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Is Fe(III) the new king of spin crossover's iron throne?

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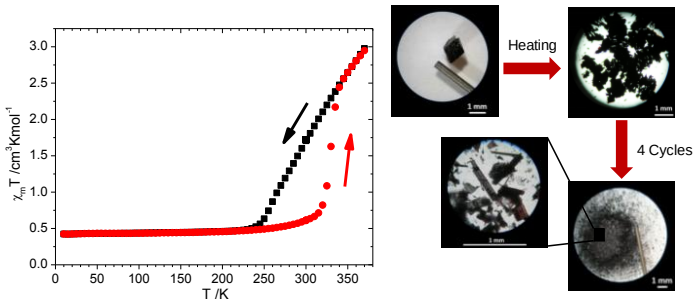
Abstract

Spin crossover compounds exist among a limited group of $3d^4$–$3d^7$ transition metal ions. The most common examples are Fe(II), Fe(III) and Co(II). Fe(III) has an advantage for fabrication of SCO materials due to its redox stability. Recently, SCO research has been producing extraordinary solutions for real applications.[1]

We recently synthesised mononuclear Fe(III) compounds, all displaying spin crossover (SCO), that show to be highly sensitive to the substituent on the ligand. For example, halogen substituted compounds show SCO profiles that range from stepped to abrupt, two of which display hysteresis centred at room temperature.[2] We found that while the bromo-substituted compound undergoes a phase transition coupled with the thermosalient effect (TSE) resulting in crystal fragmentation with no loss of both SCO and hysteresis (Figure),[3] the iodo-subsituted undergoes a irreversible TSE-SCO.[4] We have also found that in amphiphilic Fe(III) SCO compounds self-aggregation in solution forms cooperative systems in dichloromethane.[5] Here I discuss the unexpected cooperative nature of these mononuclear Fe(III) spin labile compounds and attempts to rationalise how the substituent affects the cooperativity and the thermosalient effect are also discussed.



Recent Publications (maximum 5)

1. Halcrow M. A.; Spin-Crossover Materials: Properties and Applications (John Wiley & Sons Ltd, 2013).
2. Vicente, A. I.; Ferreira, L. P.; Carvalho, M. D.; Rodrigues, V. H. N.; Dîrtu, M.; Garcia, Y.; Calhorda, M. J.; Martinho, P. N. *Dalton Trans.* 48 (2018) 4239–4247.
3. Vicente, A. I.; Joseph, A.; Ferreira, L. P.; Carvalho, M. D.; Rodrigues, V. H. N.; Duttine, M.; Diogo, H. P.; Minas Da Piedade, M. E.; Calhorda, M. J.; Martinho, P. N. *Chem. Sci.* 7 (2016) 4251–4258.
4. Martins, F. F.; Joseph, A.; Diogo, H. P.; Minas da Piedade, M. E.; Ferreira, L. P.; Carvalho, M. D.; Barroso, S.; Romão, M. J.; Calhorda, M. J.; Martinho, P. N. *Eur. J. Inorg. Chem.* 2018 (2018) 2976–2983.
5. Vicente, A. I.; Wu, X.; Ortin, Y.; Ferreira, L. P.; Carvalho, M. D.; Realista, S.; Barker, A.; Morgan, G. G.; Galamba, N.; Costa, P. J.; Calhorda, M. J.; Martinho, P. N. *Dalton Trans.* 48 (2019) 4239–4247.

Biography

P. N. Martinho completed a PhD degree in Chemistry from the University College Dublin (UCD) in 2010. After finishing his PhD, P. N. Martinho was a visiting scientist at Karlsruhe Institute of Technology (KIT) for one year. In 2012 he moved to the Faculty of Sciences at the University of Lisbon (FCUL) for a second postdoctoral appointment. Recently, P. N. Martinho was a visiting professor both at Université catholique de Louvain, Louvain-la-Neuve and Charles University, Prague. He is now a senior researcher at FCUL under the CEEC-FCT programme. His main research interests are: Molecular magnetism properties in Fe(III) and Mn(III) compounds; Self-assembly and materials development in coordination compounds; Electronic and photochemical properties in coordination compounds; Electro- and photo-chemical conversion of small molecules with first-row transition metals; Materials development for small molecule activation.. P. N Martinho published more than 20 papers and his H-index is 11 on Scopus.

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