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Synthesis of all-deuterated tris(2-phenylpyridine) iridium for highly stable electrophosphorescence: the "deuterium effect"†

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Device stability and life-time rank the key issues for PhOLEDs. We synthesized deuterated Ir(ppy)$_3$-D$_{24}$. A device based on it has a current density twenty times higher than and a life-time six times longer than devices based on Ir(ppy)$_3$. The more stable C–D bond is found to be the main contributing factor, called the "deuterium effect".

Device lifetime and stability at high current densities are the key issues for phosphorescent organic light-emitting diodes (PhOLEDs) because large scale manufacturing of real-world organic flat-panel color displays and white-lighting need thousands of hours of operating time and are often used at a high luminance. Studies have revealed some chemical and physical degradation mechanisms for PhOLEDs, such as cleavage of substituents of organic materials,[1] degradation in the HTL (hole-transport layer),[2] chemical degradation or decomposition of emitter/host,[3] concentration quenching,[4] charge-trapping problems at the sites of the dopant molecules owing to the large band gap difference between the host and dopant molecules,[5] triplet–triplet annihilation,[6] inefficient host to guest energy transfer,[7] unbalanced carrier injection/transport,[8] exciton diffusion from the emitting layer,[9] electrochemically instability of the host[10] and electric field induced quenching.[11] However, the universal key factors detrimental to PhOLED life-time remain unclear, especially why the devices suffer "roll-off" under high current densities.

In PhOLEDs, the phosphorescent materials are usually doped as emitting guests into charge-transporting and energy harvesting host materials to obtain higher efficiency and longer life-time. The presence of a heavy-metal atom in the phosphorescent matrix provides a significant spin-orbit interaction that allows the decay of a previously spin-forbidden radiative triplet to happen. Due to both singlet and triplet excited states participating in the emission, the internal quantum efficiency can potentially reach as high as 100%.[12] This paves the way for high-efficiency organic color displays and white-lighting. Iridium complexes are the most frequently used electrophosphorescent materials based on the remarkable "heavy atom effect" of the Ir^{3+} nucleus. From this, early in 2009, we came up with the idea of "all deuterating" the ligand to obtain a heavier ligand for iridium for both green and blue electrophosphorescence. Close to the end of the synthesis, we searched to find a reference and discovered that someone else had already executed the plan.[13] However, our deuterating method is different to theirs. Our direct synthesis from simple reagents creates a higher deuteration rate (more than 99% compared to the 95% reported). More importantly, we have fabricated and tested electrophosphorescent devices. In the following paragraphs, we will show that our device test results have contributed to understanding the most important issues: the device stability and operating lifetime can be greatly increased or extended and the factors for these improvements are identified.

By starting from the very simple and inexpensive reagent, deuterated benzene, we obtained deuterated bromobenzene, and then by reacting deuterated bromobenzene with another simple and inexpensive regent, deuterated pyridine, we obtained deuterated 2-phenylpyridine. After that, we obtained deuterated tris(2-phenylpyridine)iridium by using this ligand. We initially hoped that through deuteration of 2-phenylpyridine, we could greatly increase the phosphorescence efficiency of the iridium complex as a whole by introducing twenty four heavier deuterium atoms instead of the hydrogen atom and then greatly improve the device efficiency. However, contrary to

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our expectation, neither the material's nor the device's efficiency has been greatly improved, but the device stability under high current densities has been greatly improved and the device lifetime been greatly extended. This is marvellous! It is better than our initial expectation! The main factor influencing the device stability and life-time never previously reported was also identified. It can provide new insights into solving the stability issue. The deuteration can be used as a prototype for all electrophosphorescent devices. The following is the story in detail.

Scheme 1 demonstrates the synthetic routes to the deuterated ligand and the iridium complex. The detailed synthetic procedure and characterization including the absorption and emission spectra, the electrochemistry, the thermal properties, and phosphorescent life-time can be found in the ESI.†

