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Structural specifics of light-induced metastable states in copper(II)-nitroxide molecular magnets

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Although light-induced magnetostructural switching in copper(II)-nitroxide molecular magnets $Cu(hfac)_2L^R$ was known since several years, structural characterization of metastable photoinduced states was not yet accomplished due to significant technical demands. In this work we apply, for the first time, variable-temperature FTIR spectroscopy with photoexcitation to investigate structural specifics of light-induced states in $Cu(hfac)_2L^R$ family represented by (i) $Cu(hfac)_2L^{Me}$ comprising two-spin copper(II)-nitroxide clusters, and (ii) $Cu(hfac)_2L^{Pr}$ comprising three-spin nitroxide-copper(II)-nitroxide clusters. The light-induced state of $Cu(hfac)_2L^{Me}$ manifests the same set of vibrational bands as the corresponding thermally-induced state, implying their similar structures. For the second compound $Cu(hfac)_2L^{Pr}$, the coordination environment of copper(II) is similar in light- and thermally-induced states, but distinct differences are found for packing of peripheral *n*-propyl substituent of nitroxide. Thus, generally the structures of corresponding thermally- and light-induced states in molecular magnets $Cu(hfac)_2L^R$ might differ, and FTIR spectroscopy provides a useful approach for revealing and elucidating such differences.

Introduction

The possibility to employ molecular spin states as quantum bits opens new perspectives in development of data storage devices, quantum computers and multifunctional spintronics.[1-7] Along with single molecule magnets,[8-10] single-chain magnets,[10-13] valence tautomeric compounds,[14,15] nitrogen vacancy centers,[16-18] special interest is attracted to spin-crossover (SCO) compounds.[1,19-22] SCO typically occurs in transition metal ions with $d^4 - d^7$ electron configuration that can be switched between the low-spin (LS) and a high-spin (HS) state by various external stimuli (temperature, light, pressure, magnetic or electric fields, etc.).[1,23-27] Many SCO compounds also exhibit light-induced excited spin state trapping (LIESST), a phenomenon most promising for potential applications, where complex resides in photoinduced metastable state for hours-to-days at cryogenic temperatures.[28,29]

Recently, a family of principally different compounds $Cu(hfac)_2L^R$ (Fig. 1) based on copper(II) hexafluoro-acetylacetonates ($Cu(hfac)_2$) and stable nitroxide radicals (L^R) was found to manifest various SCO-like and LIESST-like phenomena.[30-37] The overwhelming majority of these compounds have polymer-chain structure with either two-spin copper(II)-nitroxide units or alternating three-spin nitroxide-copper(II)-nitroxide and one-spin copper(II) units. In contrast to classical SCO, the spin state of transition ion (copper(II), $3d^9$) in these compounds is invariable, whereas the spin configuration of whole exchange-coupled cluster of copper(II) with nitroxides can be changed by external stimuli.

This inherent bistability in $Cu(hfac)_2L^R$ owes to the switching of exchange interaction between two extreme cases: (i) the weakly-coupled spin (WS) state characterized by weak ferromagnetic exchange between spins of copper(II) and nitroxides ($|J| << kT$), and (ii) the strongly-coupled spin (SS) state with strong antiferromagnetic exchange interaction ($|J| >> kT$). These two spin states correspond to the two structural states with different geometry of CuO_6 or CuO_5N octahedral units. With respect to thermally-induced switching, WS state typically corresponds to the high-temperature structure, whereas SS state corresponds to the low-temperature structure. Both structural states are stable at relevant temperatures and can be studied in depth by X-ray diffraction (XRD).[30] However, speaking of light-induced switching, the assignment of metastable WS state (mWS) created at cryogenic temperatures to the high-temperature geometry has not yet been justified by any structural techniques. The electronic/magnetic properties of mWS states were found similar to the corresponding high-temperature WS states,[31-33,35] but the structure of mWS states was only hypothesized.

