



The atypical hysteresis of $[\text{Fe}(\text{C}_6\text{F}_5\text{Tp})_2]$: Overlay of spincrossovers and symmetry-breaking phase transition

Amina Benchohra, Yanling Li, Lise-Marie Chamoreau, Benoit Baptiste, Erik Elkaim, Nathalie Guillou, David Kreher, Rodrigue Lescouëzec

► To cite this version:

Amina Benchohra, Yanling Li, Lise-Marie Chamoreau, Benoit Baptiste, Erik Elkaim, et al.. The atypical hysteresis of $[\text{Fe}(\text{C}_6\text{F}_5\text{Tp})_2]$: Overlay of spincrossovers and symmetry-breaking phase transition. *Angewandte Chemie International Edition*, 2021, 10.1002/anie.202015994 . hal-03123596

HAL Id: hal-03123596

<https://hal.sorbonne-universite.fr/hal-03123596>

Submitted on 28 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The atypical hysteresis of $[\text{Fe}(\text{C}_6\text{F}_5\text{Tp})_2]$: Overlay of spin-crossovers and symmetry-breaking phase transition.

Amina Benchohra,^[a] Yanling Li,^[a] Lise-Marie Chamoreau,^[a] Benoit Baptiste,^[b] Erik Elkaïm^[c]
Nathalie Guillou^{[d]*} David Kreher,^{[a]*} Rodrigue Lescouëzec^{[a]*}

Abstract. The $[\text{Fe}^{\text{II}}(\text{C}_6\text{F}_5\text{Tp})_2]$ spin-crossover complex is an atypical molecular switch, which can be converted upon annealing between two archetypal spin-crossover behaviours: from an extremely gradual spin-crossover to a broad hysteretic spin-transition (of ca. 65 K). The hysteresis shows an uncommon “rounded shape” that is reproducible upon cycling temperature. In depth structural studies reveal a first crystal phase transition, which occurs upon melting and recrystallizing at high temperature. This first irreversible transition is associated with a radical change in the crystal packing. More importantly, the “rounded and broad” hysteretic transition is shown to occur in a non-cooperative SCO system and is associated with the occurrence of a symmetry-breaking phase transition that appears when roughly ca. 50% of the SCO complexes are switched.

Spin-crossover (SCO) complexes represent a prominent class of molecular switches,^[1] which can be reversibly converted between two distinct electronic configurations, a high-spin (HS) state and a low-spin (LS) state, by various stimuli such as light, temperature, pressure, electric and magnetic fields.^[2] This spin-state change can lead to drastic changes in the magnetic, optical, dielectric or mechanical properties, making these SCO complexes very interesting for the design of advanced materials.^[3–5] The spin-state switching is also attractive for the development of molecule-based electronic or spintronic devices.^[6–10] In this context, light, neutral and sublimable $\text{Fe}(\text{II})$ SCO complexes are particularly investigated because they can be easily deposited onto surfaces through high-vacuum evaporation techniques.^[11–13] In the solid-state, the spin crossover phenomenon can manifest itself in different manners depending on the interaction between the neighboring SCO units. It can be gradual when there is no (or weak) intermolecular coupling or abrupt, when efficient elastic interactions between SCO centers lead to cooperative Spin Transitions (ST).^[14] For strongly cooperative systems hysteresis can occur. These transitions are of particular interest for information storage or sensing applications.^[15,16] A possible synthetic strategy to increase the cooperativity consists in linking SCO centers through rigid bridging ligands or inorganic connectors.^[7,15,17] Alternatively one can rely on supramolecular

