Mer-Ir(ppy)₃ to fac-Ir(ppy)₃ photoisomerization

Daniel Escudero^{*[a]}

Abstract: In this contribution a detailed mechanistic investigation of *mer*-to-*fac* photoisomerization occurring in Ir(ppy)₃ is presented. Facial/meridional stereoisomerism in tris-bidentate Ir(III) complexes strongly determines their photophysical properties and thereto their efficiency and stability within a phosphorescent-based organic light-emitting diodes (PhOLED) device. Double-hybrid density functional theory (DFT) calculations are performed here to identify the photoactive species involved in the photoisomerization reaction and to assess its kinetic and thermodynamic feasibility at room temperature. These investigations highlight the protagonist role of a non-previously described ³MC state bearing one stretched *trans* Ir-N position. Finally, and in view of the computed evidences, phosphor design strategies to prevent photoisomerization are proposed.

Organometallic complexes of Ir(III) and/or Pt(II) are widely used as efficient phosphors for phosphorescent-based organic light-emitting diodes (PhOLEDs). [1,2] To further improve their device operational lifetimes, and especially in the case of blue phosphors, it is crucial to acquire durable and efficient materials that do not suffer intrinsic chemical degradation upon PhOLED operation. [3,4,5,6,7,8] Degradation of PhOLEDs' materials originates from parasitic exciton-polaron and exciton-exciton annihilation processes,[4,7] such as e.g., triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA), which also compromise PhOLEDs efficiency at high brightness levels (i.e., roll-off effect). [9] In recent years, numerous computational[10,11,12] and experimental[13,14,15,16] efforts have been made to decipher the underlying degradation mechanisms, and still many open questions remain. In the case of phosphors, ligand dissociation reactions are the most common degradation routes.[7,16] These reactions lead to the formation of products in an irreversible manner that act as nonradiative recombination sites, charge traps and/or luminescence quenchers. Thus, these final products are ultimately responsible for the significant luminance loss in the aged devices. Evidence shows that the population of higher-lying excited states, and particularly, triplet metal-centered (³MC) excited states,[10,16] strongly enhances these degradation processes. ³MC states are usually highly distorted with respect to the ground state (¹GS) and lowest triplet (¹T₁) excited state geometries,[17] the latter typically being of predominant metal-to-ligand charge transfer character, i.e., ³MLCT. For instance, in cyclometalated Ir(III) complexes, both ¹GS and ¹T₁ exhibit a pseudo-octahedral geometrical disposition while the ³MC state often displays a pentacoordinate trigonal bipyramid arrangement bearing one broken Ir-N bond.[17, 18] Therefore, ligand dissociation is more likely to occur from a ³MC state than from either ¹GS or ¹T₁. As recently disclosed, the excited state potential energy surfaces (PES) of these complexes, but also in the case of e.g., [Ru(bpy)₃]²⁺, [19] might be more complex than originally believed.[20] In many complexes different ³MC states were found to be thermally accessible at room temperature, and hence their population may open up new avenues of

photoreactivity.[19] Besides being relevant for PhOLEDs' degradation, ³MC states also act as very efficient funnels for the radiationless deactivation to the ¹GS, due to the presence of minimum energy crossing points (MECP) between the ¹GS and ³MC PES. [21,22,23] Thus, ³MC states are also responsible for the diminished photoluminescence quantum yields of phosphors at room temperature.[22] Furthermore, ³MC states are also known to play a crucial role on isomerization reactions in both homoleptic and heteroleptic Ir(III) complexes.[24,25,26] These isomerizations reactions might importantly modify the spectral features and efficiencies of PhOLEDs devices,[27] since the stereoisomers (i.e., facial (*fac*-) and meridional (*mer*-) stereoisomers) are known to possess different photophysical properties.[28,29,30] In a nutshell, it appears evident from this discussion that in order to improve PhOLEDs' efficiencies and stabilities, one should devise tailored phosphor design strategies to prevent the population of ³MC states. This is especially true in the case of blue phosphors, because for these complexes their ³MC states usually lie energetically close to T₁[21] Among the most successful strategies devised to date to impede the population of ³MC states, I highlight the use of *N*-heterocyclic carbene (NHC) ligands,[31] and/or the use of more rigid bis(tridentate) architectures.[32,33]

[a] Prof. D. Escudero
Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium
Website : <https://chem.kuleuven.be/en/research/qcpc/cpc/>
E-mail: daniel.escudero@kuleuven.be

Figure 1. Main geometrical parameters at the $^3\text{MC}_1$ (a), $^3\text{MC}_2$ (b), and $^3\text{MC}_3$ (c) minima of *mer*-Ir(ppy)₃. Zenith (left) and frontal (middle) views of the ^3MC optimized geometries.

