

Sublimation Not an Innocent Technique: A Case of Bis-Cyclometalated Iridium Emitter for OLED

Etienne Baranoff,[†] Stéphane Suàrez,[‡] Philippe Bugnon,[‡] Claudia Barolo,^{†,§} Roberto Buscaino,^{†,§} Rosario Scopelliti,[†] Libero Zuppiroli,[‡] Michael Graetzel,[†] and Md. K. Nazeeruddin^{*,†}

Laboratory for Photonics and Interfaces, Laboratoire d'Optoélectronique des Matériaux Moléculaires, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

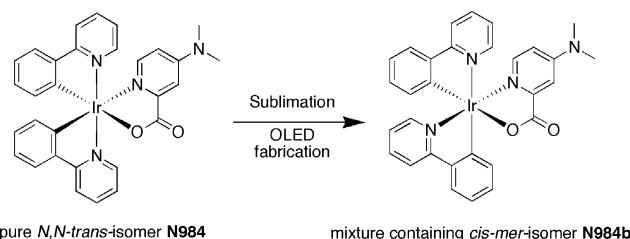
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Isomerization of a neutral bis-cyclometalated iridium(III) complex has been observed for the first time during the preparation of vacuum-processed organic light-emitting devices (OLEDs) and reproduced in solution. Isolation of the isomer revealed a cis organization of the two pyridine rings of the cyclometalating ligands. Photophysical studies show very similar emission properties of the two isomers. However, due to *in situ* isomerization, it is only possible to prepare vacuum-processed OLED devices having a mixture of isomers.

Sublimation and vacuum deposition are common techniques for the purification of compounds and thin-film preparation. They are widely used for organic light-emitting device (OLED) applications where vacuum-processed devices are usually considered as being of much better quality than simpler polymer-based devices due to, for example, the expected better purity of the sublimed emitter.

Cyclometalated iridium(III) complexes are certainly the most utilized phosphorescent emitter.¹ While tris-cyclometalated homoleptic iridium complexes have been often used,² bis-cyclometalated heteroleptic iridium complexes having one bidentate anionic ligand are becoming more and more attractive. Indeed, further tuning the photophysical properties of the complex by modulating the ancillary ligand broadens the possibilities of the design of novel complexes.

As better quality is expected from vacuum-processed devices, it has been the preparation method of choice for



pure *N,N*-trans-isomer **N984** mixture containing *cis*-*mer*-isomer **N984b**

Figure 1. Structure of starting material **N984** and of the resulting isomer after sublimation **N984b**.

OLEDs doped with heteroleptic iridium complexes.³ However, we analyzed by ¹H NMR freshly sublimed heteroleptic iridium complexes during the preparation of vacuum-processed OLEDs and noticed, in every case, independently of the sublimation conditions, the apparition of a new set of signals accounting for roughly 5–15% of the total intensity.

In this communication, we present an analysis showing the formation, during the preparation of the device, of an isomer of the starting complex (Figure 1). A supportive example of isomerization during sublimation, [Ir(2-phenylpyridine)₂(2-carboxy-4-dimethyl amino pyridine)] (**N984**)⁴ is provided along with preliminary photophysical properties of the newly isolated isomers. In every case studied, the complex purified by the vacuum process was less pure than the starting material. In addition, the new **N984b** isomer could be isolated on a pure form and has been characterized by ¹H NMR, mass spectrometry, and finally X-ray crystal

* Author to whom correspondence should be addressed. E-mail: mdkhaja.nazeeruddin@epfl.ch.

[†] Laboratory for Photonics and Interfaces.

[‡] Laboratoire d'Optoélectronique des Matériaux Moléculaires.

[§] Present address: Dipartimento di Chimica Generale e Chimica Organica, Università di Torino, Corso Massimo D'Azeglio, 48, 10125 Torino, Italy.

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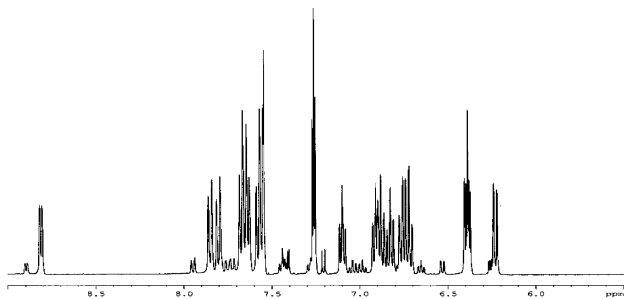


Figure 2. Aromatic part of the ^1H NMR spectrum of sublimed **N984** showing the mixture of products. Small peaks belong to the newly formed isomer.