interactions (such as H-bondings) and electrostatic interactions that can be responsible for the large hysteresis observed in some monometallic species.^[18–20] It should be noted that hysteresis can be associated with a symmetry-breaking structural phase transition (SPT). It is believed that local distortion during the spin-state change promotes displacement or motions in the SCO complexes. These motions would then propagate via intermolecular interactions through the crystal lattice giving rise to the concomitant structural phase transition. However, one cannot exclude that structural phase transition may also trigger the abrupt spin-transition.^[21] In all cases, the supramolecular framework and the topology of the crystal packing are recognized to play a major role in the ST shape. The studies on polymorphs offer a unique way to enlighten the impact of the crystal packing on the transition profile.^[22,23] The significant impact of polymorphism on SCO properties was mainly highlighted with polymorphs achieved by solution-mediated phase transitions (obtained from regular bench conditions).^[24] In contrast, polymorph examples resulting from thermally initiated phase transformations are scarce. For example, recent reinvestigations of old SCO materials showed that an annealing could lead to new phases. Salmon *et al.* who reexamined the $[\text{Fe}^{\text{II}}(\text{Tp})_2]$ (Tp = hydrottris(pyrazolyl)borate) SCO properties, demonstrated that by heating the sample near its sublimation temperature it was possible to irreversibly transform a tetragonal polymorph (a kinetic phase) into a monoclinic one (a thermodynamic phase).^[25] In that case, the conversion leads to a shift of the transition temperature and a moderate change of the SCO profile, where both phases show a gradual transition with no hysteresis. A similar phenomenon was later observed for the related $[\text{Fe}^{\text{II}}(\text{Tp}')_2]$ complex.^[26] In this context, we decided to conduct high-temperature investigations of the neutral $[\text{Fe}^{\text{II}}(\text{C}_6\text{F}_5\text{Tp})_2]$ SCO complex ($\text{C}_6\text{F}_5\text{Tp}$ = pentafluorophenyl tris(pyrazol-1-yl)borate ligand). Herein, we detail the surprising effect of a high temperature treatment on $[\text{Fe}^{\text{II}}(\text{C}_6\text{F}_5\text{Tp})_2]$ crystals: a radical change in the crystal packing that is accompanied by an unprecedented changeover of the SCO properties, from a very gradual spin-equilibrium to one of the broadest hysteretic transition found in monometallic SCO complexes. Moreover, further in-depth single crystal and powder diffraction studies revealed the origins of the unprecedented “gradual and rounded” hysteresis loop observed after thermal treatment.

The synthesis of the $[\text{Fe}^{\text{II}}(\text{C}_6\text{F}_5\text{Tp})_2]$ complex was first reported by Wagner *et al.* together with its X-ray structure obtained from crystals grown at room temperature. However, the magnetic properties of this triclinic phase (noted phase 1) were not investigated.^[27] We will first describe the magnetic properties of phase 1 (kinetic phase) and then those of the new phase obtained after thermal treatment: the phase 2 (thermodynamic phase) that otherwise undergoes a reversible structural phase transition between 2-LT and 2-HT. The $\chi_M T$ versus T curve of 1 (χ_M is the molar magnetic susceptibility) is shown in figure 1. The $\chi_M T$ measured at 300 K, ca. $0.06 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, indicates the occurrence of a low-spin $\text{Fe}(\text{II})$ state ($S = 0$). This agrees with

[a] A. Benchohra, Y. Li, L.-M. Chamoreau, D. Kreher, R. Lescouëzec
Institut Parisien de Chimie Moléculaire, CNRS UMR 8232
Sorbonne Université

4 place Jussieu F-75252 Paris cedex 5

E-mail: Rodrigue.lescouezec@sorbonne-universite.fr

[b] B. Baptiste
Institut de Mineralogie, de Physique des Matériaux et de
Cosmochimie (IMPMC), Sorbonne Université, UMR 7590 CNRS,
UMR 206 IRD, Muséum National d'Histoire Naturelle MNHN, 4
place Jussieu, F-75252 Paris cedex 5

[c] E. Elkaïm,
Synchrotron Soleil, L'Orme des Merisiers, Saint-Aubin - BP 48
91192 Gif-sur-Yvette CEDEX

[d] N. Guillou
Université Paris-Saclay, UVSQ, Institut Lavoisier de Versailles,
CNRS UMR 8180, 45 Avenue des Etats-Unis 78035, Versailles.

