Switchable Molecular Magnets

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Ultrafast Photoswitching in a Copper-Nitroxide-Based Molecular Magnet[**]

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Abstract: *Molecular compounds with photoswitchable magnetic properties have been intensively investigated over the last decades due to their prospective applications in nanoelectronics, sensing and magnetic data storage. The family of copper-nitroxide-based molecular magnets represents a new promising type of photoswitchable compounds. We report the first study of these appealing systems using femtosecond optical spectroscopy. We unveil the mechanism of ultrafast (< 50 fs) spin state photoswitching and establish its principal differences compared to other photoswitchable magnets. On this basis, we propose potential advantages of copper-nitroxide-based molecular magnets for the future design of ultrafast magnetic materials.*

Among various photoswitchable materials, special attention has been given to spin-crossover (SCO) compounds and the light-induced excited spin state trapping (LIESST) phenomenon, which allow optical manipulation of the magnetization by switching the molecules between high- and low-spin states.[1,2] In the solid state it is also possible to reach new phases through light-control of structural order between SCO molecules.[3] LIESST has been extensively investigated in common SCO compounds, with the complete photocycle revealed and dynamics of photoswitching studied on femtosecond timescale in solution[4] and the solid state.[5] More recently, another type of promising spin-crossover-like compounds has emerged. These copper-nitroxide-based molecular magnets undergo reversible magneto-structural rearrangements between weakly and strongly exchange-coupled states of spin triads nitroxide–copper(II)–nitroxide (WS/SS states). They are often called "breathing crystals" because of the large-scale changes of the unit cell volume upon transition (Figure 1 a,b).[6,7] A number of similarities between "classical" SCO compounds and "breathing crystals" have been identified, despite the principal difference in the origin of switching, arising either within a transition ion or on the scale of the exchange-coupled cluster, respectively. Among these similarities is the ability for light-induced spin state switching, with a long lifetime of the photoinduced state at cryogenic temperatures (hours to days, LIESST-like phenomenon). However, the mechanism of photoswitching in breathing crystals has not yet been understood. Moreover, studies of photoinduced dynamics in copper complexes on sub-ns scale are extremely scarce, especially for paramagnetic copper(II).[8] Therefore proposing the photoswitching pathway and the intermediate electronic states for "breathing crystals" is both demanding and vital for shaping further research in this field. Here we report the first study of ultrafast photoswitching in a copper(II)-nitroxide-based molecular magnet of the breathing-crystal family using femtosecond optical

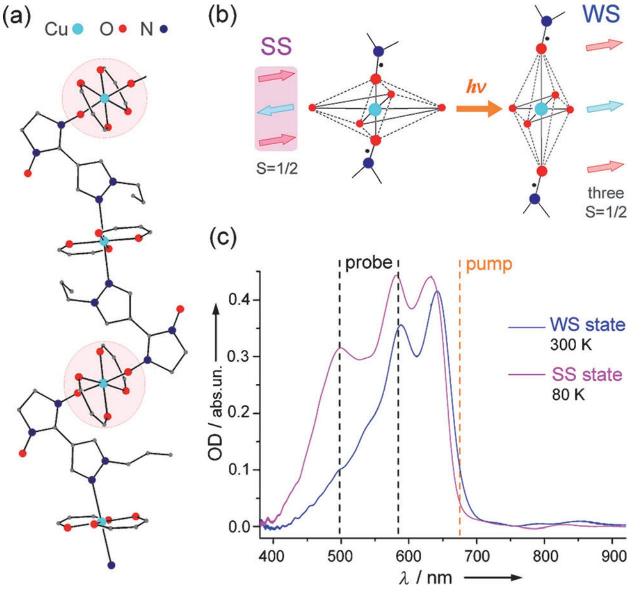

Figure 1. a) Polymer chain structure of molecular magnet [Cu(hfac)$_2$L^{Pr}] (spin triads are circled). b) Structure and key properties of the SS and WS states of spin triads. c) Optical absorption spectra of [Cu(hfac)$_2$L^{Pr}] in SS and WS states (pump and probe positions in femtosecond experiment are indicated). λ is the wavelength.

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spectroscopy, unveil the mechanism, and determine the timescale of the phenomenon.

