Highly phosphorescent perfect green emitting iridium(III) complex for application in OLEDs†

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A novel iridium complex, [bis-(2-phenylpyridine)(2-carboxy-4-dimethylaminopyridine)iridium(III)] (N984), was synthesized and characterized using spectroscopic and electrochemical methods; a solution processable OLED device incorporating the N984 complex displays electroluminescence spectra with a narrow bandwidth of 70 nm at half of its intensity, with colour coordinates of $x = 0.322$; $y = 0.529$ that are very close to those suggested by the PAL standard for a green emitter.

Organic light emitting diodes (OLEDs) are becoming increasingly successful as a new display technology.[1,2] Although OLED displays have reached commercialization, there is still a need for improvement of the efficiency, colour purity and stability. This is true for multilayered OLEDs prepared *via* vacuum evaporation and even more so for OLED architectures obtained *via* solution processing. The latter technique offers a more economic production route and hence is of great interest for the more widespread application of the OLED technology. The introduction of iridium(III) containing complexes led to very efficient multilayered OLEDs, reaching internal conversion efficiency of almost 100%.[3] These high efficiencies originate from the strong spin orbit coupling present in these heavy metal complexes which makes it possible for both singlet and triplet excitons generated to decay radiatively.[4,5] A large number of iridium complexes have been utilized for this purpose, which are mostly based on the cyclometalating ligand 2-phenylpyridine (ppy) with an auxiliary ligand such as acetylacetonate (acac) or picolinate (pic).[6–10] Several groups have demonstrated tuning of the phosphorescence wavelength from blue to red by functionalization of the ligands with electron withdrawing and electron donating substituents.[11–13] Nevertheless, no attempts were made to tune the colour purity by decreasing the emission bandwidth, which of course is attractive for both fundamental research and practical applications. Therefore, in this communication we report a novel approach for tuning bandwidth by modulating the LUMO levels of the ancillary ligand.

The N984 complex was synthesized in one step by reacting the dimeric iridium(III) complex [Ir(ppy)$_2$(Cl)]$_2$ with methyl-dimethyl-amino-picolinate and sodium carbonate in 2-ethoxy-ethanol affording the N984 compound as a yellow powder.‡ The ^{1}H NMR spectrum of the N984 complex shows 19 resonance signals (two doublets (d), five doublet of doublets (dd), six doublet of doublet of doublets (ddd) and six doublet of triplets (dt); see Fig. S1) in the aromatic region. The pyridine 6-H protons of the 2-phenylpyridine ligands are assigned to ddd at δ 7.64 and δ 8.82 on the basis of the distinctive pattern of the coupling constants expected for these substituted pyridines ($J_{3,6}$ 0.8, $J_{4,6}$ 1.6 and $J_{5,6}$ 5.8). The different magnetic environments of these protons are a result of the *trans* geometry of the pyridine rings which directs one 6-H proton towards the 4-dimethylaminopyridine ring and the other towards the carboxylate group of the ancillary ligand. The dimethylamino group protons are observed as a singlet at δ 3.05; the integrated ratio of 19 : 6 between the aromatic and aliphatic protons confirms the proposed structure. The carbon-13 NMR spectrum (see Fig. S2) exhibits 25 distinct signals for the 27 aromatic carbon atoms present in the N984 complex and the inequivalence of the 2-phenylpyridine ligands is again attributable to the asymmetry imposed on the complex by the ancillary ligand. The signal from the dimethylamino group of the ancillary ligand is found at δ 38.7 and that of the carboxylate group at δ 172.9.