To date, little attention has been paid to understand the actual mechanisms of the photoisomerization reactions taking place in cyclometalated Ir(III) complexes. In this contribution, a complete and detailed mechanism of the *mer*-to-*fac* photoisomerization occurring in Ir(ppy)₃ (ppy=phenylpyridine),[28] is provided for the first time. Ir(ppy)₃ is the most widely used complex for green emission in PhOLEDs. Most of the investigations focus on the *fac*-isomer, because it corresponds to the thermodynamic isomer. Both thermal and photochemical *mer*-to-*fac* isomerizations are generally observed for Ir(ppy)₃ and more generally for tris(bidentate) Ir(III) complexes.[28] As compared to their *mer*-counterparts, the *fac*-isomers are characterized by significantly larger photoluminescence efficiencies. This trend can be traced back to the larger nonradiative decay rates of the *mer*-isomers.[28] As recently disclosed in a computational investigation, the larger nonradiative rates in *mer*-isomers are due to the presence of several $^3\text{MLCT} \rightarrow ^3\text{MC} \rightarrow ^1\text{GS}$ deactivation pathways characterized by small activation barriers to populate the different ^3MC states.[20] Conversely only one ^3MC state, and generally characterized by larger activation barriers, is found for the *fac*-isomers.[20]

For *mer*-Ir(ppy)₃, which bears two Ir-N bonds in trans position, three different ^3MC states (i.e., $^3\text{MC}_1$, $^3\text{MC}_2$ and $^3\text{MC}_3$) were found (see their most relevant geometric features in Figure 1).[20] $^3\text{MC}_1$ involves the d_{z^2} -like orbital and displays stretched trans Ir-N bond distances (2.45 and 2.55 Å). Conversely, $^3\text{MC}_2$ involves the $d_{x^2-y^2}$ -like orbital. In the latter species, the trans Ir-N bond distances are antisymmetrically enlarged (2.33 and 2.57 Å, see Figure 2b). In both $^3\text{MC}_1$ and $^3\text{MC}_2$, none of the Ir-N bonds is completely cleaved and thus, they display a highly distorted pseudo-octahedral disposition. A more conventional pentacoordinate trigonal bipyramid arrangement was obtained for $^3\text{MC}_3$. Thus, in $^3\text{MC}_3$, a complete rupture of the Ir-N position located trans to the Ir-C bond is observed (3.39 Å, see Figure 1). The energetic profiles of the $^3\text{MLCT} \rightarrow ^3\text{MC}_{1-3} \rightarrow ^1\text{GS}$ deactivation pathways were computed,[20] and in view of the significant activation barriers for the $^3\text{MLCT} \rightarrow ^3\text{MC}_1 \rightarrow ^1\text{GS}$ and $^3\text{MLCT} \rightarrow ^3\text{MC}_2 \rightarrow ^1\text{GS}$ deactivation pathways (17.6 and 16.3 kcal/mol; respectively), it was concluded that these pathways can hardly be populated at room temperature. Conversely, the $^3\text{MLCT} \rightarrow ^3\text{MC}_3 \rightarrow ^1\text{GS}$ pathway, characterized by an activation barrier of ca. 8 kcal/mol, is fully accessible and it is thus responsible for the enhanced nonradiative decay of *mer*-Ir(ppy)₃ as compared to that of *fac*-Ir(ppy)₃. [20] The question that arises now is whether $^3\text{MC}_3$ is also the excited state species responsible for *mer*-to-*fac* photoisomerization. Let us evaluate this in more detail. At the $^3\text{MC}_3$ geometry, the monocoordinated ligand (ligand 1 in Figure 1c) can rotate itself 180° without steric hindrance with respect to the other ligands. However, this rotation only regenerates the *mer*-isomer. The only possibility to produce the *fac*-isomer is through a rotation of ligand 2 at the $^3\text{MC}_3$ geometry. However, ligand 2 is strongly bound to the Ir atom and furthermore its rotation is sterically hindered through the interactions with the other ligands. Other possible ligand rotations starting from the $^3\text{MC}_1$ or $^3\text{MC}_2$ states are disregarded here because these states are not significantly populated at room temperature.[20] In conclusion, none of the so far reported ^3MC states for *mer*-Ir(ppy)₃ seems to have an active role on the *mer*-to-*fac* photoisomerization. Therefore, to shed some light into this reaction, the triplet excited state potential energy surface (PES) of *mer*-Ir(ppy)₃ have been further explored.