Photoswitching in breathing crystals has mostly been studied by using steady-state electron paramagnetic resonance (EPR) with laser excitation.[7a,b] Although the peculiarities of magneto-structural relaxation occurring within a few hours at $T<20$ K were successfully investigated, probing the photoswitching process has been far beyond the temporal resolution of the method. Recently, we employed another advanced approach, time-resolved (TR) EPR, to probe photoinduced spin dynamics with ca. 100 ns temporal resolution—but still the results evidenced that the photoswitching occurs much faster.[7c] Time-resolved studies with sub-ns temporal resolution are the way to access the information on intermediate states and corresponding transition rates. Femtosecond optical spectroscopy is a powerful technique for studying photoswitching dynamics, especially when the optical spectra of ground and photoinduced states are noticeably different.[9] In the present case, a particular complication came from the fact that the optical spectra of the SS and WS states are very broad and inexpressive, and they strongly overlap. Still, with broadband spectroscopy a reliable spectral assignment can be accomplished.

Thin polyvinylchloride films with embedded breathing microcrystals $[\mathrm{Cu(hfac)_2L^{Pr}}]$ (hfac = hexafluoroacetylacetonate, $\mathrm{L^{Pr}}$ = nitronyl nitroxide; see Figure 1 a) were prepared. They were placed on a quartz glass support and used in the following pump–probe fs optical spectroscopy experiments. $[\mathrm{Cu(hfac)_2L^{Pr}}]$ exhibits gradual thermal spin transition and is found in the SS state at $T<100$ K and in the WS state at $T>250$ K.[6] The absorption spectra of both WS and SS states are dominated by the bands of nitronyl nitroxides ($\lambda=450$–700 nm) (Figure 1 c and Supporting Information). A strong, broad band assigned to a metal–ligand charge transfer (MLCT) transition ($\lambda_{\max}=500$ nm) arises at low temperatures, because Cu−O$_L$ distances in spin triads drastically shorten upon conversion to the SS state. Thus, the most pronounced spectral change upon SS⇄WS conversion occurs in the $\lambda=500$–600 nm region, where a characteristic bleaching of optical density (OD) is found during SS→WS thermal conversion. It is this spectral zone which was probed by femtosecond optical spectroscopy to monitor the ultrafast light-induced SS→WS photoswitching by means of broad band as well as two-color pump–probe measurements. The photoswitching was triggered by exciting the system at 675 nm at the tail of the broad band for maximizing the laser penetration depth. Attempts to excite the crystals at the absorption peak (600 nm) resulted in sample damage due to local heating on the crystal surface.

Figure 2 a shows the relative optical density change of the thermally induced ($\Delta\mathrm{OD_{therm}}$) and light-induced ($\Delta\mathrm{OD_{photo}}$) SS→WS transition. The photoinduced spectral change measured at $t=15$ ps after 675 nm laser excitation agrees well with the thermally induced bleaching and gives a clear fingerprint of the SS→WS photoswitching. Comparison of $\Delta\mathrm{OD_{therm}}$ and $\Delta\mathrm{OD_{photo}}$ allows us to estimate the photoinduced conversion yield as 0.6–0.7 % (see Ref. [5b] for details). Figure 2 b does not show significant changes between the absorption spectra immediately after laser excitation ($t=100$ fs) and 15 ps later, indicating that an ultrafast process occurs in a step-like manner at $t<100$ fs. Since there is no isosbestic point between the SS and WS states (the crossing at 650 nm in Figure 1 c results from band shift rather than population transfer), only a monopolar signal (OD decrease) is recorded in the visible range (Figure 3). This interpretation, which leads to the identification of the photoinduced state, is enabled by the ability to record the spectra of SS and WS states at thermal equilibrium.

