

# Ultrafast charge transfer excited state dynamics in trifluoromethyl-substituted iridium(III) complexes

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Time-resolved spectroscopy was exploited to gain new insights into the nature and dynamics of charge transfer excited states of bis-cyclometalated Ir(III) complexes. We showed that its dynamics is strongly influenced by the nature of the diimine ligand due to the existence of a ligand-ligand charge transfer process in the picosecond timescale. All the results are supported by DFT/TD-DFT calculations and spectroelectrochemistry.

## Introduction

Iridium(III)-based compounds have recently emerged as powerful systems for the design of supramolecular devices relying on photo-induced energy<sup>1, 2</sup> or electron transfer.<sup>3, 4</sup> Especially, cyclometalated Ir(III) complexes have attracted the interest of the scientific community due to their unconventional optoelectronic properties. Due to the unique capacity of Ir(III) to accommodate up to three carbometalated bonds,<sup>5</sup> a wide variety of spectroelectrochemical properties are available, depending on the number of C-Ir bonds present in the resulting complex. Homoleptic complexes of the type Ir(C<sup>^</sup>N)<sub>3</sub> (C<sup>^</sup>N = cyclometalated ligand) have been extensively studied as phosphorescent dopants in organic light-emitting diodes.<sup>6-8</sup> Alternatively, researchers have been interested in replacing a C<sup>^</sup>N ligand by a N<sup>^</sup>N ligand. This modification in the architecture of the complexes allows the development of heteroleptic [Ir(C<sup>^</sup>N)<sub>2</sub>(N<sup>^</sup>N)]<sup>+</sup> compounds. Such bis-cyclometalated Ir(III) complexes are highly interesting for the development of new charged materials used in light-emitting electrochemical cells<sup>9</sup> and as photosensitizers in light-driven hydrogen production.<sup>10</sup> In addition, these Ir(III) complexes have found applications in biological media thanks to their net positive charge. Similarly to their homoleptic counterparts, their absorption, emission and electrochemical behaviour can be easily tuned by choosing the right ligands, making them ideal candidates as biosensors<sup>11</sup>, subcellular markers<sup>12</sup> and photodrugs.<sup>13</sup> Over the last two

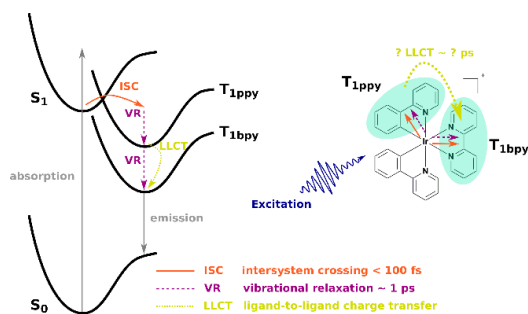
decades, research has been mainly focused on the relationship between the structure and the photophysical properties of Ir(III) complexes.<sup>14-16</sup> Study on the ultrafast dynamics of primary intramolecular light-induced processes in Ir(III) complexes are scarcely reported in the literature, particularly concerning [Ir(C<sup>^</sup>N)<sub>2</sub>(N<sup>^</sup>N)]<sup>+</sup>.<sup>17-21</sup> For the archetypal complex [Ir(ppy)<sub>2</sub>bpy]<sup>+</sup> (ppy = 2-phenylpyridine; bpy = 2,2'-bipyridine), it is generally accepted that the emission occurs from a low-lying triplet state which corresponds to a metal-ligand to ligand charge transfer state (MLLCT), involving the metal and the ppy ligand as electron donor, and the bpy ligand as electron acceptor.<sup>22</sup> Other CT states, higher in energy, are also present, such as MLCT located on the ppy ligand. Upon light excitation, a manifold of singlet CT states are thus populated. Based on time-resolved spectroscopic studies,<sup>17, 18</sup> from this manifold of singlet states, the low lying triplet MLLCT emitting state seems to be reached in several steps. As shown in scheme 1, first a singlet metal-to-ligand charge transfer (MLCT; S<sub>1</sub>) excited state is populated upon direct photoexcitation (or ultrafast internal conversion and relaxation from higher populated <sup>1</sup>MLCT). Then, an intersystem crossing occurs within 100 fs, followed by internal vibrational relaxation to the lowest <sup>3</sup>MLCT in approximately 1 ps. This <sup>3</sup>MLCT state seems to be mainly directed towards the C<sup>^</sup>N ppy ligand. Consequently, an internal conversion to yield the so-called MLLCT excited state, corresponding to the final charge separated state from T<sub>1ppy</sub> to T<sub>1bpy</sub>, must take place. This late event and its associated time constant are unfortunately difficult to evaluate and differ from papers,<sup>17, 18</sup> because of difficulties to distinguish the spectroscopic responses of the two involved ligands. In addition, mixture of different absorption bands from ground and excited state are convolved by different vibrational relaxation that lead to some difficulties to retrieve pure species and their kinetic parameters.

