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Remarkable impact of the *fac/mer* isomerism and its geometrical control on the excited states lifetimes of pyridyl-carbene Fe(II) complexes

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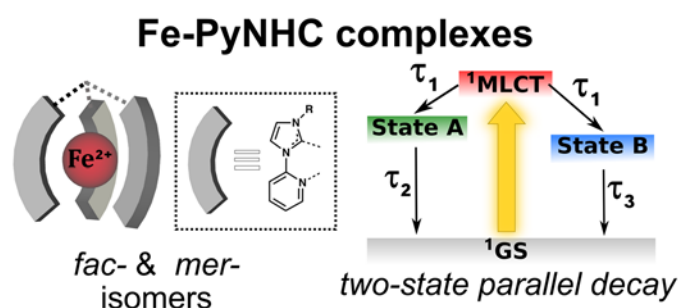
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ABSTRACT

The control of photophysical properties of iron complexes and especially of their excited states decay is a great challenge in the search for sustainable alternatives to noble metals in photochemical applications. Herein we report the synthesis and investigations of the photophysics of *mer* and *fac* iron complexes bearing bidentate pyridyl-NHC ligands,

coordinating the Fe with three ligand-field enhancing carbene bonds. Ultrafast transient absorption spectroscopy reveals two distinct excited state populations for both *mer* and *fac* forms, ascribed to the populations of the T1 and the T2 states, respectively, which decay to the ground state via parallel pathways. We find 3-4 ps and 15-20 ps excited state lifetimes, with respective amplitudes depending on the isomer. The longer lifetime exceeds the one reported for tridentate-liganded complex analogue with four carbene bonds. By combining experimental and computational results, a mechanism based on the differential trapping of the triplet states in spin-crossover regions is proposed for the first time to explain the impact of the *fac/mer* isomerism on the overall excited-state lifetimes. Our results clearly highlight the impact of bidentate Pyridyl-NHC ligands on the photophysics of iron complexes, especially the paramount role of *fac/mer* isomerism in modulating the overall decay process, which can be potentially exploited in the design of new Fe(II)-based photoactive compound.

TOC GRAPHIC



KEYWORDS. *fac/mer* isomerism, iron complexes, NHC, photophysics, TD-DFT, Minimum Energy Path, decay process

INTRODUCTION

The replacement of platinumoids (Pt, Ru, Ir) by other more accessible metals in photoactive systems constitutes a great scientific and technological challenge. This accomplishment is crucial for the development of cheaper and more eco-friendly light-driven devices such as organic light-emitting diodes (OLEDs)¹ or dye-sensitized solar cells (DSSCs).² As a matter of fact, in the DSSCs field, ruthenium complexes have dominated the scene and boosted the technological development thanks to their optimal electrochemical and photophysical properties, such as an efficient coverage of the solar spectrum and a fast electron transfer via long-lived metal-to-ligand charge transfer (MLCT) excited states.^{3,4} However, the low abundance, high price and non-negligible toxicity of ruthenium definitely represent a major limit in view of large-scale technological applications. Thus, the quest for sustainable alternatives has pushed the scientific community to develop analogous iron-based compounds, the latter being a cheaper, more abundant and less toxic element, as it was pioneered by Ferrere two decades ago.^{5,6}

Nevertheless, the population of low-energy metal-centered (MC) states in typical iron polyimine complexes leads to the ultra-fast deactivation of the MLCT states initially accessed upon light excitation of the complex and as a consequence to the loss of the suitable photophysical properties.^{7,8}

Hence, the development of iron-based optically active devices will necessarily imply the synthesis and production of systems presenting long-lived MLCT states. In turn, this task is a veritable scientific challenge and necessitates to achieve a thorough understanding of the fine photophysical process dictating the MLCT deactivation and most importantly the non-trivial coupling between electronic and vibrational effects. In this respect, the fine comprehension of the fundamental factors tuning the excited state relaxation and of their subtle interplay is fundamental.

Considerable success in increasing the excited-state lifetime of organometallic iron complexes has been achieved in the very last years thanks to the use of *N*-heterocyclic carbenes (NHC) as ligands. Indeed, the combined strong σ -donating and weak-to-moderate π -accepting character of NHC induces a higher splitting of the iron d orbitals, resulting in a destabilisation of the MC states over the MLCT manifold and consequently a hampering of the deactivation pathways. For instance, the use of tridentate pyridyldicarbene ligands allowed achieving a remarkable $^3\text{MLCT}$ lifetime of 9 ps for complex **C0** (Fig. 1).⁹ Confirming the subtle interplay between different structural and chemical effects, our group also showed¹⁰ that the presence of a carboxylic group on the central pyridyl ring is non-innocent and almost doubled the $^3\text{MLCT}$ lifetime up to 16.5 ps.¹¹ Switching from imidazolylidenes to benzimidazolylidenes moieties in the chromophoric ligand further increased the excited state lifetime, attaining a record lifetime of 26 ps.¹² This experimental observation has also been rationalized by molecular modelling revealing, for the first time, an inversion of the MLCT/MC energy levels for an iron complex. In addition, the inclusion of carboxylic group allowed the sensitization of TiO_2 surface and the production of the first working DSSC device based on iron NHC, although with a low efficiency of light-to-electricity conversion.^{11,13}

An alternative strategy to increase the ligand-field splitting, and hence the MLCT lifetime, is to employ ligands that reduce the angular strain around the metal centre upon coordination.^{14,15,16,17,18,19} This effect is invoked to justify the different photophysical behaviour of the angularly strained $[\text{Ru}(\text{tpy})_2]^{2+}$ complex (tpy = 2,2':6',2''-terpyridine) that experiences an ultra-fast non-radiative via MC states population,²⁰ and the weakly distorted bidentate homologue $[\text{Ru}(\text{bpy})_2]^{2+}$ (bpy = 2,2'-bipyridine)²¹ that is instead strongly luminescent at room temperature since the deactivation channels are not

accessible.²² As a consequence, the selection of tridentate or bidentate coordinating ligands can have a deep impact on the photophysical properties of the final complex.

However, the photophysical phenomena taking place in transition metal complexes are extremely complicated also due to the high density of excited states and their high coupling. Therefore, many different relaxation channels may compete, and a simple rationalization based on very intuitive concepts, such as the ligand-field splitting, although useful, does not allow to catch all the subtle details of the processes. More elaborate modelling strategies, involving the full exploration of the potential energy surfaces (PESs) of the involved states are needed to complete the picture.

Recently, and as a way to influence the angular strain, we have reported the first example of bidentate-liganded iron complexes containing pyridylcarbene ligands **C1**.²³ The asymmetric nature of the employed ligand led to different geometrical isomers. In fact, **C1** was obtained as a mixture of mostly the meridional (*mer*) isomer with a concomitant fraction of the facial (*fac*) isomer in a 14:1 ratio. A thorough molecular modelling of the different singlet, triplet and quintet excited states PES involved in the photoresponse evidenced totally different landscapes for the two isomers. In particular, the low-lying triplet PES of the *mer* isomer, leading to the MC population and deactivation, was found to be much steeper than the one of the corresponding *fac* isomer.²³ This aspect is intimately linked to the larger stabilization of the ³MC state in the *mer* arrangement as compared to the *fac* one. Altogether, our molecular modelling results indicate a much faster deactivation for the *mer* isomer.

This result represented, to the best of our knowledge, the first hypothesis on the possibility of tuning and controlling the excited states life-time by the effects of *fac/mer* isomerism. As such, it also represents a fundamental aspect of the inherent photophysics

of organometallic compounds that should be precisely investigated and whose implication can go far beyond the production of photoactive iron complexes.

