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ABSTRACT

Oligonuclear complexes of d^4 – d^7 transition metal ion centers that undergo spin-switching have long been developed for their practical role in molecular electronics. Recently, they also have appeared as promising photochemical reactants demonstrating improved stability. However, the lack of knowledge about their photophysical properties in the solution phase compared to mononuclear complexes is currently

hampering their inclusion into advanced light-driven reactions. In the present study, the ultrafast photoinduced dynamics in a solvated $[2 \times 2]$ iron(II) metallogrid complex are characterized by combining measurements with transient optical-infrared absorption and x-ray emission spectroscopy on the femtosecond time scale. The analysis is supported by density functional theory calculations. The photocycle can be described in terms of intra-site transitions, where the Fe^{II} centers in the low-spin state are independently photoexcited. The Franck–Condon state decays via the formation of a vibrationally hot high-spin (HS) state that displays coherent behavior within a few picoseconds and thermalizes within tens of picoseconds to yield a metastable HS state living for several hundreds of nanoseconds. Systematic comparison with the closely related mononuclear complex $[\text{Fe}(\text{terpy})_2]^{2+}$ reveals that nuclearity has a profound impact on the photoinduced dynamics. More generally, this work provides guidelines for expanding the integration of oligonuclear complexes into new photoconversion schemes that may be triggered by ultrafast spin-switching.

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INTRODUCTION

Photoinduced spin-switching (PSS) in solvated d^4 – d^7 transition metal (TM) complexes is a fundamental molecular process, which is driving a growing number of advanced technologies, including ion sensing, photocatalysis, and drug delivery (Kumar and Ruben, 2017; Halcrow, 2013). The vast majority of solvated TM compounds that operate through efficient PSS are mononuclear Fe^{II} complexes that switch from the low-spin (LS) $(t_{2g})^6\ ^1A_1$ state to the high-spin (HS) $(t_{2g})^4(e_g)^2\ ^5T_1$ state upon light irradiation. Despite definite success in laboratory settings, the efficiencies reported so far cannot yet meet the demands of chemical applications in real-life because of the limitations associated with rather restricted intramolecular distortions and photodecomposition. The prospect of overcoming these hurdles is currently spurring a significant synthetic effort toward oligonuclear complexes, since they often interconvert between stable and adaptable conformers that respond to the changes in the surroundings (Bodenthin *et al.*, 2009; Halder, 2002; and Wang *et al.*, 2013). For example, homometallic, heterometallic, and mixed valence $[2 \times 2]$ grid complexes, which are actively pursued for high-density data storage and miniaturization in the field of molecular electronics, have recently emerged as self-assembling nanosized platforms that can sustain multiple spin-switching (Schäfer *et al.*, 2016; Matsumoto *et al.*, 2014; Schneider *et al.*, 2013; Schneider *et al.*, 2010; Wu *et al.*, 2009; and Nihei *et al.*, 2005), charge transfer (Ohkoshi *et al.*, 2011; Liu *et al.*, 2010; and Zhang *et al.*, 2010), and redox modulation (Shen *et al.*, 2015; Wang *et al.*, 2013; Schneider *et al.*, 2010; Ruben *et al.*, 2004; and Uppadine *et al.*, 2004). The optimization of these properties could ultimately produce photosensitizers, reactive centers, or catalysts achieving superior operando performances. However, unlike for the single-crystal and film morphologies, functionalities based on manipulating the spin degrees of freedom with visible photons have not been demonstrated to date for solvated metallogrid complexes (Kumar and Ruben, 2017). This status can be ascribed to the fact that their basic photophysical properties have rarely been investigated in the solution phase. A fundamental difficulty lies in tracing the detailed map of the competing deactivation pathways that are mediated by intersystem crossing (ISC), internal conversion (IC), internal vibrational relaxation (IVR), and vibrational cooling (VC) to the solvent. Consequently, establishing clear correlations between the nuclearity of the large molecular assembly, the connectivity of the multi-site ligand scaffold, and the intrinsic rate of the PSS process requires combining the quantitative results

