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Pyridine-Containing Bipolar Host Materials for Highly Efficient Blue Phosphorescent OLEDs

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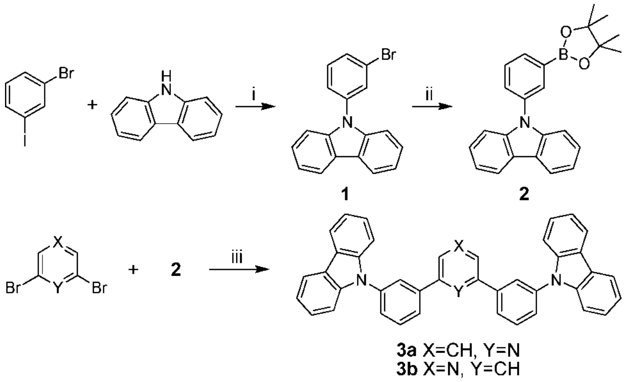
As one of the three primary colors, blue emission from organic light-emitting devices (OLEDs) is of importance for application to full color flat-panel display. In addition, white light emission can be obtained combining blue, green, and red light from one device.[1] So highly efficient blue emission is indispensable for the commercialization of OLEDs in flat-panel display and lighting. Forrest and Thompson's groups have developed transition metal complexes, which emit phosphorescence from their triplet states, realizing nearly 100% internal quantum efficiencies of electroluminescence.[2] In such phosphorescent OLEDs, triplet emitters are normally doped into a host material to reduce concentration quenching. Development of effective host materials are thus of equal importance for efficient phosphorescent OLEDs. Generally, it is essential that the triplet excited state of the host material should be higher than that of the triplet emitter to prevent reverse energy transfer from the guest back to the host and to effectively confine triplet excitons on the guest molecules.[3] Such a requirement becomes particularly challenging for a blue triplet emitter, in which the conjugation length of the host molecules must be extremely limited to achieve a triplet energy level higher than photon energies of blue light. Unfortunately, it is difficult to meet these requirements because there is a tradeoff between increasing the band gap of the material to increase singlet and triplet energies and decreasing the π-conjugation system, which may adversely affect the charge transport properties.[4] As an example, silicon-containing wide-band gap insulating host materials have been developed for blue phosphorescent emitters. The charge hopping occurred between the adjacent dopant materials, leading to increased operating voltage and thus lower power efficiency.[5] To obtain a host material with carrier transport property and high triplet energy level, it was generally designed by introducing a well-known carbazole electron donor.[6] However, this may induce an unbalanced carrier injection and transport into the emitting layer and thus a limited device performance.

Scheme 1. Synthetic Routes of 26DCzPPy and 35DCzPPy[a]



[a] i: Cu, K_2CO_3, DMF. ii: bis(pinacolato)diboron, $Pd_2(dba)_3$, KOAc, PCy_3, dioxane. iii: $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene/ethanol.

In this communication, we report a unique molecular design strategy of combining carbazole electron donor with high triplet energy and pyridine electron acceptor with high electron affinity to give novel bipolar host materials of 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy) (**3a**) and 3,5-bis(3-(carbazol-9-yl)phenyl)pyridine (35DCzPPy) (**3b**). Their synthetic routes are shown as Scheme 1. An external quantum efficiency (EQE) of 24% and a power efficiency (PE) of 46 lm/W were achieved at the practical brightness of 100 cd/m^2 by using 26DCzPPy as the host for the iridium(III) bis(4,6-(difluorophenyl)pyridinato-*N*,$C^{2'}$) picolinate (FIrpic)-based blue phosphorescent OLEDs. Even at a brighter emission of 1000 cd/m^2, the efficiencies remain above 22% and 34 lm/W, which are the highest ever values for blue phosphorescent OLEDs.

The phosphorescence spectra of 26DCzPPy and 35DCzPPy were obtained under excitation by a nitrogen gas laser ($\lambda = 337$ nm) at 4.2 K. They both have the highest energy peak ($\nu_{0,0}$) at 457 nm corresponding to a triplet energy (E_T) of 2.71 eV, compared to 2.65 eV for FIrpic[3b] and 2.56 eV for a general host material of *N*,*N*′-dicarbazolyl-4,4′-biphenyl (CBP).[7] From the energy alignments, it can be speculated

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that there should be an efficient exothermic energy transfer from the 26DCzPPy and 35DCzPPy triplet states to the FIrpic triplet states and an excellent triplet energy confinement on the FIrpic molecules. To confirm this, the transient photoluminescence (PL) decay of 3% (by weight) FIrpic doped into 35DCzPPy and 26DCzPPy was measured under excitation by a nitrogen gas laser (λ = 337 nm) at room temperature. Both the 35DCzPPy:FIrpic and the 26DCzPPy:FIrpic films clearly exhibit a monoexponential decay curve with a relatively long lifetime of 1.59 and 1.73 μs, respectively. The transient photoluminescence observation indicates that the triplet energy transfer from FIrpic to 35DCzPPy and 26DCzPPy was completely suppressed and the energy was well confined on FIrpic due to higher E_T of 35DCzPPy and 26DCzPPy than FIrpic.

