

Multiresponsive Spin Crossover Driven by Rotation of Tetraphenylborate Anion in an Iron(III) Complex

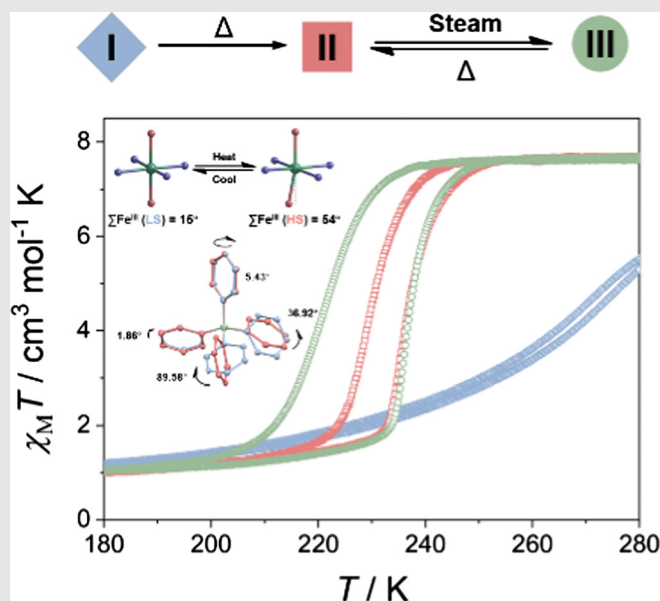
Si-Guo Wu^{1†}, Md. Najbul Hoque^{1†}, Jie-Yu Zheng¹, Guo-Zhang Huang¹, Nguyen Vu Ha Anh², Liviu Ungur², Wei-Xiong Zhang¹, Zhao-Ping Ni^{1*} & Ming-Liang Tong^{1*}

¹Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, ²Department of Chemistry, National University of Singapore, Singapore 117543.

*Corresponding author(s): nizhp@mail.sysu.edu.cn; tongml@mail.sysu.edu.cn; [†]These authors contributed equally to this work.

Cite this: *CCS Chem.* **2020**, 2, 453–459

Dynamic molecular materials, which involve mechanical motions in crystals, usually exhibit tunable properties related to conformational polymorphs. Herein, we describe a solvent-free molecular crystal [$\{\text{Fe}^{\text{III}}(\text{salten})\}_2(\text{TPB})\}(\text{BPh}_4)_2$ (I) developed by associating the rotatable tetraphenylborate anion with the spin crossover (SCO) binuclear iron(III) cation. The solvent-free phase I can undergo a temperature-induced phase transformation to phase II, during which rotation of the BPh_4^- anion interplays with the SCO component, giving rise to fascinating variations in SCO (from gradual to abrupt) and dielectric properties. Most importantly, an unexpected polymorphic transformation from II to III or IV, with increasing magnetic hysteresis, is realized by exposing II to water or ethanol vapor; the transition is reversible by heating. This rare successive transformation is further rationalized by theoretical calculations. Hence, this multiresponse system provides a new way for modulating synergistic effects and designing dynamic SCO materials by integrating intramolecular motions in the crystal lattice.



Keywords: intramolecular motion, iron(III), spin crossover, polymorph, single-crystal-to-single-crystal transformation

Introduction

Spin crossover (SCO) materials exhibiting bistable spin states are conceivable candidates for magneto-memory devices and molecular switches.^{1,2} The magnetic bistability of high-spin (HS) and low-spin (LS) states can be modulated by external stimuli such as temperature, light irradiation, or pressure, in a detectable and reversible way.^{3–6} Yet, the spin transition dynamics strongly depend on the cooperativity among spin centers. For a weak synergetic effect, the thermal SCO process can be gradual or incomplete.⁷ Once the cooperativity exceeds a threshold value, an abrupt or hysteretic spin transition can be observed. Indeed, a hysteretic event is essential for binary switching applications since the encoded information can be easily written in or read out through different electronic states. Extensive research efforts have been dedicated to promoting the SCO cooperativity through a supramolecular strategy⁸ via enhancing intermolecular interactions (e.g., hydrogen bonding^{9,10} and π - π stacking^{11,12}) or a polymeric strategy^{13–15} via introducing covalent linkages between spin centers. However, the modulation of the characteristics of SCO usually remains ineffective due to the weak perturbation of metal sites and the inadequate propagation of synergy in the lattice.

