Tracking the Light-induced Excited-State Dynamics and Structural Configurations of an Extraordinarily Long-lived Metastable State at Room Temperature

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Abstract: Time-resolved X-ray (Tr-XAS) and optical transient absorption (OTA) spectroscopy in the pico-microsecond time scale coupled with Density Functional theory calculations are applied to study the light-induced spin crossover processes of a Fe-based macrocyclic complex in solution. Tr-XAS analysis after light illumination shows the formation of a seven-coordinated high spin quintet metastable state which relaxes to a six-coordinated high spin configuration before decaying to ground state. Kinetic analysis of the macrocyclic complex reveals an unprecedented long-lived decay lifetime of ~42.6 μ s. Comparative studies with a non-macrocyclic counterpart illustrate a significantly shortened ~568-fold decay lifetime of ~75 ns, and highlight the importance of the ligand arrangement in stabilizing the reactivity of the excited state. Lastly, OTA analysis shows the seven-coordinated high spin state to be formed within ~6.2 ps. These findings provide a complete understanding of the spin crossover reaction and relaxation pathways of the macrocyclic complex, and reveal the importance of a flexible coordination environment for their rational design.

Introduction

Light-induced single molecule switching is a central topic in modern science covering a long range of applications from optical-readout to biological functions.^[1] Among these photo-conversion processes, transition metal complexes (Scheme 1) exhibiting spin crossover (SCO) phenomenon between the low spin (LS) and high spin (HS) electronic configurations give rise to one of the most spectacular switching processes. A single

molecule can adopt reversibly both spin states in a controlled manner through external perturbation factors such as temperature, pressure, chemical *stimuli* or light irradiation. The latest process from LS to HS is called the LIESST effect by "light-induced excited state spin trapping" and the opposite (from HS to LS) reverse-LIESST.^[1e, 2]

Scheme 1. General roadmap of the SCO complexes studied in this work, including a chemdraw illustration of the macrocyclic and tridentate-based organic ligands. **[1]** refers to $[Fe^{II}(LN_5)(CN_2)]^{2+}$ (LN_5 = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12-14,16-pentaene); **[2]**^[2f] refers to $[Fe^{II}(bpp)(H_2L)]^{2+}$ where bpp = 2,6-bis-(pyrazol-3-yl) pyridine and H_2L = bpp -based ligand, 2,6-bis(5-(2-methoxyphenyl)pyrazol-3-yl)pyridine.

In this process, ultraviolet or visible light excitation of the LS ground state relaxes through an inter-system crossing cascade by first leading to the formations of single and triplet metal-to-ligand charge transfer (1MLCT and 3MLCT) states (Scheme 2), followed by population to a quintet HS state. The HS state subsequently decays back to the ground state.^[3] Several studies involving the application of femto to picosecond time-resolved optical transient absorption^[3a-c, 4] and tabletop^[5], soft and hard X-ray spectroscopy^[3-4, 4e, 4i, 6] have been employed to unravel the photocycle, solvation effects, and relaxation processes of Iron(II)-based SCO complexes. These works have provided valuable insights into the fundamental electronic and solvation dynamics that govern octahedral spin-state switching and light-triggered molecular phenomena^[6c]. Nevertheless, a major drawback for the real applications of these SCO materials in optical data storage in information technology involves the short lifetime (order of picoseconds) of the metastable state formed upon light excitation at room temperature. As previously illustrated^[2h], the

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Supporting information for this article is given via a link at the end of the document. The supporting information (SI) includes the experimental information, the UV-vis absorption measurements, EXAFS fit parameters, determination of high spin excited state fractions, optical transient absorption analysis as well as results of the TD-DFT calculations.

main limitation in the design of materials capable of storing information on a single molecular level or on molecular assemblies stems from the instability of the photoinduced metastable HS state at room temperature.”

Finding means of extending the lifetime of the photoexcited metastable state formed is therefore a critical task. In particular, the ability to control and prolong the magnetic excited state of iron-based earth abundant complexes using light is an important way of enhancing the performance of molecular devices for digital processing, communication and magnetic data storage applications.^[2a-e] It has been long believed that one means of extending the relaxation process of the excited state lifetime lies in inducing large structural distortions over the course of the SCO phenomena.^[2b]

Scheme 2 A. General energy level scheme of Fe-based octahedral spin cross over complexes following photo-excitation from the low spin (LS) ground state to the high spin (HS) excited state after MLCT charge transfer. **B.** Energy level scheme of Fe-based SCO macrocyclic complex **[1]** described in this work involving a change to a seven-coordinated HS structural conformation.

