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Azaullazine-driven frontier orbital engineering enables nanosecond-lived singlet MLCT states in Fe(II) NHC complexes

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Iron(II) complexes are promising sustainable alternatives to noble-metal photosensitizers, yet their practical application is limited by ultrafast deactivation of metal-to-ligand charge-transfer (MLCT) states into low-lying metal-centred (MC) states. Here we report a Fe(II) complex displaying long-lived singlet MLCT excited states, with a fluorescence lifetime of 3.5 ± 0.5 ns and a quantum yield of 1.5%, representing record performances for iron-based chromophores. By introducing heteroleptic NHC–azaullazine ligands that combine high-energy π -donor and low-energy π^* acceptor orbitals with suitable energy and symmetry matching to the Fe $3d$ manifold, we achieve controlled metal–ligand orbital mixing that induces both *HOMO inversion* and an unusual reordering of the lowest unoccupied molecular orbitals (*LUMO inversion*). This electronic structure enhances visible-light absorption and suppresses the detrimental $^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^3\text{MC}$ relaxation pathway. Ultrafast spectroscopy and spin–orbit coupling calculations reveal that intersystem crossing from the lowest-energy $^1\text{MLCT}$ states, i. e. excitation into the two lowest-lying acceptor orbitals, is selectively inhibited, thereby preventing population transfer into MC states. In contrast, conventional ultrafast deactivation occurs only for higher-lying $^1\text{MLCT}$ states involving excitation into higher-energy acceptor orbitals. These findings establish frontier-orbital symmetry control as a general strategy for stabilizing emissive charge-transfer singlet states in Earth-abundant transition-metal complexes.

Introduction

The development of sustainable photoactive materials for solar energy conversion has driven growing interest in replacing noble metals with environmentally benign, earth-abundant alternatives.^{1–4} Iron, the most abundant metal on Earth, emerges as a particularly compelling candidate for this transition. However, harnessing the photophysical properties of iron complexes for practical applications remains highly challenging. Unlike their ruthenium counterparts, the weaker ligand field in Fe(II) polypyridines promotes ultrafast decay of the possibly emissive metal-to-ligand charge-transfer (MLCT) states via rapid population of low-lying metal-centred (MC) states.^{5–8} As a result, these short-lived MLCT states cannot be readily exploited for photophysical applications.

Over the years, various ligand-design strategies have been successfully employed to strengthen the iron ligand field and achieve long-lived MLCT excited states.^{9–11} The most successful examples reported in the literature include exploiting the strong σ -donation of N-heterocyclic carbene (NHC) ligands,¹² combining σ - and π -donation through cyclometalating ligands,¹³ and employing mesoionic carbenes that function simultaneously as σ -donors and π -acceptors.¹² In particular, the association of NHCs with pyridine units has revitalized research on iron(II) complexes featuring long-lived MLCT states. The introduction of these ligands boosted the MLCT lifetime to tens of picoseconds for complexes with tridentate C^N^C ligands,^{14–16} making iron complexes applicable in photochemical applications such as dye-sensitized solar cells.^{4,17–19} By coordinating iron(II) with six carbene units in an octahedral geometry, record $^3\text{MLCT}$ lifetimes of up to 528 ps have been achieved.²⁰ The increased electron density at the metal center can also promote the formation of Fe(III) species under aerobic conditions, which exhibit long-lived (nanosecond) luminescent LMCT states.²¹

However, this enhancement in the lifetime of Fe(II)-NHC complexes came, with a few exceptions,²² at the cost of a reduced absorption window, which is undesirable for light-to-energy conversion, where broad light-harvesting is essential. To address this challenge, the possibility of combining panchromatic absorption with sufficiently long MLCT lifetimes has been proposed through the “*HOMO inversion*” strategy introduced by Jakubikova and co-workers.²³ This concept relies on imparting partial ligand character to the highest-occupied molecular orbital (HOMO): by mixing the metal t_{2g} and higher-energy ligand π orbitals, the HOMO effectively shifts from a metal-centered to a mainly ligand-centered orbital. This metal–ligand hybridization in the highest occupied molecular orbitals promotes the emergence of mixed MLCT, ligand-centered (LC), and ligand-to-ligand charge-transfer (LLCT) transitions, resulting in broader and more intense absorption throughout the visible region.^{24–26}

However, its beneficial effect on MLCT lifetimes has not yet been conclusively demonstrated. Some of us recently showed that replacing the central pyridine unit in pyridyl-NHC ligands with fused polythiophenes induces a pronounced red shift of the $^1\text{MLCT}$ transition together with a two- to three-fold increase in the molar extinction coefficient. The electron-donating thiophene fragments promote delocalization of the

MLCT state onto the ligands, resulting in a two-fold enhancement of the excited-state lifetime (13–18 ps) compared with the unsubstituted analogue.²⁶ Conversely, the Fe-amido complexes reported by Herbert and co-workers,^{24,25} despite exhibiting strong Fe-ligand orbital mixing²⁷ and the resulting panchromatic absorption, display ultrafast excited-state deactivation into a ⁵MC state.²⁸

To advance this design strategy for optimizing metal-ligand mixing and photophysical properties, we turn to ullazines and azaullazines as an intriguing class of conjugated heterocycles. These molecules feature a prominent electron-rich character, arising from an internal pyrrole nitrogen within the conjugated framework, which promotes an intramolecular charge-transfer (ICT) resonance. The resulting ICT absorption band extends strongly across the visible spectrum, a property that has been exploited in diverse applications, including organic field-effect transistors (OFETs)²⁹ or solar cells.³⁰

Here, we report the first Fe(II)–NHC complex incorporating an azaullazine core, **C2** (Figure 1), which displays a broad and intense 350–580 nm absorption window and, notably, an emissive singlet MLCT state with a lifetime of a few nanoseconds. These unprecedented photophysical properties arise from two key features. First, *HOMO inversion* generates a dense manifold of bright mixed MLCT, LC, and LLCT excited states in the visible region while reducing the MLCT character of the lowest-lying singlet and triplet states. Second, the distinctive symmetry of the lowest-energy unoccupied molecular orbitals (LUMOs) suppresses spin–orbit coupling between the low-lying ¹MLCT states and nearby ³MLCT states, an exceptional behaviour in transition-metal complexes.^{31,32} Collectively, these findings establish frontier-orbital engineering as a powerful strategy for designing photoactive and emissive iron-based sensitizers, in which the energy, symmetry, and topology of frontier molecular orbitals can be rationally tuned to control optical and excited-state properties.

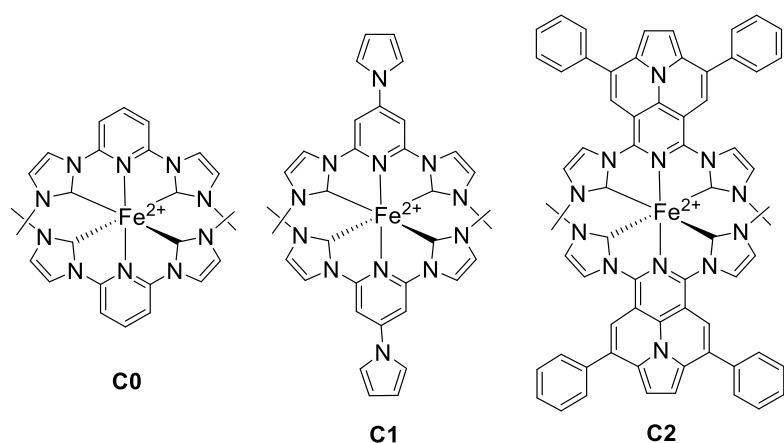
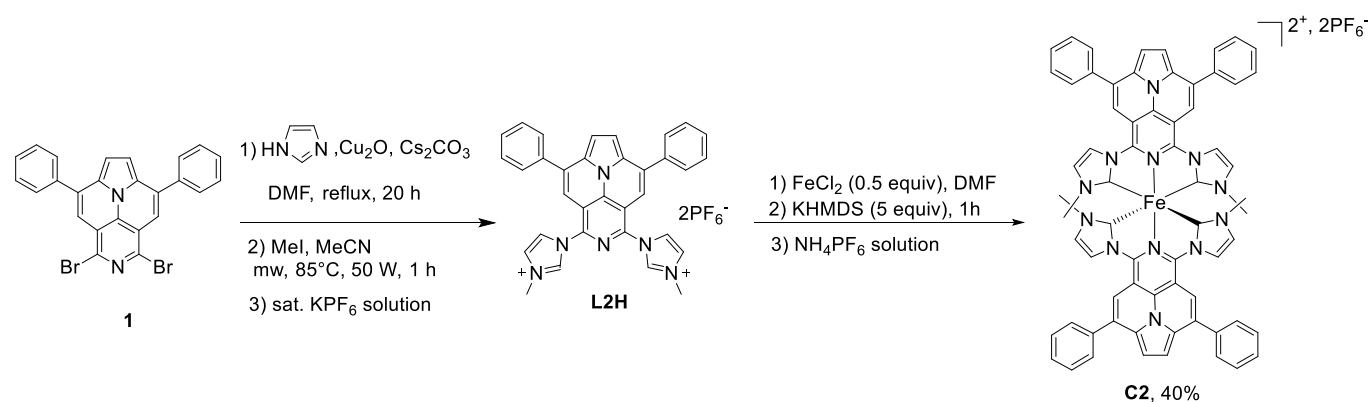


Figure 1. Complexes **C1** and **C2** studied in this work, compared to **C0** from Ref. 14. The counterion is PF₆[−] throughout.

Results

Synthesis and ground state properties

The imidazolium salts **L1H** and **L2H**, which are the required precursors of the pyridyl-NHC ligands, used to synthesize **C1** and **C2**, respectively (Figure 1), were first synthesized (Scheme 1 for **LH2**, and SI for **L1H**). **L1H** bears only the pyrrole unit to evaluate the impact of the fused system present in **C2**. **L2H** was prepared in good yield by reacting the 2,6-dibromo azaullazine **1**³³ with imidazole, followed by quaternization. The target complexes **C1** and **C2** (Figure 1, Scheme 1) were finally obtained using an in-situ coordination protocol. FeCl₂ was first mixed with the appropriate ligand precursor in DMF, and then KHMDS was added to generate the carbene in situ, which was trapped by the iron salt.



