Light- and Temperature-Assisted Spin State Annealing: Accessing the Hidden Multistability

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Abstract: Among the responsive multistable materials, spin crossover (SCO) systems are of particular interest for stabilizing multiple spin states with various stimulus inputs and physical outputs. Here in a 2D Hofmann-type coordination polymer $[Fe(isoq)_2{Au(CN)_2}_2]$ (isoq = isoquinoline), hidden multistability of the spin state is accessed by introducing an medium-temperature annealing after a light/temperature stimulation. With the combined effort of magnetic, crystallographic and Mössbauer spectral investigation, these distinct spin states are identified and the lightand temperature-assisted transition pathways are clarified. Such excitation-relaxation and trapping-relaxation joint mechanisms, as ingenious interplays between the kinetic and thermodynamic effects, uncover hidden possibilities for the discovery of multistable materials and the development of multistate intelligent devices.

Introduction

Responsive multistable materials are one of the most attractive topics for designing switchable devices with potential applications in nonvolatile memory, switches and sensors.^[1-4] Among them, multistable spin crossover (SCO) materials are of particular interest,^[5-9] since the spin transition is accompanied by multifaceted magnetic, electronic, optical and mechanical outputs.^[10-19] In fundamental, a spin center can be stabilized in a high spin (HS) or low spin (LS) state^[20] according to different temperature, pressure, guest, etc.^[21-27] In most cases, the spin state switching is realized by varying the temperature, where the HS/LS state is obtained at higher/lower temperature, respectively, but only one spin state can be stabilized in a set of given condition.

The first step toward multistability relies on the strong cooperativity between multiple spin centers, in which case an energy barrier can be formed and hinders the transition process.

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Consequently, the thermal SCO behavior become hysteretic with notable bistability between $T_{c,cool}$ and $T_{c,warm}$,^[28] where the spin state can be trapped in the HS/LS state under the same condition, mimicking the 1/0 states in a binary numeral system. The switching between these bistable states can be achieved by cooling/warming beyond the hysteretic region, or by directly stimulating inside the hysteresis by external stimulus. ^[29-30] Multistep SCO systems have brought about more possibilities by accommodating different spatial organizations of the HS and LS centers due to elastic frustration.^[31] Each state would have different HS:LS fractions, which results in the multiple staircaselike transitions.^[32-37] Nevertheless, it remains a great challenge to achieve multistability from multistep SCO systems, unless the stepwise transition is combined with hysteresis (Scheme 1a).^{[38-} ^{39]} Such scenario usually requires symmetry-breaking SCO, in which the locations of HS/LS sites must be re-arranged in the crystal structure.^[40] As a result, the dramatic change of the lattice can further raise the transition barrier, thus the hysteretic region is widen and coupled with the multistep transition into multistability.



Scheme 1. Representative types of multistable spin crossover systems (a-d), and the LASSA and TASSA process reported in this work (e-f).

On the other hand, multistability can also be achieved by kinetically trapping the system in multiple excited states at low

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temperature. For SCO materials, the light-induced spin state trapping (LIESST) effect facilely accommodates the lightinduced excited state below T_{LIESST} , where the thermal vibration of the lattice is not strong enough for the relaxation back to its ground state.^[41] Therefore, a bistable system is achieved as the spin centers can be stabilized in either of the HS/LS state. Based on such mechanism, a few SCO complexes can further exhibit a multistable LIESST effect when different spin centers and/or additional intermediate states are involved, which produces multiple excited states and thus multistability (Scheme 1b).^[42-45] When the initial spin state is a mixed spin (MS) state, it is also possible to observe a bidirectional LIESST effect, where different irradiations can promote HS and LS state, respectively (Scheme 1c), and the subsequent transitions between these states may further reveal hidden hysteresis.^[46-47] In these cases, the HS/MS/LS states can be regarded as the 2/1/0 states in a ternary numeral system, namely tristability. Last but not least, there is also an successful approach by combing the LIESST effect with the magnetic polarities, [48-49] so that the system can be stabilized in one of the nonmagnetic/up/down tristable states in a light-actuated Magnet (Scheme 1d), mimicking the 0/+1/-1 states in a balanced ternary numeral system.