An elegant approach for introducing distortion during the switchable process involved the use of a macrocyclic Schiff-base ligand.^[2b, 2h] Derivative of the Fe(II) macrocyclic-based complexes have shown impressive and atypical abilities to change their local coordination geometry and undergo a reversible structural rearrangement from a six to seven-coordination configuration (Schemes 1,2).^[2b, 2h] Precisely, **[1]** is a hexa-coordinated complex (Schemes 1,2) at room temperature, with a low spin (LS₆) Fe(II) in a distorted octahedral geometry.

The stabilization of the seven-coordinated geometry (HS₇) obtained upon thermal and photoexcitation was achieved through the additional formation of a Fe-N coordination bond within the macrocyclic ligand arrangement and a symmetry change of the metal center from octahedral to pentagonal bipyramidal (Schemes 1, 2).^[2b, 2h] Although the seven coordinated geometry, HS₇, was recently characterized by X-ray diffraction (XRD) at low temperature under continuous light irradiation^[2b], a full understanding of the “real-time” photo-induced SCO processes under realistic conditions at room temperature, and the relaxation dynamics of the various electronic states that are responsible for the increased coordination and geometrical changes of complex **[1]** have not been reported.

Towards this aim, ultrafast pump (laser)/X-ray (probe) time-resolved X-ray absorption (tr-XAS) spectroscopy with pico-microsecond time resolution coupled with time-dependent Density Functional theory calculations (TD-DFT) are employed to capture snapshots of the HS excited state of the macrocyclic complex **[1]**. In this scenario, a laser pulse (pump) initiates the photoinduced reaction and an X-ray pulse (probe) at varying delays is used to interrogate the local electronic and structural change. Comparison of the excited-state dynamics of complex **[1]** with various octahedral-based Fe(II) SCO complexes studied in solution phase remark an unprecedented longer excited state lifetime in the order of microseconds (Table 1).

Table 1. Decay lifetimes of the HS quintet excited states of some previously studied Fe(II)-based SCO complex in solution. Comparisons with the complexes reported in this work are provided.

Examples of Fe-based SCO complexes	Lifetime of quintet state at room temperature (solvent)	Ref.
[Fe ^{II} (bpy) ₃] ²⁺ (bpy = 2,2'-bipyridine)	665 ± 35 ps (H ₂ O), 980 ± 50 ps (CH ₃ CN)	[3a, 3b, 4a, 4e, 4h, 6h, 7]
[Fe(terpy) ₂] ²⁺ (terpy = 2,2':6',2''-terpyridine)	5.4 ± 0.1 ns (CH ₃ CN)	[4h, 7]
[Fe ^{II} (mbpy) ₃] ²⁺ (mbpy = 4,4'-dimethyl-2,2'-bipyridine)	865 ± 11 ps (H ₂ O), 1295 ± 10 ps (CH ₃ CN)	[3c]
[Fe(tren)(py) ₃] ²⁺ ; (tren(py) ₃ = tris(2-pyridyl-methyliminoethyl)amine)	60 ± 5 ns (CH ₃ CN)	[4i, 6f, 7]
[Fe(phen) ₃](BF ₄) ₂ (phen = 1,10-phenanthroline)	1.1 ± 0.1 ns (CH ₃ CN)	[3d]
[Fe(2CH ₃ -phen) ₃](BF ₄) ₂	3.6 ± 0.2 ns (CH ₃ CN)	[4g]
[Fe(dcpp) ₂] ²⁺ (dcpp = 2,6-dicarboxypyridyl pyridine)	272 ± 4 ps (CH ₃ CN)	[6d]
[Fe(dmb) ₃] ²⁺ (dmb = 4,4'-dimethyl-2,2'-bipyridine)	1.32 ± 0.02 ns (CH ₃ CN)	[4h]
[Fe(dtbb) ₃] ²⁺ (dtbb = 4,4'-di-ter-butyl-2,2'-bipyridine)	1.07 ± 0.01 ns (CH ₃ CN)	[4h]
Complex [1] (Scheme 1)	42.6 ± 9.30 μs (CH ₃ OH)	This work
Complex [2] (Scheme 1)	75.2 ± 20.5 ns (CH ₃ OH)	This work

This work thus starts by describing the experimental and theoretical X-ray spectroscopic results of **[1]**^[2b, 8] in contrast to an Fe(II) octahedral reference SCO compound^[2f] **[2]** (Scheme 1).