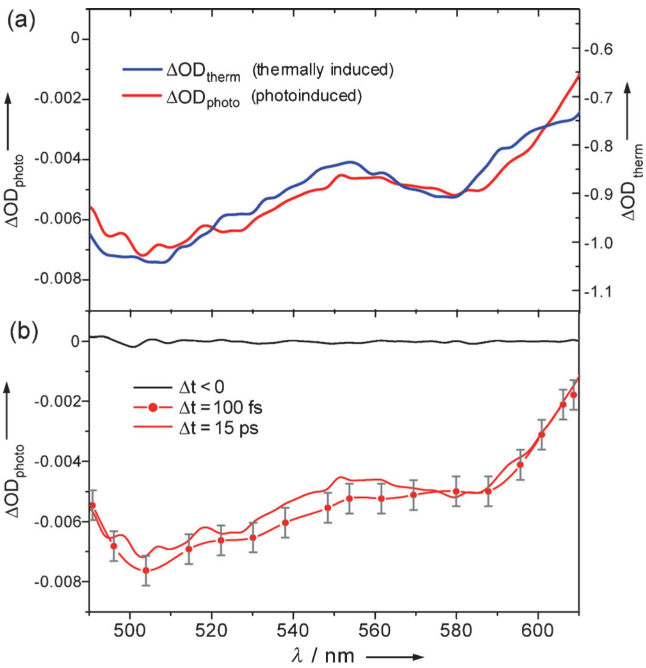

Figure 2. a) Relative change of optical density (OD) between SS and WS states of $[\mathrm{Cu(hfac)_2L^{Pr}}]$ in PVC as a function of λ. Thermally induced change ($\Delta\mathrm{OD_{therm}}$) is the difference of spectra measured for WS state at 293 K and SS state at 90 K, both at thermal equilibrium. The photoinduced change ($\Delta\mathrm{OD_{photo}}$) is the difference of spectra measured at 90 K 15 ps after the pump excitation (675 nm) and before excitation. b) $\Delta\mathrm{OD_{photo}}$ before ($t<0$), shortly after ($t=100$ fs), and at $t=15$ ps after laser excitation. The photoinduced change of OD occurs within 100 fs, without any indication of transient states within the 0–15 ps time window.

Two-color femtosecond pump–probe measurements allow us to track the photoswitching dynamics induced by laser excitation at 675 nm in more detail. By this approach we can probe the time evolution of OD at the characteristic absorption band and thus kinetically resolve, with better accuracy, the pathway of the light-induced SS→WS transition. Figure 3 shows the time traces recorded at 500 nm and 580 nm. The bleaching is a clear evidence of the SS→WS transition. Taking into account the temporal resolution of our setup (140 fs), the fitted time traces indicate the upper limit of the photoswitching time to be 50 fs. We also notice that after the step-like bleaching, a slower process takes place resulting in a slower decrease of OD (ca. 5 % of initial amplitude) with a time constant of 0.6 ps for 580 nm and 1.5 ps for 500 nm (inset of Figure 3). The second process can be attributed to vibrational cooling because 1) its time scale corresponds well to the values expected for such process, and 2) the depend-

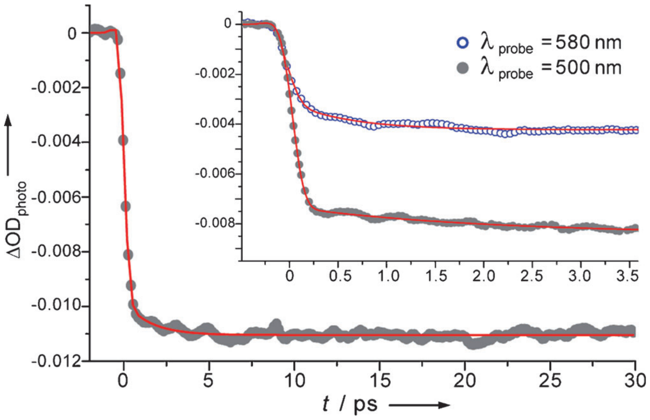

Figure 3. Transient absorption kinetics of [Cu(hfac)$_2$L^{Pr}] in PVC measured by pumping at 675 nm and probing at 500 nm (t is the time delay between the pump and the probe pulses). Inset expands the short time scale for different data sets obtained at 500 nm and 580 nm. Red curves show biexponential fits of the data. Rapid bleaching occurs within less than 50 fs at both probe wavelengths, and a slower wavelength-dependent process is attributed to vibrational cooling with characteristic times τ_2 (500 nm) = 1.5 ps, τ_2 (580 nm) = 0.6 ps.

