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# Nearly 100% internal phosphorescence efficiency in a polymer light-emitting diode using a new iridium complex phosphor†

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**A new iridium complex with a phenylphthalazine ligand has been prepared by an unexpected method and polymer light-emitting devices doped with the complex have been achieved with nearly 100% internal phosphorescence efficiency.**

Organic light-emitting diodes (OLEDs) have attracted great attention because they are amongst the most promising devices for full-color flat-panel displays.[1] The emissive layers of the earliest OLEDs were composed of fluorescent polymers and/or small molecules, in which only the singlet excitons could decay radiatively.[2,3] A significant step in the development of highly efficient OLEDs was the addition of phosphorescent complex dopants to these layers in order to harvest both the singlet and triplet excitons as light.[4] The presence of a heavy-metal atom in the phosphorescent complex provides a significant spin–orbit interaction that allows the normally spin-forbidden radiative triplet decay. In addition, the same effect allows for rapid intersystem crossing from the singlet to the lower-energy triplet state and, as a result, all emission is observed from the triplet state. Among phosphorescent heavy-metal compounds reported, cyclometalated iridium(III) complexes are the most promising candidates due to their higher stability, larger photoluminescence efficiency and relatively shorter excited-state lifetime.[5] Moreover, wavelength tunability over the entire visible spectrum can be achieved by using different ligands.[6]

Generally, to maximize the performance of electrophosphorescent devices, it is necessary to disperse the iridium(III) guest in a suitable host material to reduce triplet–triplet annihilation and concentration quenching. These highly efficient phosphorescent OLEDs have been formed by evaporation techniques of small molecules.[7] For green emitting OLEDs, the most efficient devices have been based around [Ir(ppy)$_3$] (ppy = 2-phenylpyridinyl) with an external efficiency ($\eta_{ext}$) of 19.2% being demonstrated.[8] However, these devices have a complicated structure and consist of multiple layers deposited sequentially under high vacuum conditions by thermal evaporation. There is thus hope to simplify the manufacturing process of these exceptionally efficient devices. Using a polymer as the host material is attractive, since it allows the light-emitting diodes to be made with a spin-coating or printing technique. Despite extensive works in many research groups,[9,10] $\eta_{ext}$ values of solution-processed polymeric electrophosphorescent organic light-emitting diodes (PLEDs) are still much lower than those of vacuum-deposited small-molecule-based devices. Generally, Ir(III) complexes are not sufficiently compatible to form homogeneous molecular dispersions in polymer films. This poor solubility, in turn, restricts device efficiency and lifetime. A widely used approach to enhancing the solubility of Ir(III) complexes has been to attach solubilizing alkyl moieties or to introduce dendritic architectures.[11] However, the introduction of alkyl groups perturbs charge carrier transport and lowers the glass transition temperature ($T_g$). Hence, sterically hindered aromatic substituents, which give rise to fewer side effects, are considered to be better solubilizing groups. In this communication, we reported a highly efficient phosphorescent Ir(III) complex of a 4-phenylphthalazine derivative. The sterically hindered phenolic groups were introduced into the Ir(III) complex to improve its solubility.

With chelating aromatic ligands iridium(III) preferentially form bis-cyclometalated complexes.[12] To synthesize tris-cyclometalated Ir(III) complexes, two different synthetic routes can be used.[13,14] The fist method involves treating Ir(III) organic complexes, such as Ir(O^O)$_3$ (O^O = β-diketonate anion), (C^N)$_2$Ir(μ-Cl)$_2$ Ir(C^N)$_2$ (C^N = cyclometalating ligand anion) and (C^N)$_2$Ir(O^O), with excessive free cyclometalating ligand precursors. The tris-cyclometalated complexes can also be prepared by reaction of $IrCl_3 \cdot nH_2O$ with a large excess of free ligand in the presence of a silver salt. However, these methods employ either expensive materials and high temperatures (>170 °C) or a silver catalyst. In our experiment, tris(1-(2,6-dimethylphenoxy)-4-(4-chlorophenyl)phthalazine)iridium(III) [Ir(MPCPPZ)$_3$] was unexpectedly synthesized using $IrCl_3 \cdot 3H_2O$ as starting material in the absence of any catalyst (Fig. 1a). Under mild reaction condition (80 °C, 12 h), air-stable red powders were obtained. Purification of the mixture by column chromatography furnished homoleptic *fac*-[Ir(MPCPPZ)$_3$] in moderate yield (41%). The facial geometry around the Ir center was confirmed by a single-crystal X-ray analysis (Fig. 1b). The complexes show excellent thermal stability, with their onset decomposition temperatures ($T_d$) higher than 388 °C, as revealed by thermogravimetric analysis (TGA). Studies on the mechanism of preferentially forming triscyclometalated Ir(III) complexes are currently under way.