In this work we attempt to characterize structurally the photoinduced mWS states in molecular magnets $Cu(hfac)_2L^R$

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Electronic Supplementary Information (ESI) available: Manifestation of light and thermally-induced structural changes in FTIR spectra of $Cu(hfac)_2^R$, relaxation properties of light-induced spin state. See DOI: 10.1039/x0xx00000x and compare the obtained data with those of thermally-induced WS states. For this task we employ FTIR spectroscopy that recently has proven to be a valuable tool for monitoring thermal spin state and structural switching in Cu(hfac)$_2$L^R.[37] Most direct structural method, XRD, could not be applied for light-induced studies of these systems, because the crystals are optically dense ($\varepsilon > 10^3$ M^{-1}cm^{-1}) and effective illumination of large enough crystals was not feasible up to date. At the same time, FTIR is highly sensitive to the structural changes and is capable to detect spin state switching in both SCO compounds and in Cu(hfac)$_2$L^R family.[37-43] We have selected two representative compounds Cu(hfac)$_2$L^R, both having polymer-chain structure and containing (i) two-spin copper(II)-nitroxide clusters (Cu(hfac)$_2$L^{Me}), and (ii) three-spin nitroxide-copper(II)-nitroxide clusters (Cu(hfac)$_2$L^{Pr}).

Thermal switching in these two compounds has been studied by FTIR combined with quantum-chemistry calculations in our recent work;[37] therefore we rely on these data for interpreting the light-induced phenomena attained here by FTIR for the first time.

Experimental

Preparation of the samples

The studied compounds Cu(hfac)$_2$L^{Pr}, Cu(hfac)$_2$L$^{i\text{-}Pr}$ and Cu(hfac)$_2$L^{Me} have been synthesized according to the developed procedures,[44,45] their physicochemical properties were previously characterized by X-ray, SQUID, EPR.[32-37] Usual pelleting technique was applied for mid-FTIR experiments (Figure 3): 1–2 mg of studied compound was ground and then mixed with 140 mg of KBr powder; the mixture was pressed in vacuo at room temperature using ≈5 ton pressure applied for 5 minutes. Although the compression procedure leads to partial suppression of magnetostructural transition (that becomes smoothed and lagged), its manifestations in FTIR spectra were found similar in both single crystals and pellets.[37] Figure 4 used thin single crystals of Cu(hfac)$_2$L^{Pr} and Cu(hfac)$_2$L$^{i\text{-}Pr}$.

IR measurements

The IR spectra of polycrystalline powders of studied compounds were recorded in the range of 4000–550 cm^{-1} (mid-IR) at T=5-300 K using FTIR spectrometer Bruker Vertex 80v (Bruker Optics, Germany) equipped with continuous flow liquid He cryostat Oxford OptistatCF and with a liquid N$_2$ cooled MCT detector. Infrared microscope HYPERION 2000 (Bruker Optics, Germany) equipped with sample stage Linkam FTIR600 (Linkam Scientific Instruments, United Kingdom) was used for measurements on single crystals at T=80 and 300 K. Spectral resolution was 2 cm^{-1}. The sample was thermally equilibrated during 5 min for each temperature-dependent measurement.

Irradiation conditions

For the photoswitching experiments steady-state halogen light source of illumination was used with average power around 20 mW/cm^2. The steady-state halogen light was applied to the pellet perpendicular to IR scanning irradiation. The surface of pellet was inclined by 45 deg with respect to the scanning irradiation in order to be irradiated by both IR and visible light. The typical time of irradiation before spectra measurement was ~10 minutes; after this time no significant spectral changes were observed.

EPR measurements

Continuous wave (CW) EPR measurements were carried out at X-band (9 GHz) using a commercial EPR spectrometer Bruker Elexsys E580 equipped with Oxford Instruments temperature control system (T=4-300 K). *In situ* illumination was done using the same halogen light source as in FTIR experiments.

