1170 *Inorg. Chem.* **2011**, *50*, 1170–1172
DOI: 10.1021/ic102231j

Inorganic Chemistry
Communication

Making Spin-Crossover Crystals by Successive Polymorphic Transformations

Rong-Jia Wei,[†] Bao Li,[†] Jun Tao,*[,†] Rong-Bin Huang,[†] Lan-Sun Zheng,[†] and Zhiping Zheng*[,†,‡]

[†]*State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry,*
College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005,
People's Republic of China, and [‡]*Department of Chemistry and Biochemistry,*
University of Arizona, Tucson, Arizona 85721, United States

Received November 7, 2010

The complex [Fe(tpa)$(NCS)_2$] showed successive polymorphic transformations (polymorphs II−IV) that produced crystals with distinct changes in color, crystal structure, and spin-crossover behavior.

Polymorphism arises when a complex is able to crystallize in more than one form (polymorph) possessing different conformations and/or arrangements of the molecules in the unit cell.[1] Though chemically identical, the physical and chemical properties of polymorphs of the same substance may vary significantly. Nowadays, polymorphism has been maintaining its significance in crystal engineering based on the very idea of the rational design and construction of functional materials with predefined architectures and physical properties starting from the choice of the molecular components.[2] Spin-crossover (SCO) complexes, whose intra-ionic electron transfer between different spin states could occur upon external stimuli, are a class of fundamentally interesting materials.[3] The effects of polymorphism on SCO have been known since the first example was reported by König and co-workers,[4] where differences in the abruptness and residual high-spin (hs) molecules at temperatures below T_c are found between polymorphs arising from different preparative methods. The importance of polymorphism in monomeric SCO is that polymorphs show different intermolecular interactions in long-range order, which, in turn, greatly influence the transition behavior of SCO complexes. In view of this, a number of such SCO complexes with polymorphs were investigated, and the correlation between the polymorph and the nature of the spin transition was well studied.[5] However, although up to four polymorphs of one SCO complex have been found,[5d] the obtainment of polymorphs of SCO complexes is still a result of serendipity, such as the coexistence of polymorphs in supersaturated solutions[5a,f] or crystallization under different conditions.[4,5c,5d] To the best of our knowledge, no polymorphs of the SCO complex have been found to be generated from other polymorph(s) through polymorphic transformation.

We have recently reported the crystal structure of a well-studied SCO complex [Fe(tpa)$(NCS)_2$],[6a,b] here named as p**I**, and its interesting methanol-vapor-induced single-crystal-to-single-crystal transformation behavior.[6c] It is when we attempted to synthesize other solvates of the same complex and to investigate the possible solvent influence on their SCO properties that we came across three new polymorphs

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*To whom correspondence should be addressed. E-mail: taojun@xmu.edu.cn (J.T.), zhiping@u.arizona.edu (Z.Z.).

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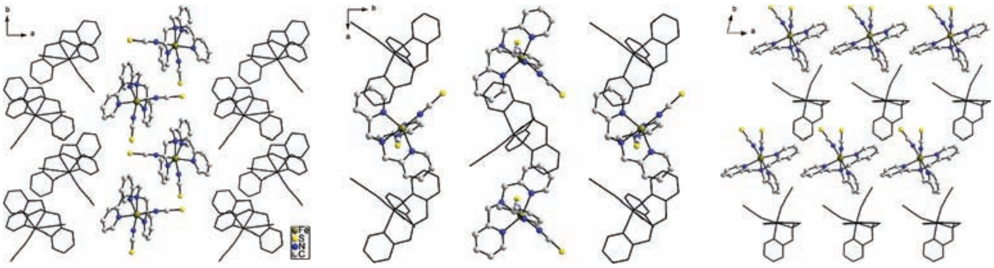

Figure 1. Crystal packing of p**II**−p**IV** (from left to right). Fe_A units are displayed in capped-stick form and Fe_B in ball-and-stick form.

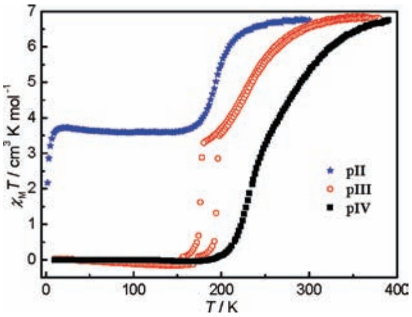

Figure 2. $\chi_M T$ versus T plots of p**II**, p**III**, and p**IV** (per Fe_2 unit).

(p**II**−p**IV**), not by *simultaneous* crystallization from the same solution but via *successive* polymorphic transformations.

