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Light-induced spin transitions

Light-Induced Excited Spin State Trapping in an Exchange-Coupled Nitroxide-Copper(II)-Nitroxide Cluster**

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The discovery of light-induced excited spin state trapping (LIESST) on a spin-crossover complex of iron(II) in 1984 attracted much attention in the field of photomagnetism and triggered a large number of subsequent studies.[1] Apart from being an interesting photophysical phenomenon, LIESST is one of the most promising effects for potential applications in molecular-level light-operated magnetic devices, because the metastable multiplet state excited by light may be trapped for hours to days at sufficiently low temperatures (typically below $T_c \approx 50$ K).[1] Recent research on LIESST has been aimed at increasing the blocking temperature T_c and expanding the range of compounds exhibiting this effect. To date, LIESST has been observed on compounds containing spin-crossover complexes of iron(II) and, more recently, iron(III).[2, 1i] In all of these cases, including exchange-coupled dinuclear complexes,[3] LIESST is based on the spin-crossover nature of iron. Herein, we report the first example of a LIESST-like effect observed in a system of principally different type, that is, an exchange cluster of copper(II) with two nitronyl nitroxide ligands. This compound does not contain any metals displaying spin crossover, and an efficient trapping of the light-induced state of a cluster on a timescale of hours originates from highly cooperative structural rearrangements in a one-dimensional system. Photoswitching of the exchange interaction has been studied in other one-dimensional systems aiming at ultrafast switching times.[4] In contrast, the present system shows a behavior more similar to the LIESST effect in iron compounds and is characterized by a long lifetime of the photoinduced state. Our finding introduces a new class of photoswitchable compounds and thus broadens the scope and range of potential applications of such systems.

The polymeric complex [Cu(hfac)$_2$L^{Pr}] (Figure 1) belongs to the family of so-called "breathing crystals" that we have studied extensively over the last few years.[5,6] Breathing crystals [Cu(hfac)$_2$L^R] have been found to exhibit thermally induced structural rearrangements accompanied by magnetic anomalies that are, in many respects, similar to a classical spin crossover (Figure 1). During these reversible rearrangements, the elongated (Jahn–Teller) axis of the octahedron is rotated, and the exchange interaction J in a spin triad between copper(II) and the nitroxide spins changes by up to one order of magnitude owing to the shortening or lengthening of interspin distances.[6d] This situation results in a change of the magnetic moment (i.e. spin transition), since at high temperatures the spins are weakly coupled ($|J| \ll kT$, referred to as the weakly coupled spin (WS) state), whereas at low temperatures strong antiferromagnetic exchange effectively couples two of the three spins ($|J| \gg kT$), and thus the spin triad converts to the strongly coupled spin (SS) state. We have found that EPR spectroscopy of breathing crystals allows us to monitor the spin transitions between WS and SS states and to measure the exchange interactions.[6] Herein, we report the first observation that light irradiation of breathing crystals

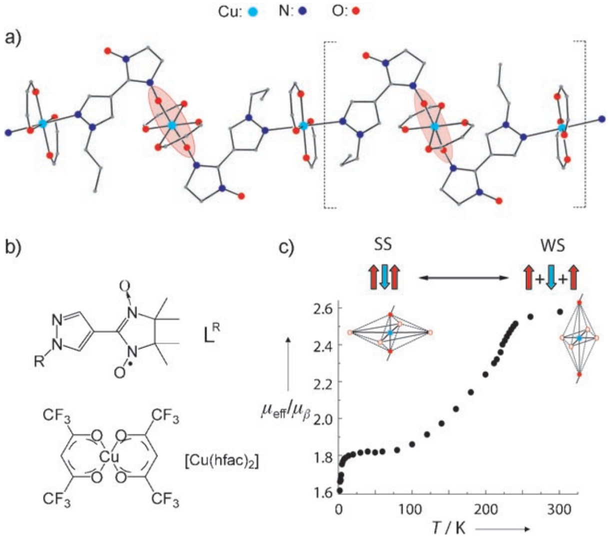

Figure 1. a) Polymeric structure of [Cu(hfac)$_2$L^{Pr}]; spin triads are circled. b) Chemical structure of [Cu(hfac)$_2$] and nitroxide ligand L^R. c) Temperature dependence of the effective magnetic moment $\mu_{eff}(T)$, defined as $\sqrt{0.5}\mu_{eff}$ of the bracketed fragment in (a); the arrow and structural diagrams illustrate spin transition between SS and WS states and corresponding geometry changes.

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[Cu(hfac)$_2$L$^{\text{Pr}}$] also leads to spin transitions between the WS and SS states. EPR spectroscopy at Q-band frequencies (34 GHz) is used to enhance the sensitivity and spectral resolution of our experiments.