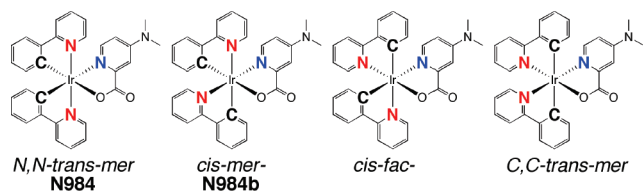


Figure 3. Structure of possible isomers of **N984**. Nitrogen atoms are highlighted for clarity.

structure, showing unambiguously the *cis* orientation of pyridine rings of the cyclometalating ligands, different from the *trans* orientation in the starting complex. A vacuum-processed OLED device has been made using the mixture of isomers.

N984 was synthesized as reported,⁴ and the complex was purified by gradient sublimation. The solid obtained after one sublimation has been characterized by ^1H NMR, which exhibits a new set of signals with integrated peak intensity accounting for about 15% of the total intensity (Figure 2). High-pressure liquid chromatography (HPLC) coupled to mass spectrometry was used to separate and analyze the mixture, showing the main impurity to be an isomer of **N984** (see the Supporting Information). To see if this isomer was coming from the analysis process, the starting **N984** material has been subjected to the same analysis and shows purity higher than 98%. When the main peak was separated and reinjected under the same conditions in the HPLC column, no isomers remained, showing that the complex is stable under the conditions used for the analytical HPLC. Therefore, confirming the presence of the isomer, *cis-mer*-[Ir(2-phenylpyridine)₂(2-carboxy-4-dimethylaminopyridine)] (**N984b**) has to be formed during the sublimation process. All possible isomers are shown in Figure 3. The nomenclature used gives first the relative orientation of the cyclometalating ligands (red nitrogen atoms), which can be either *N,N-trans*, *cis*, or *C,C-trans*-, followed by the relative orientation of the three nitrogen atoms, either meridional or facial (red and blue nitrogen atoms).

Single crystals of **N984** (Supporting Information) and **N984b** (Figure 4) suitable for X-ray diffraction analysis have been obtained. They have been grown separately from a solution containing the pure respective complex. **N984** is a heteroleptic complex with, as expected for such a heteroleptic complex, the two pyridines of the main phenyl-pyridine ligands in *trans* position to each other. In the case of **N984b**, the two pyridines are in the *cis* position to each other,

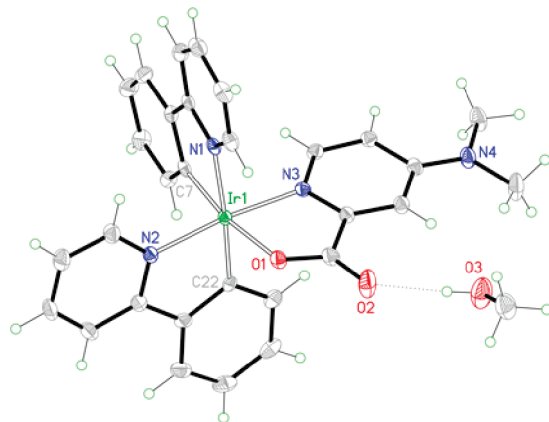


Figure 4. ORTEP drawing of **N984b**.

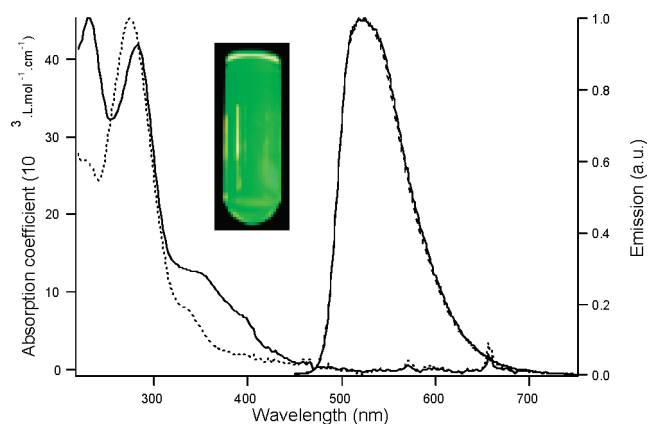


Figure 5. Absorption (left) and emission (right) of **N984** (dotted lines) and **N984b** (full lines) in solution in acetonitrile. The insert shows a photo of the 10^{-5} M **N984b** solution emission exhibiting a very strong green color when excited at 365 nm.

reminiscent of the facial organization of the cyclometalating ligand in tris-homoleptic complexes.⁵ Most remarkable are the lengthening of the distance N(1)–Ir from 2.059 Å in **N984** to 2.121 Å in **N984b** and the shortening of the distance N(3)–Ir from 2.144 Å in **N984** to 2.038 Å in **N984b**. This can be explained by the change of the coordinated *trans* atom: in **N984**, N(1) is *trans* to a nitrogen atom and N(3) is *trans* to a carbon atom, whereas in **N984b**, N(1) is *trans* to a carbon atom and N(3) is *trans* to a nitrogen atom.