In the UV-visible absorption spectrum of Ir(MPCPPZ)$_3$ (Fig. 2a), the absorption band around 296 nm is assigned to a typical spin-allowed $^1\pi$–$\pi^*$ transition of the MPCPPZ ligand because the corresponding transition was also observed in the free ligand 1-(2,6-dimethylphenoxy)-4-(4-chlorophenyl)phthalazine (HMPCPPZ) based UV spectral profile (Fig. 2b). On the other hand, the band at 392 nm, which is not observed in the spectrum of the free ligand, is assignable to the singlet metal-to-ligand charge-transfer ($^1$MLCT).

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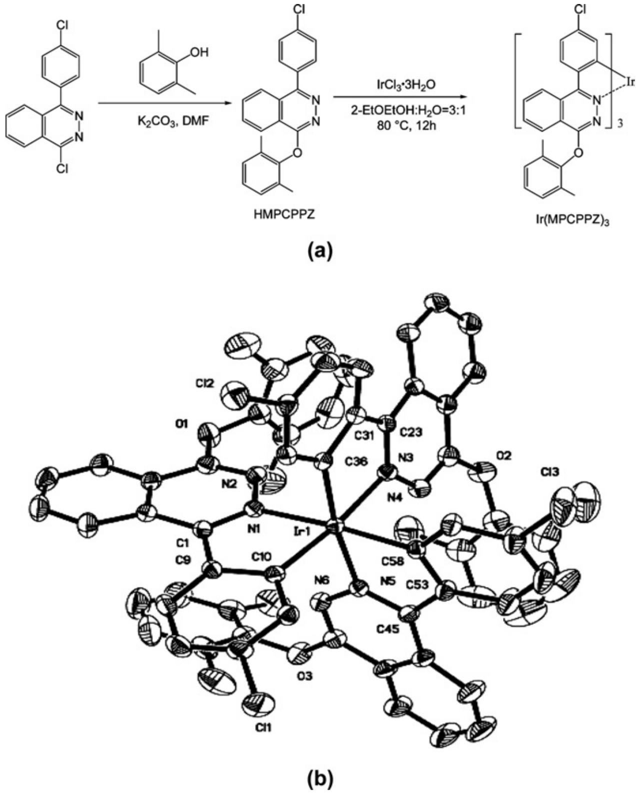

**Fig. 1** (a) Synthesis of Ir(MPCPPZ)$_3$; (b) ORTEP plot of Ir(MPCPPZ)$_3$, with the hydrogen atoms omitted for clarity.

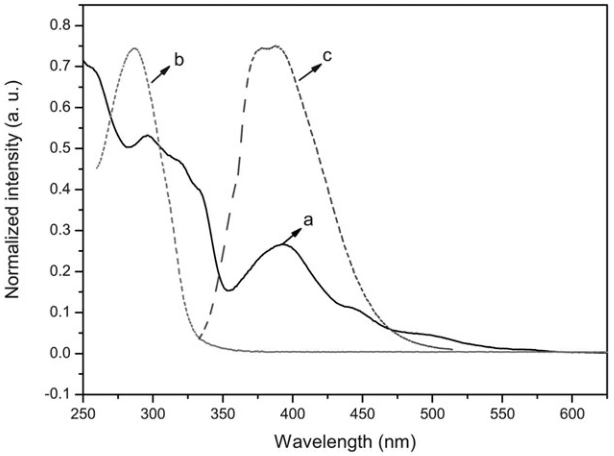

**Fig. 2** UV absorption spectra of Ir(MPCPPZ)$_3$ (a) and HMPCPPZ (b) in $CH_2Cl_2$ and emission spectrum of a PVK-CBP blend (c) at 298 K.

