Monitoring spin-crossover behaviour in novel iron coordination complexes

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The study of spin-crossover (SCO) phenomena between high-spin (HS) and low-spin (LS) states of octahedral $3d^4$-$3d^7$ transition-metal ions represents an important area of coordination chemistry. SCO compounds involving Fe(II) in an octahedral ligand field are the most commonly studied systems and are interesting both from a fundamental and an application standpoint. The transition between LS and HS states can be triggered by external stimuli such as temperature, pressure and electromagnetic radiation, giving rise to variations in colour, spin state, metal-donor distances as well as the dielectric constant. Such complexes have several potential applications. However, the design and successful construction of SCO systems with the required defined properties still represents a significant challenge. This investigation sought to identify if the Fe2p splitting could be seen at intermediate temperatures in a mononuclear high temperature iron(II) SCO complex, allowing the spin transition to be followed using XPS measurements, and to identify how the trend in variable temperature (VT) XPS matches that of the squid magnetic susceptibility experiments. Our interests also lay in how these XPS spectra differed when the number of Fe(II) metal centres in the discrete compound changed from mononuclear to dinuclear. A dinuclear triple-stranded helicate iron(II) complex that displays a complete spin transition with a gradual-abrupt character at high T1/2 is also reported [1, 2]. VT-XPS shows the spin behaviour is completely reversible between HS and LS. The spin state of an Fe(II) centre can be clearly traced by three distinct 'phases' of the XPS spectrum [fig1]. The ability of XPS to analyse the surface layers of SCO materials serves as a strong advantage to the technique, as this allows for thin-film analysis of future electronic or sensing SCO devices without interference of the underlying substrate. In this study we have done preliminary work of analysing thin film of the mononuclear SCO complex. Above room temperature, the HS fraction of the film appears lower than expected. Future work will confirm if the film properties differ somehow from a bulk solid material.

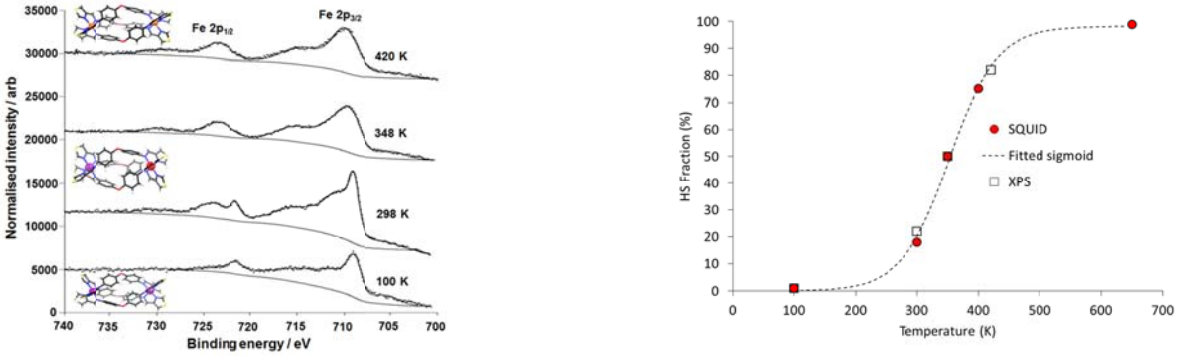

Fig 1: a) Fe2p spectra of dinuclear triple-stranded helicate Fe(II) complex, b) HS fraction of VT-XPS and magnetic data as function of temperature.

References:
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