of several ultrafast spectroscopic measurements. From the accumulated experience about the PSS in solvated mononuclear Fe^{II} complexes, transient optical absorption (TOA) spectroscopy in the UV–visible range can monitor the population of the bright states reached through dipole-allowed transitions, such as the metal-to-ligand-charge-transfer (MLCT) state, which subsequently leads to the formation of the lowest-lying quintet HS state. The technique also delivers the lifetime of the metastable state through the kinetics of the ground-state bleach recovery (i.e., HS $\rightarrow$ LS transition). In few cases, transient infrared absorption (TIA) spectroscopy (Wolf *et al.*, 2008; Zerdane *et al.*, 2018a; Collet *et al.*, 2019) and transient Raman spectroscopy (Smeigh *et al.*, 2008 and Collet *et al.*, 2019) have been used to follow the vibrational relaxation toward the dark thermalized HS state in related mononuclear Fe^{II} complexes. Utilizing the high photon energies delivered by the X-ray Free Electron Laser (XFEL) facilities, transient x-ray emission (TXE) spectroscopies of the Fe^{II} K α lines ($2p_{3/2,1/2} \rightarrow 1s$) and Fe^{II} K β lines ($3p_{3/2,1/2} \rightarrow 1s$) have been employed to uncover the spin multiplicity of the optically dark metal-centered (MC) states involved in the formation of the HS state (Zhang *et al.*, 2014; Zhang and Gaffney, 2015) and, more generally, to map out the photoinduced spin-dynamics in homoleptic and heteroleptic mononuclear Fe^{II} complexes (Zhang *et al.*, 2017; Kjær *et al.*, 2018; 2019; and Kunnus *et al.*, 2020). The present work reports the first steps toward obtaining exhaustive characterizations of the photoinduced dynamics in oligonuclear TM complexes using mid-IR, UV–vis, and x-ray femtosecond pulses. The reversible photocycle of a solvated pyrazolate-bridged $[2 \times 2]$ Fe^{II} metallogrid complex is probed with femtosecond TOA and TIA spectroscopies along with TXE spectroscopy at the FXE instrument (Galler *et al.*, 2019; Khakhulin *et al.*, 2020) of the European XFEL (EuXFEL) facility (Altarelli, 2015; Tschentscher *et al.*, 2017). Correlating the relevant time scales associated with the coupled electronic, vibrational, and spin dynamics allows building a detailed picture of the PSS process in this important family of oligonuclear TM complexes that will guide the development of their light-driven applications based on spin-switching in the solution phase.

RESULTS

The $[2 \times 2]$ metallogrid complex $[\text{Fe}_4(\text{L})_4](\text{BF}_4)_4$ (noted Fe4) is formed around the pyrazole-based compartmental ligand bis(2,2′-bipyridine)-6,6′-(3,5-pyrazol) [noted HL, see Fig. 1(a)] (van der Vlugt *et al.*, 2008). The coordination sphere of each Fe^{II}

FIG. 1. (a) Compartmental ligand HL. Crystallographic structures at (b) 133 K and (c) 233 K reported by Schneider *et al.* (2010), with schematic illustration of their respective molecular structures with spin composition [(d) and (e)]. The LS and HS centers are displayed in blue and red, respectively.

center consists of two quasi-orthogonal terpyridine-like binding units, each belonging to two compartmental deprotonated ligands L. The molecular structure of Fe4 with the BF_4^- counter-anion determined through x-ray crystallography depends on the temperature (Schneider *et al.*, 2010). At 133 K, a single Fe^{II} center is in the $(t_{2g})^6$ LS configuration, while three Fe^{II} centers are in the $(t_{2g})^4(e_g)^2$ HS configurations [Fig. 1(b)]. The average metal-ligand bond lengths, R_{av} , are 1.99 Å for the LS center and 2.17 Å, 2.18 Å, and 2.19 Å for the 3 HS centers. At 233 K, the Fe^{II} center in the LS state undergoes a thermal transition to the HS state [Fig. 1(c)]. The R_{av} are then 2.16 Å for the switching center and 2.18 Å for the other 3 HS centers. The LS $\rightarrow$ HS transition at room temperature is also accompanied by a greater degree of angular distortion (Schneider *et al.*, 2010). Figures 1(d) and 1(e) provide the simplified sketches of the molecular structures that will be employed to illustrate the changes in spin speciation upon solvation and photoexcitation.

Figure 2(a) shows the Mössbauer measurements on Fe4 in frozen in MeCN at 80 K, which indicates a spin-state ratio LS:HS of 52:48. For the magnetic characterization, dimethylformamide (DMF) was chosen as a solvent since the solubility of Fe4 in MeCN is not sufficiently high to allow meaningful superconducting quantum interference device (SQUID) magnetometry. Figure 2(b) displays the magnetic measurements for the Fe4 complex dissolved in DMF as a function of temperature from 2 K to 350 K. Over the range 40–200 K, the [2LS–2HS] species is exclusively present in solution. As the temperature rises, the population of HS centers increases. Using $\chi_{\text{M}}T$ ([1LS–3HS]) = $9.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (i.e., 100% of [1LS–3HS]) and $\chi_{\text{M}}T$ ([2LS–2HS]) = $6.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (i.e., 0% of [1LS–3HS]), the experimental value $\chi_{\text{M}}T$ of $8.09 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ obtained at 295 K gives 39:61 for the ratio [2LS–2HS]:[1LS–3HS], which translates into an overall LS:HS ratio of $35:65\% \pm 5\%$.