Here, we present a 2D Hofmann-type coordination polymer $[Fe(isoq)_2(Au(CN)_2)_2]$ (1). In addition to the symmetry-breaking SCO, after a light or temperature stimulus, a further annealing process for 1 around liquid nitrogen temperature can lead to a hidden LS state, which generates genuine multistability (Scheme 1e-1f) together with the MS and LIESST-HS states. Such two-stage manipulations, named as the Light- and Temperature-Assisted Spin State Annealing (LASSA and TASSA) mechanisms, are investigated by a combination of magnetism, structure and Mössbauer spectroscopy technique. It is demonstrated that, both the light- or temperature-induced excited state and the medium-temperature annealing process are crucial for accessing the multistability that is hidden under normal circumstances.

Results and Discussion

The title compound was synthesized by the slow diffusion of a 1:2:2 molar ratio of FeSO₄·7H₂O, isoq, and K[Au(CN)₂] in the mixed solvents of methanol and water. **1** is a two-dimensional Hofmann-type coordination polymer (see the crystal structure section for detail discussions), which is solvent-free and ideal for comprehensive investigations.

Variable-temperature magnetic susceptibility data were recorded in the temperature range of 10-300 K on polycrystalline samples. At first glance, **1** exhibit an adjacent two-step spin crossover behavior (orange line in Figure 1) centered at 143 K and 132 K, respectively. The $\chi_M T$ values fall from 4 cm³ K mol⁻¹ at high temperature to 2 cm³ K mol⁻¹ below 130 K, indicating a half spin transition from the HS state to an intermediate spin (MS, where HS:LS = 1:1) state. Also, varying the temperature sweeping rate does not give rise to any significant impact on the spin crossover behavior (Supporting Information, Figure S1).



Figure 1. Temperature dependence of the molar magnetic susceptibility $\chi_M T$ products for **1** in normal cooling mode (orange); in warming mode after LIESST at 5 K (green) and annealed at 75 K (green to red) and then in warming mode (from 10 K) after the annealing process (red); in quench mode and annealed at 80 K (blue to purple) and then in warming mode (from 10 K) after the annealing process (purple).

LASSA: LIESST + Anneal

When **1** was excited by a 532 nm laser at 5 K, a LIESST effect (MS \rightarrow HS) was obtained just in several minutes (green arrow in Figure 1, and Supporting Information, Figure S2). However, the following warming from such excited HS state reveals a clear trough just above the temperature of liquid nitrogen (75~100 K, Supporting Information, Figure S3), suggesting an unusual relaxation behavior. Therefore, an annealing test was performed by keeping **1** at 75 K (green-to-red line in Figure 1) after a complete LIESST. During such a annealing process, the $\chi_M T$ values keep falling from ~2 cm³ K mol⁻¹ (MS) to 0.5 cm³ K mol⁻¹, revealing a hidden low spin (LS) state.

The annealing dynamics were also studied at a series of nearby temperatures. Below 80 K, all of the annealing processes bring 1 to the LS state (Figure 2). The time dependence of the $\chi_M T$ values shows a rapid pseudo-exponential decay at the beginning, followed by a sigmoidal relax to the final LS state, but such two-stage relaxation behavior hampers further analysis on the dynamics using a classical $d\gamma_{HS}/dt = -k \gamma_{HS}$ model. Nevertheless, the deviation from a simple exponential decay is clear evidence of strong cooperativity, where the spin centers are coupled into domains and relax altogether. As the temperature rises, a clear speedup of the annealing rates is observed. At 65 K, the relaxation to the LS state takes ca. 10 hours, while at 80 K it takes only an hour, which is in line with the thermal-activating nature of an annealing process. For higher temperatures, the relaxations do not lead to the LS state. but gradually turn to the MS state instead (Supporting Information, Figure S4). Therefore, hidden tristability of the spin states is revealed for 1 at low temperature, which consist of: 1) an MS state accessed by normal slow cooling; 2) a HS state accessed by LIESST effect; and 3) a hidden LS state accessed by the combination of LIESST at low temperature and annealing at medium temperature, the last of which we hereby refer to the Light-Assisted Spin State Annealing (LASSA) mechanism.



Figure 2. Time dependence of the molar magnetic susceptibility $\chi_M T$ products for 1 during Light-Assisted Spin State Annealing (LASSA): firstly LIESST (MS \rightarrow HS) at 5 K and then annealed at various temperatures to the LASSA-LS state. Note the largely different time scale for 60 K in the inset.