The copper ion in a spin triad of [Cu(hfac)$_2$L$^{\text{Pr}}$] is antiferromagnetically coupled to each nitroxide ligand, yielding ground and intermediate $S=1/2$ states and an upper $S=3/2$ state. Temperature-dependent EPR spectra of [Cu(hfac)$_2$L$^{\text{Pr}}$] have been studied.[6] Each spectrum is a superposition of signals from a one-spin copper ion in the CuN$_2$O$_4$ unit and from a spin triad in the CuO$_6$ unit of interest (Figure 2). At temperatures above the spin transition (WS state), the observed broad signal of a spin triad has an almost isotropic g tensor owing to dynamic averaging processes between different multiplets[6b] (Figure 2a). At temperatures below the spin transition (SS state), the ground $S=1/2$ state becomes better isolated owing to the increase of J, and the observed signal displays typical anisotropic g values with $g_i<2$ ($i=$ any of x,y,z; Figure 2b).[6] Irradiation with light at 900 nm for 90 seconds at 7 K has a dramatic effect on the EPR spectrum (Figure 2c). The signal of the SS state strongly decreases, and the broad line assigned to the WS state appears instead. Simulations show that the observed signal contains approximately 82 % of the WS state and 18 % of the SS states, that is, light-induced SS→WS conversion shows a conversion depth $\delta \approx 82\,\%$. After the laser excitation, the spin triad slowly relaxes back to the SS state on a time scale of hours (Figure 2d–e). Presumably, two different processes contribute to this relaxation, because after relatively fast recovery during the first hour, the system gets trapped more stably at approximately 40 % conversion depth and can remain close to this value for hours (Figure 3). However, if afterwards this sample is warmed up to 20 K for several minutes and then cooled back to 7 K, the EPR signal completely reverts to that of the initial unperturbed state (Figure 2f). These observations are similar to the LIESST effect observed on numerous spin-crossover compounds using Mössbauer, optical,[1] and very recently also hard X-ray spectroscopy.[7]

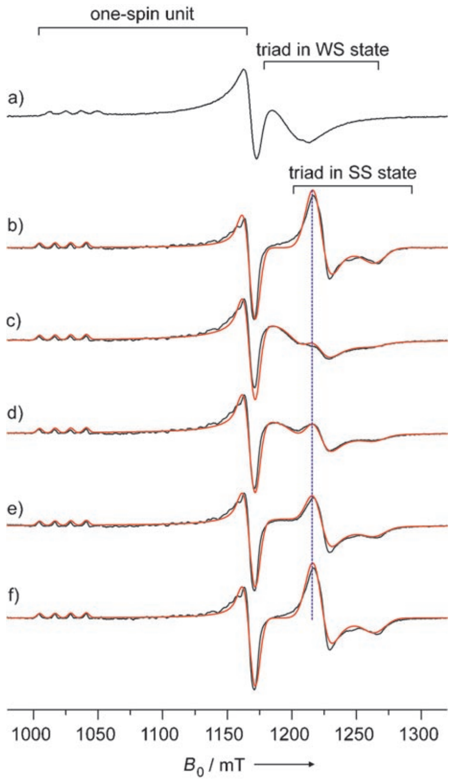

Figure 2. CW EPR spectra of pure polycrystalline powder of [Cu(hfac)$_2$L$^{\text{Pr}}$] at $T=210$ K, $\nu_{\text{mw}}=33.98$ GHz (a), and of [Cu(hfac)$_2$L$^{\text{Pr}}$] mixed with glycerol at $T=7$ K, $\nu_{\text{mw}}=33.94$ GHz (b–f). b) dark spectrum; c) immediately after irradiation (900 nm); d) 5 min and e) 210 min after irradiation; f) after warming the irradiated sample up to 20 K and then cooling back to 7 K. Simulations (red lines) yield an estimation of the SS→WS state conversion depth: approximately 82 (c), 65 (d), and 40 % (e; details in the Supporting Information). The vertical dashed line indicates the field position for the data shown in Figure 3.

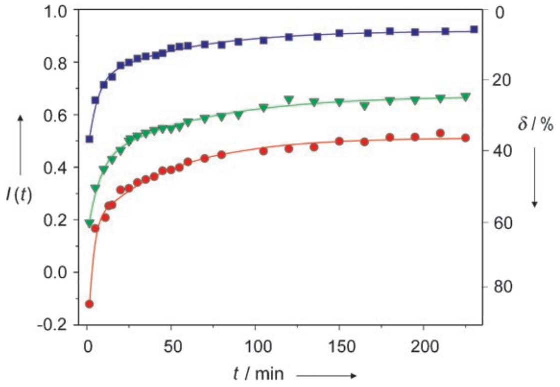

Figure 3. Recovery of the EPR signal $I(t)$ (at $B_0=1216$ mT, see vertical dashed line in Figure 2) after light irradiation at 7 K (●), 10 K (▼), and 13 K (■). Curves are normalized to the intensity of the dark spectra; estimations of the conversion depth δ are given.