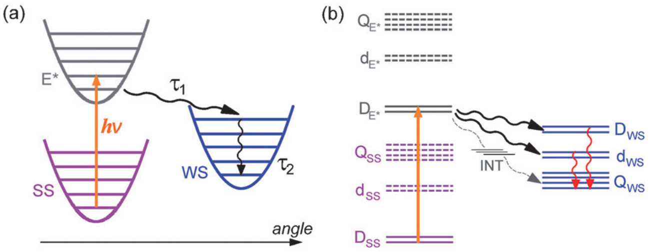

Figure 4. Photoswitching scheme of [Cu(hfac)$_2$L^{Pr}]. a) General mechanism in terms of potential energy surfaces, electronic and vibronic transitions. τ_1 describes relaxation from excited electronic state E* to WS state, τ_2 refers to vibrational cooling. Bottom axis indicates the reaction coordinate, which is the direction (angle) of the elongated •O–Cu–O• axis in CuO$_6$ octahedron (sketched in Figure 1 b). b) Photoswitching mechanism shown in terms of spin states. Each vibronic level in part (a) is split into 8 spin levels corresponding to two doublets (D, d) and one quartet (Q) (see Supporting Information for details). The reversal of spin levels in WS state compared to SS state owes to the switching of exchange coupling from antiferromagnetic to ferromagnetic one. Thermally populated levels are shown by solid lines, and noncontributing ones by dashed lines. Spin-allowed relaxation pathways are shown by black solid lines, and spin-forbidden transition $D_{E*} \rightarrow Q_{WS}$ by gray dashed line. Red arrows show electronic relaxation between spin multiplets of WS state.

ence of time constant on probe wavelength is commonly attributed to spectral narrowing caused by vibrational cooling.[5a] This process may also include a change of the structural reaction coordinate for reaching the equilibrium position. After 2–3 ps the SS→WS photoswitching is complete and the signal does not show any further evolution (Figure 3). Likewise, the spectrum recorded 150 ps after the excitation (Supporting Information) is identical to those shown in Figure 2b. The photoinduced WS state relaxes back to SS state within 1 ms at 90 K, in agreement with a rapid shortening of the lifetime on increasing temperature, as has been found previously by EPR.[7b] Note also that the SS→WS transition does not show signs of cooperative response to light excitation (at least within the range of tolerable excitation densities), as ΔOD_{photo} follows a single-step change of the amplitude which is linearly dependent on the pump laser power (Supporting Information). This is very likely due to the local nature of the structural trapping of the photo-excited state.

One would tentatively expect a more complex kinetics along the SS→WS photoswitching pathway, involving one or several intermediate states (INT) as often found in systems exhibiting intersystem crossing.[4,5,9] However, in breathing crystals such differences could not be detected, and the shape of the kinetics is the same for $\lambda_{probe} = 500$–600 nm, whereas outside this region photoinduced change of OD becomes very weak. It seems that the whole photoswitching pathway is reduced to a quasi three-state scheme sketched in Figure 4a, that is, SS→E*→WS, where E* refers to the electronically excited state having lower OD than the SS in the probed spectral range. Because optical absorption bands of nitroxides, MLCT, and d–d transitions of copper(II) strongly overlap (Figure 1c and Supporting Information), and since E* state is extremely short-lived (<50 fs, Figure 2 and Figure 3) it is not possible to exactly identify the nature of E* even by means of femtosecond optical spectroscopy. More importantly, the obtained data clearly reveal that the E*→WS relaxation proceeds within 50 fs, and they contain no signatures of any intermediate electronic states (INT).

Figure 4b shows a plausible explanation why E*→WS transition is so fast and occurs through bypassing intermediate states. It represents the same processes as those shown in Figure 4a, but exaggerates for clarity the spin sublevels structure (of SS, WS, E* states). Due to exchange coupling (J) in spin triads nitroxide–copper(II)–nitroxide each vibronic level is split into 8 spin sublevels: two doublets (D, d) and one quartet (Q) (see Supporting Information for details). In the SS state J is strongly antiferromagnetic, and the energy splitting $E(Q_{SS})-E(D_{SS}) = 3J \approx 400\ \text{cm}^{-1}$.[6c] Therefore, only the ground spin multiplet D_{SS} is thermally populated. In WS state J is weakly ferromagnetic, and $E(D_{WS})-E(Q_{WS}) = 3J < 20\ \text{cm}^{-1}$;[6c] therefore all three spin multiplets are thermally accessible. Assuming the same spin sublevels structure in E* and SS states, we find that the relaxational transitions $D_{E*} \rightarrow D_{WS}$ and $D_{E*} \rightarrow d_{WS}$ are spin-allowed. Therefore, the conversion E*→WS through these spin states does not require intersystem crossing and intermediate states. The third pathway $D_{E*} \rightarrow Q_{WS}$ is spin-forbidden, since spin multiplicity must change, and should hypothetically proceed through intermediate states (INT) and thus take noticeably longer compared to spin-allowed transitions $D_{E*} \rightarrow D_{WS}$ and $D_{E*} \rightarrow d_{WS}$. However, as was mentioned above, we did not observe any signatures of INT states, therefore the role of $D_{E*} \rightarrow Q_{WS}$ pathway is negligible. The electronic relaxation from thermally excited mutliplets D_{WS} and d_{WS} to Q_{WS} may take relatively long time up to several microseconds depending on temperature,[7c] but such relaxation in the already photoswitched WS state is indiscernible for transient VIS absorption.

