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Solution-Processable, High-Molecule-Based Trifluoromethyl-Iridium Complex for Extraordinarily High Efficiency Blue-Green Organic Light-Emitting Diode

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Organic light-emitting diodes (OLEDs) possess high potential in flat panel displays and solid-state illumination applications.[1] To replace current display and illumination technologies, and to make the resultant products more energy saving and make them last longer, OLEDs with higher power efficiency are demanded. Recently, phosphorescent materials have drawn great attention because of their ability to harvest both singlet and triplet excitons, achieving nearly 100% internal quantum efficiency.[2] Among them, green light-emitting iridium complexes show relatively high efficiency.[3,4] For example, Chi's group reported a green device with efficiency of 23.2 cd A^{-1} by using an pyrazolyl-containing iridium complex that exhibited a short excited-state lifetime.[5] Lin's group achieved 61 cd A^{-1} with an iridium complex containing 1,2-diphenyl-1H-benzoimidazole that exhibited high quantum yield.[6] Designing new phosphorescent materials, such as iridium-based complexes, that possess both short excited-state lifetime and high quantum yield may markedly enhance the efficiency. However, different functional groups may consequently be needed to introduce to the base molecules. This will inevitably result in an increase in molecular weight, which will in turn make the resultant molecules difficult, if not at all impossible, to vacuum-evaporate. This will hence make solution process a must choice, especially when the molecular weight of employed materials is further increased. In fact, the wet process is a requirement for large-area devices or roll-to-roll production.[7]

In this study, we report a novel high-molecular-based iridium complex, bis[5-methyl-7-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one]iridium(picolinate) (CF_3BNO), which exhibits both a short excited-state lifetime and a high quantum yield. Although CF_3BNO has a comparatively high molecular weight (869 g mol^{-1}), which is difficult to vacuum-evaporate, the resultant blue-green device via solution process shows a current efficiency of 89.1 cd A^{-1} at 100 cd m^{-2}, which is the highest among all the reported green devices via a solution process.

Scheme 1 shows the synthesis of CF_3BNO and bis[5-methyl-5H-benzo[c][1,5] naphthyridin-6-one]iridium(picolinate) (BNO). Iridium trichloride hydrate was reacted with 5-methyl-7-trifluoromethyl-5H-benzo[c][1,5]naphthyridin-6-one or 5-methyl-5H-benzo[c][1, 5]naphthyridin-6-one to give the corresponding cyclometalated Ir(III)-μ-chloro-bridged dimers. Further reaction of the dimers with picolinic acid and sodium carbonate formed the desired iridium complex, CF_3BNO or BNO.

Table 1 lists the physical characteristics of the novel blue-green guest, CF_3BNO, and the other two compared counterparts, BNO and tris(2-phenylpyridine) iridium(III) ($Ir(ppy)_3$). The excited-state lifetimes were 0.30, 0.32, and 1.2 μs for CF_3BNO, BNO, and $Ir(ppy)_3$, respectively. Compared with that in $Ir(ppy)_3$, the shorter excited-state lifetime exhibited in CF_3BNO and BNO should presumably favor the fabrication of a high-efficiency device, as mentioned above.

The quantum yields in solution were 95, 42, and 38% for CF_3BNO, BNO, and $Ir(ppy)_3$, respectively. The quantum-yield exhibited in CF_3BNO was markedly higher than those in BNO and $Ir(ppy)_3$. It is known that the high quantum yield of an emissive material in solution could be correlated to a high quantum efficiency of the emitter-composing device.[8]