The described response to irradiation of breathing crystals of [Cu(hfac)$_2$L$^{\text{Pr}}$] detected by EPR spectroscopy has also been demonstrated using FTIR spectroscopy.[8] Heating and photoacoustic effects during the experiment could reliably be ruled out. Although SQUID magnetometry under irradiation was not feasible for this compound, the magnetic susceptibility $\chi \propto \mu_{\text{eff}}{}^2$ could be reliably estimated using double integration of the whole EPR spectrum (see the Supporting Information). The value of χ was found to increase under irradiation by a factor of approximately 1.6–1.8 (for traces b and c in Figure 2). This finding agrees well with expectations, since for $\mu_{\text{eff}}(\text{SS})=1.8\,\mu_{\text{B}}$ and $\mu_{\text{eff}}(\text{WS})=2.5\,\mu_{\text{B}}$ (Figure 1c) and a conversion depth of $\delta=82\,\%$, a factor of approximately 1.76 is calculated. This light-induced increase of χ is an additional strong argument for the assignment of the light-induced state to the WS state.

The mechanism of the observed LIESST-like effect in exchange-coupled clusters of breathing crystals is expected to be generally similar to that in iron compounds. The excitation at 900 nm most likely corresponds to a d–d absorption band of copper (see UV/Vis spectra in the Supporting Information). After the light-induced promotion of an electron to the vacancy in the $d_{x^2-y^2}$ orbital, the system can relax from this excited state back to the unperturbed SS state or, alternatively, undergo structural rearrangement and convert to the WS state. The latter process involves the rotation of the Jahn–

Teller axis and thus lowers the energy of the system because of the interchange of equatorial and axial d orbitals, so that the electronically excited state becomes a ground state. Our experiments indicate that the conversion into the WS state after photoexcitation is significant. As in classical LIESST, the potential barrier between WS and SS states is mainly due to their geometrical differences; it provides for a slow WS→SS relaxation and an efficient trapping of the WS state on a timescale of hours. However, our experiments indicate that the WS→SS relaxation and its temperature dependence are somewhat different from iron compounds. The EPR signal recovery curves at $T = 7$, 10, and 13 K are shown in Figure 3. It is remarkable that both the initial conversion depth (immediately after laser irradiation) and the depth at the "plateau" achieved after several hours strongly decrease with increasing temperature. At $T > 15$ K, the LIESST-like effect becomes negligible for the studied compound. These observations imply that the competition between excitation and relaxation takes place during the formation of the trapped excited state.

We have also observed this LIESST-like effect on several other compounds of the family $[Cu(hfac)_2L^R]$. This finding shows the general manifestation of this phenomenon in breathing crystals and makes such systems interesting for applications in optically operated molecular spin devices and magnetic data storage. There are many similarities between LIESST in spin-crossover transition-metal complexes and in exchange clusters of breathing crystals. However, the specific characteristics of the latter need to be further investigated. The mechanism must be elucidated in detail, including the excitation pathway and wavelength dependence; we must search for possibilities to reverse the photoswitching; and detailed relaxation studies are needed. The correlation of conversion depth and relaxation characteristics with structure is also of interest, as it might give us further insight into the nature of the phenomenon and enable us to develop methods for increasing blocking temperature and conversion depth. We believe that the first observation of LIESST in this new type of system will stimulate many future studies and open new vistas in the exciting field of photomagnetism.

Experimental Section

The compound $[Cu(hfac)_2L^{Pr}]$ was synthesized as described previously.[4a] Because of the high optical density of crystals, the direct study of the light effect (e.g. using magnetic susceptibility or optical detection) is hindered. To make the irradiation efficient, crystals were ground, mixed with an excess of glass-forming liquid to form a suspension, and then frozen at cryogenic temperatures. Glycerol was found suitable for this purpose, as it is a weak solvent of $[Cu(hfac)_2L^{Pr}]$. A Bruker ER200D continuous-wave Q-band (34 GHz) EPR spectrometer equipped with a home-built resonator (TE_{011}) and Oxford CF935 flow cryostat was used for the experiments in Mülheim. In situ irradiation was performed using a Vibrant/Opotek Nd-YAG laser and OPO system. Pulse irradiation was carried out at 10 Hz with 1–2 mJ per pulse. The calculation[9] and other details are given in the Supporting Information.

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