Integrating intramolecular motions, especially those that cooperate with the SCO moiety, is a judicious approach to regulate the synergism. The material undergoes single-crystal-to-single-crystal (SCSC) transformation, affording an ideal platform for the exploration of structure-property relationships. Then, the comprehension of structural factors contributing to spin transitions can aid the design of high-performance SCO materials.

Moreover, reversible motions such as the generation/breakage of chemical bonds^{16–18} and intramolecular rotation/flipping¹⁹ are collectively accompanied by conformational isomerization,²⁰ and significantly affect material properties, not to mention the SCO behavior. Herein, by introducing the tetraphenylborate anion as the rotary element, we report a solvent-free binuclear iron(III) complex $[\{\text{Fe}^{\text{III}}(\text{salten})\}_2(\text{TPB})](\text{BPh}_4)_2$ [**I**, TPB = 1,2,4,5-tetra(4-pyridyl) benzene, H_2salten = *N,N'*-bis[2-hydroxyphenyl]methylene-4-azaheptane-1,7-diamine] (Figure 1). Intriguingly, complex **I**, isolated as a kinetic product, can convert to the related thermodynamically stable phase (**II**) by heating. This irreversible phase transition, accompanied by remarkable phenyl rotations of the BPh_4^- anion, associates with dramatic changes in SCO and dielectric properties. Moreover, after exposing **II** to water or ethanol vapor, polymorphic transformations to **III** or **IV** are observed, which exhibit wider thermal hysteresis loops. The solvent-free phases **III** and **IV** can revert to **II** by heating.

Results and Discussion

Complex **I** was synthesized via self-assembly of the precursor $\text{Fe}(\text{salten})\text{Cl}$ and TPB ligand in the presence of BPh_4^- anion. More experimental details and characterizations are available in [Supporting Information](#). Thermogravimetric analysis (TGA) indicates that **I** is solvent-free and maintains thermal stability until 450 K ([Supporting Information Figure S2](#)). Differential scanning calorimetry (DSC) data show a pair of weak exothermic/endothermic peaks around 270 K during cooling/heating, with a small enthalpy change ($\Delta H = 2 \text{ kJ mol}^{-1}$). Unexpectedly, after holding **I** at 380 K for 2 h, the DSC peaks shift to 229 and

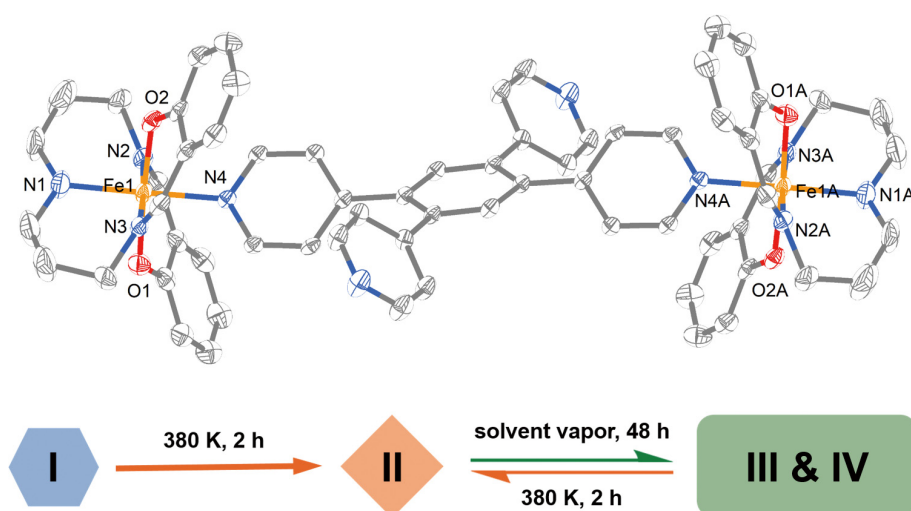


Figure 1 | The moiety $[\{\text{Fe}^{\text{III}}(\text{salten})\}_2(\text{TPB})]^{2+}$ (top) and the schematic single-crystal-to-single-crystal (SCSC) transformation pathways (bottom). Hydrogen and anions are omitted for clarity. Color code: gray (C), blue (N), red (O), and orange (Fe^{III}).

