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Ultrafast Photoswitching

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Femtosecond Spin-State Photoswitching of Molecular Nanocrystals Evidenced by Optical Spectroscopy**

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In the field of control science, which aims at switching the physical properties of materials, photoinduced phase transitions[1] open fascinating perspectives for driving a material towards a new state, far from thermal equilibrium. Such photoswitching will impact future technologies as it provides doorways to the light-control of various photoswitchable functions (for example, magnetic, optical, conducting, and ferroelectric).[2] In control science, tailored laser pulses are widely regarded as the most likely source for achieving that goal.[3] In that respect, the great challenge for molecular-based materials is directing the functionality, both at the relevant size and time scales. If we attempt simple parallels here, the goal is to achieve at the level of a material what femtochemistry has accomplished at the level of a molecule.[4] In observing and understanding how materials work during elementary dynamical processes, several challenging basic questions are confronted. For instance, ultrafast information processing based on the control of light-driven switching of the physical properties of materials requires that such systems be directed through a complex pathway from atomic to material scales, and that the fundamental limits of transformation speed be overcome, or circumvented. Molecular magnets,[5] and especially the spin-crossover compounds (SCO),[6] are ideal candidates for photo-active prototypes, which show photomagnetic and photochromic properties driven by the switching of the constituent molecules between their electronic low spin (LS) and high spin (HS) states. Herein we report the ultrafast spin state photoswitching of a spin-crossover nanocrystal of an Fe^{III} complex, $[Fe(3\text{-}MeO\text{-}SalEen)_2]PF_6$ (Figure 1), as studied through femtosecond optical spectroscopy (H-3-MeO-SalEen being the condensation product of 3-methoxy-substituted salicylaldehyde and *N*-ethyl-ethylenediamine). This result provides proof-of-principle for femtosecond switching at the nanoscale in SCO materials showing photomagnetic and photochromic responses.

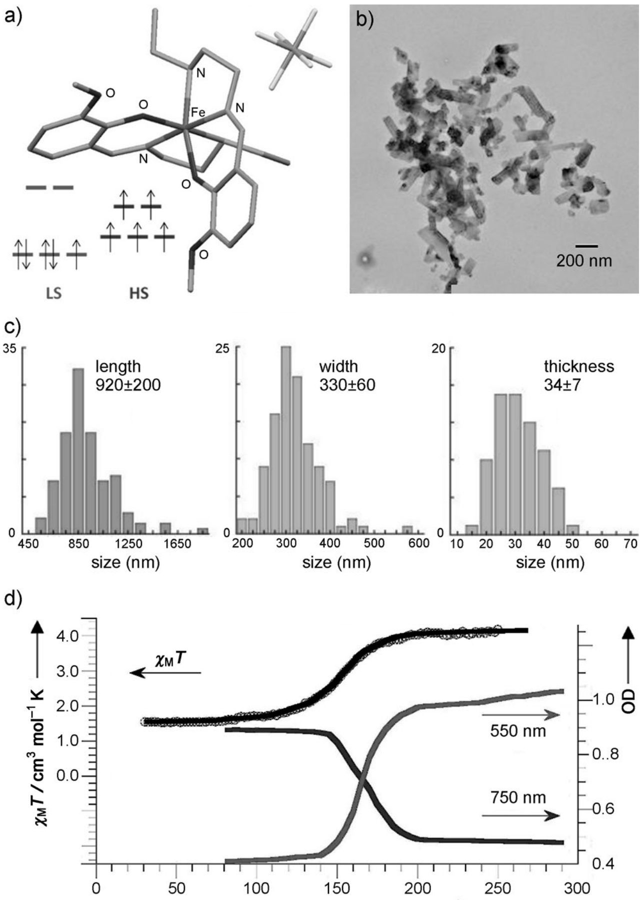

Figure 1. Fe^{III} spin-crossover nanocrystals. a) The $[Fe(3\text{-}MeO\text{-}SalEen)_2]$ cation and PF_6 anion with the LS and HS electronic configurations. b) TEM image of the nanocrystals. c) Size distribution of the nanocrystals. d) $\chi_M T$ vs. T plot of the nanocrystal film and OD versus T at 550 and 750 nm.