We prepared single crystals of Ir(ppy)$_3$-D$_{24}$. The atomic arrangement in space for both Ir(ppy)$_3$-D$_{24}$ and Ir(ppy)$_3$ is facial. (The facial isomer can be easily identified from Fig. 1. The eleven ^{13}C NMR signals also provided evidence for the facial isomer, rather than the meridional isomer, in which many more than eleven ^{13}C NMR signals would be found.) The distance between phenylpyridine fragments and the Ir–Ir separation distance of the two proximal complexes are calculated to be too far to create probable inter-molecular interactions. However, the topology of the molecular packing is different with that of Ir(ppy)$_3$. The cell setting for Ir(ppy)$_3$-D$_{24}$ is tetragonal in contrast to trigonal for Ir(ppy)$_3$.[14] The space group is $P\bar{4}$ for Ir(ppy)$_3$-D$_{24}$ in contrast to $P\bar{3}$ for Ir(ppy)$_3$. Considering that the crystal formation conditions are different in that Ir(ppy)$_3$-D$_{24}$ crystals were prepared by sublimation while Ir(ppy)$_3$ crystals were prepared in solution, these differences are not so surprising. In addition, in OLEDs, materials are fabricated into devices in the morphological state not in the crystal state. We thus exclude the possible contribution of crystal packing to device performances.

We turn our attention to the structural difference between the two materials. Fig. 2(a) is a comparison of the IR spectra between Ir(ppy)$_3$ and Ir(ppy)$_3$-D$_{24}$. The most evident is that the highest energy for C–H stretching has been shifted from 3040 to 2274 cm^{-1} by deuteration (the small peak at $\sim$3020 cm^{-1} may be due to some kind of O–H stretching from a residual crystal water). This reduced 766 cm^{-1} energy equals to 2.2 kcal mol^{-1}. In addition, the C=C stretching, C=N stretching, and C–H bending at $\sim$1600 cm^{-1}, $\sim$1470 cm^{-1}, and 755 cm^{-1} for Ir(ppy)$_3$ obviously moves to the lower energy of $\sim$1566 cm^{-1}, $\sim$1400 cm^{-1} and 611 cm^{-1} for Ir(ppy)$_3$-D$_{24}$ instead. The reduced energy for C–H bending is 155 cm^{-1}, equalling 0.45 kcal mol^{-1}. Therefore, we conclude that the deuteration decreases the stretching and bending energy of the entire Ir(ppy)$_3$-D$_{24}$ molecule, especially the C–H stretching and bending. In other words, the C-D stretching and bending in Ir(ppy)$_3$-D$_{24}$ possess much lower energy than the C–H stretching and bending in Ir(ppy)$_3$. Fig. 2(b) compares the total internal energy between Ir(ppy)$_3$-D$_{24}$ and Ir(ppy)$_3$ by density functional theory (DFT) calculation. We can see that the former has a lower internal energy of 25.4 kcal mol^{-1} than the latter.

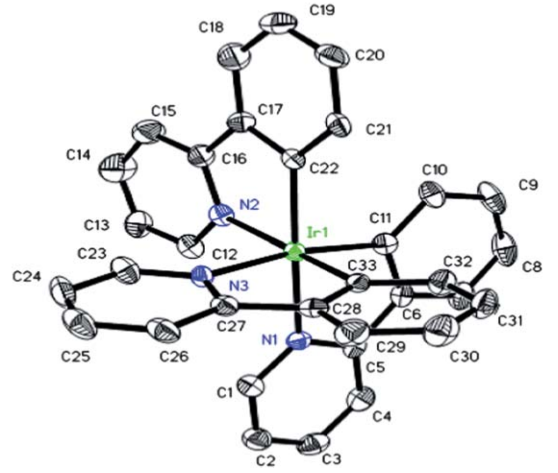
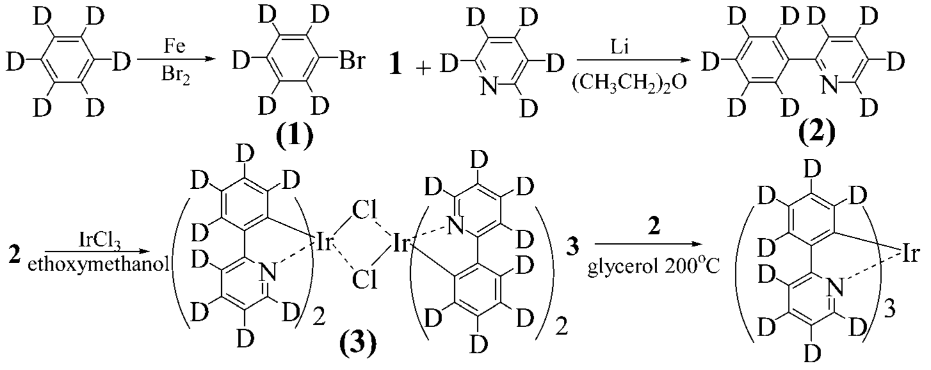


Fig. 1 ORTEP diagram of Ir(ppy)$_3$-D$_{24}$. Selected bond distances (Å): Ir–C(11) = 2.017(5), Ir–C(22) = 2.011(5), Ir–C(33) = 2.018(5), Ir–N(1) = 2.133(4), Ir–N(2) = 2.120(4), Ir–N(3)–2.138(4) and angles (deg): C(22)–Ir–N(2) = 79.58(18), C(11)–Ir–N(1) = 78.96(19), C(33)–Ir–N(3) = 79.08(19).