However, the two isomers could not be separated, hence precluding the possibility to perform time-resolved spectroscopy to obtain the two separate life-times. To overcome this problem, we propose a different strategy based on the precise control of the geometrical arrangement of the ligands to selectively obtain only one of the two isomers. This leads to the synthesis of a new C_3 -symmetric hemicage ligand **L2** based on bidentate pyridine-imidazolylidene moieties, subsequently used to prepare the corresponding pure *fac* iron(II) complex **C2** (Fig. 1).

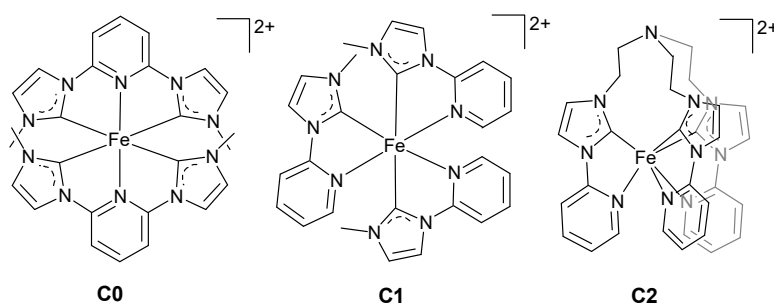


Figure 1. Complexes studied in this work. In all cases, counter ion is PF_6^- .

In this contribution we report the full characterization of both **C1** and **C2** including molecular modelling and time-resolved spectroscopy, thereby allowing for the quantification and the rationalisation of the *fac/mer* isomerism on the properties of these iron-based compounds. Most importantly, while globally confirming the difference in relaxation times of the two isomers, we also show how this effect is due to a quite complex interplay between two decay pathways that are, in turn, affected differentially by the PES topologies.

This work represents the first direct observation of different decay characteristic times in *fac* and *mer* isomers of iron compounds. As such, it opens the way to a novel strategy

that can be synthetically pursued to achieve the precise tuning of important photophysical properties of materials.

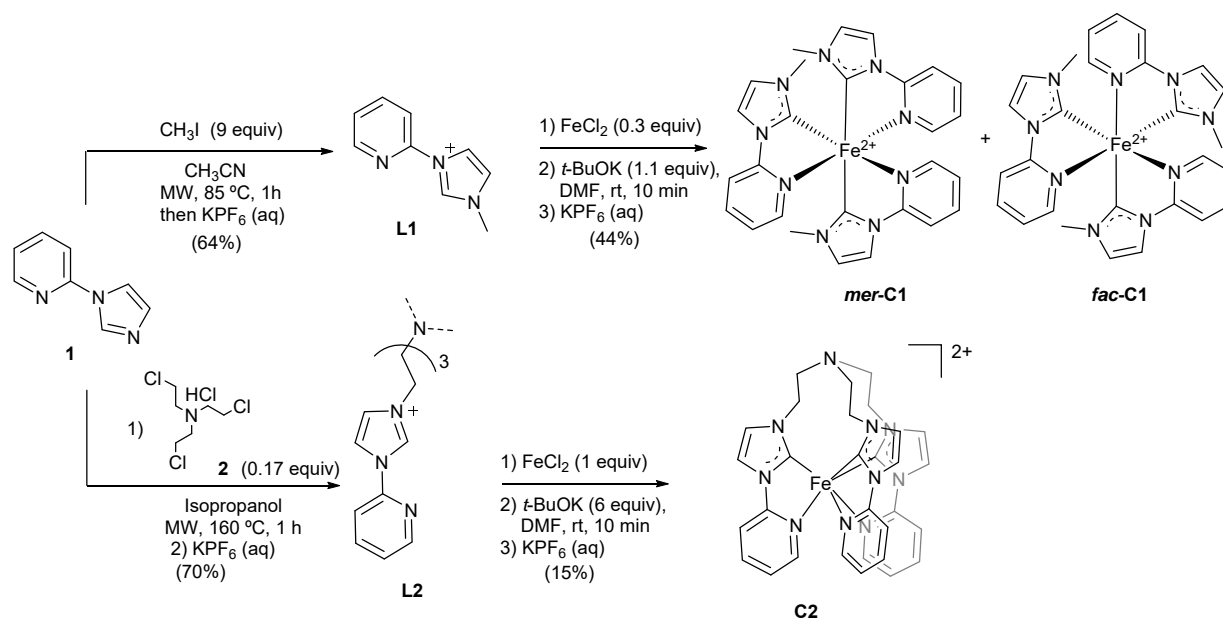
RESULTS AND DISCUSSION

Synthesis and characterization

The preparation of pyridylimidazolium salts precursors **L1** and **L2** was achieved by reacting 2-(1*H*-imidazol-1-yl)pyridine **1** with the appropriate haloalkane. In the case of **L1**, the quaternisation reaction was performed with methyl iodide in acetonitrile at 85°C (Scheme 1).^{24,25} As for **L2**, tris(2-chloroethyl)amine **2** was selected as the alkylating agent. Temperatures as high as 150 °C and isopropanol as solvent were required to attain the triple-fold substitution. It is noteworthy to mention the dramatic effect of the microwave heating in both substitution reactions, which were performed in only 1h while similar reactions performed under classical thermal conditions have been previously reported to last up to 7 days.²⁶

The target complexes **C1** and **C2** were obtained following a recently reported protocol by our group. Upon *in situ* generation of the carbene species by deprotonation of the pyridylimidazolium salts in the presence of *t*-BuOK, the resulting ligand is then coordinated to iron *via* FeCl₂ metal precursor in DMF (Scheme 1). It should be noted the importance of adding the base at the end in order to reduce possible detrimental side-reactions, *e.g.* carbene degradation or iron precipitation.^{26,27} In the case of tripodal ligand **L2**, the protocol required more diluted conditions in order to reduce the formation of oligomeric side-products. Successful coordination was confirmed in both cases by analysing the variation of the chemical shifts in ¹H-NMR spectra. As expected, the pro-carbenic proton was absent in the final complexes. Moreover, the coordination of the three pyridine rings in **C2** was nicely confirmed by the noticeable shift change of the

alpha pyridine hydrogens, excluding a possible coordination of the central amine moiety (See Fig. S1).



Scheme 1. Overall synthesis of pro-carbene ligands **L1** and **L2**, together with final iron(II) complexes **C1** and **C2**. Counterion is PF_6 for all charged compounds.

As aforementioned, **C1** was obtained as a non-separable mixture of *mer* and *fac* isomers in a 14:1 ratio. This remarkably high ratio might be attributed to the steric requirements of the ligand, that would particularly disfavour a facial arrangement, along with the employed reaction conditions.^{28,28,29} Nevertheless, the identification and characterisation of both isomers was carried out unambiguously by NMR analysis due to their differences in signal intensity and pattern. Concerning **C2**, the three bidentate units are magnetically equivalent, which correlates well with the inherent C_3 symmetry of the complex. It is worth noting that the constrained geometry causes the four hydrogens of the ethylene units to be non-equivalent. Despite all our attempts, we were unsuccessful in growing quality crystals suitable for diffraction XRay analysis so we have resorted to high-level molecular modelling to get the molecular structures of **C0**, **C1** and **C2**. The ground

state equilibrium geometry of the tridentate and bidentate compounds has been obtained by molecular modelling (Fig. 2) and the details are reported (Table S2).