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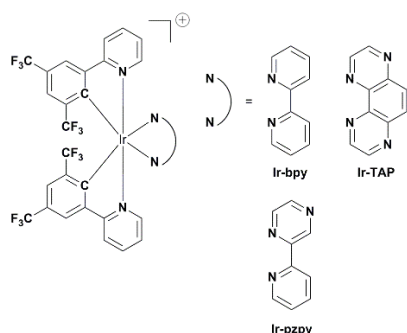
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**Scheme 1.** Schematic and molecular representations of the ultrafast relaxation processes occurring in  $[\text{Ir}(\text{ppy})_2\text{bpy}]^+$ .

In consequence, we have been interested in characterizing this ligand-ligand charge separation process in the picosecond timescale for different bis-cyclometalated Ir(III) complexes. We report in this paper the ultrafast photo-dynamics of three complexes synthesized and reported recently by our group<sup>23</sup>. These compounds are made of two trifluoromethyl-substituted phenylpyridine ( $\text{ppyCF}_3$ ;  $\text{C}^{\wedge}\text{N}$  ligands) and one diimine species, *i.e.* either a bpy, a TAP or a pzpy ligand (TAP = 1,4,5,8-tetraazaphenanthrene; pzpy = 2-(pyridin-2-yl)pyrazine;  $\text{N}^{\wedge}\text{N}$  ligand - Chart 1). As reported in our previous paper<sup>23</sup>, the introduction of the trifluoromethyl-substituted  $\text{C}^{\wedge}\text{N}$  ligand and the use of highly  $\pi$ -deficient ligand such as pzpy and TAP allows to tune the energy gap between the different CT excited states involving either the  $\text{C}^{\wedge}\text{N}$  or the  $\text{N}^{\wedge}\text{N}$  ligands, a parameter expected to play a pivotal role in the kinetics of the LLCT process. By ultrafast transient absorption, we obtained clear-cut evidence that a charge separation occurs in the picosecond timescale. Besides, by changing the nature of the  $\text{N}^{\wedge}\text{N}$  chelating ligand, we investigated the influence of the electron withdrawing ability and the symmetry of this ligand on the complete excited state dynamics of the resulting Ir(III) complexes. All the results are supported by spectroelectrochemistry measurements and DFT/TD-DFT calculations.



**Chart 1.** Structure of the bis-cyclometalated Ir(III) complexes investigated in this study.

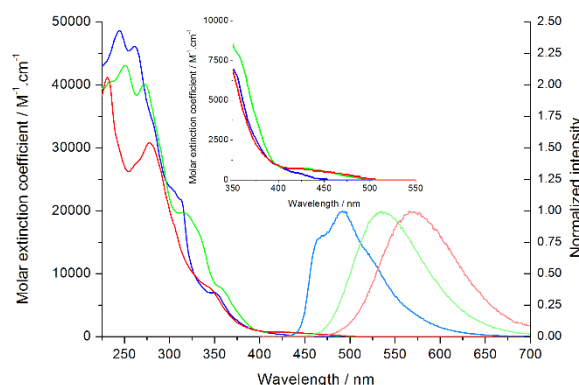
## Results and discussion

The three heteroleptic Ir(III) complexes, namely **Ir-bpy**, **Ir-TAP** and **Ir-pzpy** (Chart 1), have been synthesized and purified as previously described.<sup>23</sup> There were unambiguously characterized by  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR spectroscopy and high-resolution mass spectrometry (HRMS) (ESI).