Scheme 1. Synthesis of preligand **L2H** and complex **C2**.

The complexes **C0** and **C1** exhibit three distinct absorption bands in their UV-Vis spectra recorded in acetonitrile (Figure 2, Table 1). The high-energy band (250-350 nm) is attributed to LC and LLCT π - π^* transitions. The two lower-energy bands are generally assigned to Fe(II)-NHC transitions (340-420 nm) and Fe-pyridine MLCT transitions (420-520 nm). The electron-donating pyrrole moiety in **C1** induces a slight red shift (0.09 eV) of the lowest-energy band relative to **C0**. In contrast to **C1**, the annulated azaullazine structure in **C2** promotes a very broad and intense absorption spanning the visible region (350-580 nm). Notably, both the proligand **L2H** and complex **C2** share an intense visible absorption band centered at 430 nm, characteristic of the azaullazine moiety (see Figure S15).³³

The redox properties of **C1** and **C2**, investigated by cyclic voltammetry, are summarized in Table 1 (see Figures S16 and S17). For **C2**, several redox processes are observed. The first oxidation process occurs at around +0.3 V vs Fc/Fc⁺, similarly to the two other complexes, and is assigned to the Fe^{III}/Fe^{II} redox couple. On the cathodic side, an irreversible reduction process is observed below -2.20 V, attributed to the reduction of the ligand, with its potential shifting notably across the series. Interestingly, the potential difference between these two redox systems aligns with the UV-Vis data, as the electrochemical gap decreases significantly from **C0** to **C2**. This trend correlates with a ~0.2 eV redshift of the lowest-energy band upon introducing azaullazine as the central azine.

C0 and **C1** complexes are not luminescent; in contrast, **C2** is emissive with a fluorescence quantum yield of $\Phi_f = 1.5 \pm 0.1$ % when excited at 520 nm (see SI, §7.1). At this excitation wavelength, **C2** presents a broad emission band in acetonitrile extending from 500 nm to 850 nm with a peak at 578 nm. The right panel of Figure 2 displays the red shift of the fluorescence spectra while increasing the solvent's polarity (peak at 625 nm for DMSO). According to the Lippert-Mataga formalism,²⁹ the observed red-shift indicates a clear charge transfer (CT) character of the emissive HOMO-LUMO transition (see details of electronic structure below).

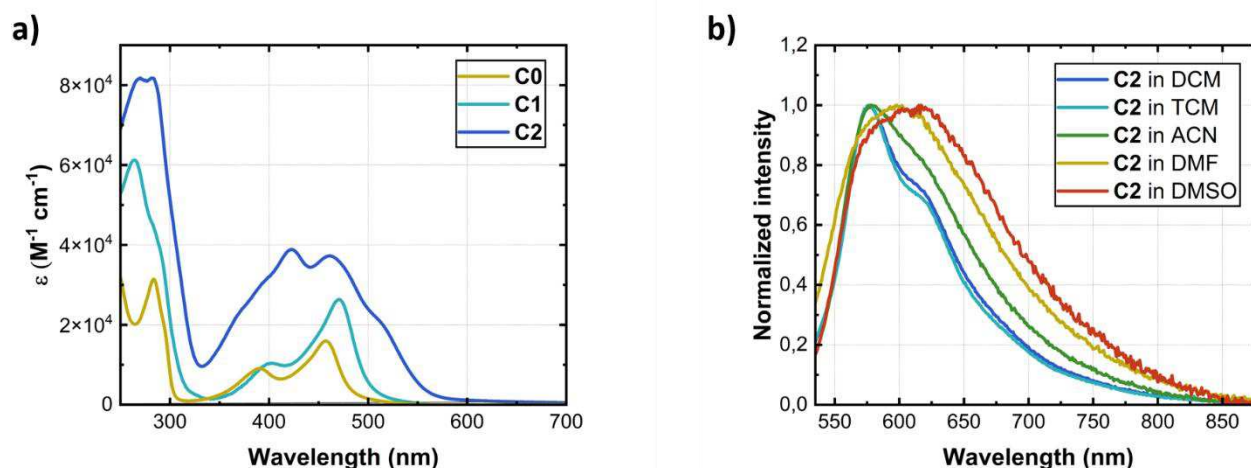


Figure 2. a) UV-Vis absorption spectra of the investigated complexes in acetonitrile; b) Normalized emission spectra of **C2** in solvents of varying polarity: dichloromethane (DCM), chloroform (TCM), acetonitrile (ACN), N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Solvents are ordered by increasing polarity index.³⁴

Table 1. Spectroscopic and electrochemical properties of the investigated complexes

Complex	$\lambda_{\max}$ (nm)	$E_{\max}^a$ (eV)	ϵ (M ⁻¹ .cm ⁻¹)	$E_{1/2}^{ox}(Fe^{II}/Fe^{III})/V$ (ΔV / mV) ^b	E_{pc}^{Red} / V^a	ΔE^c (eV)
C0 ¹⁴	457	2.71	15955	0.31 (rev)	-2.39 (irr)	2.70
C1	473	2.62	11034	0.29 (rev, 90)	-2.37 (irr)	2.66
C2	515	2.41	4049	0.28 (rev, 65)	-2.20 (irr)	2.48

^a Calculated optical gap. ^b vs Fc/Fc⁺. ^c $\Delta E = E_{1/2}^{ox} - E_{pc}^{Red}$

UV-Vis spectroelectrochemistry and EPR spectroscopy: characterization of the metal-centred one-electron oxidized species

The UV-Vis spectroelectrochemistry of the first oxidation system of **C2** is shown in Figure 3a (see Figures S20 and S21 for **C1**). Upon oxidation, the characteristic transitions of **C2** disappear, and new bands emerge at 335 nm, 450 nm, and 605 nm. The presence of isosbestic points at 358 nm, 434 nm, 470 nm, and 550 nm attests to a clean oxidation process, converting **C2** into a unique species. Returning the potential to its initial value (Figure 3b) fully restores the original bands, confirming the reversibility of the process (conversion of 0.20 C, corresponding to 1 electron exchange). To determine whether oxidation occurs at the ligand or the metal center, X-band cw-EPR spectroscopy experiments were carried out. As expected, the **C2** spectrum is EPR silent, consistent with a diamagnetic low-spin Fe(II) complex. Upon oxidation, the resulting EPR spectrum exhibits a quasi-axial signature in agreement with a low-spin Fe(III) complex ($S = 1/2$).³⁵ The large anisotropy of the g -tensor ($\Delta g = 0.445$) indicates that the main spin density is localized on the Fe center, confirming that the oxidation is metal-centered (Figures S22 and S23).

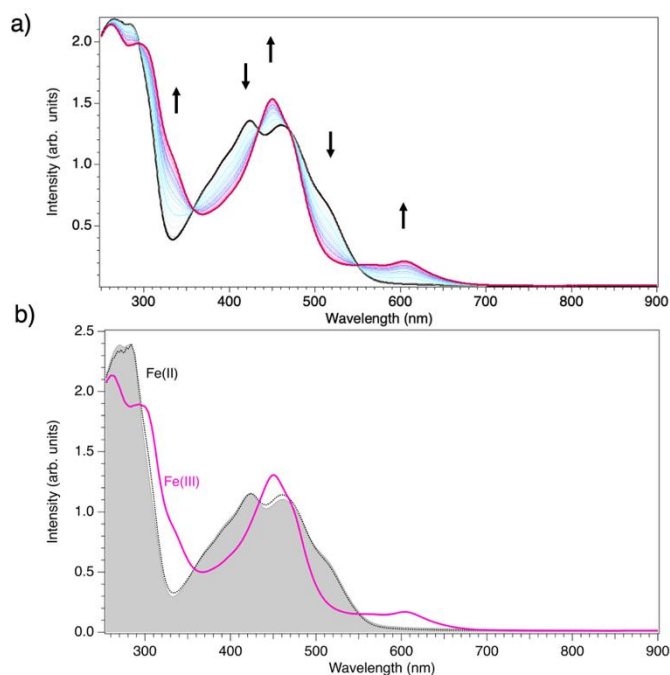


Figure 3. (a) UV-vis spectra of **C2** (0.35 mM) recorded in acetonitrile (MeCN) containing 0.1 M TBAPF₆ during exhaustive oxidation at $E_{app} = 0.42$ V vs Fc/Fc⁺. Pathlength: 1 mm; scan interval: 550 s (final scan at 990 s). (b) UV-vis spectra of **C2** (0.35 mM): initial spectrum (grey), after oxidation (magenta), and after subsequent reduction at $E_{app} = -0.09$ V vs Fc/Fc⁺ (black dashed), regenerating the initial complex.

Frontier-orbital engineering and excited-state properties

This section provides a detailed understanding of the differences in the electronic structure of **C1** and **C2** and how these differences affect their absorption spectra in terms of spectral range and nature of the optical transitions (MLCT, LC and LLCT). As a starting point, it is important to note that, in both **C1** and **C2** complexes, the octahedral O_h symmetry of the ideal six-fold coordination of the metal ion is lowered to a slightly distorted D_{2d} symmetry. This can be seen in Figure 1, where the ligands of **C1** and **C2** define a vertical symmetry axis along the Fe-N bond and further across both pyrrole and azaallazine moieties. Within the D_{2d} symmetry and taking the z axis along the Fe-N bond, the Fe 3*d* atomic orbitals belong to the “ e ” (d_{xz} and d_{yz}), “ b_2 ” (d_{xy}), “ b_1 ” ($d_{x^2-y^2}$), and “ a_1 ” (d_{z^2}) irreducible representations (*irreps*) instead of “ t_{2g} ” and “ e_g ” for the O_h symmetry.