X-ray emission spectroscopy (XES) measurements of the $\text{K}\alpha_{1,2}$ and $\text{K}\beta$ lines were then conducted in order to establish the spin speciation in MeCN at room temperature. When the orbital angular momentum of the valence shell is equal to zero and when relativistic interactions can be neglected, the multiplet theory predicts a linear

FIG. 2. (a) Zero-field ^{57}Fe Mössbauer spectrum of Fe4 in frozen MeCN at 80 K. The lines represent simulations with Lorentzian doublets for HS- Fe^{II} (red; $\delta = 1.05 \text{ mm s}^{-1}$, $\Delta E_Q = 2.81 \text{ mm s}^{-1}$, and rel. intensity: 48%) and LS- Fe^{II} (blue; $\delta = 0.35 \text{ mm s}^{-1}$, $\Delta E_Q = 1.01 \text{ mm s}^{-1}$, and rel. intensity: 52%). (b) Magnetic susceptibility measurement of Fe4 in DMF from 2 to 350 K. The dotted lines represent the expected values for the [1LS–3HS] and [2LS–2HS] states. The LS and HS centers are displayed in blue and red, respectively.

relationship between the (2p, 3d) exchange energy splitting and the number of unpaired electrons (Glatzel). As a result, the width of the ($2p_{3/2} \rightarrow 1s$) $\text{K}\alpha_1$ line reflects the spin at the 3d metal center. Figure 3(a) shows the $\text{K}\alpha_{1,2}$ ($2p_{3/2,1/2} \rightarrow 1s$) lines for Fe4 in MeCN after normalization by the total area. The asymmetry in the $\text{K}\alpha_1$ line shape is related to the significant fraction of the HS state in the solvated sample. Figure 3(b) shows the $\text{K}\beta$ ($3p_{3/2,1/2} \rightarrow 1s$) lines for the Fe4 metallogrid complex in MeCN after normalization by the area. The accurate determination of the spin-state from these lines is achieved through monitoring the satellite feature at 7045 eV. Spectral decomposition as a linear combination fit (LCF) based on the solvated mononuclear LS and HS references $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$ (where bpy = 2,2'-bipyridine) in MeCN and $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ in H_2O yields $37\% \pm 3\%$ of LS and $63\% \pm 3\%$ of HS for Fe4 in MeCN. The spin state composition is illustrated with the sketch in Fig. 3(c). The $\text{K}\beta$ profiles for the mononuclear reference complexes are reported in Sec. S.I.1. The comparison between the spin distributions in the solution, powder, and single-crystalline phases summarized in Table S.I.2 shows that the Fe4 metallogrid complex is strongly affected by the environment.

FIG. 3. (a) $\text{K}\alpha_{1,2}$ lines, (b) $\text{K}\beta$ lines, and (c) spin composition for Fe4 solvated in MeCN at room temperature. The LS and HS centers are displayed in blue and red, respectively.

The UV–visible absorption spectrum of Fe4 in MeCN at room temperature is displayed in Fig. 4. The line shape is consistent with the one reported in the literature (Schneider *et al.*, 2010). The oscillator strength below 350 nm is attributed to overlapping ligand-based transitions, while the broad band spanning the 450–700 nm range is assigned to a metal-to-ligand-charge-transfer (MLCT) transition of mixed singlet–triplet character. The values of the extinction coefficient are given in Sec. S.I.3 for the selected wavelengths. Assuming that the individual Fe^{II} centers are only weakly electronically coupled, they should retain their isolated properties once they are linked. Therefore, the absorbance of the [2LS–2HS] species should be around twice that of the [1LS–3HS] species in the visible range. Temperature-dependent measurements show that the oscillator strength is due to the LS units and that a thermalized HS state does not contribute to the absorbance in this spectral region (see Sec. S.I.4).

Figure 5(a) presents the photoinduced dynamics following the femtosecond laser excitation of Fe4 in MeCN at 385 nm at room temperature for a fluence of about 0.3–1.1 mJ/cm². The setup is described in Sec. S.I.5. The singular value decomposition (SVD) analysis based on a simple sequential model identifies three clear components with distinct time constants (Sec. S.I.6). The decay associated spectra (DAS) are displayed in Fig. 5(b). The first component (red line) is formed instantaneously with a time constant τ_1 of about 200 fs, which is instrument-limited. It comprises a bleach signal (B1) and a broad excited state absorption (ESA) signal that cover the blue (A₁) and red (A₁') regions of DAS₁. The second component (blue line) that corresponds to the time constant τ_2 of 15 ps reflects the growth of the bleach (B₂) and a weaker ESA in the blue (A₂) and red (A₂') regions of DAS₂. The third component matches the negative of the absorption spectrum (B₃), which is shown as the gray trace in Fig. 5(b). It decays over a time scale exceeding the temporal window covered by the transient absorption setup employed for this measurement. Figure 5(c) shows the optical kinetics that track the temporal evolution of the ground state bleach at 460 nm and the excited manifold at 360 nm. The high-frequency oscillations in the first few picoseconds are presented in the inset. It should be noted that the oscillatory behavior is not observed in the 460 nm kinetics so that there is no impulsive excitation on the PES of the LS (Cannizzo *et al.*, 2010). Fitting a double-exponential to the kinetics trace at 360 nm and subtracting it in order to extract the residual oscillations deliver a period of 600 ± 20 fs (Sec. S.I.7). The schematic in Fig. 5(d) illustrates the global PSS in Fe4 solvated

FIG. 4. Extinction coefficient of Fe4 in MeCN over the UV–visible spectral range.