The electronic configurations and structural conformations of the macrocyclic complex's **[1]** excited state are discussed. The dynamics of the high state excited species of **[1]** in the sub 100 ps and ps- μ s time scales are then determined through complementary optical transient absorption (OTA) and tr-XAS spectroscopy. Finally, the relaxation pathway of **[1]** to a six coordinated HS state (Scheme 2) and its significantly longer excited state lifetime in comparison to **[2]** are elaborated upon.

Results and Discussion

Electronic and Structural Nature of Complexes [1] and [2] in solid and solution. Complexes **[1]** and **[2]** illustrated in Scheme 1, were studied in both solid and solution forms by X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) spectroscopy (Figure 1). Similar to the majority of reported Fe(II) SCO complexes^[3a, 3c], the distorted octahedral iron-based complexes illustrated in scheme 1 display atomic-like 3 d^6 levels with filled d_{xy} , d_{xz} and d_{yz} molecular orbitals in D_{5h} symmetry (Scheme 2 A). Local distortions of the octahedron around Fe in both complexes result in splitting of the d levels thus causing them to exhibit a multiplet pre-edge feature.^[9] Presence of pre-edge features correspond to weak 1s to 3d quadrupole transitions which gain intensity through the dipole excitations of the core electrons into the valence 3d states hybridized with the N/C ligand p orbitals.^[9a, 10] Interestingly, both the solid and solution states of **[1]** demonstrate very similar pre-edge features at 7113 and 7116 eV and rising edge trends from 7120-7140 eV (Figure 1 A) indicating nearly identical electronic and local geometrical configurations. Negligible changes are observed upon the dissolution of **[1]** in solution thus highlighting the robust and inflexible nature of its macrocyclic coordination arrangement. In sharp contrast to **[1]**, the octahedral-based nature of the local coordination arrangement of complex **[2]** is characterized by a 2.4 eV shift of the rising edge towards lower energy of the XANES spectrum upon its dissolution in methanol (Figure 1 A). Although complex **[2]** in both solid and solution states have the same formal oxidation states, they demonstrate large symmetrical and geometrical changes as will be elaborated in the EXAFS discussion below (Figure 1 B and compare Fe-N distances in Table 2/Table S2). The solution complex **[2]** further demonstrates a more prominent multiplet pre-edge feature compared to its solid-based counterpart which is attributed to the local geometrical and symmetrical changes^[10] occurring upon its dissolution in methanol (Figure 1 A inset).

The EXAFS spectra of **[1]** and **[2]** in both solid and solution states are shown in Figure 1 B and C. Three peaks denoted in Figure 1 B as I, II and III are observed in the solid and solution EXAFS spectra of **[1]** corresponding to the distinctive Fe-N/C and elongated Fe-C distances. EXAFS fits for the first coordination sphere and the entire spectrum for **[1]** in both solid and solution forms are shown in Table 2 and S2. Analysis of the solid-state EXAFS peaks in **[1]** clearly resolves 6 Fe-N/C bonds at 1.96 Å in agreement with the reported X-ray diffraction structure by Aromí et al.^[2b] (Table 2) and relaxed structures from DFT geometry optimizations (Table 2). Interestingly, the solution-state EXAFS of **[1]** exhibit Fe-N/C distances of 1.93 Å, thus displaying very similar geometrical configurations. The practically identical structural arrangements of **[1]** in solid and

solution states thus ascertain its robust macrocyclic ligand arrangement as previously demonstrated through the XANES experiments (Figure 1 A).

Figure 1. A. Top: Experimental normalized Fe K-edge XANES of **[1]** in solution (black), solid (blue) and **[2]** in solution (red) and solid (magenta) forms. Inset: Zoom-in of the pre-edge details. B. Experimental Fourier transforms of k^2 -weighted Fe EXAFS of **[1]** in solution (black) and solid (blue). Inset: Back Fourier transforms, experimental results (solid lines) and fitted (dashed lines) $k^2\chi(k)$ of **[1]** in solid (Fit 2, Table S2) and solution (Fit 4, Table S2). Experimental spectra were calculated for k values of 2 to 11.533 Å⁻¹. C. Experimental Fourier transforms of k^2 -weighted Fe EXAFS of **[2]** in solid (magenta) and solution (red). Inset: Back Fourier transforms, experimental results (solid lines) and fitted (dashed lines) $k^2\chi(k)$ of **[2]** in solid (Fit 6, Table S2) and solution (Fit 8, Table S2). Experimental spectra were calculated for k values of 2 to 11.533 Å⁻¹.