**Table 1.** Emission data in MeCN and  $\text{H}_2\text{O}$  at 298 K under air for **Ir-bpy**, **Ir-TAP** and **Ir-pzpy**.

| Complex        | $\lambda_{\text{max}} / \text{nm}$ |                      | $\tau / \text{ns}$ |                      | $\Phi_{\text{Argon}}$<br>MeCN <sup>1</sup> | $k_{\text{r}} / 10^3 \text{ s}^{-1}$ |
|----------------|------------------------------------|----------------------|--------------------|----------------------|--------------------------------------------|--------------------------------------|
|                | MeCN                               | $\text{H}_2\text{O}$ | MeCN               | $\text{H}_2\text{O}$ |                                            |                                      |
| <b>Ir-bpy</b>  | 493                                | 496                  | 665                | 1217                 | 0.108                                      | 50.4                                 |
| <b>Ir-TAP</b>  | 574                                | 608                  | 795                | 56                   | 0.154                                      | 137.4                                |
| <b>Ir-pzpy</b> | 539                                | 565                  | 1036               | 297                  | 0.133                                      | 87.9                                 |

<sup>1</sup>Relative to quinine ( $\Phi = 0.546$  in 0.5 M  $\text{H}_2\text{SO}_4$  in  $\text{H}_2\text{O}$ ,  $\lambda_{\text{ex}} = 366 \text{ nm}$ , 298 K)<sup>25</sup>.

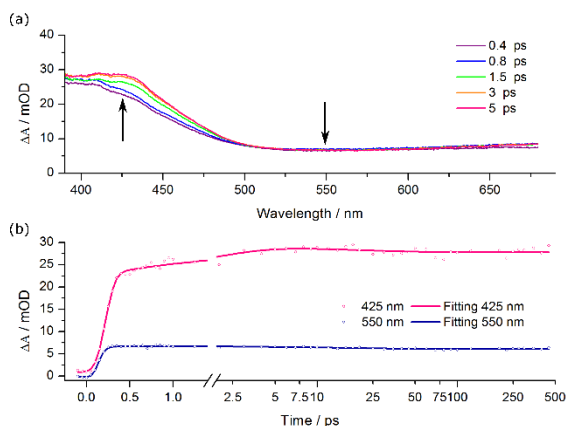


**Figure 1.** Steady-state absorption spectra and emission spectra of **Ir-bpy** (blue), **Ir-pzpy** (green) and **Ir-TAP** (red) in MeCN at room temperature. Inset: enlarged absorption spectra for the 350-550 nm region.

Their absorption spectra in MeCN at room temperature (Fig. 1) are similar and exhibit strong absorption bands in the UV attributed to ligand centered (LC) transitions. Bands of lower energy ( $\lambda > 340 \text{ nm}$ ) are assigned to charge transfer (CT) transitions. They usually correspond to mixed ligand to ligand, metal-ligand to ligand and metal to ligand charge transfer transitions. They involve the metal and the  $\text{C}^{\wedge}\text{N}$   $\text{ppyCF}_3$  ligand as the electron donor and the  $\text{N}^{\wedge}\text{N}$  diimine ligand as the electron acceptor. Bands from 340 to 400 nm are attributed to spin-allowed CT transitions whereas the weak absorption features above 400 nm arises from spin-forbidden CT transitions resulting from the iridium-induced spin-orbit coupling.<sup>24</sup> Upon excitation at 380 nm, the wavelength of the excitation source used for ultrafast studies, a set of  $^1\text{CT}$  excited state are thus populated.

In agreement with a MLLCT emissive state, the luminescence of the three complexes is strongly influenced by (i) the solvent and (ii) the nature of  $\text{N}^{\wedge}\text{N}$  chelating ligand (Table 1 and Fig. 1). For each additional heteroaromatic nitrogen, the maximum of the emission spectrum in MeCN is red-shifted by *ca.* 40 nm. Water induces strong modifications on their emissive properties, *i.e.* (i) a bathochromic shift of their emission, (ii) a strong decrease of the emission lifetime for complexes with at least one non-chelating nitrogen. All these results confirm that the lowest-energy state is a charge transfer state involving the  $\text{N}^{\wedge}\text{N}$  ligand as electron acceptor.

To gain further insight into the formation and the evolution of this charge separated state, picosecond time-resolved absorption measurements were performed in MeCN upon 380 nm femtosecond-laser pulses ( $\approx 100 \text{ fs}$ ) at the magic angle.