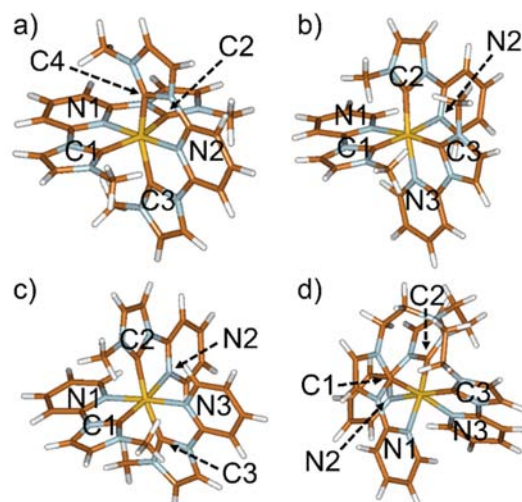


Figure 2. Atom labelling and ground-state equilibrium geometries for a) **C0**, b) *fac*-**C1**, c) *mer*-**C1** and d) **C2**. The optimization procedures have been conducted with very tight convergence thresholds

C0 with the tridentate ligand has shorter distances between the iron atom and the coordinating nitrogen atoms and slightly longer Fe-C distance. On the other hand, the impact on the angular strain measured via the N-Fe-C bite angles appears marginal, **C0** having smaller bite angles (less than 2°). Most importantly the geometry of **C2** is globally equivalent to the one of the *fac*-**C1** isomer.

The redox properties of both complexes were analyzed using cyclic voltammetry, and full results are provided in SI (Table S1). In comparison with the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ oxidation potential of the tridentate complex **C0** (0.71 V), less positive values were obtained for **C1** (0.65 V) and **C2** (0.61 V). These latter values were much lower compared with $[\text{Fe}(\text{bpy})_3]^{2+}$ (1.05 V/SCE) confirming the induction of important ligand-field effects.

The complexes were also characterized by UV-vis spectroscopy (Fig. 3 and Table S1). For all the systems, the absorption spectrum, shows three bands in the 200-700 nm

region. Usually, the intense bands near 250-300 nm can be assigned to intraligand (IL) [$\pi \rightarrow \pi^*$] transitions. In the lower energy region, the two less intense, broader bands are attributed to MLCT transitions as previously reported for **C0**,⁹ **C1**,²³ and other related Fe(II) complexes. The band in the 450-500 nm area is clearly blue shifted by 30 nm for **C1** and **C2** compared with **C0**.

The optical properties have also been modelled by TD-DFT allowing also to characterize the nature of the electronic excited states. Figure S11 displays the calculated UV-Vis spectrum of **C2**, which shows an intense band centred at $\lambda \sim 443$ nm, in reasonably good agreement with the experimental recordings (see Fig. 3). Note that the small red shift of **C2** with respect to **C1** observed in the experimental band maxima (see Fig. 3) is also captured by our theoretical protocol, since the convoluted spectrum of the 1:14 *fac/mer*-**C1** mixture has an absorption band peaking at ~ 415 nm.²³

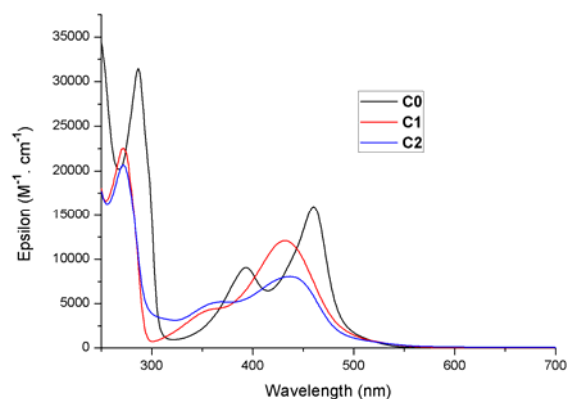


Figure 3. UV-Vis spectra of **C0**, **C1** and **C2** in air-equilibrated CH₃CN solution

This is indeed confirmed by the analysis of the excited states topology (Fig. S12). Interestingly, **C2** has additional electronic transitions from the nitrogen atom of the ‘bridge’ amino group to the π^* orbitals of the pyridyl-carbene ligands (n_{NL}). The excitation energies lie in the 350 – 450 nm range, although the associated oscillator

strengths are small as compared to the MLCT transitions (see Fig. S13). However, certain MLCT/ $\pi\pi^*$ mixing, also enhanced by the symmetry breaking induced by the tertiary amine ‘bridge’, might be responsible for the absorption intensity loss displayed by **C2** in that region, with respect to the more efficient absorption of **C1**.

Excited-state computational studies

As already stated, important differences in the excited states PES landscapes have been found between *fac* and *mer* isomers.²³ Hence, it is necessary to prove that the **C2** complex represents a good model for a pure *fac*-FeNHC complex and does not alter this energetic landscape.

The PESs and the associated geometrical distortions that drive the **C2** decay to the ground state have been modelled using DFT and TD-DFT methods. Given the ultrafast population of the triplet manifold determined for this compounds and other Fe(II) derivatives in the literature,^{8,18,30,31,32,33} it is thus expected that the triplet states can be accessed already at the Franck-Condon or S_1 ($^1\text{MLCT}$) equilibrium geometry, taking also into account the structural similarity of both geometries (see Table S3), as it is also analysed in our previous report.²³

Fig. 4 tracks the low-lying singlet, triplet and quintet states along the key structures involved in the decay process, namely the S_0 min, S_1 ($^1\text{MLCT}$) min, T_1 (^3MC) min and Q_1 min geometries. As in the case of *fac*-**C1**,²³ the triplet PESs of **C2** evolve adiabatically from MLCT to MC nature as the system approaches to the T_1 (^3MC) min structure. The natural transition orbitals (NTOs) isosurfaces for the lowest-lying singlet and triplet states are shown in Figure S14. Coherently with what observed for *fac*-**C1** and *mer*-**C1**,²³ the main coordinate driving the process is the enlargement of the Fe-N1 bond, which has a bond distance of 2.82 Å at the T_1 (^3MC) min geometry (Fig. 4a). Further Fe-

N1 stretching is required to reach the T₁-S₀ singlet-triplet crossing (STC) at 3.05 Å (Fig. 4b).