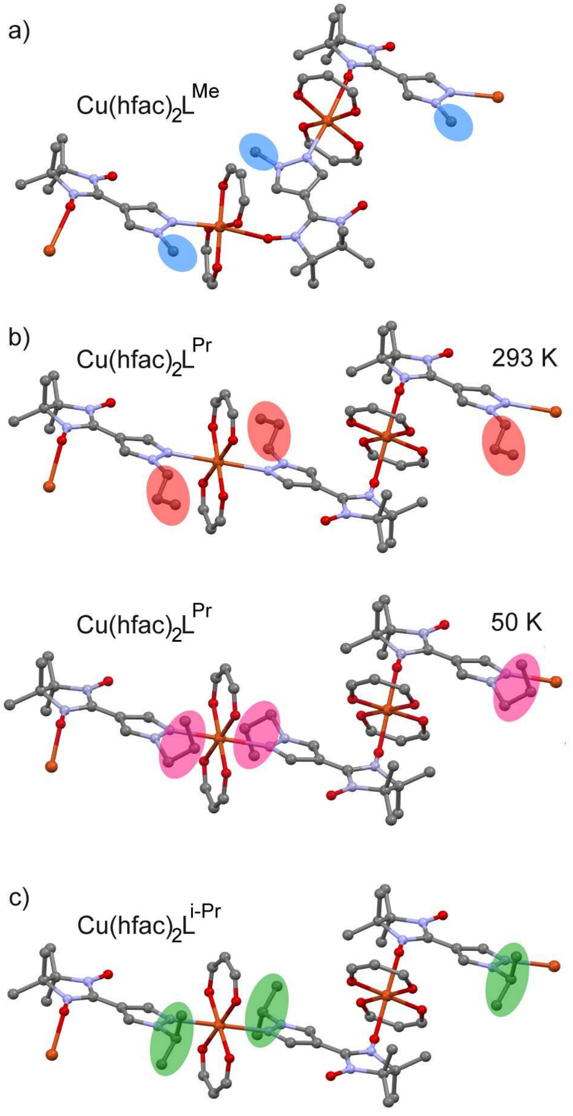

Fig. 1 The polymer-chain structures of the studied compounds. (a) Cu(hfac)$_2$L^{Me} with head-to-tail coordination motif (293 K). (b) Cu(hfac)$_2$L^{Pr} with head-to-head coordination motif at temperatures above (293 K) and below (50 K) magneto-structural transition. (c) Cu(hfac)$_2$L$^{i\text{-}Pr}$ with head-to-head coordination motif (293 K). Alkyl substituents of nitroxide radical are highlighted with corresponding colors.

Results and discussion

Fig. 2 shows the dependence of the effective magnetic moment on temperature $\mu_{eff}(T)$ for Cu(hfac)$_2$L^{Me} and Cu(hfac)$_2$L^{Pr}, and sketches the corresponding structures of SS and WS states. LIESST-like phenomena were previously observed and studied for Cu(hfac)$_2$L^{Pr}; photoinduced WS state was found to be metastable at T<25 K (Fig.2).[31-34] For Cu(hfac)$_2$L^{Me} photoswitching was not known before. Moreover, these phenomena were never demonstrated for Cu(hfac)$_2$L^{R} compounds with two-spin copper(II)-nitroxide clusters in polymer chains; all previous work concerned transitions in three-spin clusters, and we expand the type of Cu(hfac)$_2$L^{R} compounds exhibiting LIESST-like phenomena here for the first time.

Fig. 3 shows FTIR spectra of Cu(hfac)$_2$L^{Me} (a) and Cu(hfac)$_2$L^{Pr} (b) obtained in corresponding thermal SS, WS and photoinduced mWS states in the most informative mid-IR range 1100–800 cm^{-1} (the full-range mid-IR spectra are shown in Fig. S1 and S2 of ESI). Most of the vibrational bands in these chain-polymeric compounds involve sets of entangled vibrations, and the assignment of each band to a particular vibration is not instructive.[37] Spectra of thermally-accessed WS states were measured at T=150 K for Cu(hfac)$_2$L^{Me} and T=300 K for Cu(hfac)$_2$L^{Pr}, i.e. above spin transition for both compounds (Fig. 2). Light-induced mWS states were created and measured at T=5 K for both compounds to maximize photoswitching efficiency. The corresponding SS states were measured at T=25 K, where photoswitching becomes negligible for both compounds and any possible effects of scanning light on SS state are avoided (see Fig. S5 of ESI).