Azaallazine-induced HOMO and LUMO inversion and frontier-orbital symmetry. DFT electronic structure calculations at the structurally relaxed ground-state geometries reveal pronounced differences in the energy, symmetry, and compositions of frontier molecular orbitals (MOs) upon introducing the fused azaallazine framework in **C2** relative to the pyrrole-substituted **C1** (Figure 4 a and b). The extended aromatic core narrows the HOMO-LUMO gap from 3.27 eV in **C1** to 2.71 eV in **C2**, mainly due to an upward shift of the HOMO energy level, calculated at -5.16 eV and -5.57 eV for **C2** and **C1**, respectively (Figure 4). The differences in the electronic structures of the two complexes can be readily rationalized by considering the energetics and symmetry of the ligand HOMOs and LUMOs: In both complexes, the HOMO arises from the in-phase combination of the ligand π HOMOs (hereafter indicated with π_1 , Figure S27), of b_2 symmetry, enabling mixing with the Fe 3*d*_{xy} orbital belonging to the same *irrep*. Owing to the extended conjugation of the azaallazine unit, the π_1 orbital lies substantially higher in energy in **C2** than in **C1** (-4.92 vs -6.08 eV; Figure S27), resulting in a markedly different energetic alignment with the Fe 3*d*_{xy} orbital and consequently distinct degrees of metal-ligand hybridization. Accordingly, the HOMO in **C2** is predominantly ligand-localized with a moderate Fe contribution ($\sim 30\%$), whereas in **C1**, it exhibits substantial metal character ($\sim 60\%$). On the other hand, the out-of-phase combination of the ligand π_1 orbitals transforms as a_2 and is therefore symmetry-forbidden from mixing with the Fe 3*d* manifold, which does not contain any orbital belonging to this *irrep*; this leads to a fully ligand-localized orbital. The energy difference exceeding 1 eV between the ligand π_1 orbitals in **C1** and **C2** accounts for the higher energetic position of this orbital in **C2** (HOMO-1, -5.43 eV) relative to **C1** (HOMO-5, -6.83 eV), as displayed in Figure 4. These results thus show that the azaallazine unit enables *HOMO inversion* in **C2**, while **C1** retains the electronic structure characteristic of typical Fe-py-NHC complexes. At lower energies, a pair of quasi-degenerate occupied orbitals is found with e symmetry (HOMO-2/HOMO-3 in **C2** and HOMO-1/HOMO-2 in **C1**). These orbitals are largely metal-localised ($\sim 70\%$) and arise from combinations of the two ligand π_2 (HOMO-1) orbitals of e symmetry (Figure S27) with the Fe 3*d*_{xz} and 3*d*_{yz} orbitals. Interestingly, in **C2**, HOMO-4 (Figure 4a), calculated at -5.81 eV, closely resembles the HOMO in spatial distribution, with only $\sim 30\%$ iron character.

In the following we formalize the concept of *LUMO inversion* by comparing the symmetry properties of the unoccupied molecular orbitals of **C1** and **C2**. Significant differences in the unoccupied frontier MOs are observed, indeed, between of the two complexes, arising from an energetic reordering of the empty MOs of the ligands upon introduction of the azaallazine unit. As shown in Figure S27, in terms of symmetry and spatial shape of orbitals along the metal-coordinating bonds, π_1^* of the **C2** ligand is topologically equivalent to π_2^* of the **C1** ligand, whereas π_1^* of **C1** corresponds to π_3^* of **C2**. As a consequence of this reordering in the empty ligand MOs, in **C2**, the LUMO and LUMO+1 belong to the a_2 and b_2 irreducible representations and correspond to the out-of-phase and in-phase combinations, respectively, of the ligand

LUMO (π_1^* in Figure S27). Thus, a notable consequence of the extended π system of the azauallazine ligand is that in the complex the symmetry and topology of LUMO/LUMO+1 mirror those of the HOMO/HOMO-1 (Figure 4a). However, a slight distortion from the perfect D_{2d} symmetry accounts for the appearance of a very small electron density (d_z^2) on the metal in the LUMO isodensity plot (Figure 4a). The LUMO+2 and LUMO+3 orbitals (e symmetry) arise from a weak interaction between the ligand π_3^* orbital (Figure S27) and the Fe $3d_{xz}$ and $3d_{yz}$ orbitals and lie about 0.2 eV higher in energy. In **C1** the ordering of these orbitals is reversed, consistent with the different energetic ordering of the ligand unoccupied MOs. Thus, the LUMO and LUMO+1 in **C1** derive from the combination of the two ligand π_1^* (e symmetry) and correspond to the LUMO+2 and LUMO+3 of **C2**. In contrast, the LUMO+2 and LUMO+3 orbitals of **C1**, originate from π_2^* combinations (b_2 and a_2 symmetry), and therefore correspond to the LUMO and LUMO+1 in **C2**.

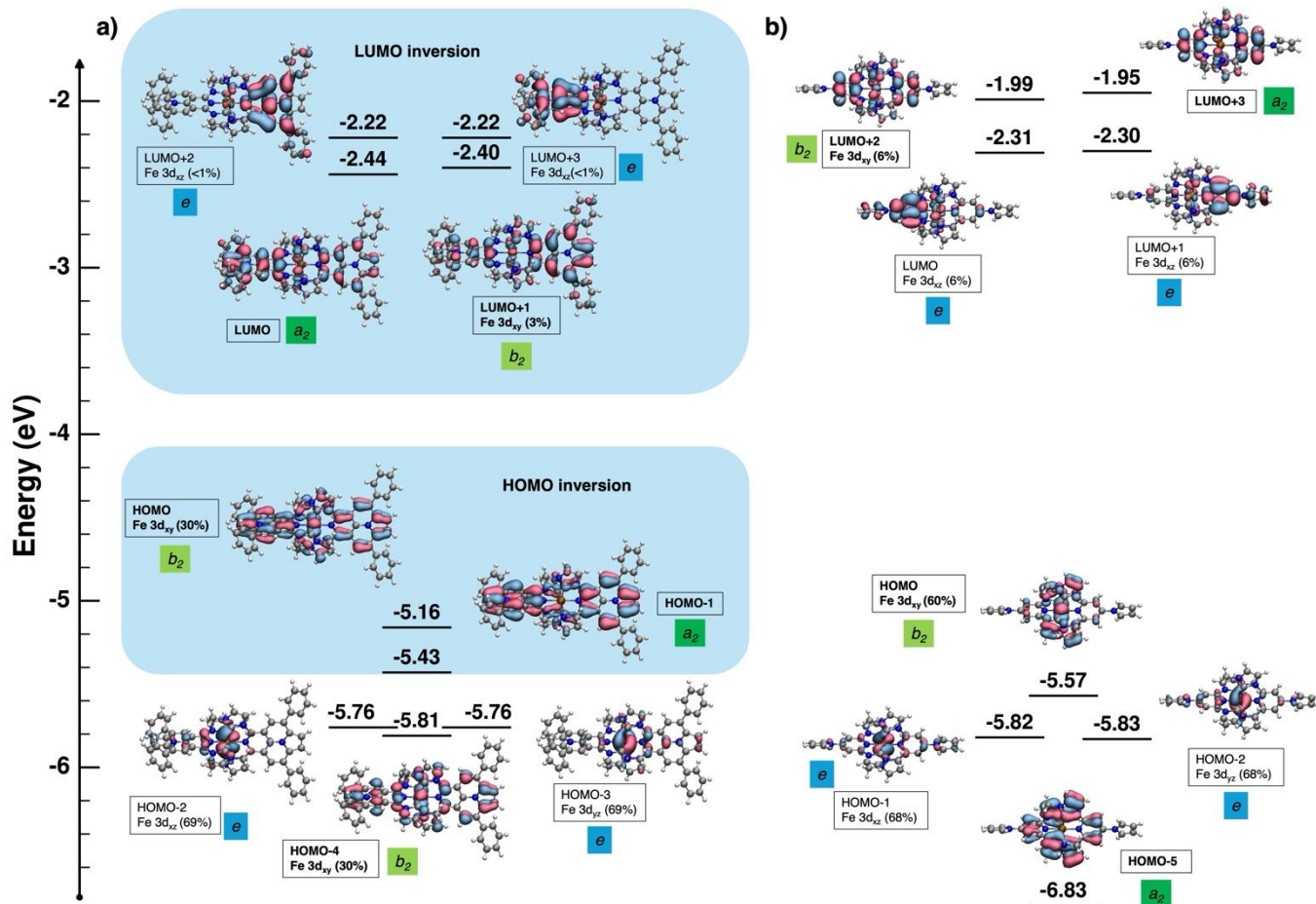


Figure 4. Calculated energy levels (B3LYP*/6-311G*) and isodensity plots (isosurface value = 0.025 a.u.) of the highest occupied and lowest unoccupied molecular orbitals (HOMOs and LUMOs) of **C2** (a) and **C1** (b). The percentage Fe 3d character (when non-zero) and the orbital symmetry in the D_{2d} point group are given for each orbital.

Rationalizing the absorption and emission spectra of C2. Based on the different electronic structure of **C1** and **C2**, the differences observed in the absorption spectra recorded for the two complexes (Figure 2a) can be readily rationalized. The simulated broad absorption band of **C2**, extending from approximately 350 nm to 600 nm (Figure S28), arises from a rich manifold of bright electronic excitations with mixed MLCT, LC, and LLCT character. As shown in the inset of Figure S28, the low-energy band, corresponding to the experimental shoulder at 520 nm, is mainly due to the S_1 (HOMO $\rightarrow$ LUMO) transition at 521 nm. This excitation has a mixed MLCT (40%)/LLCT (32%)/LC (25%) character (Table S5), with the hole distributed over the metal and ligands ($\approx 40\%$ and $\approx 60\%$, respectively) and the electron fully delocalized on the ligands. Two other weak transitions are calculated very close in energy, i.e., S_2 , at 518 nm, mainly described by the HOMO $\rightarrow$ LUMO+2 excitation, and S_3 , at 517 nm, originating from the HOMO $\rightarrow$ LUMO+3 electronic transition. In the Franck-Condon region, the HOMO $\rightarrow$ LUMO+1 excitation (S_4) is almost dark and calculated at 506 nm. Comparison of the simulated and experimental absorption profiles shows that the present level of theory, omitting finite-temperature broadening, explicit solvation, and vibronic effects,^{36,37} predicts an absorption band dominated by a single bright S_1 transition, thereby underestimating the intensity of the three higher-energy excitations. Experimentally, however, the broad low energy shoulder (500-550 nm, Figure 2a) arises from comparable contributions of the four lowest excited states, which collectively define the spectral envelope and, as discussed below, influence the excited state photophysics.

