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Using Ultrafast X-ray Spectroscopy to Address Questions in Ligand-field Theory: The Excited State Spin and Structure of $[\text{Fe}(\text{dcpp})_2]^{2+}$

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ABSTRACT

We have employed a range of ultrafast x-ray spectroscopies in an effort to characterize the lowest energy excited state of $[\text{Fe}(\text{dcpp})_2]^{2+}$ (where dcpp is 2,6-(dicarboxypyridyl)pyridine). This compound exhibits an unusually short excited-state lifetime for a low-spin Fe(II) polypyridyl complex of 270 ps in room-temperature fluid solution, raising questions as to whether the ligand-field strength of dcpp had pushed this system beyond the $^5\text{T}_2/{}^3\text{T}_1$ crossing point and stabilizing the latter as the lowest energy excited state. $\text{K}\alpha$ and $\text{K}\beta$ x-ray emission spectroscopies have been used to unambiguously determine the quintet spin multiplicity of the long-lived excited state, thereby establishing the $^5\text{T}_2$ state as the lowest energy excited state of this compound. Geometric changes associated with the photo-induced ligand-field state conversion have also been monitored with extended x-ray absorption fine structure. The data show the typical average Fe-ligand bond length elongation of $\sim 0.18 \text{ \AA}$ for a $^5\text{T}_2$ state and suggest a high anisotropy of the primary coordination sphere around the metal center in the excited $^5\text{T}_2$ state, in stark contrast to the nearly perfect octahedral symmetry that characterizes the low-spin $^1\text{A}_1$ ground state structure. This study illustrates how the application of time-resolved x-ray techniques can provide insights into the electronic structures of molecules - particularly transition metal complexes - that are difficult if not impossible to obtain by other means.

INTRODUCTION

The capture and conversion of light into electrical and/or chemical energy is one of the most promising venues for addressing energy needs on a global scale. As in nature, molecular or materials-based approaches require as a first step the separation of charge: the chemical potential this charge separation creates is what drives subsequent processes such as current generation in solar cells¹ or the coupling of redox equivalents to catalysts for the formation of energy-dense compounds². In terms of kinetics, the lifetime of this charge separated state must be sufficiently long relative to the processes reliant on the redox activity of the excited state to effect subsequent chemical dynamics. For strategies that employ transition metal-based compounds, complexes of the second- and third-row transition series (e.g., Ru, Ir) are characterized by metal-to-ligand charge transfer (MLCT) excited states possessing excited-state lifetimes that can range from tens of nanoseconds to many microseconds, thereby allowing for their use in a wide range of settings, including bimolecular reaction chemistry³. Unfortunately, these elements represent some of the least abundant of the entire periodic table. Although this is not necessarily a problem when incorporated into catalysts – many large-scale industrial reactions use compounds based on rhenium, for example – the diffuse nature of sunlight makes the light capture part of the solar energy conversion problem material-intensive. The elemental availability of the components making up the chromophore is therefore a critical issue when it comes to scalability.

To overcome this problem in the context of transition metal-based chromophores, one would want to replace rare 4d/5d complexes with more earth-abundant first-row (3d) complexes. Successful efforts along these lines have employed Cu(I). For example, a Cu-based photosensitizer has been employed in a homogeneous water splitting system;⁴ and Cu(I)-based polypyridyl complexes have been used as chromophores in dye-sensitized solar cells (DSSCs).⁵ The d¹⁰

configuration of Cu(I) gives it an electronic structure reminiscent of Ru(II) (i.e., the lowest-energy excited state of polypyridyl complexes of Cu(I) is a $^3\text{MLCT}$), so the ability of these complexes to engage in photo-induced electron transfer is not surprising. More challenging has been the use of iron, the first-row congener of ruthenium. An enormous number of low-spin (LS) Fe(II) complexes are known, including the thoroughly studied Fe(II) polypyridyl complexes $[\text{Fe}(\text{bpy})_3]^{2+}$ ^{6–8} and $[\text{Fe}(\text{terpy})_2]^{2+}$ ^{9–12}. Their absorption spectra are dominated by strong MLCT transitions in the visible regime, however, these Fe(II)-based complexes have been difficult to employ in solar energy conversion schemes⁵ due primarily to the fact the MLCT states convert to lower-lying metal-centered ligand-field (LF) states on the ~100 fs timescale^{8,13–16}. Although the underlying reason(s) driving these surprisingly rapid dynamics are still the subject of active research,¹⁷ recent calculations suggest that the potential energy surfaces of these ligand-field excited states cross those of the MLCT states in proximity of the Franck-Condon regime.^{18,19} This can lead to efficient non-radiative decay through coupling of states at conical intersections.

One approach to eliminating the problem of rapid deactivation of MLCT states in Fe-based chromophores has been to design ligands that impart substantially stronger ligand fields to the metal center. This should result in destabilization of multielectronic terms states that arise due to population of the e_g^* orbitals and, potentially, alter the dynamics associated with the MLCT state(s). Warnmark and co-workers have pioneered this approach by replacing the bidentate and tridentate polypyridyl ligands with N-heterocyclic carbenes (NHCs)^{20–23}. The strongly sigma-electron donating nature of the carbene-based ligands does in fact result in dramatic increases in MLCT lifetimes due to significant destabilization of the high-spin ($^5\text{T}_2$) state.^{23,24} Complementary approaches include stabilizing the MLCT states by using strongly pi-accepting ligands²⁵ or the use

of sterics which Damrauer and co-workers have successfully employed to increase the lifetime of the $^5\text{MLCT}$ lifetime of a high-spin Fe(II)-terpyridine complex^{26,27}.

More subtle changes in the coordination sphere have also been observed to give rise to unexpected perturbations to the excited-state dynamics of Fe(II) polypyridyls. One of us (McCusker) recently reported the synthesis, structure, and fundamental photophysics of a new class of Fe(II) chromophores in which the basic terpyridine motif was modified by the incorporation of a C=O group between the C-C links of the pyridyl rings.²⁸ This new complex – $[\text{Fe}(\text{dcpp})_2]^{2+}$ (where dcpp is di(carboxypyridyl)pyridine) – exhibited a number of structural and dynamic features quite distinct from its polypyridyl cousins $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{terpy})_2]^{2+}$ (Figure 1). The primary coordination sphere of this compound is a near-perfect octahedron due to the six-membered metallocycle that is formed upon binding (as opposed to the 5-membered ring that results upon ligation of both bpy and terpy). More surprising was the excited-state. With regard to the compound's photo-induced properties, the time constant for ground-state recovery in fluid CH_3CN solution was measured to be 280 ± 10 ps, significantly shorter than that of $[\text{Fe}(\text{bpy})_3]^{2+}$ (960 ± 20 ps) and $[\text{Fe}(\text{terpy})_2]^{2+}$ (5.35 ± 0.15 ns) under identical conditions.²⁸

The shorter lifetime coupled with data indicating that dcpp presents a significantly stronger ligand-field to Fe(II) than bpy raised a question as to whether this system was the first example of a six-coordinate all-polypyridyl Fe(II) complex whose ligand-field strength pushed the system past the $^3\text{T}_1/{}^5\text{T}_2$ crossing point in the Tanabe-Sugano diagram, i.e., a pseudo-octahedral polypyridyl compound whose lowest-energy excited state was *not* the $^5\text{T}_2$, but rather the intermediate $^3\text{T}_1$ state. The data available at the time of this earlier report were insufficient to

Figure 1. Left: Structural formula of $[\text{Fe}(\text{dcpp})_2]^+$, the nitrogen atoms constituting the first coordination shell around Fe are grouped into axial N_{ax} and equatorial N_{eq} , the carbon atoms of the second coordination shell into C_{ax} , C_{eq1} and C_{eq2} . Right: 3-D structure of $[\text{Fe}(\text{dcpp})_2]^{2+}$ obtained from the single-crystal x-ray structure reported in ²⁸. (H atoms omitted for clarity).