Further study shows that 1 can maintain in the LASSA-LS state at low temperatures regardless of repeatedly cooling and warming. Above 90 K, an adjacent two-step SCO behavior is activated from LS to MS (red line in Figure 1) centered at 94 K and 99 K. The plateau of the MS state lasts for ca. 30 K, and then another adjacent two-step SCO from MS to HS is observed in good agreement with the conventional SCO. The temperature regions of such transitions are far separated from the relaxation of HS states, which rules out the possibility for overlapping kinetic effects.^[50-51] Judging from the $\chi_M T$ values, the subtle small steps at 99 K and 132 K were tentatively attributed to the 1/3 HS and 2/3 HS as transient states, but they are not stable enough for further characterizations. Second pass LASSA effect were also studied between 70~85 K (Supporting Information, Figures S5-S6): Starting from the LASSA-LS state obtained at 75 K, 1 can be excited again by a 532 nm laser to a fraction of HS state. The following annealing process shows that 1 will relax back to LS state for $T \le 80$ K, proving that the LASSA-LS state is not a kinetically-trapped excited state but a thermodynamically stable state. For higher temperatures such as 85 K, both the LIESST process and the annealing process become inefficient, which may due to the destabilization of the HS and LS state upon warming. As a result, the final outcome at high temperature is dominated by the thermal equilibrium between the HS, LS and MS states.

Other light sources, namely UV (355 nm), blue (473 nm), red (671 nm) and infrared (830, 905, 1064 nm) lasers, were also investigated for their impact on the spin states of **1**. Starting from the conventional MS state, the LIESST result shows that both the 473 nm and 1064 nm lasers can promote a full HS state, while only partial excitation is observed for the 355 nm and 671 nm lasers (Supporting Information, Figures S7-S8). The 830 nm and 905 nm lasers, however, tend to stabilize the LS state following a bidirectional LIESST effect, no matter starting from the MS state or from the HS state (obtained by 532 nm LIESST). With the higher final χ_{MT} values of 0.6~0.8 cm³ K mol⁻¹ and the signs of further relaxations upon warming, such light-only

transitions are less effective than the LASSA pathway. This situation may be due to the insufficient structural relaxation at low temperatures, which emphasizes the thermodynamic nature of the annealing process and thus clearly differs the LASSA mechanism from the kinetic bidirectional LIESST effects.



Figure 3. Time dependence of the molar magnetic susceptibility $\chi_M T$ products for **1** during Temperature-Assisted Spin State Annealing (TASSA): firstly quenched from room temperature and then annealed at various temperatures to the TASSA-LS state (for 80 K and 75 K). Inset shows the relaxation with slower cooling rate than quenching and note the largely different time scales.

TASSA: Quench + Anneal

To gain further insight into the unusual LS state, we tried to quench the sample from the room-temperature HS state. When **1** was quenched to 85 K or above, the $\chi_{\rm M}T$ value reads ~2 cm³ K mol⁻¹ and basically maintains, indicating the acquisition of an MS state rather than trapping in the HS state. However, when 1 was quenched to 80 K or 75 K, a following annealing process from MS to LS state was observed as evidenced by the continuous dropping of $\chi_{\rm M}T$ values from 2 cm³ K mol⁻¹ to 0.3 cm³ K mol⁻¹ (blue-to-purple line in Figure 1, and Figure 3). With a cooling rate of 10 K/min, which is much slower than quenching, 1 can maintain in the MS state for much longer before annealing to the LS state (inset of Figure 3). Recalling the lack of sweeping-rate dependence of the conventional SCO process for 1, such behavior is opposite to the kinetically trapping mechanism (where slow cooling rates reveal new states).^[52] Therefore, it is suggested that the normal MS state from slow cooling might be different from the quenched MS* state here, despite their similar $\chi_{\rm M}T$ values (~2 cm³ K mol⁻¹) from the magnetic point of view. From such MS* state, 1 can anneal to a hidden LS state, which is partially similar to the aforementioned LASSA-LS state and indeed shares similar SCO behaviors in the following warming process toward MS and then HS states (purple line in Figure 1, and Supporting Information, Figure S9). Hereby, we refer such mechanism to Temperature-Assisted Spin State Annealing (TASSA), where the combination of quenching from high temperature and annealing at medium temperature finally accesses the hidden LS state.