Moving at shorter wavelengths, the main excitations contributing to the 440 nm band (Figure S28) are S_{10} and S_{12} . While the former display a mixed LLCT (40%)/LC (36%)/MLCT (20%) nature, S_{12} is essentially ligand-based (Table S5). In the 420–350 nm region (third absorption band in Figure S28), the calculations indicate a manifold of closely spaced excited states with mixed electronic character. These excitations involve deeper-lying occupied orbitals with increased metal contribution, together with ligand-based transitions, resulting in a highly intricate

excited-state landscape. At higher excitation energies, the spectrum becomes dominated by predominantly LC and MC excitations. The calculated absorption spectrum of **C1** is reported (Figure S29) and shortly discussed in the ESI.

Concerning the fluorescence spectrum of **C2**, TDDFT calculations in acetonitrile at the S_1 minimum yield a vertical emission energy of 592 nm for the LUMO $\rightarrow$ HOMO transition, in excellent agreement with the experimental maximum at 578 nm. In the next section, we will provide the experimental evidence for the singlet character of that charge transfer state and for its exceptionally long lifetime.

Time-resolved fluorescence

Measurements were performed with a time-gated Hamamatsu C10627 streak camera (time resolution 10 ps) to address the luminescence lifetime of **C2** in acetonitrile. Since steady-state luminescence measurements of **C1** gave no detectable signal, it was not considered for the time-resolved luminescence study. An excitation wavelength of 515 nm excites the MLCT/LLCT/LC transition band (composed of S_1 , S_2 , S_3 , and S_4 according to TDDFT calculations, Figure 2b and Table S5). The time-dependent spectra are displayed in Figure 5a. The emission band spans from 540 nm to 750 nm, peaking at 581 nm (Figure 2). The spectrum slightly blue-shifts until it almost completely decays by 20 ns. The kinetic traces at different emission wavelengths are curved when plotted on a logarithmic intensity scale, indicating multiple decay times rather than a single exponential decay. To determine their values, a global fitting analysis (GF) was performed using a multiexponential decay function convolved with the Gaussian instrument response function (IRF). Four exponential decay times are needed for a satisfactory fit, with values of 160 ps, 1.2 ns, 4.3 ns, and 11 ns. Fitted kinetics and the fit residuals are plotted at 560 nm, 580 nm, and 640 nm for the first 5 ns (Figure 5c) and in a 20 ns window (Figure 5d), attesting the fit quality. The corresponding decay-associated spectra (DAS) (Figure 5b) show blue-shifted peaks for longer time components in agreement with the time-resolved spectra. The main decay component at 4.3 ns accounts for 55% of the intensity decay. The amplitudes of the 11 ns and 160 ps components are roughly four times smaller, and their origins will be discussed below.

The amplitude-weighted average excited state lifetime is $\langle \tau_{fluo} \rangle = 3.5 \pm 0.5$ ns (Figure S25). The fluorescence QY Φ_F of 1.45%, determined for excitation at 520 nm, can then be converted into an average radiative rate, $k_r = \Phi_F / \langle \tau_{fluo} \rangle$, assuming that laser pulses excite only the S_0 to S_1 transition. For **C2**, a radiative rate of $k_r = 4.1 \times 10^6 \text{ s}^{-1}$ was measured, which indicates a singlet nature of the emissive state since radiative rates of triplet-to-singlet transitions are generally smaller than 10^6 s^{-1} .³⁸ However, compared to the values of $\approx 20'000$ for the extinction coefficient at $\lambda > 500$ nm (Figure 2), and assuming that the Strickler-Berg relation holds,²⁹ k_r is nevertheless one order of magnitude lower than expected. The critical point is that, as shown in the next section, excitation in the 500-520 nm range populates emissive and non-emissive excited states in parallel, which explains in part the relatively low Φ_F value, and hence an underestimated low k_r . Nevertheless, the theoretically predicted emissive S_1 - S_0 transition at 592 nm, with some MLCT character, is confirmed experimentally. While the origin of the different nanosecond decay components is unclear for the moment, the real novelty of **C2** is the suppression of the common singlet-to-triplet ISC, usually occurring on sub-ps time scales for Fe(II) complexes.³⁹

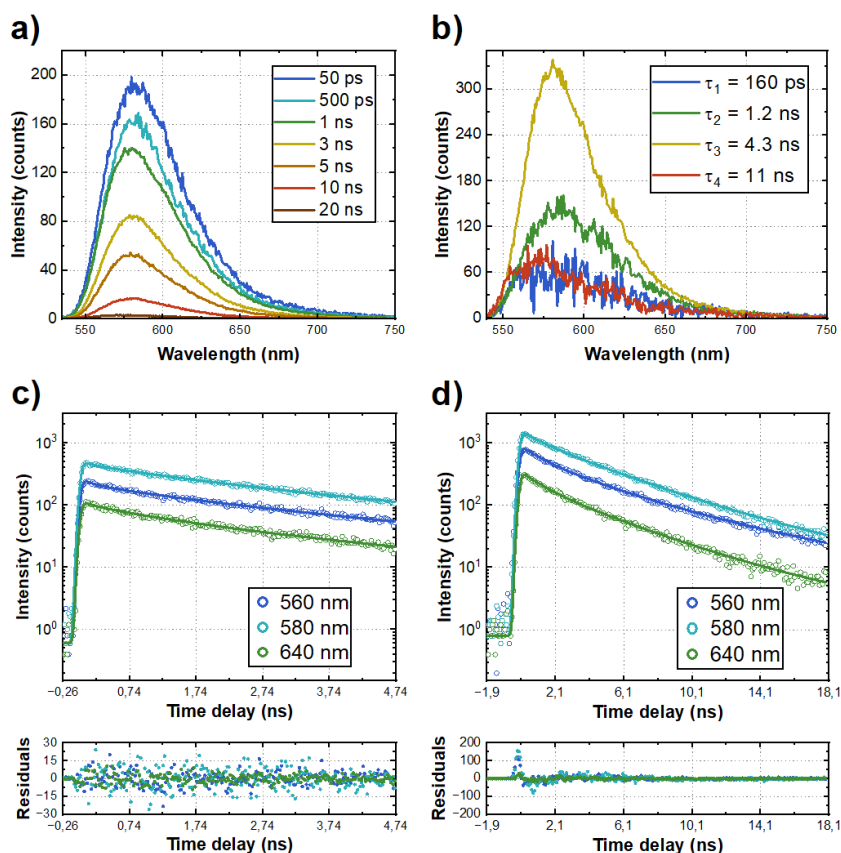


Figure 5: Time-resolved luminescence spectroscopy of **C2**. Time-dependent spectra in acetonitrile excited at 515 nm (a). Decay-associated spectra obtained via global fitting analysis described by four exponential fitting convolved with the IRF (b). Fitted kinetics traces at different wavelengths and their respective residuals are plotted for the 5 ns (c) and 20 ns (d) detection windows.

Excited state relaxation dynamics

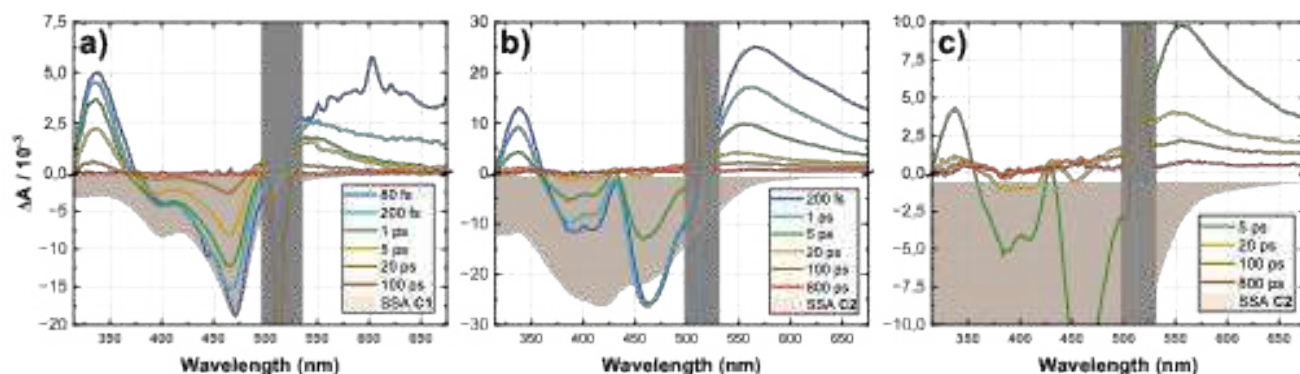


Figure 6: Femtosecond transient absorption spectroscopy (fs-TAS) of **C1** and **C2** complexes. Time-dependent spectra are shown for **C1** (a) and **C2** (b and c) for different time delays. The shaded spectra correspond to the sign-inverted ground-state absorption of each complex. For **C2**, the spectra of the last four delay times are shown in (c) to visualize the long-lived signal. Grey shaded areas cover residual scattering of the pump beam.

