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First observation of hidden hysteresis in an Fe(III) spin crossover complex

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Abstract: Molecular magnetic switches are expected to form the functional components of future nanodevices. Herein we combine detailed (photo-) crystallography and magnetic studies to reveal the unusual switching properties of an iron(III) complex, between low (LS) and high (HS) spin states. On cooling, it exhibits a partial thermal conversion associated with a reconstructive phase transition from a [HS-HS] to a [LS-HS] phase with a hysteresis of 25 K. Photoexcitation at low temperature allows access to a [LS-LS] phase, never observed at thermal equilibrium. This work, reporting the first iron(III) spin crossover complex to exhibit reverse-LIESST (light-induced excited spin state trapping), also reveals a hidden hysteresis of 30 K between the hidden [LS-LS] and [HS-LS] phases. It also demonstrates that Fe(III) SCO complexes can be just as effective as Fe(II) systems, and with the advantage of being air-stable, makes them ideally suited for use in molecular electronics.

Molecular switches are attractive targets in the development of new materials. Among the many possible switches, those based on the spin crossover (SCO) phenomenon are particularly attractive as a range of perturbations can be used to affect switching including temperature, chemical and physical pressure, application of a magnetic field and light.^[1–5] Spin crossover involves a transition between a high spin (HS) and a low spin (LS) state and is most common in octahedral complexes with a d^4 – d^7

electron configuration. While the vast majority of SCO complexes are d^6 Fe(II) systems,^[2] recent studies have demonstrated that Fe(III) complexes can exhibit equally abrupt and hysteretic SCO behaviour.^[6–8] The Fe(III) complexes have the advantage of being air stable and robust making their implementation in devices more straightforward.

Spin crossover in Fe(III) occurs between a $S = 5/2$ (6A_1) HS state and a $S = 1/2$ (2T_2) LS state and differs from Fe(II) in that both spin states are paramagnetic.^[9–11] This has a profound influence on the change in Fe-ligand bond lengths that occurs upon SCO with values typically between 0.10–0.13 Å compared with ca. 0.20 Å for Fe(II) systems.^[9,12,13] This is important as the smaller change in the bond lengths between the two spin states renders light-activated Fe(III) SCO systems extremely rare since the light-induced HS state can rapidly relax to the LS state. Such optical switching in SCO is termed light-induced excited spin state trapping, or LIESST. The first example of LIESST in an Fe(III) complex was reported in 2000 in $[\text{Fe}(\text{pap})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$.^[14] Subsequent studies have shown that larger changes in the Fe-ligand bond distances and greater distortion of the coordination sphere in the HS state both favour LIESST.^[15–20] It is also apparent that a large thermal hysteresis does not necessarily result in efficient LIESST. While thermal hysteresis results from a collective response due to long-range elastic interactions and the associated energy cost due to the volume change, the structural reorganization of the ligand^[21] is a key factor in the efficiency of LIESST processes in Fe(III) complexes.

Another more recent finding in photoactivated SCO complexes has been the discovery of bidirectional switching from a thermally trapped HS state. This was first reported by Hauser and coworkers in the Fe(II) 2D coordination polymer $\{[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2\}_n$, (bbtr = 1,4-di(1,2,3-triazol-1-yl)butane). This compound is HS down to 10 K but upon irradiation at 830 nm converts to the LS state via reverse-LIESST.^[22] Irradiation at 472 nm then switches the Fe(II) centres back to the HS state. A particularly interesting feature of this type of optical switching is that it occurs between *two infinitely long-lived states*. More recently, the Triki group reported the Hoffmann-type network $[\text{Fe}(\text{trz-py})_2\{\text{Pt}(\text{CN})_4\}]\cdot 3\text{H}_2\text{O}$ (trz-py = 4-(2-pyridyl)-1,2,4-triazole) which exhibits a HS-LS state at low temperature due to the presence of two independent Fe(II) centres in the asymmetric unit.^[23] Irradiation with near-IR light allowed access to the full LS state with the HS-LS state restored with green light, again showing bidirectional switching. The authors were also able to show that warming, and subsequent cooling of the sample reveals a hidden hysteresis of 25 K. In a follow-up paper, the related compound, $[\text{Fe}(\text{3PhOH-trz})_2\{\text{Pt}(\text{CN})_4\}]\cdot 2\text{H}_2\text{O}$ {3PhOH-trz = 4-(3-hydroxy-phenyl)-1,2,4-triazole} was found to be HS even

