

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

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### 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)<sub>2</sub>Li-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)<sub>2</sub>Li-Pr are very similar to those in its sister compound Cu(hfac)<sub>2</sub>Ln-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)<sub>2</sub>Li-Pr paves the way for photoswitching applications of this and similar compounds in the remarkably broad temperature range of 2-350 K. © 2014 American Chemical Society.

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