Spin state switching in copper-nitroxide based molecular magnets using the low-energy photons

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Molecular magnets switchable by external stimuli are perspective systems for realization of high-density magnetic memory and quantum information processing devices. Among them, copper(II)-nitroxide based complexes $Cu(hfac)_2L^R$ (also called "breathing crystals") exhibit spin-crossover-like (SCO-like) behavior and can be switched between two magnetostructural states by temperature, pressure or light [1]. Light-induced switching is most promising for potential applications, and long-lived photoinduced states at cryogenic temperatures have been experimentally evidenced, similar to LIESST in classical iron-based SCO compounds. However, the absorption spectrum of copper-nitroxide compounds is drastically different. While iron-based SCO compounds most often feature well-defined d-d or charge-transfer bands in UV-vis region, copper-nitroxide magnets show poorly resolved broad bands spreading at least to the near IR region. At the same time, ultrafast photoswitching (<50 fs) and excited state relaxation point out at existence of low-lying excited states [2]. These specifics altogether imply that a very low-energy radiation quanta, far-IR-to-THz range, can possibly induce photoswitching of copper-nitroxide magnets.

We report that as low energy as mid-IR is sufficient to switch the breathing crystal $Cu(hfac)_2L^{Pr}$ from ground to excited long-lived state, which was observed at temperature below 10 K with FTIR or EPR detection. Furthermore, Novosibirsk Free Electron Laser (NovoFEL) provides unique opportunity of tunable excitation within 1040-1180 cm^{-1}, yielding solid confirmations of the low-energy photoswitching. Thus, we show that the excitation energy necessary for photoswitching of breathing crystals can be drastically downscaled from UV-vis to mid-IR region (~20 times). At the moment, this is a rather fundamental finding; however, decent advantages of using low-energy quanta may lead to the new and promising potential applications.

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