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at low temperature but optical switching this time revealed a hidden hysteresis of 37 K.^[24] In this work we report the first example of an iron(III) SCO complex to exhibit hidden hysteresis and show that this phenomenon is possible in molecular systems as well as in the coordination polymers previously reported.

The complex was prepared by reacting a solution of the Schiff base ligand, HnaphBzen (1-([2-(benzylamino)ethylimino]methyl)-2-naphthol) with $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ to give $[\text{Fe}(\text{naphBzen})_2]\text{NO}_3$ which was isolated as a dark green solid. Anion exchange with KI gives, after crystallization, $[\text{Fe}(\text{naphBzen})_2]\text{I}$ **1**. Spectroscopic characterization and elemental analysis are consistent with the proposed structure and are included in the ESI (Figure S1).

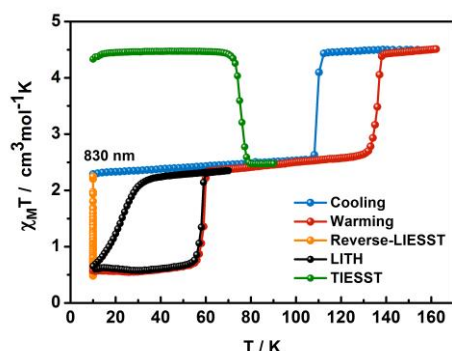


Figure 1. $\Delta M T$ vs. T plot of $[\text{Fe}(\text{naphBzen})_2]\text{I}$ showing the thermal hysteresis (red and blue), the thermal trapping of the HS state, TIESST (green), reverse-LIESST (orange) and LITH (black) curves showing the hidden hysteresis between the [LS-LS] and [HS-LS] states. Measurement recorded in settle mode at a mean temperature scan rate of 0.4 K/mn.

Temperature dependent magnetic studies show that **1** exhibits a reversible 50% spin crossover, with a thermal hysteresis of 25 K with $T_{1/2}(\uparrow) = 135$ K and $T_{1/2}(\downarrow) = 110$ K (Figure 1). SCXRD reveals that $[\text{Fe}(\text{naphBzen})_2]\text{I}$ **1** crystallizes with two $[\text{Fe}(\text{naphBzen})_2]^+$ cations and iodide anions in the asymmetric unit in monoclinic Pc at 100 K and monoclinic Pn at 120 K and 150 K (Table S1 and Figure 2). The SCO is therefore associated with a symmetry change, but since there is no group-subgroup relationship between the two space groups, and they share the same a , b , c lattice parameters, the phase transition is reconstructive^[25] (Figure 3a). In contrast, the network $[\text{Fe}(\text{trzpy})_2\{\text{Pt}(\text{CN})_4\}] \cdot 3\text{H}_2\text{O}$ exhibits an isostructural switching to the [HS-LS] state.^[23] Reconstructive phase transitions are associated with a large structural reorganization modifying the molecular packing and interactions, which implies a cooperative and first-order phase transition. By comparison, $[\text{Fe}(\text{naphEen})_2]\text{I}$ (naphEen = 1-([2-(ethylamino)ethylimino]methyl)-2-naphthol) crystallizes in monoclinic $I2/a$ with a single Fe(III) centre in the asymmetric unit.^[26]