Figure 4. Crystal structure for 1 in the HS state at 170 K (a-b); in the ordered MS state at 80 K (c-d, by slow cooling); and in the LS state at 80 K (e-f, by rapid quench and annealed), showing the coordination environment of Fe (a, c, e) and the 2D double-layer (b, d, f) connected by Au…Au interactions. Color codes: Fe(HS), red; Fe(LS), blue; Au, yellow; N, cyan; C, gray. H atoms are omitted and the back layer is faded out for clarity.

Single crystal structure.

The comprehensive magnetic study above not only demonstrates the fascinating mechanisms that lead to the multistability for 1, but also provides a guideline for the crystallographic measurements, which can be precisely followed to capture the structural evidence for the corresponding spin states. To avoid any unnecessary interference, all single-crystal X-ray diffraction data for 1 were collected using the same piece of crystal. At 170 K, 1 crystallizes in the monoclinic P21/c space group and each asymmetric unit contains one formula unit (Figure 4a). Each iron atom is octahedrally coordinated by six nitrogen atoms, in which two nitrogen atoms come from monodentate isoq ligands in the axial positions and remaining come from four [Au(CN)₂]⁻ species in the equatorial positions. The average Fe-N bond length is 2.17 Å, indicating a full HS state for Fe(II). Each Fe(II) ions are linked equatorially by four [Au(CN)₂]⁻, and each [Au(CN)₂]⁻ connects two Fe(II) ions, generating 2D [Fe{Au(CN)₂}₂]_∞ layers along the *bc* plane. Furthermore, the undulated 2D layers are linked together into double layers through aurophilic (Au···Au = 3.05 Å) interactions (Figure 4b), and then packed into 3D supramolecular structure with offset face-to-face π ··· π interactions (Supporting Information, Figures S10-S11).

When **1** is slowly cooled to 80 K as in the conventional SCO characterization, the single crystal structure here reveals a symmetry-breaking transition into a *P*-1 space group. Unlike the single Fe(II) site in a P_{21}/c space group, two crystallographically inequivalent Fe(II) sites were presented in the crystal structure (Figure 4c), and the average Fe-N bond length is 2.12 and 2.00 Å, respectively, which indicates a ordered mixed spin (MS) state

with the HS:LS ratio of 1:1. Within the 2D [Fe{Au(CN)₂}₂]_{∞} layers along the *bc* plane (Figure 4d), these HS and LS Fe(II) sites are arranged alternatively with each other, which could be referred to as the antiferroelastic pattern.^[31]

Following the TASSA process, the single-crystal X-ray diffraction data for **1** was also collected after rapid quenching from room temperature to 80 K (the lowest temperature that can be stabilized by our cryostat) and annealing until equilibrium. The single crystal structure at this stage shows that **1** turns back to the monoclinic space group $P2_1/c$ and each asymmetric unit contains only one formula unit with only one crystallographically inequivalent Fe(II) (Figure 4e). The average Fe-N bond length is 2.00 Å, indicating a full TASSA-LS state. The 2D layer also dramatically shrinks as evidenced by the shortening of the average Fe...(NCAuCN)...Fe distance from 10.40 Å in the HS state to 10.10 Å, as well as the shortening of the nearest interlayer Fe...Fe distances from 7.66 Å to 7.45 Å.

Table 1. Selected structural parameters at different states for 1.

<i>T /</i> K		<fe-n>ª/Å</fe-n>	∑Fe ^b /°	Assignment
170		2.17	13.1	HS
80 (MS-Order)	Fe1	2.12	16.5	HS
	Fe2	2.00	12.9	LS
80 (MS-Disorder)		2.05	12.9	HS/LS
80		2.00	11.2	LS
80		2.00	11.2	LS

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The last piece of the puzzle is completed by capturing the MS* state just after the quenching. Recalling the steady plateau of magnetic susceptibility just after cooling (inset of Figure 3), it is evident that the transient structure can be maintained longer with a slower cooling rate. After some trials, a set of diffraction data was successfully collected within the first few hours just after cooling to 80 K at 6 K/min. Single crystal analysis at this point, whether solved in a triclinic or monoclinic space group, only shows an intermediate structure with the average Fe-N bond length of 2.05 Å. Therefore, it cannot be assigned to a pure HS or LS state, but it corresponds to a disordered arrangement of HS and LS Fe(II) ions within the lattice. Indeed, such average Fe-N bond length is just at the middle of those for HS state (2.12 Å in the ordered MS state) and LS state (2.00 Å in both the ordered MS state and pure LS state) at 80 K. We hold back from further discussing the structural details in this disordered scenario, as it merely represent an averaged picture from the crystallographic point of view. Nevertheless, judging from the magnetic susceptibility, such state shall consist of HS:LS = 1:1. namely a disordered MS* state. From here on, the TASSA process will subsequently bring 1 to the LS state, which clearly differs such disordered MS* state from the ordered MS state in slow cooling.

