Covalency-Driven Preservation of Local Charge Densities in a Metal-to-Ligand Charge-Transfer Excited Iron Photosensitizer

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A. Chemicals and materials

$\text{K}_2[\text{Fe(bpy)}(\text{CN})_4]\cdot3\text{H}_2\text{O}$ was purchased from HetCat and used without further purification. For measurements in aqueous solution, the sample was dissolved in deionized water at a concentration of 100 mM. For the measurements of $[\text{Fe(bpy)}(\text{CN})_4]^{2-}$ in DMSO, the K$^+$ counter ions of the sample were exchanged with $[\text{N(C}_4\text{H}_9)_4]^+$ following the procedures by Schilt [1] and Toma and Takasugi [2]. The product of the ion exchange was then dissolved in DMSO (purchased from Sigma-Aldrich) at a concentration of 130 mM for the time-resolved experiments and 90 mM for the steady-state measurements.

B. Experimental methods

All data were recorded using the transmission flatjet endstation described by Fondell et al. [3]. In this setup, two colliding jets form a thin liquid sample sheet inside the experimental vacuum chamber [4]. The thickness of the sheet ranges from sub-$\mu$m to several $\mu$m as estimated from the comparison of the transmission before the absorption onset at 700 eV to tabulated values [5]. This allows for transmission experiments in the soft X-ray regime of transition metal L-edges [6], while simultaneously avoiding potential X-ray-induced sample damage [7]. The sample thickness during measurements amounted to 2.3 $\mu$m in DMSO and 2.2 $\mu$m in aqueous solution at flow rates of 1.6 and 2.0 ml/min, respectively. The X-ray intensity transmitted through the liquid sample is detected by an optically blind avalanche photodiode with an active area of 3x3 mm$^2$. The measurements were performed at the UE52-SGM beamline [8] located at BESSY II. The difference spectra and delay traces are measured by consecutively detecting pumped and unpumped X-ray intensity $I_p$ and $I_u$ originating from the hybrid bunch in the fill pattern of the synchrotron. Thereby, small jet instabilities are inherently accounted for. The difference spectra and their temporal evolution are then generated via $-\log (I_p/I_u)$ as function of energy and delay, respectively. Due to the small jet instabilities, the steady-state spectrum is measured separately. In this case, the signal of the full multi-bunch transmitted through the flatjet $I$ is detected using a gallium arsenide photodiode and compared to the signal of the direct beam $I_0$. The spectrum is then generated via $A = -\log_{10}[I/I_0]$ and corrected for solvent absorption by a linear fit of the spectrum before the absorption onset.
The synchrotron was operated in the Low-Alpha mode [9], where the temporally compressed electron bunches resulted in an experimental time-resolution of $(19 \pm 2) \text{ps FWHM}$ as determined from the instrument response function. The bandwidth of the X-ray radiation was 290 meV at 700 eV excitation energy. For the time-resolved measurements in DMSO, an optical parametric amplifier was used to generate the 680 nm excitation. The aqueous sample was excited at 515 nm using the second harmonic of a 1030 nm fiber laser. The repetition rate of the laser was set to 208 kHz for all measurements and the laser pulse length was approximately 300 fs. Laser fluences of 100 mJ/cm$^2$ were used for the 680 nm excitation and 200 mJ/cm$^2$ for 515 nm. The time-resolved difference spectra are averaged over 20 individual scans for measurements in DMSO and 12 for water. The delay traces in DMSO are averaged over 3 scans for the ground state depletion and 7 scans for the positive transient feature. Both delay traces in water are averaged over 2 scans. The steady-state spectra are averaged over 8 scans.

C. Time-resolved L-edge XAS of $[\text{Fe(bpy})(\text{CN})_4]^2^−$ in water

The solvent-dependent variation of the valence excited-state landscape can be clearly seen in Fig. 1, when comparing the shape of the transient $L_3$-edge absorption difference spectra of $[\text{Fe(bpy})(\text{CN})_4]^2^−$ in water and DMSO in panel c and d. The delay-dependent signals in water are simultaneously modeled with a single-exponential function on top of the appearance of a meta-stable intermediate. Thereby, a $(10 \pm 3) \text{ps}$ exponential decay is determined. This is in good agreement with the 13 ps lifetime of the $^3\text{MC}$ state previously determined by Kjær et al. with $K\beta$ emission and transient absorption spectroscopy [10]. The concomitant occurrence of an additional meta-stable signal in aqueous solution for delays beyond 30 ps is also consistent with previous findings. It has been reported that an aqueous environment facilitates the creation of solvated electrons via UV-photon-induced ionization of the complex [11]. The applied 515 nm laser fluence (see Experimental methods) is likely to facilitate such a process via two-photon absorption, which was also observed by Kjær et al. [10]. While the exponential decay can therefore be robustly assigned to the $^3\text{MC}$ state, its spectral signature overlaps with the transient spectrum of $[\text{Fe(bpy})(\text{CN})_4]^{1−}$ that is meta-stable within the measured delay range.
FIG. 1. Extension of Fig. 1 from the main text additionally showing the transient L$_3$-edge absorption spectra as well as the delay-dependent evolution of [Fe(bpy)(CN)$_4$]$^{2-}$ in aqueous solution in panel (c). The spectrum in water can be partly assigned to the formation of the $^3$MC as well as photo-oxidized [Fe(bpy)(CN)$_4$]$^{2-}$. The delay traces in water yield a $^3$MC lifetime of (10±3) ps on top of the occurrence of meta-stable [Fe(bpy)(CN)$_4$]$^{1-}$.