The Fe-ligand bond lengths at the Fe2 centre in **1** at 100 K are consistent with LS Fe(III) while those at the Fe1 centre are HS, giving a [HS-LS] state.^[27–31] Heating the crystals to 150 K results in an increase in the Fe2-O, Fe2-N_{imine} and Fe2-N_{amine} bond distances by 0.05, 0.16 and 0.18 Å, respectively (Table S2). In contrast, the Fe1 bond lengths change very little, which is

unsurprising given that even at 100 K it is HS. Thus, at 120 and 150 K the complex adopts a [HS-HS] state. The octahedral distortion parameters are consistent with the above spin assignments and with $\Delta\Sigma$ ca. 26° it is evident that complete SCO occurs at the Fe2 centre.

A key feature of the structure is that a combination of N-H...I and C-H...I interactions link all the complexes (Figure S2). Notably, the N-H...I contacts at Fe1 and Fe2 are different by 0.13 Å at 100 K, and even at 120 K, when both Fe centres are HS, the difference is still 0.07 Å (Table S3). Consequently, the change in this distance upon HS \rightarrow LS SCO is 0.053 Å (the thermal contraction between 100 K and 120 K is expected to be small). This suggests that the LS state favours shorter N-H...I contacts and that there is an upper limit, beyond which the Fe centre is unlikely to undergo thermal SCO. There is also a difference in the C-H...I interactions with the SCO active Fe2 centre forming two such contacts with neighbouring $[\text{Fe}(\text{naphBzen})_2]^+$ cations while at the Fe1 centre the C-H...I contacts come from aromatic C-Hs of the phenyl rings. Interestingly, the same interactions are found at the HS Fe2 $[\text{Fe}(\text{naphBzen})_2]^+$ cation at 120 and 150 K. This involves a rotation of the phenyl rings evident in the torsion angle, α . The rotation of the phenyl ring is higher around Fe2 than Fe1, which could be linked to the bigger variation of the distortion parameter around Fe2.

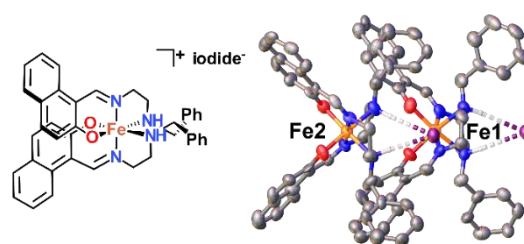


Figure 2. View of the molecular structure and asymmetric unit of **1** at 100 K. All hydrogen atoms, except the amine hydrogens are omitted for clarity.

The overall packing consists of 1D chains of $[\text{Fe}(\text{naphBzen})_2]\text{I}$ which at 100 K contain alternating LS and HS centres (Figure S3). Neighbouring chains are linked via C-H... π contacts and the aforementioned C-H...I interactions to form a 2D sheet on the ab plane with a checkerboard pattern of LS and HS centres at 100 K (Figure 3a). Further C-H... π interactions then link these sheets to create a highly cooperative supramolecular network. The gap between the sheets, coincident with the c -axis, lengthens significantly upon SCO to the full [HS-HS] state by ca. 0.9 Å (Figure S4). It is noteworthy that the packing closely resembles that of the related compound $[\text{Fe}(\text{salEen-Br})_2]\text{ClO}_4$ which exhibits abrupt SCO.^[30] An important difference however, is that in **1** two sub-lattices of independent Fe(III) centres exist in the [HS-HS] phase (HS-Fe1 and HS-Fe2). During the reconstructive phase transition, the molecular packing reorganises to form another set of sub-lattices: one that is HS and one is LS (Figure 3). Moreover, the relative position of the Fe1 and Fe2 networks changes considerably upon SCO with some of the Fe...Fe distances altering by as much as 0.52 Å (Table S4; Figure S5). This difference is all the more remarkable when one considers that the

a- and *b*-axes, which form the edge of the 2D sheets, change by only 0.15–0.22 Å upon SCO.