233 K with prominent enthalpy change ($\Delta H = 13 \text{ kJ mol}^{-1}$), suggesting the formation of a new phase **II** via a thermal-induced phase transition (Supporting Information Figure S3).²¹

To better understand the aforementioned phase transition, in situ variable-temperature single-crystal X-ray diffraction measurements were carried out. **I** crystallizes in the triclinic $P\bar{1}$ space group, consisting of a binuclear [$\{\text{Fe}^{\text{III}}(\text{salten})\}_2(\text{TPB})\}^{2+}$ cation and two BPh_4^- anions (Figure 1 and Supporting Information Table S1). The asymmetric unit cell only contains half of the binuclear molecule. Two $\text{Fe}(\text{salten})^+$ moieties are linked by a TPB ligand in *trans* geometry, which can be related to each other via an inversion at the center of TPB. The $\text{Fe}(\text{III})$ center adopts a distorted octahedral geometry, with three nitrogen atoms and two oxygen atoms from the pentadentate salten^{2-} ligand and one nitrogen atom from the TPB ligand. The salten^{2-} ligand shows twofold disorder relative to temperature, wherein the occupancy ratio of configurations A:B changes from 66:34 at 120 K to 60:40 at 298 K. In configuration A, the secondary amine group (N1) from salten^{2-} ligand interacts with phenyl ring from BPh_4^- anion, giving the $\text{N1-H1A}\cdots\pi_{(\text{C40-C45})}$ distance

of 3.3568(1) Å at 120 K and 3.4965(2) Å at 298 K (Figure 2c). Meanwhile, the $\text{C-H}\cdots\pi_{(\text{C15-C20})}$ interactions are formed between the alkyl chain from the salten^{2-} ligand and the phenyl ring from the neighboring cation (Supporting Information Table S6). In contrast, the N1 atom and aliphatic chain in configuration B are involved in the $\text{N1-H1B}\cdots\pi_{(\text{C15-C20})}$ and $\text{C-H}\cdots\pi_{(\text{C40-C45})}$ interactions, respectively. When the two structures at 120 and 298 K (Supporting Information Figure S9) are compared by the overlay, it can be observed that the cation moiety does not change much. The most obvious difference is in the bond length related to $\text{Fe}(\text{III})$ ion. The average bond lengths of Fe-N and Fe-O are 1.984(2) and 1.878(2) Å at 120 K, while 2.105(4) and 1.909(3) Å at 298 K, indicating the occurrence of a spin transition. For the BPh_4^- anion, rotational motions of phenyl rings are revealed through structural comparison. The largest rotation occurs in the C34–C39 phenyl ring with a rotation angle of 36.72° , which results in subtle modulation of $\text{C-H}\cdots\pi$ interactions (see the Supporting Information).

Phase **II**, obtained via a thermal-induced SCSC transformation from **I**, shows the same molecular components but with distinct conformational changes (Figure 2).