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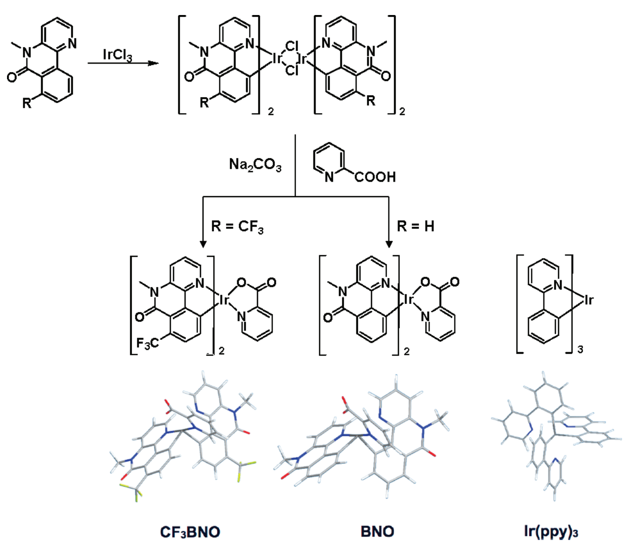
Table 1. Physical Characteristics of the Novel Blue-Green Light-Emitting Dopant, CF_3BNO, Compared against Those of the Two Comparing Counterparts, BNO and $Ir(ppy)_3$[a]

guest	τ (μs)	Φ_{em} (%)	MW (g mol^{-1})	T_d (°C)
CF_3BNO	0.30	95	869	290
BNO	0.32	42	733	200
$Ir(ppy)_3$	1.15	38	655	395

[a] τ, Excited state lifetime; Φ_{em}, quantum yield; MW, molecular weight; T_d, decomposition temperature.

Scheme 1. Schematic Illustration of the Synthesis of the Novel Blue-Green Dopant CF_3BNO and the Comparing Counterpart, BNO. Also Shown Is the Chemical Structure of $Ir(ppy)_3$



The high quantum yield in solution of CF_3BNO should also favor the fabrication of a high efficiency device.

The molecular weights were 869, 733, and 655 g mol^{-1} for CF_3BNO, BNO, and $Ir(ppy)_3$, respectively. The CF_3BNO guest possesses the highest molecular weight, which would make it the most difficult to deposit by vacuum evaporation, especially by realizing its decomposition temperature of 290 °C to be comparatively low.

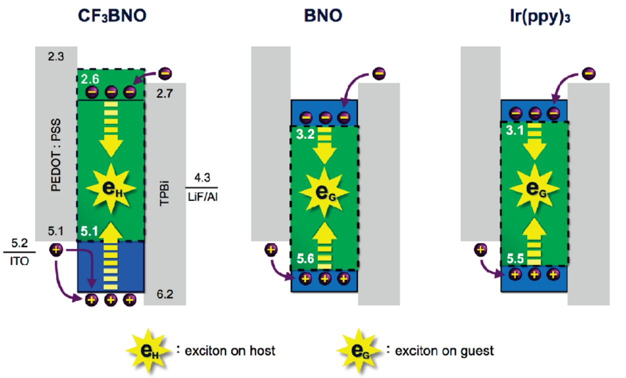
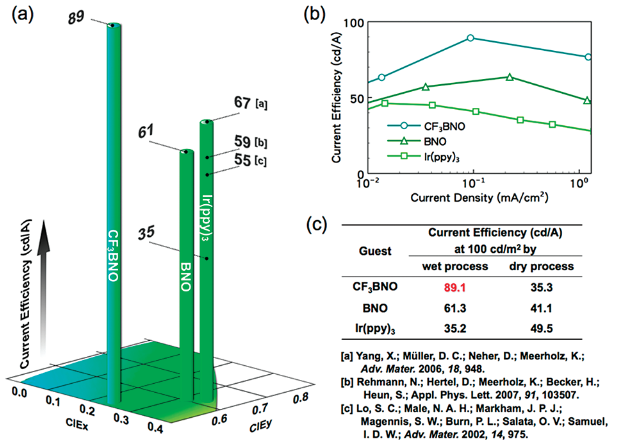


Figure 1. Energy-level diagram of the CF_3BNO-composing blue-green device with a CBP host. For comparison, also shown are the energy levels of the two dopants, BNO and $Ir(ppy)_3$. It is noteworthy that only in the CF_3BNO-composing system can the electrons, injected from the TPBi electron-transporting layer, freely enter the host rather than guest, leading excitons to form on host and hence favoring energy transfer from host to guest, which would in turn result in high device efficiency.