The irradiation with white light results in clear transformations of the SS-state FTIR spectrum of Cu(hfac)$_2$L^{Me} (Fig. 3a). All vibrational bands characteristic for SS state disappear (1334, 1201, 1098, 1086, 1034, 890 cm-1). At the same time, vibrational bands characteristic for WS state grow in intensity (1645, 1356, 1325, 884, 815 cm^{-1}). Comparison of Fig. 3a (top vs. bottom) shows striking similarities between FTIR spectra of thermally-accessed WS and light-induced mWS states. Although the line widths are slightly different, which is reasonable for noticeably different detection temperatures, the rest of the spectral information coincides (and this coincidence takes place in the whole mid-IR range, Fig. S1). Thus, we conclude that the changes of the bond lengths in Cu(hfac)$_2$L^{Me} occur similarly for thermal (SS$\rightarrow$WS) and light-induced (SS$\rightarrow$mWS) conversion, implying that the crystal structures of WS and mWS states are very similar.

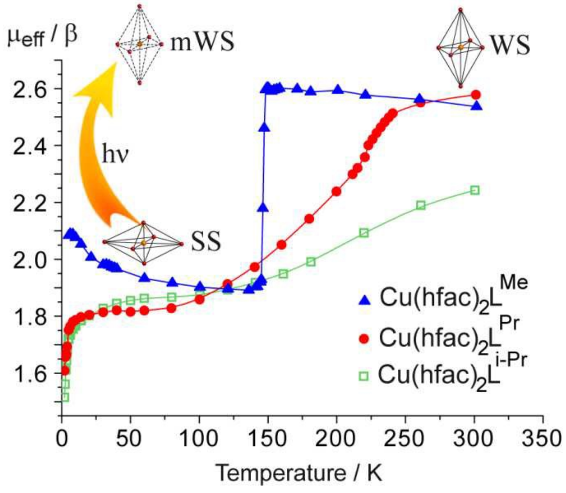

Fig. 2 The temperature dependence of effective magnetic moment for Cu(hfac)$_2$L^{Me} (blue), Cu(hfac)$_2$L^{Pr} (red), Cu(hfac)$_2$L^{i-Pr} (green). SQUID data were taken from Ref. 51; μ_{eff} was calculated for one Cu(hfac)$_2$L^{R} fragment. Diagrams sketch structures of CuO$_6$ units in SS, WS and mWS states.