differentiate between these two possibilities. Indeed, this ambiguity underscores a fundamental problem that arises when studying the photophysics of the vast majority of first-row metal complexes. Whereas the energetics of charge-transfer states are usually quite easily determined either through emission spectroscopy or electrochemistry, determining the nature and identity of ligand-field excited states can be exceedingly difficult. With rare exceptions (e.g., the ^2E state of Cr(III) complexes), ligand-field excited states are usually non-emissive even at low temperature. This is certainly the case for a $^5\text{T}_2$ state, whose radiative coupling to the $^1\text{A}_1$ state is virtually zero due to the $\Delta S = 2$ difference between the two states. Electrochemistry is likewise not useful in this regard: ligand-field excited states are not redox in nature and therefore cannot be simulated in a manner similar to charge-transfer states. Finally, with the exception of spin-crossover systems in which the lowest-energy excited state can be accessed either with temperature or through simple

chemical modifications of the ligand²⁹, data from traditional time-resolved optical measurements are generally not diagnostic for the identity of any specific excited state.

With this report, we will show that the combined application of various time-resolved x-ray spectroscopies can succeed in identifying the exact nature of a ligand-field excited state where other methods cannot. Specifically, we have exploited ultrafast x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) to meticulously characterize both the geometry and spin of the lowest-energy excited state of $[\text{Fe}(\text{dcpp})_2]^{2+}$. In addition to resolving ligand-field theory questions about this specific compound, we will demonstrate the power of these methods to not only determine the geometric structures of excited states, but to provide insights into the electronic structures that are difficult if not impossible to acquire by other means.

EXPERIMENTAL AND THEORETICAL METHODOLOGY

Time resolved XAS and XES have been measured at beamline 7ID-D of the Advanced Photon Source at Argonne National Laboratory. The experimental setup has been described previously.³⁰ The APS storage ring was operated in 24 bunch mode with an average ring current of 102 mA in top-up mode.³⁰ The laser system, synchronized to the storage ring, generated 10 ps pulses at MHz repetition rates. x-rays were monochromatized to $\Delta E/E=5.4\times 10^{-5}$ with a double-crystal diamond (111) monochromator³¹. The sample consisted of a ~10 mM solution of $[\text{Fe}(\text{dcpp})_2]^{2+}$ in CH_3CN flown through a sapphire nozzle with rectangular 0.1 mm $\times$ 6 mm orifice, which created a 100 μm thick flat sheet liquid jet. The liquid jet was tilted to about 45° with respect to the x-ray propagation direction, allowing a quasi-simultaneous measurement of XES and XAS spectra, i.e. at the front and backside of the liquid jet at 90° in the vertical plane parallel to the x-ray polarization direction. In order to reduce the amount of sample required, efforts were made to minimize the necessary sample volume to around 20 mL by employing a peristaltic pump to

circulate the solution. Evaporation of CH_3CN was largely suppressed by i) fully enclosing the sample environment, and ii) cooling the sample reservoir by placing it in a chilled water container. Furthermore, a second automated and remote-controlled pump was set up to refill the sample with solvent, allowing frequent (about once per hour) injections of small quantities (on the order of 1 mL) without entering the experimental hutch and disturbing the data acquisition.

XAS spectra were measured by scanning the incident x-ray energy from 7.08 to 7.60 keV and measuring the total fluorescence yield (TFY) with a gated scintillator coupled to a photomultiplier tube (S/PMT). The XANES part of the recorded XAS can be found in Figure 2. The laser repetition rate was set to 1.304 MHz, i.e. the fifth subharmonic of the x-ray repetition rate of 6.52 MHz. The laser power was set to 1.5 W exciting the sample with a pulse energy of 1.15 μJ . The lifetime of the excited state was determined by measuring the transient intensity at the strong B-feature of the XANES spectrum while scanning the laser-x-ray delay (Fig. 3). $\text{K}\alpha_1$ XES (Fig. 4) was measured at equivalent laser excitation conditions with a Johann type³² scanning XES spectrometer employing a 100 cm radius spherically bent Ge(440) analyzer crystal, which focused the monochromatized fluorescence photons onto a second S/PMT. Full XES spectra were obtained by scanning the Bragg angle over the corresponding range. Reference XES spectra were collected on the powder samples as described previously.⁸ The spectra were normalized by the incident x-ray flux and further background subtracted by setting the high energy tail of the spectrum to zero. The areas of all spectra are normalized to unity to facilitate a comparison between the sample and the reference measurements. Furthermore, reference spectra are arbitrarily shifted as the sample plane of the reference powder was slightly different than the one of the liquid jet.

In a second measurement campaign, $\text{K}\beta$ XES (Fig. 5) were obtained with a von Hamos spectrometer³³ employing a 25 cm radius cylindrically bent Si(531) analyzer crystal dispersing

the spectra onto a gated ³⁴ Pilatus 100k detector. Here, the laser repetition rate was set to 0.931 MHz (the 7th subharmonic of the 6.52 MHz x-ray repetition rate). Owing to the slightly larger laser spot size on the sample, a higher optical laser pulse energy of 2.7 μ J (corresponding to 2.5 W) was chosen in order to match the amplitude of the transient signal (normalized to the absorption edge-jump) edge-jump normalized transient signal strength of the first measurement campaign (simultaneous XAS and $K\alpha_1$ XES) and ensure the creation of an identical excited state fraction. The full spectra were obtained by selecting a region of interest of the detector and integrating the signal perpendicular to the dispersive axis of the spectrometer. The total area underneath all emission lines are normalized to unity; normalization to the incident x-ray flux is not needed, as the x-ray emission over the full spectral width is acquired within each x-ray pulse.

The structural optimizations for singlet, triplet and quintet spin states of $[\text{Fe}(\text{dcp})_2]^{2+}$ were done employing the B3LYP functional^{35–38} and Grimme's D2 dispersion correction³⁹. An SDD effective core potential and associated basis set⁴⁰ was utilized for Fe along with 6-311G* basis set^{41–43} for all other atoms (C, H, O, N). Geometry optimizations were performed with polarizable continuum model (PCM)⁴⁴ for water as a solvent. The computational approach was chosen based on our previous work, as it provided for reliable optimized structures and spin-state energetics for $[\text{Fe}(\text{terpy})_2]^{2+}$ and $[\text{Fe}(\text{dcp})_2]^{2+}$ based compounds.^{45,46} The local minima on the potential energy surface were confirmed with the vibrational frequency analysis for all the equilibrium structures. Cartesian coordinates of all optimized complexes are provided in a xyz file format as Supplemental Information. These calculations were carried out using Gaussian 09 software package.⁴⁷

We carried out additional geometry optimizations utilizing the BP86^{48,49} exchange-correlation functional in combination with the TZP Slater atomic basis set, as implemented in the ADF2013 program package.^{50–52} In these calculations, we constrained the occupation of molecular

orbitals by D_2 point group symmetry for the three components of the 5T_2 manifold (5B_2 , 5A , and 5B_3).