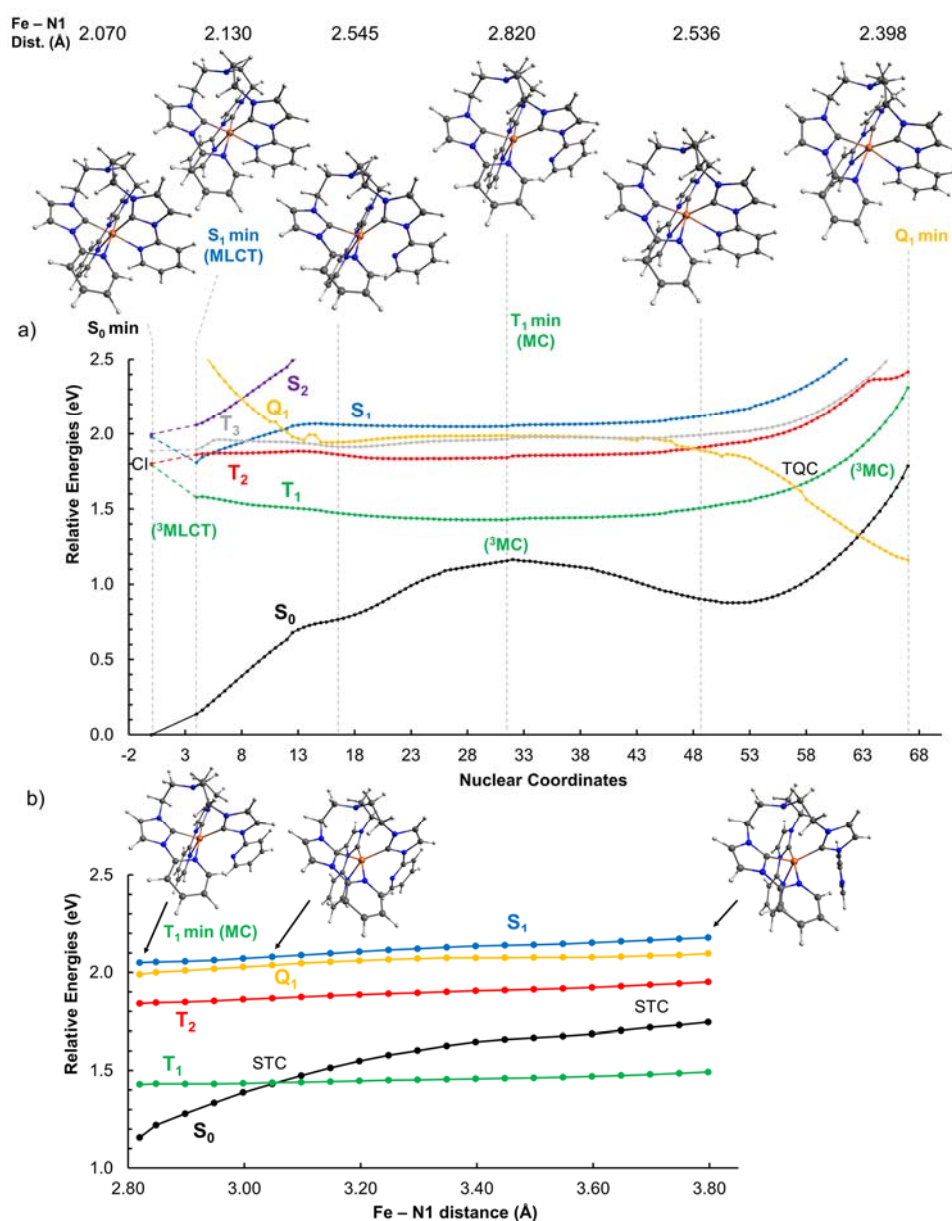


Figure 4. a) Photochemical landscape of C2. Arbitrary nuclear coordinate values are used to label the structures obtained along the decay path. The nuclear coordinates 0, 4.0, 31.5 and 67.0 correspond to the S₀ min, S₁ min (¹MLCT), T₁ min (³MC) and Q₁ min, respectively. T₁ and T₂ energies at the T₂ min (³MC) structure (nuclear coordinates = 24.5) are also shown. b) Energies of the most relevant states mapped upon Fe-N1 bond stretching by means of relaxed scan calculations on the T₁ surface starting from the T₁ min (³MC) geometry of C2. All energies are relative to the S₀ minimum. STC = singlet-triplet crossing, TQC = triplet-quintet crossing.

On the other hand, the T₂-S₀ STC area is achieved at larger Fe-N1 elongations. It shall be noted that the Fe-N1 enlargement has a small impact on the triplet PESs but greatly destabilizes the ground state, giving rise to relatively planar triplet surfaces and unveiling the absence of significant energy barriers throughout the decay process.

Interestingly, the T₁ (³MC) min geometry lies at a relative energy of 1.43 eV, similar to the 1.35 eV determined for *fac*-C1 and higher in energy with respect to *mer*-C1 (1.13 eV).²³

It can also be readily seen that the T₁-Q₁ triplet-quintet crossing (TQC) is less accessible from the T₁ (³MC) min structure as compared to the S₀-T₁ STC, since an energy barrier has to be surmounted in order to populate the quintet state, whereas the access to the S₀-T₁ STC is barrierless. Therefore, we may conclude that the PES landscape of C2 can be considered globally equivalent to the one of *fac*-C1 and is significantly different from the one of the *mer* isomer.

Femtosecond transient absorption spectroscopy

In order to understand the photophysics of C1 and C2, their solutions in ACN are studied using transient absorption spectroscopy (TAS), under excitation with ≈50 fs pulses at 400 nm. In Fig. 5A, some relevant spectra at different time delays are reported for the *fac*-only C2. The negative signal is the ground state bleach (GSB), i.e this band mirrors the depletion of the population of the ground state induced by the pump.

Such signal is broad, from 300 up to 475 nm, but two main peaks are detected at 427 nm and another, less intense and narrow, at 364 nm. The first one, at 0.3 ps overlaps with the inverse Steady State Absorption SSA, (blue dash- dot line) in the region 410-450 nm, while outside of this interval, a broad positive signal, due to excited state absorption (ESA), reduces the negative intensity. Indeed, the smaller GSB amplitude as compared

to the SSA for $\lambda < 380$ nm (25% reduction at 0.3 ps) is due to a hidden ESA for these wavelengths. ESA appears as a dominant positive signal for $\lambda > 475$ nm and even 460 nm for longer delay times (> 5 ps). This band is broad, extending from 475 to beyond 650 nm at 0.3 ps, narrows down and blue-shifts for longer delay times.

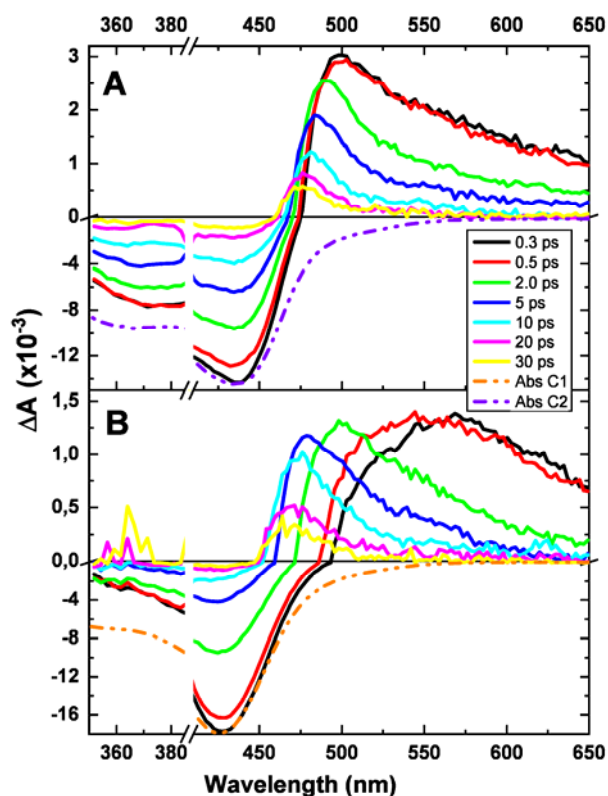


Figure 5. Transient absorption spectra at relevant time of (A) *fac*-only **C2** and (B) **C1** *fac/mer* 1/14 in CH₃CN after excitation at 400 nm. Data at 390-415 nm are not shown (pump laser scattering). Dash-dotted lines are the respective inverted and scaled ground state absorption spectra. Note the different scales for positive and negative signals.

This is highlighted when the ΔA spectra are normalized at the ESA peak (Fig. S19). Spectral evolution stops only after 20 ps, when a ≈ 50 nm narrow spectrum with a maximum at 475 nm remains. Note that these ΔA spectra are significantly different from the ones we reported for tridentate-liganded complexes of NHC-Fe(II).^{10,11,12} Here, the extinction coefficients of the ESA transitions are 4, or even ≈ 10 (cf. **C1** below), times

smaller than for the $S_0 \rightarrow {}^1\text{MLCT}$ transitions dominating the GSB, while for the tridentate-liganded complexes, the ratio is not larger than 3. In addition, tridentate-liganded complexes display additional positive ESA bands below 450 nm, which are not observed, or probably hidden in the GSB signal for C1 and C2, here.

The result of the continuous spectral shifts and narrowing is a strong wavelength dependence of the kinetic traces in the ESA region (Fig. 5A, and S20, S21).

