Supporting Information

High-field EPR of copper(II)–nitroxide compound exhibiting three-step phase transition: structural insights from the field-induced sample orientation

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1. FTIR spectroscopy data processing

Figure S1 shows temperature dynamics of mid-IR spectrum of $Cu(hfac)_2L^{MeMe}$ in the 300 K (red) – 10 K (blue) temperature range (only 20 spectra are shown for clarity). In 700–1700 cm^{-1} energy range a multitude of lines change their shape and intensity as a function of temperature. The temperature dependence of most of the absorption lines of $Cu(hfac)_2L^{MeMe}$ reflects the two-step magnetostructural transitions. We have highlighted seven lines in 700–1700 cm^{-1} range that best demonstrate stepwise features at the temperatures of magnetostructural transitions. Figure S2 shows that integral absorption of every characteristic line indicates two-step character of the transition. Comparing to magnetometry data, the FTIR changes are more gradual. Presumably, this is a result of compound grinding, that is required for FTIR experiments.

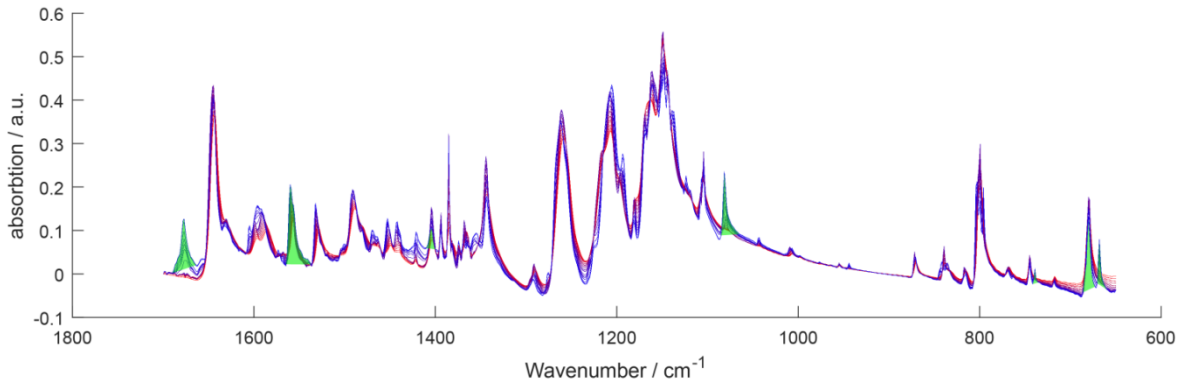

Figure S1. FTIR spectra of $Cu(hfac)_2L^{MeMe}$ in temperature range 300 (red) - 10 (blue) K