RESULTS AND DISCUSSION

The iron K-edge XANES spectra of $[\text{Fe}(\text{dcpp})_2]^{2+}$ in CH_3CN with and without laser excitation are shown in Figure 2. The most prominent features are labeled A-E; in terms of the qualitative spectral features, transient changes in the XANES spectra are almost identical to those observed following photoexcitation of $[\text{Fe}(\text{bpy})_3]^{2+}$ ⁶ and $[\text{Fe}(\text{terpy})_2]^{2+}$ ^{9–11}. The spectral range labeled A is assigned to the so-called pre-edge region where bound-bound transition to unoccupied molecular orbitals can be found. These transitions correspond to formally dipole-forbidden $1s \rightarrow 3d$ transitions, of both t_{2g} and e_g^* character. Spectral changes in this region reflect directly the change in occupancy of different $3d$ metal orbitals due to spin transition. In fact the final states of these weak resonances are the same as in case of transition metal L-edge spectra, however in the latter case the XAS spectra are dominated by dipole-allowed $2p \rightarrow 3d$ transitions and therefore bearing much higher sensitivity to the occupancy of $3d(t_{2g})$ and $3d(e_g^*)$ orbitals as has been reported earlier for similar Fe(II)-based complexes.^{53,54} The other spectral features visible in the XANES spectrum in Fig. 2 correspond to multiple scattering resonances in the vicinity of the ionization potential and therefore they are quite sensitive to the overall molecular structure of the complex, similarly to other K-edge spectra of Fe complexes^{6,9,55}. However, none of the spectral features in the XAS spectrum allows for an unambiguous determination of the spin multiplicity of the metal, which is one of the primary goals of our study. The temporal decay of the B feature together with a fit is shown in Figure 3. The fit is a convolution of a Gaussian-broadened step function with an exponential decay and results in a (77 ± 3) ps risetime reflecting the x-ray pulse duration and a (272 ± 4) ps decay, in excellent agreement with the known lifetime of the lowest-energy excited

state of $[\text{Fe}(\text{dcpp})_2]^{2+}$ in CH_3CN solution²⁸. This lifetime is significantly shorter than that observed for $[\text{Fe}(\text{bpy})_3]^{2+}$ (0.96 ns in CH_3CN ²⁸) and $[\text{Fe}(\text{terpy})_2]^{2+}$ (5.35 ns in CH_3CN ²⁸) under identical experimental conditions. As mentioned above, this observation coupled with the increased ligand-field strength imparted by the dcpp ligand relative to both bpy and terpy prompted consideration that the lowest-energy excited state of $[\text{Fe}(\text{dcpp})_2]^{2+}$ was the $^3\text{T}_1$ state as opposed to the $^5\text{T}_2$ state characteristic of other Fe(II) polypyridyl complexes.

Figure 2. The XANES region of the K-edge spectra of the $^1\text{A}_1$ ground state $[\text{Fe}(\text{dcpp})_2](\text{PF}_6)_2$ in CH_3CN solution (blue), ~ 50 ps after 532 nm laser excitation (red), the transient difference spectrum (green), and of the compound's lowest-energy excited state assuming an excited-state fraction of $f = 78\%$ has been produced (grey).

Figure 3. Kinetics trace for $[\text{Fe}(\text{dcpp})_2](\text{PF}_6)_2$ in CH_3CN solution at the B feature (7123 eV) following $^1\text{A}_1 \rightarrow ^1\text{MLCT}$ excitation. The data can be described by a single exponential kinetic model with $\tau_{\text{obs}} = (272 \pm 4)$ ps.

To address this unresolved question, we have measured $K\alpha_1$ XES in analogy to the measurements on $[\text{Fe}(\text{bpy})_3]^{2+}$ ^{7,56,57} and $[\text{Fe}(\text{terpy})_2]^{2+}$ ⁹ in order to determine the spin of the excited-state being sampled in the ground-state recovery dynamics of $[\text{Fe}(\text{dcpp})_2]^{2+}$. The spectra of the GS, about 50 ps after laser excitation and their respective difference, as well as the

Figure 4. a) $K\alpha_1$ XES spectra of the ground state of $[\text{Fe}(\text{dcpp})_2]^{2+}$ (blue), 50 ps after laser excitation (red), and the excited-state/ground-state transient difference (green). The corresponding spectrum of a standard which possesses a high-spin, $S=2$ ground state, is also shown (grey). b) A plot of the $K\alpha_1$ XES data for a series of Fe(II) and Fe(III) complexes (yellow points), revealing an approximately linear correlation between spin-state and spectral line width.. The spectrum acquired subsequent to photoexcitation of $[\text{Fe}(\text{dcpp})_2]^{2+}$ corresponds to an average spin of $S_{\text{dcpp,LON}} = 1.56$, a value consistent with sampling a $S=2$ excited state with a $f = 78\%$ excited-state fraction.

spectrum of a high-spin ($S=2$) reference complex can be seen in Figure 4a. It can be seen that the laser ON spectrum is virtually identical to the $S=2$ reference spectrum, an indication that the

excited state for $[\text{Fe}(\text{dcpp})_2]^{2+}$ is likely $S = 2$ in character. A more detailed assessment of the average spin-state of the photo-excited ensemble is facilitated by the approximately linear relation that exists between the number of unpaired $3d$ electrons and the $K\alpha_1$ linewidth^{58,59}. The line shape of the ground- and photo-induced excited states of $[\text{Fe}(\text{dcpp})_2]^{2+}$ along with a series of static references having $S=3/2$ and $S=2$ have been analyzed based on the approach by Vankó et al.⁵⁸ This relationship is highlighted in Figure 4b, which shows a plot of the $K\alpha_1$ line width as a function of S for a series of Fe(II) and Fe(III) complexes. The experimentally determined line width of the photoexcited sample of $[\text{Fe}(\text{dcpp})_2]^{2+}$ corresponds to a spin of $S = 1.56$, however, this value represents a superposition of the excited state being sampled as well as any residual ground state not upconverted upon excitation. The fraction of sample that is actually excited and sampled will vary depending on pulse power, pump-probe cross-section, and the molar absorptivity of the absorption feature among other factors, and in principle can range from 0 to 100%. Assuming that only a single excited state is being sampled following photoexcitation, we can use the excitation fraction as a weighting factor and describe the spin-state value obtained from the correlation in Figure 4b as

$$S_{\text{exp}} = (1-f) S_{\text{GS}} + f S_{\text{ES}} \quad (1)$$

where S_{GS} and S_{ES} are the spin values corresponding to the ground and excited states, respectively, and f is the excitation fraction. For $[\text{Fe}(\text{dcpp})_2]^{2+}$, $S_{\text{GS}} = 0$ and $S_{\text{exp}} = 1.56$; since the excitation fraction cannot be larger than 1 (i.e., you cannot produce more excited state than you have ground state to begin with), a value of $S_{\text{exp}} = 1.56$ in eq. 1 effectively rules out an isolated 3T_1 term as the lowest energy excited state of $[\text{Fe}(\text{dcpp})_2]^{2+}$. The experimental data can be interpreted in terms of a 5T_2 excited state for $[\text{Fe}(\text{dcpp})_2]^{2+}$ assuming $f = 0.78$, i.e., photoexcitation results in 78% of the sample being converted to the excited state. This represents a large but plausible excitation cross-

section given that the molar absorptivity at the excitation wavelength (532 nm) is on the order of $10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