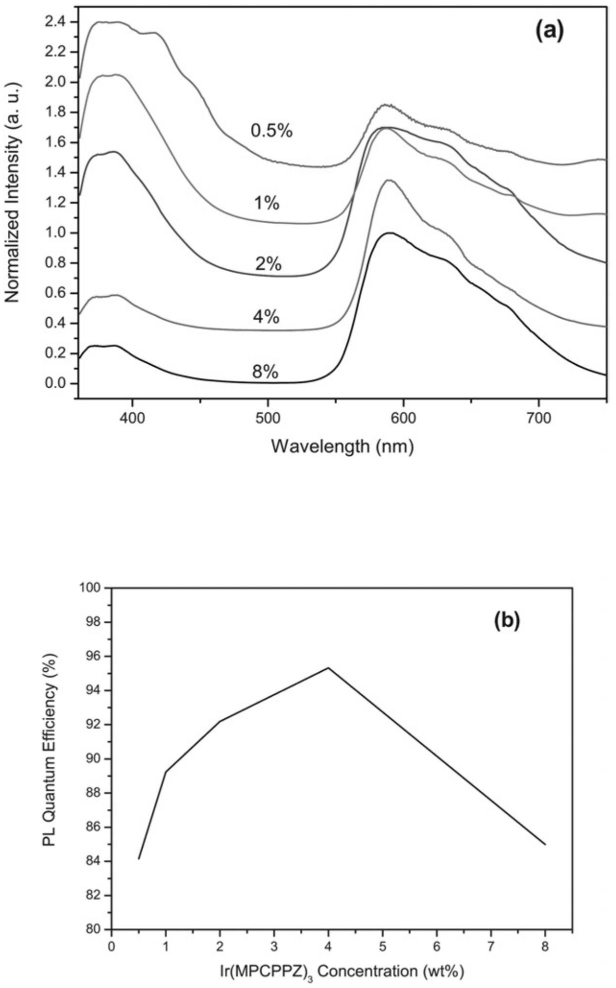

**Fig. 3** The PL spectra (a) and PL quantum efficiency (b) of Ir(MPCPPZ)$_3$/PVK-CBP films with different doping concentrations.

The moderately intense absorptions at *ca.* 450–550 nm and weaker absorptions above 550 nm can be assigned to a spin-forbidden triplet metal-to-ligand charge-transfer ($^3$MLCT).

A reasonable overlap between the emission profile (Fig. 2c) of a PVK-CBP blend (12:80, wt:wt, PVK = poly(*N*-vinylcarbazole), CBP = 4,4′-dicarbazolyl-1,1-biphenyl) and the absorption bands of this iridium complex is observed, which enables a Förster energy transfer from the singlet-excited states of the host to the MLCT states of the iridium complex. Fig. 3a shows the photophosphorescence (PL) spectra of Ir(MPCPPZ)$_3$ doped into the PVK-CBP blend at different doping ratios under excitation of 325 nm line from a He–Cd laser. The extent of energy transfer from the PVK-CBP blend to the Ir(MPCPPZ)$_3$ dopant is presented in the PL spectral profiles at the dopant concentrations of 0.5–8 wt%. All these PL profiles contain two components: one component peaks around 380 nm, which originates from the excited emission of the PVK-CBP blend; another component peaks at 590 nm with a shoulder at 630 nm corresponding to the triplet emission of the Ir(III) complex. With increasing dopant concentration from 2 wt% to 4 wt%, the contribution of PVK-CBP emission decreased very quickly. A further increase in the dopant concentration from 4 wt% to 8 wt% resulted in little change in the contribution of the PVK-CBP emission. Complete quenching of the PVK-CBP emission is not observed even at the dopant concentration of 8 wt%. This implies that energy transfer from the PVK-CBP blend to the Ir(III) complex is inefficient under photo-excitation. Fig. 3b shows the absolute photophosphorescence quantum efficiency ($\eta_{PL}$) of the above blend films. The $\eta_{PL}$ increased from 84.2% to a maximum of 95.3% going from low to intermediate dopant concentration (0.5–4 wt%) and then decreased with increasing concentration. Since a small amount of emission from the host was observed at high doping concentration, the increase of $\eta_{PL}$ at low concentrations can be attributable to incomplete energy transfer process from the triplet state of the PVK-CBP blend to Ir(MPCPPZ)$_3$, suggesting that the value of $\eta_{PL}$ is in excess of

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95.3%. The room temperature decay characteristics of Ir(MPCPPZ)$_3$ are monoexponential with emission lifetime of about 1 μs as a neat film and 2 μs in degassed CH$_2$Cl$_2$.

The electrophosphorescent properties of the Ir(III) complex were characterized and PLEDs were fabricated with the structure of ITO/PEDOT(50 nm)/PVK:CBP:Ir(MPCPPZ)$_3$(12 wt%)(55 nm)/TPBI(30 nm)/Ba(4 nm)/Al(120 nm). Commercially available PEDOT (Baytron P4083, Bayer AG), a conductive polymer blend that is composed of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) and acts as a hole-transport layer, was spin coated on a precleaned ITO substrate and dried by baking in vacuum at 80 °C for 12 h. PVK-CBP blends doped with Ir(MPCPPZ)$_3$ were spin coated from a mixed solution of chloroform and chlorobenzene. 1,3,5-Tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) instead of the commonly used BCP or BAlq was deposited onto the emitting material layer to confine excitons within the emissive zone. Then a layer of Ba and a capping layer of Al were deposited through a shadow mask. Consistent with the excellent compatibility of the Ir(III) complex with PVK-CBP blends, a high-quality spin-coated film was easily realized during device fabrication. The polymer organic light-emitting devices based on the Ir(III) complex exhibited a peak electrophosphorescence wavelength of 597 nm along with a shoulder around 635 nm (Fig. 4a). A peak external quantum efficiency of 20.2% ph el$^{-1}$ and luminance efficiency of 18.4 cd A$^{-1}$ were recorded at a current density of 0.49 mA cm$^{-2}$, and a luminance of 5870 cd m$^{-2}$ was observed at a current density of 114 mA cm$^{-2}$ (Fig. 4b). The turn-on voltages are 8 V with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.62, 0.36). The electroluminescence (EL) spectra exhibit no residual emission from the host and/or adjacent layers, even at high drive currents. Typical efficiency roll-off at higher currents, attributable to a combination of triplet–triplet annihilation and field-induced quenching effects, is also observed here. To the best of our knowledge, this is the first report of polymer-based phosphorescent devices with external quantum efficiencies that achieve 20% ph el$^{-1}$. The OLED external quantum efficiency follows:

