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Electronic Supplementary Information for "Ultrafast ³MLCT quenching and vibrational coherence: excited-state dynamics of the first-discovered Fe(II)-carbene sensitiser resolved"

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Contents

S1 Methodological Details	2
S2 Model Parameters	5
S3 Supplementary Results	6

S1 Methodological Details

Similarly to our previous study on the $[Fe(terpy)_2]^{2+}$ complex¹ (terpy = 2,2':6',2"-terpyridine), the methodology utilised in this work is based on full-dimensional trajectory surface hopping (TSH). We carried out the TSH simulations both on linear vibronic coupling²⁻⁴ (LVC) and on-the-fly potential energy surfaces.

The LVC potential, which is based on the harmonic oscillator approximation and normal modes, is calculated as:

$$V^{(\alpha\alpha)} = \varepsilon^{(\alpha)} + \sum_{i} \kappa_{i}^{(\alpha)} q_{i} + \frac{1}{2} \sum_{i} \hbar \omega_{i} q_{i}^{2}$$
(1)

$$V^{(\alpha\beta)} = \sum_{i} \lambda_i^{(\alpha\beta)} q_i + s^{(\alpha\beta)} , \qquad (2)$$

Equation 1 defines the diagonal terms; here $\varepsilon^{(\alpha)}$ is the vertical excitation energy at the FC geometry for electronic state α , q_i the normal mode coordinate for mode i, $\kappa_i^{(\alpha)}$ the linear diagonal coupling constants, ω_i the ground-state vibrational frequencies, and \hbar the reduced Planck constant. Equation 2 defines the off-diagonal part with $\lambda_i^{(\alpha\beta)}$ being the vibronic coupling constants, and $s^{(\alpha\beta)}$ the SOC matrix elements. While the $\lambda_i^{(\alpha\beta)}$ coupling constants are calculated by overlaps of electronic wave functions, and the resulting vibronic term is linearly dependent on the given normal mode coordinate q_i , the $s^{(\alpha\beta)}$ SOCs are obtained directly by quantum chemistry at the ground-state equilibrium geometry, and are taken to independent on the nuclear geometry. The inclusion of SOC into the LVC model leads to the construction of the spin-vibronic⁵ Hamiltonian matrix defined in Equations 1 and 2.

The parameters of our model are given in Section S2, Table S1 and in the provided supplementary data files.

The quantum chemistry calculations were performed at the density functional theory (DFT)/time-dependent (TD-DFT) level of theory based on the B3LYP^{*6} exchangecorrelation functional and the TZVP basis set. The B3LYP^{*} functional was chosen for its known accuracy for the excited-state energetics of Fe complexes^{1,7-9} Two-electrons integrals were approximated using the resolution-of-identity RI-J¹⁰ and RIJCOSX¹¹ methods. In all TD-DFT calculations, we utilised the Tamm-Dancoff approximation (TDA).¹² The SOC matrix elements were calculated using an approach based on second-quantised spin operators and SOC integrals written in a spherical basis.¹³ In these SOC calculations we applied a mean-field/effective potential SOC operator.¹⁴ We did not include solvation in the calculations, as it was found for the studied [Fe(bmip)₂]²⁺ complex (bmip = 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine) by the C-PCM method¹⁵ that solvation (using acetonitrile as solvent) does not have any significant effect on the excited-state energetics.¹⁶ All DFT/TD-DFT calculations were carried out using the ORCA5.0 implementations.^{17,18}

Our TSH methodology is based on Tully's fewest switches¹⁹ a three-step propagator technique,²⁰ and local diabatisation.^{21,22} The TSH simulations were carried out in the

diagonal basis, which is obtained by the diagonalisation of the molecular Coulombic Hamiltonian (MCH) of quantum chemistry, in which the SOCs appear as off-diagonal elements. The ground state ensemble is constructed as a Wigner distribution, leading to initial geometries and velocities. These initial conditions were then filtered for excitation from the ground state to the singlet excited states using a stochastic algorithm taking into account the oscillator strengths and excitation energies; for the latter, we used the 2.506-2.606 eV (485 nm excitation) and 3.050-3.150 eV (400 nm excitation) energy windows to select the initial state. 267/279 trajectories (for 485/400 nm excitation) were propagated for 4 ps, for the LVC case, and 100 trajectories for 200 fs, for the full on-the-fly case. In all TSH simulations, we used nuclear and electronic time steps of 0.5 fs and 0.005 fs, recpectively. We utilised the energy-based decoherence correction method 23,24 of Granucci *et al.* with a decoherence parameter of 0.1 a.u. The full on-the-fly TSH simulations were carried out for the 485 nm excitation case. All TSH simulations were performed using the SHARC2.1 implementation.²⁵⁻²⁷