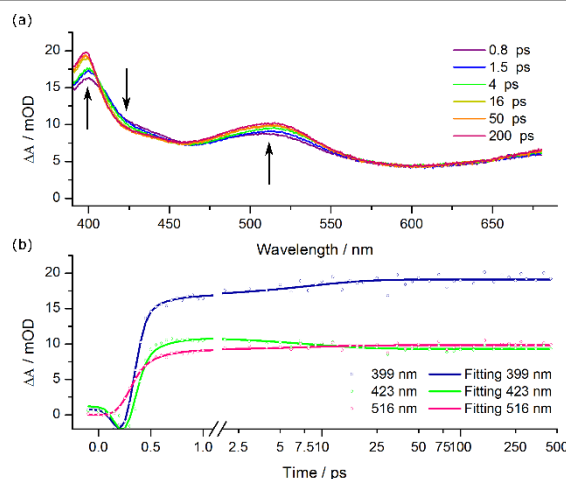
**Figure 2.** (a) Ultrafast transient absorption spectra of **Ir-bpy** in MeCN upon excitation at 380 nm. (b) Transient signals of **Ir-bpy** at 425 (red) and 550 nm (blue). The points correspond to experimental data. The lines represent the fitting with a mono-exponential model (550 nm)  $\tau = 16$  ps and a double-exponential model (425 nm)  $\tau_1 = 1.2$  ps and  $\tau_2 = 16$  ps.

Immediately after laser photoexcitation, **Ir-bpy** is characterized by a strong excited state absorption on the whole visible range corresponding to the population of triplet MLCT states (Fig. 2a). Indeed, in agreement with the literature<sup>18, 21</sup>, ISC occurs in a few tens of femtosecond and cannot be discerned with our experimental setup. We can mention that the features of the transient spectra are similar to those observed in spectroelectrochemistry and assigned to  $\text{bpy}^{\cdot-}$  (ESI). Regarding the evolution of TA signals over time, we can distinguish two distinct steps. After 0.4 ps, the TA band below 500 nm continues to increase until 5 ps, whereas absorption bands above 500 nm start to decay until 100 ps (Fig. 2a and 2b). We can thus expect that the ISC generates a set of triplet excited states, which decay to a “relaxed”  $^3\text{MLCT}$  state in less than 5 ps. A precise time constant for this relaxation step is tedious to obtain, as it is affected by a second slower step, clearly noticeable at wavelengths higher than 500 nm. This later step was adjusted to a 16 ps time constant by fitting the transient signal at 550 nm, giving us the opportunity to fit the transient signal at 425 nm with a double-exponential model. The two components found, *i.e.*  $\tau_1 = 1.2$  ps and  $\tau_2 = 16$  ps, are very similar to those previously found by Tschierlei *et al.*<sup>17</sup> for  $[\text{Ir}(\text{ppy})_2\text{bpy}]^+$ . Therefore, it is likely that the short and longer time constants correspond to vibrational cooling from vibrationally hot excited states and subsequent ligand to ligand charge transfer from  $\text{ppyCF}_3$  to  $\text{bpy}$ . Nevertheless, as previously discussed for  $[\text{Ir}(\text{ppy})_2\text{bpy}]^+$ , this assignment can be ambiguous due to similar transient spectroscopic responses of both C<sup>^</sup>N and N<sup>^</sup>N ligands. Indeed, TD-DFT calculations, performed for **Ir-bpy**, show that the triplet charge transfer states involving these ligands are extremely close in energy (within 0.1 eV, ESI).

To overcome this problem, the  $\text{bpy}$  ligand was replaced by a TAP ligand. The resulting **Ir-TAP** complex exhibits a strong excited state absorption from 390 to 700 nm directly after laser excitation (Fig. 3a). In the picosecond timescale, three bands that evolve differently can be pointed out at 399, 423 and 516 nm. The signal at 423 nm decreases whereas both signals at 399 and 516 nm show a rise of the transient absorption (Fig. 3a and

3b), giving rise to the appearance of two isosbestic points, which is in agreement of the existence of at least two coexisting transient species in equilibrium. This hypothesis is also confirmed by the negative and positive contributions of the three bands obtained by global decay analysis, in the decay associated spectra (ESI).