the crystal data obtained at the same temperature (table 1), that show, metal-ligand distances typical of low-spin Fe(II) (as observed in $[\text{Fe}^{\text{II}}(\text{Tp})_2]$) for the two Fe crystal sites that are present in phase 1.^[25] Upon heating, the $\chi_M T$ product increases over a remarkably broad temperature range (ca. 200 K), reaching $3.56 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 500 K. This value agrees with that expected for a complete spin-crossover, the expected $\chi_M T$ being ca. $3.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ($S = 2$, $g = 2.2$). The gradual conversion is also coherent with the absence of significant supramolecular interactions in 1. The weak $\text{CH}\cdots\pi$ and $\text{CF}\cdots\pi$ interactions observed are detailed in the supporting information (SI). In order to better understand the broad SCO curve, the crystal structure was recorded at 430 K, a temperature corresponding approximately to the half spin-state conversion. Interestingly, the structural data show that the two crystallographic sites, Fe1 and Fe2, exhibit different spin states, with metal-ligand distances and distortion values that are typical of low-spin and high-spin environment, respectively.^[25] As previously reported for similar bis-scorpionate Fe(II) complexes, the spin-state change is also reflected in the FeN-NB and FeN-NC torsion angles, which typically show larger distortion in the HS state (table 1).^[22,28] In summary, the overall spin-crossover in phase 1 is better described as two consecutive gradual spin-crossovers. The spin-crossover which occurs at lower temperature on the site 1 in comparison to the site 2, might be correlated to a weaker ligand field induced by a higher distortion as reflected by the distortion parameter, Σ , measured at 300 K (table1).

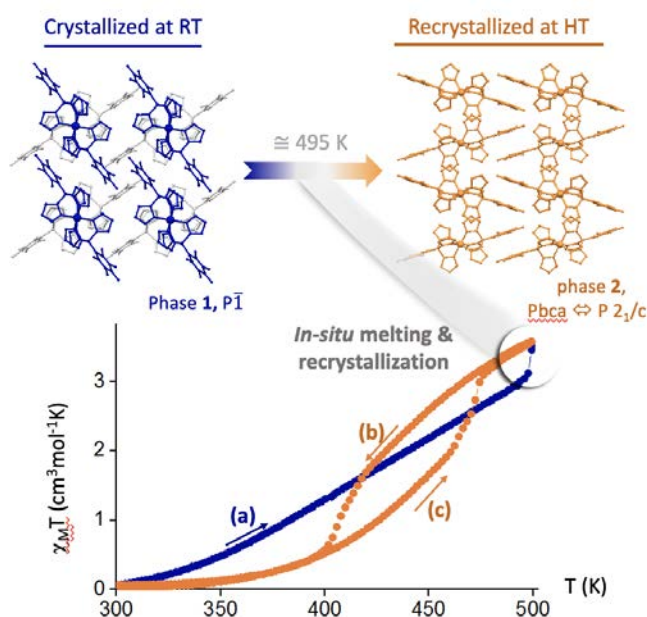


Figure 1. (top) Perspective view of the crystal packing in the phases crystallized at room temperature and high temperature (bottom). The CCDC numbers can be found in the Supporting Information. Magnetic properties of both materials, before heating up to 500 K (blue) and after melting and recrystallizing in the magnetometer (orange).

A closer look at the $\chi_M T$ vs T curve of phase 1 reveals an anomaly at high temperature, namely a sudden increase from 3.10 to $3.56 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ between 495 and 500 K . This change is associated with the melting of phase 1, which was detected at ca. 493 K at ambient pressure. It is worth noting that the FT-IR and NMR solution spectra of the sample heated to 500 K (in the

magnetometer or in the DSC apparatus) are identical to those of the fresh material (SI). Therefore, the change in the magnetic behavior is not associated with a chemical reaction but with a phase transition as confirmed by the structural study (see below). The heating up to 500 K induces an irreversible change in the magnetic behavior: the new phase (phase 2) exhibits a transition with a pronounced sigmoidal shape and displays a reversible and remarkably broad and rounded hysteresis loop of 65 K width at the widest points (at scan rate of 2 K/min). The profile of the spin transition is very uncommon. For both heating or cooling ramp, it could be described as a gradual SCO behaviour, which seems to be accelerated from threshold temperatures. These threshold temperatures roughly correspond to temperature at which half of the complexes have undergone a spin-state change. In fact, the examination of the $d(\chi_M T)/dT$ curve (see SI) shows two maxima upon each thermal ramp, reflecting spin-conversion discontinuities. For instance, upon the second heating ramp, a first inflection point is measured at $T = 461 \text{ K}$ and a second one at $T = 472 \text{ K}$. The height and the broadness of the hysteresis slightly vary with the experimental conditions (see SI) but it is always reproducible and it only appears after heating up to 500 K .