The TSH simulations lead to electronic populations corresponding to the diagonal and adiabatic (spin-diabatic = MCH) representations, the latter being the standard basis of quantum chemistry. However, the electronic character in these bases varies as function of the nuclear geometry, which is undesirable for following electronic relaxation. We thus transformed the populations to the diabatic basis according to ref. 28:

$$P_{\rm diab}^{(\alpha)}(t) = [\boldsymbol{U}^{\dagger}(t)\boldsymbol{P}_{\rm ad}(t)\boldsymbol{U}(t)]_{\alpha\alpha} , \qquad (3)$$

where P_{ad} and P_{diab} are the adiabatic (spin-diabatic) and diabatic population matrices, respectively, and U is the transformation matrix that diagonalises the diabatic potential matrix to yield the adiabatic one:

$$\boldsymbol{V}_{\mathrm{ad}} = \boldsymbol{U}^{\dagger} \boldsymbol{V}_{\mathrm{diab}} \boldsymbol{U} , \qquad (4)$$

with the diabatic potential matrix $V_{\text{diab}} = V$ defined by Equations 1 and 2. This diabatisation procedure leads to the populations shown in Figs. 3 and 4 of the main article, with the populations corresponding to the same spin multiplicity and electronic character summed up (¹MLCT, ¹MC, ³MLCT, ³MC). We note that the Franck-Condon (FC) reference states can clearly be classified as MLCT or MC, based on the dominant electronic character.

The normal mode activity displayed in Fig. 5 of the main article was calculated as the standard deviation of nuclear displacements according to:

$$\sigma_i = \sqrt{\frac{1}{N_{\text{traj}}N_{\text{step}}} \sum_{j=1}^{N_{\text{traj}}} \sum_{k=1}^{N_{\text{step}}} q_{i,j}^2(k\Delta t) - \left(\frac{1}{N_{\text{traj}}N_{\text{step}}} \sum_{j=1}^{N_{\text{traj}}} \sum_{k=1}^{N_{\text{step}}} q_{i,j}(k\Delta t)\right)^2, \quad (5)$$

where $q_{i,j}$ are the dimensionless mass-frequency scaled normal mode coordinates, and j, k run over all trajectories and time steps, respectively.

In Fig. S1, we present the mode activity resulting from the simulation with 485 nm excitation.



Fig. S1: Normal mode activity of the $[Fe(bmip)_2]^{2+}$ complex excited at 485 nm; in parantheses, the frequency of dominant modes are given (in cm⁻¹). All dominant modes possess major Fe-N or Fe-C stretching character; ν_{55} and ν_{91} are deformation modes of the middle pyridine ring.

S2 Model Parameters

normal mode frequencies The ground-state are given $_{\rm in}$ the data file "normal_modes_freq.dat", both in eV and cm^{-1} . The frequency of the Fe-N breathing normal mode ν_{14} (where the indexing corresponds to increasing frequency, i.e., ν_1 is the lowest-frequency mode), which is used in Fig. 2 of the main article, is 110.61 cm^{-1} (0.014 eV). Animations of the normal modes discussed in the main article are given in animated gif format. The Franck-Condon (FC) geometry is given in Cartesian coordinates (Å) in the data file "FC.xyz".

Our model includes the singlet ground state (¹GS), plus 14 singlet and 18 triplet excited states; these numbers were chosen by including all excited states that are below 3.1+0.5 = 3.6 eV (3.1 eV = 400 nm, corresponding to the higher-energy excitation) at the FC geometry. The $\varepsilon^{(\alpha)}$ energies, as well as the state characters and oscillator strengths (for singlet excited states) of the DFT/TD-DFT electronic states (calculated at the FC geometry) are presented in Table S1. The $\varepsilon^{(\alpha)}$ (eV) values are also provided in the data file "epsilon.dat".

The linear coefficients $\kappa_i^{(\alpha)}$ and $\lambda_i^{(\alpha\beta)}$ are given in the data files "kappa.dat" and "lambda.dat", respectively (both in eV). The SOC matrix is given in the data file "SOC.dat" (in cm⁻¹) with state ordering as defined in Table S1; for the triplet spin components, we use the following ordering: T₁ ($m_S = -1$), T₂ ($m_S = -1$), ..., T₁₈ ($m_S = -1$), T₁ ($m_S = -0$), T₂ ($m_S = -0$), ..., T₁₈ ($m_S = 0$), T₁ ($m_S = +1$), T₂ ($m_S = +1$), ..., T₁₈ ($m_S = +1$).

We note that the $\varepsilon^{(\alpha)}$ energies given in Table S1 differ somewhat from those reported in our previous quantum dynamics (QD) study²⁹ on [Fe(bmip)₂]²⁺. This is because we used Gaussian09 in ref. 29 for the ground-state optimization, while in this work, it was ORCA5.0 (which was used for all electronic structure calculations in the present work). In order to verify that our QD results are not affected by this difference in the energetics, we repeated the QD simulations with shifting the ³MC states by +0.1 eV (which is the main difference between the "old"²⁹ and "new" energies given in Table S1, that could affect the ³MLCT-³MC dynamics), as well as using the energies given in Table S1 (noe that all other parameters of the Hamiltonian were unchanged). In Figure S2, we compare the obtained population dynamics to our original QD results. As is clear from the figure, the differences in the energetics do not have any significant effect on the simulated population dynamics.