The EXAFS spectra of **[2]** in solid and solution states are contrarily largely different. The solid structure of **[2]** demonstrate

a prominent peak (Peak I in figure 1 C) within the first coordination sphere, corresponding to the averaged Fe-N distance of 1.95 Å in agreement with the reported XRD structure^[2b, 8] and relaxed structures from DFT geometry optimizations (Table 2). However, upon its dissolution in methanol, two distinctive peaks (I and II in Figure 1 C) are obtained corresponding to the likely elongation of four of the equatorial Fe-N distances within the first coordination shell (Scheme 1). Fitting of complex [2] in solution form illustrates improvement of the EXAFS fit quality upon addition of 2 Fe-N distances at 1.96 Å and 4 elongated Fe-N distances at 2.18 Å (Table 2, Table S2, Fit 8).

Table 1. Comparison of structural parameters obtained from solid state (XRD measurements), DFT calculations and EXAFS analysis. Bond lengths are given in Å.

Complexes	EXAFS(Å)	XRD (Å)	DFT (Å)
[1] LS ₆ Solid	Fe-N/C: 6 x 1.96	Fe-N: 1.854, 1.907, 2.031, 2.115 Fe-C: 1.942, 1.958 (Fe-N/C: 6 x 1.97)	Fe-N: 1.841, 1.909, 2.034, 2.155 Fe-C: 1.949, 1.954 (Fe-N/C: 6 x 1.97)
[1] LS ₆ Solution	Fe-N/C: 6 x 1.93		
[2] LS ₆ Solid	Fe-N: 6 x 1.95	Fe-N: 1.925, 1.924, 1.952, 1.952, 1.968, 1.977 (Fe-N: 6 x 1.950)	Fe-N: 1.940, 1.946, 1.979, 1.991, 1.991, 2.003 (Fe-N: 6 x 1.975)
[2] LS ₆ Solution	Fe-N: 2 x 1.96 Fe-N: 4 x 2.18		
[1] HS ₇ Excited high spin 7-coordinated state	Fe-N/C: 3 x 2.15 Fe-N: 4 x 2.27	Fe-N: 2.147, 2.252, 2.275, 2.321, 2.339 Fe-C: 2.173, 2.191 (Fe-N/C: 3 x 2.170, Fe-N: 4 x 2.297)	Fe-N: 2.127, 2.276, 2.282, 2.393, 2.395 Fe-C: 2.136, 2.136 (Fe-N/C: 3 x 2.133, Fe-N: 4 x 2.337)
[3] HS ₇ Reference high spin 7-coordinated state	Fe-N/C: 3 x 2.13 Fe-N: 4 x 2.27		
[1] - HS ₆ Calculated high spin 6-coordinated state			Fe-N: 2.044, 2.112, 2.125, 2.175 Fe-C: 1.929, 1.956 (Fe-N: 4 x 2.114, Fe-C: 2 x 1.943)

These findings show that while the macrocyclic structure of [1] remains nearly intact in solid and solution state, complex [2] contrarily bears an elongation of the Fe-N distances within the first coordination sphere thus highlighting its larger degree of flexibility. Importantly also, theoretical methods including geometry optimizations (Table 2, S2, Figure S1) as well as EXAFS analysis for the solid-state structures of [1] and [2] reproduce the experimental data well and confirm that these methods can be reliably used for analysis of the HS transient species. These results are of relevance for macrocyclic Fe-based SCO complexes and can be extrapolated to a wide range of reported complexes of similar structure.

Elucidation of the Excited State Structure of the Macrocyclic-based Complex[1] through Time-resolved X-ray Spectroscopy. Intrigued by the stable coordination environment of complex [1], its time-resolved behaviour and excited state structure was probed in the picosecond time range through time-resolved X-ray absorption spectroscopy. The complexes were optically excited in the MLCT range and probed with X-ray pulses. XAS spectra were collected both before (laser-off) and after (laser-on) laser excitation at various delays from 100 ps to ~45 μs. By subtracting the laser-off from the laser-on spectrum, a transient signal is obtained for each pump-probe delay. The transient spectrum thus provides information about the photo-induced dynamics, electronic and structural nature of the excited state configuration.

Figure 2 A. Experimental normalized Fe K-edge XANES of [1] in solution **B.** Experimental difference spectrum (laser on-laser off) corresponding to the HS state transient signal of [1]. **Inset. Top.** Simulated difference pre-edge feature for the HS state structure of [1]. **Bottom.** Zoom in the pre-edge feature of the experimental transient signal.