Despite the reasonableness of the above analysis, the $K\alpha_1$ measurements cannot completely exclude a contribution of a second excited state species (e.g., a thermally accessible 3T_1 state and/or extensive mixing between the 5T_2 and 3T_1 terms). To verify that the $S = 2$ state is the only excited state contributing to the $K\alpha_1$ signal, we therefore measured the $K\beta_{1,3}$ x-ray emission spectrum of $[\text{Fe}(\text{dcpp})_2]^{2+}$ due to the distinct features it exhibits as a function of spin-state in iron complexes⁸. The $K\beta_{1,3}$ XES data we acquired are shown in Figure 5a, together with spectra for the ground states of low-spin ($S=0$) and high-spin ($S=2$) complexes, which have previously been measured by W. Zhang *et al.*⁸, for comparison. The main feature of the laser ON spectrum exhibits a blue shift compared to the GS spectrum and exhibits a spectral profile that is virtually identical to the $S=2$ reference spectrum. Moreover, the transient difference spectrum for $[\text{Fe}(\text{dcpp})_2]^{2+}$ (Figure 5b) is wholly consistent with what has previously been observed for other compounds possessing an isolated 5T_2 term as their lower energy excited states, with the amplitude and other features reminiscent of the typical fingerprints of the singlet-quintet difference spectrum. In contrast, there are distinct qualitative disparities between the data for $[\text{Fe}(\text{dcpp})_2]^{2+}$ and the expected singlet-triplet difference spectrum. We have quantified this result further by assessing the fits of the data on $[\text{Fe}(\text{dcpp})_2]^{2+}$ in terms of their consistency with a triplet versus quintet excited state. We have calculated the transient differences spectra for linear combinations of triplet-singlet (grey in Fig. 5b) and quintet-singlet (yellow in Fig. 5b) differences for each contributing between 0% and 100%. The reduced square deviation χ^2 of this superposition and the measured difference is shown in the contour plot in Figure 5c. The minimum χ^2 , corresponding to the best agreement of the reference difference and the experimental data, was obtained for a quintet contribution of $f_Q = 72\%$ and a

triplet contribution of $f_T = 0\%$, a result that is in excellent agreement with the result obtained from the analysis of the $K\alpha$ XES data.

Figure 5. a) $K\beta$ XES spectra of $[Fe(dcpp)_2]^{2+}$ in ground state (blue) and 50 ps after laser excitation (red); spectra corresponding to model complexes having $S=0$ and $S=2$ are also shown. b) Normalized difference spectra between the ground and excited states of $[Fe(dcpp)_2]^{2+}$ (green) compared to those corresponding to excited states having $S = 1$ (grey) and $S = 2$ (yellow) (all reference spectra shown here are obtained from ref⁸). c) χ^2 contour plot of the transient $K\beta$ XES fit as a function of triplet-singlet and quintet-singlet contributions. The minimum is observed at 0% triplet and 72% quintet, consistent with $[Fe(dcpp)_2]^{2+}$ having an (isolated) $S = 2$ lowest-energy excited state.

Having established the 5T_2 state as the lowest energy excited state of $[Fe(dcpp)_2]^{2+}$, we turned our attention to characterizing the molecular structure changes accompanying the LS-HS conversion by analyzing the EXAFS part of the XAS. In the first step, the XAS of the pure excited state spectrum μ_{ES} is reconstructed from the laser ON spectrum μ_{LON} and laser OFF spectrum μ_{LOFF} using the excited state fraction f determined from the XES measurements via

$$\mu_{ES} = \mu_{LOFF} + (1/f) * (\mu_{LON} - \mu_{LOFF}) \quad (2)$$

where the laser-off spectrum corresponds to the ground-state spectrum, i.e., $\mu_{GS} = \mu_{LOFF}$. The atomic background is then subtracted and the resultant spectrum normalized to a unitary K-edge step height, yielding the EXAFS spectra $\chi_{GS}(E)$ and $\chi_{ES}(E)$ of the GS and ES, respectively, using ATHENA from the IFEFFIT toolbox ⁶⁰. The energy axis can be converted to a photo-electron wave-number k axis; to enhance the visibility of the EXAFS features at higher energies, the spectra can be additionally k^2 weighted as shown in Figures 6a and 6b. Fourier-transformation (FT) of the EXAFS spectra from k - to R -space results in pseudo-radial distribution functions (Figures 6c and 6d) ⁶¹. EXAFS spectra for $[Fe(dcpp)_2]^{2+}$ are shown in Figure 6. They have been modeled with FEFF8 ⁶² using the DFT calculated 1A_1 structure for the GS and a possible triplet 3T_1 and quintet 5T_2 structure for the excited state. These have been used as starting guesses in fitting the EXAFS spectra using the Artemis software, which is also part of IFEFFIT. In the GS fit, Fe- N_{ax} , Fe- N_{eq} , Fe- C_{ax} , Fe- C_{eq} and Fe- C_{eq2} bond lengths as well as non-structural parameters such as an energy shift, amplitude reduction factor and Debye-Waller factors are optimized. In the ES fit, the non-structural parameters are fixed to those of the GS and only the five bond-lengths are fitted (further details on the EXAFS fit can be found in the SI). For the excited state fit, both the 3T_1 and 5T_2 structures have been used as starting guesses to facilitate an unbiased structure determination, and both fits converged to the same result.

Figure 6. a) Ground-state and b) Excited-state k^2 weighted EXAFS spectra of $[\text{Fe}(\text{dcpp})_2]^{2+}$ in k -space. c) Ground-state and d) Excited-state EXAFS spectra in R -space. For the k^2 -weighted spectra, the residuals of the fit are plotted in green.

The obtained GS and ES Fe-N and Fe-C bond lengths as well as those of the three DFT structural models are summarized in Table 1. The GS structure from EXAFS is in good agreement with experiment as well as the DFT geometry-optimized structure, with only small discrepancies in the bond lengths being observed. The typical structural changes associated with a low-spin to high-spin conversion in Fe(II) are evident, with an average Fe-N bond elongation of ~ 0.18 Å due to the population of the $e_g^* \sigma$ -antibonding orbitals in the $(t_{2g})^4(e_g^*)^2$ configuration that characterizes the 5T_2 state. In contrast, an $S = 1$ state that derives from a $(t_{2g})^5(e_g^*)^1$ configuration would be expected to exhibit a much smaller average bond elongation, as has been observed in $[\text{Co}(\text{terpy})_2]^{2+}$ with an average Co-N bond elongation of ~ 0.08 Å⁶³. Nevertheless, while the primary coordination sphere for the ground state of $[\text{Fe}(\text{dcpp})_2]^{2+}$ is almost perfectly O_h in symmetry, the excited-state

structure exhibits a surprisingly anisotropic distortion with significant differences between the axial ($R(\text{Fe-N}_{\text{ax}}) = 2.05 \text{ \AA}$) and equatorial

Table 1. Experimentally determined first and second coordination shell bond lengths of $[\text{Fe}(\text{dcpp})_2]^{2+}$ in its ground state, its excited state, and their respective difference. Bond lengths obtained from x-ray crystallography as well as DFT (B3LYP+D2/SDD,6-311G* level of theory) are shown for comparison. The error estimates as estimated standard deviations obtained from ARTEMIS are given in brackets.

	$R(\text{Fe-N}_{\text{ax}}) / \text{\AA}$	$R(\text{Fe-N}_{\text{eq}}) / \text{\AA}$	$R(\text{Fe-C}_{\text{ax}}) / \text{\AA}$	$R(\text{Fe-C}_{\text{eq1}}) / \text{\AA}$	$R(\text{Fe-C}_{\text{eq2}}) / \text{\AA}$
$^1\text{A}_1$ from DFT	2.00	2.02	2.93	2.95	2.94
Ground state from x-ray cryst. ²⁸	1.974(2)	1.985(2) - 1.989(2)	2.920(5)	2.925(3)	2.931(3)
Ground state from EXAFS	1.96(1)	1.98(1)	2.91(2)	2.92(2)	2.92(2)
$^3\text{T}_1$ structure from DFT	1.98	2.14	2.92	3.02	3.06
$^5\text{T}_2$ structure from DFT	2.16	2.17	3.07	3.08	3.06
Excited state from EXAFS	2.05(2)	2.21(2)	2.97(4)	3.10(2)	3.07(2)
Diff. GS-ES	+0.09(2)	+0.23(2)	+0.06(5)	+0.17(3)	+0.15(3)