The crystals of p**II** were obtained by layering a *N*,*N*-dimethylformamide (DMF) solution of p**I** on top of water (Supporting Information). By immersion of p**II** crystals in a DMF/water (1:5) solution, dramatic color changes from yellow to red and then to dark red occurred successively within 1 month (Figure S1 in the Supporting Information). Crystallographic studies (see below) clearly indicated that two new polymorphs, **III** (red) and **IV** (dark red), were formed, and the color changes suggest that the spin states of the Fe^{II} centers might have changed. This means that an unexpected polymorphic transformation (**II** to **IV**) via an unambiguous intermediate phase (**III**) is observed. It should be noted that polymorphs **III** and **IV** could only be obtained through the transformation of **II**.

Crystal data of p**II**, p**III**, and p**IV** were collected at various temperatures in order to correlate the structures with different SCO phases identified by the magnetic studies (Figure 1). Crystal data and structural parameters are given in Tables S1 and S2 in the Supporting Information. The asymmetric unit of each of these polymorphs contains two crystallographically distinct complex units, herein denoted as $[Fe_A(tpa)(NCS)_2]$ (the Fe_A unit) and $[Fe_B(tpa)(NCS)_2]$ (the Fe_B unit), respectively. Each distorted $[FeN_6]$ octahedron is formed by four N atoms belonging to tpa and two provided by the cis-disposed NCS^- groups.

Strong correlations between the Fe−N bond lengths and the spin states of the Fe^{II} centers at various temperatures have been established. Specifically, p**II** crystallizes in the monoclinic space group $P2_1/c$. At 293 K, the Fe−N bond lengths range from 2.016(3) to 2.258(3) Å with averages of 2.154 and 2.168 Å for the Fe_A and Fe_B units, respectively. Both values are in the range expected for a hs Fe^{II}−N bond, and the spin state is consistent with the results of the room-temperature magnetic measurements (Figure 2). As a comparison, the Fe_A−N bond length has an average of 1.963 Å at 120 K, typical of a low-spin (ls) Fe^{II}−N bond, whereas the average Fe_B−N bond length remains essentially unchanged (2.169 Å) with respect to its counterpart at 293 K. A transition of p**II** from hs Fe_A/hs Fe_B to ls Fe_A/hs Fe_B upon lowering of the temperature is thus inferred.

p**III** also crystallizes in the monoclinic space group $P2_1/c$. At 293 K, the average Fe−N bond lengths are 2.135 and 2.167 Å for the Fe_A and Fe_B units, respectively, indicating that both Fe^{II} centers are in the hs states. Upon cooling to 192 K, the average Fe_A−N bond length shows a sizable decrease to 1.990 Å, whereas the corresponding value associated with the Fe_B site remains unchanged; a hs Fe_A/hs Fe_B to ls Fe_A/hs Fe_B transition of p**III** is thus suggested in this temperature range. The longer bond (Fe_B−N) was shortened to 1.959 Å at 140 K, while the Fe_A−N bond length decreases only slightly, from 1.990 to 1.956 Å, corresponding to a transition from the ls Fe_A/hs Fe_B state to a state of ls Fe_A/ls Fe_B, and the completion of a two-step spin-transition process.

p**IV** crystallizes in the triclinic space group $P\bar{1}$. Its crystal data were collected at 350 K, 250 K (inflection point as determined by magnetic studies), and 150 K. The average Fe−N bond lengths for the Fe_A and Fe_B units at these temperatures (Table S2 in the Supporting Information) indicate that p**IV** undergoes a complete two-step spin transition, from a hs Fe_A/hs Fe_B state to a ls Fe_A/hs Fe_B state and then to a ls Fe_A/ls Fe_B state. Such transitions are in good agreement with the results obtained in the following magnetic studies.

The main differences between these polymorphic structures are in their crystal-packing patterns (Figure 1). The packing of p**II** can be viewed as layers with alternate wavelike Fe_A and Fe_B chains, parallel to the *ab* plane, stacking along the *c* axis, while that of p**III** is formed by stacking along the *c* axis of layers containing parallel wavelike chains with alternating Fe_A and Fe_B units in the *ab* plane. For p**IV**, layers in the *ab* plane containing mutually parallel chains of Fe_A and Fe_B units, respectively, stack along the *c* axis. The three new structures, p**II**−p**IV**, are all stabilized by intermolecular $\pi\cdots\pi$ interactions between neighboring tpa pyridine groups and S···H−C hydrogen bonds (Table S2 in the Supporting Information) deviating from each other and may be responsible for the different SCO abruptness and transition temperature. Especially for p**III**, whose intermolecular interactions are stronger than those of p**II** and p**IV** (Table S2 in the Supporting Information), indicating stronger cooperativity within the p**III** crystals that results in an abrupt and cooperative (hysteresis) spin transition (see below).