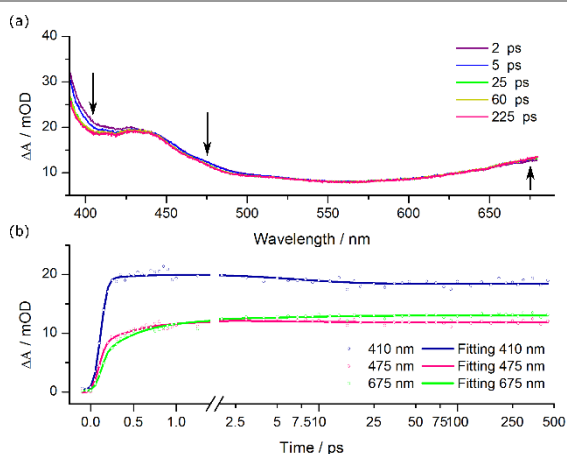
The global fitting with a two-exponential decay function (Fig. 3b) yields two time constants,  $\tau_1 = 0.20$  ps and  $\tau_2 = 8.2$  ps, which are within the same order of magnitude as those found for **Ir-bpy**. In a similar fashion, the fast component is believed to be associated to vibrational relaxation of the vibrationally hot excited states. However, there is no doubt that  $\tau_2$  is related to a transfer of population between two excited states with different spectroscopic responses. Their nature has been investigated by TD-DFT (ESI). Bands below 405 nm and above 455 nm are assigned to triplet states involving a LUMO localized on the N<sup>^</sup>N TAP ligand whereas transitions in between are characterized by a LUMO localized on the C<sup>^</sup>N  $\text{ppyCF}_3$  ligand. As a consequence, the population transfer occurring within the picosecond timescale coincides with a LLCT transition from  $\text{ppyCF}_3$  to TAP ligand. This assignment has been confirmed by spectroelectrochemistry. Indeed, the reduction of the complex, which is centred on the TAP ligand, induces the appearance of absorption bands at *ca.* 400 nm and *ca.* 530 nm (ESI).



**Figure 3.** (a) Ultrafast transient absorption spectra of **Ir-TAP** in MeCN upon excitation at 380 nm. (b) Transient signals of **Ir-TAP** at 400 (blue), 423 (green) and 516 nm (red). The points correspond to experimental data. The lines represent the fitting with a double-exponential model  $\tau_1 = 0.2$  ps and  $\tau_2 = 8.2$  ps.

To gain further insights into the influence of the N<sup>^</sup>N ligand on the ultrafast excited states dynamics, time-resolved spectroscopy has been also performed on **Ir-pzpy**. This complex shows broad excited state absorption in the visible range (Fig. 4). Once again, the global decay analysis yields two time constants,  $\tau_1 = 0.44$  ps and  $\tau_2 = 7.5$  ps. The second one corresponds to decreasing signals below 475 nm and increasing at *ca.* 675 nm (Fig. 4a and 4b). Computational investigation (ESI) seems to support a population transfer between a  $\text{ppyCF}_3$  and a  $\text{pzpy}$  state. Unfortunately, due to the asymmetry of **Ir-pzpy**, the accuracy of the energy calculated for each triplet transition is limited. However, the successive charge transfers from  $\text{ppyCF}_3$  to the pyridine part of the  $\text{pzpy}$  ligand and finally

delocalisation over the whole pzpy ligand cannot be excluded, based on the nature of the calculated LUMO and LUMO+1 (ESI). Therefore, spectroelectrochemical measurements have been carried out. Upon reduction process centered on the N<sup>^</sup>N pzpy ligand, the complex displays absorption below 500 nm and near infrared bands extending down to 600 nm (ESI). This observation provides clear-cut evidence that the signal obtained at 675 nm in transient absorption can be assigned to the N<sup>^</sup>N pzpy ligand, which clearly confirms the LLCT transition between the C<sup>^</sup>N ppyCF<sub>3</sub> and the N<sup>^</sup>N pzpy ligands.



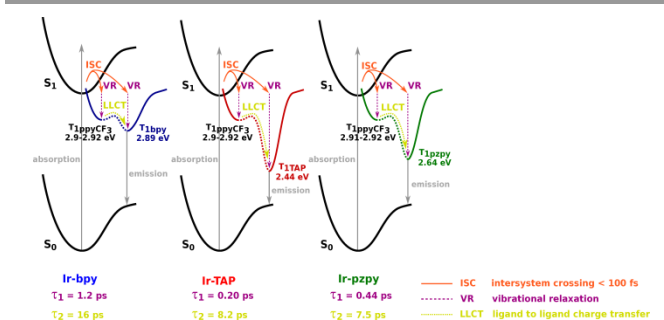
**Figure 4.** (a) Ultrafast transient absorption spectra of **Ir-pzpy** in MeCN upon excitation at 380 nm. (b) Transient signals of **Ir-pzpy** at 410 (blue), 475 (red) and 675 nm (green). The points correspond to experimental data. The lines represent the fitting with a double-exponential model  $\tau_1 = 0.44$  ps and  $\tau_2 = 7.5$  ps.