SCO materials are bistable systems, for which nanosecond laser excitation within the range of thermal hysteresis can generate LS to HS transition.[7] Ultrafast investigations of similar photo-transformations have been mainly limited to single molecules in solution,[8] and only recently also carried out on crystals.[9] Despite formidable progress in the chemistry and engineering of spin-crossover nanoparticles,[10] as well as their nano-patterning and nanoscale assembling[6b,11] while preserving their switchable properties, the ultrafast switching of such materials has not yet been observed. Herein we study the ultrafast LS-to-HS spin-state photoswitching pathway of nanocrystals (Figure 1), taking advantage of growing knowledge in the field of ultrafast chemical physics.[12]

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Hendrickson and co-workers were the first to synthesize the Fe^{III} complex [Fe(3-MeO-SalEen)$_2$] PF$_6$ (Figure 1 a).[13] Its crystalline form undergoes a first-order phase transition between LS ($S=1/2$) and HS ($S=5/2$) states around 162 K, where it also exhibits a narrow hysteresis.[9b] Nanoparticles of this compound were obtained by a precipitation method and were previously characterized with magnetic, Raman, EPR, and X-ray analysis[10e] to confirm their crystalline nature. For the investigation of ultrafast photoswitching dynamics, new nanocrystals were synthesized. These needle-shaped crystals have typical dimensions of $(34\pm7)\times(330\pm60)\times(920\pm200)$ nm^3 with a satisfactory size dispersion, when observed by TEM (Figure 1 b,c). The nanocrystals were embedded in a thin polymer film, which had been spin-coated on a glass substrate. These robust films allow for easy manipulation of nanocrystals and thus envisioning unrestricted scaffolding for nanocrystal-based devices.

The film of nanocrystals appears homogeneous at the sub-millimetric scale. The SCO properties of nanocrystals embedded in polyvinylpyrrolidone (PVP) thin films were investigated by magnetic and optical measurements, as shown in Figure 1. They undergo a thermal spin-crossover between LS and HS states centered at $T_{1/2}=$ ca. 156 K, characterized by a change in color (Figure 2 a&b) accompanying the change in magnetic susceptibility (Figure 1 d). Below about 100 K the SCO system remains fully LS, whereas it is fully HS above about 200 K. In comparison with macroscopic single crystals,[9b] the thermal conversion of the nanocrystals has somewhat lost its first-order character. For the nanocrystals embedded in the PVP film, the evolution of the fraction of the HS species appears even more gradual, and we are currently investigating whether this effect can be attributed to chemical and/or physical factors.[6b,14]

A detailed optical absorption spectroscopy study was performed to characterize the thermal LS-to-HS conversion of the nanocrystals. The variation in the optical density (ΔOD) is gradual during the thermal crossover (Figure 2 c). Figure 2 d, showing ΔOD between 90 K (pure LS state) and 230 K (pure HS state), reveals phenolate-to-iron charge-transfer (CT) bands with the distinct features of LS and HS states. The OD of the HS state, with respect to that of the LS state, is higher in the visible (VIS) and lower in the near-infrared (NIR) parts of the spectra, an observation which is in agreement with the change of color pictured in Figure 2 a,b. The evolution is marked by a well-defined isosbestic point at ca. 670 nm (Figure 2 c,d), as the HS and LS species interchange their relative concentrations during the thermal conversion. Figure 1 d, showing the temperature dependence of the OD for selected wavelengths (550 and 750 nm) on either side of the isosbestic point, marks the LS-to-HS conversion and shows a very good correlation between magnetic measurements and optical markers. All observed features were attributed to the nanocrystals, as the optical transparency of the polymer was experimentally verified in the temperature and spectral ranges considered here. We would like to emphasize a unique advantage offered here by the solid state: the molecules can be thermally switched between LS and HS states without otherwise resorting to chemical substitution. It is then straightforward to obtain spectroscopic fingerprints of the two spin states.