FIG. 5. (a) Transient optical spectra following excitation at 385 nm of Fe4 in MeCN at different time delays. (b) Decay associated spectra from the SVD with the inverted UV–visible spectrum (gray, scaled and offset for visual comparison). (c) Kinetic at 360 nm (black) and 460 nm (blue). The inset shows the oscillations extracted from the kinetics at 360 nm fitted with a damped sine curve (red). (d) Schematic of the PSS for Fe4 solvated in MeCN. The LS and HS centers are displayed in blue and red, respectively. (e) Nanosecond kinetics acquired with laser excitation at 400 nm (black dots) and single exponential fit (green line).

in MeCN. The nanosecond kinetics following excitation at 400 nm are shown in Fig. 5(e). The single-exponential lifetime is fitted to 210 ± 5 ns. As determined with SQUID and steady-state XES measurements, the Fe4 metallogrid complex solvated in MeCN is a mixture of two molecular species, namely, [2LS-2HS] and [1LS-3HS] species at room temperature. The analysis of the transient optical absorption measurements in the UV–visible indicates that a single photoexcited intermediate state leads to the formation of a long-living metastable state. This transient species is characterized by its well-defined single-exponential behavior with a time constant of 15 ps. However, its exact nature cannot be established based on the TOA measurements alone because its spectral line shape is broad and featureless.

TXE measurements with femtosecond resolution were then performed in order to assign unambiguously the spin multiplicity of the intermediate excited states. The experimental setup and the data extraction procedures are described in Sec. S.I.8. Figures 6(a) and 6(b) show the transient $K\alpha_{1,2}$ and $K\beta$ signals (black dot traces), respectively, at a time delay $\Delta t = 2$ ps following 400 nm excitation with a fluence of $55 \text{ mJ}/\text{cm}^2$ (after 3-point rebinning). Comparing with signals built from the mononuclear reference traces shows that the intermediate and metastable excited-states belong to the quintet manifold. Direct scaling to these reference signals (green line traces) delivers comparable excited state fractions of $17\% \pm 5\%$ and $20\% \pm 8\%$ from the $K\alpha_1$ and the $K\beta$ measurements, respectively. The power dependency of the $K\alpha_1$ upon the incident fluence is given in Sec. S.I.9.

Figure 7 shows the $K\alpha_1$ kinetics acquired within 6400.2–6409.4 eV (see Sec. S.I.8). Fitting the rise by a Gaussian-broadened Heaviside function suggests a $\sigma = 140 \pm 70$ fs, hence a full-width at half maximum (FWHM) of 330 ± 165 fs for the instrument response function (IRF), in agreement with published reports at the time of these XFEL experiments (Kirkwood *et al.*, 2019) (see Sec. S.I.10). In other words, the quintet character is acquired on the sub-picosecond time scale.

Further information about the relaxation dynamics from the initial Franck–Condon state is obtained with TIA spectroscopy. The first study on the sub-picosecond time scale was performed on the two related mononuclear Fe^{II} complexes $[\text{Fe}(\text{btpa})]^{2+}$ and $[\text{Fe}(\text{b(bdpa)})]^{2+}$ (where $\text{btpa} = \text{N,N,N',N'-tetrakis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-bipyridine}$

FIG. 6. (a) Transient $K\alpha_1$ and $K\alpha_2$ and (b) transient $K\beta$ signals at $\Delta t = 2$ ps for Fe4 dissolved in MeCN following 400 nm excitation (black dots). Scaling the reference traces (green lines) constructed from mononuclear LS and HS complexes delivers comparable excited state fractions of $17\% \pm 5\%$ ($K\alpha_1$ measurements) and $20\% \pm 8\%$ ($K\beta$ measurements).

FIG. 7. $K\alpha_1$ kinetics (black dots) with single-exponential fit (orange line) and the corresponding IRF (gray line).

and $\text{b(bdpa)} = \text{N,N'-bis(benzyl)-N,N'-bis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-bipyridine}$ possessing similar multidentate coordination spheres (Wolf *et al.*, 2008). For these systems, the most pronounced differences were observed in the spectral range of $1000\text{--}1065 \text{ cm}^{-1}$. Comparison with density functional theory (DFT) calculations showed that the modes responsible for the transient signals in these systems have significant metal–ligand stretching character. Figure 8(a) shows the steady-state spectrum of Fe4 in MeCN- d_3 and its evolution following photoexcitation at 385 nm in the $1400\text{--}1650 \text{ cm}^{-1}$ spectral range for a power of 0.4 mW. The steady-state spectrum resembles that of the closely related mononuclear complex $[\text{Fe}(\text{terpy})_2]^{2+}$ (see Sec. S.I.11). The transient signal is characterized by the quasi-instantaneous appearance of differential bands within the response function of the instrument. The spectral evolution is on the tens of ps time scale before reaching a line shape that remains constant over the covered temporal window. As for the UV visible data, SVD analysis can be performed with a sequential model and two single-exponential decays [Fig. 8(b)]. The first component appears within the response function of the instrument of 200 fs and displays a time constant of 14 ps. This matches the values obtained for the intermediate species monitored in the UV–vis region.