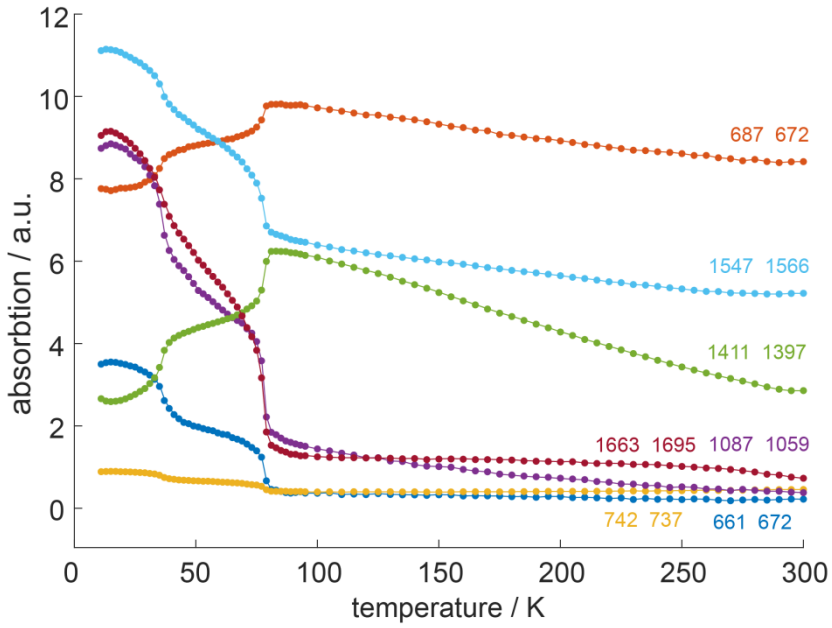

Figure S2. Integral absorption of characteristic mid-IR absorption lines of $Cu(hfac)_2L^{MeMe}$

2. Q-band EPR data processing and simulation

Figure S3 shows Q-band EPR spectra of $Cu(hfac)_2L^{MeMe}$ measured at various temperatures. Depending on the temperature, the spectra are colored in red (high-temperature range; > 90 K), in purple (intermediate-temperature range, ~ 40–90 K) and in blue (low-temperature range; < 40 K). These ranges correspond to three plateaus presented on magnetometry data. EPR spectra of these tree ranges are differing to each other. For instance, $g < 2$ signal appears at 30 K, unambiguously indicating emergence of SS state. The high-temperature transition is less pronounced, with gradual changes of EPR spectrum in 40–130 K temperature range. One of these changes is gradual disappearance of hyperfine structure of one-spin isolated copper ion (1000–1100 mT) under cooling. Same as for FTIR experiments, temperature changes of Q-band EPR spectrum of $Cu(hfac)_2L^{MeMe}$ are more gradual when comparing to the magnetometry data. It is considered to be a result of compound grinding during sample preparation.

