Crystal engineering concepts in the design and synthesis of a series of novel, structurally related spin-crossover materials, characterized by variable temperature single crystal X-ray diffraction

L. Birchall, H. Shepherd

University of Kent, School of Physical Sciences, Ingram Building, Canterbury, CT2 7NH

ltb7@kent.ac.uk

Spin-crossover (SCO) materials can change their spin state in response to a variety of stimuli such as temperature, light and guest molecules. These transitions are accompanied by changes in magnetic properties and often a colour change, making them attractive as smart materials [1].

Octahedral metal complexes containing iron(II) are known to be SCO active when certain ligands, often N-donors, are bound to the metal [2]. In framework and coordination polymer based spin-crossover materials, the cooperativity of the transition is aided by the covalent interactions present. However, in molecular complexes, the cooperativity of a transition relies on the elastic interactions that are present in the crystal structure [3]. Therefore, designing molecular SCO materials with specific properties is very challenging due to the vast number of structure-directing intermolecular interactions that need to be considered. The difficulty of design becomes even more complex due to the potential for solvate and polymorph formation [4, 5].

Thus, we have used crystal engineering concepts in the design and syntheses of a series of structurally-related SCO materials. We have used variable temperature single crystal X-ray diffraction analysis to obtain SCO curves, by following the octahedral volume at the Fe(II) center (Fig. 1). This variable temperature analysis has also provided valuable insight into the subtle structural changes such as distortions as well as the more drastic crystallographic symmetry-breaking phase transitions that we have seen in our materials [6]. This work demonstrates design tools that will greatly benefit and evolve the way in which new and desirable SCO materials will be discovered.

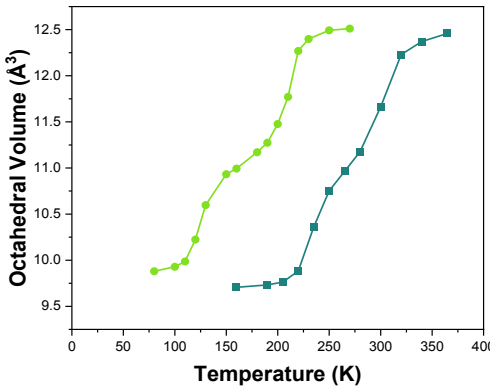

Figure 1. SCO curves where supramolecular modifications allow for modification of the SCO transition temperature. The curves were plotted by measuring the average FeN_6 octahedral volume using variable temperature single crystal X-ray diffraction.

[1] A. Bousseksou, G. Molnár, L. Salmon and W. Nicolazzi, *Chem. Soc. Rev.*, 2011, **40**, 3313–3335.

[2] J. Olguín and S. Brooker, *Coord. Chem. Rev.*, 2011, **255**, 203–240.

[3] W. Nicolazzi and A. Bousseksou, *Comptes Rendus Chim.*, 2018, **21**, 1060–1074.

[4] M. Hostettler, K. W. Törnroos, D. Chernyshov, B. Vangdal and H. B. Bürgi, *Angew. Chemie - Int. Ed.*, 2004, **43**, 4589–4594.

[5] J. Tao, R. J. Wei, R. Bin Huang and L. S. Zheng, *Chem. Soc. Rev.*, 2012, **41**, 703–737.

[6] L. Birchall and H. Shepherd, Manuscript in Preparation.

Keywords: Spin-crossover; crystal engineering; transition; responsive; design

We would like to thank the Leverhulme Trust for funding. (Grant number - RPG-2019-067)
Acta Cryst. (2021), A**77**, C803