Spin transition pathways

Finally, we were able to propose the spin transition pathways that lead to the multistablity in the spin states for **1** (Scheme 2). When the cooling/warming rate is normally slow (e.g. 2 K/min), **1** undergoes typical thermal SCO between the HS state and the ordered MS state, during which half of the Fe(II) ions alternatively change their spin states. At low temperature, **1** can be photo-excited through the LIESST mechanism back to a full HS state, which is much higher in energy. However, the relaxation from the LIESST-HS state does not lead back to the MS state, but to a hidden LS state that is inaccessible by thermal SCO. The combination of LIESST at low temperature (60~80 K) represents the key component of the LASSA mechanism, which is an excitation-relaxation process (Scheme 2b).

On the other hand, when **1** is quenched from room temperature, it is trapped in a disordered MS* state. Due to the disruption of antiferroelastic ordering (as in the ordered MS state), such MS* state could have higher energy than the ordered MS state, so that the activation energy for MS* \rightarrow LS is lower. Subsequently, the spin transition to the hidden LS state is activated during annealing at medium temperature, which represents the TASSA mechanism as a trapping-relaxation process (Scheme 2c).

Notably, the LASSA and TASSA mechanism share the same idea that firstly accommodates an excited state by external light/temperature stimulus, from which the thermodynamically or kinetically hidden states can be accessed upon annealing at medium temperature.



Scheme 2. Graphical representation of the spin transition pathways between multistable spin states for **1**, showing the relative energy at low temperature regime (a) and the two-stage manipulating processes for LASSA (b, excitation-relaxation) and TASSA (c, trapping-relaxation). The conventional SCO process is depicted in light gray for clarity.

Mössbauer spectroscopy

The spin state transition was also proved by employing ⁵⁷Fe Mössbauer spectroscopy. At 170 K, the ⁵⁷Fe Mössbauer spectrum of **1** shows only one doublet with the value of the isomer shift (δ) and quadrupole splitting (ΔE_Q) lying in the interval expected for Fe(II) in a high-spin (HS; S = 2) state (Figure 5 and Table 2). No signs of other spectral components were observed within the experimental error of the Mössbauer technique.

When **1** was slowly cooled to 80 K, two doublets emerged: one doublet for Fe(II) in HS state and another doublet for Fe(II) in a low-spin (LS; S = 0) state. If the recoil-free fraction are considered as almost identical for both spin species, the spectral ratio between the HS and LS Fe(II) doublet is 1:1, in accordance with the magnetic measurement and crystal structures.



Figure 5. ⁵⁷Fe Mössbauer spectra of 1, recorded at a temperature of 170 and 80 K after cooling from room temperature at a rate of 2 K/min and at a temperature of 80 K after rapid cooling (with liquid nitrogen and storing for 5 h at liquid nitrogen temperature before initiation of the ⁵⁷Fe Mössbauer spectroscopy measurement).

After rapid quenching and storing in liquid nitrogen for 5 h; the ⁵⁷Fe Mössbauer spectrum of **1** recorded at 80 K, shows only one doublet with δ and ΔE_Q values typical for Fe(II) in LS state. No signs of HS spectral component were observed within the experimental error of the Mössbauer technique (spectral area < 5%). Thus, with the methodology used, it was possible to fully restore the LS phase. Note that the ΔE_Q value of the LS phase, restored after rapid freezing, is somewhat smaller than that of the LS phase appearing after slow cooling (Table 2). This implies that the ligand field (its symmetry, distribution, and orientation) slightly changed with rapid quenching. The ligand field features characteristics closer to the spherical symmetry. Moreover, a slight distortion of the cation polyhedron cannot be fully excluded due to rapid freezing.

