

# White-light phosphorescence emission from a single molecule: application to OLED†

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**A simple mononuclear cyclometallated iridium(III) complex exhibits white photo- and electro- luminescence in the wavelength range from 440 to 800 nm, which originates from a single emitting excited state of mixed character.**

Organic light emitting diodes (OLEDs) are recently proposed as one of the most appealing solutions for low energy consumption solid-state lighting.<sup>1</sup> To date organic white light-emitting devices (WOLEDs) are obtained by combining the emission from red, green and blue or sky-blue and orange emitters. The combination of these emitters can be achieved by the deposition of multiple layers on top of each other,<sup>2</sup> by mixing them into one single emitting layer,<sup>3</sup> combinations of the two techniques,<sup>4</sup> and by combining them into polymeric structures.<sup>5</sup> These approaches require more complex device architectures and production processes compared to single-emitter based OLEDs, which has so far greatly hindered their market entry. Therefore, the development of a white light-emitting phosphorescent single transition-metal complex is very much desired. Multinuclear complexes<sup>6</sup> or excimers<sup>7</sup> have been designed for such a purpose. However, despite being single molecules, those approaches still rely on the combination of two emitting centers, which is expected to show color drift over time. In this paper, we describe a simple mononuclear organometallic complex that exhibits white photo- and electro-phosphorescence as a proof of concept demonstrating that WOLEDs with a single emitting center can be achieved. Theoretical calculations rationalize the reasons behind such broad emission, opening the way for generalization of this new strategy for WOLEDs development. Our result demonstrates that low-cost white light-emitting OLEDs with a single emitting center can be achieved.

An usual synthetic route was used to prepare the complex (acetylacetonato)bis(1-methyl-2-phenylimidazole)iridium(III),

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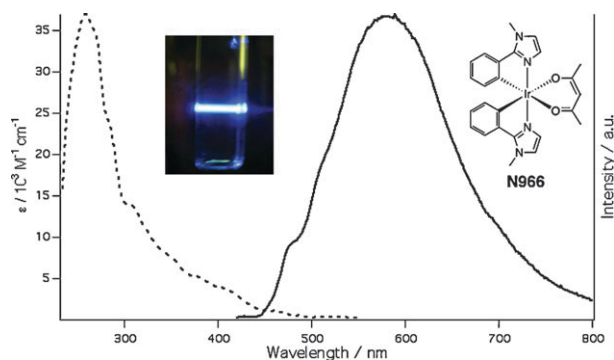
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hereafter labelled as N966 (Fig. 1 and S1 (ESI†) for the crystal structure). The UV-Vis absorption spectrum of N966 in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K displays bands in the UV at 260, 284, 308, 348 and 376 nm, and the visible region at 408 and 454<sub>sh</sub> nm due to intra-ligand ( $\pi$ - $\pi^*$ ) and metal-to-ligand charge transfer transitions (MLCT), respectively (Fig. 1). When excited at 298 K within the ligand ( $\pi$ - $\pi^*$ ) and MLCT absorption bands, the N966 complex shows a broad and almost unstructured emission covering the spectral range from 440 to 800 nm, with a maximum intensity at 570 nm,<sup>8</sup> a photoluminescence quantum yield (PLQY) of 0.015 and a radiative lifetime of  $(1.96 \pm 0.1)$   $\mu$ s over the entire spectrum (Fig. S3 and S4, ESI†). The emission spectrum is independent of the excitation wavelength. Additionally, the excitation spectrum is independent of the probed wavelength (Fig. S5, ESI†). Finally, emission spectra measured at concentrations ranging from  $10^{-3}$  to  $10^{-7}$  M exhibit the same broad shape excluding the presence of an excimer (Fig. S6, ESI†). At 77 K, the emission becomes more structured with clear peaks at 469, 504 and 544 nm, as well as unresolved shoulders at 588 and 632 nm (Fig. S7, ESI†). Those photophysical results point toward a single broad emitting center. Cyclic voltammetry in DMSO solution exhibits reversible oxidation and reduction peaks at 0.17 and  $-3.3$  V vs. ferrocene, respectively.