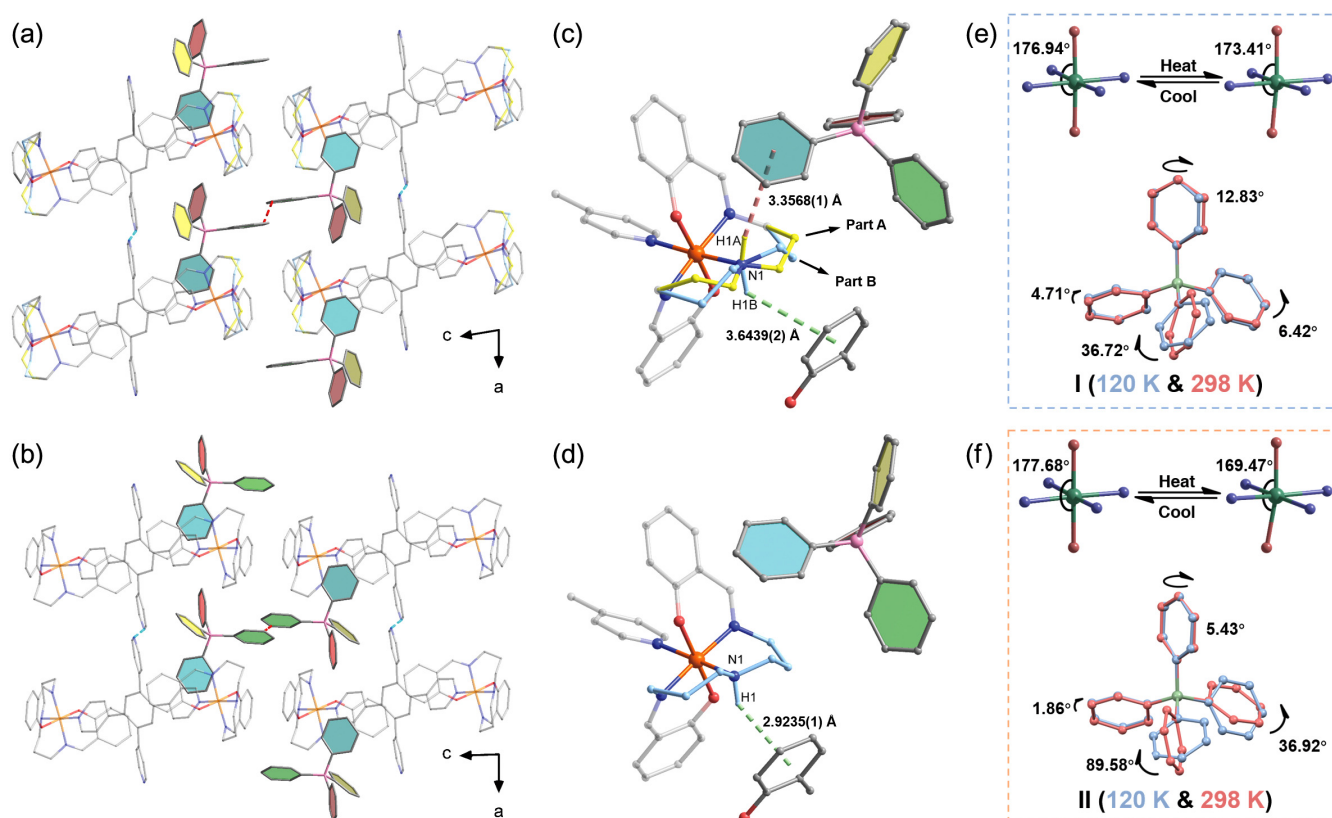


Figure 2 | Structural transformations of **I** and **II**. (a) and (b) reveal the packing views along b axis for **I** and **II** at 120 K, respectively. (c) and (d) show the related $\text{N1-H}\cdots\pi$ interactions. The disordered parts in (c) are marked in yellow (A) and light blue (B) for discrimination. The phenyl rings of BPh_4^- are shaded in different colors for identification: yellow (C34–C39), light blue (C40–C45), red (C46–C51), and green (C52–C57). (e) and (f) indicate the change of $\text{Fe}(\text{III})$ geometry as well as the rotational movements of the BPh_4^- anion for **I** and **II**.

Conspicuously, four phenyl rings of the BPh_4^- anion rotate by 41.03° , 13.87° , 21.23° , and 30.38° in **II** at 120 K when compared with **I** (Supporting Information Figure S12). Due to the movement of the C40–C45 phenyl ring away from the cation, the $\text{C–H}\cdots\pi_{(\text{C40–C45})}$ interactions in configuration B and $\text{N1–H1A}\cdots\pi_{(\text{C40–C45})}$ interaction in configuration A are weakened significantly. Meanwhile, the opposite displacement of adjacent cations enhances the $\text{N1–H1B}\cdots\pi_{(\text{C15–C20})}$ interaction in configuration B. Thus, the disorder in the alkyl chain disappears and only configuration B is retained in **II**. Additionally, the crystal packing in **II** becomes tighter, which is proven by a 2.2% decrease in unit cell volume when compared to **I** at 120 K. Hence, a stronger cooperativity is realized in polymorph **II**.

The average Fe–N/Fe–O distances in **II** increase from 1.986(1)/1.882(1) Å at 120 K to 2.142(2)/1.920(2) Å at 298 K, suggesting a more significant change of bond length than that in **I**. Structural transformations between different spin states are more prominent in **II**. In particular, the four phenyl rings of the BPh_4^- anion experience different degrees of rotation, with the C34–C39 phenyl ring rotating the most by 89.58° . Hence, a thoroughgoing change in the surrounding intermolecular interactions is triggered (Supporting Information Figure S6). Moreover, the uncoordinated pyridine rings of the TPB ligand also rotate concertedly (Supporting Information Figures S11 and S13), leading to the changes in hydrogen-bonding interactions [$\text{C5–H5}\cdots\text{N5}$: 2.527(2) Å at 120 K and 2.397(2) Å at 298 K; $\text{C32–H32}\cdots\text{N5}$: 2.607(1) Å at 120 K and 3.375(2) Å at 298 K] (Supporting Information Table S6). Given all these structural rearrangements, the O1–Fe1–O2 angles as well as the octahedral distortion parameters ΣFe alter from 177.68° to 169.47° and from 15.48° to 54.26° , respectively.