Table 2. Values of the Mössbauer hyperfine parameters, derived from the least-square fitting of the $^{57}{\rm Fe}$ Mössbauer spectra of 1. a

T	δ	ΔE_Q	Г	Area	Assignment
(K)	(mm/s)	(mm/s)	(mm/s)	(%)	
170	1.09	1.22	0.35	100	Fe(II), S = 2
00	1.18	1.77	0.24	51	Fe(II), $S = 2$
80	0.38	0.29	0.24	49	Fe(II), S = 0
80*	0.39	0.23	0.23	100	Fe(II), $S = 0$

^a*T* is the temperature of measurement, δ is the isomer shift, ΔE_Q is the quadrupole splitting, and Γ is the linewidth. The errors in δ , ΔE_Q , and Γ are ± 0.01 mm/s, the error in area is ± 2%.

Such subtle variation can be clearly evaluated by the fingerprint plots based on the Hirshfeld surface analysis,^[53] which facilely visualizes the close interactions between the asymmetric units in 1 (Figure 6, and Supporting Information, Figures S12-S16). In general, the distances from the surface to the nearest internal (d_i) and external (d_e) atoms are both shorten upon the HS \rightarrow LS transition, with the whole pattern shifting from the upper right corner toward the lower left corner. Since 1 is a coordination polymer, such analysis also reveals the bonding information at the terminal of the asymmetric units. Most sharply, the closest Fe...N / N...Fe contacts change from $(d_i, d_e) = (1.10, 1.05)/(1.05, 1.10)$ in the HS state to (1.01, 0.96)/(0.97, 1.00) in the LS state, which directly represents the shortening of Fe...N bond lengths during SCO. At the same time, the closest Au...Au interactions change from (1.52, 1.52) to (1.48, 1.48), and the C...C, C...H and H...H interactions that mainly contributed by the inter-ligand $\pi \cdots \pi$ interactions also shorten, which is in line with the shrinkage of the lattice during SCO and cooling.



Figure 6. Fingerprint plot of 1 in the HS state at 170 K (a); in the LS state at 80 K (b) and in the ordered MS state at 80 K (c-d), resolved into Fe...N (red), Au...Au (yellow), C...C (green), C...H (blue) and H...H (gray) contacts. Individual fingerprint plots are depicted in Supporting Information, Figure 11-S15.

The ordered MS state, however, shows asymmetric fingerprint plots with respect to the diagonal line (Figure 7c-d), while those for the disordered MS* state are basically an averaged result (Supporting Information, Figure S16). Such asymmetry is mainly due to the fact that, in the ordered MS state each HS Fe(II) is linking to a LS one, and *vice versa*, which enhance the waviness of the 2D plane. Indeed, the HS Fe1 in the MS state is similar but not identical to those in the HS state (Supporting Information, Figure S17), the former of which shows higher octahedral distortion parameter (Σ Fe) and larger quadrupole splitting (ΔE_{α})

(Table 2). Such antiferroelastic ...HS-LS-HS-LS... pattern, as a direct consequence of the symmetry-breaking SCO, not only stabilizes the ordered MS state but also create a relatively high energy barrier that hides the LS state, so that the thermodynamic annealing is crucial to the multistability.

Conclusion

In summary, a pair of two-stage manipulations, namely lightand temperature-assisted spin state annealing (LASSA and TASSA) processes, are successfully applied to 1 and reveal a hidden spin state that is inaccessible by conventional pathways. Contrary to most kinetic effects, the key to success here is an additional medium-temperature thermodynamic annealing following a light or temperature stimulus: either from the excited HS state by LIESST or from the trapped disordered MS* state by quenching. The mechanism for such behavior is rationalized by a comprehensive investigation and attributed to the excitationrelaxation and trapping-relaxation process, respectively, in such a coordination polymer with strong cooperativities between spin centers. Thanks to the thermodynamically higher stability of the annealed spin state, in addition to the symmetry-breaking SCO and LIESST effect, 1 exhibits genuine tristability for its spin states within one of the widest temperature ranges (T < 65 K). The multistage transition pathways presented here not only uncover the hidden multistability for 1 as a multistable SCO material, but also convey a generalized idea that the impacts of the external stimuli on multistable materials are not limited to the stimulating stage. The subsequent relaxation upon mediumtemperature annealing, under certain circumstances, may open up new windows for unexpected hidden stable states, which shall pave the way toward the excavating of a growing number of responsive multistable materials and multistable devices.

Experimental Section

General Procedure. All reagents for the synthesis were commercially available and used as purchased without further purification. The FT-IR spectra were recorded in the range of 4000-400 cm⁻¹ on a Bio-Rad FTS-7 spectrometer with KBr pellets. The C, H and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer.

