

An inconvenient influence of iridium(III) isomer on OLED efficiency†

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The recently reported heteroleptic cyclometallated iridium(III) complex [Ir(2-phenylpyridine)₂(2-carboxy-4-dimethylaminopyridine)] N984 and its isomer N984b have been studied more in detail. While photo- and electrochemical properties are very similar, DFT/TDDFT calculations show that the two isomers have different HOMO orbital characteristics. As a consequence, solution processed OLEDs made using a mixture of N984 and isomer N984b similar to vacuum processed devices show that the isomer has a dramatic detrimental effect on the performances of the device. In addition, commonly used thermogravimetric analysis is not suitable for showing the isomerization process. The isomer could impact performances of vacuum processed OLEDs using heteroleptic cyclometallated iridium(III) complexes as dopant.

Introduction

Organic light emitting devices using phosphorescent emitters are subject of intense research for low energy consumption solid state lighting and display applications.^{1–6} For many years now, cyclometallated iridium(III) complexes are the most utilized phosphorescent emitters due to excellent photophysical properties and the possibility to tune the emitted color over the entire visible spectrum.^{7–11}

Two designs have been mainly used to prepare new cyclometallated iridium(III) phosphorescent emitters. The first design is the tris-homoleptic cyclometallated iridium(III) complex. In this design, the complex has the general formula [Ir(C[∧]N)₃] where C[∧]N is a cyclometallated monoanionic bidentate ligand. With this design, two isomers can be obtained: the facial isomer where each anionic ring is in *trans* position of the neutral ring and the meridional isomer where only one anionic ring is in *trans* position to a neutral ring.¹² The meridional isomer is obtained at lower temperature and can be easily isomerized to the facial isomer at higher temperature or by shining UV light. The facial isomer cannot be isomerized back to the meridional isomer.

The second important design has the general formula [Ir(C[∧]N)₂(L)] where L is again a monoanionic bidentate ligand, but different from the C[∧]N ligand. In addition, it isn't necessarily a C[∧]N type of ligand; O[∧]O (for example acetylacetonate) or

O[∧]N (like picolinate) type of ligands are often used. This design is advantageous because the compounds are obtained using a synthesis with softer conditions. While facial tris-homoleptic complexes are commonly obtained at temperatures higher than 200 °C, heteroleptic complexes can be usually obtained by reacting the chloro-bridged dimer in low boiling solvents like dichloromethane. A second advantage is the increased possibility of tuning the properties of the complex as two different ligand types are accessible for substitution. It is only recently that the thermal isomerization has been shown to happen as well for this class of complexes.¹³

Using those two designs, enormous progress has been made over the last decade leading to devices with very high efficiencies.^{14–16} This is largely due to improved materials purity and photophysical properties. In this respect, sublimation has been the technique of choice for purification and thermogravimetric analysis (TGA) a common characterization tool to assess the thermal stability of the materials in view of preparing vacuum-processed devices.

We recently reported the thermal isomerization of a bis-cyclometallated heteroleptic iridium(III) complex, [Ir(2-phenylpyridine)₂(2-carboxy-4-dimethylaminopyridine)] (N984) leading to the bis-cyclometallated complex N984b (see Table 1 for chemical structures) where the pyridine rings of the cyclometallated ligands are in *cis* position one to each other.¹³ Such isomerization has been reported for heteroleptic complexes during the synthesis.¹⁷ In our case, as this isomerization is happening during the preparation of the device, it has not been possible to prepare vacuum processed devices without having a mixture of isomers as dopant emitter. It therefore looks interesting to examine the impact of the isomer on the performance of the device.

We report here the photo- and electrochemical properties of N984 and N984b as well as DFT/TDDFT calculations performed on the two isomers. Finally we compare two devices, one containing pure N984 (device A) and one containing a mixture of N984 and N984b (device B) as dopant in the emissive layer. Both devices have the same architecture and are solution processed in order to control the amount of isomer. We observed a dramatic and inconvenient effect of the isomer on the device performances.