We compared the photophysical properties of the two complexes in detail. The absorption and emission spectra, the thermal and electrochemical values for deuterated Ir(ppy)$_3$-D$_{24}$ and un-deuterated Ir(ppy)$_3$ are almost identical (see ESI†). However, for deuterated Ir(ppy)$_3$-D$_{24}$, the quantum efficiency at 77 K/in degassed solution and the phosphorescent life-time at 77 K/solid powder is slightly higher than those of un-deuterated



Scheme 1 Synthetic route for Ir(ppy)$_3$-D$_{24}$.

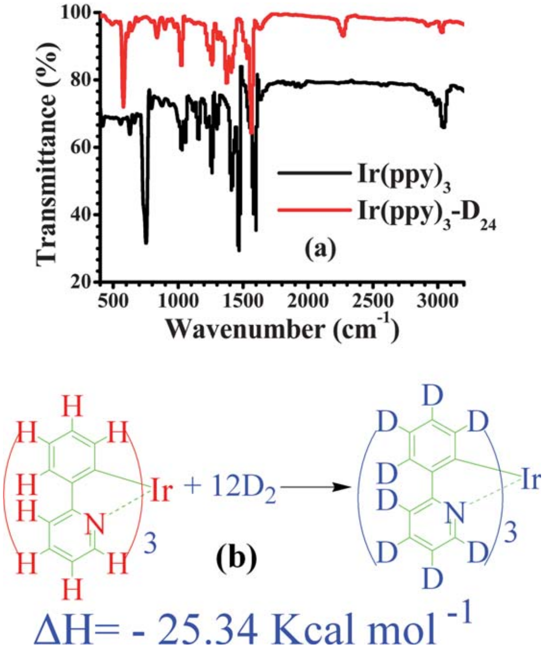


Fig. 2 (a) IR spectra of the two complexes. (b) DFT calculation of the enthalpy of Ir(ppy)$_3$-D$_{24}$ from Ir(ppy)$_3$.

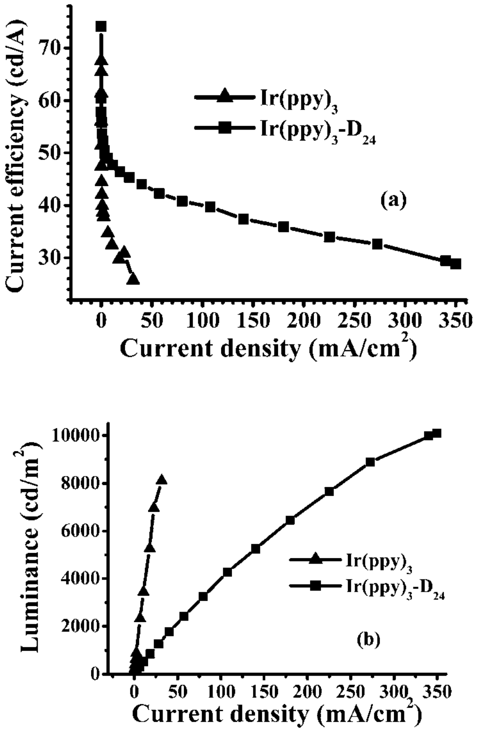


Fig. 3 (a) Current efficiency (cd A^{-1}) *vs.* current density (mA cm^{-2}) curve. (b) Luminance (cd m^{-2}) *vs.* current density (mA cm^{-2}). The device architecture is glass/ITO (150 nm)/2T-NATA (25 nm)/NPB (5 nm)/TCTA (10 nm)/iridium complex 6% doped CBP (20 nm)/TPBi (30 nm)/LiF (0.3 nm)/Al (100 nm), where 2T-NATA is 4,4′,4′′-tris-*N*-naphthyl-*N*-phenylamino-triphenylamine, NPB is *N*,*N*′-bis-(1-naphthyl)-*N*,*N*$_0$-diphenyl-1,10-biphenyl-4,40-diamine, TCTA is 4,4′,4′′-tri(*N*-carbazolyl) triphenylamine CBP is 4,4′-*N*,*N*′-dicarbazolyl-1,10-biphenyl, TPBi is 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene.

