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Photoswitching of a thermally unswitchable molecular magnet Cu(hfac) 2Li-Pr evidenced by steady-state and time-resolved electron paramagnetic resonance

Barskaya I., Tretyakov E., Sagdeev R., Ovcharenko V., Bagryanskaya E., Maryunina K., Takui T., Sato K., Fedin M.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

Most photoswitchable molecular magnets exhibit thermally induced switching, as is typical of spin crossover (SCO), valence tautomerism and SCO-like phenomena. We report a rare case of a copper-nitroxide based molecular magnet Cu(hfac)2Li-Pr that does not exhibit quantitative SCO-like behavior in the temperature range of its chemical stability (2-350 K); however, it can be switched to a metastable thermally inaccessible spin state via visible/near-IR light at cryogenic temperatures. By means of photogeneration, unique information on this otherwise unobservable spin state has been obtained using steady-state Q-band (34 GHz) and time-resolved W-band (94 GHz) electron paramagnetic resonance (EPR) spectroscopy. In particular, we have found that the electronic structure and relaxation properties of the photoinduced state in Cu(hfac)2Li-Pr are very similar to those in its sister compound Cu(hfac)2Ln-Pr that is thermally switchable and has been exhaustively characterized by many analytical methods, previously. The first observation of photoswitchable behavior in a thermally unswitchable copper-nitroxide based molecular magnet Cu(hfac)2Li-Pr paves the way for photoswitching applications of this and similar compounds in the remarkably broad temperature range of 2-350 K.

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