D. Computational details

All electronic structure and spectrum simulations were performed using the ORCA quantum chemistry package [12]. Geometries were optimized at the B3LYP level [13, 14] employing the all-electron def2-TZVP(-f) basis set [15]. Dispersion correction was utilized with the Becke-Johnson damping scheme [16, 17]. The resulting geometries were verified using frequency calculations. The solvent-effects of DMSO were approximated with the conductor-like polarizable continuum (CPCM) model [18]. To speed up the SCF iterations, the RIJCOSX method [19] was used with the def2-TZV/J auxiliary basis set [20]. Energies and intensities of core-excitations were calculated on the same level of theory using the restricted open shell configuration interaction singles (ROCIS) method with the parameters $c_1 = 0.18$, $c_2 = 0.20$ and $c_3 = 0.40$ [21]. All spectra are generated by convoluting the individual calculated core-excitations with a Voigt profile. The Voigt function entails a Gaussian
broadening of 0.3 eV to account for the bandwidth of the incident photons as well as a 1.5 eV Lorentzian lifetime broadening for best agreement with the experimental data. To account for the mismatch in energy between experiment and theory, shifts of 15.7 eV were applied to all spectra.

E. The Fe 2p → CN⁻ (2π⁺) resonance seen through DFT/ROCIS

Fig. 2a shows the theoretical spectra from the manuscript for an extended range including the L₂-edge. It can be observed that in the case of the ³MLCT state the Fe 2p → CN⁻ (2π⁺) resonance begins to overlap with the L₂-edge and almost fully merges with it in the case of the Fe(III) species. This is due to a combined effect of the systematic overestimation of the energy of the CN⁻ (2π⁺) resonance by DFT/ROCIS as well as an underestimation of the L₃ - L₂ splitting possibly caused by the perturbative treatment of spin-orbit coupling via the approximate spin-orbit mean field (SOMF) operator.[21]. We therefore turn to Fig. 2b, where the spectra from panel (a) are plotted without spin-orbit coupling. This has no significant effect on the relative shifts of the CN⁻ (2π⁺) resonance between the three species and thus allows for a more intuitive discussion.
As deduced for the case of ferrous and ferric hexacyanide, reducing the \( t_{2g} \) occupation is reflected in a decrease in intensity of the \( \text{Fe} \ 2p \rightarrow \text{CN}^- \ (2\pi^*) \) resonance as well as an increase in its energy\[22\]. This is reproduced by our calculations for both, the \( ^3\text{MLCT} \) as well as the Fe(III) species. Interestingly, the intensity of the resonance is the same for both species reflecting their shared \( t_{5g}^5 \) occupation. The resonance of the \( ^3\text{MLCT} \) state is however slightly lower in energy as in the case of the fully oxidized one, which thus can be attributed to the presence of the extra electron in the \( ^3\text{MLCT} \) state and the resulting different mixing of configurations in the CI expansion.

F. Radial electron density function calculation

The radial distribution functions were computed by carrying out a single point calculation at the level described in the main text. The electron density \( \rho(x, y, z) \) was sampled on a cartesian grid with the orca_plot program for further processing. The charge of the molecule, as a function of the radius around the metal center, is defined in spherical coordinates as

\[
Q(r) = e \int_0^r \int_0^\pi \int_0^{2\pi} dr' d\theta d\phi \ r'^2 \sin \theta \rho(r', \theta, \phi).
\]

Identically, we compute this integral numerically in cartesian coordinates as

\[
Q(r) = e \int \int \int_{\sqrt{x^2+y^2+z^2} \leq r} dx dy dz \ \rho(x, y, z).
\]

Finally, the radial charge density may be computed by the following derivative

\[
\rho(r) = \frac{d}{dr} Q(r).
\]

We note that two independent grids were used in the numerical calculation of the radial distributions: A fine grid of \( 500^3 \) in the range \(-1.5 \text{ a.u.} \leq x, y, z \leq 1.5 \text{ a.u.} \) was used to properly resolve the K, L and M shells of the metal center. Then, a ten times coarser grid was used for describing the remaining part of the molecule with \( 500^3 \) points in a \(-15.0 \text{ a.u.} \leq x, y, z \leq 15.0 \text{ a.u.} \) range.
G. DFT optimized molecular structures

TABLE I. Optimized geometries of ground state (GS) \([\text{Fe(bpy)(CN)}_4]^{2−}\), the triplet metal-to-ligand charge-transfer state (\(^3\text{MLCT}\)) and \([\text{Fe(bpy)(CN)}_4]^{1−}\) (Fe(III)).