Note, that it is the existence of low-lying excited spin levels (D_{WS}, d_{WS}) in breathing crystals that makes spin state switching partially spin-allowed and overall SS→WS switching ultrafast. We believe that the switching time is so short because during displacive transformations along the potential energy curve, a fast transition is associated with an efficient activation of the reaction coordinate, resulting from efficient spin–orbit or electron–phonon interactions, allowing to reach the final potential.[10] The latter occurs faster than the oscillation period of the reaction coordinate, and this was experimentaly observed in several molecular systems.[4,5,9] For breathing crystals the reaction coordinate is mainly the direction (angle) of the elongated $^{\bullet}$O–Cu–O$^{\bullet}$ axis, with typical oscillation frequency of 200–300 cm^{-1}, and half period in the 50 fs range.

In summary, the first study of photoswitching in copper-nitroxide-based breathing crystals on the femtosecond scale revealed two findings of great importance. First, the photoswitching is ultrafast and occurs within 50 fs. This kind of photoswitching is different from that occurring in classical SCO compounds, as it proceeds on the larger scale of exchange-coupled cluster and, hypothetically, could be noticeably slower. Notwithstanding such expectations, the observed photoswitching time is very short and similar to the values found in several coordination compounds. The second important finding is that the photoswitching mechanism can basically be described by three-state dynamics involving ground SS state, intermediate excited state, and final WS state (Figure 4a). The transition from excited to WS state is partly spin-allowed, therefore the overall SS→WS photoswitching represents an interesting alternative for developing ultrafast photo-magnetic materials, thus promoting breathing crystals for applications in spintronics.

Experimental Section

Synthesis of $[Cu(hfac)_2L^{Pr}]$ was described previously.[6b] To fabricate $[Cu(hfac)_2L^{Pr}]$ embedded in poly(vinyl chloride) (PVC) films, 1–2 mg of the complex was dissolved in 1 mL of solution prepared from 1 g of a low molecular weight PVC and 200 mL of dichloroethane. This solution was equally sprayed onto a thin quartz plate to give a brown-colored transparent film. During drying for 24 h on the air, the film changed its color to blue that visually indicated a formation of microcrystal particles of $[Cu(hfac)_2L^{Pr}]$ within PVC films to be used for this study.

Two-color pump–probe heterodyne detection and white light spectroscopy were performed on thin microcrystalline film of $[Cu(hfac)_2L^{Pr}]$ embedded in PVC. In all ultrafast experiments the sample temperature was controlled with a standard N_2 flow cryocooler (Oxford Instruments Cryojet). The experiments were performed at 90 K in the SS state. For two-color ultrafast pump–probe spectroscopy the SS-to-WS photoswitching was generated by pumping the system by a 100 fs laser pulse at 675 nm. The temporal evolution of OD was obtained from the change of transmitted probe signal, by using a lock-in amplifier. In order to build up statistics, stroboscopic measurements were performed at the repetition rate of 1 kHz and data were averaged over several scans. Data treatment involved iterative fitting of a double exponential test function convoluted with a Gaussian instrumental response function (IRF) of 140 fs FWHM. Measurements with femtosecond white light recorded spectral response of the sample to 675 nm excitation. White light was generated by a femtosecond laser pulse at 800 nm focused into a sapphire window. Thus generated light covers the 400–700 nm range on the CCD detector (Princeton Instruments, PIXIS 100) preceded by a spectrometer (Acton Research Corp., SPEC-TRAPro 2500i). For every Δt, 10000 spectra were collected, averaged, and analyzed using a double-reference method to improve the signal-to-noise ratio. The raw data are the ratios between the transmitted signal at each wavelength in the presence of the pump and that in the absence of the pump. More details can be found in Refs. [9b,c] and the Supporting Information.

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