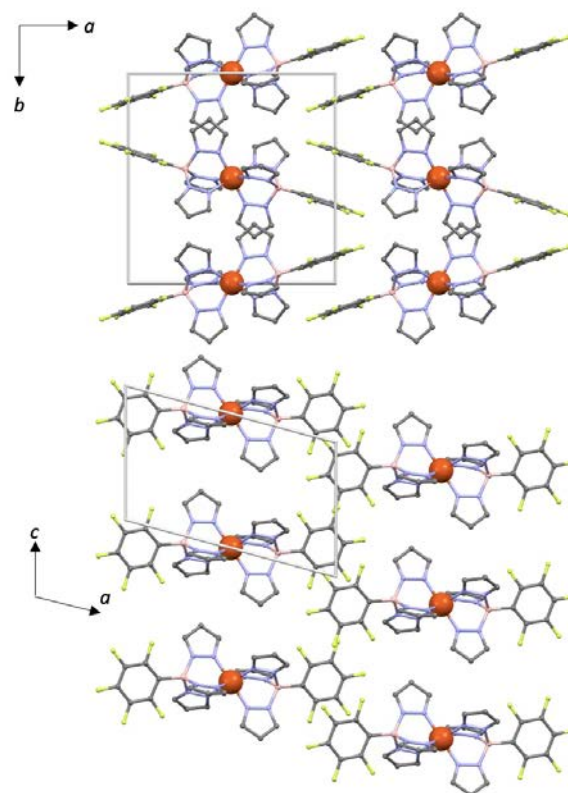


Figure 2. Perspective view of phase 2-LT phase along the c (top) and the b (bottom) axes.

In order to shed light on the unusual behavior of the $[\text{Fe}^{\text{II}}(\text{C}_6\text{F}_5\text{Tp})_2]$ complex, various single-crystal and powder X-ray diffraction experiments were carried out. First of all, we measured several crystals of the phase 1 upon heating. As mentioned above, a crystal structure of the phase 1 was obtained at 430 K . Beyond this temperature, the quality of the crystal data decreases and measurements above 490 K showed that the colorless crystals (in the high-spin state) shrink and melt. Therefore, we could not follow the phase transition *in-situ*. Nonetheless, we managed to study single crystals of the new phase obtained after the melting of

phase **1** and recrystallization. Despite their poor crystallinity, a satisfactory structural model was obtained through XRD analysis

diffraction patterns recorded in the 298-503 K range are depicted in Figure 3. First, the data obtained at room temperature display