Femtosecond transient absorption spectroscopy (fs-TAS) was performed on **C1** and **C2** in acetonitrile to identify signatures of $^1/{}^3\text{MLCT}$ states as well as the signature of the long-lived CT states in **C2**. Upon excitation at 520 nm, chosen to favour the low-energy MLCT/LLCT/LC transitions (Figure 2a), the differential transient spectra of **C1** display a negative and two positive signals (Figure 6a). The former corresponds to the ground-state bleach (GSB), with a peak near the ground-state absorption maximum (470 nm). The two positive signals correspond to excited state absorption (ESA). At early times (80–200 fs), the UV-ESA (300–375 nm) blue-shifts, as does the VIS-ESA (490–670 nm), which by 1 ps forms a narrow band peaking at 535 nm. These spectral changes are usually indicative of the $^1\text{MLCT}$ to $^3\text{MLCT}$ transition,^{40,41} with the broad VIS-ESA being characteristic of the reduction of the pyridine ligands.²⁶ These ESA features, and the GSB, largely decay within 20 ps without further spectral shifts.

The dynamics of the fs-TAS for **C1** data can be described by a 3-component exponential decay as explained in detail in the supplementary information. Global fitting provides three decay components: 100 fs, 3 ± 1 ps, and 13 ± 1 ps. As discussed above, **C1** follows the standard excited state relaxation of previously studied Fe(II)-NHC complexes:^{16, 26, 40} the 100 fs time constant corresponds to the $^1\text{MLCT}$ -to- $^3\text{MLCT}$ transition, followed by vibrational relaxation within the triplet state (3 ± 1 ps). The latter then decays to the ground state on the 13-ps timescale, most likely via a transient population of a very short-lived (< 1 ps) ^3MC state.

In the case of **C2**, the differential transient spectra show features similar to those of **C1**, for delay times up to 20 ps: GSB splits in two bands extending from 360 nm to 500 nm, plus the UV-ESA in the 300–360 nm and the VIS-ESA in the 500–670 nm range (Figure 6b). No stimulated emission (SE) is observed, in contrast to the time-resolved fluorescence data, most likely due to the intense VIS-ESA that obscures the negative SE signal. After 20 ps, all transient signals have decayed to $\approx 10\%$ of their initial amplitude, but a long-lived, low-amplitude, positive signal persists to the longest measured delays (800 ps, Figure 6c). Note that the GSB signal reaches zero within the tens-of-ps range. Clearly, the long-lived ESA showcases a different process in **C2** dynamics than in **C1** (Figure 6c). The **C2** data can be described by a 4-component exponential decay. Global fitting (Figure S26) yields decay time components of 380 fs, 5.2 ps, 42 ps, and 1.2 ns. Comparison of the decay-associated differential spectra (DADS) obtained for **C1** and **C2** suggests the presence of two parallel decay pathways. Some excitation populates the classical $^1\text{MLCT}$ state, with the 380 fs decay time corresponding to a subsequent ultrafast vibrational relaxation. The 5.2 ps time component is assigned to the $^3\text{MLCT}$ decay of **C2**, since its DADS closely resembles that of **C1** (see ESI). The assignment of the intermediate 42-ps time constant is not straightforward. The GSB and ESA signatures in the 42-ps DADS (Figure S26) suggest the population of a ^3MC state, such that the excitation of the $^1\text{MLCT}$ state would lead to the classical reaction scheme $^1\text{MLCT} \xrightarrow{380 \text{ fs}} ^3\text{MLCT} \xrightarrow{5.2 \text{ ps}} ^3\text{MC} \xrightarrow{42 \text{ ps}} S_0$, but it might also be related to short-lived emissive excited states, which contribute to the 160-ps component in the fluorescence DAS (Figure 5b). Since the GSB is almost zero after the decay of the $^3\text{MLCT}$, the 1.2 ns decay component must belong to states of a different parallel relaxation pathway. The obvious candidate is the S_1 - S_0 transition giving rise to the 1.2-ns fluorescence decay component (Figure 5). Note that a ΔA spectrum without a GSB component indicates that it is covered by a positive ESA of larger amplitude. Unfortunately, this prevents us from evaluating the amount of GSB and hence the relative population of the singlet low-energy CT state. Since the maximum delay is limited to ≈ 1 ns, it was not possible to explore the longer lifetimes revealed in the time-resolved fluorescence.

Rationalising the excited states dynamics and the suppressed intersystem crossing

In the above TAS experiments on **C2**, excitation with a ≈ 30 nm (FWHM) broad pulse centred at 520 nm gives rise to both a long-lived singlet CT state, identified by the time-resolved fluorescence, as well as to the conventional $^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^3\text{MC} \rightarrow S_0$ deactivation cascade, occurring on timescales of 0.38 ps, 5.2 ps, and 42 ps. Indeed, just above S_1 , only 10–20 meV higher in energy, two LC/MLCT/LLCT excited states are predicted (left panel of Figure S30, ESI), primarily arising from $\text{HOMO} \rightarrow \text{LUMO}+2$ (S_2) and $\text{HOMO} \rightarrow \text{LUMO}+3$ (S_3) transitions. The S_4 ($\text{HOMO} \rightarrow \text{LUMO}+1$) transition, calculated to lie only 70 meV higher in energy, is also covered by the 200 meV spectral width of the laser

pulse. As the calculated energy differences among these four states are significantly smaller than the intrinsic TDDFT uncertainty (0.15–0.20 eV),⁴² all are considered in the following discussion to rationalize the excited-state dynamics.

For **C2**, and in the Franck–Condon region, ten triplet states are calculated to lie below the four lowest energy singlet states considered here, with different degrees of LC, MC, MLCT, LLCT, and ligand-to-metal CT (LMCT) contributions (Figure S30). A first qualitative observation is that, as a direct consequence of the *HOMO inversion* in **C2**, the low-energy triplet states exhibit a predominance of LC character over MLCT (Figure S30). In particular, states T_1 , T_2 , T_5 , and T_6 display up to ~80% ligand-centered character. This reduced metal contribution leads to relatively small, calculated SOC values (Tables S7), which are overall notably lower than those predicted for **C1** (Tables S9).

Focusing on the highest-energy triplet states, T_9 and T_{10} , featuring a mixed MC/MLCT/LC nature and lying sufficiently close in energy to the singlet manifold to enable efficient population transfer, an interesting difference appears among the four low-lying singlet states regarding the predicted SOC values. Notably, S_1 and S_4 show negligible SOC values with these triplet states (1–2 cm^{-1} ; Table S7), suggesting that ultrafast singlet-triplet ISC from these states is effectively suppressed. By contrast, S_2 and S_3 exhibit quite large SOC values (~80 cm^{-1} ; Table S7) with the nearby triplet state T_{10} , suggesting that, upon S_2/S_3 population, efficient ISC may occur on an ultrafast timescale, which explains the $^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^3\text{MC} \rightarrow S_0$ deactivation cascade observed in TAS.

Furthermore, upon structural relaxation to the S_1 minimum, five triplet states are predicted to be lower in energy than S_1 , with one predominantly MC state (T_6) becoming nearly degenerate with S_1 (right panel of Figure S30). Even at this geometry, however, the calculated SOC values remain modest, with the highest values amounting to 46 cm^{-1} and 40 cm^{-1} for T_4 and T_6 , respectively (see Table S8), indicating that the ISC rate remains relatively inefficient even at the S_1 minimum, as it scales with the square of the SOC.

The calculated SOC values thus provide strong evidence for the unusual excited-state dynamics in **C2**, corroborating the experimental observation of two parallel relaxation pathways: excitation to the LUMO and LUMO+1 (S_1/S_4) gives rise to the long-lived component observed in transient absorption and fluorescence experiments, while the S_2/S_3 states ($\text{HOMO} \rightarrow \text{LUMO}+2$ and $\text{HOMO} \rightarrow \text{LUMO}+3$) follow a conventional ultrafast ISC pathway to the triplet manifold, ultimately leading to population of ^3MC states, as shown in Figure S32 and discussed in ESI.

