When Iron Changes Its Spin: A Pressure-Temperature Phase Story

Benjamin BERTIN[1], Almudena INCHAUSTI[1], Elodie TAILLEUR[2], Nathalie DARO[1], Patrick ROSA[1], Guillaume CHASTANET[1], Mathieu MARCHIVIE[1], Philippe GUIONNEAU[1]

[1]Université de Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR5026, 33600 Pessac, France.
[2]Université Lorraine, CRM2, 54506 Vandoeuvre Les Nancy, France.

Spin crossover (SCO) materials are attracting growing interest for many applications due to their ability to switch reversibly between high spin (HS) and low spin (LS) states under numerous external stimuli such as temperature, light or pressure. According to this last stimulus and due to their ability to switch reversibly between HS and LS associated with a high entropy variation, SCO complexes have been recently identified as potential candidates for solid-state barocaloric refrigerant[1] (for the cooling systems of the future). Within this context, designing molecular-based spin transition materials that are optimal for barocaloric application requires a thorough understanding of SCO behavior under extreme conditions.

In this work, we focused on a Fe(II)-based complex already known as a model for the general understanding of the behavior under temperature and pressure: **$[Fe(PM\text{-}BiA)_2(NCS)_2]$** (PM-BiA = N-(2'-pyridylmethylene)-4-amino-bi-phenyl), which crystallizes in two polymorphic forms, with distinct SCO transition characteristics[2]. Previous attempts were made to draw a phase diagram but first some proposed features were controversial and then many data were missing[3]. The principal aim of this study is to clarify the complete and finally reveal its definitive **phase diagram (P, T)** including the contribution of the two polymorphs and their corresponding spin state. To implement it, measures under pressures using X-ray diffraction and Raman spectroscopy were made, notably on synchrotron beam lines. The X-Ray diffraction patterns were analyzed and compared with previously reported crystal structures to clearly identify and correlate the observed phases under pressure. This work presents thus an in-depth study of this compound, enlighten new features and contributes to a better understanding of its behavior under pressure, which constitutes a key point for the study of other Fe(II) complexes.

Beyond the targeted SCO properties ($T_{1/2}$, abruptness, …), finding good candidates for barocaloric applications implies to perfectly know the properties and the stability of the different phases under pressure. The results presented here constitute then one example of the mandatory steps that one has to perform prior to envisage a SCO material for barocaloric applications.

(1) Sandeman, K. G. Research Update: The Mechanocaloric Potential of Spin Crossover Compounds. *APL Mater.* **2016**, *4* (11), 111102. https://doi.org/10.1063/1.4967282.

(2) Létard, J.-F.; Chastanet, G.; Nguyen, O.; Marcén, S.; Marchivie, M.; Guionneau, P.; Chasseau, D.; Gütlich, P. Spin Crossover Properties of the [Fe(PM-BiA)2(NCS)2] Complex – Phases I and II. *Monatshefte Für Chem. Chem. Mon.* **2003**, *134* (2), 165–182. https://doi.org/10.1007/s00706-002-0537-0.

(3) Matar, S. F.; Guionneau, P.; Chastanet, G. Multiscale Experimental and Theoretical Investigations of Spin Crossover FeII Complexes: Examples of [Fe(Phen)2(NCS)2] and [Fe(PM-BiA)2(NCS)2]. *Int. J. Mol. Sci.* **2015**, *16* (2), 4007–4027. https://doi.org/10.3390/ijms16024007.

Acknowledgments: The authors acknowledge the French Agency of Research, ANR BREF (ANR-23-CE08-0022-01) for the financial support of this study.