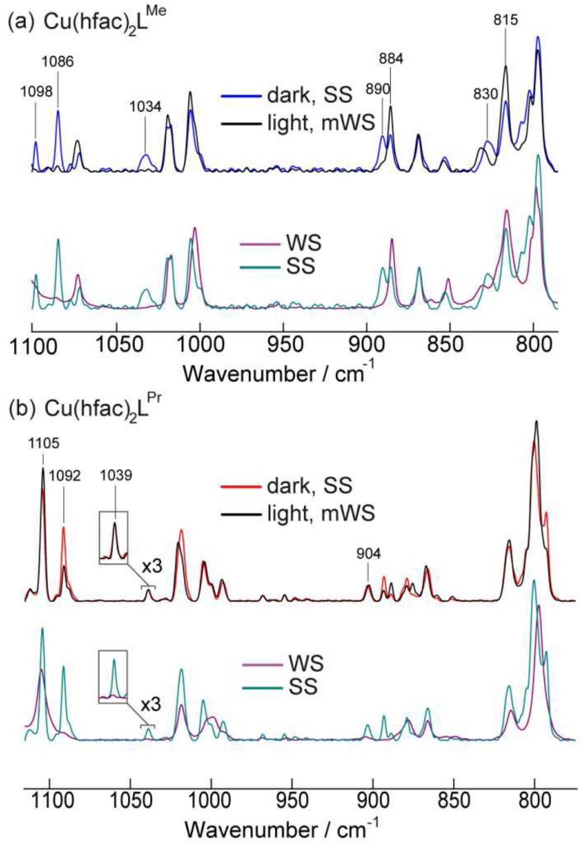

Fig. 3 (a) Mid range FTIR absorbance spectra of Cu(hfac)$_2$L^{Me}: (top) SS state (dark, 25 K), and mWS state (irradiated with light, 5 K); (bottom) temperature-induced WS and SS states (150 and 25 K, respectively). (b) Mid range FTIR absorbance spectra of Cu(hfac)$_2$L^{Pr}: (top) SS state (dark, 25 K) and mWS state (irradiated with light, 5 K); (bottom) temperature-induced WS and SS states (300 and 25 K, respectively).

In case of the second compound Cu(hfac)$_2$L^{Pr}, quite similar trends are observed (Fig.3b and Fig. S2 of ESI). Irradiation with white light reduces the intensity of characteristic vibrational bands of SS state (1649, 1553, 1504, 1193, 1139, 1092, 893, 793 and 672 cm^{-1}); at the same time vibrational bands characteristic for thermal WS state (1641, 1558, 1355, 1105 and 798 cm^{-1}) grow in intensity. Photoswitching efficiency is not as high as in Cu(hfac)$_2$L^{Me} (to be addressed in detail in the future), but characteristic spectral changes are undoubted (see e.g. bands at 1105, 1091, 893 and 792 cm^{-1}).

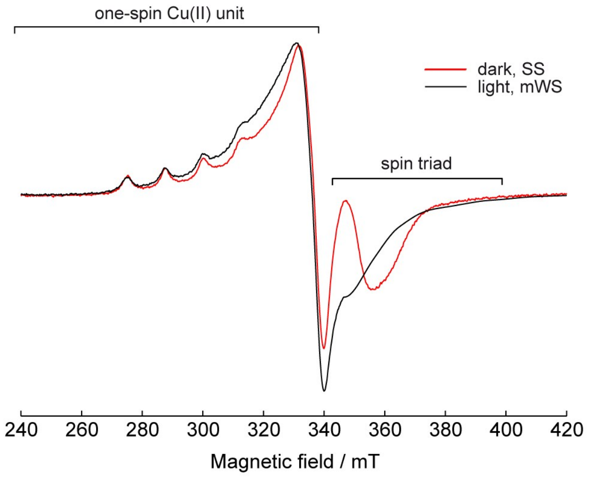

Fig. 4 X-band continuous wave EPR spectra of $Cu(hfac)_2L^{Pr}$ recorded at 5 K before irradiation in SS state (dark) and after irradiation in mWS state (light). The contributions of the spin triads and one-spin copper(II) units are indicated on top.

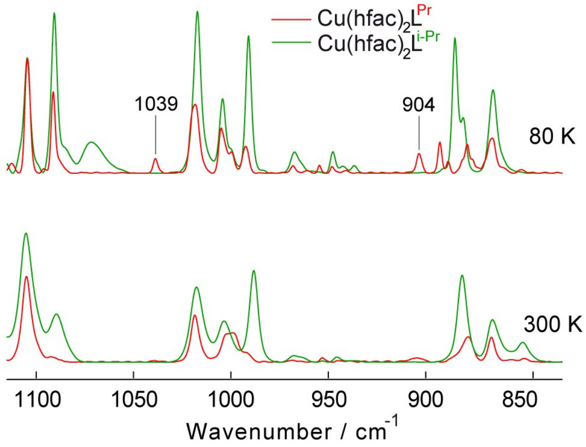

Fig. 5 Mid range FTIR absorbance spectra of $Cu(hfac)_2L^{Pr}$ (red) and $Cu(hfac)_2L^{i\text{-}Pr}$ (green) at 80 and 300 K. The characteristic bands of $Cu(hfac)_2L^{Pr}$, which are insensitive to light-induced SS→mWS conversion, are indicated.