Ir(ppy)$_3$. There are reports on the quenching effects of C–H oscillators and substitution of these quenching C–H modes for C–D bonds in lanthanide complexes leads to significant enhancement of the luminescent lifetime and quantum yields.[16] However, from the data above, it can be concluded that deuteration has only a minor effect on the photophysical properties of the materials. This might be understood in terms of a "heaviest atom effect", that is, an electron will search the heaviest nucleus nearby (in this case, the heaviest nucleus is Ir^{3+} rather than D) and completes its spin-flip to facilitate the coupling of the spin angular moment to the orbital angular momentum. In addition, the mechanism to generate phosphorescence in heavy-metal complexes is different from that to generate luminescence in lanthanide complexes in that the former stems mainly from ^{3}MLCT and the latter comes from the low-lying 4f atomic orbital of the lanthanide ion. Table 1 summarizes the main photophysical comparison between Ir(ppy)$_3$ and Ir(ppy)$_3$-D$_{24}$.

Fig. 3 compares the efficiency (a) and luminance (b) *vs.* current density curves based on deuterated Ir(ppy)$_3$-D$_{24}$ and un-deuterated Ir(ppy)$_3$. The highest efficiency for the device based on deuterated Ir(ppy)$_3$-D$_{24}$ and un-deuterated Ir(ppy)$_3$ reaches as high as 74 and 68 cd A^{-1} respectively. At the initial current densities (0.6–3 mA cm^2, corresponding to ~200 cd m^{-2} @ 8.5 V), efficiency of both device types decays very fast. This is common for many OLEDs because at the beginning, the luminance is very low but corresponding to even lower a current density and as a result, the efficiency turns out to be quite high. This continues until the device reaches ~50 cd A^{-1}. Then the device based on Ir(ppy)$_3$-D$_{24}$ experiences a slower decay while the device based on Ir(ppy)$_3$ still decays very fast. In other words, the device based on Ir(ppy)$_3$-D$_{24}$ endures high current densities much better. The efficiency decays to half of its initial value until the current density reaches 140 mA cm^{-2} for the device

Table 1 Photophysical properties of the deuterated Ir(ppy)$_3$-D$_{24}$ and un-deuterated Ir(ppy)$_3$

Entry unit	$\lambda_{abs}{}^a$ nm	$\lambda_{em}{}^b$ nm	Φ^c %	Φ^d %	Φ^e %	τ^f µs	τ^g µs	τ^h µs	T_d °C	V_{ox} V	Isomeric
Ir(ppy)$_3$	380	509/540	33	81	88	7.0/3.1	3.5/0.87	11	410	0.68	Facial
Ir(ppy)$_3$-D$_{24}$	380	511/541	40	100	85	11/4.3	4.0/0.93	11	400	0.66	Facial

[a] In CH$_2$Cl$_2$ room temperature. [b] In CH$_2$Cl$_2$ degassed, 77 K, excited by 365 nm. [c] In CH$_2$Cl$_2$ degassed, room temperature, excited by 365 nm, contrast to quinine sulfate which is reported to have a Φ value of 54%.[15] [d] In CH$_2$Cl$_2$, 77 K, no reference can be used, so the value for Ir(ppy)$_3$ is relative to Ir(ppy)$_3$-D$_{24}$ which is set as 100%. [e] 6%(wt) doped in CBP thin solid film. [f] Double-exponential decay, in CH$_2$Cl$_2$, 77 K. [g] Double-exponential decay, solid sample, room temperature. [h] Single-exponential decay, 6%(wt) doped in CBP thin solid film.

based on $Ir(ppy)_3$-D_{24} while the efficiency decays to half of its initial value earlier at ~7 mA cm^{-2} for the device based on $Ir(ppy)_3$. In this sense, we can say that the device based on $Ir(ppy)_3$-D_{24} is 20 times more stable than the device based on $Ir(ppy)_3$! Fig. 3b indicates that the device based on $Ir(ppy)_3$-D_{24} moves toward high luminance more steadily. Fig. 4a is the device luminance *vs.* time curve. At an initial driven luminance of 1000 cd m^{-2}, both devices experience accelerating decay. For the device based on $Ir(ppy)_3$-D_{24}, the half life-time ($t_{1/2}$) was ~38.5 hours and for the device based on $Ir(ppy)_3$, $t_{1/2}$ is ~6.5 hours, so the former has about 6 times longer life-time than the latter in the test. We can reasonably expect a much longer life time for the former than the latter at a lower driven luminance, ex. 100 cd m^{-2}, because the decay curve for the former is much flatter at the latter part of the curve.[17] Fig. 4(b) outlines the electrophosphorescent spectra of the two devices. The emissions are almost identical to $Ir(ppy)_3$-D_{24} but with a narrower peak.