The magnetic susceptibilities of p**II**, p**III**, and p**IV** measured in an applied field of 5000 Oe are shown in the form of $\chi_M T$ versus T plots (Figure 2). p**II** (two SCO centers) shows a transition similar to that of p**I** (only one SCO center)[6c] but without hysteresis. Between 250 and 300 K, the $\chi_M T$ value remains essentially constant at 6.76 cm^3 K mol^{-1}, suggesting

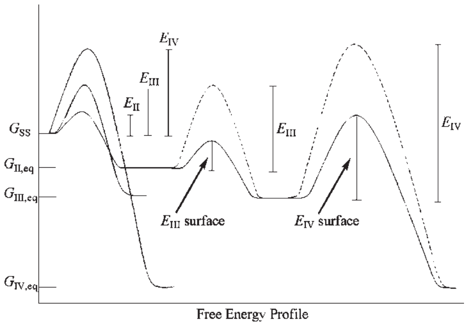

Figure 3. Energy (G) versus reaction coordinate profile for the nucleation of polymorphs of [Fe(tpa)(NCS)$_2$].

two hs Fe^{II} ions. The $\chi_M T$ value decreases upon cooling, and a value of 3.60 cm^3 K mol^{-1} was reached at 160 K. Following the wide plateau between 160 and 20 K, a sudden decrease of the $\chi_M T$ value was observed, possibly because of the zero-field effect of the residual hs Fe^{II} ions,[7] that is, the Fe$_B$ unit, as revealed by crystallographic studies detailed above.

pIII displays a two-step spin-transition process, with the transition temperature at 235 and 176 K, respectively, separated by a narrow plateau between 200 and 180 K. The existence of three separate phases with distinct spin states is thus suggested. At 360 K, the $\chi_M T$ value is 6.76 cm^3 K mol^{-1}, corresponding to a hs Fe$_A$/hs Fe$_B$ state. The $\chi_M T$ value decreases upon temperature lowering, and a complete transition to a ls Fe$_A$/hs Fe$_B$ state is reached at approximately 180 K. Interestingly, a hysteresis loop with a width of ca. 20 K was observed in the lower-temperature transition step, indicating a cooperative transition. **pIV** displays a complete two-step transition with critical temperatures at 293 and 230 K, respectively. The intermediate inflection point is located at 250 K with a $\chi_M T$ value of 3.34 cm^3 K mol^{-1}, suggesting an authentic hs Fe$_A$/ls Fe$_B$ state.

Thermodynamically, the polymorph representing the lowest free-energy state is preferred for a given set of conditions.[1] The nucleation of this particular form, however, may suffer from a higher activation energy. If the common view that nucleation defines crystallization holds, one would expect the metastable phase with the lowest energy barrier for nucleation to crystallize out first, followed by its transformation to the thermodynamically most stable form by way of any intermediates that may be energetically accessible.[1,8] The present successive polymorphic transformations thus provide a perfect crystallization paradigm that follows Ostwald's Rule of Stages.[9] Accordingly, a generic depiction of the free energy versus nucleation coordinate is shown in Figure 3, where G_{SS} stands for the energy state of the supersaturated solution of **pI** in DMF/H$_2$O, while $G_{II,eq}$, $G_{III,eq}$, and $G_{IV,eq}$ stand for the energy states at equilibria of **pII**, **pIII**, and **pIV**, respectively. **pII**, kinetically favored because of its smaller activation energy E_{II} would nucleate at a faster rate than **pIII** or **pIV**. Driven by the lower free energy of **pIII**, solution-mediated polymorphic transformation ensued with the partial dissolution of **pII** and concomitant crystallization of **pIII**; the nucleation of **pIII** was presumably facilitated by the sympathetic surface of the continuously dissolving **pII** because the nucleation barrier E_{III}(surface) is lower than the corresponding activation energy if **pIII** nucleated directly from the supersaturated solution. In other words, the preexisting polymorph acts as a template that guides the nucleation of the next metastable form with a pathway significantly different and with much lower energy than the one without the preexisting polymorph. The subsequent transformation from **pIII** to **pIV** followed a similar pathway but was much lengthier than the one from **pII** to **pIII**.

In summary, we report herein the isolation and identification of three new polymorphs of the SCO complex [Fe(tpa)(NCS)$_2$] and their extraordinary successive transformations. Such transformations are accompanied with dramatic color changes, originating from their distinct, structurally dependent electronic spin states, affording crystalline materials with altered SCO properties, as indicated by the magnetic measurements. This is the first example that shows successive polymorphic transformation in the SCO system. The present study contributes to the fundamental understanding of the crystallization of polymorphs. Furthermore, the ability to systematically investigate a material's structure−property relationship, as exemplified here for a SCO complex, portends the opportunity to fine-tune and optimize the material's properties and to realize even better materials.

Acknowledgment. This work was supported by the NNSF of China (Grants 90922012, 20971106, and 20721001), the NSF of Fujian Province for Distinguished Young Scientists (Grant 2009J06006), and the National Basic Research Program of China (973 program, Grant 2007CB815301).

Supporting Information Available: Experimental details, figures, tables, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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