Figure 2A shows the ground-state XANES spectrum of complex[1] and Figure 2B shows the time-resolved XAS spectra at a time delay of 100 ps between laser and X-ray pulses. A transient signal with maximum peak energy of 7125 eV together with a broad feature at 7147 eV is obtained (Figure 2B), typical of the signature of a Fe-based quintet HS state's configuration.^[3a, 3c, 4a, 6b, 6d, 6h] Interestingly, clear changes are additionally observed in the pre-edge features at low photon energies at

7113, 7116 and 7118 eV (Figure 2B), indicating significant deviations in the electronic configurations and local symmetry of the excited state's structure. Upon laser excitation, d level atomic rearrangements in the excited state structure (Scheme 2B) are further accompanied by structure relaxation and increased hybridization of the valence 3d states with N/C ligand orbitals, thus explaining the prominent change in the pre-edge features between the low and high states. The differences in energy for the three subsequent pre-edge transitions at 7113, 7116 and 7118 eV observed in the transient signal was calculated to be ~3 and ~2 eV respectively for the high spin derivative, comparable to that observed in the experimental pre-edge XAS (Figure 2B). Furthermore, the pre-edge features of the time-resolved XAS spectrum agree well with the calculated ones (Figure 2B inset) showing the close agreement of the DFT-optimized HS₇ state's structure with the experimentally observed one (Figure 2B).

The XANES spectra of the macrocyclic complex **[1]** before (laser-off) (in black) and after (laser-on) (in blue) light illumination are shown in Figure 3 A. A proportion of the excited state of around ~9% was determined in the laser-on spectra and further used to plot the actual or reconstructed spectrum (magenta trace in Figure 3 A). The excited state fraction after light illumination was determined by two methods of analysis. On the one hand, the percentage of the HS excited state species in the laser-on spectrum was determined to be ~10 % by integrating the pre-edge region of the excited state and comparing to a pure HS₇ reference complex^[11] (Figure S2) that was synthesized for this purpose. On the other hand, the pre-edge of the laser-on spectra was determined to be ~8 % upon comparison to the TD-DFT calculated XANES profile of the seven-coordinated HS state (Figure S3). Both methods of analysis yield comparable results thus narrowing the percentage of excited state species after light excitation to be around 8-10 %, and further confirm the validity of the TD-DFT simulations.

It should be noted that the XANES and EXAFS of the high spin, HS₇, reference complex **[3]** (Figure S2) was studied in solution after fast freezing (within 30 s) in a cryostat at 20 K to minimize radiation damage and due to its instability in solution state as evidenced by UV-visible absorption kinetic analysis (Figure S4). Analysis of the reconstructed XANES spectrum of the excited state complex compared to the ground state spectrum reveals several prominent changes in the pre-edge and rising edge regions from 7110-7140 eV, labeled here as **P**, **A**, **B** and **C** (Figure 3 A), that are typical of iron-based HS complexes.^[3c] Three peaks in the pre-edge region (**P**) of the reconstructed laser-on spectrum at 7109 eV (Figure 3 A inset), 7113 and 7118 eV are observed corresponding to the dipole allowed excitations of the core electrons hybridized with carbon and nitrogen ligand p orbitals.^[9a, 10] (Figure 3 A and inset) The significant changes in the pre-edge regions of the excited state conformations indicates a large variation in the local coordination geometry as elaborated in section 2.2 above.^[9a, 12] Interestingly, feature **A** at 7127 eV shows a relative red shift of 3 eV in comparison to its ground state XANES spectral feature (Figure 3 A). The red energy shift of feature **A** is attributed to the lowering of the energy of the unoccupied Fe(4s,4p)-N(2p) states.^[6f] Light excitation causes the electrons in the d_{xy} , d_{xz} , and d_{yz} orbitals as depicted in scheme 2 B to be rearranged and promoted to d_{xy} , $d_{x^2-y^2}$, and d_{z^2} which involve orbitals that are formally antibonding in nature, thus causing the unoccupied states to

lower in energy. Features **B** (7137 eV) and **C** (7151 eV) lastly correspond to the multiple and single scattering processes of the photoelectron.^[3c, 13] The decrease in intensity and shift in energies of these features are attributed to the geometrical differences between the LS and HS states.^[6f]