UV–Vis absorption spectra of the N984 complex measured in acetonitrile solution at 298 K display bands in the UV (208, 274, 334 and 398 nm) and the visible region (at 428, 448 and 480$_{sh}$ nm) due to intra ligand (π–π*) and metal to ligand charge transfer transitions (MLCT), respectively (Fig. 1). When excited at 298 K within the π–π* and MLCT absorption bands, the N984 shows emission maxima at 508 nm with an excited state lifetime of 32 ns. The argon-degassed methanol solution of the N984 shows bright
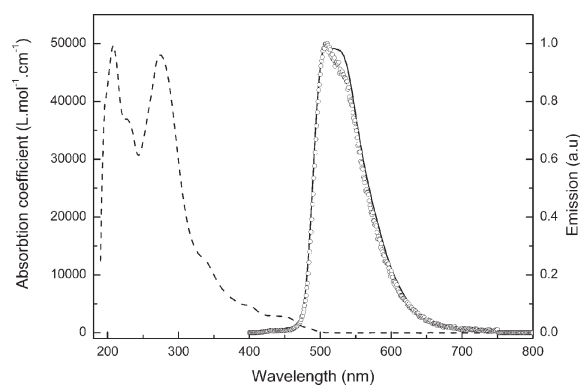
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Fig. 1 Absorption (dashed line) and emission (open circles) spectra of the N984 complex measured in acetonitrile and doped in a PMMA film (solid line) at 298 K.

green luminescence with an excited state lifetime of 1.95 μs. The phosphorescence quantum yield of the N984 complex is $70 \pm 10\%$ in solution at room temperature. The emission spectrum of a solid-state film prepared by dissolving 1% N984 complex in a PMMA matrix shows maxima at 506 with a distinct shoulder at 535 nm similar to the solution based emission spectrum. The excited state lifetime of N984 in the solid-state film is 2.42 μs which is comparable to that observed in an argon-degassed acetonitrile solution (2.19 μs). The electroluminescence spectrum maximum, however, is slightly (15 nm) red shifted compared to that observed *via* photo-excitation in solution and in the solid-state film (see below).

The cyclic voltammogram of the N984 complex measured in an ethylenecarbonate solution containing 0.1 M lithium hexafluorophosphate with a 0.5 V s^{-1} scan rate shows a reversible couple at 0.61 V *vs.* ferrocene (Fc) due to the iridium(III/IV) couple. The separation between the anodic and cathodic peak is 75 mV. Upon scanning cathodically a reversible reduction wave at -2.55 V *vs.* Fc is observed, which is assigned to the reduction of the 2-phenylpyridine based on analogous complexes. The reduction potential data demonstrate that the first LUMO is located on the 2-phenylpyridine rather than on the 4-dimethylamino-2-carboxy-pyridine whose LUMO is destabilized because of the presence of the 4-dimethylamino group. On the other hand the oxidation potential in the N984 complex is shifted cathodically by 0.1 V compared to the [Ir(ppy)$_2$(pic)] complex due to destabilization of the iridium HOMO orbitals caused by the insertion of the dimethylamino group on the 4-position of 2-pyridinecarboxylate ligand.

A simple polymer light emitting diode is fabricated utilizing N984, which is blended with the large bandgap polymer poly(*N*-vinylcarbazole) (PVK).[14] In order to improve the electron transporting properties, 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) is added to the PVK.[14,15] The introduction of the dimethylamino group on N984 makes it more soluble and facilitates its dispersion into polymeric charge transporting materials. OLEDs were prepared by spin coating a chlorobenzene solution containing PVK:PBD:N984 in a ratio of 3 : 1 : 0.25 on an indium tin oxide (ITO) coated patterned substrate. Previously, a 100 nm thick PEDOT:PSS (obtained from HC-Starck) was deposited to enhance the hole injection and the device stability.[16] To confine the excitons to the emissive layer and to prevent the loss of holes by recombination at the cathode a 20 nm layer of 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) is thermally evaporated.[15] Finally a barium cathode protected by an 80 nm silver layer is deposited *via* thermal vacuum deposition.

The peak of the electroemission spectrum of the N984 containing OLED is located at 513 nm (Fig. 2). This results in CIE[17] colour coordinates of $x = 0.322$ $y = 0.529$, very close to those suggested by the PAL standard for a green emitter, making the N984 a good candidate for use in display and illumination applications.