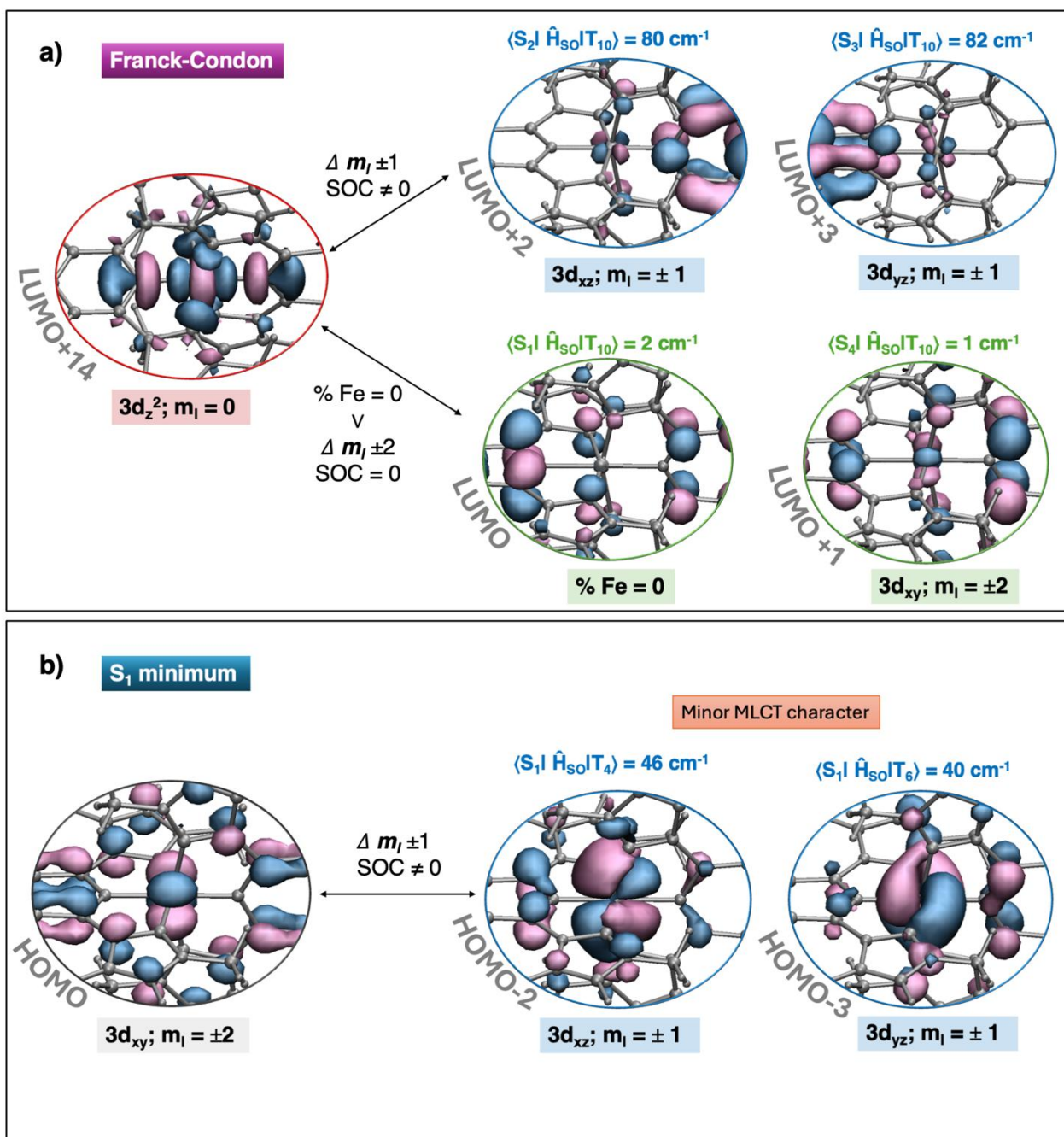


Figure 7. Zoomed-in view of the molecular orbitals involved in spin–orbit coupling (SOC) between the low-lying singlet and triplet states of **C2**, shown in the Franck–Condon region (a) and at the S_1 minimum (b). The allowed or forbidden nature of the SOC is determined by the change in the magnetic quantum number (m_l) of the Fe $3d$ orbitals contributing to the one-electron spin–orbit operator integral (see Section 8.3 in the ESI for details).

However, qualitative considerations of the character of the four low-lying singlet states, all involving excitations between orbitals with only modest or negligible metal contribution, are not sufficient to fully rationalize the differences in the calculated SOC. Indeed, it is necessary to examine the electronic configurations and molecular orbitals coupled through the spin–orbit operator. Since we adopt a simple one-electron spin–orbit Hamiltonian with effective nuclear charges,^{43,44} coupling is restricted to singlet and triplet configurations differing by at most one orbital, in accordance with the Slater–Condon rules.⁴⁵ Thus, among the configurations contributing to T_{10} (Table S7), only the MC HOMO→LUMO+14 configuration can couple to the lowest singlet states (S_1 to S_4), as they share the same hole orbital (HOMO). It is therefore necessary to evaluate the matrix elements of the spin–orbit operator between the orbitals that differ, namely between LUMO+14 and LUMO, LUMO+1, LUMO+2, and LUMO+3, respectively. Within this approximation, in the idealized limit of a free Fe ion, the SOC is dominated by the integrals of the three components of the angular momentum $\vec{l}$ between the two $3d$ Fe atomic orbitals. These matrix elements are non-zero only when the two orbitals are identical (l_z operator) or when their magnetic quantum numbers differ by one ($\Delta m_l = \pm 1$, corresponding to the l_x and l_y operators). Given that d_{z^2} has $m_l=0$, d_{xz} and d_{yz} are linear combinations of d_1 and d_{-1} ($m_l=\pm 1$), while $d_{x^2-y^2}$ and d_{xy} are linear combinations of d_2 and d_{-2} ($m_l=\pm 2$) (see section 8.3. in ESI for more details), one can note that the integrals involving d_{xy} vanish with d_z^2 . The

same can easily be verified also in the reduced D_{2d} symmetry, the SOC integrals of the I_x and I_y operators (e symmetry) involving the d_{xy} (b_2 symmetry) and d_z^2 (a_1 symmetry) orbitals are zero. As a consequence, and as displayed in Figure 7a, for S_1 , the absence of iron character in the LUMO (being strictly zero in the D_{2d} symmetry) results in vanishing SOC with the MC state. For S_4 , the Fe $3d$ projections of LUMO+1 (predominantly d_{xy}) and LUMO+14 (predominantly d_z^2), show that the coupling is symmetry-forbidden and therefore expected to be vanishingly small, even when accounting for the pseudo- D_{2d} symmetry of the complex. In contrast, SOC between S_2/S_3 and T_{10} is symmetry-allowed, as LUMO+2 and LUMO+3 have d_{xz} and d_{yz} character. On the other hand, for **C1**, the LUMO possesses Fe $3d_{xz}$ character (Figure 4b), enabling S_1 to couple with the closest-energy triplet T_4 (SOC $\approx 130\text{ cm}^{-1}$, Table S9) via a metal-centred configuration involving excitation from the HOMO to the Fe $3d_z^2$ orbital (LUMO+6).

A similar analysis can be performed at the equilibrium geometry of the $^1\text{MLCT}$ state (Figure S30 and Table S8), where six triplet states of primarily LC (T_1 , T_2 , T_3 , and T_5) and MC (T_4 and T_6) character lie below S_1 . The electronic configurations of T_6 and T_4 that can couple with S_1 (HOMO $\rightarrow$ LUMO) are the two MLCT excitations HOMO $\rightarrow$ 3 $\rightarrow$ LUMO in T_6 ($\approx 13\%$) and HOMO $\rightarrow$ 2 $\rightarrow$ LUMO in T_4 ($\approx 11\%$) (Table S8), as they differ by only one orbital. In this case, as displayed in Figure 7b, the relevant matrix elements involve the SOC operator between the HOMO and HOMO $\rightarrow$ 3 or HOMO $\rightarrow$ 2 orbitals, respectively. As these transitions involve the Fe $3d_{xy}$ orbital ($m_l = \pm 2$) in the HOMO and the $3d_{xz}/3d_{yz}$ orbitals ($m_l = \pm 1$) in HOMO-2/HOMO-3 of e symmetry, the coupling is symmetry-allowed. Nevertheless, the small weight of these MLCT configurations in the triplet states and the modest Fe content in the HOMO result in relatively modest calculated SOC values.

Discussion

The incorporation of NHC-fused π -extended azaullazine ligands, featuring high-energy π -donor and low-energy π^* acceptor orbitals, enables precise tuning of the frontier orbital manifold in the Fe(II)–NHC complex **C2**. The unusual electronic structure and the associated optical and photophysical properties of **C2** originate from two fundamental characteristics of the azaullazine–NHC framework: the energetic positioning and the symmetry of its frontier molecular orbitals. The π HOMO of the ligand lies relatively high in energy with respect to the Fe t_{2g} manifold. As a result, the in-phase combination (b_2 symmetry in D_{2d}) of the two tridentate ligand molecular orbital interacts only weakly with Fe $3d_{xy}$, resulting in a HOMO with only 30% metal character. In contrast, the out-of-phase combination (a_2 symmetry) is symmetry-forbidden from interacting with the Fe $3d$ manifold, giving rise to a fully ligand-centered HOMO $\rightarrow$ 1 and thus to *HOMO inversion*. Furthermore, the extended π -conjugation of the azaullazine ligand in **C2** induces an energetic reordering of the ligand-based virtual orbitals with respect to the pyrrole-substituted ligand of **C1**, leading in the complex to *LUMO inversion*, where the symmetry and topology of the LUMO and LUMO+1 (a_2 and b_1 , respectively) mirror those of the HOMO $\rightarrow$ 1 and HOMO. This frontier orbital arrangement gives rise to intense, broad UV–vis absorption, with mixed MLCT, LC and LLCT excitations, and suppresses otherwise efficient MLCT $\rightarrow$ MC deactivation pathways from the lowest-energy singlet state. Spin–orbit coupling calculations and excited-state relaxation analyses confirm, indeed, that ISC and subsequent MC-mediated quenching are strongly suppressed, in the Franck-Condon region, for HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 excitations due to symmetry-based selection rules. Notably, even at the $^1\text{MLCT}$ (S_1) minimum, the calculated spin–orbit couplings remain modest owing to *HOMO inversion*, which decreases the MLCT character of the lowest-lying singlet and triplet excited states. As a result, **C2** exhibits fluorescence with an average excited-state lifetime of $3.5 \pm 0.5\text{ ns}$ and a quantum yield (Φ_F) of 1.5%, representing record values for Fe(II) complexes and addressing a long-standing limitation for their photocatalytic applications. However, the overall fluorescence efficiency and most likely also the photocatalytic performance of **C2** are presently limited by the fact that higher-energy states, involving LUMO+2 and LUMO+3 (e symmetry), remain accessible to ISC and that they follow the conventional, non-productive MLCT $\rightarrow$ MC pathway.

This behaviour contrasts sharply with previously reported systems in which a conjugated chromophore (e.g., pyrene or anthracene) was covalently linked, without fusion to the pyridine ring, as in azaullazine, to a similar Fe–NHC complex.⁴⁶ In those cases, the resulting complexes exhibited room-temperature luminescence with excited-state lifetimes on the nanosecond timescale. However, the emission originated from an internal conversion process from the chromophore singlet state to the $^1\text{MLCT}$ state of the complex, without suppressing the subsequent deactivation pathway involving $^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^3\text{MC}$, hence limiting Φ_F . In contrast, in **C2**, this decay cascade is effectively inhibited, for the lowest energy singlets.