Figure 3 A. Experimental transient X-ray absorption spectrum of **[1]** measured before (black) and at 100 ps (blue) after laser excitation, together with the reconstructed XANES spectrum of its HS state configuration. The reconstructed “Laser ON” spectrum corresponds in this case to the subtraction of 91 % of the ground state spectrum from the “Laser ON” spectrum. **Inset.** Zoom-in of the pre-edge region of **[1]** before laser excitation (black) and the reconstructed spectrum after laser excitation. **B.** Fourier transforms of k^2 -weighted Fe EXAFS of the laser off and reconstructed excited state. **Inset:** Back Fourier transforms, experimental results (solid lines) and fitting (dashed

lines) $k^2\chi(k)$ (Fit 12 for reconstructed [1], HS₇ state, Table S2) Fourier transforms were calculated for k values of 2 to 10.5 Å⁻¹. **C.** Simulated EXAFS spectra. Atomic coordinates were obtained from single crystal X-ray diffraction structure of [1]^[2b, 8] (black) and its HS state configurations. The XRD crystal structure for the HS state configuration^[2b] were obtained at 82 K under white light (magenta) and 455 nm LED lamp irradiation (dashed magenta line).

The reconstructed EXAFS for the HS₇ state, shown in Figure 3 C, reveals 3 peaks (I, II and III) corresponding to the elongated Fe-N/C and Fe-C distances. Analysis of the EXAFS data clearly shows an elongation in the Fe-N bond lengths of 0.22-0.34 Å, with 3 Fe-N/C at 2.15 Å and 4 Fe-N at 2.27 Å (Table 2, S2 and Figure S5). The fitted Fe-N/C distances are in agreement with the extracted distances of the HS₇ reference complex [3] (Figure S2, Tables 2, S2).

The derived EXAFS spectra for the reconstructed high spin states further agree with the relaxed structures from DFT geometry optimization and reported XRD structures^[2b] of the high spin seven-coordinated state obtained under both white and 455 nm LED light illumination (Figure 3 C, Table 2). It is important to remark that the EXAFS spectrum of the derived excited state is in sharp contrast to the DFT-optimized structure (Table 2) and calculated EXAFS profile of a six-coordinated HS structure (Figure S6). The experimental EXAFS spectrum of the [1]HS₇ conformation reconstructed with an excited state fraction of ~8-10 % (Figure 3 C, Figure S7) lastly matches very well with the calculated EXAFS profile obtained from XRD structures. This analysis additionally confirms the correct percentage of excited state fraction used in the estimation of complex [1]'s laser on spectrum. The excitation state fraction of less than 10 % obtained for the reconstruction of the HS state can be explained by the lower photon flux (photons/pulse/molecules) employed in this set of experiments (Table S1). Our experimental conditions however ensures that the experiments are carried out in the linear regime, while ruling out multi-photon effects, and further helps in minimizing any radiation and laser-induced damage. As illustrated in Figure S8, no damage was observed to the sample scan after scan over the course of several hours.

Kinetic analysis and dynamics of [1] in sub 100 picosecond time scales. The time-frame of formation of the high spin excited state species and relaxation pathways of [1] was determined through complementary OTA and tr-XAS spectroscopy. Limited by the 100 ps pulse duration of the X-rays, OTA spectroscopy in the 0–200 ps time regime was first performed in order to resolve its time frame of formation (Figure 4).

The steady-state optical absorption spectrum of [1] in CH₃OH displays two absorption bands at 490 and 600 nm corresponding to the singlet ¹MLCT^[4e] transitions as previously discussed (Figure 4B inset, S9). A broad photo-induced absorption feature is observed at ~430 nm corresponding to the signature of the ³MLCT state and the absorption of the reduced ligand, as already established from optical transient absorption^[3a] and spectroelectrochemical studies^[14] of Fe(II) spin crossover polypyridine complexes. The decay of the triplet excited state at ~430 nm was fitted to be ~6.20±0.84 ps (Figure 4) through a first order rate equation, suggesting a sub-ps d level atomic arrangement of the electrons (Scheme 2B), and the direct population of the ³MLCT triplet state to the high spin seven-coordinated state within the time frame of ~6.2 ps.