($R(\text{Fe-N}_{\text{eq}}) = 2.21 \text{ \AA}$) bond distances. Nevertheless, this fit result is in contrast to the DFT geometries, which predicts an almost perfectly octahedral structure in the $^5\text{T}_2$ state. The reasons for disagreement between the DFT-optimized geometries and experimental data are unclear. With the analyzed k-range from $2.5 \text{ \AA}^{-1}$ - $10.5 \text{ \AA}^{-1}$ we cannot observe the Fe-N_{ax} and Fe-N_{eq} bonds as separate peaks in the pseudo radial distribution functions (Figs 6c and 6d) and resolve their relative bond length difference of $\sim 0.02 \text{ \AA}$ in the GS. Nevertheless, the bond length changes of the inequivalent Fe-N bonds during the LS-HS transition of $[\text{Fe}(\text{terpy})_2]^{2+}$ ^{9,11} and $[\text{Fe}(\text{tpen})]^{2+}$ ⁶⁴ have been characterized with a similar k-range and we can analogously use the change in peak width and intensity to quantify the change in symmetry in the first coordination shell of $[\text{Fe}(\text{dcpp})_2]^{2+}$. The increased asymmetry in the ES is reflected in the broadening and strong peak intensity

decrease, which could otherwise only be explained by a large change in the Debye-Waller factor, although within the ~100 ps temporal resolution of the measurement the largest part of the ensemble of molecules in the ES have thermalized. To further test the excited state EXAFS fit result we have constrained the geometry to a symmetric one, which leads to a comparably good symmetric fit, but with a significant and almost unreasonable (~6-fold for the first coordination shell compared to the ground state) increase in the Debye-Waller factors and amplitude reduction factor (see Table S3). Constrained optimizations of $[\text{Fe}(\text{dcpp})_2]^{2+}$ in the $^5\text{T}_2$ state with Fe-N_{ax} and Fe-N_{eq} bond lengths fixed at 2.05 Å and 2.21 Å, respectively, yielded two different structures that are only 4.8 kcal/mol and 2.6 kcal/mol higher in energy than the fully optimized $^5\text{T}_2$ structure. The two structures differ from each other by orbital occupancy and inter-ligand interactions (natural orbitals showing d orbital occupation as well as a table with structural parameters for fully-optimized and constrained-optimized structures can be found in the SI). This suggests that the PES of $^5\text{T}_2$ state is flat with respect to the asymmetric distortions along the axial and equatorial Fe-N bond lengths. Unlike $[\text{Fe}(\text{terpy})_2]^{2+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$ complexes, $[\text{Fe}(\text{dcpp})_2]^{2+}$ displays significant inter-ligand interactions between the CO bridging groups of one dcpp ligand and pyridine moieties of the second dcpp ligand (see Figure 1), calculated C (CO) – N (pyridine) distance is 2.90 Å (2.84-2.87 Å in the crystal structure). It is possible that these inter-ligand interactions affect the structure of the complex in the ES, and that our chosen computational methodology is unable to describe them with sufficient accuracy.

We have also attempted to find fully-optimized asymmetric structures. The pseudo-octahedral ligand field of molecules possessing D_2 molecular symmetry, as is the $[\text{Fe}(\text{dcpp})_2]^{2+}$ complex, splits the $^5\text{T}_2$ state into three components: the $^5\text{B}_2$, ^5A , and $^5\text{B}_3$. Geometry optimizations utilizing the BP86 exchange-correlation functional^{48,49} show that the energy splitting of these states

is below 50 meV (the lowest being the 5B_3). Furthermore, while the 5B_2 structure reflects an almost completely symmetric FeN6 core, the one of the 5A and 5B_3 exhibits a Fe-N anisotropy of ca. 0.05 Å and 0.03 Å, respectively. These results hint at the existence of an energetically accessible distorted HS structure, even if the theory-predicted anisotropy is significantly smaller than the one obtained from the EXAFS experiment (0.16 Å).^{50–52}

To further verify the anisotropically distorted excited state we have compared the EXAFS spectra to those of $[Fe(terpy)_2]^{2+}$ in its ground and excited states (Figure 7). The ground-state EXAFS spectrum for $[Fe(terpy)_2]^{2+}$ differs significantly from that of $[Fe(dcpp)_2]^{2+}$, reflecting the distinctly different ground-state structures of the two compounds. Interestingly, the compounds become far more similar in the excited state: the first coordination shell of the excited state of $[Fe(terpy)_2]^{2+}$ is very similar to that of $[Fe(dcpp)_2]^{2+}$, with $R(Fe-N_{ax}) = 2.08$ Å and $R(Fe-N_{eq}) = 2.20$ Å⁹ (Figure 7e). This leads to almost identical excited-state EXAFS spectra for the two compounds (Figures 7f). The overall result is therefore rather intriguing: whereas the low-spin to high-spin conversion in $[Fe(terpy)_2]^{2+}$ is more or less isotropic, the same process in $[Fe(dcpp)_2]^{2+}$ is very anisotropic. The reasons underlying this difference in behavior is still unclear but likely relates to the greater degree of geometric constraint associated with the terpy ligand (which creates 5-membered rings upon chelation to a metal center) as compared to the more structurally accommodating 6-membered metallocycles that result from dcpp complexation.

Figure 7. a) Ground-state XANES spectra of $[\text{Fe}(\text{dcpp})_2]^{2+}$ (from this work) and $[\text{Fe}(\text{terpy})_2]^{2+}$ (reproduced from ref 4). b) k^2 -weighted ground-state EXAFS spectra of $[\text{Fe}(\text{dcpp})_2]^{2+}$ and $[\text{Fe}(\text{terpy})_2]^{2+}$. c) Transient XANES spectrum for $[\text{Fe}(\text{dcpp})_2]^{2+}$ at a delay of ~ 50 ps following $^1A_1 \rightarrow ^1MLCT$ excitation at 532 nm. d) Transient k^2 -weighted EXAFS spectra. e) Reconstructed excited state XANES spectra. f) Reconstructed excited state k^2 -weighted EXAFS spectra.

CONCLUDING COMMENTS

We have employed time-resolved x-ray absorption and emission spectroscopies in an effort to characterize the electronic and geometric structure of $[\text{Fe}(\text{dcpp})_2]^{2+}$, an Fe(II) polypyridyl complex whose photophysical properties were sufficiently anomalous that it called into question the nature of its lowest-energy excited state. Whereas more traditional forms of steady-state and time-resolved spectroscopies were unable to definitively answer this question, the quintet spin multiplicity of this excited state has been unambiguously determined via $K\alpha$ and $K\beta$ XES, thereby establishing the lowest-energy excited state as a 5T_2 . Additional insights into the geometric changes that accompany conversion between the high-spin excited and low-spin ground states of this compound were obtained from an analysis of EXAFS data. While the average Fe-N bond elongation of ~ 0.18 Å is consistent with structural changes associated with LS $\rightarrow$ HS conversions

in a number of other Fe(II) polypyridyl complexes,^{6,9,44,61} the distortion in $[\text{Fe}(\text{dcpp})_2]^{2+}$ appears to be highly anisotropic, leading to a structure that is best described in terms of pseudo Jahn-Teller distortion. This somewhat unexpected result is tentatively attributed to the nature of the dcpp ligand which allows for a degree of structural flexibility due to the manner in which it chelates to a metal as compared to complexes such as $[\text{Fe}(\text{terpy})_2]^{2+}$,⁹ where the geometric constraints are expected to be more severe. . Further systematic analyses of EXAFS-derived structures of the ground and excited states of a range of Fe(II) polypyridyl complexes will be required in order to understand this as yet unresolved aspect of the present study.