The device performance is shown in Fig. 3 which depicts the current density–brightness–voltage properties and the luminous and power efficiencies. The turn-on voltage is somewhat high for polymer type OLEDs and is in part caused by the TPBI hole blocking layer. The current density and the brightness increase rapidly after the turn-on voltage, reaching a brightness level of 20000 cd m^{-2} at 14 volts. The efficacy reaches 32 cd A^{-1} at an
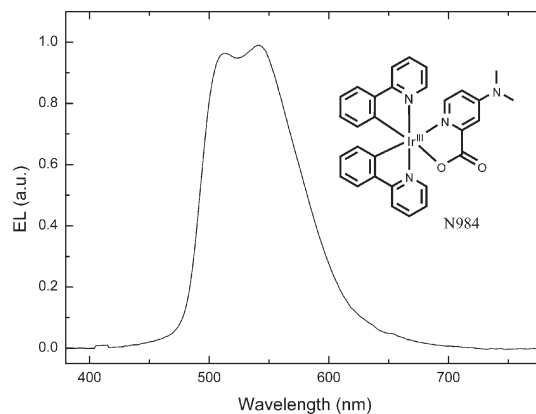

Fig. 2 Electroluminescent spectra of N984 containing OLED device. The inset shows the chemical structure of N984.
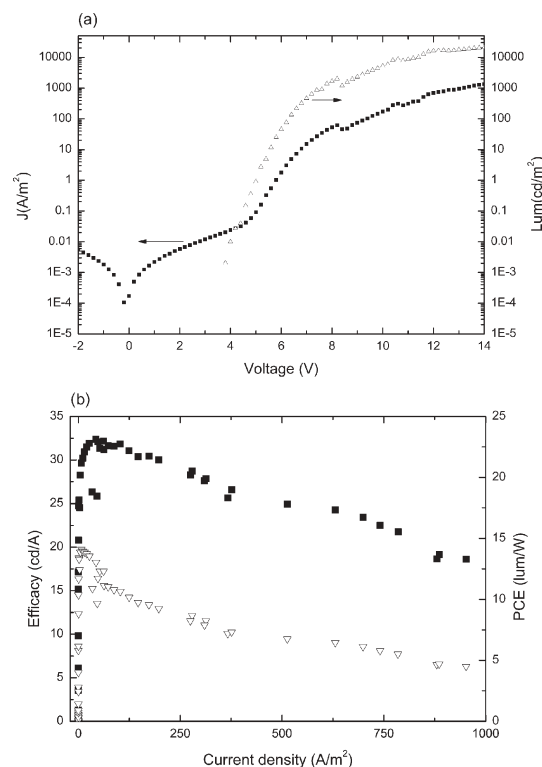

Fig. 3 (a) Current density (solid squares) and luminance (open up triangles) *versus* applied bias of the N984 containing OLED device. (b) The corresponding efficacy (solid squares) and power conversion efficiency (open down triangles) curves as a function of the luminance.

operation voltage of 8 volts; this is among the highest values obtained for a polymer OLED using a simple low work function cathode. Similarly, the power efficiency is among the best reported for a simple solution processable OLED (13.5 lm W^{-1} at 1000 cd m^{-2}), indicating the potential of this new approach to Ir complexes for use in OLEDs.

It has been reported that when optimizing the cathode by using ultrathin LiF and CsF deposited in between the electroluminescent layer and a metal an additional enhancement of the device efficacy can be obtained.[18] In such a device structure the operation voltage is decreased by approximately 5 volts. Additionally, when making use of a crosslinked and partially oxidized hole injection layer

record power efficiencies as high as 29.7 lm W^{-1} at a brightness of 1000 cd m^{-2} were reported using the commercially available tris[2-(4-methylphenyl)pyridine]iridium(III) complex.[19] The implementation of these device optimizations while using the title complex should result in even higher values for the device efficiencies.

In conclusion, by introducing a donor group on the ancillary ligand 2-picolinate we have been able to move the LUMO from this chemically weakly bound ligand to the cyclo-metalating ppy ligand, resulting in a highly phosphorescent green emitter with high electroluminescence efficiency, which is very close to the perfect green desired for display and illumination applications. Additionally, the introduction of the dimethylamino group imparts to the complex good solution processability. This work, therefore, shows the potential of this new class of phosphorescent complexes for OLED applications.