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Table 1 Photophysical and electrochemical properties of complexes

	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}^a/\text{nm}$	Φ_p^a	$\tau^a/\mu\text{s}$	$\tau_{\text{rad}}^a/\mu\text{s}$	$k_r/10^5\text{ s}^{-1}$	$k_{\text{nr}}/10^5\text{ s}^{-1}$	E_{ox}^b/V	$E_{\text{red}}^b/\text{V}$
N984	274, 334, 398, 428, 448, 480 sh	520	0.70	2.19	3.13	3.2	1.4	0.51	-2.55
N984b	231, 284, 350, 400, 450 sh	520	0.65	2.12	3.36	3.0	1.6	0.53	-2.58

^a In degassed acetonitrile solution at 298 K. ^b In acetonitrile containing TBAPF₆ 0.1 M, potential vs. ferrocene.

Synthesis and characterization

A N984/N984b mixture was obtained by refluxing N984 in glycerol for 24 h under argon, as previously described. After cooling, the crude was precipitated with water and filtered on fritted glass. Silica gel chromatography column was used for partial purification leading to the mixture used for device preparation (*vide infra*). In addition to those two main constituents, the scale of reaction allowed us to identify additional side products present in a small amount. In particular, we could observe the presence of the facial and meridional tris-homoleptic complexes [Ir(ppy)₃]. This shows that, at least in the case of thermal isomerization in solution, complete decoordination of the bidentate phenylpyridine ligand happens, leading to a scrambling of ligands.† This is similar to what has been previously observed in the case of heteroleptic tris-cyclometallated iridium complexes.¹⁸ It could reasonably be expected to happen as well during sublimation, as the formation of meridional tris-homoleptic complexes has been reported during sublimation of the iridium chloro-bridged dimer.¹⁹

Electrochemical and photophysical properties of N984 and N984b are reported in Table 1. The two isomers exhibit almost identical phosphorescent properties. Indeed, they both emit at 520 nm when excited in acetonitrile solution, with similar photoluminescent quantum yield (0.70 for N984 compared to 0.65 for N984b) and a slightly longer radiative lifetime of excited state for N984b (3.36 μs compared to 3.12 μs for N984). Electrochemical data show that N984b is slightly more stable towards reduction and oxidation than N984. Overall, properties of N984 and N984b in solution are very similar. In case of phosphine-based ancillary ligand, differences are more pronounced.¹⁷

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of N984 have been performed under vacuum at 10⁻⁵ mBar in the 30–420 °C temperature range (Fig. 1). The TGA trace shows only one onset at 403.3 °C attributed to the sublimation process as DC exhibits an endothermic process. Just before this endothermic process, a weak exothermic process in the DSC trace could indicate either isomerization or a more severe degradation of the dopant. It is important to note that only the sublimation is observed in TGA, not the isomerization. As a

† One reviewer suggested that the 4-dimethylamino substituent could be the reason why isomerization of N984 is observed. Therefore we attempted the isomerization in solution and under sublimation conditions, of complex Ir(ppy)₂(pic), that is N984 without -NMe₂ group. Both experiments shows new peaks appearing in ¹H NMR which are tentatively attributed to the *cis* isomer. See ESI for more details.†

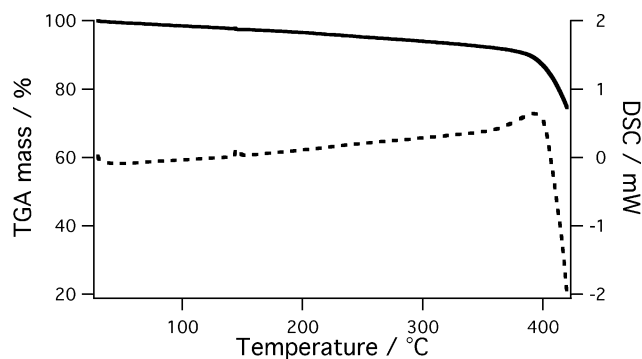
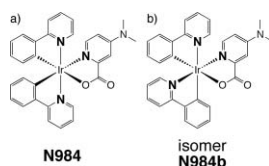


Fig. 1 TGA (solid line) and DSC (dashed line) traces of pure N984.

consequence the dopant could be considered sufficiently stable for vacuum processed devices. Hence TGA is not sufficient to assert the full thermal stability of bis-cyclometallated iridium emitters, since isomerization is a hidden process for TGA.

DFT/TDDFT calculations

To provide insight into the electronic structure and absorption and emission properties of the N984 and N984b complexes, we performed DFT/TDDFT calculations on the two Ir(III) complexes. The frontier molecular orbitals of N984 and N984b are displayed in Fig. 2 (see Fig. S1, ESI for a larger view†).

