Crystallographic studies of the spin state transition of three Fe(II) metallogrids: thermal vs ultra-fast photoswitching

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Diffraction techniques has been employed to study the molecular reorganisation of three oligonuclear spin crossover (SCO) complexes of the form $[Fe(II)_X L^R_4]BF_3 \cdot MeCN$ (X = 2,3,4; L = R-3,5-bis{6-(2,2'-bipyridyl)}pyrazole; R = H, CH_3), with a grid-like arrangement [1-2]. A multi-temperature crystallographic investigation exhibits the gradual phase transition in all compounds and a cross-talk between strongly linked metal centres. A systematic comparison between metallogrids suggests that the intramolecular cooperativity results from the complex interplay between grid flexibility and nuclearity. The latter has also a key role in molecular geometry of the ephemeral species formed after light irradiation with a femto-second laser pulse, as observed by time-resolved crystallography. The metallogrid with two non-linked metal centres shows a single molecular rearrangement during the first nanosecond after excitation, while the tetranuclear grid has multiple structural arrangements during the same span of time. More in general, this work exhibits the structural modifications accompanying the thermal and ultra-fast photo-induced spin transition of three metallogrids complexes.

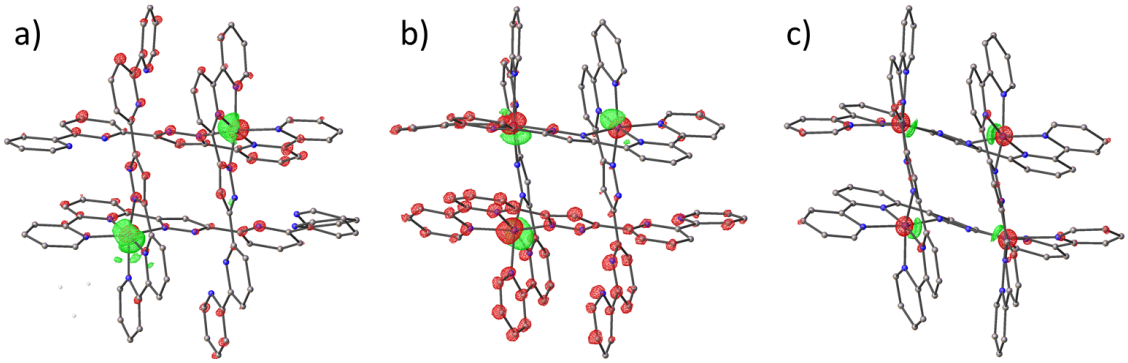

Figure 1. Thermal-difference Fourier maps of metallogrids with a) two, b) three, and c) four Fe(II) metal centres.

[1] Schneider, B., Demeshko, S., Neudeck, S., Dechert, S. & Meyer, F. (2013) *Inorg. Chem*. **52**, 13230.

[2] Steinert, M., Schneider, B., Dechert, S., Demeshko, S. & Meyer, F. (2014) Angew. Chem. Int. Ed. 53, 6135.

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