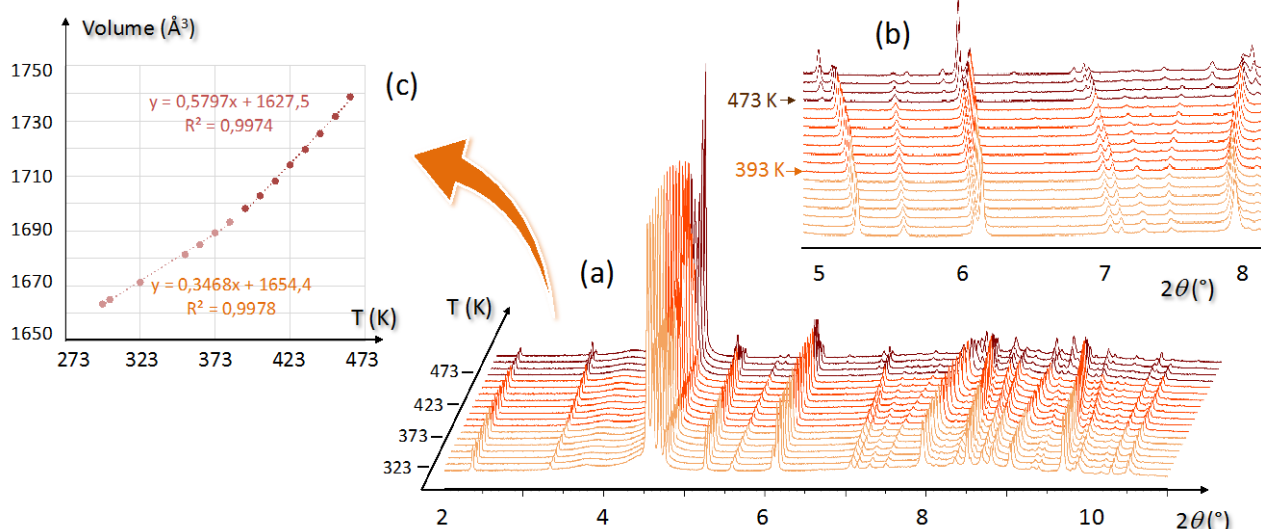


Figure 3. $[\text{Fe}^{\text{II}}(\text{C}_6\text{F}_5\text{Tp})_2]$ (phase 2, obtained from melting of phase 1) (a) Thermal evolution of diffractograms in the 298 - 503 K range ($\lambda = 0.57039 \text{ \AA}$); (b) zoom in the 2θ range 4.8 - 8.15 ° is shown in inset; (c) Temperature dependence of the unit cell volume of the 2-LT phase in the range 298 - 473 K.

using synchrotron radiation (SI). The structure of this new phase was measured at low-temperature (100 K) and is noted from now **2-LT**. Two observations can be made on its crystal structure. Firstly, the approximate Fe-N distances (1.97 Å) and the distortion of the coordination sphere ($\Sigma = 28.5^\circ$) measured at low temperature agrees with a low-spin state, coherently with the magnetic measurements. Secondly, the supramolecular arrangement of the complexes in the **2-LT** crystal structure is completely reorganized in comparison with that of **1** (Figure 1).

Table 1. Selected Structural Data of phase 1

T / K	Fe-N (Range)		Σ (Fe)		FeN-NB (average value)		FeN-NC (average value)	
	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2
300	1.952(3) 1.981(3)	1.966(3) 2.001(3)	22.0	28.2	2.8	2.6	170.3	168.2
430	1.967(4) 1.997(4)	2.080(4) 2.131(4)	28.9	56.6	3.6	5.6	169.4	165.3
490	1.99(1) 2.057(9)	2.106(9) 2.14(1)	38.0	72.6	4.8	7.9	168.3	164.0

Angles (°) Distance (Å); Σ : sum of the deviation of the twelve pseudo-orthogonal angles of the Fe coordination sphere.

Views along *b* and *c* axes show an alternation of layers of $\{\text{Fe}^{\text{II}}(\text{Tp})_2\}$ core complexes and pentafluorophenyl groups (Figure 2). A close examination of the crystal packing did not reveal a significant enhancement of supramolecular interactions (see details in SI). Only very weak C-F \cdots H, C-H \cdots π and C-F \cdots π interactions^[29] are observed, with distances that are similar or even longer than those measured in phase **1**. From these observations, we can conclude that the observed hysteresis does not arise from a strong cooperativity that would be mediated by the supramolecular interaction. Besides this experiment, several attempts were made to follow structural changes of this new phase by SC-XRD. However, the crystalline quality decreased upon heating preventing a reliable collection of data.

In order to overcome this problem, we then carried out powder X-ray diffraction experiments on the sample recovered from DSC measurement after heating up **1** to 500 K. Satisfactory diffraction data were obtained by using synchrotron radiation. The powder