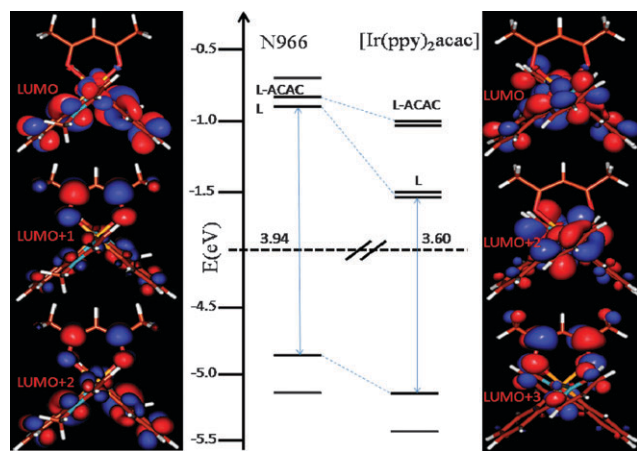
To provide insight into the electronic structure and the optical properties of the N966 complex we performed DFT/TDDFT calculations on its ground singlet and on the two lowest triplet excited states, the latter corresponding to the lowest SCF triplet states obtained by population of the LUMO and LUMO+2 ( $T_1$  and  $T_2$ , respectively). For



**Fig. 1** Absorption (left dotted line) and emission spectra (right full line) of N966 in dichloromethane. The inset shows the chemical structure of N966. The photo shows the white-light emission of N966 obtained upon excitation using 355 nm laser light.

comparison, we also investigated the well-known (acetylacetonato)bis(2-phenylpyridine)iridium(III), hereafter [Ir(ppy)<sub>2</sub>acac], which shows green luminescence at 516 nm in CH<sub>2</sub>Cl<sub>2</sub> with a much less broad emission spectrum, spanning the 470–650 nm range.<sup>9</sup> The main structural parameters of the ground (S<sub>0</sub>) and lowest excited states (T<sub>1</sub> and T<sub>2</sub>) for N966 and [Ir(ppy)<sub>2</sub>acac] are rather similar, see Table S1 (ESI†) for a comparison with crystallographic data. The two complexes share the same HOMO of Ir(t<sub>2g</sub>; d<sub>xy</sub>)-ppy(π) character lying at −4.84 and −5.13 eV in N966 and [Ir(ppy)<sub>2</sub>acac], respectively (not shown). This decrease in the oxidation potential in N966 is in agreement with the trend of electrochemical data, which locates the [Ir(ppy)<sub>2</sub>acac] (N966) oxidation potential at 0.37 (0.17) V vs. ferrocene. The HOMO destabilization in N966 is due to the increased donor capability of the N966 cyclometallated ligands compared to the phenylpyridine ligands of [Ir(ppy)<sub>2</sub>acac]. For [Ir(ppy)<sub>2</sub>acac] the LUMO/LUMO + 1, see Fig. 2, are degenerate π\* orbitals of the ppy ligands, lying at −1.53/−1.51 eV, followed at higher energy (ca. 0.5 eV above) by a second degenerate couple of antibonding orbitals localized on the ppy and acac ligands at −1.04/−1.00 eV (LUMO + 2 and LUMO + 3, respectively). Notice that, given the energetic proximity of LUMO + 2/LUMO + 3, at the [Ir(ppy)<sub>2</sub>acac] T<sub>1</sub> optimized geometry, the order of these two orbitals is inverted. For N966, the LUMO is a π\* orbital delocalized over the cyclometallated ligands. However, in relation to the destabilization of this orbital due to the increased donor capability of the bis(1-methyl-2-phenylimidazole) ligands, a considerable mixing of the cyclometallated and acac-based π\* orbitals in the LUMO + 1 and LUMO + 2 occurs. This provides a set of three almost degenerate LUMOs, Fig. 2.