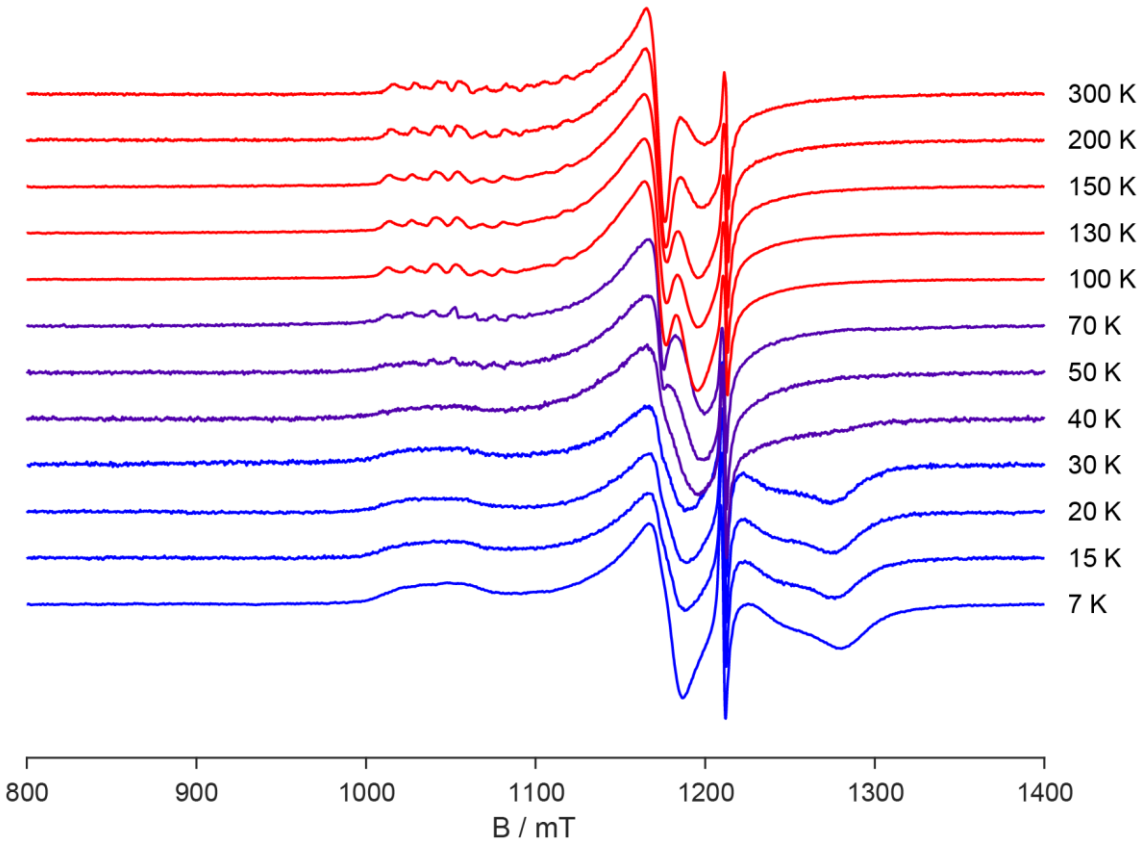

Figure S3. Temperature changes in Q-band EPR spectrum of $Cu(hfac)_2L^{MeMe}$. Red spectra – high-temperature phase, purple spectra – intermediate-temperature phase, blue spectra – low-temperature phase.

Figure S4 shows simulation of representative spectrum of each temperature range (30, 70, and 300 K). Simulation parameters are in accordance with high-field EPR data: A_{zz} = 450 MHz = 15.7 mT, g_R = 2.007. 30 K: $g_{single\ Cu}$ = [2.056, 2.347], g_{Triad} = [1.98 1.91]; 70 K: $g_{single\ Cu}$ = [2.072, 2.35], g_{Triad} = [2.048]; 300K: $g_{single\ Cu}$ = [2.073 2.35], g_{Triad} = [2.05]. Q-band spectra simulation show unidentified line with g ≈ 2.05 and 60 mT width contributing to the spectra at low temperatures. Presumably, this signal is attributed to the clusters of polymer chain that affected by grinding of compound during sample preparation.