Overall, these results establish the benefits of the *HOMO inversion* strategy and introduce the concept of *LUMO inversion* as a synergistic design principle, highlighting the role of symmetry-adapted combinations of azaullazine π^* orbitals in stabilizing long-lived, electronically robust $^1\text{MLCT}$ states. Suppression of non-radiative decay pathways can be further achieved either by increasing the number of π^* orbitals with appropriate symmetry or by widening the energetic separation between the LUMO/LUMO+1 manifold and higher-lying e -symmetry orbitals. Beyond reinforcing the *HOMO inversion* framework, this work identifies the symmetry of low-lying unoccupied molecular orbitals as a critical descriptor and establishes transferable structure–property relationships for the rational design of next-generation transition-metal photocatalysts.

References

1. Housecroft, C. E. & Constable, E. C. Solar energy conversion using first row d-block metal coordination compound sensitizers and redox mediators. *Chem. Sci.* **13**, 1225–1262 (2022).
2. Sinha, N., Wegeberg, C., Häussinger, D., Prescimone, A. & Wenger, O. S. Photoredox-active Cr(0) luminophores featuring photophysical properties competitive with Ru(II) and Os(II) complexes. *Nat. Chem.* **15**, 1730–1736 (2023).
3. Sinha, N. & Wenger, O. S. Photoactive Metal-to-Ligand Charge Transfer Excited States in 3d⁶ Complexes with Cr⁰, Mn^I, Fe^{II}, and Co^{III}. *J. Am. Chem. Soc.* **145**, 4903–4920 (2023).
4. Pastore, M., Caramori, S. & Gros, P. C. Iron-Sensitized Solar Cells (FeSSCs). *Acc. Chem. Res.* **57**, 439–449 (2024).
5. Monat, J. E. & McCusker, J. K. Femtosecond Excited-State Dynamics of an Iron(II) Polypyridyl Solar Cell Sensitizer Model. *J. Am. Chem. Soc.* **122**, 4092–4097 (2000).
6. Auböck, G. & Chergui, M. Sub-50-fs photoinduced spin crossover in [Fe(bpy)₃]²⁺. *Nat. Chem.* **7**, 629–633 (2015).
7. Smeigh, A. L., Creelman, M., Mathies, R. A. & McCusker, J. K. Femtosecond Time-Resolved Optical and Raman Spectroscopy of Photoinduced Spin Crossover: Temporal Resolution of Low-to-High Spin Optical Switching. *J. Am. Chem. Soc.* **130**, 14105–14107 (2008).
8. Cammarata, M. *et al.* Sequential Activation of Molecular Breathing and Bending during Spin-Crossover Photoswitching Revealed by Femtosecond Optical and X-Ray Absorption Spectroscopy. *Phys. Rev. Lett.* **113**, 227402 (2014).
9. Wenger, O. S. Is Iron the New Ruthenium? *Chem. – Eur. J.* **25**, 6043–6052 (2019).
10. Lindh, L. *et al.* Photophysics and Photochemistry of Iron Carbene Complexes for Solar Energy Conversion and Photocatalysis. *Catalysts* **10**, 315 (2020).
11. Satheesh, L. N., Achilleos, K., Abudayyeh, A. M. & Troian-Gautier, L. Challenges and Opportunities in the Use of Iron Photosensitizers for Dye-Sensitized Solar Cells and Photoelectrosynthetic Cells Applications. *EcoEnergy* **3**, e70001 (2025).
12. Liu, Y., Persson, P., Sundström, V. & Wärnmark, K. Fe N-Heterocyclic Carbene Complexes as Promising Photosensitizers. *Acc. Chem. Res.* **49**, 1477–1485 (2016).

13. Leis, W., Argüello Cordero, M. A., Lochbrunner, S., Schubert, H. & Berkefeld, A. A Photoreactive Iron(II) Complex Luminophore. *J. Am. Chem. Soc.* **144**, 1169–1173 (2022).
14. Liu, Y. *et al.* Towards longer-lived metal-to-ligand charge transfer states of iron(II) complexes: an N-heterocyclic carbene approach. *Chem. Commun.* **49**, 6412 (2013).
15. Liu, L. *et al.* A new record excited state ³ MLCT lifetime for metalorganic iron(II) complexes. *Phys Chem Chem Phys* **18**, 12550–12556 (2016).
16. Darari, M. *et al.* Iron(II) complexes with diazanyl-NHC ligands: impact of π -deficiency of the azine core on photophysical properties. *Dalton Trans.* **48**, 10915–10926 (2019).
17. Lindh, L. *et al.* Dye-sensitized solar cells based on Fe N-heterocyclic carbene photosensitizers with improved rod-like push-pull functionality. *Chem. Sci.* **12**, 16035–16053 (2021).
18. Reddy-Marri, A. *et al.* Panchromatic light harvesting and record power conversion efficiency for carboxylic/cyanoacrylic Fe(II) NHC co-sensitized FeSSCs. *Chem. Sci.* **14**, 4288–4301 (2023).
19. Shalhoub, N. *et al.* Tuning the electronic properties of Fe(II)–NHC sensitizers with thienyl π -extended ligands. *Dalton Trans.* **54**, 17662–17673 (2025).
20. Chábera, P. *et al.* Fe^{II} Hexa *N* -Heterocyclic Carbene Complex with a 528 ps Metal-to-Ligand Charge-Transfer Excited-State Lifetime. *J. Phys. Chem. Lett.* **9**, 459–463 (2018).
21. Chábera, P. *et al.* A low-spin Fe(III) complex with 100-ps ligand-to-metal charge transfer photoluminescence. *Nature* **543**, 695–699 (2017).
22. Leis, W., Argüello Cordero, M. A., Lochbrunner, S., Schubert, H. & Berkefeld, A. A Photoreactive Iron(II) Complex Luminophore. *J. Am. Chem. Soc.* **144**, 1169–1173 (2022).
23. Mukherjee, S., Torres, D. E. & Jakubikova, E. HOMO inversion as a strategy for improving the light-absorption properties of Fe(II) chromophores. *Chem. Sci.* **8**, 8115–8126 (2017).
24. Braun, J. D., Lozada, I. B. & Herbert, D. E. In Pursuit of Panchromatic Absorption in Metal Coordination Complexes: Experimental Delineation of the HOMO Inversion Model Using Pseudo-Octahedral Complexes of Diarylamido Ligands. *Inorg. Chem.* **59**, 17746–17757 (2020).

25. Braun, J. D. *et al.* Iron(II) coordination complexes with panchromatic absorption and nanosecond charge-transfer excited state lifetimes. *Nat. Chem.* **11**, 1144–1150 (2019).
26. Marri, A. R., Marekha, B., Penfold, T., Haacke, S. & Gros, P. C. Towards panchromatic Fe(II) NHC sensitizers via HOMO inversion. *Inorg. Chem. Front.* **10**, 118–126 (2023).
27. Larsen, C. B. *et al.* Reduction of Electron Repulsion in Highly Covalent Fe-Amido Complexes Counteracts the Impact of a Weak Ligand Field on Excited-State Ordering. *J. Am. Chem. Soc.* **143**, 20645–20656 (2021).
28. Reinhard, M. E. *et al.* Time-Resolved X-ray Emission Spectroscopy and Synthetic High-Spin Model Complexes Resolve Ambiguities in Excited-State Assignments of Transition-Metal Chromophores: A Case Study of Fe-Amido Complexes. *J. Am. Chem. Soc.* **146**, 17908–17916 (2024).
29. Skabeev, A. *et al.* Carbonyl-Functionalized Cyclazines as Colorants and Air-Stable *n*-Type Semiconductors. *Org. Lett.* **20**, 1409–1412 (2018).
30. Delcamp, J. H., Yella, A., Holcombe, T. W., Nazeeruddin, M. K. & Grätzel, M. The Molecular Engineering of Organic Sensitizers for Solar-Cell Applications. *Angew. Chem. Int. Ed.* **52**, 376–380 (2013).
31. Chia, Y. Y. & Tay, M. G. An insight into fluorescent transition metal complexes. *Dalton Trans* **43**, 13159–13168 (2014).
32. Housecroft, C. E. & Sharpe, A. G. *Inorganic Chemistry Fifth Edition*. (Pearson, 2018).
33. Ibrahim, D., Boulet, P., Gros, P. C. & Pierrat, P. Efficient Access to Arylated Aza-ullazines by Regioselective Functionalization of their Pyridine Ring by H–Li Exchange and Electrophilic Substitution. *Eur. J. Org. Chem.* **2021**, 3331–3339 (2021).
34. <https://www.organometallics.it/wp-content/uploads/2022/01/Solvent-Miscibility-and-Polarity-Chart.pdf>.
35. Girerd, J.-J., Boillot, M.-L., Blain, G. & Rivière, E. An EPR investigation of the electronic structure of pseudo-octahedral and spin crossover catecholato-iron(III) complexes in the low-spin state. *Inorganica Chim. Acta* **361**, 4012–4016 (2008).
36. Cerezo, J. *et al.* Non-Phenomenological Description of the Time-Resolved Emission in Solution with Quantum–Classical Vibronic Approaches—Application to Coumarin C153 in Methanol. *Molecules* **28**, 3910 (2023).

37. Segalina, A., Cerezo, J., Prampolini, G., Santoro, F. & Pastore, M. Accounting for Vibronic Features through a Mixed Quantum-Classical Scheme: Structure, Dynamics, and Absorption Spectra of a Perylene Diimide Dye in Solution. *J. Chem. Theory Comput.* **16**, 7061–7077 (2020).
38. Turro, N. J., Ramamurthy, V. & Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction*. (2009).
39. Chergui, M. & Collet, E. Photoinduced Structural Dynamics of Molecular Systems Mapped by Time-Resolved X-ray Methods. *Chem. Rev.* **117**, 11025–11065 (2017).
40. Cebrián, C. *et al.* Ultrafast Spectroscopy of Fe(II) Complexes Designed for Solar-Energy Conversion: Current Status and Open Questions. *ChemPhysChem* **23**, e202100659 (2022).
41. Lindh, L. *et al.* Photophysics and Photochemistry of Iron Carbene Complexes for Solar Energy Conversion and Photocatalysis. *Catalysts* **10**, 315 (2020).
42. Kaur, J., Ospadov, E. & Staroverov, V. N. What Is the Accuracy Limit of Adiabatic Linear-Response TDDFT Using Exact Exchange–Correlation Potentials and Approximate Kernels? *J. Chem. Theory Comput.* **15**, 4956–4964 (2019).
43. Heinemann, C., Koch, W. & Schwarz, H. An approximate method for treating spin-orbit effects in platinum. *Chem. Phys. Lett.* **245**, 509–518 (1995).
44. Marian, C. M. Spin–orbit coupling and intersystem crossing in molecules. *WIREs Comput. Mol. Sci.* **2**, 187–203 (2012).
45. Szabo, A. & Ostlund, N. S. *Quantum Chemistry Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theor.* (Dover, 1996).
46. Dierks, P. *et al.* Ground- and Excited-State Properties of Iron(II) Complexes Linked to Organic Chromophores. *Inorg. Chem.* **59**, 14746–14761 (2020).