The results of TDDFT excited-state calculations are summarized in Table 1. The calculated absorption spectrum for N966 (Fig. S9, ESI†) is in good agreement with the experimental one, being slightly shifted towards higher energies by only ca. 0.15 eV. As found for related Ir(III) cyclometallated complexes,<sup>10</sup> the visible region is dominated by MLCT transitions, while at higher energy the π–π\* excitations of the cyclometallated ligands are found. At the ground state geometries (S<sub>0</sub> in Table 1), the lowest excited state of



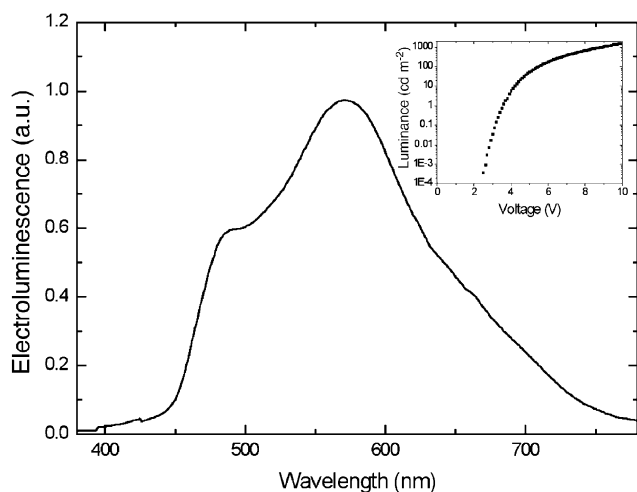
**Fig. 2** Schematic representation of the frontier molecular orbitals for the N966 and [Ir(ppy)<sub>2</sub>acac] complexes calculated at the S<sub>0</sub> geometries. Plots of relevant unoccupied orbitals are also reported.

**Table 1** Selected lowest calculated S<sub>0</sub>–T<sub>n</sub> and S<sub>0</sub>–S<sub>n</sub> transitions (nm) for [Ir(ppy)<sub>2</sub>acac] and N966 along with their numbering and composition in terms of main orbital contributions. For S<sub>0</sub>–S<sub>n</sub> transitions the oscillator strength is also reported (data in parentheses)

Transition	[Ir(ppy) <sub>2</sub> acac]			N966				
		<i>n</i>	S <sub>0</sub>	T <sub>1</sub>	<i>n</i>	S <sub>0</sub>	T <sub>1</sub>	T <sub>2</sub>
S <sub>0</sub> –T <sub>n</sub>	H → L	1	482	537	1	440	494	480
S <sub>0</sub> –T <sub>n</sub>	H → L + 1	2	479	515	2	433	472	469
S <sub>0</sub> –T <sub>n</sub>	H → L + 2	3/5	—	429	3	431	431	439
	H → L + 3	—	432	—	—	—	—	—
S <sub>0</sub> –S <sub>n</sub>	H → L	1	440 (0.047)	—	1	390 (0.078)	—	—
S <sub>0</sub> –S <sub>n</sub>	H → L + 1	2	434 (0.001)	—	2	383 (0.007)	—	—
S <sub>0</sub> –S <sub>n</sub>	H → L + 2	6/5	366 (0.023)	—	3	369 (0.000)	—	—

N966 is calculated to be of triplet character at 440 nm; the lowest singlet excited state is calculated as a quite intense transition (*f* = 0.078) at 390 nm. Both S<sub>0</sub>–T<sub>1</sub> and S<sub>0</sub>–S<sub>1</sub> originate from excitation from the metal-based HOMO to the π\* LUMO of the cyclometallated ligands; the calculated transition wavelengths nicely compare with the 454 nm shoulder and more intense 408 nm band found in the absorption spectrum, suggesting that the 454 nm shoulder originates from spin-forbidden singlet–triplet excitations, which become allowed due to the strong spin–orbit coupling of the Ir(III) metal centre. In [Ir(ppy)<sub>2</sub>acac] the S<sub>0</sub>–T<sub>1</sub> and S<sub>0</sub>–T<sub>2</sub> transitions are almost degenerate (482 and 479 nm), reflecting the degeneracy of the phenylpyridine based LUMO/LUMO + 1. The lowest triplet transition involving a sizable amount (ca. 35%) of acac-based LUMO + 3 is calculated at higher energy, 432 nm, reflecting the molecular orbital energies discussed above. In N966 the lowest S<sub>0</sub>–T<sub>n</sub> transitions, related to population of the cyclometallated-based LUMO, LUMO + 1 and acac-based LUMO + 2, are, on the other hand, found at essentially the same energy (440, 433 and 431 nm, respectively); recalling the degeneracy and character of the three N966 LUMOs, our data indicate comparable contributions to the lowest excited states by the cyclometallated and acac ligands. This degeneracy is only partly resolved at the excited state relaxed geometries, for which we still calculate the two lowest excited states to lie within ca. 0.1 eV. This is opposed to the [Ir(ppy)<sub>2</sub>acac] case for which TDDFT calculations performed at the T<sub>1</sub> geometry indicate that the acac-based lowest triplet state is very energetically separated from lowest excited state (0.58 eV).