To confirm FTIR-detected photoswitching, we performed additional EPR experiment using similar sample (KBr pellet) $Cu(hfac)_2L^{Pr}$ are contributed by two types of paramagnetic centers, namely spin triads and one-spin copper(II) units (see Fig. 4). It is evident that the signal of spin triad dramatically changes under light: the characteristic signal of SS state with g-factor <2 is replaced by a broad signal of mWS state with g>2. Similar spectral changes have been previously observed and interpreted for the same compound dispersed in frozen glycerol or embedded in polyvinylchloride (PVC) film.[31,33] The achieved photoswitching efficiency in KBr sample (~50 %) is smaller compared to that in PVC (~100%) or glycerol (~80%), that can be attributed to different sample preparation approaches leading to different illumination conditions.[31,34,37] Nevertheless, the temperature dependence of photoswitching efficiency obtained by FTIR (in KBr) and EPR (in glycerol) is closely the same (Fig. S6), and observed self-decelerating relaxation is typical for $Cu(hfac)_2L^R$ family (Fig.S5b).[33] Altogether, these trends unambiguously confirm the assignment of observed changes in FTIR spectra to photoinduced SS→mWS conversion.

Contrary to $Cu(hfac)_2L^{Me}$, in case of $Cu(hfac)_2L^{Pr}$ some of the characteristic changes occurring upon thermal SS→WS conversion do not occur at all upon light-induced SS→mWS conversion. No changes are observed for the bands at 1039 and 904 cm^{-1} under irradiation, whereas nearly complete disappearance of these bands occurs by switching temperature from 25 to 300 K (Fig. 3b and insets). This fact signifies some structural differences between thermal WS and light-induced mWS states of $Cu(hfac)_2L^{Pr}$.

Previous XRD studies of thermal WS and SS states of $Cu(hfac)_2L^{Pr}$ have shown that the orientation of n-propyl substituent in nitroxide radical is different in these two magnetostructural states (see Fig. 1b).[36] Since n-propyl substituent is remote from the main sites of magnetostructural rearrangements (i.e. CuO_6 units containing spin triads), it is plausible that orientation of propyl group may change upon slow thermal SS→WS conversion, but may not change upon ultrafast (<50 fs)[35] light-induced SS→mWS conversion.

To verify this hypothesis we additionally investigated the sister compound to $Cu(hfac)_2L^{Pr}$, the complex $Cu(hfac)_2L^{i\text{-}Pr}$ with almost identical structure and magnetic properties, but having isopropyl substituent in pirazole ring of nitroxide instead of n-propyl (Fig. 1 and 2). It was reasonably anticipated that structural difference in substituents would lead to the difference in corresponding vibrational bands. FTIR spectra of $Cu(hfac)_2L^{i\text{-}Pr}$ and $Cu(hfac)_2L^{Pr}$ are quite similar at low and high temperatures (Fig. 5). Note that at 80 K both compounds reside in SS state, whereas at 300 K $Cu(hfac)_2L^{Pr}$ is found in thermal WS state, but $Cu(hfac)_2L^{i\text{-}Pr}$ is found in mixed SS/WS state (~44/56%, respectively).[34] It is evident that the characteristic bands of $Cu(hfac)_2L^{Pr}$ that are insensitive to light-induced SS→mWS conversion (1039 and 904 cm^{-1}), are completely absent in the spectra of $Cu(hfac)_2L^{i\text{-}Pr}$. Thus, comparison with $Cu(hfac)_2L^{i\text{-}Pr}$ confirms our assignment of 1039 and 904 cm^{-1} bands in $Cu(hfac)_2L^{Pr}$ to vibrations of propyl substituent. In addition, quantum chemical calculations also predict the presence of propyl substituent's absorption bands in the discussed frequency range.[37] Thereby, we have demonstrated that the structure of light-induced mWS state in $Cu(hfac)_2L^{Pr}$ is not identical to the structure of corresponding thermally-accessed WS state: although it is similar for the "heart" of the compound, i.e. CuO_6 unit containing spin triads, at periphery it rather resembles the ground SS state, at least with respect to the packing geometry of n-propyl substituent.[46] Note that certain differences between crystal structures of light- and thermally-induced high-spin states have been broadly discussed for SCO compounds.[39,47-52] Thus, the first observation of such differences in SCO-like molecular magnets $Cu(hfac)_2L^R$ adds up to the similarities between these principally different systems.