The N984 highest occupied molecular orbital (HOMO) is an almost isolated orbital composed by a combination of Ir (t_{2g}) d_{xy} and π orbitals on both the phenyl rings of the phenylpyridine ligands, with the HOMO-1 lying more than 0.5 eV below the HOMO. The N984b HOMO is somehow similar to that of N984 complex, albeit lying at slightly lower energy (0.1 eV), but the charge density shared between the metal and the phenylpyridine ligand is localized on a different plane. The HOMO energy downshift calculated for N984b nicely compares with the increased oxidation potential measured for this isomer and is related to the isomeric arrangement of the N and C binding sites of the phenylpyridines. Apart from this HOMO energy shift, the most noticeable difference between N984 and N984b is that in the latter the HOMO is followed within 0.2 eV by two close-lying orbitals, that in N984 are lying at considerably lower energy, see Fig. 2. In both N984 and N984b the lowest unoccupied molecular orbital (LUMO) and LUMO+1 are a couple of almost degenerate orbitals, essentially delocalized on both the phenylpyridine ligands. At higher energy the LUMO+2 and LUMO+3 are delocalized on

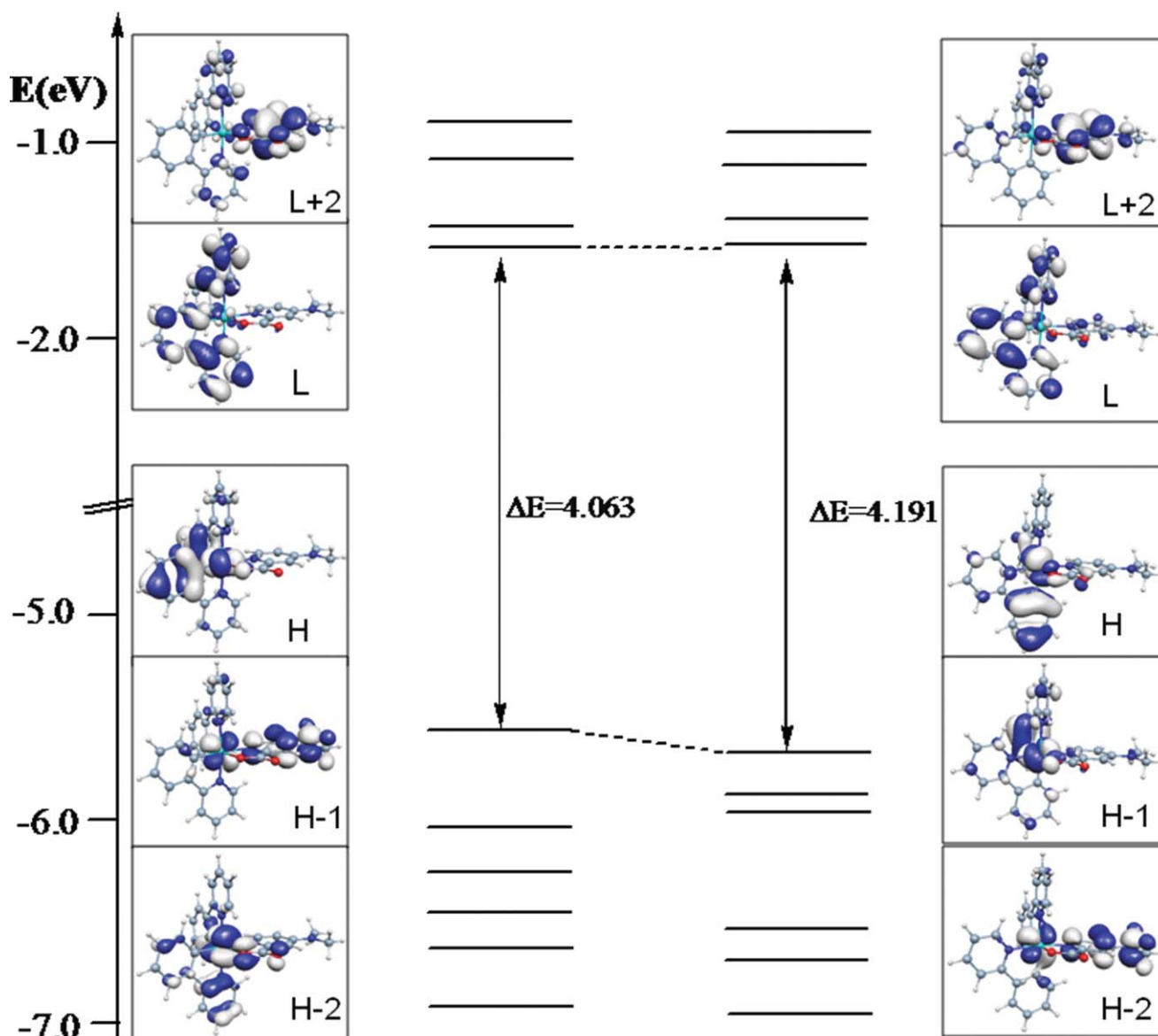


Fig. 2 Frontier molecular orbitals of N984 (left) and N984b (right).

the 2-carboxy-4-dimethylaminopyridine ligand and lie at similar energies for both isomers.

We individuate several differences in the absorption spectra consistent with the experiment. In particular, in the 340–400 nm region N984b shows a stronger absorption, due to a series of medium intensity transitions, which on the other hand show negligible intensity in the N984 absorption spectrum (Fig. S2 and Fig. S3, ESI†). The N984 computed absorption spectrum shows a transition at 400 nm ($f = 0.07$) of HOMO \rightarrow LUMO character assigned to a MLCT transition with a partial π - π^* character, which in N984b is shifted at 387 nm ($f = 0.03$) and involves the HOMO as starting state and the LUMO and LUMO+1 as arriving states.

To characterize the nature of the emitting excited states of both N984 and N984b complexes, TDDFT calculations on the optimized lowest triplet excited state geometries have been performed. The optimized triplet geometries are similar to those