Magnetic susceptibility measurements (Figure 3) reveal a gradual and incomplete SCO behavior for **I**. The $\chi_{\text{M}}T$ value is $7.57 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 380 K, which is lower than the theoretical value of $8.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for two HS Fe(III) ions. Hence, they are mainly in the HS state. Upon cooling, the $\chi_{\text{M}}T$ value decreases slowly to $1.01 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 160 K, corresponding to two isolated LS Fe(III) ions. During multiple annealing cycles from 160 to 380 K, the SCO dynamics shift to lower temperature, with an obvious change of T_{c1} values: 268 K $\rightarrow$ 246 K $\rightarrow$ 231 K $\rightarrow$ 227 K during cycles 1–4. Meanwhile, the phase transition process is accompanied by progressive amplification of hysteresis as well as a slight increase in $\chi_{\text{M}}T$ value. Ultimately, an abrupt spin transition with $T_{1/2\downarrow} = 229 \text{ K}$ and $T_{1/2\uparrow} = 236 \text{ K}$ is observed after four thermal cycles.

Indeed, the cycle-dependent SCO behavior can be ascribed to the phase transition **I** $\rightarrow$ **II**. During the endothermic process, the metastable phase can transform into a more thermodynamically stable one with significant conformational isomerization.²² The polymorphic movements effectively propagate across the lattice

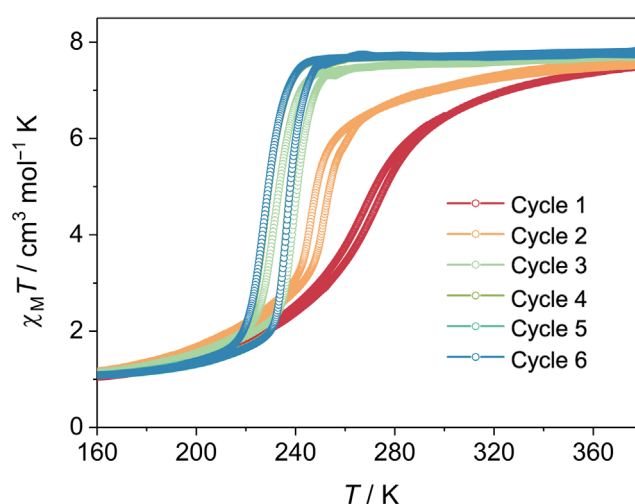


Figure 3 | Variable-temperature magnetization (160–380 K) of **I** $\rightarrow$ **II** with a sweep rate of 2 K min^{-1} under 0.5 T dc field.

through intermolecular interactions, which facilitate the SCO cooperativity between spin centers. As a result, more robust phenyl rotations of the BPh_4^- anion and striking variations of Fe(III) geometry are achieved between LS and HS states, leading to an abrupt spin transition in **II**.

To gain further insight into the alterations of electronic polarizability caused by the structural transformations and electron rearrangements, dynamic dielectric susceptibility was monitored with a pelleted powder sample (Figure 4). Upon cooling, the in-phase dielectric constant ϵ' shows a slight decline due to the less voluminous and ionic nature of the LS state. However, the ϵ' value

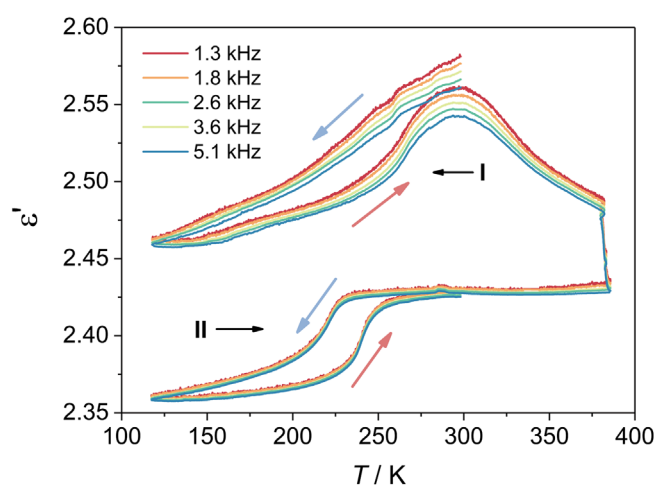


Figure 4 | Temperature dependence of in-phase dielectric constant ϵ' performed on powdered sample of **I** following: 298 K $\rightarrow$ 120 K $\rightarrow$ 380 K (hold for 2 h) $\rightarrow$ 120 K $\rightarrow$ 298 K with a sweep rate of 2 K min^{-1} .