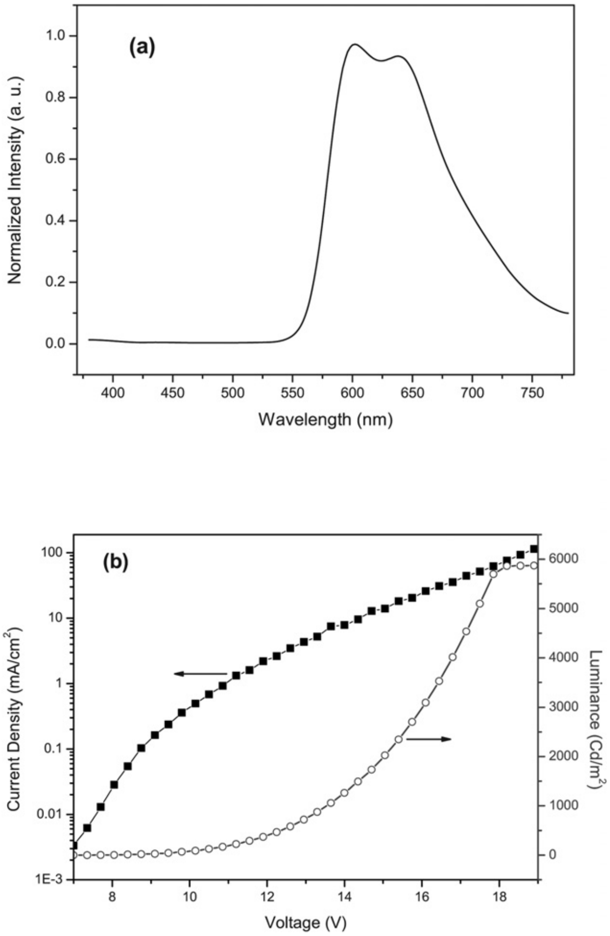

**Fig. 4** The EL spectrum (a) and current–voltage–luminance characteristics (b) for Ir(MPCPPZ)$_3$.

$$\eta_{\text{ext}} = \eta_{\text{int}}\eta_{\text{c}} \quad (1)$$

where $\eta_{\text{int}}$ is the internal quantum efficiency and $\eta_{\text{c}}$ is the light out-coupling efficiency. Assuming $\eta_{\text{c}}$ is around 20%,[7] $\eta_{\text{int}}$ is calculated to be nearly 100% at 10 V in this device. The extra-high efficiency is an indication of balanced electron and hole recombination in the host matrix, and complete energy and/or charge transfer from the host exciton to the phosphor upon electrical excitation, and is also consistent with the very high $\eta_{\text{PL}}$ of Ir(MPCPPZ)$_3$ established above. Since we found in our experimentation the solubility of the free ligand was greatly improved after the introduction of the sterically hindered phenolic moiety, we can also surmise that it is probably the sterically hindered phenolic moiety that results in a rigid spacer which plays a assistant role in alleviating the self-quenching of the phosphor, and consequently increases the emission efficiency.

In summary, a new Ir(III) complex with excellent solubility and efficiency have been synthesized by an abnormal method. The sterically hindered phenolic substituents successfully facilitated higher phase homogeneity of the Ir(III) complex inside a PVK-CBP host. Polymer organic light-emitting devices based on the Ir(III) complex exhibited the highest external quantum efficiency of 20.2% ph el$^{-1}$ and luminance efficiency of 18.4 cd A$^{-1}$. The efficiency remains as high as $\eta_{\text{ext}} = 6.6\%$ ph el$^{-1}$ at a high current density of 100 mA cm$^{-2}$. The high internal phosphorescence efficiency and charge balance in the structure are responsible for the high efficiency. The results demonstrate that high-efficiency electrophosphorescent organic light-emitting diodes are possible with a polymer as the host and a heavy-metal complex as the guest by a simple and low-cost solution-processing technique. If material efficiencies can be maintained as color tuning occurs by changing the substituents and their positions then these materials will provide a unique platform for full color display devices of the future.

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