of the ground singlet state for both complexes. The Ir–C/N/O distances and the related angles of the core of both N984 and N984b compounds slightly change going from singlet to triplet geometries increasing (or decreasing) by 0.011–0.048 Å and up to 5°, respectively. The energy and character of the three computed lowest excited singlet and triplet states for both complexes are reported in Table S1, ESI.† The lowest excited state of both N984 and N984b is of $^3\text{MLCT}$ character (T_1), involving a single orbital excitation of HOMO–LUMO character. The T_1 excitation at the triplet geometries are almost identical in the two isomers, 558 nm vs. 561 nm for N984 and N984b, to be compared to the coincident experimental emission values of 520 nm. Thus, the calculated T_1 excitation energies are in good agreement with experimental emission maxima, with deviations of 0.17–0.18 eV, within the accuracy of our computational set-up.

Overall our computational investigation basically confirms the similarity of the optical properties of the two isomers. The most

noticeable difference turns out to be the presence in N984b of a manifold of three HOMOs lying within 0.2 eV, while in N984 the HOMO-1 lies more than 0.5 eV below the HOMO. This observation suggests that N984b might be a better hole transporter than N984, whereby the charge hole would be shared among the manifold of HOMOs in N984b, while it would be trapped in the isolated HOMO, lying at higher energy, in N984 (Fig. S4, ESI†).

Devices

The efficiency of OLEDs is in part dependent on the balanced transportation of electrons and holes as it impacts the charge recombination efficiency. Based on DFT/TDDFT calculation pointing towards both isomers having a difference in charge transporting properties, we anticipate that the presence of the isomer in the emissive layer could impact the performances of the device.

A mixture composed of N984 and N984b (92:8 ratio) has been obtained from column chromatography purification and used in partly solution-processed devices.²⁰ The devices are fabricated by spin coating a chlorobenzene solution containing PVK:PBD:N984/N984b mixture in a ratio of 15.25:4.5:1 on an indium tin oxide (ITO) coated patterned substrate on which a 100 nm thick PEDOT:PSS layer was first deposited to enhance the hole injection and the device stability.²¹ Poly(*N*-vinylcarbazole) (PVK) is used as a polymeric host and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) to improve the electron transporting properties.^{22,23} A 20 nm layer of 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) is thermally evaporated to confine the excitons to the emissive layer and to prevent the loss of holes by recombination at the cathode. Finally a barium cathode protected by an 80 nm silver layer is deposited *via* thermal vacuum deposition. It should be noted that the ratio for the mixture of isomers used as dopant in device B is in the range expected for the ratio of isomers obtained during the preparation of the vacuum-processed device.