Data availability

The data supporting this article have been included as part of the Supplementary Information.

Methods

General procedures

Solvents and commercially available reagents were used as received. NMR spectra were recorded on a DRX400 Bruker spectrometer at ambient temperature at 400MHz (^1H) and 100MHz ($^{13}\text{C}\{^1\text{H}\}$). All resonances are reported in ppm versus the solvent signal as an internal standard [CD_3CN (^1H : $\delta=1.94$ ppm), ($^{13}\text{C}\{^1\text{H}\}$: $\delta=1.3$ ppm, $\delta=118.3$ ppm)] and [CDCl_3 (^1H : $\delta=7.26$ ppm), ($^{13}\text{C}\{^1\text{H}\}$: $\delta=77.4$ ppm)]. Multiplicities are abbreviated as follows: (s) = singlet, (d) = doublet, (t) = triplet. High-resolution mass spectrometry (HRMS) data was obtained by using a Waters Xevo G2-XS Q-ToF spectrometer. UV-vis spectra were recorded in a 1 cm path length quartz cell on a LAMBDA 1050 (Perkin Elmer), spectrophotometer.

Electrochemistry was performed on a Metrohm Autolab PGStat100 potentiostat using a conventional three-electrode cell in glove box under argon atmosphere. Complexes were dissolved at 0.5 mM in acetonitrile containing 0.1 M Bu_4NPF_6 as supporting electrolyte. The reference electrode was Ag/Ag^+ in electrolytic solution (AgNO_3 10 mM) and the counter-electrode was a platinum wire. The working electrode was a commercial 3 mm-diameter glassy carbon disk for cyclic voltammetry, and a glassy carbon foam (of around 0.4 cm^3 and 80 ppi) for bulk electrolysis. After the measurement, ferrocene was added as the internal reference for calibration. All potentials were quoted versus Ag/Ag^+ . In these conditions the redox potential of the couple Fc^+/Fc was found at 0.084V. In all the experiments the scan rate was 100 mV/s.

In situ UV-visible spectrometry was performed with a Xenon lamp and a Avaspec detector from Avantes connected by optical fibers to a Hellma immersion probe with a pathlength of 1 mm. UV-vis-NIR spectra were recorded with a Perkin Elmer Lambda 1050 spectrometer in a 2 mm cuvette.

X-band EPR spectra were recorded at 100K with a EMX Plus Bruker spectrometer equipped with a ER4119HS Bruker cavity. All spectra presented were recorded under non-saturating conditions. EPR spectral simulation was carried out using Easyspin program.

Ab initio calculations

Optimized geometries of **C1** and **C2** in their ground-state low-spin singlet electronic configuration (S_0) and lowest energy singlet excited state (S_1) were obtained at the density functional theory (DFT) and time-dependent DFT (TDDFT) levels, respectively, using the 6-311G** basis set and the modified B3LYP* exchange–correlation functional, which contains 15% of non-local Hartree-Fock exchange. This approach has been successfully applied to the description of excited states in Fe(II) complexes.^{47,48} Solvent effects (acetonitrile) were included via the conductor-like polarizable continuum model (C-PCM),^{49,50} as implemented in Gaussian16.⁵¹

Simulated steady-state absorption spectra were obtained by convoluting the 80 lowest-energy singlet TDDFT vertical transitions at the S_0 optimized structures (Franck-Condon region) with Gaussian functions of 0.17 eV full width at half maximum. Low-lying triplet states were computed by TDDFT at the B3LYP*/6-311G**/ACN level at both the ground-state S_0 (Franck-Condon region) and the S_1 -optimized geometries. To achieve a reliable assignment of the lowest-lying excited states, the one-particle transition density matrix was analysed with the TheoDOR package⁵² at the Franck-Condon geometry (S_0) and at the optimized S_1 minimum. This enabled us to determine the nature of the electronic excitations and to map the hole (h^+) and electron (e^-) distributions across the different fragments of the complex. For each model system, the spin-orbit coupling (SOC) matrix elements, $\langle S_n | \hat{H}_{\text{SO}} | T_m \rangle$, were evaluated at the S_0 and S_1 equilibrium geometries using the Breit-Pauli spin-orbit Hamiltonian with effective charge approximation, as implemented in the PySOC.⁵³

Steady-state absorption and fluorescence spectroscopy

Absorption spectra were recorded on an Analytik Jena Specord UV-VIS spectrometer with a spectral bandwidth and step size of 1 nm. Measurements were performed in a Hellma quartz cuvette with an optical path length of 10 mm. Fluorescence emission spectra were acquired using an Edinburgh FLS1000 spectrofluorometer, with excitation and emission slit widths set to 6 and 2 nm, respectively. The integration time was chosen to be 0.5 s, and two scanned spectra were averaged. Emission data were corrected for the detector's wavelength-dependent sensitivity using the corresponding correction file, and the detector's dark count rates.

Transient Absorption spectroscopy

The experimental setup for transient absorption spectroscopy (TAS) used to study the C1 and C2 complexes consists of a 5 kHz Ti:Sapphire regenerative amplifier that produces an 800 nm pulse with a 40 fs duration. This pulse goes through a beam splitter to generate the pump and probe beams. One of the beams is focused on a 2mm oscillating CaF_2 crystal to create the supercontinuum probe beam, which extends from 300 to 700 nm. The pump beam is generated via the commercial optical parametric amplifier TOPAS (Light Conversion). The sum-frequency generation arrangement is then used to produce the pump beam peaking at 520 nm with a 10-nm FWHM and a pulse duration of between 60 and 80 fs. The pump power is reduced so that the transient absorption signal stays in the linear-excitation regime. The pump and probe beams are then focused with a spot size of approximately 60 and 30 μm FWHM, respectively, into the 1-mm Hellma quartz cuvette containing the sample. Their linear polarizations are set to form a 54.7-degree angle (magic angle). Data sets are recorded for different spectrometer configurations corresponding to the spectral windows in the UV (300-420 nm) and in the Vis (350-700 nm) regions. For each sample, the corresponding solvent artifacts due to the pump-probe overlap around the zero-time delay are recorded using the same cuvette with only the solvent. This allows for the removal of these signals during the treatment of the raw data. The treatment consists of removing the above-mentioned solvent signal, merging the UV and Vis data sets, and correcting for the group velocity dispersion in the probe signal over the full spectral window. Quantitative analysis of the data is done by performing a fit with a multi-exponential function convolved with

a Gaussian function accounting for the instrument response. The global fit is carried out using a Python implementation of the VARPRO algorithm, allowing for minimizing the residuals.^{54,55}

Picosecond Fluorescence Spectroscopy

We used a Hamamatsu C10627 streak camera with 10 ps time resolution (fast single sweep unit), in photon counting mode, coupled to a 25-cm focal length Jobin-Yvon spectrograph (spectral resolution 5 nm).⁵⁶ Excitation pulses at 515 nm (0.3 ps duration, 100 kHz) were produced by frequency doubling the 1030nm fundamental of a Yb:fiber laser (Tangerine, Amplitude). The excitation density was typically $\leq 50 \mu\text{J}/\text{cm}^2$. The linear polarisation of the excitation beam was oriented at magic angle with respect to the one of an analyser placed in front of the spectrograph. Multi-exponential fits of the fluorescence decay kinetics are carried out with the same home-made Python software, used for the TAS data (see above).

References

47. Fredin, L. A. *et al.* Exceptional Excited-State Lifetime of an Iron(II)– *N* -Heterocyclic Carbene Complex Explained. *J. Phys. Chem. Lett.* **5**, 2066–2071 (2014).
48. Francés-Monerris, A., Gros, P. C., Assfeld, X., Monari, A. & Pastore, M. Toward Luminescent Iron Complexes: Unravelling the Photophysics by Computing Potential Energy Surfaces. *ChemPhotoChem* **3**, 666–683 (2019).
49. Barone, V. & Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **102**, 1995–2001 (1998).
50. Cossi, M., Rega, N., Scalmani, G. & Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* **24**, 669–681 (2003).
51. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
52. Plasser, F. TheoDORE: A toolbox for a detailed and automated analysis of electronic excited state computations. *J. Chem. Phys.* **152**, 084108 (2020).

53. Gao, X. *et al.* Evaluation of Spin-Orbit Couplings with Linear-Response Time-Dependent Density Functional Methods. *J. Chem. Theory Comput.* **13**, 515–524 (2017).
54. O’Leary, D. P. & Rust, B. W. Variable projection for nonlinear least squares problems. *Comput. Optim. Appl.* **54**, 579–593 (2013).
55. Tkach, O. *et al.* Exploring excited-state proton transfer reactions in isothiazologuanosine, an isofunctional fluorescent analogue of guanosine. *Phys. Chem. Chem. Phys.* **27**, 19820–19836 (2025).
56. Jouaiti, A. *et al.* Binuclear Copper(I) Complexes for Near-Infrared Light-Emitting Electrochemical Cells. *Angew. Chem. Int. Ed.* **62**, e202305569 (2023).

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Competing interests

The authors declare no competing interests.

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