The QD simulations were carried out using the Heidelberg multiconfiguration timedependent Hartree (MCTDH) QD software³⁰ utilising the Hamiltonian reported in ref. 29. 15 single particle functions (SPFs) were used for all ¹MLCT, ³MLCT, and ³MC states; for the ground state and ¹MC states, we used 2 SPFs (as these states do not play a role in the dynamics simulated at this level of theory). The QD simulations were initiated from a single component of the pair of lowest-lying ¹MLCT states that are degenerate at the FC geometry; this technique avoids artificial interference of relaxation pathways.³¹



Fig. S2: Effect of the utilised $\varepsilon^{(\alpha)}$ energies on the simulated population dynamics of $[Fe(bmip)_2]^{2+}$, as obtained from 4D QD simulations. Full lines – original energies from ref. 29, dashed lines – same, but all ³MC states shifted by +0.1 eV, dotted lines – energies from Table S1, this work.

S3 Supplementary Results

We analysed the diabatic populations for a representative set of 90 trajectories (400 nm excitation case). The purpose of this investigation was twofold: i) to check whether the ³MC states could also be populated directly from the ¹MLCTs (in addition to the ¹MLCT \rightarrow ³MLCT \rightarrow ³MC pathway), and ii) to inspect the mechanisms according to which the ground state is populated. Out of the 90 analysed trajectories, only one is indicative of a direct ¹MLCT \rightarrow ³MC pathway; this single case is illustrated in Fig. S3, which shows the diabatic populations of the trajectory. As this direct transition occurs very rarely (~1%) it is negligible.

The dominant pathway for populating the ³MC states is ¹MLCT \rightarrow ³MLCT \rightarrow ³MC; an example for this mechanism is shown in Fig. S4. As can be seen in this figure, the ground state is populated from the ³MC, which turned out to be the dominant mechanism (~90%)for populating ¹GS. The analysis of trajectories revealed that, as shown in Fig. S5, the ground state can also be populated from ³MLCT states, however, this pathway only appears as a minor component due its low occurrence (~10%)

Finally, in Fig. S6, we present the oscillations in the Fe-N/Fe-C bond lengths and



Fig. S3: The single case of a trajectory for the direct ¹MLCT \rightarrow ³MC pathway.



Fig. S4: Example trajectory for the ¹MLCT \rightarrow ³MLCT \rightarrow ³MC \rightarrow ¹GS pathway.

along the breathing mode ν_{14} for the 485 nm excitation case. These results are very similar to those obtained for the 400 nm excitation case, shown in Fig. 8 in the main article.



Fig. S5: Example trajectory for the ³MLCT \rightarrow ¹GS pathway.



Fig. S6: Average trajectories of $[Fe(bmip)_2]^{2+}$ along the Fe-N and Fe-C bond, as well as the breathing normal mode ν_{14} , as obtained from the simulation with 400 nm excitation.

Table S1: $\varepsilon^{(\alpha)}$ energies, electronic character, and oscillator strengths for excitation from the ground state of the DFT/TD-DFT electronic states calculated at the B3LYP*/TZVP level at the FC geometry.

State (character)	$\varepsilon^{(\alpha)}$ (eV)	Osc. strength
S_0 (¹ GS)	0.000	_
S_1 (¹ MLCT)	2.622	0.002
S_2 (¹ MLCT)	2.622	0.002
S_3 (¹ MLCT)	2.853	0.000
S_4 (¹ MLCT)	2.857	0.000
S_5 (¹ MC)	2.891	0.000
S_6 (¹ MC)	2.891	0.000
S_7 (¹ MLCT)	3.009	0.000
S_8 (¹ MLCT)	3.110	0.026
S_9 (¹ MLCT)	3.250	0.010
S_{10} (¹ MLCT)	3.250	0.010
S_{11} (¹ MC)	3.338	0.000
S_{12} (¹ MLCT)	3.343	0.258
S_{13} (¹ MLCT)	3.468	0.005
S_{14} (¹ MLCT)	3.468	0.005
T_1 (³ MC)	2.206	0.000
T_2 (³ MC)	2.206	0.000
T_3 (³ MC)	2.329	0.000
T_4 (³ MLCT)	2.495	0.000
T_5 (³ MLCT)	2.508	0.000
T_6 (³ MLCT)	2.508	0.000
T_7 (³ MLCT)	2.594	0.000
T_8 (³ MLCT)	2.718	0.000
T_9 (³ MLCT)	2.747	0.000
T_{10} (³ MC)	2.797	0.000
T_{11} (³ MLCT)	2.861	0.000
T_{12} (³ MC)	3.004	0.000
T_{13} (³ MC)	3.004	0.000
T_{14} (³ MLCT)	3.061	0.000
T_{15} (³ MLCT)	3.078	0.000
T_{16} (³ MLCT)	3.078	0.000
T_{17} (³ MLCT)	3.395	0.000
T_{18} (³ MLCT)	3.395	0.000

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