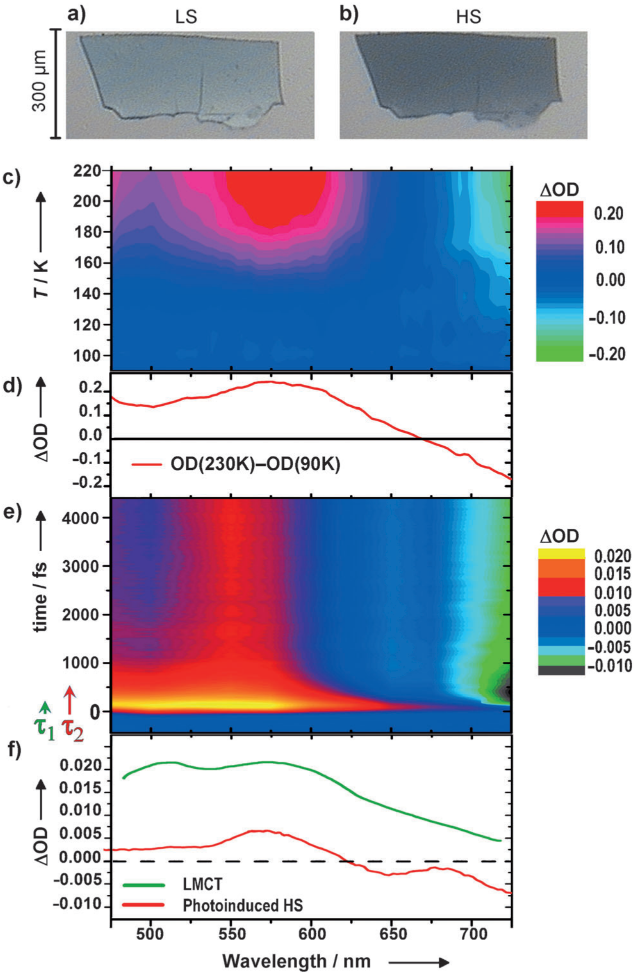

Figure 2. Optical analysis. a,b) Microscope photographs obtained by back illumination of a slice of PVP polymer film containing homogeneously dispersed nanocrystals, changing color between LS (80 K) and HS (280 K) states. c) Thermal variation of the optical density (ΔOD) recorded with a white-light spectrometer during LS to HS conversion. d) ΔOD between the complete HS (230 K) and LS (90 K) states. e) 2D time–wavelength plot of ΔOD after femtosecond laser excitation obtained by a two-color pump–probe experiment; the color coded change follows the characteristic τ_1 and τ_2 time constants. f) ΔOD spectra obtained by white-light spectroscopy at time 0 (—, LMCT and INT states) and at 15 ps (—, photoinduced HS).

We exploit these spectroscopic fingerprints to study the ultrafast dynamics of nanoscaled SCO crystals at far from thermal equilibrium. To track the photoinduced spin-state switching dynamics in real time, we employed two different transient absorption experiments, one kinetically resolved and the other spectrally resolved (see the Supporting Information). The pump wavelength was set to 850 nm, where it efficiently induces LS-to-HS transition at 90 K from the pure LS state. Single-wavelength measurements probed the resulting dynamics through OD change in the identified spectral zones (475–725 nm). The overall instantaneous response function (IRF) of this experiment, conducted with a fine time step of 10 fs, is ca. 140 fs.

Selected time traces are shown in Figure 3 a,b. The two dimensional time–wavelength plot of ΔOD following femtosecond laser excitation is shown in Figure 2 e. These figures indicate two main steps, a transient peak appearing immediately after laser excitation and a plateau reached with a time constant shorter than one picosecond. ΔOD recorded on this plateau, positive in VIS and negative in NIR, reveals the formation of a HS state less than 1 ps after laser excitation of the nanocrystals. The transient response recorded during the first 100 fs differs significantly, showing a broad and strong absorption band dominating the VIS–NIR spectrum, indicating that the observed transient species are neither LS nor HS. These findings suggest that the HS formation mechanism involves a short-lived intermediate step resulting from the population of the ligand-to-metal charge-transfer (LMCT) state, as is similarly proposed for the macroscopic single crystal,[9] and for molecules in solution.[8]