Notes and references

‡ **Synthesis**

4-N,N′-dimethylamino-2-methoxycarbonylpyridine: To a solution of 2-bromo-4-dimethylaminopyridine (1.45 g, 7.2 mmol) in THF (100 ml) cooled to −78 °C was dropwise added *n*BuLi (1.6 M, 6.3 ml, 10 mmol). The resulting orange solution was stirred at −78 °C for 40 minutes under nitrogen. CO_2 (from dry-ice) was then bubbled into the solution during 3 hours while the temperature was allowed to reach room temperature. MeOH (2 ml) was then added and the solvent removed under vacuum. MeOH (100 ml) and conc. H_2SO_4 (4 ml) were added and the resulting mixture refluxed overnight. The solvent was removed under vacuum and water (100 ml) was added. The mixture was neutralized with aqueous K_2CO_3 and extracted with CH_2Cl_2 (3 × 50 ml). The combined organic fractions were washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (SiO_2, CH_2Cl_2–MeOH 95 : 5). The obtained orange oil was dissolved in CH_2Cl_2 (1 ml) and petroleum ether (100 ml) was added. The solution was stood in a refrigerator overnight. The precipitate formed was filtered and washed with small portions of cold petroleum ether to afford 600 mg (46%) of the desired compound as a slightly yellow solid.

^{1}H NMR (CDCl$_3$, 298 K, 200 MHz, δ ppm) δ 3.09 (s, 6H), 3.96 (s, 3H), 6.94 (dd, J = 2.5 × 9 Hz, 1H), 7.99 (d, J = 9 Hz, 1H), 8.17 (d, J = 2.5 Hz, 1H). ^{13}C NMR (CDCl$_3$, 298 K, 50 MHz, δ ppm) δ 39.7, 52.2, 116.8, 126.2, 133.9, 134.9, 147.7, 166.1.

Synthesis of [Ir(2-phenylpyridine)₂(4-dimethylamino-2-carboxy-pyridine)]
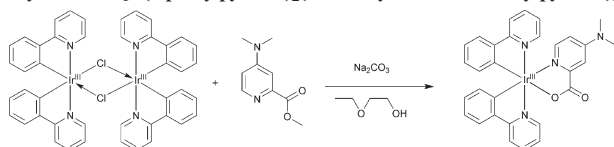
The dimeric iridium(III) complex [Ir(ppy)₂(Cl)]₂ (199 mg, 0.185 mmol), methyl-dimethylamino-picolinate (103 mg, 0.57 mmol, 3.1 equiv.) and

sodium carbonate (102 mg, 0.96 mmol, 5 equiv.) were suspended in a mixture of 2-ethoxy-ethanol (44 ml) and deionised water (6 ml) under argon. This mixture was heated at 110 °C for 12 hours and cooled down to room temperature. Water (100 ml) was added and the mixture stored in a refrigerator for 2 hours. The precipitate was filtered off, washed with deionised water (3 × 50 ml) and dried under vacuum to afford the target compound as a yellow powder (215 mg, 0.32 mmol, 87% yield).

Device preparation: PEDOT:PSS was purchased from HC-Starck, TPBI was obtained from Sensient GmbH, PVK, PBD and solvents used were obtained from Aldrich. The pre-patterned ITO glass plates were extensively cleaned, using chemical and UV–ozone methods, just before the deposition of the organic layers. The thickness of the films was determined using an Ambios XP1 profilometer, resulting in a 100 nm and a 70 nm thick PEDOT:PSS and PVK:PBD:N984 film, respectively. TPBI was thermally evaporated to a layer thickness of 20 nm using temperature controlled sources and an evacuation chamber integrated in an inert atmosphere glovebox (<0.1 ppm O_2 and H_2O). In a separate evaporation chamber integrated in the same inert atmosphere glovebox the barium and silver metals were evaporated. The base pressure for both evaporators is <1 × 10^{-6} mbarr. Current density and luminance *versus* voltage were measured using a Keithley 2400 source meter and a photodiode coupled to a Keithley 6485 picoampmeter using a Minolta LS100 to calibrate the photocurrent. An Avantes luminance spectrometer was used to measure the EL spectrum. Devices were characterised in inert atmosphere.

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