For a molecular assembly as large as the Fe4 metallogrid complex, calculating the IR frequencies was beyond the computational resources that could be accessed at the time of this study. However, useful insight can be obtained from simple considerations. The first component (green trace) matches very well the derivative (gray trace) of the GS spectrum (black trace), which is the signature of a global shift for all the frequencies to lower wavenumbers (i.e., to lower energies). This can be ascribed to a weakening of the elongated metal–ligand bonds, resulting in lower force constants. For the long-lived nanosecond component (purple trace), some of the initial frequencies gain intensities (features A, B, C, and D in the purple trace) while narrowing (features A and B in the purple trace). This finding follows the general trend observed in the photoexcited Fe^{II} mononuclear complexes, where the absorption cross section in the infrared (IR) is enhanced upon $\text{LS} \rightarrow \text{HS}$ transition (Wolf *et al.*, 2008; Lawson Daku and Hauser, 2010; Lawson Daku, 2018; and Lawson Daku, 2019), associated with increased entropy.

FIG. 8. (a) Spectral evolution of the transient signal in the IR region for different time delays. (b) Decay associated spectra from the SVD analysis (green and purple lines), compared to the steady state spectrum (black line) and its derivative (gray line).

DISCUSSIONS

The analysis of kinetics obtained from TOA, TXE, and TIA delivers several time scales that should be correlated in order to yield a detailed description of the PSS process within the Fe4 metallo-grid complexes solvated in MeCN. The ultrafast optical kinetics in the UV-visible and IR range indicate that a well-defined photoexcited species, characterized by its specific single-exponential behavior, evolves with a time constant of tens of ps toward a metastable state that lives for hundreds of ns. The ultrafast $K\alpha_1$ x-ray kinetics show that this intermediate state possesses a quintet character. Photoexcitation of the solvated Fe4 does not appreciably change the vibrational spectrum in the IR region but induces a sub-ps weakening of all the force constants attributed to the population of the antibonding orbitals of e_g character in the HS manifold. The vibra-

tional coherence observed during the single-exponential decay is particularly notable considering the fact that the initial sample is a mixture of two large molecular species. These findings suggest that the Fe^{II} LS centers in the two types of metallo-grids can be independently photoexcited to HS states, as anticipated from an assembly that is weakly electronically coupled. DFT calculations using BLYP-d3 in the gas phase and with a COSMO model for solvation were performed in order to establish the structures and energetics of the [4LS-0HS], [3LS-1HS], [2LS-2HS], [1LS-3HS], and [0LS-4HS] species. The average metal-ligand bond lengths, R_{av} , for the four centers in each species are summarized in Sec. S.I.12. The gas phase structures are in good agreement with the ones obtained in previous computational studies conducted with a similar methodology (Zueva *et al.*, 2011; Borshch and Zueva, 2012). The calculated R_{av} of the [1LS-3HS] and [0LS-4HS] species reproduce the tendency reported upon thermal switching in the crystallographic structures measured at 133 K and 233 K, considering the expected solid-state effects, e.g., packing forces. The energy diagram for the solvated species is displayed in Fig. 9, with $[\text{Fe}(\text{terpy})_2]^{2+}$ in MeCN for comparison (see Sec. S.I.12). The values of the energy gaps are given in Sec. S.I.12.

It should be noted here that state-of-the-art DFT methods are still generally failing to provide accurate predictions of the HS-LS energy difference, even for mononuclear transition metal complexes. In this work, the choice of BLYP-d3 was motivated by the fact that it belongs to the family of the so-called GGA functionals. This made it possible to carry out the efficient computational study of the large

FIG. 9. Energy diagram for Fe4 in MeCN compared with the mononuclear $[\text{Fe}(\text{terpy})_2]^{2+}$ in MeCN for D_{2d} and D_2 symmetries. The LS and HS centers are displayed in blue and red, respectively. The calculations were performed with the BLYP-d3 functional.