Conclusions

The first application of FTIR spectroscopy to light-induced metastable states of molecular magnets $Cu(hfac)_2L^R$ has demonstrated the capabilities of this method and provided valuable insights into the structural specifics of such states. In particular, the comparison of structures of thermal WS and light-induced mWS states is straightforward using FTIR with photoexcitation. Two selected compounds, which essentially represent the diversity of $Cu(hfac)_2L^R$ family, have been investigated. For one of them, $Cu(hfac)_2L^{Me}$, no differences in FTIR spectra were found for thermal WS and light-induced mWS states, implying that the corresponding structures are closely similar. For the second compound $Cu(hfac)_2L^{Pr}$ we observed distinct differences in FTIR spectra of WS and mWS states. Based on comparison with sister compound $Cu(hfac)_2L^{i\text{-}Pr}$ and quantum chemical calculations, different geometry of peripheral propyl group in WS and mWS states was established. Although major structural rearrangements in nitroxide-copper(II)-nitroxide cluster do occur under irradiation with light, minor structural changes on periphery may be suppressed, so that the remote propyl group of nitroxide radical retains the geometry of the ground SS state despite exchange clusters adopt the geometry of WS state. Deep understanding of structural peculiarities of mWS states is indispensable for future studies of photoswitching and relaxation phenomena in molecular magnets $Cu(hfac)_2L^R$. In particular, the relaxation rates from photoinduced mWS to the ground SS state are strongly dependent on local structural perturbations created by photoswitched clusters.[33,34] Therefore, the development of sound approach for structural characterization of mWS states reported here is a significant step forward for improving functional properties of molecular magnets $Cu(hfac)_2L^R$.

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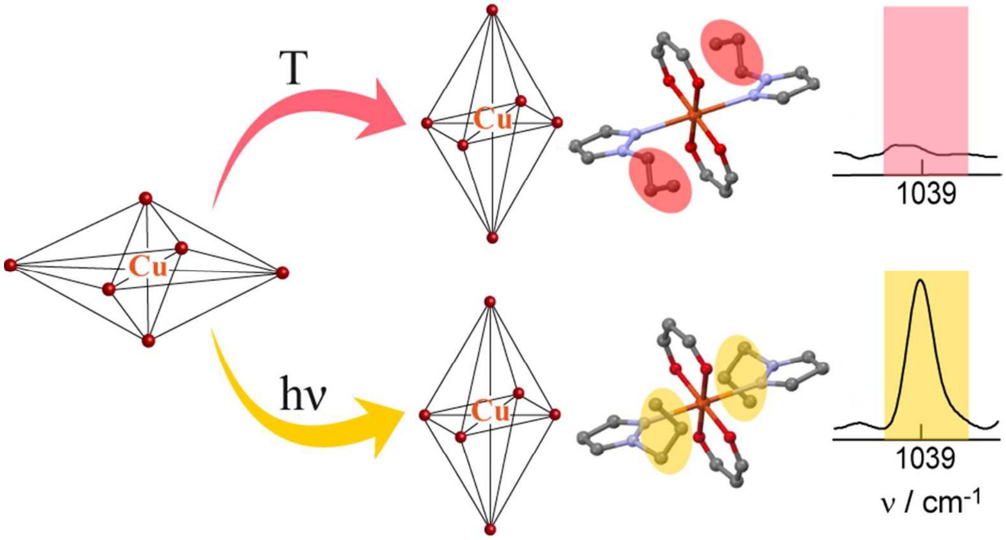

TOC graphic
78x43mm (300 x 300 DPI)

Although thermally- and light-induced structures of molecular magnets $Cu(hfac)_2L^R$ are principally similar, FTIR reveals differences in packing of peripheral groups.