sharp peaks, which match well with those calculated from the crystal structure of **2-LT** phase. Then, in order to understand its thermal behavior, Rietveld refinements of all the powder patterns recorded up to 503 K were carried out. The model of **2-LT** phase determined from single crystal data was used as a starting point, treating the organic ligand as rigid body (see SI). Upon heating up to 383 K, the peaks remain thin and undergo some small shifts toward lower 2θ values, which is characteristic for thermal expansion (inset Fig.3). From 393 K, the unit cell parameters show a different evolution, not simply due to the thermal effect but coherent with the occurrence of a gradual SCO (see SI), as seen in the $\chi_M T$ vs *T* curve. Although the standard deviations on the Fe-N distances are quite high, it seems that the average Fe-N distances tend to increase, which is also consistent with a spin-state change from LS Fe(II) to HS Fe(II) (SI). Then, nearby 473 K, the occurrence of a structural phase transition is evidenced (insert Fig.3, details in SI). This is revealed by the appearance of new peaks on the powder patterns, whose intensity increases with rising temperature, while a decrease of the peaks ascribed to the **2-LT** phase is concomitantly observed. The conversion from **2-LT** to the high-temperature phase, **2-HT**, is not complete at 503 K, as peaks of both phases coexist. Since the compound starts decomposing at higher temperature, it was not possible to obtain a pure **2-HT** phase by further heating. Nevertheless, indexing of the **2-HT** phase was made possible by excluding the diffraction peaks attributed to the **2-LT** phase, which have been identified by a careful analysis of the thermal dependence of **2-LT** unit cell parameters above 473 K. This analysis allows converging to an orthorhombic unit cell (space group *Pbca*), with a doubling of the *a* parameter compared to the monoclinic **2-LT** one (and a doubling of the unit cell volume). The structural determination of the **2-HT** phase was then undertaken by using the simulated annealing approach, considering ($\text{C}_6\text{F}_5\text{Tp}$) as a rigid body, the scattering contribution of the **2-LT** phase being calculated together by the Rietveld method analysis. In the 473-503 K range, structural models of both phases were refined. The final Rietveld plots correspond to satisfactory model indicators and profile factors (see SI). The quantitative analysis deduced from the Rietveld refinements led to the following **2-LT/2-HT** ratios (%): 93(2)/7(2)

at 473 K, 74(2)/26(2) at 483 K, 46(2)/54(2) at 493 K and finally, 29(1)/71(1) at 503 K. The conversion from **2-LT** ($P2_1/c$) to **2-HT** ($Pbca$) is associated with a slight rotation of the F_6C_5 groups, together with an increase of the intermolecular Fe-Fe distances as a likely effect of the Fe-N lengthening. In summary, the powder X-ray study supports the occurrence of a gradual nature of the spin conversion in the **2-LT** phase, as observed by magnetometry below 470 K. Above that temperature, the material undergoes a phase transition to the higher symmetry **2-HT** phase. This phase transition is reflected in the magnetic curve by the sudden increase of the $\chi_M T$ product near 473 K. The **2-HT** phase also shows a gradual spin-crossover and converts back to the **2-LT** near 410 K, which leads to the very unusual “round-shaped” hysteresis. The calorimetry experiments are fully consistent with the observations made in magnetometry and crystallography. The differential scanning calorimetry (DSC) measurements performed on crystalline samples (2K/min) of phase **1** do not show endothermic peaks during the first heating ramp from 300 to 497 K (see SI). This agrees with the occurrence of a large gradual spin-crossover. A series of sharp endothermic peaks associated with the fusion of the crystallites (also observed during the XRD experiments) is then observed above 496 K. Similarly to the magnetic measurements, a new behavior is observed after heating to 500 K. Exothermic and endothermic signals are observed at 405 and 468 K, respectively. These temperatures match well with those corresponding to the sudden changes in the $\chi_M T$ curves in phase **2** (in other words **2-HT/2-LT**) (see $d(\chi_M T)/dT$ curve, SI) and support the occurrence of abrupt phase transition between **2-HT** and **2-LT**.

In conclusion, we showed that $[Fe^{II}(C_6F_5Tp)_2]$ SCO complex undergoes a first crystalline phase transition after a high-temperature melting and recrystallization from phase **1** to phase **2-HT**. This irreversible transition leads to a profound reorganization of the crystal packing and a radical change in the SCO profile: from an extended spin-equilibrium to a broad and ‘rounded’ hysteresis. Despite this change, the spin-state change remains essentially non-cooperative, in agreement with the absence of significant intermolecular interactions. In fact, we demonstrated that the hysteresis opening results from a second reversible abrupt structural transition occurring between two phases which both show gradual spin transition at different temperatures. The structural phase transition is accompanied by a more abrupt spin-state change and it occurs when roughly over 50% of the SCO complexes underwent the gradual spin-state change. Upon cooling, the process seems perfectly symmetrical. Overall, these observations suggest that the molecular volume change that accompanied the gradual spin-state change would trigger the abrupt structural phase change once a threshold spin-conversion ratio is achieved. To our knowledge such interplay between gradual SCO and a symmetry-breaking transition is rare.^[30] The present phenomenon contrasts with the much well known “rectangle-like” hysteretic spin-transitions, generally associated to strong cooperativity, where both structural changes and spin-state change occur concomitantly in a sharp temperature range. Overall, this result provides a new example of the wealth and complexity of the spin-crossover behaviors.