increases first and then falls down in the warming mode, resulting in an atypical peak at 294 K. This abnormal dielectric behavior, which might be relative to lattice effects (e.g., hydrogen bonding and orientation of the anion),²³ has rarely been reported in SCO materials.²⁴ In our case, the decrease of ϵ' value upon heating above room temperature is likely attributed to the **I** $\rightarrow$ **II** phase transition. During this process, the molecule experiences anion reorientation as well as the extinction of alkyl chain disorder in lattice. The ϵ' value at room temperature decreases ca. 5%, corresponding to the concomitant consequence of closer packing of molecules. Finally, a typical dielectric bistability, which mainly comes from electron rearrangements, is recorded in **II** with a hysteresis width of 20 K. The dielectric dynamics shifting toward low temperature matches well with the magnetic change from **I** to **II**.

Surprisingly, **II** exhibits reversible polymorphic transformation to **III** or **IV**. As shown in Figure 5, the solvent-free phases **III** and **IV** were obtained by exposing **II** to the saturated vapors of water and ethanol for 48 h. **III** and **IV** display larger thermal hysteresis loops up to 15 and 11 K, respectively. The $T_{1/2}$ values of **III** and **IV** move down to 221 and 225 K, while the warming dynamics are unchanged. In addition, **III** and **IV** can convert to **II** by annealing at 380 K for 2 h (Supporting Information Figure S15). The SCO behaviors of **III** and **IV** were further verified by DSC measurements. The endothermic peaks of **III** and **IV** shift to 215 and 217 K while the exothermic peaks remain at 234 K (Supporting Information Figure S3). Although similar in molecular structure and packing to **II**, subtle differences in **III** and **IV** were revealed by carefully checking the structural deviations (Supporting Information Table S9). In the LS state, we noticed small deflections of the BPh_4^- anion by 0.54° and

0.14° for the C46–C51 phenyl ring, while 0.06° and 0.28° for the C40–C45 phenyl ring in **III** and **IV**, respectively. In addition, the ΣFe values of **III** and **IV** slightly change to 54.33° and 53.48° at HS states, suggesting the inevitable change of ligand field of Fe(III). Hence, the SCO properties of **III** and **IV** are sensitive to these subtle structural rearrangements. The polymorphic transformation from **II** to **III** or **IV** may be induced by interfacial hydrogen-bonding interactions between the polar solvents and the external molecules, which then trigger a cascade of the subtle structural rearrangement throughout the whole crystal.

In order to clarify the SCO behavior in **I–IV**, the spin structure of an individual Fe ion and the magnetic interaction between Fe sites were computed by density functional theory (DFT) methods (see the Supporting Information). It was found that the individual Fe site in **I** at low temperature (120 K) is in the LS state ($S=1/2$). This fact correlates well with the magnetic susceptibility value at low temperature. It is also in the LS state at high temperature (298 K), in which the energy of HS state ($S=5/2$) is only 405 cm^{-1} higher than that of LS state (Supporting Information Table S10). The rise of magnetic susceptibility with temperature in **I** derive from the gradual thermal population of the HS state on the Fe site. For compounds **II–IV**, all Fe sites are in LS states at low temperature, while they turn to HS states at high temperature (Supporting Information Tables S10 and S11), which exhibits a drastic difference to **I**. Their LS $\rightarrow$ HS transitions are the reason for the sharp rise of the magnetic susceptibility. The values of $\chi_M T$ at high temperatures for **II–IV** are close to the sum of two independent HS Fe(III) ions. From the electronic point of view, the presence of two axial Fe–O bonds leads to a strong, mostly axial splitting of the 3d orbitals of Fe sites. This large orbital splitting favors the LS state in **I–IV**, overcoming the energy gain of the Hund's coupling of spins in a HS configuration. Upon heating, the lengths of both Fe–O and Fe–N bonds increase to stabilize the HS state, which has an opposite effect on the orbital splitting. For compound **I**, the increase in the bond lengths is smaller than those in **II–IV**, explaining why the spin transition is not complete. Having established the ground state spin values of all Fe sites, we computed the magnetic interactions via the broken-symmetry approach. As shown in Supporting Information Table S13, the magnetic interactions between Fe sites in **I–IV** are rather weak ($<5\text{ cm}^{-1}$) and ineffective at the investigated temperatures.