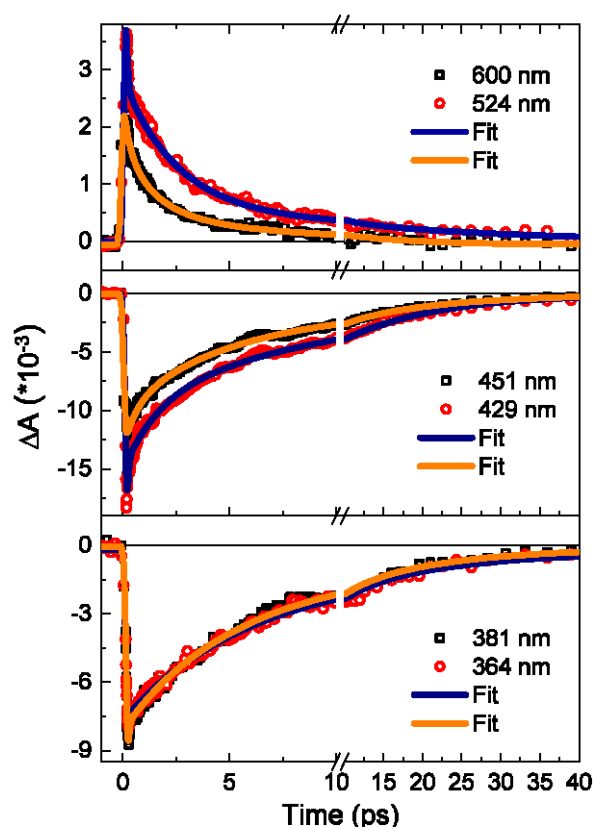
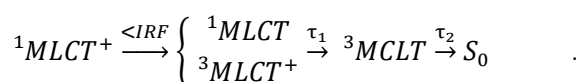


Figure 6. Kinetic traces (dots) and relative fits (line) of C2 in different wavelength regions: ESA in the top panel, main GSB in the centre and short wavelength GSB in the bottom.

Kinetic traces at >550 nm decay faster than for shorter wavelengths, due to the presence of a sub-picosecond component. A detailed inspection of the kinetic traces on a semi-log scale (Fig. S20) allows to identify three characteristic wavelength-dependent lifetimes describing all the kinetic traces and spectral evolution. They are clearly distinct, and the three slopes of the semi-log traces allow to estimate their values: $\tau_1 = 0.2\text{-}0.5$ ps,

$\tau_2 = 3\text{-}4\text{ ps}$, $\tau_3 = 15\text{-}20\text{ ps}$. These are the used for and refined by single wavelength fits as explained in SI. The agreement between the fitted curves and the experimental data is very good as highlighted in Fig. 6, and remaining residuals are due to the noise level (pump intensity fluctuations).

While τ_1 is attributed to electronic relaxation from the optically excited $^1\text{MLCT}$ state and subsequent vibrational relaxation, the occurrence of two distinct excited state lifetimes is unusual for NHC-Fe(II) complexes. Indeed, previous reports agreed in the description of a sequential relaxation process attributing one single ps lifetime τ_2 to the population of the $^3\text{MLCT}$ state (Fig. 7A):



In the present case, for **C2** containing only the *fac* isomer, the question arises, whether τ_2 reflects an internal conversion between two excited state A and B, the latter decaying in a second stage with τ_3 (Fig. 7B), or whether states A and B decay in parallel with these two lifetimes (FigC).

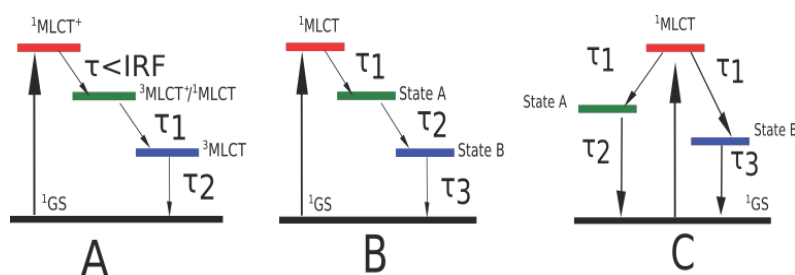


Figure 7. Excited state relaxation schemes in the presence of a single dominant ps excited state (A), or for the co-existence of 2 states labelled A and B (schemes B and C), as found for the bidentate-liganded **C1** and **C2** here.

A partial answer comes from an inspection of the time-resolved ΔA spectra. Indeed, τ_3 is associated with the long-lived quasi-static narrow ESA component dominating the spectra for $t \geq 10\text{ ps}$, characterising state B (Fig. 5). In Fig. S19B, we display the results of a subtraction approach that removes the smoothed and normalized $\Delta A^*(t=15.0\text{ ps})$

spectrum from the normalized ΔA^* at earlier times (the ‘*’ denotes normalisation to the max. ESA signal). To a good degree of approximation, one may consider these double difference spectra $\Delta(\Delta A^*(t)) = \Delta A^*(t) - \Delta A^*(t=15.0 \text{ ps})$, as the time-dependent spectra of the earlier time populations, associated with τ_1 ($^1\text{MLCT}$) and τ_2 (state A). For delays $t > 0.5 \text{ ps}$, the ESA part of $\Delta(\Delta A^*(t))$, representative of state A, is much broader than the ESA of state B. It displays only a slight dynamic blue-shift, so that a quasi-isobestic point appears at 485 nm, for $t > 1.6 \text{ ps}$, with the GSB part of $\Delta(\Delta A^*(t))$.

In Fig. 8, we summarize the results of the 3-exp. fits (see SI for details) performed for 20 single wavelengths.

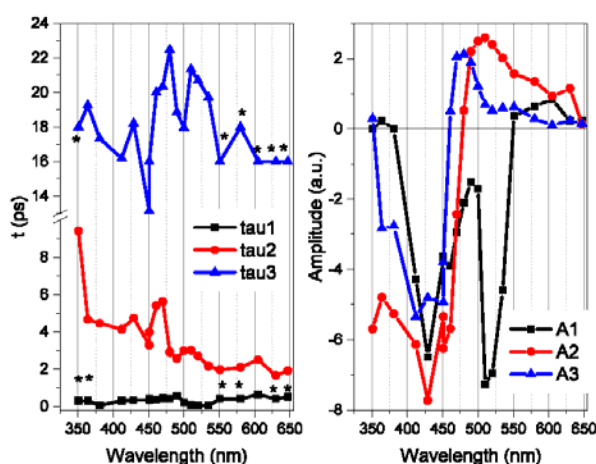


Figure 8. Results of single wavelength 3-exp. fits of C2. Left: Decay times vs wavelength. Right: Decay time associated amplitudes vs wavelength. Values are from table S4. ‘*’ denote lifetime values kept fixed for fit convergence.

As anticipated above, at longer wavelengths ($>550 \text{ nm}$) the ESA band is dominated by the amplitudes of τ_1 ($^1\text{MLCT}$) and τ_2 (state A), A1 and A2, while A3 (state B) is negligible. τ_1 has an average value of $0.4 \pm 0.1 \text{ ps}$. It appears both in the ESA and GSB decay and is related to intersystem crossing from the $^1\text{MLCT}$ state and subsequent intramolecular vibrational cooling in states A and B. As such it appears as a rise time for the

ESA in the 500-540 nm range ($A_1 < 0$). In the bleach region ($\lambda < 450$ nm), τ_2 and τ_3 are only slightly wavelength dependent with average values of 4 ± 1 ps and 18 ± 3 ps, respectively, while τ_2 effectively decreases down to ≈ 2.0 ps for the longest ESA wavelengths. In Table S4 all the parameters are reported, together with details for the fit procedure, used for meaningful convergence of the fits. The A_3 amplitude associated with τ_3 , agrees with the 15 ps spectrum of Fig. S19B. In the range 440-600 nm, it has a positive amplitude, while below it is always negative (GSB). This decay associated amplitude spectrum demonstrates that the decay of state B leads to filling of the ground state (GS), in agreement with schemes A and B of Fig. A2, the amplitude of τ_2 agrees with the evolution described in Figs. S19: The spectral shape of A_2 is consistent with the long-wavelength ESA component revealed after subtraction of the 15 ps spectrum (Fig. S19B). Most importantly, A_2 has a significant amplitude (30-40% larger than a_3) throughout the entire GSB region.