Photoluminescence quantum efficiency (η_{PL}) of FIrpic doped into 35DCzPPy and 26DCzPPy was measured under N_2 flow using an integrating sphere excited at 330 nm with a multichannel spectrometer as the optical detector. FIrpic:35DCzPPy and FIrpic:26DCzPPy exhibited a maximum η_{PL} of 88% ± 1% and 87% ± 1% at 5 wt %, respectively, which is comparable to that of FIrpic:mCP[8] and can be attributed to good confinement of triplet energy on the FIrpic molecules when doped into 35DCzPPy and 26DCzPPy. At these low doping concentrations, it is expected that most of the excitation energy is absorbed by the hosts. The high η_{PL} here also arise from an efficient energy transfer from 35DCzPPy and 26DCzPPy to FIrpic.

To evaluate 26DCzPPy and 35DCzPPy as host materials, OLEDs were fabricated with FIrpic and doped at 11 wt % via coevaporation with 26DCzPPy or 35DCzPPy. Poly(arylene amine ether sulfone)-containing tetraphenylbenzidine (TPDPES) doped with 10 wt % tris(4-bromophenyl)aminium hexachloroantimonate (TBPAH) was spun onto the precleaned substrate from its dichloroethane solution as a buffer layer.[9] 2,2′-Bis(*m*-di-*p*-tolylaminophenyl)-1,1′-biphenyl (3DTAPBP) was then deposited as the hole transport layer.[6a] A 40-nm-thick electron transport layer of 3,5,3′,5′-tetra(*m*-pyrid-3-yl)phenyl-[1,1′]-biphenyl (TmPyPBP) was deposited onto the emissive layer to block holes and to confine excitons in the emissive zone. Figure 1 shows the luminance and current density versus the applied voltage characteristics of the devices with 35DCzPPy and 26DCzPPy as the host. The charge injection and transport in 35DCzPPy- and 26DCzPPy-based devices are nearly identical but give higher luminance for the device based on 26DCzPPy.

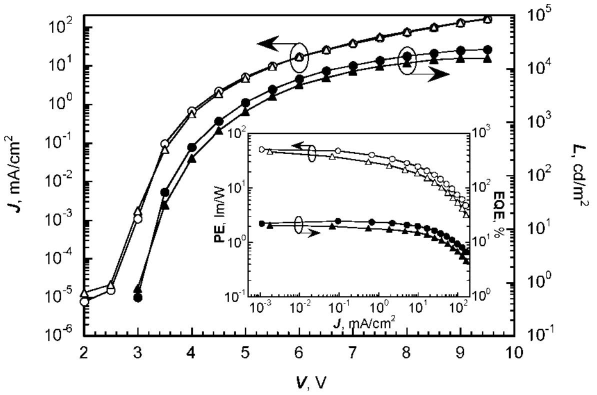

Figure 1. Luminance and current density vs driving voltage characteristics and efficiency vs driving current density characteristics (inset) for ITO/TPDPES:TBPAH (20nm)/3DTAPBP (30nm)/35DCzPPy (triangles) or 26DCzPPy (circles):11 wt % FIrpic (10nm)/TmPyPBP (40nm)/LiF (0.5 nm)/Al (100 nm).

Although efficiency roll-off at a high driving current, which is a typical phenomenon in phosphorescent OLEDs and may be associated with triplet–triplet annihilation, is also observed, high efficiencies of 19.1%, 34.6 lm/W, and 17.9%, 24.1 lm/W, were realized at 100 cd/m^2 and 1000 cd/m^2, respectively, for the 35DCzPPy-based device. For the 26DCzPPy-based device, further improved efficiencies of 24.3% and 46.1 lm/W at 100 cd/m^2 and 22.6% and 34.5 lm/W at 1000 cd/m^2 were achieved, indicating reduced efficiency roll-off at a high driving current. To the best of our knowledge, this is the most efficient FIrpic-based blue phosphorescent OLED up to now.