Conclusion

In summary, a multiresponse system was constructed by integrating a rotatable tetraphenylborate anion into the SCO active module. The synergy effect was modulated and propagated across the lattice with significant conformational isomerization amid thermal treatment.

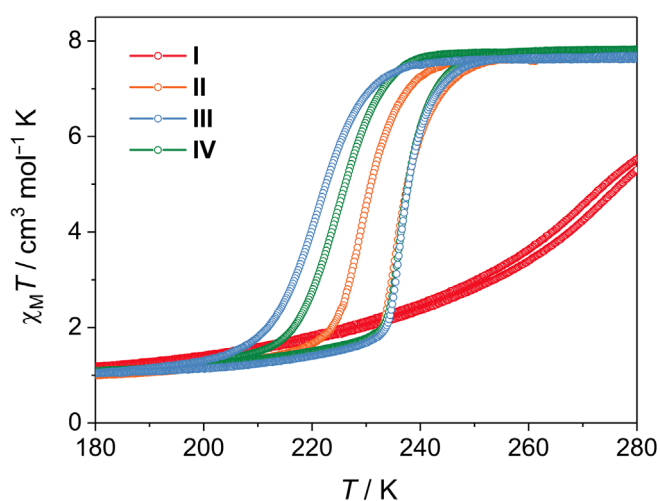


Figure 5 | Variable-temperature magnetization of the polymorphs **I–IV** with a sweep rate of 2 K min^{-1} .

Taking advantage of the enhancement of cooperativity, SCO behavior was implemented from gradual to abrupt via intramolecular motions. Simultaneously, the relevant dielectric dynamics were observed to correspond to the structural transition. Most importantly, the nonporous annealed phase (II) shows reversible solvent-vapor and temperature-induced polymorphic transformations, which could be applicable as solvent sensors. Hence, this work provides a strategy to enhance cooperativity in the SCO field by introducing intramolecular motions to the lattice, which might also be extended to switchable molecule-based materials.

Supporting Information

Supporting Information is available.

Conflict of Interest

There is no conflict of interest to report.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2018YFA0306001), the NSFC (21773316, 21771200, and 21821003), and the Pearl River Talent Plan of Guangdong (2017BT01C161). The scientific grants R-143-000-A80-114 and R-143-000-A65-133 from the National University of Singapore are gratefully acknowledged. Computational resources from NSCC (ASPIRE-1, grant no. 11001278) were used for this study.