The spectral shape of A_2 allows us to discriminate between the parallel and sequential excited state relaxation schemes (Fig. 7, A and B). In the sequential scheme, the population moves from state A to state B without any ground state bleach recovery. The 4 ps component should thus appear as a rise time (neg. A_2) for the ESA of B in the 450-500 nm range. This is partly true since A_2 is negative for $\lambda < 470$ nm, but not for the wavelengths of maximum ESA of state B (470-490nm). Hence, a clear indication of state A giving rise to population of state B is lacking. More importantly is the observation of the GSB recovery occurring dominantly with τ_2 for $\lambda < 470$ nm. This is in contradiction to the sequential relaxation scheme, but fully in agreement with the parallel one. Indeed, both the decays of the population of A and B lead to ground state recovery.

As far as **C1** is concerned, even though this complex contains only 6.7% of the *fac* isomer, the transient absorption data show, at first sight, a high resemblance with those of **C2** (Fig. 5B). The main differences are in the smaller ratio of ESA to GSB amplitude, which is 1:10, and in a more drastic evolution (dynamic shift and spectral narrowing) of the ESA in the early 2-5 ps. The ESA and GSB kinetics are significantly faster than for **C2**, as can be seen from Fig. 9, and from Figs. S24 and S26. Like **C2**, a detailed visual inspection of the kinetic traces in semi-log scales reveals three distinct lifetimes (Fig. S24): $\tau_1 = 0.2\text{-}0.5$ ps, $\tau_2 = 2\text{-}3$ ps, $\tau_3 = 15\text{-}20$ ps. Note that τ_2 is shorter for **C1** than for **C2**. A comparison of kinetic traces obtained for the 1:14 and a 1:8 mixture of *fac/mer* shows that they are identical (Fig. S25 and related discussion), which indicates that the contribution of the *fac* isomers is negligible in the mixtures. We will therefore attribute the following excited state dynamics to *mer* isomers only.

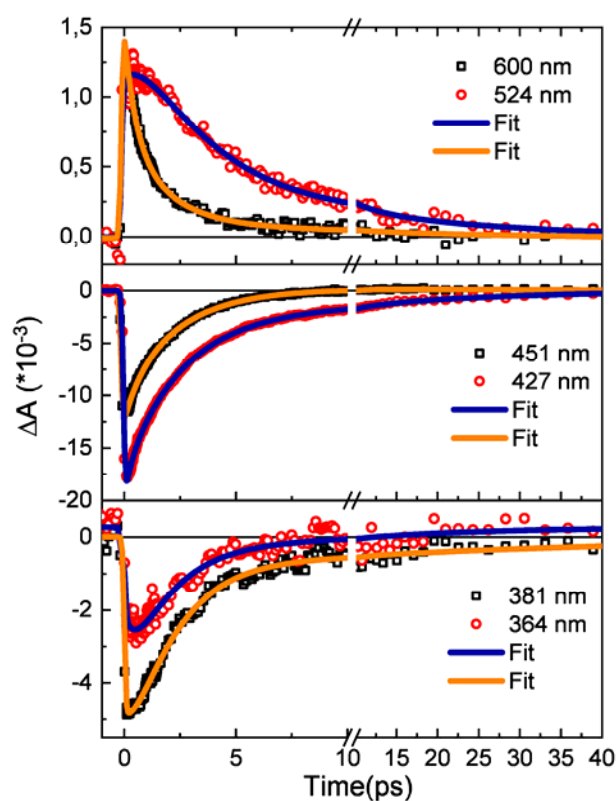


Figure 9. Kinetic traces (dots) and relative fits (line) of **C1** in different wavelength regions: ESA in the top panel, main GSB in the centre and short wavelength GSB in the bottom.

A similar analysis of the normalised time-resolved spectra, as performed for **C2**, allows to identify two distinct ESA bands and thus excited state populations, corresponding to lifetimes τ_2 and τ_3 (Fig. S23). As suggested by Fig.5B, the short wavelength ESA associated with τ_2 is blue-shifting and decaying on that same timescale, leading to strongly wavelength dependent ESA kinetics and values for τ_2 , as can be readily seen from visual inspection (Fig. 9 top, Fig. S24 bottom). Global fitting is therefore not an option. Fig. S26 and S27 present the results of the 3-exp. fits carried out for individual wavelengths, and a detailed discussion is in the SI. Most importantly, the τ_2 component associated with the short-lived long-wavelength ESA, characterising state A in Fig. 7, is the dominating channel for ground state recovery (Fig. S27). Also, the decay of state B (lifetime τ_3 and amplitude A_3), leads directly back into the ground state, since the latter is observed in the GSB recovery times, very clearly for (410-450 nm), where the signal-to-noise ratio is sufficiently large. We therefore conclude, that, as for **C2**, the parallel relaxation scheme of two distinct excited state populations (Fig. 7C) also applies for **C1**. If one wants to characterize the excited state lifetime by an average of the two populations, the experiments demonstrate that *mer* isomers have, in average, a 3-4 times shorter excited state lifetime than *fac*. It turns out that the faster overall decay of ESA and GSB of **C1** with respect to **C2** is mainly due to a larger relative amplitude for τ_2 , and its shorter value (2.0-2.5 ps). Fig. S23 shows that, in the GSB region, the ratio of A_2/A_3 is $\approx 7:1$, while for **C2**, this ratio is $\approx 4:3$, on average. Other differences are in the smaller ESA amplitude and slightly red-shifted ESA spectra for *mer* with respect to *fac*.

Overall interpretation of the excited-state decay

With the computational results of the excited state manifold in mind, the first obvious question concerns the assignment of states A and B and their location in the excited state

landscape (Fig. 4). We can unambiguously rule out that the metal-centered quintet 5T_2 participates in the relaxation scheme since the latter is characterised by a sharp (10-15 nm broad) excited state absorption in the 340-360 nm range for tridentate ligands.^{10,12} No sign of such an ESA is indicated by the ΔA spectra (Fig. 5). Furthermore, the calculated PES for both isomers of **C1** and **C2** consistently rule out the possible population of the quintet state due to its high energy. As a consequence, and in extension to previous reports,^{10,34} we conclude that “3” is the minimum number of carbene bonds necessary to avoid the quintet population and hence photo-induced spin crossover in NHC-Fe(II) complexes.

One initial motivation for the design of bidentate ligands was the prospect to produce NHC complexes with bite angles closer to 180° , preserving the octahedral coordination of Fe, and thus increasing the ligand field, with respect to tridentate ligands. So far, to the best of our knowledge, a heteroleptic tridentate-liganded complex with 3 carbene bonds has not been reported, making it difficult to identify a direct effect of the coordination geometry only. The present study definitely points to an important modification of the excited state energy landscape since, for both *mer* and *fac* isomers, we observe the co-existence of two excited state populations, while in all homoleptic tridentate-liganded Fe(II)-NHC complexes reported so far, a single excited state population was observed,^{9, 10, 11,12, 34,18} always assigned to 3MLCT states.

The assignment of states A and B in terms of their electronic character is difficult on the sole basis of the TAS data. We can, however, safely exclude them to be singlet states since these would display stimulated emission, i.e. negative ΔA on the low-energy side of the GSB bands. Triplet states, as the 3MLCT 's reported for tridentate-liganded Fe(II)-NHCs, do not show sizeable stimulated emission since the radiative rate of the $^3MLCT \rightarrow S_0$ transition has a ≈ 3 orders of magnitude smaller radiative rate than the allowed singlet-

singlet transitions.³⁵ It is therefore most likely that the observed states A and B are located on the triplet excited state PES presented in the computational studies. TAS could potentially differentiate the MC or MLCT character on the basis of the ESA spectra, however a clear fingerprint differentiating one from the other has only been reported for the very specific case of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$, where the $^3\text{MLCT}/\text{MC}$ crossover goes along with a strong solvatochromism.³³

A possible interpretation of the time-resolved spectroscopy results and in particular the existence of a parallel decay model with a branching ratio between the fast and slow component that is strongly dependent on the isomerism, can be formulated taking into account the results from molecular modelling reported here and in previous contributions.²³

The slower decay from the first triplet state may be explained by a closer examination of the PES. Figure 10 displays a schematic representation of the two-state decay model. Indeed, in the case of T_1 the system will be trapped in the T_1 minimum region where the S_0 PES is higher in energy than T_1 displaying a spin-crossover region. Hence, some vibrational cycles will be necessary to allow the crossing between the S_0 and T_1 states and subsequently transfer the population back to S_0 . This process is thus ascribed to the slower decay component, τ_3 . On the other hand, a much larger region of the T_2 PES lies at higher energies with respect to S_0 , having a much smaller spin-crossover area and thus being able to funnel the population to the available low-lying S_0 state in a much more efficient way, leading thus to shorter triplet excited-state lifetimes (τ_3 component).