Guest	Current Efficiency (cd/A) at 100 cd/m² by	
	wet process	dry process
CF_3BNO	89.1	35.3
BNO	61.3	41.1
$Ir(ppy)_3$	35.2	49.5

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Figure 2. Current efficiency results of the three studied OLEDs and previously reported green ones via wet process on the (a) CIE diagram and (b) current density. (c) Current efficiency of the CF_3BNO-composing devices fabricated via wet and dry process, compared with those of the BNO-, $Ir(ppy)_3$-composing counterparts.

The resultant CF_3BNO was then fabricated into a blue-green OLED device mainly via solution process because of its high molecular weight. To compare material characteristics, we also fabricated green OLED devices composed of BNO and $Ir(ppy)_3$ via solution process. The device architecture consisted of a 1250 Å indium tin oxide layer, a 350 Å poly(3,4-ethylene-dioxythiophene)-poly-(styrenesulfonate) (PEDOT: PSS) hole-transporting layer, a 220 Å green emissive layer, a 320 Å 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) electron-transporting layer, an 8 Å lithium fluoride layer, and a 1500 Å aluminum layer, as shown in Figure 1. The employed host for the emissive layer was 4,4′-bis(carbazol-9-yl)biphenyl (CBP). A series of doping concentrations were studied for the resultant blue-green light-emitting CF_3BNO as well as for the two compared counterparts, BNO and $Ir(ppy)_3$. The respective doping concentrations for achieving the highest power efficiency were 12.5, 10.0, and 12.5 wt % for CF_3BNO, BNO, and $Ir(ppy)_3$. To compare the effect of the processing method, CF_3BNO-, BNO-, and $Ir(ppy)_3$-composing devices were also fabricated via a dry process.[9]

Figure 2a shows the current efficiency result of the CF_3BNO-composing device via wet-process on the Commission Internationale de l'Eclairage (CIE) diagram, compared with those of the BNO- and $Ir(ppy)_3$-composing devices and the previously reported green ones via wet-process. The current efficiency versus current density of these three devices is shown in Figure 2b. As seen, the CF_3BNO-composing device via wet-process exhibited the highest current efficiency at all applied current densities compared to other wet-processed ones. At lower current density, such as 1 × 10^{-1} mA cm^{-2} for example, its resultant current efficiency is 89.2 cd A^{-1}, corresponding to a luminance of 88 cd m^{-2}. Meanwhile, the device efficiency was 59.4 cd A^{-1} (62 cd m^{-2}) for the BNO-composing counterpart and 41.0 cd A^{-1} (538 cd m^{-2}) for the $Ir(ppy)_3$-composing one. At higher current density of 100 mA cm^{-2}, the efficiencies show 79.2 (770 cd m^{-2}),

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51.2 (488 cd m^{-2}), and 29.8 cd A^{-1} (3503 cd m^{-2}) for the CF_3BNO-, BNO-, and Ir(ppy)$_3$-composing device, respectively. These results indicate that the CF_3BNO would have high potential for display and lighting applications. The discussion on the high resultant efficiency of the CF_3BNO-composing device will be mentioned later.

Figure 2c also shows the current efficiency results of the green OLEDs composing the novel blue-green dye CF_3BNO and the two other comparing ones, BNO and Ir(ppy)$_3$, via wet- and dry-processes. Among them, the CF_3BNO-composing device via wet-process exhibited the highest current efficiency, which was 89.1 cd A^{-1} at 100 cd m^{-2} with CIE coordinates of (0.22, 0.51). In contrast, the same CF_3BNO-composing one via dry-process exhibited a much lower current efficiency of 35.3 cd A^{-1}. The reason why the dry-processed device had exhibited lower device efficiency may be attributed to the high molecular weight (869 g mol^{-1}) and low decomposition temperature (290 °C) characters of CF_3BNO, which would make it difficult to be vacuum-evaporated, leading to a graded electroluminescent structure that restrains the carrier-injection and -transport and hence the low device efficiency.[10] Similarly, the BNO-composing device exhibited a current efficiency of 61.3 cd A^{-1} via wet-process, but only 41.1 cd A^{-1} via dry-process. The high molecular weight (733 g mol^{-1}) and low decomposition temperature (222 °C) of BNO would also make the film of BNO difficult to form via vacuum-evaporation.