Acknowledgements

In the framework of the CNRS RÉCIPROCS network, this work has been accepted for synchrotron beamtime by the Soleil

scientific proposal committee (BAG proposals 20171078 and 20180913). The authors would like to thank Erik Elkaïm and Pierre Fertey for their help on CRISTAL beamline at SOLEIL and Kamel Boukheddaden for the useful discussions.

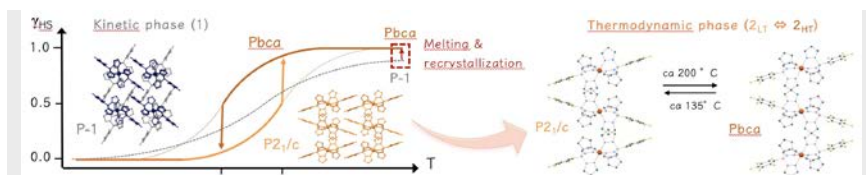
Funding

This work has been funded by the LabEx michem, by the CNRS and the Ministère de l'Education et de la Recherche.

- [1] B. L. Feringa, Ed., *Molecular Switches*, Wiley-VCH-Verl, Weinheim, **2011**.
- [2] M. A. Halcrow, Ed., *Spin-Crossover Materials: Properties and Applications*, Wiley, Chichester, **2013**.
- [3] Y.-S. Koo, J. R. Galán-Mascarós, *Advanced Materials* **2014**, *26*, 6785–6789.
- [4] G. Molnár, S. Rat, L. Salmon, W. Nicolazzi, A. Bousseksou, *Advanced Materials* **2018**, *30*, 1703862.
- [5] F. Valverde-Muñoz, M. Seredyuk, M. C. Muñoz, G. Molnár, Y. S. Bibik, J. A. Real, *Angew. Chem.* **2020**, *132*, 18791–18797.
- [6] K. Senthil Kumar, M. Ruben, *Coordination Chemistry Reviews* **2017**, *346*, 176–205.
- [7] J. Dugay, M. Aarts, M. Giménez-Marqués, T. Kozlova, H. W. Zandbergen, E. Coronado, H. S. J. van der Zant, *Nano Letters* **2017**, *17*, 186–193.
- [8] A. C. Aragonès, D. Aravena, J. I. Cerdá, Z. Acís-Castillo, H. Li, J. A. Real, F. Sanz, J. Hihath, E. Ruiz, I. Díez-Pérez, *Nano Letters* **2016**, *16*, 218–226.
- [9] T. Miyamachi, M. Gruber, V. Davesne, M. Bowen, S. Boukari, L. Joly, F. Scheurer, G. Rogez, T. K. Yamada, P. Ohresser, E. Beaurepaire, W. Wulfhekel, *Nature Communications* **2012**, *3*, DOI 10.1038/ncomms1940.
- [10] F. Prins, M. Monrabal-Capilla, E. A. Osorio, E. Coronado, H. S. J. van der Zant, *Advanced Materials* **2011**, *23*, 1545–1549.
- [11] X. Zhang, P. S. Costa, J. Hooper, D. P. Miller, A. T. N'Diaye, S. Beniwal, X. Jiang, Y. Yin, P. Rosa, L. Routaboul, M. Gonidec, L. Poggini, P. Braunstein, B. Doudin, X. Xu, A. Enders, E. Zurek, P. A. Dowben, *Advanced Materials* **2017**, *29*, 1702257.
- [12] M. Gruber, T. Miyamachi, V. Davesne, M. Bowen, S. Boukari, W. Wulfhekel, M. Alouani, E. Beaurepaire, *The Journal of Chemical Physics* **2017**, *146*, 092312.
- [13] C. Lefter, S. Rat, J. S. Costa, M. D. Manrique-Juárez, C. M. Quintero, L. Salmon, I. Séguy, T. Leichle, L. Nicu, P. Demont, A. Rotaru, G. Molnár, A. Bousseksou, *Advanced Materials* **2016**, *28*, 7508–7514.
- [14] K. Boukheddaden, S. Miyashita, M. Nishino, *Physical Review B* **2007**, *75*, DOI 10.1103/PhysRevB.75.094112.
- [15] O. Kahn, *Science* **1998**, *279*, 44–48.
- [16] M. Ohba, K. Yoneda, G. Agustí, M. C. Muñoz, A. B. Gaspar, J. A. Real, M. Yamasaki, H. Ando, Y. Nakao, S. Sakaki, S. Kitagawa, *Angewandte Chemie International Edition* **2009**, *48*, 4767–4771.
- [17] J. A. Real, A. B. Gaspar, V. Niel, M. C. Muñoz, *Coordination Chemistry Reviews* **2003**, *236*, 121–141.
- [18] J.-F. Létard, P. Guionneau, E. Codjovi, O. Lavastre, G. Bravic, D. Chasseau, O. Kahn, *J. Am. Chem. Soc.* **1997**, *119*, 10861–10862.
- [19] B. Weber, W. Bauer, J. Obel, *Angewandte Chemie International Edition* **2008**, *47*, 10098–10101.
- [20] M. Kepenekian, B. Le Guennic, V. Robert, *J. Am. Chem. Soc.* **2009**, *131*, 11498–11502.
- [21] M. Shatruk, H. Phan, B. A. Chrisostomo, A. Suleimenova, *Coordination Chemistry Reviews* **2015**, *289–290*, 62–73.
- [22] D. L. Reger, J. R. Gardinier, M. D. Smith, A. M. Shahin, G. J. Long, L. Rebhoun, F. Grandjean, *Inorg. Chem.* **2005**, *44*, 1852–1866.
- [23] S. Vela, H. Paulsen, *Inorg. Chem.* **2018**, *57*, 9478–9488.