|        | GS         | 3MLCT      | Fe(III)    |
|--------|------------|------------|------------|
|        | x (Å) y (Å) z(Å) | x (Å) y (Å) z(Å) | x (Å) y (Å) z(Å) |
| C      | 2.08031 1.87106 -3.28727 | 2.06203 1.85374 -3.30145 | 2.07312 1.86505 -3.28740 |
| Fe     | -0.00529 0.01637 0.00115 | 0.02598 0.03818 0.00424 | 0.02300 0.03671 0.00366 |
| C      | 2.26955 1.52695 0.89533 | 2.28757 1.54227 0.86850 | 2.28223 1.53584 0.89493 |
| C      | 3.22378 2.10393 1.73067 | 3.23788 2.11501 1.75274 | 3.22933 2.10756 1.73658 |
| C      | 3.14733 1.89263 3.09722 | 3.14602 1.89717 3.09999 | 3.14000 1.88799 3.10176 |
| C      | 2.11523 1.10684 3.59443 | 2.09336 1.09453 3.60630 | 2.10691 1.10209 3.59403 |
| C      | 1.20161 0.56302 2.70644 | 1.19521 0.55905 2.71082 | 1.19665 0.56033 2.70267 |
| N      | 1.26926 0.72689 1.38533 | 1.26650 0.75856 1.38678 | 1.28215 0.77202 1.38541 |
| H      | 4.01637 2.70966 1.31764 | 4.03533 2.72438 1.35129 | 4.02467 2.71414 1.33118 |
| H      | 3.87960 2.33285 3.76059 | 3.87227 2.33468 3.77292 | 3.86826 2.32498 3.77118 |
| H      | 2.01328 0.91319 4.65317 | 1.95577 0.89841 4.66319 | 1.99989 0.90559 4.65104 |
| H      | 0.38451 -0.05429 3.04871 | 0.37661 -0.05975 3.05038 | 0.37831 -0.05767 3.03910 |
| C      | 2.26122 1.68957 -0.56347 | 2.27948 1.69853 -0.53339 | 2.27415 1.69782 -0.56080 |
| C      | 3.20334 2.44289 -1.26054 | 3.21973 2.45424 -1.28008 | 3.20964 2.44670 -1.26503 |
| C      | 3.11369 2.53610 -2.63938 | 3.11618 2.53351 -2.64160 | 3.10757 2.53104 -2.64427 |
| C      | 1.17748 1.14099 -2.53162 | 1.17267 1.13347 -2.53605 | 1.17300 1.13700 -2.52806 |
| N      | 1.25754 1.04686 -1.19951 | 1.25394 1.04344 -1.20059 | 1.27070 1.05550 -1.19729 |
| H      | 3.99597 2.95023 -0.73153 | 4.01812 2.96699 -0.76242 | 4.00491 2.95644 -0.74315 |
| H      | 3.83671 3.11661 -3.19640 | 3.83459 3.11111 -3.20918 | 3.82684 3.10935 -3.20780 |
| H      | 1.96837 1.91308 -4.36173 | 1.94588 1.89051 -4.37486 | 1.95663 1.90382 -4.36081 |
| H      | 0.35873 0.60970 -2.99331 | 0.35278 0.59913 -2.99476 | 0.35244 0.60451 -2.98401 |
| C      | -1.12470 -0.61089 -1.43552 | -1.14672 -0.63417 -1.39705 | -1.14223 -0.62972 -1.38831 |
| N      | -1.80047 -0.98787 -2.30954 | -1.84599 -1.03500 -2.23217 | -1.83337 -1.02337 -2.23185 |
| C      | -1.11072 -0.91329 1.27527 | -1.13812 -0.91951 1.23693 | -1.12858 -0.91947 1.22832 |
| N      | -1.77849 -1.47642 2.04971 | -1.83011 -1.49392 1.97069 | -1.81187 -1.48941 1.97166 |
| C      | -1.12607 1.60922 0.18253 | -1.10346 1.64959 0.20210 | -1.11243 1.63927 0.18573 |
| C      | 1.12668 -1.56958 -0.17528 | 1.16991 -1.56344 -0.19354 | 1.15961 -1.56488 -0.17906 |
| N      | 1.81650 -2.50520 -0.27167 | 1.85859 -2.48986 -0.30836 | 1.84370 -2.49454 -0.28147 |
| N      | -1.77819 2.57036 0.28964 | -1.74870 2.60645 0.31968 | -1.76214 2.59276 0.29311 |
TABLE II. Average metal-ligand bond distances

|                | Fe — Ligand (Å) | Fe — C (Å) | Fe — N (Å) |
|----------------|-----------------|------------|------------|
| GS             | 1.969           | 1.941      | 2.024      |
| $^3$MLCT       | 1.972           | 1.963      | 1.992      |
| Fe(III)        | 1.972           | 1.953      | 2.009      |

H. Structure dependence of the $^3$MLCT spectra

![Graph showing DFT/ROCIS spectra of $^3$MLCT in its optimized structure as well as the Franck-Condon (FC) region showing an almost identical spectral shape.]

FIG. 3. DFT/ROCIS spectra of the $^3$MLCT in its optimized structure as well as the Franck-Condon (FC) region showing an almost identical spectral shape.

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