The difference in the branching ratio between the two paths in the case of *fac* and *mer* isomers can also be rationalized in terms of the different shape of the PES (Fig.10). In the case of *mer* (**C1**) one can observe an initially steep PES; furthermore, T_1 is significantly lower in energy than T_2 at the Franck-Condon region. The situation is

totally different for the *fac* (**C2**) isomer where the PESs are globally flatter and the two triplet states are degenerated at Franck-Condon area. As such, in the case of the *mer* isomer a large population of T₂ should be expected in an ultrafast time scale, driving the system rapidly towards the central regions of the PES.²³ On the other hand, in the case of *fac*, and in the τ_1 time-scale, *i.e.* close to the Franck-Condon region, the population of the triplet manifold will distribute more equally between T₁ and T₂ since the PESs are flatter and accessible T₁/T₂ energy degeneracy areas are predicted at the surroundings of the mentioned Franck-Condon region. Remarkably enough, the steeper PES calculated for the *mer* isomer is also in agreement with the shorter value observed for the τ_2 component of this isomer as compared to the τ_2 measured for *fac*.

Theoretical determinations of the triplet ESA spectra support the present interpretation. Although the calculation of ESA spectra has more technical difficulties as compared to the steady-state ones, and hence the results should be taken only as semi-quantitative, the overall experimentally observed trend of separate ESA bands with different lifetimes is confirmed by our simulations. Figures S15 to S18 show the simulated ESA for the T₁→T_X and T₂→T_X excitations computed for both **C2** and *mer-C1* complexes along some important points of their respective PES. At all Fe-N1 distances, the lowest-energy T₂→T_X absorptions appear at longer wavelengths with respect to the lowest-energy T₁→T_X excitations, explaining the apparent blue shift at the 450-500 nm region observed in the transient absorption spectra (see Figure 5) because of the faster T₂ decay. In other words, the faster disappearance of the T₂→T_X absorptions causes the mentioned apparent blue shift displayed in Figure 5.

Importantly, and in contrast with what is usually taken as a model, it should be noted that the two low-lying triplet states cannot clearly be identified within the diabatic notation as MC or MLCT. Instead, their nature changes adiabatically along the PES, and

following the iron nitrogen enlargement, leads to a progressive deactivation rather than a sharp non-adiabatic transition from a ligand- to a metal-centred surface.

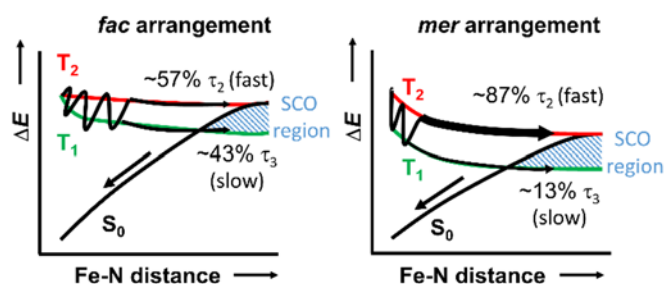


Fig. 10. Schematic interpretation of the τ_2 and τ_3 excited-state components on the basis of the singlet and triplet PES topologies of the *fac* and *mer* arrangements.

METHODOLOGY

All general experimental considerations may be found in the ESI.†

Synthesis

Methylimidazoliumpyridine (L1)²⁵

2-pyridylimidazole (200 mg, 1.38 mmol) and iodomethane (1.76mg, 0.77 mL, 12.40 mmol) were heated one hour in 2 mL of acetonitrile at 100°C under microwaves irradiation (60W). After evaporation of solvent, the resulting mixture was dissolved in water. Then the metathesis was made by addition of saturated solution of KPF₆. Solid was filtered, washed twice with Et₂O and dried under vacuum to give yellow powder (67 %). The obtained NMR data for the ligand L1: ¹H NMR (400 MHz, DMSO-d₆) : δ = 10.01, (s, 1H), 8.65 (ddd, J = 4.8, 1.8, 0.8 Hz, 1H), 8.50 (t, J = 2.0 Hz, 1H), 8.22 (td, J = 7.6, 2.0 Hz, 1H), 7.99 (dt, J = 13.6 Hz, 1H), 7.94(t, J = 1.8 Hz, 1H), 7.65 (ddd, J = 7.6, 5.0, 0.8 Hz, 1H), 3.97 (s, 3H) ppm.

[Fe^{II}(MeIm-Py)](PF₆)₂ (C1)

Using schlenk techniques, the ligand L1 (600 mg, 1.97 mmol) and FeCl₂, (82 mg, 0.65 mmol) were dissolved in 4 mL of DMF. Potassium tert-butoxide (243 m, 2.16 mmol)

was then added. The dark red solution was stirred at rt for 10 min. After evaporation of DMF, the residue was purified by column chromatography using water/acetone/ KNO_3 (6/3/1) as eluent. The red fractions were evaporated and a saturated solution of KPF_6 was added. The obtained solid was filtered, washed twice with Et_2O and dried under vacuum to give a non-separable mixture of both *fac*- and *mer*-**C1** in a 1:14 ratio (41 %) as an orange solid.

mer-**C1**: ^1H NMR (400 MHz, CD_3CN) : δ = 8.22 (d, J = 2.2 Hz, 1H), 8.15 (d, J = 2.2 Hz, 1H), 8.11–8.08 (m, 1H), 8.06 (d, J = 2.3 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.87–7.80 (m, 3H), 7.69 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 2.2 Hz, 1H), 7.38 (d, J = 2.2 Hz, 1H), 7.32 (dd, J = 5.8, 0.6 Hz, 1H), 7.29 (td, J = 5.6, 1.2 Hz, 1H), 7.19 (d, J = 2.3 Hz, 1H), 6.91–6.89 (m, 2H), 6.85–6.83 (dd, J = 5.8, 0.7 Hz, 1H), 3.25 (s, 3H), 2.82 (s, 3H), 2.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, CD_3CN) : δ = 209.5, 205.1, 204.5, 157.1, 156.3, 155.9, 155.7, 155.3, 152.5, 141.5, 140.2, 139.1, 129.0, 128.9, 128.8, 124.7, 123.4, 122.7, 118.9, 118.0, 117.8, 113.2, 112.4, 112.1, 37.0, 36.0, 35.8 ppm.

fac-**C1**: ^1H NMR (400 MHz, CD_3CN) : δ = 8.11 (d, J = 1.6 Hz, 1H), 8.11–8.06 (m, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.24–7.21 (m, 1H), 7.18 (d, J = 2.5 Hz, 1H), 7.07 (dd, J = 5.7, 0.7 Hz, 1H), 2.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, CD_3CN) : δ = 200.3, 151.1, 140.7, 128.5, 124.1, 118.2, 112.9, 36.7 ppm. HR-MS calcd for $\text{C}_{27}\text{H}_{27}\text{FeN}_9\text{P}_2\text{F}_{12}$ m/z: 266.5864 $[\text{M} - 2\text{PF}_6]^{2+}$, found 266.5873.