Returning to the question that catalyzed this work, namely the nearly 4-fold increase in the rate constant for ground-state recovery for $[\text{Fe}(\text{dcpp})_2]^{2+}$ as compared to $[\text{Fe}(\text{bpy})_3]^{2+}$, our determination of quintet spin multiplicity for the lowest-energy excited state of $[\text{Fe}(\text{dcpp})_2]^{2+}$ means that we cannot attribute the observed difference in kinetics to a significant change in the electronic coupling between the two states (i.e., a $\Delta S = 1$ versus $\Delta S = 2$ spin change). The excited-state relaxation kinetics of $[\text{Fe}(\text{bpy})_3]^{2+}$ in solution have long been considered to be at⁶⁵ or near⁶⁶ the barrierless limit, i.e., $\Delta G_0 \approx \lambda$. This was indeed one of the assumptions that led to the suggestion that perhaps the lowest energy excited state of $[\text{Fe}(\text{dcpp})_2]^{2+}$ was a $^3\text{T}_1$ as opposed to $^5\text{T}_2$.²⁸ However, it has recently been determined that ground-state recovery for $[\text{Fe}(\text{bpy})_3]^{2+}$ in fluid solution has a small but nevertheless measurable barrier of $\sim 300 \text{ cm}^{-1}$,⁶⁷ whereas corresponding studies on $[\text{Fe}(\text{dcpp})_2]^{2+}$ under identical conditions reveal an essentially barrierless process with measured rate constants at 295 K and 215 K that are within experimental error of each other.⁶⁸ Interestingly, the pre-exponential term in an Arrhenius treatment of the data on $[\text{Fe}(\text{bpy})_3]^{2+}$ yields a value of ca. 250 ps^{-1} , i.e., very close to the observed ground-state recovery time for $[\text{Fe}(\text{dcpp})_2]^{2+}$. Since the pre-exponential Arrhenius term is the time constant expected in the limit of zero barrier,

we can conclude that the experimentally observed 4-fold difference in ground-state recovery time between $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{dcp})_2]^{2+}$ is simply a reflection of a $\sim 300 \text{ cm}^{-1}$ difference in their respective activation energies as manifested at room temperature. Given that the Arrhenius activation energy equates to $((\Delta G_0 + \lambda)^2/4\lambda)$, it's difficult to push this analysis any further absent an independent measure of either ΔG_0 or λ . That stated, it seems plausible that the reorganization energy associated with ground-state recovery for $[\text{Fe}(\text{dcp})_2]^{2+}$ could be larger than that of $[\text{Fe}(\text{bpy})_3]^{2+}$ given the more complex structural changes that appear to be occurring in $[\text{Fe}(\text{dcp})_2]^{2+}$ based on the data and analysis we have presented herein. Whether that would require a larger or smaller driving force in order to compensate will depend on whether these systems lie in the normal or inverted region, an interesting question that is beyond the scope of the present study.

ASSOCIATED CONTENT

Supporting Information. UV-vis absorption spectrum, details on EXAFS analysis, estimation of activation barrier height, energies, structural parameters and natural orbitals for various electronic states of $[\text{Fe}(\text{dcp})_2]^{2+}$, Cartesian coordinates (xyz format) for optimized singlet, quintet and triplet structures of $[\text{Fe}(\text{dcp})_2]^{2+}$ complex.

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Notes

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References.

- (1) Grätzel, M. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. *Inorg. Chem.* **2005**, *44* (20), 6841–6851.
- (2) Goldsmith, J. I.; Hudson, W. R.; Lowry, M. S.; Anderson, T. H.; Bernhard, S. Discovery and High-Throughput Screening of Heteroleptic Iridium Complexes for Photoinduced Hydrogen Production. *J. Am. Chem. Soc.* **2005**, *127* (20), 7502–7510.
- (3) Ardo, S.; Meyer, G. J. Photodriven Heterogeneous Charge Transfer with Transition-Metal Compounds Anchored to TiO₂ Semiconductor Surfaces. *Chem. Soc. Rev.* **2009**, *38* (1), 115–164.
- (4) Luo, S.-P.; Mejía, E.; Friedrich, A.; Pazidis, A.; Junge, H.; Surkus, E.; Jackstell, R.; Denurra, S.; Gladiali, S.; Lochbrunner, S.; et al. Photocatalytic Water Reduction with Copper-Based Photosensitizers: A Noble-Metal-Free System. *Angew. Chemie - Int. Ed.* **2013**, *52*, 419–423.
- (5) Malzner, F.; Housecroft, C.; Constable, E. The Versatile SALSAC Approach to Heteroleptic Copper(I) Dye Assembly in Dye-Sensitized Solar Cells. *Inorganics* **2018**, *6* (57), 1-17 and references therein.
- (6) Gawelda, W.; Pham, V.-T.; Benfatto, M.; Zaushitsyn, Y.; Kaiser, M.; Grolimund, D.; Johnson, S.; Abela, R.; Hauser, A.; Bressler, C.; et al. Structural Determination of a Short-Lived Excited Iron(II) Complex by Picosecond X-Ray Absorption Spectroscopy. *Phys. Rev. Lett.* **2007**, *98* (5), 057401.
- (7) Haldrup, K.; Vankó, G.; Gawelda, W.; Galler, A.; Doumy, G.; March, a M.; Kanter, E. P.; Bordage, A.; Dohn, A.; van Driel, T. B.; et al. Guest-Host Interactions Investigated by Time-Resolved X-ray Spectroscopies and Scattering at MHz Rates: Solvation Dynamics and Photoinduced Spin Transition in Aqueous Fe(bipy)₃⁽²⁺⁾. *J. Phys. Chem. A* **2012**, *116* (40), 9878–9887.
- (8) Zhang, W.; Alonso-Mori, R.; Bergmann, U.; Bressler, C.; Chollet, M.; Galler, A.; Gawelda, W.; Hadt, R. G.; Hartsock, R. W.; Kroll, T.; et al. Tracking Excited-State

- Charge and Spin Dynamics in Iron Coordination Complexes. *Nature* **2014**, *509*, 345–348.
- (9) Vankó, G.; Bordage, A.; Pápai, M.; Haldrup, K.; Glatzel, P.; March, A. M.; Doumy, G.; Britz, A.; Galler, A.; Assefa, T. A.; et al. Detailed Characterization of a Nanosecond-Lived Excited State : X-Ray and Theoretical Investigation of the Quintet State in Photoexcited $[\text{Fe}(\text{terpy})_2]^{2+}$. *J. Phys. Chem. C* **2015**, *119* (11), 5888–5902.
- (10) Canton, S. E.; Zhang, X.; Lawson Daku, M. L.; Smeigh, A. L.; Zhang, J.; Liu, Y.; Wallentin, C.; Attenkofer, K.; Jennings, G.; Kurtz, C. A.; et al. Probing the Anisotropic Distortion of Photoexcited Spin Crossover Complexes with Picosecond X-ray Absorption Spectroscopy. *J. Phys. Chem. C* **2014**, *118* (8), 4536.
- (11) Zhang, X.; Lawson Daku, M. L.; Zhang, J.; Suarez-Alcantara, K.; Jennings, G.; Kurtz, C. A.; Canton, S. E. Dynamic Jahn-Teller Effect in the Metastable High-Spin State of Solvated $[\text{Fe}(\text{terpy})_2]^{2+}$. *J. Phys. Chem. C* **2015**, *119* (6), 3312–3321.
- (12) March, A. M.; Assefa, T. A.; Boemer, C.; Bressler, C.; Britz, A.; Doumy, G.; Galler, A.; Harder, M.; Khakhulin, D. V.; Németh, Z.; et al. Probing Transient Valence Orbital Changes with Picosecond Valence-to-Core X-Ray Emission Spectroscopy. *J. Phys. Chem. C* **2017**, *121*, 2620–2626.
- (13) Auböck, G.; Chergui, M. Sub-50-Fs Photoinduced Spin Crossover in $[\text{Fe}(\text{bpy})_3]^{2+}$. *Nat. Chem.* **2015**, *7*, 629–633.
- (14) Ferrere, S.; Gregg, B. A. Photosensitization of TiO_2 by $[\text{FeII}(2,2'\text{-bipyridine-4,4'}\text{-dicarboxylic acid})_2(\text{CN})_2]$: Band Selective Electron Injection from Ultra-Short-Lived Excited States. *J. Am. Chem. Soc.* **1998**, *120* (4), 843–844.
- (15) McCusker, J. K.; Walda, K. N.; Dum, R. C.; Simon, J. D.; Magde, D.; Hendrickson, D. N. Subpicosecond $^1\text{MLCT}$ $^5\text{T}_2$ Intersystem Crossing of Low-Spin Polypyridyl Ferrous Complexes. *J. Am. Chem. Soc.* **1993**, *115* (1), 298–307.
- (16) Monat, J. E.; McCusker, J. K. Femtosecond Excited-State Dynamics of an Iron(II) Polypyridyl Solar Cell Sensitizer Model. *J. Am. Chem. Soc.* **2000**, *122* (17), 4092–4097.