Attempts to optimize alternative ^3MC states on the lowest adiabatic triplet PES were successful. Figure 2 displays the main geometrical features at the optimized geometry of the newly found ^3MC state, herein named as $^3\text{MC}_4$. One of the trans Ir-N positions of $^3\text{MC}_4$ is largely stretched (see 2.87 Å in Figure 2), whilst the other trans Ir-N position remains unaffected (2.30 Å). In addition, $^3\text{MC}_4$ reveals strong distortions from the pseudo-octahedral arrangement. Notably, the monocoordinated ligand (ligand 2) tilts ca. 36° from the square plane (see Figure 2), and thus $^3\text{MC}_4$ reaches a pseudo-trigonal bipyramid arrangement. Consequently, at the $^3\text{MC}_4$ state, ligand 2 can in principle rotate 180° itself to generate the *fac*-isomer. Such a process should not strongly be affected by the steric hindrance with the other ligands since $^3\text{MC}_4$ strongly deviates from a pseudo-octahedral arrangement. In order to ascertain the putative role of $^3\text{MC}_4$ on the *mer*-to-*fac* photoisomerization, one needs to i) assess whether $^3\text{MC}_4$ is significantly populated at room temperature and ii) assess the thermodynamical feasibility of the 180° rotation of ligand 2 by mapping the lowest triplet excited state PES starting from $^3\text{MC}_4$. These investigations are presented below.

Figure 2. Main geometrical parameters at the $^3\text{MC}_4$ minimum of *mer*-Ir(ppy)₃. Frontal (left) and diagonal (middle) view of $^3\text{MC}_4$.

Figure 3. PWPB95/6-31G*(ecp-60-mwb for Ir) energetic profile for the $^3\text{MLCT} \rightarrow ^3\text{MC}_4$ reaction pathway. Relevant geometrical parameters at the optimized geometry of ^3TS are highlighted.

First, the transition state connecting both $^3\text{MLCT}$ and $^3\text{MC}_4$ minima was optimized (see main geometrical parameters of the ^3TS in Figure 3). In the ^3TS , the trans Ir-N position is less stretched than at the $^3\text{MC}_4$ (compare 2.76 Å at ^3TS with 2.87 Å at $^3\text{MC}_4$). Its characteristic imaginary mode (31i cm⁻¹) involves the torsion out of the coordination sphere of the pyridyl unit of

ligand 2. Its associated PWPB95 activation barrier (8.9 kcal/mol) is similar to the one obtained for $^3\text{MC}_3$, and thus, the population of the $^3\text{MC}_4$ well is also possible at room temperature. Next, starting from $^3\text{MC}_4$, the triplet excited state PES was mapped along the 180° rotation of ligand 2. As shown in Figure 4, this rotation ultimately yields the $^3\text{MLCT}$ state of the *fac*-isomer. The scan was done along the dihedral φ angle highlighted in Figure 4. Several local minima (I_{1-3}) along this reaction coordinate were optimized imposing fixed values of the dihedral φ angle. In addition, two transition state structures (TS_1 and TS_2) were optimized, but in those cases without imposing any geometrical constraint. TS_1 connects I_2 and I_3 and it determines the activation barrier of the *mer*-to-*fac* photoisomerization, which amounts to 20.4 kcal/mol. Due to the steric hindrance between the three ligands, TS_1 displays a pseudo-square pyramidal arrangement where the φ dihedral angle amounts to 98° . The characteristic imaginary mode ($24i\text{ cm}^{-1}$) involves the torsion of this angle; and thus it further corroborates the role of this stationary point in the photoisomerization reaction. A further twist of the φ dihedral angle leads to I_3 and subsequently to TS_2 . Note that in TS_2 the nitrogen atom of the pyridyl unit of ligand 2 is out of the coordination sphere of the Ir center. Thus, in order to ultimately yield the $^3\text{MLCT}$ state of *fac*-Ir(ppy) $_3$, the pyridyl unit must rotate itself in order that its nitrogen atom faces the Ir center. Indeed, the characteristic imaginary mode of TS_2 ($39i\text{ cm}^{-1}$) involves the torsion of the pyridyl unit of ligand 2. Experimentally, the *mer*-to-*fac* photoisomerization takes place in an irreversible manner for Ir(ppy) $_3$.^[28] The above mechanistic investigations agree well with these experimental evidences. Thus, upon continuous irradiation of *mer*-Ir(ppy) $_3$, the $^3\text{MC}_4$ state is populated because it is thermally accessible from the $^3\text{MLCT}$ state. The $^3\text{MC}_4$ state displays, in contrast with $^3\text{MC}_1$, a stretched trans Ir-N position which is necessary for the photoreaction to take place. Starting from the $^3\text{MC}_4$ state, the *mer*-to-*fac* photoisomerization can then proceed at room temperature because the activation barrier is not extremely large (20.4 kcal/mol). Furthermore, in view of the larger activation barrier obtained for the back reaction, we can explain why the reverse reaction, i.e., *fac*-to-*mer* photoisomerization, does not take place experimentally. In addition, *mer*-to-*fac* isomerization is in practical terms irreversible because both the ^1GS and $^3\text{MLCT}$ states of the *fac*-isomer are deeper in energy than their *mer*-counterparts.