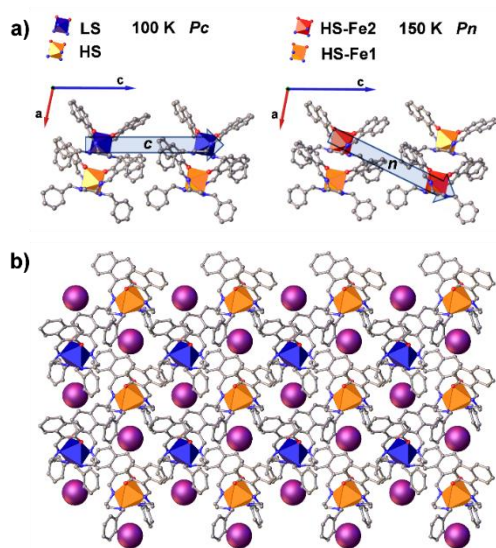


Figure 3. View of a) the reconstructive phase transition involving the Fe1 and Fe2 networks showing the LS and HS sub-lattices at 100 K, equivalent through the *c* glide plane, and the HS-Fe1 and HS-Fe2 sub-lattices at 150 K, related through the *n* glide plane, and b) the 2D sheets (on the *ab* plane) with the iodide shown as a spacefill model.

The reversible 50% SCO with thermal hysteresis in **1** contrasts with the behaviour of $[\text{Fe}(\text{naphEen})_2]\text{I}$, which is LS up to 350 K and confirms that the benzyl group is vital for accessing SCO active systems.^[26] The presence of hysteresis is uncommon and is directly related to the reconstructive nature of the phase transition, associated with the large structural reorganization of the 2D sheets in **1**. An additional indication of high cooperativity is that rapid cooling of **1** results in thermal trapping of the compound in the full HS state. As shown in Figure 1, warming results in relaxation back to the [HS-LS] state with the relaxation temperature $T(\text{TIESST}) = 75$ K (TIESST = temperature-induced excited spin state trapping). Comparatively few iron(III) systems have been reported to exhibit TIESST,^[18,29] and to the best of our knowledge **1** has the highest $T(\text{TIESST})$ known in Fe(III) SCO chemistry.

The photomagnetic properties of crystals of **1** were studied at 10 K and reveal a small increase in χ_{MT} from 2.37 to 2.70 $\text{cm}^3\text{mol}^{-1}\text{K}$ after irradiation at 650 nm, consistent with partial LIESST (Figure S6). The χ_{MT} product remains constant up to 40 K at which point it gradually decreases to a value indicative of the [HS-LS] state at 70 K. The weak photoconversion efficiency of only 15%, could be due to the strong absorption by **1** in the visible region but also the unfavourable rotation of the phenyl ring associated with SCO. Indeed, if the structure of the full photoinduced [HS-HS] phase is similar to the one at high temperature, a large amount of energy would be required to drive the opposite reconstructive phase transition from *Pc* in the [HS-LS] phase to *Pn* in the photoinduced [HS-HS] one. At low

temperature there is probably not enough thermal energy to support these structural reorganizations.

Irradiation of the sample at 830 or 980 nm shows a reverse-LIESST to a full LS state that is not accessible thermally (Figure 1). Re-heating results in an increase in χ_{MT} at $T_{1/2}(\uparrow) = 60$ K to the [HS-LS] state after which it follows the original magnetic profile. Provided that the sample is not heated above 130 K, subsequent cooling produces the [HS-LS] state down to 10 K, leading to an open hysteresis of 60 K. If the same experiment (irradiation at 830 nm at 10 K, followed by warming up to 100 K and cooling down to 10 K) is performed under constant light irradiation, a Light-Induced Thermal Hysteresis, LITH,^[32,33] is observed with a return to the [LS-LS] state at $T_{1/2}(\downarrow) = 30$ K and thus a hysteresis of 30 K. We note that without continuous irradiation the [HS-LS] \rightarrow [LS-LS] conversion is not observed. Indeed, time dependence of χ_{MT} recorded between 10 and 56 K shows no evidence of any relaxation of the [HS-LS] state (Figure S7). This is the first time that *hidden hysteresis* has been observed in an Fe(III) SCO complex. The thermally quenched [HS-HS] state also exhibits reverse-LIESST by exposure to 830 nm light with conversion to the full LS state, but interestingly no evidence of the [HS-LS] state (Figure S8). Subsequent heating follows the previous magnetic profile of **1** generated by reverse-LIESST from the [HS-LS] state. Relaxation kinetics at 54, 56 and 58 K reveal relaxation towards the [HS-LS] state (Figure S7). In this system, 3 competing states may be stable at low temperature, but the global study shows that the true ground state is the [HS-LS] state, whereas the [HS-HS] and [LS-LS] states are competing false ground states.