- (17) McCusker, J. K. Electronic Structure in the Transition Metal Block and Its Implications for Light Harvesting. *Science* (80-.). **2019**, 363 (6426), 484–488.
- (18) De Graaf, C.; Sousa, C. Study of the Light-Induced Spin Crossover Process of the [Fe II(bpy)₃]²⁺ Complex. *Chem. - A Eur. J.* **2010**, 16 (15), 4550–4556.
- (19) Ashley, D. C.; Jakubikova, E. Ironing out the Photochemical and Spin-Crossover Behavior of Fe(II) Coordination Compounds with Computational Chemistry. *Coord. Chem. Rev.* **2017**, 337, 97–111.
- (20) Liu, Y.; Harlang, T.; Canton, S. E.; Chábera, P.; Suárez-Alcántara, K.; Fleckhaus, A.; Vithanage, D. A.; Göransson, E.; Corani, A.; Lomoth, R.; et al. Towards Longer-Lived Metal-to-Ligand Charge Transfer States of Iron(II) Complexes: An N-Heterocyclic Carbene Approach. *Chem. Commun.* **2013**, 49 (57), 6412–6414.
- (21) Liu, Y.; Kjaer, K. S.; Fredin, L. A.; Chabera, P.; Harlang, T.; Canton, S. E.; Lidin, S.; Zhang, J.; Lomoth, R.; Bergquist, K.-E.; et al. A Heteroleptic Ferrous Complex with Mesoionic bis(1,2,3-triazol-5-ylidene) Ligands: Taming the MLCT Excited State of Iron(II). *Chem. - A Eur. J.* **2015**, 21 (9), 3628–3639.
- (22) Harlang, T. C. B.; Liu, Y.; Gordivska, O.; Fredin, L. A.; Ponseca, C. S.; Huang, P.; Chábera, P.; Kjaer, K. S.; Mateos, H.; Uhlig, J.; et al. Iron Sensitizer Converts Light to Electrons with 92% Yield. *Nat. Chem.* **2015**, 7 (11), 883–889.
- (23) Chábera, P.; Kjaer, K. S.; Prakash, O.; Honarfar, A.; Liu, Y.; Fredin, L. A.; Harlang, T. C. B.; Lidin, S.; Uhlig, J.; Sundström, V.; 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.* **2018**, 9 (3), 459–463.
- (24) Fredin, L. A.; Papai, M.; Rozsályi, E.; Vanko, G.; Warnmark, K.; Sundström, V.; Persson, P. Exceptional Excited-State Lifetime of an Iron(II)-M-Heterocyclic Carbene Complex Explained. *J. Phys. Chem. Lett.* **2014**, 5 (12), 2066–2071.
- (25) Zhang, W.; Kjær, K. S.; Alonso-Mori, R.; Bergmann, U.; Chollet, M.; Fredin, L. A.; Hadt, R. G.; Hartsock, R. W.; Harlang, T.; Kroll, T.; et al. Manipulating Charge Transfer

Excited State Relaxation and Spin Crossover in Iron Coordination Complexes with Ligand Substitution. *Chem. Sci.* **2017**, 8, 515–523.

- (26) Shepard, S. G.; Fatur, S. M.; Rappe, A. K.; Damrauer, N. H. Highly-Strained Iron(II) Polypyridines: Exploiting the Quintet Manifold to Extend the Lifetime of MLCT Excited States. *J. Am. Chem. Soc.* **2016**, 138 (9), 2949–2952.
- (27) Fatur, S. M.; Shepard, S. G.; Higgins, R. F.; Shores, M. P.; Damrauer, N. H. A Synthetically Tunable System to Control MLCT Excited-State Lifetimes and Spin States in Iron(II) Polypyridines. *J. Am. Chem. Soc.* **2017**, 139 (12), 4493–4505.
- (28) Jamula, L. L.; Brown, A. M.; Guo, D.; McCusker, J. K. Synthesis and Characterization of a High-Symmetry Ferrous Polypyridyl Complex: Approaching the $^5T_2/{}^3T_1$ Crossing Point for Fe(II). *Inorg. Chem.* **2014**, 53 (1), 15–17.
- (29) Smeigh, A. L.; Creelman, M.; Mathies, R. A.; McCusker, J. K. Femtosecond Time-Resolved Optical and Raman Spectroscopy of Photo-Induced Spin-Crossover: Temporal Resolution of Low Spin-to-High Spin Optical Switching. *J. Am. Chem. Soc.* **2008**, 130 (43), 14105–14107.
- (30) March, A. M.; Stickrath, A.; Doumy, G.; Kanter, E. P.; Krässig, B.; Southworth, S. H.; Attenkofer, K.; Kurtz, C. A.; Chen, L. X.; Young, L. Development of High-Repetition-Rate Laser Pump/x-Ray Probe Methodologies for Synchrotron Facilities. *Rev. Sci. Instrum.* **2011**, 82 (7), 73110.
- (31) Walko, D. A.; Adams, B. W.; Doumy, G.; Dufresne, E. M.; Li, Y.; March, A. M.; Sandy, A. R.; Wang, J.; Wen, H.; Zhu, Y. Developments in Time-Resolved x-Ray Research at APS Beamline 7ID. *AIP Conf. Proc.* **2016**, 1741, 1–5.
- (32) Johann, H. H. Die Erzeugung Lichtstarker Röntgenspektren Mit Hilfe von Konkavkristallen. *Zeitschrift für Phys.* **1931**, 69 (3–4), 185–206.
- (33) Szlachetko, J.; Nachtegaal, M.; de Boni, E.; Willimann, M.; Safonova, O.; Sa, J.; Smolentsev, G.; Szlachetko, M.; van Bokhoven, J. A.; Dousse, J.-C.; et al. A von Hamos X-Ray Spectrometer Based on a Segmented-Type Diffraction Crystal for Single-Shot x-

Ray Emission Spectroscopy and Time-Resolved Resonant Inelastic x-Ray Scattering Studies. *Rev. Sci. Instrum.* **2012**, 83, 103105.

- (34) Ejdrup, T.; Lemke, H. T.; Haldrup, K.; Nielsen, T. N.; Arms, D. A.; Walko, D. A.; Miceli, A.; Landahl, E. C.; Dufresne, E. M.; Nielsen, M. M. Picosecond Time-Resolved Laser Pump/X-Ray Probe Experiments Using a Gated Single-Photon-Counting Area Detector. *J. Synchrotron Radiat.* **2009**, 16 (3), 387–390.
- (35) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, 98 (7), 5648–5652.
- (36) Becke, A. D. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, 98 (2), 1372–1377.
- (37) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, 37 (2), 785–789.
- (38) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, 98 (45), 11623–11627.
- (39) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, 27 (15), 1787–1799.
- (40) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. Energy-Adjusted Ab Initio Pseudopotentials for the First Row Transition Elements. *J. Chem. Phys.* **1987**, 86 (2), 866–872.
- (41) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-Type Basis Set for Second-Row Elements. *J. Chem. Phys.* **1982**, 77 (7), 3654–3665.
- (42) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, 28 (3), 213–222.
- (43) Hehre, W. J.; Ditchfield, K.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII.

- Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56* (5), 2257–2261.
- (44) Scalmani, G.; Frisch, M. J. Continuous Surface Charge Polarizable Continuum Models of Solvation. I. General Formalism. *J. Chem. Phys.* **2010**, *132* (11), 1–15.
- (45) Bowman, D. N.; Bondarev, A.; Mukherjee, S.; Jakubikova, E. Tuning the Electronic Structure of Fe(II) Polypyridines via Donor Atom and Ligand Scaffold Modifications: A Computational Study. *Inorg. Chem.* **2015**, *54* (17), 8786–8793.
- (46) Nance, J.; Bowman, D. N.; Mukherjee, S.; Kelley, C. T.; Jakubikova, E. Insights into the Spin-State Transitions in $[\text{Fe}(\text{tpy})_2]^{2+}$: Importance of the Terpyridine Rocking Motion. *Inorg. Chem.* **2015**, *54* (23), 11259–11268.
- (47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09 Rev. D.01; Gaussian, Inc.: Wallingford, CT, USA. 2009.
- (48) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38* (6), 3098–3100.
- (49) Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. *Phys. Rev. B* **1986**, *33* (2), 8822–8824.
- (50) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22* (9), 931–967.
- (51) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. Towards and Order-N DFT Method. *Theor. Chem. Acc.* **1998**, *99*, 391–403.
- (52) ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands <http://www.scm.com> (accessed May 3, 2018).
- (53) Huse, N.; Kim, T. K.; Jamula, L.; McCusker, J. K.; de Groot, F. M. F.; Schoenlein, R. W.

- Photo-Induced Spin-State Conversion in Solvated Transition Metal Complexes Probed via Time-Resolved Soft X-Ray Spectroscopy. *J. Am. Chem. Soc.* **2010**, *132* (19), 6809–6816.
- (54) Cho, H.; Strader, M. L.; Hong, K.; Jamula, L.; Gullikson, E. M.; Kim, T. K.; de Groot, F. M. F.; McCusker, J. K.; Schoenlein, R. W.; Huse, N. Ligand-Field Symmetry Effects in Fe(II) Polypyridyl Compounds Probed by Transient X-Ray Absorption Spectroscopy. *Faraday Discuss.* **2012**, *157*, 463.
- (55) Van Kuiken, B. E.; Khalil, M. Simulating Picosecond Iron K-Edge X-Ray Absorption Spectra by Ab Initio Methods To Study Photoinduced Changes in the Electronic Structure of Fe(II) Spin Crossover Complexes. *J. Phys. Chem. A* **2011**, *115* (39), 10749–10761.
- (56) Vankó, G.; Glatzel, P.; Pham, V.-T.; Abela, R.; Grolimund, D.; Borca, C. N.; Johnson, S. L.; Milne, C. J.; Bressler, C. Picosecond Time-Resolved X-Ray Emission Spectroscopy: Ultrafast Spin-State Determination in an Iron Complex. *Angew. Chemie - Int. Ed.* **2010**, *49*, 5910–5912.
- (57) Vankó, G.; Bordage, A.; Glatzel, P.; Gallo, E.; Rovezzi, M.; Gawelda, W.; Galler, A.; Bressler, C.; Doumy, G.; March, A. M.; et al. Spin-State Studies with XES and RIXS: From Static to Ultrafast. *J. Electron Spectros. Relat. Phenomena* **2013**, *188*, 166–171.
- (58) Vankó, G.; Neisius, T.; Molnar, G.; Renz, F.; Karpáti, S.; Shukla, A.; de Groot, F. M. F. Probing the 3d Spin Momentum with X-Ray Emission Spectroscopy: The Case of Molecular-Spin Transitions. *J. Phys. Chem. B* **2006**, *110* (24), 11647–11653.
- (59) Glatzel, P.; Bergmann, U. High Resolution 1s Core Hole X-Ray Spectroscopy in 3d Transition Metal Complexes - Electronic and Structural Information. *Coord. Chem. Rev.* **2005**, *249* (1–2), 65–95.
- (60) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12* (Pt 4), 537–541.
- (61) Sayers, D. E.; Stern, E. A.; Lytle, F. New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray— Absorption Fine Structure*. *Phys.*

Chem. Lett. **1971**, 27 (18), 1204.

- (62) Ankudinov, A. L.; Rehr, J. J.; Conradson, S. D. Real-Space Multiple-Scattering Calculation and Interpretation of x-Ray-Absorption near-Edge Structure. *Phys. Rev. B* **1998**, 58 (12), 7565–7576.
- (63) Biasin, E.; Driel, T. B. Van; Kjær, K. S.; Dohn, A. O.; Christensen, M.; Harlang, T.; Chabera, P.; Liu, Y.; Uhlig, J.; Pápai, M.; et al. Femtosecond X-Ray Scattering Study of Ultrafast Photoinduced Structural Dynamics in Solvated [Co(Terpy)₂]²⁺. *Phys. Rev. Lett.* **2016**, 117, 013002.
- (64) Zhang, J.; Zhang, X.; Suarez-alcantara, K.; Jennings, G.; Kurtz, C. A.; Daku, L.; Canton, S. E. Resolving the Ultrafast Changes of Chemically Inequivalent Metal – Ligand Bonds in Photoexcited Molecular Complexes with Transient X - Ray Absorption Spectroscopy. *ACS Omega* **2019**, 4, 6375–6381.
- (65) Khalil, M.; Marcus, M. a; Smeigh, A. L.; McCusker, J. K.; Chong, H. H. W.; Schoenlein, R. W. Picosecond X-Ray Absorption Spectroscopy of a Photoinduced Iron(II) Spin Crossover Reaction in Solution. *J. Phys. Chem. A* **2006**, 110, 38–44.
- (66) Sutin, N. Nuclear, Electronic, and Frequency Factors in Electron Transfer Reactions. *Acc. Chem. Res.* **1982**, 15 (14), 275–282.
- (67) Hauser, A.; Vef, A.; Adler, P. Intersystem Crossing Dynamics in Fe(II) Coordination Compounds. *J. Chem. Phys.* **1991**, 95 (12), 8710–8717.
- (68) Carey, M. C.; Adelman, S. L.; McCusker, J. K. Insights in the Excited State Dynamics of Fe(II) Polypyridyl Complexes from Variable-Temperature Ultrafast Spectroscopy. *Chem. Sci.* **2018**, 10 (134).
- (69) Carey, M. C. Achieving a Long-Lived Charge-Separated Fe(II) Chromophore: Insights into the Role of Reorganization Energy on the Ultrafast Photophysical Processes of D6 Polypyridyl Complexes, Ph.D. Dissertation, Michigan State University, East Lansing, MI, 2018.

FOR TABLE OF CONTENTS ONLY

SYNOPSIS

Time-resolved x-ray emission and absorption spectroscopies have been used to probe the excited-state electronic and geometric structure of an Fe(II) polypyridyl complex. Analysis of the data revealed that the lowest energy excited state is high-spin ($S = 2$) in character. This determination had not been possible using other experimental techniques (e.g., time-resolved optical spectroscopy), demonstrating the potential for ultrafast x-ray methods to address scientific questions that are difficult to resolve by other means.