Compared to **N984**, UV–vis absorption spectra of **N984b** measured in acetonitrile solution at 298 K display slightly red-shifted bands in the UV (231, 284, 350, and 400 nm) and the visible (at 450 nm) regions due to intraligand (π – π^*) and metal-to-ligand charge transfer transitions (MLCT), respectively (Figure 5). Surprisingly, when excited at 298 K within the π – π^* and MLCT absorption bands, **N984b** shows an identical emission band shape to that of **N984**. On the other hand, the photoluminescence quantum yield has been measured as being slightly lower for **N984b** (0.65 compared to 0.70 for **N984**). Overall, the emission properties of **N984** and **N984b** are nearly identical.

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To reproduce the isomerization process, isomerization in solution has been achieved in refluxing glycerol as reported for the meridional-to-facial isomerization of tris-cyclometalated homoleptic complexes.⁵ However, after 20 h of reaction, only about 40% of the *cis-mer*-isomer **N984b** was obtained. Photochemical isomerization of *dms**o*-*d**6* solution, either using UV light or visible light. This shows the excellent photochemical stability of **N984** (see Supporting Information). Qualitatively, the same results are obtained with **FIrpic** (iridium(III)bis[(4,6-difluoro phenyl)-pyridinato-*N,C*2'] picolinate (see Supporting Information)). This commercially available complex has been widely used and studied for blue-emitting vacuum-processed OLEDs.⁶ These preliminary results show that isomerization during sublimation is indeed thermally induced and that devices made of those compounds are likely to contain mixture of isomers.

Finally, a standard organic light-emitting diode is fabricated by thermal vapor deposition using the **N984–N984b** mixture of isomers in a layer-by-layer architecture as follows: ITO/CuPc/NPB/N984/BCP/Alq3/LiF/Al. CuPc (copper phthalocyanine), NPB (*N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine), Alq3 (Tris(8-hydroxyquinoline) aluminum), and LiF (lithium fluoride) were used as the hole injection layer, hole transporting layer, electron transporting layer, and electron injection layer, respectively. The entire device is 114-nm-thick between the two electrodes. As, in such a structure, holes migrate faster than electrons, the hole-blocking layer BCP was therefore introduced to impose the recombination zone at the **N984**/BCP interface. The electroluminescent spectrum shows a green emission centered at 532 nm with a 73 nm half-bandwidth, showing excellent color purity (see the Supporting Information).

Figure 6 shows the density of current and the luminance characteristics of the OLED device. At 7.5 V, the luminance and the density of current achieve 1700 cd/m² and 120 A/m², respectively, with a turn-on voltage at 3 V. The power conversion efficiency and the external quantum efficiency reach a maximum of 14.4 lm/W at 4.2 V and 6.4% at 5.5 V, respectively. These results show that, in addition to being a very high-performing emitter for polymer-based light emitting diodes,⁴ **N984** is a good candidate for vacuum-processed architectures, even in a nonfavorable layer-by-layer archi-

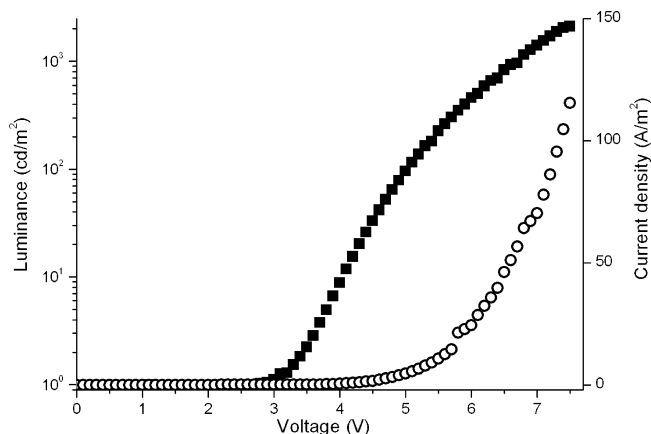


Figure 6. Luminance (solid squares) and current density (open circles) versus applied bias voltage of the **N984**-based OLED device.

ture, despite the presence of an isomer in the emissive layer.

In summary, we have shown that the *N,N*-*trans-mer*-heteroleptic iridium complex isomerizes to an apparently more stable *cis-mer*-isomer. However, contrary to the tris-cyclometalated complexes, the *cis-mer*-isomer exhibits slightly lower emission quantum yields than the *N,N*-*trans-mer*-isomer. More generally speaking, vacuum sublimation is not an innocent technique, as thermal isomerization occurs. It leads to OLED devices made of a mixture of isomers, and polymer-based devices can be considered as using an emitter of better purity. As *fac*- and *mer*-tris-cyclometalated complexes behave differently in OLED devices,⁷ the bis-cyclometalated isomer mixture is likely to have an impact when highperforming OLEDs are studied.

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Supporting Information Available: Experimental procedures, crystal structures tables, NMR spectra, and HPLC chromatograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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