Recently, *mer*-isomers have been proposed to be more interesting than their *fac*-counterparts, especially in the case of NHC-based tris-bidentate Ir(III) complexes.^[31] Thus, if one aims preventing *mer*-to-*fac* photoisomerization, possible design strategies arise from introducing bulky substituents in the aromatic rings, with the final aim of increasing the steric hindrance between the ligands at TS_1 . In the case of Ir(ppy) $_3$ this could be achieved for instance by replacing the ppy ligand for a 6-methyl-2-phenylpyridine or a 2-(3-methylphenyl)pyridine ligand.

In conclusion, a “from first principles” mechanistic investigation of *mer*-to-*fac* photoisomerization occurring in Ir(ppy) $_3$ is presented in this paper. A non-previously described ^3MC state for the *mer*-isomer, i.e., $^3\text{MC}_4$, is the active species in this photoreaction. The thermodynamical feasibility of the reaction at room temperature has been ascertained by mapping the lowest triplet excited state PES along the photoisomerization reaction. In addition, its irreversibility has been demonstrated. In line with a previous study of the author of this paper,^[20] this work highlights the complex nature of the triplet excited state PES of tris(bidentate) Ir(III) complexes involving different ^3MC states. The excited state reactivity arising from these ^3MC states might

also strongly differ, from e.g., playing a protagonist role in the efficient radiationless deactivation to the ground state to foster photoreactivity. Finally, as photoisomerization reactions may strongly influence PhOLEDs’ efficiency and stability,^[16,27] this study provides also phosphor design strategies to prevent photoisomerization reactions in Ir(III) complexes.

Computational Details

All calculations on Ir(ppy) $_3$ are based on density functional theory (DFT). The geometries of all stationary points including local minima and transition states (TS) were optimized using the hybrid functional B3LYP^[34, 35] in combination with the 6 31G* basis set for all atoms. Relativistic effects were taken into account for the Ir atom by using the ECP-60-mwb pseudopotential.^[36] The nature of all stationary points was confirmed by computing the Hessian at the same level of theory. In order to obtain accurate energies, singlet point calculations using the double-hybrid PWPB95 functional^[37] in combination with the def2-SVP basis set (ECP-60-mwb pseudopotential for Ir) were performed. The PWPB95 functional has been shown to outperform other hybrid and other double-hybrid functionals for the kinetics and thermochemistry of 5d transition metal complexes.^[23,38] All the calculations were carried out with the Gaussian16 program package,^[39] except the single point PWPB95 calculations that were performed with the ORCA software.^[40]

Keywords: facial/meridional stereoisomerism • photoisomerization • OLEDs • Ir(III) complexes • computational photochemistry

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Figure 4. PWPB95/6-31G* (ecp-60-mwb for Ir) energetic profile for the *mer*-to-*fac* photoisomerization starting from $^3\text{MC}_4$. Relevant geometrical parameters at the optimized geometries of $^3\text{MC}_4$, I_2 , TS_1 , TS_2 , and $^3\text{MLCT fac-Ir(ppy)}_3$ stationary points are highlighted.