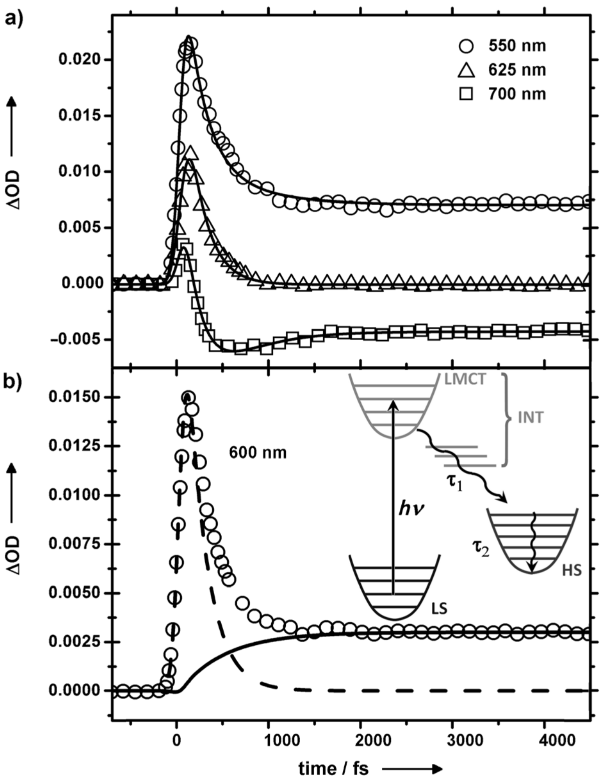

Figure 3. Kinetic traces of ΔOD at selected wavelengths obtained by a two-color pump–probe experiment at $T = 90$ K. a) Raw data (○,△,□) and fits with the biexponential model (——). b) Deconvolution of raw data (○) for the 600 nm probe into the relaxation kinetic of the intermediate electronic states (– – –) and the population kinetic of the HS state (——). The inset shows a schematic representation of the photoswitching pathway with time constants τ_1 for the relaxation of short-lived intermediate states (INT), and τ_2 for the vibrational cooling of the photoinduced HS state.

For more detailed characterization through ΔOD of the transient LMCT and the photoinduced HS states, we performed time-resolved broad band spectroscopy at 90 K (see the Supporting Information). The transient LMCT spectrum around time zero is compared in Figure 2 f to the spectrum of the photoinduced HS state taken at 15 ps, which does not change on the plateau (at least up to 100 ps). Here again the observed photoinduced absorption in the VIS range and bleaching in the NIR obey the spectral behavior expected for LS-to-HS switching. The spectrum at time zero differs significantly from that of the LS ground state and that of the HS photoinduced state; the VIS part (Figure 2) shows neither a bleach signal nor an isosbestic point, which prevents assignment of the species to LS or HS.

Spin state photoswitching dynamics are known to proceed through transient states, as the direct low energy excitation from a LS to a HS state is forbidden by spin parity. Photoswitching is now understood at the molecular level[8] to a degree that allows the following description: the femtosecond pump pulse promotes the d electrons of the metal ion in the LS state into a Franck-Condon state (charge-transfer state). This electronic excited state relaxes through intersystem crossing[15] and through different intermediate states to a state with higher parity (HS). Our time-resolved data lead us to a similar description of the LS-to-HS transformation pathway of the Fe^{III} complex in nanocrystals. Specifically, the simple model used here for reproducing the kinetics of this photoswitching is biexponential (inset Figure 3 b). The shorter time constant (τ_1) describes the population of the HS state by the depopulation of intermediate (INT) electronic states (including LMCT and other possible intermediates) before the final electronic HS state is reached. The longer time constant (τ_2) describes the vibrational cooling of the HS state, which is populated with excess vibrational energy as most of the absorbed energy is still localized at the molecular level on this time scale.

Figure 2 e and Figure 3 show that the contributions from HS or LS states to ΔOD cancel out around 625 nm on the picosecond plateau. Therefore, the corresponding kinetic trace (Figure 3 a) can be used to track the INT electronic states, which are expected to have distinct absorption spectra.

