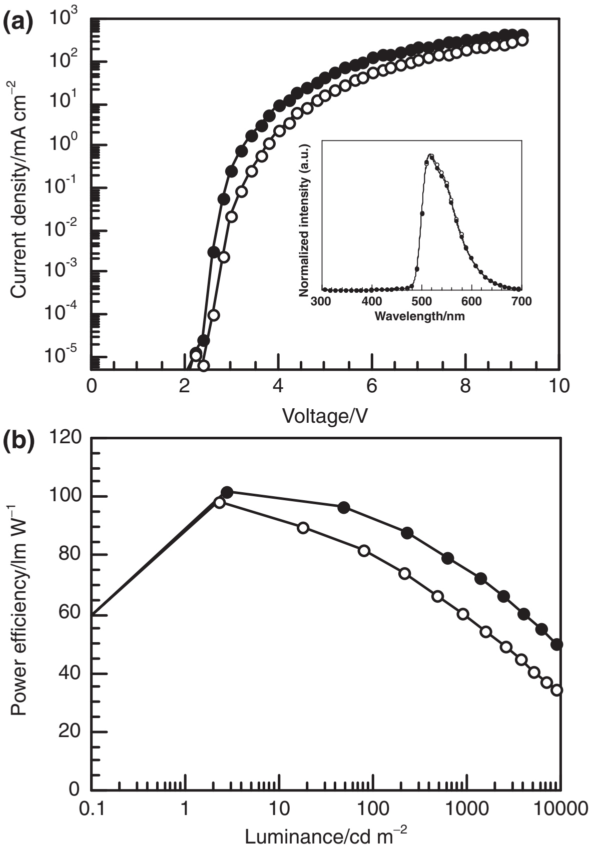


Figure 2. (a) *J–V* characteristics and (b) *PE–L* characteristics of green PHOLED using mCaP (closed circle) and mCP (open circle) as a host material. Inset: EL spectra of the devices.

temperature (see SI in detail[17]). These results indicate that the effective suppression of the FIrpic exciton quenching can be realized and a superior performance can be obtainable using mCaP as a host material.

To investigate the function of mCaP as a host material, a blue phosphorescent OLED with a structure of [ITO (110 nm)/1,1-bis{4-[*N*,*N*-di(4-tolyl)amino]phenyl}cyclohexane (TAPC) (20 nm)/FIrpic (10 wt %)-doped mCaP or mCP (10 nm)/3,5,3′′,5′′-tetra-3-pyridyl-1,1′;3′,1′′-terphenyl (B3PyPB)[15] (50 nm)/LiF (0.5 nm)/Al (100 nm)] were fabricated. All the materials, TAPC, mCaP, mCP, and B3PyPB have higher triplet energy (E_{T}) than that of FIrpic. Therefore, the triplet exciton quenching of FIrpic at the hole-transport layer/EML interface and/or EML/electron-transport layer interface can be minimized in these blue OLEDs. Both EL spectra were only from FIrpic with no emission from neighboring materials. The current density–voltage (*J–V*) characteristics are shown in Figure 1a. Although these two hosts have similar $I_{\mathrm{p}}/E_{\mathrm{a}}$ and η_{PL} values, mCaP-based OLED showed much greater current density than that with mCP, and gave much reduced operating voltage of 3.1 V at 100 cd m^{-2}, which is 0.6 V lower than that with mCP (3.7 V). The power efficiency–luminance (*PE–L*) characteristics are shown in Figure 1b. mCaP device showed an $\eta_{\mathrm{p,100}}$ of 37 lm W^{-1} (36 cd A^{-1}, EQE 17%) at 100 cd m^{-2} and 21 lm W^{-1} (25 cd A^{-1}, EQE 12%) at 1000 cd m^{-2}, respectively. These performances are approximately 1.2–1.6 times higher than that with mCP.

Further, we also tried to estimate green OLED performance using a common green phosphorescent emitter *fac*-tris(2-phenylpyridyl)iridium(III) (Ir(ppy)$_3$). Prior to the device fabrication, the photophysical properties of 8 wt % Ir(ppy)$_3$–doped host films were evaluated. The η_{PL} of mCaP/Ir(ppy)$_3$ film was estimated to be 75 ± 1%, that is almost the same as in mCP/Ir(ppy)$_3$ film (72 ± 1%). The transient PL decay curve of mCaP/Ir(ppy)$_3$ film exhibited single-exponential decay with a τ_{p} of 1.2 μs at room temperature (see SI in detail[17]). These results clearly indicate that a high-performance green OLED can be realized by use of mCaP.