The temperature dependent Mössbauer spectra consist of two overlapping asymmetric quadrupole doublets in different proportions corresponding to HS and LS Fe(III); Figure S9. The parameters derived from the spectra (Table S5) are comparable to previous related compounds.^[26] The %HS determined from the Mössbauer spectra is lower than expected based on the structural and magnetic studies (Figure S10). One reason may be that iodine is a strong absorber of the 14.4 keV Mössbauer radiation of ^{57}Fe and thus 80 mg of sample was required to obtain spectra (see ESI for further details). Even under these conditions, the spectra required long collection times and they exhibited asymmetric linewidths and absorptions. Moreover, the different Lamb-Mössbauer factors of the HS and LS states may cause the %HS to be underestimated.^[34,35] However, the Mössbauer does confirm a frozen-in HS state at low temperatures (< 60 K) and a thermal hysteresis centred at 120 K, in excellent agreement with the structural and magnetic data.

Photocrystallographic studies were conducted on **1** irradiating at 980 nm with a 10 mW laser at 10 K. While the data are not ideal, due to twinning, the reconstructive phase transition during cooling and weak diffraction, the structural features are clear. The average Fe-N/O bond lengths are 1.96(4) (Fe1) and 1.92(3) Å (Fe2), confirming that both Fe centres are now LS. The basic structural features of the [LS-LS] structure in the *Pc* space group match those described above at higher temperatures. In line with the changes observed between 100 and 120 K, the *a*- and *b*-axes lengthen slightly while the *c*-axis shortens by almost 0.50 Å as a result of SCO at Fe1. However, the relative position of the Fe1 and Fe2 networks changes markedly by between 0.61–0.80 Å compared to the structure at 100 K, and is far larger than that observed upon thermal SCO (Table S3; Figure S5). We also see

rotation of the phenyl rings such that they more closely resemble those found in the [HS-HS] state. The large change in the relative position of the two networks and the concomitant rotation of the phenyl ring may explain why the [LS-LS] state is not thermally accessible.

In conclusion, we have shown that judicious ligand choice not only gives rise to strongly hysteretic SCO but also hidden hysteresis as the result of an extremely rare *reverse-LIESST* process. The two supramolecular networks within the structure facilitate this photomagnetic behaviour moving relative to each other upon SCO, resulting in reorganisation of the C-H...I and weaker C-H... π interactions. The presence of hidden hysteresis in a *molecular* SCO compound suggests that cooperativity is the key factor for observing this behaviour. The results also indicate that the ligand plays a more significant role in Fe(III) SCO systems than those of Fe(II) in determining whether the complex will exhibit LIESST or *reverse-LIESST*. The design elements presented here, flexible groups on the ligand and strong anion-cation interactions, will hopefully serve as a route into more photomagnetically active Fe(III) SCO materials and ultimately functional devices.

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Keywords: spin crossover • hidden hysteresis • photomagnetism • iron(III) complexes • light-induced thermal hysteresis

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Light revealing: Thermal and optical switching in an iron(III) spin crossover complex reveals a hidden hysteresis of 30 K

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