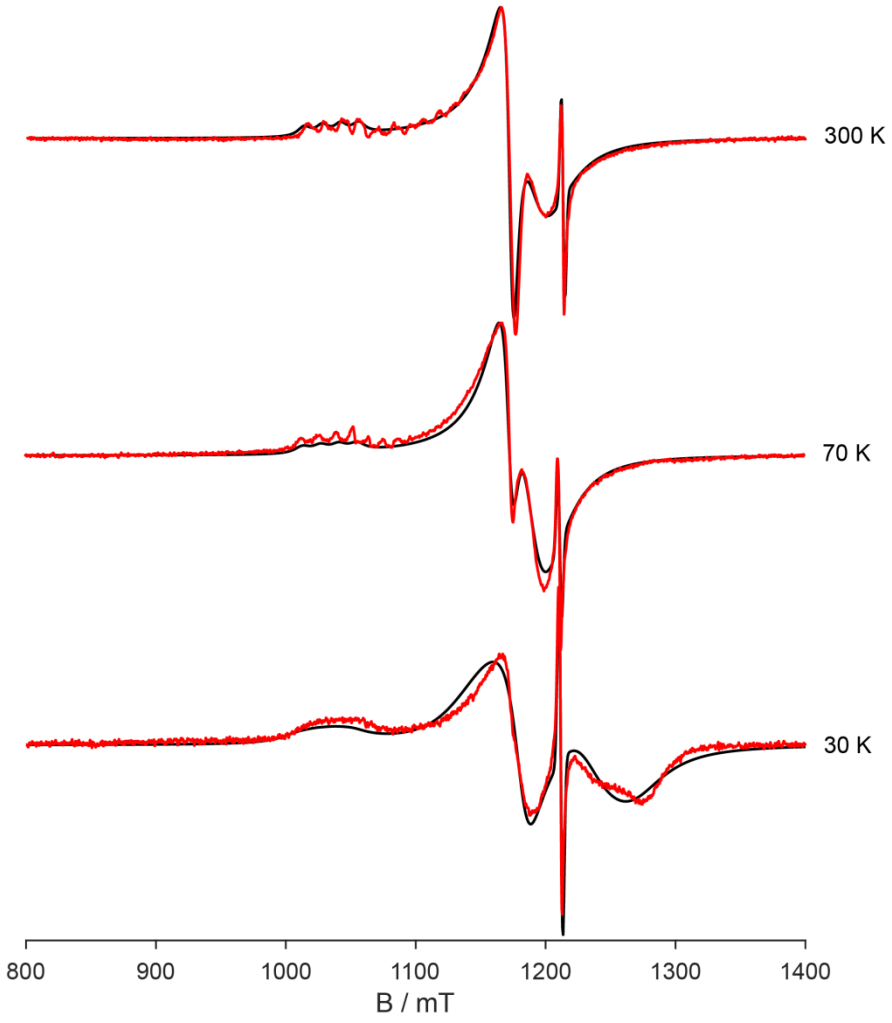

Figure S4. Simulation of Q-band EPR spectra of $Cu(hfac)_2L^{MeMe}$ in high (300 K), medium (70 K), and low-temperature (30 K) states. Experimental spectra are shown in red, simulated spectra are shown in black.

3. High-field EPR data processing and estimation of the alignment time

Figure S5 shows experimental data from two sequential high-field EPR experiments. The intensity of the signal is proportional to the radiation power absorbed by the sample, measured using bolometric detector in transmission mode. The only processing of the raw data is the subtraction of linear baseline and conversion from transition to absorption-type spectra. Peaks in the lowest (21 T) and highest (26 T) magnetic fields of the compound spectra appear as a result of powder sample alignment in the magnetic field. The data shows that the ratio of aligned to disordered powder fractions in each spectrum is similar under the field ramping up and falling down (within the given signal-to-noise ratio). Thus, the powder partial orientation happens during the first 200 ms of the magnetic field sweep, prior to magnetic field reaching 21 T.

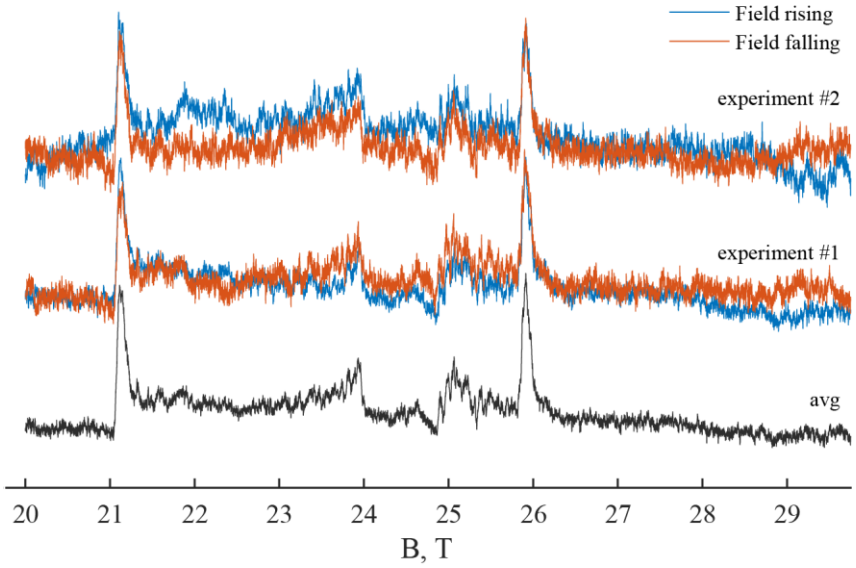

Figure S5. 693 GHz experimental EPR spectra of $Cu(hfac)_2L^{MeMe}$ at 4 K under the magnetic field ramping up and falling down (red and blue respectively) and the resulting summary spectrum (black).