Tris(2-imidazoliumpyridineethyl)amine (L2)

Tris(2-chloroethyl)amine (100 mg, 0.41 mmol) and 2-pyridylimidazole (362 mg, 2.46 mmol) were reacted for one hour in 2 mL of isopropanol at 160°C under microwave irradiation (70W). After evaporation of the solvent, the resulting mixture was dissolved in water. After addition of a saturated solution of KPF_6 the obtained solid was filtered,

washed twice with Et₂O and dried under vacuum to give **L2** (98 % yield). ¹H NMR (400 MHz, DMSO-d₆) : δ = 9.92 (s, 3H), 8.56 (dd, *J* = 4.8, 1.0 Hz, 3H), 8.44 (t, *J* = 2.0 Hz, 3H), 8.18 (td, *J* = 7.6, 2.0 Hz, 6H), 7.92–7.89 (m, 6H), 7.62 (dd, *J* = 7.6, 4.8 Hz, 3H), 4.40 (t, *J* = 6.0 Hz, 6H), 3.17 (t, *J* = 6.0 Hz, 6H) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ = 149.2, 146.1, 140.6, 135.0, 125.2, 132.7, 119.0, 113.9, 51.3, 46.4 ppm. HR-MS calcd for C₃₀H₃₃N₁₀P₃F₁₈ m/z: 823.2168 [M - PF₆]⁺, found 823.2258.

[Fe^{II}(N-Et-Im-Py)](PF₆)₂ (C2)

Using schlenk techniques, the ligand **L2** (400 mg, 0.42 mmol) and FeCl₂ (4 mg, 0.38 mmol) were dissolved in 15 mL of DMF. Potassium tert-butoxide (281 mg, 2.50 mmol) was then added. The dark red solution stirred at rt for 10 min. After evaporation of DMF, the resulting crude was purified by column chromatography using water/acetone/KNO₃ (6/3/1) as eluent. The red fractions were evaporated and a saturated solution of KPF₆ was added. The solid was filtered, washed twice with Et₂O and dried under vacuum to give **C2** as an orange solid (15 % yield). ¹H NMR (400 MHz, CD₃CN) : δ = 8.16 (s, 3H), 8.06 (t, *J* = 6.6 Hz, 6H), 7.90 (dd, *J* = 8.6 Hz, 3H), 7.21–7.18 (m, 6H), 7.04 (d, *J* = 5.6 Hz, 3H), 3.60 (d, *J* = 14.6 Hz, 3H), 3.14 (d, *J* = 13.6 Hz, 3H), 2.84 (t, *J* = 14.6 Hz, 3H), 1.95 (t, 3H) ppm. ¹³C NMR (100 MHz, CD₃CN): δ = 207.5, 154.6, 150.7, 140.2, 127.2, 123.7, 119.2, 112.6, 63.8, 52.9 ppm. HR-MS calcd for C₃₀H₃₀FeN₁₀P₂F₁₂ m/z : 293.0997 [M - 2PF₆]²⁺, found 293.1020.

Computational methods

The computational methods employed in this work have been fully detailed elsewhere²³ and only a brief description will be provided here. All computations have been performed with the GAUSSIAN 09 (D01 revision) software package.³⁶ The S₀ and Q₁

equilibrium geometries of **C2** have been obtained with the standard DFT/B3LYP method, whereas optimizations and MEPs of the T₁ state have been performed using the unrestricted DFT/HCTH407 method (hereafter, DFT/HCTH).³⁷ On the other hand, the S₁ and T₂ states have been optimized at the TD-DFT/HCTH level. All energies discussed in the present work have been obtained with the TD-DFT/HCTH method. The GAUSSIAN 09 standard optimization thresholds have been used in all minimizations except for the S₀ equilibrium structures of **C0**, *fac-C1*, *mer-C1* and **C2** shown in Fig.4 and Table 1. In these cases, very tight optimization thresholds (opt=verytight) have been used to provide highly accurate geometrical parameters. The NTOs³⁸ have been obtained by post-processing the GAUSSIAN output using the Nancy_EX code.^{39,40} The photochemical landscape displayed in Fig.4 has been built by combining MEP calculations (relaxing the T₁ state) starting from the S₁ (¹MLCT) min (nuclear coordinate = 4.0) and the Q₁ min geometry (nuclear coordinate = 67.0). Both MEP computations ended up at the T₁ (³MC) min structure (nuclear coordinate = 31.5), identified in a separated calculation using the standard optimization algorithm. The Tamm-Dancoff approximation⁴¹ has been used in all TD-DFT calculations and the 6-31+G(d,p) basis set has been used throughout. The solvent effects (acetonitrile) have been included in all optimization and single-point computations by means of the polarizable continuum model (PCM) method, employing the GAUSSIAN 09 default settings.

Femtosecond transient absorption spectroscopy

In the transient absorption setup, an amplified 5kHz Ti: sapphire laser generates 30 fs pulses to pump a commercial optical parametric amplifier (TOPAS: Light Conversion), from which 60 fs pulses at 400 nm are derived to excite the samples. The white light continuum probe beam is generated in a 2 mm thick CaF₂ crystal and split in two: the

probe that is sent through the sample, and a reference beam is used for measuring and compensating the white-light intensity fluctuations. The polarization of the probe beam is set at magic angle (54.7°) with respect to the pump.

A 1 mm path length cuvette in fused silica contains the complexes dissolved in CH_3CN . Time-resolved spectra are acquired in the range 350-650 nm as a function of pump-probe delay, by a Peltier-cooled CCD with 220Hz acquisition rate. A solvent-only sample is measured, and the data are processed to (i) remove the background at negative delay times, (ii) the solvent Raman signal and the coherent interactions of the pump and probe in the cell, (iii) to correct for the group velocity dispersion of the probe beam, characterized in the solvent-only data set. The temporal resolution is characterized by the 70 ± 5 fs FWHM of the solvent Raman response. For more details see Ref ⁴². The multi-exponential fit procedure is described in the SI.

CONCLUSIONS

In the present contribution, we report the synthesis and the detailed experimental and computational characterization of an original iron-carbene bidentate compound. The complex is obtained with a 100% *fac* isomerism, in contrast to previous conventional synthetic procedures which only lead to mixtures dominated by the *mer* isomer. The excited-state lifetimes of the pure *fac* compound have been compared with those of the *mer* isomer. It is shown that, as it was the case for tridentate-liganded complexes reported before, the inclusion of carbene moieties increases the MLCT lifetime from the subpicosecond range to a maximum of about 20 ps.

By producing the constrained *fac*-only bidentate-liganded iron-carbene complex we have confirmed large differences in the photophysics of bidentate-liganded and tridentate-liganded complexes. Our transient absorption spectroscopy measurements and the computational results unveil crucial differences in the photophysics of the *fac* and

mer isomers. We show that bidentate-liganded iron-carbene complexes decay to the ground state via a parallel two-state mechanism composed by a fast and a slow component. The former component is ascribed to the population of the T₂ state whereas the latter is ascribed to the T₁ state. Differences in the excited-state lifetime are interpreted based on a large spin-crossover region in T₁ as compared to T₂, which will act as a more efficient trap for the triplet state slowing down its decay.

While in the case of the *fac* isomer the two pathways appear as equally probable, a preference for the fastest decay is observed in the *mer* dominated mixture, hence globally leading to a faster decay for the latter.

Our results clearly confirm the peculiarity of the photophysics of iron bidentate-liganded compounds, especially the crucial role of *fac/mer* isomerism in driving the overall decay process, illustrating how the simple diabatic picture relying in the competition between well separated MC and MLCT states is largely insufficient to provide a full coherent explanation of the time resolved photophysics.

ASSOCIATED CONTENT

NMR, spectroscopic and electrochemical data for complexes as well as additional computational and photophysical details can be found in the Supporting Information.

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