It is well-known that external quantum efficiency is correlated to η_{PL}, light outcoupling efficiency, and carrier balance. It is interesting that a light outcoupling efficiency of about 30% is already achieved for the present device structures, greater than ~20% given by the classical ray optics.[10] It strongly supports the numerical results that as much as 30−50% of the light could be emitted externally in a planar device when subjected to optical interference effects.[11] It is speculated that light outcoupling efficiencies of the devices demonstrated here are comparable to each other because of their similar device structure. As such, the difference in device performance, especially reduced efficiency roll-off in the 26DCzPPy-based device, should arise from the difference in carrier balance injected and/or transport through the emission layer, which is determined by characteristics of the host materials in the present devices. In fact, most of host materials ever developed contain solely carbazole electron donor[3,6] or electron acceptor of phosphine oxide.[4,12] This may induce an unbalanced carrier injection and transport and thus a limited device performance. For comparison, a device with none-pyridine-containing CBP as a host material was also fabricated. The current density of the devices based on 35DCzPPy and 26DCzPPy is identical to that of the device based on CBP, indicating no decrease of carrier injection and transport for 35DCzPPy and 26DCzPPy compared to CBP with insertion of a pyridine unit. Improved device performance for the device based on 35DCzPPy and 26DCzPPy should arise from an improvement of carrier balance besides η_{PL} by using 35DCzPPy or 26DCzPPy instead of CBP due to bipolar property of 35DCzPPy and 26DCzPPy consisting of both the electron donor and the electron acceptor units.

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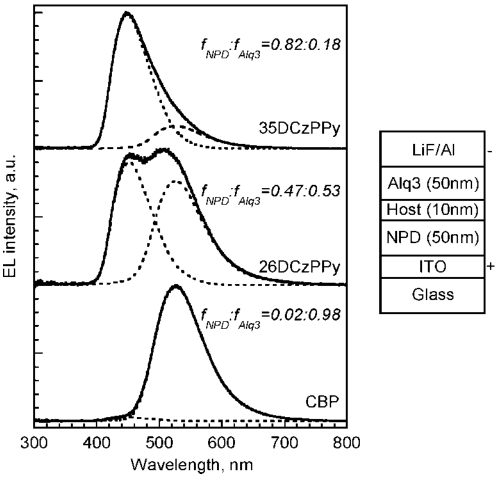

Figure 2. Electroluminescent spectra of devices in the structure of ITO/NPD (50nm)/35DCzPPy, 26DCzPPy, or CBP (10nm)/Alq3 (50 nm)/LiF (0.5 nm)/Al (100 nm) measured at a driving current density of 0.625 mA/cm^2. The dotted lines are the fitted emissions corresponding to NPD and Alq3.

To verify the bipolar property of 35DCzPPy and 26DCzPPy, each 35DCzPPy, 26DCzPPy, and CBP was inserted between *N*,*N*′-bis((1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPD) and tris(8-hydroquinolinato)aluminum (Alq3) to form devices in the structure of ITO/NPD (50 nm)/35DCzPPy, 26DCzPPy or CBP (10 nm)/Alq3 (50 nm)/LiF (0.5 nm)/Al (100 nm). Figure 2 shows their electroluminescent spectra measured at a driving current density of 0.625 mA/cm^2. It can be seen that the emission from Alq3 dominated the emission for the CBP-based device (f_{NPD}:f_{Alq3} = 0.02:0.98), indicating lack of electron passing through the thin CBP layer. In contrast, for the device based on 35DCzPPy, the emission from the hole transport layer of NPD combined with that from the electron transport layer of Alq3 was observed because of the improved bipolar property of 35DCzPPy. But the emission from NPD dominated the emission (f_{NPD}:f_{Alq3} = 0.82:0.18), indicating that 35DCzPPy was electron-rich. For the device based on 26DCzPPy, the emission from the hole transport layer of NPD and that from the electron transport layer of Alq3 were quite similar (f_{NPD}:f_{Alq3} = 0.47:0.53), indicating a better bipolar property of 26DCzPPy and thus a well balanced hole and electron injection and transport through 26DCzPPy. Note that there is no emission from the CBP, 35DCzPPy, or 26DCzPPy interlayer of the corresponding device, indicating both hole and electron transport through the interlayer without combination to form their excitons. From these results, it can be clearly seen that both hole and electron can be easily injected and then transported to the emissive layer when 26DCzPPy was used as the host material, leading to an improved carrier balance and thus a higher efficiency in comparison to CBP- and 35DCzPPy-based devices.

In conclusion, we have demonstrated a unique molecular design of bipolar host material by introducing both carbazole electron donor and pyridine electron acceptor. A record high efficiency and reduced efficiency roll-off at a high driving current were achieved for FIrpic-based blue phosphorescent OLEDs by using the present bipolar host materials as a result of good confinement of the triplet excitons on the guest molecules in the emissive layer and improved carrier balance injected into the emissive layer. The present findings suggest a new route to further improve performance of phosphorescent OLEDs, especially at a high driving current.

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Supporting Information Available: Experimental procedures, analytical and spectroscopic data of compounds, Tables S1 and S2, and Figures S1, S2, and S3 (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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