-
- [24] J. Tao, R.-J. Wei, R.-B. Huang, L.-S. Zheng, *Chem. Soc. Rev.* **2012**, *41*, 703–737.
- [25] L. Salmon, G. Molnár, S. Cobo, P. Oulié, M. Etienne, T. Mahfoud, P. Demont, A. Eguchi, H. Watanabe, K. Tanaka, A. Bousseksou, *New Journal of Chemistry* **2009**, *33*, 1283.
- [26] O. Iasco, M.-L. Boillot, A. Bellec, R. Guillot, E. Rivière, S. Mazerat, S. Nowak, D. Morineau, A. Brosseau, F. Miserque, V. Repain, T. Mallah, *J. Mater. Chem. C* **2017**, *5*, 11067–11075.
- [27] H. Vitze, M. Bolte, H.-W. Lerner, M. Wagner, *European Journal of Inorganic Chemistry* **2016**, *2016*, 2443–2454.
- [28] D. L. Reger, J. R. Gardinier, W. R. Gemmill, M. D. Smith, A. M. Shahin, G. J. Long, L. Rebbouh, F. Grandjean, *J. Am. Chem. Soc.* **2005**, *127*, 2303–2316.
- [29] K. Reichenbacher, H. I. Süss, J. Hulliger, *Chem. Soc. Rev.* **2005**, *34*, 22–30.
- [30] A. Lennartson, A. D. Bond, S. Piligkos, C. J. McKenzie, *Angew. Chem. Int. Ed.* **2012**, *51*, 11049–11052.

COMMUNICATION



A. Benchohra, Y. Li, L.-M. Chamoreau, B. Baptiste, E. Elkaïm, N. Guillou*, D. Kreher,*, R. Lescouëzec*

Page No. – Page No.

The atypical hysteresis of [Fe(C₆F₅Tp)₂] : Overlay of spin-crossovers and symmetry-breaking phase transition

A rounded switch: The [Fe^{II}(C₆F₅Tp)₂] complex is converted through melting from a crystal phase showing a very gradual spin-crossover to another one showing a broad hysteretic spin-transition. The uncommon “rounded” hysteresis occurs in a non-cooperative SCO system. It is due to a symmetry-breaking phase transition that is triggered when roughly ca. 50% of the SCO complexes are switched.