Current density and luminance *versus* voltage and efficacy *versus* voltage curves of the devices are depicted in Fig. 3 and 4. High efficacies (41 cd A⁻¹) are obtained for the device employing the pure complex (device A), similar to what was reported previously. The efficacy of the device containing N984b (device B, 10.4 cd A⁻¹) is almost four times lower. This unexpected and dramatic drop in performance is due to a lower luminance and a slightly higher

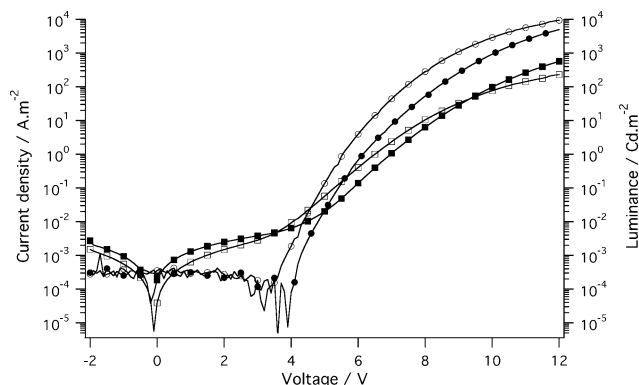


Fig. 3 Current density (squares) and luminance (circles) *versus* applied voltage for device A (open symbol) and device B (solid symbol).

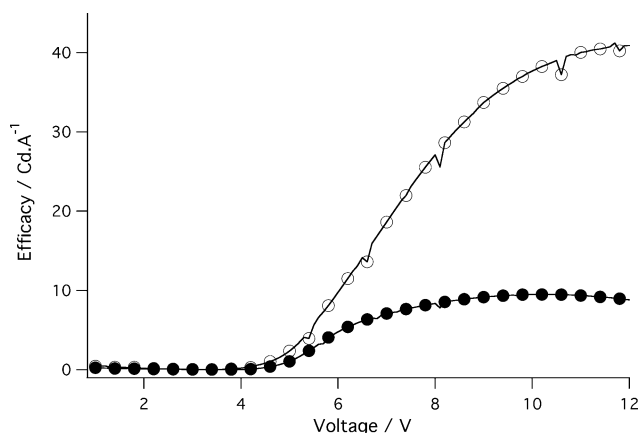


Fig. 4 Efficacy curves *versus* applied voltage for device A (open symbol) and device B (solid symbol).

current density of the device employing the complex containing the isomer. A difference in turn-on voltage can be observed in this device. However, we do not believe it is significant. Indeed, while we could easily reproduce the drop in efficiency in different devices, the turn-on voltage was not. In addition, due to the position of the HOMO and LUMO energy levels of the isomer relative to other constituents of the device, it is not expected to significantly impact the turn-on voltage. The small differences observed are therefore attributed to small differences in morphology at the interfaces.

In the case of the vacuum processed device, the efficiency barely reaches 21 cd A⁻¹,¹³ which is better than solution processed device B containing the isomer, but still much less than the solution processed device A containing only N984 as dopant. While this can be partly attributed to the layer-by-layer architecture of the reported vacuum-processed device, it is expected that the presence of the isomer, which is not possible to avoid due to isomerization occurring during sublimation, would impact the efficiency as it is observed in the solution processed device. In this case, solution processed devices are superior to vacuum-processed devices from an efficiency point of view.

Conclusions

In summary we have shown unambiguously that the presence of isomers in the dopant is strongly detrimental to the performance of the light-emitting device. The reasons are an increase of the current density and a drop of luminance. This is at the moment attributed to the differences in HOMO orbitals between N984 and N984b. Unfortunately, complete studies and clearer explanation are at the moment hampered by the difficulty to obtain reasonable quantities of the pure isomer. The problem with bis-cyclometallated iridium complexes is that thermal isomerization is an intrinsic thermal instability of such family of dopant.^{24,25} When happening during vacuum sublimation, it is not possible to prepare vacuum processed devices without contamination by the isomer. As a result, efficiency of vacuum processed OLED is expected to drop considerably due to contamination by isomer produced *in situ* during the processing of the device. In such cases, a solution processed device is likely to be superior to the vacuum processed one. An important consequence of the reported results is that commonly trusted thermogravimetric analysis is not

sufficient to assess the thermal stability of the dopants as it cannot detect the isomerization of the compound. Finally it can be fairly assumed that some efficiencies reported in the literature of vacuum processed devices using bis-cyclometallated iridium complexes as emitters are lowered due to contamination with the isomer and could be considered as lower limits.

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