Fe4 grid targeted in this work. It is well-known that GGA functionals tend to overestimate the stability of the LS state with respect to the HS state in mononuclear Fe(II) complexes (Lawson Daku *et al.*, 2012). In addition, a purely electronic calculation does not account for the crucial vibrational and entropic contributions. For both reasons, the absolute energy differences obtained through the present DFT optimizations are not expected to be strictly comparable to the ones of relevance in the experiment, including kT at room temperature. However, intensive benchmarking has established that the relative energy spacings in closely related complexes are accurately captured by DFT calculations (e.g., Lawson Daku, 2019; 2005; Vargas *et al.*, 2013; Phan *et al.*, 2017; Bowman and Jakubikova, 2012; and Petzold *et al.*, 2017). This argument can be used to explain certain trends in physicochemical observables, e.g., here the lifetime of the photoexcited [1LS-3HS] and [0LS-4HS] in Fe4 and of the HS in $[\text{Fe}(\text{terpy})_2]^{2+}$. The rates of HS $\rightarrow$ LS transitions vary in accordance with the inverse energy gap law, which is holding in the solution phase (Hauser *et al.*, 1991; Hauser, 1995; 2004; and Liu *et al.*, 2017). Since $\Delta E_0([1\text{LS}-3\text{HS}] - [2\text{LS}-2\text{HS}]) = 0.9812$ eV and $\Delta E_0([0\text{LS}-4\text{HS}] - [1\text{LS}-3\text{HS}]) = 0.9807$ eV, the decay kinetics of the metastable HS states back to their respective ground state [1LS-3HS] $\rightarrow$ [2LS-2HS] and [0LS-4HS] $\rightarrow$ [1LS-3HS] are expected to be very similar.

Overall, the photoinduced dynamics do not exhibit any detectable dependency upon the spin composition of a given metallogrid. Therefore, they can be described in terms of intra-site transitions. Upon photoexcitation, a vibrational wavepacket is created in the quintet manifold on the few hundreds of fs by the coherent excitation of modes that are similar to the ones in the LS state, but downshifted in energy. The vibrationally hot HS state thermalizes within tens of ps to a long-living HS state. This time scale is typical for the equilibration of the photoinduced HS state in mononuclear Fe^{II} complexes with a flexible coordination sphere (Wolf *et al.*, 2008). The reversible photocycle is summarized in Fig. 10.

The photoinduced dynamics in Fe4 can be compared to the ones reported for the closely related mononuclear complex $[\text{Fe}(\text{terpy})_2]^{2+}$ that also imposes a tridentate coordination sphere for the Fe^{II} center. In this complex, photoabsorption in the visible range creates a coherent superposition of excited vibrational modes (i.e., a nuclear wavepacket) in the quintet manifold. The vibrationally hot HS thermalizes and decays back to the LS ground state within a few nanoseconds in MeCN and water (Liu *et al.*, 2017; Canton *et al.*,

2014; Zhang *et al.*, 2015; and Vankó *et al.*, 2015). The prolonged lifetimes are in line with the larger energy gap $\Delta E_0([\text{HS}] - [\text{LS}])$ calculated for the LS and HS state of $[\text{Fe}(\text{terpy})_2]^{2+}$ in D_{2d} and D_2 symmetries (see Fig. 9).

Besides energetic factors, further modulation of the HS $\rightarrow$ LS transition rate in $[\text{Fe}(\text{terpy})_2]^{2+}$ arises due to the deviation of the reaction coordinate from an isotropic single configuration coordinate. For this complex, the reaction coordinate cannot be approximated by a simple average Fe-N bond elongation, e.g., it is anisotropic (Nance *et al.*, 2015; Canton *et al.*, 2014; 2015; and Zhang *et al.*, 2015). As revealed by powerful studies combining ligand design, crystallography, and modeling tools, such anisotropy is the key to stabilizing the HS state (Steinert *et al.*, 2016; Stock *et al.*, 2016; 2012; 2017a; 2017b; Phan *et al.*, 2017; and Kroll *et al.*, 2019). A significant increase in the HS lifetime of mononuclear complexes occurs when radial and angular motions are coupled during the rearrangement of the ligand scaffold (Marchivie *et al.*, 2005; Buhks *et al.*, 1980; Hauser *et al.*, 1991; 1995; 2004; and Gülich *et al.*, 1994), e.g., through a trigonal prismatic deformation known as the Bailar twist (Bailar, 1958), which was already proposed in the 1980s (Rodger and Johnson, 1988; Vanquickenborne and Pierloot, 1981; McCusker *et al.*, 1992; and McCusker *et al.*, 1993). The present work illustrates how linking several metal centers into oligonuclear complexes can be developed as an efficient synthetic strategy to increase the lifetime of the photoinduced metastable spin-state, hence preventing thermal spin-scrambling. Comparing the lifetime observed for photoexcited Fe4 (~ 210 ns) with the one reported for photoexcited Fe3 (~ 123 ns) (Naumova *et al.*, 2020) pinpoints the global nuclearity of the architecture as a tailoring parameter. Eventually, the balance between the connectivity and the rigidity of the molecular assembly can be further tuned toward promoting vibrational coherence while influencing the overall kinetics.

Finally, Fig. 10 suggests that the metallogrid architecture will be well-suited for creating non-Boltzmann distributions of spin multiplicities. In the particular case of Fe4, the decay [1LS-3HS] $\rightarrow$ [2LS-2HS] and [0LS-4HS] $\rightarrow$ [1LS-3HS] takes place on very similar time scales. However, for example, if [0LS-4HS] $\rightarrow$ [1LS-3HS] could be accelerated (e.g., in a heteroleptic oligonuclear assembly), the photoinduced population of the [1LS-3HS] species would be strongly out of equilibrium on the ns to μs time scale, thereby imparting unusual transient properties to the mixture of species.