Similar decay kinetics within comparable error bars of 5.23 ± 0.33 ps are observed at 490 nm (Figure 4 B), corresponding to the photobleach, in agreement with the fast (< 0.6 ps) formation of the triplet excited state. A positive photoinduced absorption band between 650-730 nm (Figure 4 B) could further be observed at pump-probe delays between 16-197 ps corresponding to the optical signature of the seven-coordinated excited state configuration. The global spectra fits of the optical transient absorption spectra (Figures S10, S11 Tables S3,S4) shows the absorption maxima of the high spin excited state to be 675±5 nm. It is important to remark that the assignment of coordination and structure is difficult through optical transient absorption spectroscopy due to its direct insensitivity. The decay kinetics and relaxation pathways of the HS state to a six-coordinated octahedral state was consequently determined after the 100 ps time scale through time-resolved X-ray absorption spectroscopy as elaborated below.

Figure 4 A. “Ball and Stick” schematic for the molecular structures of [1] in the ground and excited states. **B.** Optical transient absorption spectra of a solution of [1] collected at varying pump-probe delays between 6 to 197 ps. **Inset. Left** Kinetic decay profile of the transient absorption signal at $\lambda = 430$ nm and 490

nm after excitation at $\lambda_{\text{exc}} = 378$ nm. The solid lines are fittings to a first order decay kinetics, and T is the resulted lifetime. **Right.** Steady-state optical absorption of Complex [1].

Unusually long-lived metastable quintet state of Complex [1] and relaxation to a HS six-coordinated conformation.

Figure 5. Stacked spectra corresponding to a series of time delays between laser and X-ray pulses of **A.** 5 mM [1]. These measurements were carried out for a range of averaged time delays from 0 to 45 μ s. **Inset** X-ray kinetics taken at 7125 eV corresponding to the decay of the HS state structure for complex [1] from 0 to 1 μ s and two more relaxation pathways up till $\sim$ 45 μ s. **B.** Stacked spectra corresponding to a series of time delays between laser and X-ray pulses of 1.2 mM [2]. These measurements were carried out for a range of averaged time delays from 0 to 1 μ s. **Inset.** X-ray kinetics taken at 7125 eV corresponding to the decay of the HS state structure of [2] from 0 to 1 μ s.

The HS state configuration of [1] appears with the 100 ps X-ray pulse duration of the X-rays. A strong transient signal is observed from 100 ps to 45 μ s in [1] (Figure 5 A). The gradual decays of the transient signal from 0 to $\sim$ 100 ns was monitored by fixing the photon energy to 7125 eV, corresponding to the formation of the HS state's configuration, and varying the time delays between the laser and X-ray pulses. The transient signals of the HS state structure at longer time delays from 153 ns- 45 μ s were obtained by averaging multiple X-ray pulses after laser excitation (See Experimental Section in SI).

As illustrated in Figure 5 A inset, the HS excited state of [1] clearly demonstrates 3 structural relaxation times with lifetimes of $T_1 = 94.2 \pm 10.4$ ns, $T_2 = 1.50 \pm 0.54$ μ s and $T_3 = 42.6 \pm 9.3$ μ s. A zoom-in comparison of the transient signal XANES spectrum at various delays (Figure S12) illustrates a shift of the $1s \rightarrow 4p$ main peak transition at 7120 eV indicating a change in the electronic configuration at longer pump-probe delays. Changes in the XANES spectral features at 7135 eV corresponding to changes in the multiple scattering processes^[3c, 13] are additionally observed reflecting the geometrical changes of the HS state's excited state structures at microsecond delay time scales (Figure S12).

Figure 6. Reconstructed XANES spectra of the HS state configuration of [1] at various delays ranging from 100 ps to $\sim$ 41 μ s after laser excitation. The dashed XANES spectra represent the raw data while the solid line represents the smoothed spectra. A HS₆ structural conformation is observed for longer delay time from $\sim$ 2.5 to $\sim$ 41 μ s. **Inset.** Zoom-in of the raw XANES data's pre-edge region.

The transient signals of the HS state structure at time delays of 2.5- 45 μ s are significantly decreased by factors of $\sim$ 11-23 (Figure S12) compared to the one observed at 100 ps (Figure 2 B) such that the EXAFS and structural conformation of the HS state could not be resolved during those time intervals. However, the reconstructed HS XANES spectra ranging in the microsecond time scales from 2.5-40.2 μ s (Figure 6) clearly show an increase in the pre-edge intensity and a shift of the rising edge energy to lower energy. Both the increase in the pre-edge intensity (Figure 6 inset) and negative shift in the XANES rising-edge energy region point towards the population of the seven-coordinated HS₇ state to a six-coordinated HS₆ state

before its eventual decay to the LS_6 coordinated complex. As demonstrated by Solomon and coworkers^[9], the pre-edge intensity due to metal 4p mixing into 3d orbitals has been shown to increase with a decrease in the coordination number due to a decrease in the dipole allowed $1s \rightarrow 4p$ character contribution to this transition. Moreover the negative shift in the rising K-edge energy region reflects the lesser ionization energy^[10] required to eject a core 1s electron from a six-coordinated HS_6 versus the seven-coordinated HS_7 geometrical conformation.