This kinetic trace, which shows a rapid rise followed by a rapid drop in ΔOD was deconvoluted from the IRF by a single exponential model and gave a decay time constant for the INT state of 200 ± 20 fs. This is in excellent agreement with earlier reports on the SCO of metal complexes both in solution[8] and in macroscopic crystals,[9] as well as a femtosecond Raman experiment,[8c] which probed the charge density shift timescale within a Fe^{II} complex upon Franck–Condon excitation.

As the photoinduced HS state is OD silent only around this isosbestic point, the variation of OD at other wavelengths involves both INT and HS states. Thus, INT states are the bottleneck for the relaxation process. Therefore, τ_1 should not vary with wavelength and was fixed in the model to 200 fs, whereas τ_2 was left as a free parameter. The fitting (lines in Figure 3 a) yields a τ_2 in the 500–800 fs range, depending on the probe wavelength. The existence of two time constants is clearly seen on the 2D map in Figure 2 e. The strong absorption in the VIS range (yellow), vanishing within the first 200 fs, marks the very short INT states. The slower increase of bleaching in the NIR, as well as the global spectral narrowing, which is easily visualized by band narrowing around 575 nm and 725 nm, all occur within less than 1 ps. Spectral narrowing is a well-known marker of vibrational cooling[8c,16] and is associated here with a downslide of the vibrationally hot HS molecules to the bottom of the HS potential (inset Figure 3b). Compared to the cooling constants reported for such molecules in solution in the 1–10 ps range,[8] the process reported here is faster. Vibrational cooling dissipates excess energy to the environment, on which the efficiency of this process will depend. Thus, the same molecules in different solvents cool down differently.[8d] In the case of crystalline solids, additional cooling channels may exist. Namely, lattice phonons, which allow efficient coupling of the locally photoexcited molecules with the environment.[9a,17] The direct comparison of the optical signatures of LS-to-HS switching driven by temperature with those driven by the laser pulse (Figure 2) provides clear-cut evidence of a photoinduced HS state. However, a more detailed description of the ultrafast relaxation to this state is difficult, as theoretical studies have shown that the intersystem crossing is complex;[15] several pathways involving different excited spin states and different crossing between the potential energy curves of the states exist and are hidden here in the INT state (or manyfold state). The physical mechanism underlying the inter-system crossing dynamics is poorly understood and awaits the development of theoretical studies and simulations, including spin-orbit coupling of the excited states. Unlike cooperative materials,[1,2d] where the electronic excitation can be delocalized, thus allowing one photon to transform several molecules,[18] in SCO materials the excitation is localized at the intramolecular scale. Therefore, one photon transforms a single molecule on the femtosecond timescale, even though the cooperative elastic effect and thermal activation may exist on significantly longer time scales.[9,17]

The fraction of molecules photoswitched from LS to HS states can be reliably estimated by a comparison of the OD change resulting from photoexcitation to that of the OD change from a complete thermal conversion. Compared to macroscopic crystals under similar excitation,[9b] we find an intriguing difference in the case of nanocrystals studied here. The fraction of photoconverted molecules on the picosecond plateau in these nanocrystals is 50 times higher and reaches 10%. Such an improvement in the switched fraction can be put down to a very good penetration of the pump laser through minute nanocrystals.

In conclusion, femtosecond laser pulses should ultimately allow for control over molecules, and open new perspectives for nanoscale molecular materials. Downsizing SCO materials is a very encouraging route to efficient photoswitchable solids. Our main motivation was to study the possibility of photoswitching a SCO system whose volume size is nine orders of magnitude smaller than common molecular crystals, and unveiling the associated photoswitching pathway. Herein, we have demonstrated a one-way laser pulse switching between LS and HS states in a solid compound of nanometric size embedded in a PVP film. This morphological modification does not deteriorate the ultrafast photoswitching ability of the SCO material in the optically silent polymer. Application prospects have already been recognized for SCO materials, and seem even more appealing in the case of nanocrystals. They should be downsizeable at will, and switchable with relatively low laser power. Despite their minute size, the nanocrystals studied here are still far above the infinite system size limit, precluding first-order phase transition and thereby prompting finite size scaling as an interesting aspect for device design.[19] Now that ultrafast switching of SCO nanoparticles has been demonstrated, the next challenge is to control a single nanoparticle on a femtosecond timescale.

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