To sum up, the ultrafast relaxation dynamics of bis-cyclometalated Ir(III) complexes occurs in a few steps. The population of a <sup>1</sup>MLCT excited state is immediately followed by a very fast intersystem crossing (< 100 fs) and vibrational relaxation to a <sup>3</sup>MLCT state involving at least the C<sup>^</sup>N ppyCF<sub>3</sub> ligand as electron acceptor. Finally, a LLCT transition takes place from ppyCF<sub>3</sub> towards the N<sup>^</sup>N ligand. Even if the excited state dynamics are similar for each complex, the kinetic rate constants of the deactivation processes are influenced by the nature of both C<sup>^</sup>N and N<sup>^</sup>N ligands (Table 2). Kinetic rate constants obtained for our complexes are within the same order of magnitude than those reported for [Ir(ppy)<sub>2</sub>bpy]<sup>+</sup>.<sup>17</sup> However, **Ir-bpy**, which bears the same N<sup>^</sup>N ligand, exhibits a longer  $\tau_1$  due to the CF<sub>3</sub> electron-withdrawing groups of the ppy ligands. This result confirms that the first step involved in the excited state deactivation implies this C<sup>^</sup>N ligand. Comparison of our complexes shows that  $\tau_1$  also decreases with the  $\pi$ -acceptor character of the N<sup>^</sup>N ligand, revealing that the first step of the relaxation dynamics is altered by the nature of the diimine ligand (Table 2). As shown on scheme 2, both last results suggest that the vibrational relaxation occurring in the first step leads to a double-potential well involving T<sub>1C<sup>^</sup>N</sub> and T<sub>1N<sup>^</sup>N</sub> respectively, as previously proposed by Cho *et al.*<sup>19</sup> It is also worth mentioning that the second kinetic rate constant, corresponding to the LLCT transition, is influenced by the N<sup>^</sup>N ligand (Table 2). Indeed, for a N<sup>^</sup>N bpy ligand,  $\tau_2$  is approximatively equal to 16 ps (Table 2) but, for **Ir-TAP** and **Ir-**

**pzpy**,  $\tau_2$  is two times faster (8 ps). The increased  $\pi$ -acceptor ability of the TAP or pzpy actually facilitates the final delocalization of the excited electron over the N<sup>^</sup>N ligand to yield the lowest-energy excited state, which in turn relaxes to the ground state in the nano-microsecond time regime.

**Table 2.** Associated kinetic time constants from the global decay analysis with a two-exponential model for the transient spectra of **Ir-bpy**, **Ir-TAP** and **Ir-pzpy** in MeCN upon excitation at 380 nm.

| Complex                                    | $\tau_1$ / ps | $\tau_2$ / ps |
|--------------------------------------------|---------------|---------------|
| [Ir(ppy) <sub>2</sub> bpy] <sup>+</sup> 17 | 0.7           | 16            |
| <b>Ir-bpy</b>                              | 1.2           | 16            |
| <b>Ir-TAP</b>                              | 0.20          | 8.2           |
| <b>Ir-pzpy</b>                             | 0.44          | 7.5           |



**Scheme 2.** Schematic representation of the ultrafast processes occurring in **Ir-bpy**, **Ir-TAP** and **Ir-pzpy** based on time-resolved spectroscopy and computational calculations.

## Conclusions

Through a combination of experimental and theoretical approaches, we studied the ultrafast excited state relaxation dynamics of three bis-cyclometalated Ir(III) complexes recently published by our group<sup>23</sup>. We showed that their lowest-energy excited state, which arises from a metal-ligand to ligand charge transfer, is obtained in three kinetics steps within a few dozen picoseconds after photoexcitation. By time-resolved transient absorption spectroscopy, we showed that the ultrafast intersystem crossing process, leading to a triplet excited state, is followed by vibrational relaxation and, finally, a charge transfer process. Thanks to computational calculations and spectroelectrochemical experiments, we attributed this late process to a ligand to ligand charge transfer from the trifluoromethyl-substituted phenylpyridine towards the N<sup>^</sup>N ligand. Finally, we established that the kinetic constants associated to the whole relaxation process are dependent on the nature of the ligands chelated onto the iridium(III) center. Increasing the  $\pi$ -acceptor ability of the N<sup>^</sup>N diimine ligand induces faster excited state interconversion decays. Therefore, thanks to different ligand substitution, we were able to unambiguously determine the excited state interplay followed for the deactivation pathway.

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## Conflicts of interest

There are no conflicts of interest to declare.

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