As previously discussed, the severe coordination and geometrical change around the Fe(II) center strongly affects the kinetics of its structural relaxation process. The HS_7 species is hereby shown to strongly decelerate the HS to LS relaxation state by acting on the vibrational properties of the inner macrocyclic core. This study further shows for the first time that the HS_7 excited state first relaxes to the HS_6 state before finally recovering to the LS_6 ground state.

The transient spectrum of **[2]** contrarily decays within 99.1 ± 55.8 ns (Figure 5 B and inset) highlighting the remarkably longer-lived excited state species in **[1]**. Due to the large error bar derived in the kinetic analysis of **[2]** (Figure 5 B inset), its decay lifetime was further corroborated through OTA spectroscopy carried out in the nanosecond time regime (Figure S13). The steady-state optical absorption spectrum of **[2]** in CH_3OH displays a broad band at 456 and 550 nm (Figure S9B) corresponding to the singlet $^1MLCT^{[4e]}$ transitions. Time-resolved nanosecond OTA analysis (Figure S13) reveals a ground state bleach with a maximum negative peak at 456 nm and decay constant of $\sim 75.2 \pm 20.5$ ns (Figure S13 inset), consistent with the X-ray kinetic analysis (Figure 5 B inset).

Conclusion

In summary, this work reports the application of steady-state and time-resolved X-ray absorption spectroscopy coupled with DFT calculations in monitoring the electronic and structural dynamics of a macrocyclic Fe-based SCO complex. Importantly, structural comparisons of the macrocyclic **[1]** with a non-macrocyclic counterpart **[2]** illustrate the intact and rigid nature of the ligand arrangement in both solid and solution states. While the structural arrangement of **[1]** is unchanged upon its dissolution in methanol, **[2]** contrarily demonstrates a significant elongation of the Fe-N distances in solution.

Light excitation of macrocyclic complex **[1]** further triggers d level atomic rearrangements within the molecule forming a quintet HS state within 6.20 ± 0.84 ps which simultaneously undergoes an increased coordination change from a six to a seven-coordinated conformation change. The obtained Fe-N/C bond distance elongation of 0.22-0.34 Å within the first coordination sphere is in agreement with theoretical relaxed DFT optimizations and reported XRD structures. This finding confirms the influence of the $Fe-C_2N_5$ coordination sphere in stabilizing the seven-coordinated excited state's configuration.

Significantly also, time-resolved X-ray kinetics studies show for the first time that the seven-coordinated HS_7 state first relaxes to the HS_6 state before finally decaying back to the LS_6 ground state within a time scale of $\sim 42.6 \pm 9.3$ μs . In sharp contrast, coupled X-ray and OTA kinetic analysis of **[2]** demonstrates a significantly ~ 568 -fold shortened decay lifetime of $\sim 75.2 \pm 20.5$ ns.

The relatively slow rate (microseconds) associated with the decay of the HS state of **[1]** in comparison to previously reported Fe(II)-based SCO complexes (Table 1, Figure 5) is a consequence of the low reactivity of the seven-coordinated excited state's geometry that is highly stabilized by the macrocyclic nature of the ligand surrounding the Fe(II) coordination sphere. Future efforts to control and prolong the lifetime of the metastable state include further introduction of rigid equatorial-based ligands that can help in enhancing the stability and lifetime of the excited state. Development of such types of complexes will provide novel promising avenues for practical applications in magnetic devices and in molecular spintronics while opening an interesting new pathway in the area of light-induced SCO in transition-metal compounds.

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Keywords: Iron spin crossover complexes • time-resolved X-ray absorption spectroscopy • optical transient absorption spectroscopy • Time-dependent density functional theory • excited state structures

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FULL PAPER

A multi-method approach was used to study the light-induced spin crossover dynamic process and relaxation pathway of an Fe-based macrocyclic complex. Comparison of its excited state dynamics with other Fe(II) spin crossover complexes remark an excited state lifetime in the order of microseconds. These findings show the importance of the ligand arrangement in stabilizing the reactivity of the excited state.

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Tracking the Light-induced Excited-State Dynamics and Structural Configurations of an Extraordinarily Long-Lived Metastable State at Room Temperature