On the basis of the same solution-process, the BNO-composing device showed efficiency significantly higher than that of the Ir(ppy)$_3$ counterpart. This may be attributed mainly to the much shorter excited-state lifetime of BNO, 0.32 μs, whereas it is 1.2 μs for Ir(ppy)$_3$, especially by realizing the fact that BNO and Ir(ppy)$_3$ have exhibited nearly the same quantum yield. The quantum yield was 42% for BNO and 38% for Ir(ppy)$_3$. By introducing a trifluoromethyl group into BNO, the quantum yield of the resultant CF_3BNO markedly increased to 95%. It is noteworthy that CF_3BNO and BNO exhibited nearly the same excited-state lifetimes of 0.30 and 0.32 μs, respectively. Therefore, the remarkable efficiency of the CF_3BNO-composing device may be at least partly attributed to its outstanding quantum-yield of 95% compared with 42% for BNO. Besides having excellent optoelectronic properties, i.e., very short excited-state lifetime and relatively high quantum ield, this CF_3BNO-composing device possessed an additional efficiency-improving effect in its device architecture. CF_3BNO exhibits a LUMO value of −2.6 eV, which is higher than that of the host CBP (−2.9 eV), as shown in Figure 1. Therefore, electrons almost preferably inject into the host CBP rather than into the guest CF_3BNO. In contrast, CF_3BNO shows a higher HOMO value of −5.1 eV compared to that of CBP (−6.2 eV), resulting in two possible hole injection alternatives. First, some holes would inject into the host and then recombine with electrons to form excitons. Second, part of holes could inject into the guest and then hop into the host to form excitons. The excitons formed by these two ways on the host can favor energy transfer from host to guest. Meanwhile, lesser excitons formed on the guest would also prevent undesired quenching phenomenon.[11] These two factors may partly explain why the CF_3BNO-composing device exhibited the relatively high efficiency observed. In contrast, both carriers, electrons and holes, would be trapped on the guests of Ir(ppy)$_3$ and BNO, because the LUMOs of the guests (−3.0 eV) are lower than that of the host CBP (−2.9 eV) and their HOMO (−5.6 eV) values are higher than that of the host (−6.0 eV). Trapping both electron and hole on guest would result in excessive excitons formed thereon, which would in turn cause efficiency-unfavorable exciton quenching, resulting in low device efficiency.

Compared with previous literatures, the CF_3BNO-composing device exhibits an extraordinarily high-efficiency and a blue-green emission (Figure 2a), the EQE of which is as high as 23.6%, greater than the generally accepted theoretical limit of 20%.[12] However, Kido's group has recently reported that the EQE of the OLEDs can reach 30−50% under the condition of out-coupling efficiency of 30−50% with IQE of 100%.[13] Hence, the reasons why the CF_3BNO-composing device shows such a high efficiency may partly result from its high out-coupling efficiency, besides the high quantum yield and short excited-state lifetime of the CF_3BNO molecule, as well as the proper fabrication process and the effective device architecture mentioned above.

In conclusion, a novel CF_3BNO iridium complex with a short excited-state lifetime (0.30 μs) and relatively high quantum yield (95%) was presented. With the use of CBP host, a blue-green OLED device with a markedly high current efficiency of 89.1 cd A^{-1} (69.8 lm W^{-1}) at 100 cd m^{-2} with CIE coordinates of (0.22, 0.51) was fabricated via solution-process. Besides the intrinsically good phosphorescence properties, the high efficiency may also be partly attributed to the device architecture, which enables excitons to form on the host and hence favors efficiency-favorable energy transfer from host to guest.

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Supporting Information Available: Syntheses of these novel green iridium complexes, measurements of physical properties, and device fabrication (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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