These results are very important. Many reports have already confirmed the "roll-off" degeneracy of PhOLEDs.[1–11] our findings here with improved device stability and prolonged device lifetime can be helpful to solve the "roll off" problem. Through the analysis above, the improvements are closely related to the reduced internal energy of the C–D bond, which may be helpful to prevent the degradation of the emitter. The C–D bond also partially take part in the excited state electro-generated phosphorescence as evidenced by the slightly improved photoluminescence efficiency and narrowed electrophosphorescent spectrum, and as supported by the reports in lanthanide luminescent materials of ref. 16. Adachi *et al.* recently identified the interface between the HTL and the emissive layer $Ir(ppy)_3$ as the most susceptive region to degration.[18] In this interface, the C–H/D bonds are just in close contact with the HTL and might influence the degradation. We herein term the influential factors in which the C–D bond takes part in as "the deuterium effect". The detailed mechanism needs further investigation.

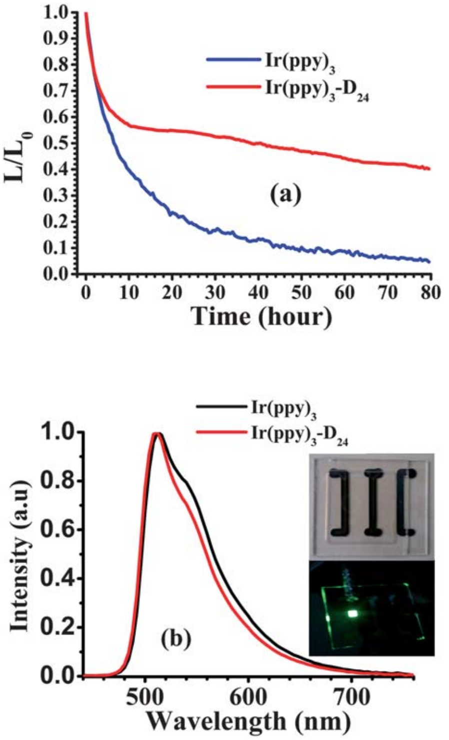


Fig. 4 (a) Luminance (L)/initial luminance (L_0) for glass/ITO (150 nm)/2T-NATA (25 nm)/NPB (5 nm)/TCTA (10 nm)/iridium complex 6% doped CBP (20 nm)/TPBi (30 nm)/LiF (0.3 nm)/Al (100 nm). Both devices were operated at 2.2 mA cm^{-2} and the initial luminance L_0 for both devices was 1000 cd m^{-2}. (b) Electrophosphorescent spectra of the devices based on the iridium complexes. Inset: top, picture of the sealed device turning-off; bottom, picture of the sealed device turning-on.

In conclusion, we have synthesized deuterated $Ir(ppy)_3$-D_{24} by starting from simple deuterated reagents. So, the cost of deuteration is reasonably low. Deuteration of $Ir(ppy)_3$ creates only minor improvements in its photophysical properties but has significant effects on the device stability and life-time. The device based on $Ir(ppy)_3$-D_{24} has high current density 20 times better and a life-time 6 times longer than the device based on $Ir(ppy)_3$ at an initial luminance of 1000 cd m^{-2}. From the IR spectra comparison and the DFT calculation, we can prove that $Ir(ppy)_3$-D_{24} possesses much lower internal energy than $Ir(ppy)_3$, especially the C–D stretching and bending. This is the main contributing factor toward a higher device stability and longer device life-time and we call it a "deuterium effect". Our findings provide a prototype for improving the device stability and lifetime, which are the most important issues regarding the fate of PhOLEDs in the future: maybe we should deuterate all phosphorescent complexes from now on.

Experimental

Details of the synthetic procedures and characterization, absorption spectra, emission spectra, electrochemistry, thermal analysis, computational studies and device fabrication are described in the ESI.†

Acknowledgements

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