A green phosphorescent OLED with a structure of [ITO (110 nm)/TAPC (20 nm)/Ir(ppy)$_3$ (8 wt %)-doped mCaP or mCP (10 nm)/B3PyPB (50 nm)/LiF (0.5 nm)/Al (100 nm)] was prepared. The *J–V* and *PE–L* characteristics are shown in Figure 2. Compared with mCP-based OLED, mCaP-based OLED showed much reduced operating voltage of 2.9 V at 100 cd m^{-2}, which is 0.3 V lower than that with mCP (3.2 V). This tendency is very similar to that in blue OLEDs. An mCaP device showed an $\eta_{\mathrm{p,100}}$ of 94 lm W^{-1} (85 cd A^{-1}, EQE 24%) at 100 cd m^{-2}, 76 lm W^{-1} (80 cd A^{-1}, EQE 22%) at 1000 cd m^{-2}, respectively. These performances are approximately 1.1–1.3 times higher than that with mCP.

Although mCaP shows similar $I_{\mathrm{p}}/E_{\mathrm{a}}$ and η_{PL} values to those of mCP, mCaP tends to reduce the driving voltage of OLEDs. Because the only difference in these hosts is the presence of

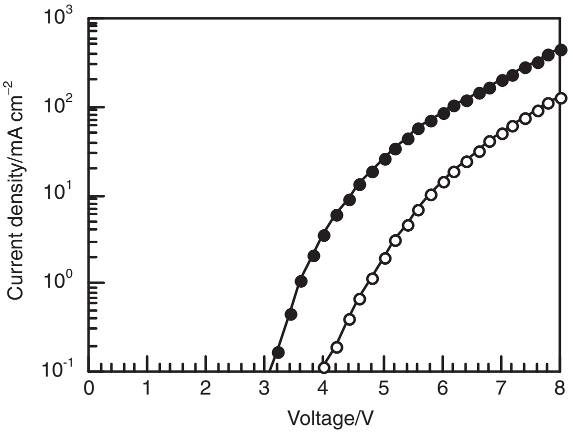


Figure 3. *J–V* characteristics of electron-only device using mCaP (closed circle) and mCP (open circle).

C=N double bonds, these favorable results can be mainly attributed to the weak electron-accepting nature of C=N double bonds. To investigate the electron-transport properties of mCaP, we fabricated electron-only devices with a structure of [ITO (110 nm)/B3PyPB (20 nm)/mCaP or mCP (10 nm)/B3PyPB (50 nm)/LiF (0.5 nm)/Al (100 nm)]. In this device, we used B3PyPB as a hole-blocking layer because this material has deep I_p at 6.67 eV to prevent the hole injection from ITO.[15] Figure 3 shows the *J–V* characteristics. The mCaP exhibited much higher current density than that of mCP. Thus, it can be concluded that the weak electron-accepting nature of the C=N double bond effectively promotes the electron injection in mCaP devices.

Compared with Ir(ppy)$_3$-based devices, FIrpic-based devices showed greater improvement by using mCaP in terms of the efficiency (see SI Figures S-7 and S-8 in detail[17]). In blue and green OLEDs, we used the same materials, TAPC, mCP, mCaP, and B3PyPB except the emitters. Therefore, these differences can be attributed to the emitters. To investigate the effect of emitters, we fabricated FIrpic-based electron-only devices with a structure of [ITO (110 nm)/B3PyPB (20 nm)/10 wt% FIrpic-doped host (10 nm)/B3PyPB (50 nm)/LiF (0.5 nm)/Al (100 nm)] (see SI Figure S-9 in detail[17]). mCaP/FIrpic device exhibited much higher current density than that of mCP/FIrpic devices. On the other hand, holes are preferably injected to host in FIrpic-based OLEDs because of the deeper I_p of FIrpic (6.15 eV). Thus, injection of both holes and electrons to EML can be enhanced in mCaP/FIrpic devices more than in mCP/FIrpic devices. We also fabricated Ir(ppy)$_3$-based electron-only devices (see SI Figure S-10 in detail[17]). mCaP/Ir(ppy)$_3$ device showed slightly higher current density than that in mCP/Ir(ppy)$_3$ devices. Unlike FIrpic-based OLEDs, holes are preferably injected to Ir(ppy)$_3$ ($I_p = 5.36$ eV) from TAPC ($I_p = 5.60$ eV) in Ir(ppy)$_3$-based OLEDs due to the favorable overlapping of the density-of-state (DOS) distributions.[16] Thus, mCaP/FIrpic-based devices can realize greater improvement than that of mCaP/Ir(ppy)$_3$-based device in terms of the efficiency.

In summary, we developed a novel host material mCaP with two C=N double bonds for phosphorescent OLED. By using mCaP as a host material, we successfully developed high-performance blue and green OLEDs. These performances are the highest levels in the scientific literature.

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