The present study highlights the fact that tapping into the reactivity of the hot spin-states produced by PSS in metallogrid complexes is well within reach. However, several open questions have to be answered before mechanistic models can be built to guide their systematic integration into new photoconversion schemes. Synergetic methodologies based on synthetic chemistry, ultrafast spectroscopies, and theoretical modeling should be devised in order to refine the current understanding of the PSS process as a function of fluence (Bertoni *et al.*, 2015; Zerdane *et al.*, 2018a), excitation wavelength (Zerdane *et al.*, 2018a; 2019), and solvent (Zerdane *et al.*, 2018b). The impact of the local coordination geometry on the lifetime of the HS state has been reported in mononuclear complexes, e.g., bidentate in $[\text{Fe}(\text{bpy})_3]^{2+}$ (Gawelda *et al.*, 2007; Cannizzo *et al.*, 2010; Auböck and Chergui, 2015; Chergui and Collet, 2017; and Lawson Daku, 2018) vs tridentate in $[\text{Fe}(\text{terpy})_2]^{2+}$ (Canton *et al.*, 2014; Zhang *et al.*, 2015;

FIG. 10. Schematic photocycle for Fe4 in MeCN.

Bowman and Jakubikova, 2012; Petzold *et al.*, 2017; and Lawson Daku, 2019). Improving the monodispersity of the oligonuclear samples in their ground state would clarify all the spectroscopic measurements since the mixtures of species complicate their analysis. Architectures where the number of connected units can be systematically incremented from the mononuclear building block to the complete metallogrid complex would be particularly valuable for studies aiming at determining accurate absorption cross sections and unraveling the impact of multiple excitation events. Capabilities for large-scale calculations of vibrational manifolds should be implemented for assigning the IR-active marker bands to vibrational modes of the complex undergoing PSS. Transient XES measurements with higher temporal resolution and higher signal to noise ratios will clarify the exact nature of the intermediate manifold and the role of metal centers, as for mononuclear Fe^{II} complexes. Finally, transient x-ray absorption spectroscopy (Bressler *et al.*, 2009; Cammarata *et al.*, 2014; Lemke *et al.*, 2013; 2017; and Britz *et al.*, 2020) and transient wide-angle x-ray scattering displaying increased structural sensitivity with hard x rays (Khakhulin *et al.*, 2019) could also be applied to capture the local and global structural dynamics on the relevant time scales and length-scales associated with the photoactivity triggered by the PSS process in solvated metallogrid complexes.

CONCLUSIONS

In conclusion, the present work initiates multi-spectroscopic studies of the PSS in solvated $[2 \times 2]$ iron(II) metallogrid complexes. The ultrafast dynamics are characterized with femtosecond pulses in the mid-infrared, UV-visible, and x-ray spectral ranges. The reversible photocycle can be described in terms of independent intra-sites transitions. Following photoexcitation, the Franck-Condon state of the mixed singlet-triplet MLCT character rapidly evolves into a vibrationally hot quintet state while exhibiting coherent behavior over 1–2 ps. The thermalization toward the equilibrated state takes around 15 ps. The metastable HS state lives for several hundreds of nanoseconds, in stark contrast with the few nanosecond lifetimes reported for the related mononuclear complex $[\text{Fe}(\text{terpy})_2]^{2+}$. This finding evidences the crucial role of the ligand connectivity and global nuclearity in stabilizing the photo-products of the PSS. Independently addressable, energy-rich, and long-lived metastable states are favorable for achieving selective manipulation of the transient spin-state in oligonuclear complexes at the atomic level. With the rapid progress expected from cross-disciplinary investigations, the control of PSS in oligonuclear complexes will contribute to the elaboration of photoconversion schemes that can be efficiently triggered by ultrafast spin-switching.

MATERIALS AND METHODS

Synthesis

The ligand HL and the complex $[\text{Fe}_4(\text{L})_4](\text{BF}_4)_4$ (noted Fe4) were synthesized according to the previously reported procedures (van der Vlugt *et al.*, 2008; Schneider *et al.*, 2010). The crystallographic structures in the CCDC are CCDC-768536 $[1(\text{BF}_4)4 \cdot 4 \text{ DMF} (133 \text{ K})]$ and CCDC-768537 $[1(\text{BF}_4)4 \cdot 4 \text{ DMF} (233 \text{ K})]$.

The complex bis(2,2':6',2''-terpyridine iron(II)) dihexafluorophosphate $[\text{Fe}^{\text{II}}(\text{terpy})_2](\text{PF}_6)_2$ was synthesized according to a previously published method (Machan *et al.*, 2012) and was additionally recrystallized from the water/acetone mixture (1:2.5 v/v) and dried under vacuum before use. The synthesis of $[\text{Fe}^{\text{II}}(\text{bpy})_3](\text{PF}_6)_2$ was performed according to literature procedures (Kumar *et al.*, 2016).