References

1. Gütllich, P.; Goodwin, H. A. *Spin Crossover in Transition Metal Compounds III*. Springer-Verlag: Berlin Heidelberg, New York, **2004**.
2. Halcrow, M. A. *Spin-Crossover Materials: Properties and Applications*. John Wiley & Sons, **2013**.
3. Halcrow, M. A. Structure: Function Relationships in Molecular Spin-Crossover Complexes. *Chem. Soc. Rev.* **2011**, *40*, 4119–4142.
4. Hogue, R. W.; Singh, S.; Brooker, S. Spin Crossover in Discrete Polynuclear Iron(II) Complexes. *Chem. Soc. Rev.* **2018**, *47*, 7303–7338.
5. Ohkoshi, S.-i.; Imoto, K.; Tsunobuchi, Y.; Takano, S.; Tokoro, H. Light-Induced Spin-Crossover Magnet. *Nat. Chem.* **2011**, *3*, 564–569.
6. Sato, O. Dynamic Molecular Crystals with Switchable Physical Properties. *Nat. Chem.* **2016**, *8*, 644–656.
7. Nihei, M.; Shiga, T.; Maeda, Y.; Oshio, H. Spin Crossover Iron(III) Complexes. *Coord. Chem. Rev.* **2007**, *251*, 2606–2621.
8. Muñoz, M. C.; Real, J. A. Thermo-, Piezo-, Photo- and Chemo-Switchable Spin Crossover Ion(II)-Metallocyanate Based Coordination Polymers. *Coord. Chem. Rev.* **2011**, *255*, 2068–2093.
9. Weber, B.; Bauer, W.; Obel, J. An Iron(II) Spin-Crossover Complex with a 70 K Wide Thermal Hysteresis Loop. *Angew. Chem. Int. Ed.* **2008**, *47*, 10098–10101.
10. Ye, Y.-S.; Chen, X.-Q.; Cai, Y.-D.; Fei, B.; Dechambenoit, P.; Rouzières, M.; Mathonière, C.; Clérac, R.; Bao, X. Slow Dynamics of the Spin-Crossover Process in an Apparent High-Spin Mononuclear Fe^{II} Complex. *Angew. Chem. Int. Ed.* **2019**, *58*, 18888–18891.
11. Létard, J.-F.; Guionneau, P.; Codjovi, E.; Lavastre, O.; Bravic, G.; Chasseau, D.; Kahn, O. Wide Thermal Hysteresis for the Mononuclear Spin-Crossover Compound *cis*-bis(thiocyanato)bis[N-(2'-pyridylmethylene)-4-(phenylethynyl)anilino]iron(II). *J. Am. Chem. Soc.* **1997**, *119*, 10861–10862.
12. Hayami, S.; Gu, Z.-z.; Yoshiki, H.; Fujishima, A.; Sato, O. Iron(III) Spin-Crossover Compounds with a Wide Apparent Thermal Hysteresis Around Room Temperature. *J. Am. Chem. Soc.* **2001**, *123*, 11644–11650.
13. Kahn, O.; Martinez, C. J. Spin-Transition Polymers: From Molecular Materials Toward Memory Devices. *Science* **1998**, *279*, 44–48.
14. Real, J. A.; Andrés, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. Spin Crossover in a Catenane Supramolecular System. *Science* **1995**, *268*, 265–267.
15. Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. Guest-Dependent Spin Crossover in a Nanoporous Molecular Framework Material. *Science* **2002**, *298*, 1762–1765.
16. Venkataramani, S.; Jana, U.; Dommaschk, M.; Sonnichsen, F. D.; Tuczek, F.; Herges, R. Magnetic Bistability of Molecules in Homogeneous Solution at Room Temperature. *Science* **2011**, *331*, 445–448.
17. Aguilà, D.; Dechambenoit, P.; Rouzières, M.; Mathonière, C.; Clérac, R. Direct Crystallographic Evidence of the Reversible Photo-Formation and Thermo-Rupture of a Coordination Bond Inducing Spin-Crossover Phenomenon. *Chem. Commun.* **2017**, *53*, 11588–11591.
18. Nowak, R.; Prasetyanto, E. A.; De Cola, L.; Bojer, B.; Siegel, R.; Senker, J.; Rössler, E.; Weber, B. Proton-Driven Coordination-Induced Spin State Switch (PD-CISSS) of Iron (II) Complexes. *Chem. Commun.* **2017**, *53*, 971–974.
19. Rodríguez-Velamazán, J. A.; González, M. A.; Real, J. A.; Castro, M.; Muñoz, M. C.; Gaspar, A. B.; Ohtani, R.; Ohba, M.; Yoneda, K.; Hijikata, Y.; Yanai, N.; Mizuno, M.; Ando, H.; Kitagawa, S. A Switchable Molecular Rotator: Neutron Spectroscopy Study on a Polymeric Spin-Crossover Compound. *J. Am. Chem. Soc.* **2012**, *134*, 5083–5089.
20. Tao, J.; Wei, R.-J.; Huang, R.-B.; Zheng, L.-S. Polymorphism in Spin-Crossover Systems. *Chem. Soc. Rev.* **2012**, *41*, 703–737.
21. Zhang, W.; Xiong, R.-G. Ferroelectric Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 1163–1195.
22. Chen, Y.-C.; Meng, Y.; Dong, Y.-J.; Song, X.-W.; Huang, G.-Z.; Zhang, C.-L.; Ni, Z.-P.; Navařík, J.; Malina, O.; Zbořek, R.; Tong, M.-L. Light- and Temperature-Assisted Spin State Annealing: Accessing the Hidden Multistability. *Chem. Sci.* **2020**, *11*, 3281–3289.

23. Lefter, C.; Davesne, V.; Salmon, L.; Molnár, G.; Demont, P.; Rotaru, A.; Bousseksou, A. Charge Transport and Electrical Properties of Spin Crossover Materials: Towards Nanoelectronic and Spintronic Devices. *Magnetochemistry* **2016**, *2*, 18.
24. Bousseksou, A.; Molnár, G.; Demont, P.; Menegotto, J. Observation of a Thermal Hysteresis Loop in the Dielectric Constant of Spin Crossover Complexes: Towards Molecular Memory Devices. *J. Mater. Chem.* **2003**, *13*, 2069–2071.