The proximity of the lowest cyclometallated- and acac-based excited states in N966 is opposed to well characterized ppy-based emission found in [Ir(ppy)<sub>2</sub>acac], suggesting the origin for the broad emission spectrum observed for N966. Vibronic coupling between bright and dark almost degenerate excited states is indeed considered to be a major source of spectral broadening in small to medium size molecules.<sup>11</sup> The room-temperature emission spectra can be fitted with five gaussians, each separated by about 1300 cm<sup>−1</sup>, that is about one vibrational quantum of typical C–C aromatic stretching vibration (Fig. S8, ESI†). These are indeed the geometrical parameters which are mostly varied on going from S<sub>0</sub> to T<sub>1</sub> (Table S1, ESI†) and correspondingly, the modes mainly involved in the vibrational sub-structure of emission spectra in related iridium complexes.<sup>12</sup> We stress here that we have no evidence of dual-emission for N966, rather a single emitting



**Fig. 3** Device: (ITO/PEDOT:PSS/TCTA:N966/TPBI|Ba|Ag, ratio TCTA : N966 = 6 : 4). Inset shows the luminance vs. voltage.

excited state of mixed character seems to be the origin of the broad emission.

To verify the emission spectra of N966 under electronic excitation, a simple, partly solution processed, light emitting diode was fabricated, the emitting layer consisting only of N966 and a hole transporting molecule 4,4',4''-tri(*N*-carbazolyl)-triphenylamine (TCTA) in a 4 : 6 ratio. Due to the presence of the methyl groups on the 2-phenylimidazole ligand, the N966 complex rapidly dissolves in a wide range of commonly used solvents (see ESI†).

The electroluminescence spectrum of the N966-containing OLED, Fig. 3, is very broad with maxima around 570 nm, having a FWHM of 165 nm (FWHM  $\approx 5490 \text{ cm}^{-1}$ ; CIE:  $x = 0.281$ ;  $y = 0.360$ ). It should be noted that TCTA has its electroluminescence maximum around 410 nm<sup>13</sup> and therefore does not contribute to the emission observed in the N966 device. The electroluminescence profile coincides with that observed from the solution emission spectra, indicating their similar origin and it rules out the formation of excimers as the source for the broad emission. The device reaches a luminance value of more than  $1000 \text{ cd m}^{-2}$  at a driving voltage of 9 V and an efficiency of  $1 \text{ cd A}^{-1}$ . Efficient injection and transport of the two carriers is manifested by the low turn-on voltage (3.1 V). *I-V-L* curves of the device are shown in Fig. S10 (ESI†). PLQY of N966 in a PMMA matrix (5 wt%) and in a thin film of the same composition as the emissive layer of the OLED have been measured by means of an integrated sphere, and are 0.07 and 0.05, respectively. Hence the PLQY is increased by one order of magnitude in the solid state (photo- and electroluminescence) compared to that in solution, in accordance with observations recently published for another phosphorescent complex.<sup>14</sup>

In summary, an iridium(III) complex is developed to have degenerate emitting states of mixed character, inducing a very

broad emission perceived as white light upon photoexcitation and electro-excitation. Though the device efficiency is rather low, the preparation of a single component white light-emitting phosphorescent emitter is significant as it demonstrates the large potential that simple single organo-metallic complexes have for the development of white LEDs.

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