MAGNETIC CHARACTERIZATION

Mössbauer spectroscopy measurements

Mössbauer spectra were recorded with a ^{57}Co source in a Rh matrix using an alternating constant acceleration Wissel Mössbauer spectrometer operated in the transmission mode and equipped with a Janis closed-cycle helium cryostat. Isomer shifts are given relative to iron metal at ambient temperature. Simulation of the experimental data was performed with the Mfit program using Lorentzian line doublets: E. Bill, Max-Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, Germany.

Magnetic susceptibility measurements

Temperature-dependent magnetic susceptibility data were measured using a Quantum-Design MPMS-XL-5 SQUID magnetometer at a magnetic field of 5000 Oe. The sample was prepared by dissolving crystalline Fe4 in MeCN and sealing the solution in an nuclear magnetic resonance (NMR)-tube. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of MeCN. The molar susceptibility data were corrected for the diamagnetic contribution according to $\chi_{\text{Mdia}}(\text{sample}) = -0.5 \text{ M} \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

Ultrafast optical characterization

The ultrafast optical characterization was performed on two setups achieving femtosecond and nanosecond temporal resolution. They are described in Sec. S.I.5. The details for the data treatment and subsequent analysis are given in Secs. S.I.5–S.I.7.

Femtosecond TXE experiments at the FXE instrument of EuXFEL

The TXE measurements with femtosecond resolution were performed at the FXE instrument of the European XFEL facility in the standard optical pump–x-ray probe configuration. The incoming x-ray energy was set to 9.3 keV. The filling pattern was the standard 40 pulses at 374 kHz in a 110 μs train with energy $\sim 1 \text{ mJ/pulse}$. The x-ray beam was focused down to a 20 μm spot. The $\text{K}\alpha_{1,2}$ and $\text{K}\beta$ emission lines were collected by 5 Ge(440) and 8 Si(531) crystals, respectively, in the von Hamos geometry and focused, in turn, on a 2D CCD GreatEyes detector. The optical excitation wavelength of the PPLS I laser system was 400 nm. The pump pattern was fixed to 40 pulses/train at 374 kHz. The pulse duration was 15 fs fwhm, and the spot size was 30 μm . The pump and the probe were overlapped in time and space on a flowing liquid round jet of 100 μm diameter. The jet speed was adjusted to insure a refreshed spot for each pump–probe event. The concentration of Fe4 was $\sim 3 \text{ mmol}$ in MeCN. No sample damage

was observed either in the laser_off XES spectra or in the UV-vis absorption spectra taken before/after the x-ray measurements. The details of the XES data processing and analysis are given in Sec. S.I.8.

DFT optimizations

The geometries of the metallogrid complex Fe4 in the different spin states have been optimized in the gas phase and in acetonitrile (MeCN) with the ADF program package [1], using the COSMO (conductor like screening model) implicit model of solvation for MeCN [2] and the dispersion-corrected BLYP-d3 functional [3], combined both with the Slater-type TZP basis set of triple-zeta polarized quality from the ADF basis set database [4]. The calculations were carried out within the frozen core approximation with the cores frozen up to the 1s level for the C and N and up to the 2p level for the Fe atoms. They were run restricted for the [4LS-0HS] state and unrestricted for the [3LS-1HS], [2LS-2HS], [1LS-3HS], and [0LS-4HS] states for which the z-component (quantum number M_S) of the total electronic spin (quantum number S) was constrained to $M_S = +2$ ($S = 2$), $M_S = +4$ ($S = 4$), $M_S = +6$ ($S = 6$), and $M_S = +8$ ($S = 8$), respectively. The Fe-N bond lengths and the electronic energy gaps, ΔE_0 , are given in the tables of S.I.12. The complete reference list for this section is given in Sec. S.I.13.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for (Sec. S.I.1) a linear combination fit for the $K\beta$ line of Fe4 in MeCN, (Sec. S.I.2) comparison of the spin-state speciation in Fe4 solvated in MeCN with magnetic and spectroscopic techniques, (Sec. S.I.3) extinction coefficient at the selected wavelengths, (Sec. S.I.4) temperature dependent measurements of the UV-visible spectrum, (Sec. S.I.5) ultrafast optical characterization of photoexcited Fe4 in MeCN, (Sec. S.I.6) SVD analysis of the transient optical and infrared spectra, (Sec. S.I.7) fitting of the oscillations in the transient optical absorption signal, (Sec. S.I.8) acquisition and extraction of steady-state and time-resolved $K\alpha$ and $K\beta$ XES at the FXE instrument of the European XFEL, (Sec. S.I.9) intensity dependency of the transient XES signal at 2 ps for 400 nm excitation, (Sec. S.I.10) fit of the XES kinetics, (Sec. S.I.11) infrared spectrum of $[\text{Fe}(\text{terpy})_2]^{2+}$, (Sec. S.I.12) selected structural and energetic parameters for Fe4 from DFT optimizations, and (Sec. S.I.13) complete reference list for the DFT optimizations.

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