Synthesis of [Fe(isoq)₂{Au(CN)₂}₂] (1). An aqueous solution (0.25 mL) of K[Au(CN)₂] (14.4 mg, 0.05 mmol), a buffer solution (MeOH:H₂O = 2:1, 0.2 mL), and a MeOH solution (0.25 mL) of isoq (6.5 mg, 0.05 mmol) was successively placed in a 0.7 mL test tube. Eight of such tubes were placed in a 40 mL bottle. Then an aqueous solution (2 mL) of FeSO₄·7H₂O (55.6 mg, 0.2 mmol) was put into the bottle, followed by adding a buffer solution (MeOH:H₂O = 2:1, 6 mL) that completely immerse the tubes. Yellow crystals of **1** were obtained after one week, which were manually separated and collected with a yield of 17.1mg (10%). IR (cm⁻¹) for **1**: 2168 (s), v(C \equiv N). Elemental analysis: Calcd (Found) for C₂₂H₁₄Au₂FeN₆: C 32.53 (32.72), H 1.74 (1.71), N 10.35 (10.41).

X-ray Crystallography. Single-crystal X-ray diffraction data for 1 were collected on a Bruker D8 QUEST diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Low temperature down to 80 K (turbo mode) was maintained

by an Oxford cryostat operating with liquid nitrogen. The structures were solved by direct method and refined by least-squares on F^2 using the SHELX program.^[54] Hydrogen atoms on organic ligands were generated by the riding mode and some of the light atoms are restrained with ISOR to reduce the heavy-atom effect from the gold atoms. Crystal Data and structural refinement values are listed in Table S1. Powder X-ray diffraction measurements were obtained on a Bruker D8 Advance diffractometer with Cu_{Ka} radiation by scanning over the range of 5-50° with a step of 0.12 °/s at room temperature. Simulated powder XRD pattern was calculated based on the single-crystal structure with Mercury software (Supporting Information, Figure S18). CCDC 1918986-1918989 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ structures/

Magnetic Measurements. Temperature-dependent magnetic susceptibility was measured by a Quantum Design MPMS XL-7 SQUID magnetometer and a Quantum Design MPMS3 magnetometer at a standard rate of 2 K/min unless otherwise stated. Diamagnetic correction was performed based on Pascal's coefficients. Photomagnetic behaviors were studied on the standard fiber optic sample holder (FOSH) using various laser source (355/473/532/671/830/905/1064 nm, ~20 mW/cm²). For sufficient light penetration, only a small amount (~ 1.5 mg) of sample was used, and the exact weight was corrected by matching the curve with that of a heavier sample (~ 20 mg) used for normal variabletemperature magnetic susceptibility. Unless otherwise mentioned, the sample was firstly slowly cooled to 5 K, irradiated by laser until photosaturation, and then warmed at 2 K/min in dark. The magnetic susceptibility was continuously measured in DC mode and the slight photo-thermal warming of ~2 K was corrected based on the magnetization. Quenching experiment was performed using the RSO Airlock of MPMS and the slight introduction of air oxygen is subtracted. The sample was firstly kept at room temperature and then rapidly loaded into the pre-cooled sample chamber in <10 s. The target temperature was immediately reset to minimize temperature fluctuation. The magnetic susceptibility was then continuously measured in RSO mode during the annealing process.

Mössbauer spectra. 57 Fe Mössbauer spectra were recorded employing a home-made Mössbauer spectrometer, operating in a transmission measuring geometry and in a constant acceleration regime, equipped with a ⁵⁷Co(Rh) radioactive source with an activity of 50 mCi, emitting yrays. The samples were placed inside the chamber of the cryomagnetic system (Oxford Instrument, UK), to which the Mössbauer spectrometer is mounted, providing setting temperatures in the interval from 5 to 300 K. For Mössbauer spectroscopy measurements at a temperature of 170 and 80 K, the sample was cooled from room temperature with vapors of helium inside the sample chamber at a rate of 2 K/min. For measurement at 80 K, the sample already mounted in the sample holder was rapidly cooled by putting to liquid nitrogen basin and left immersed for 5 h. Then, the rapidly guenched sample was guickly transferred to the sample chamber pre-cooled holding at 100 K. After inserting the sample into the pre-cooled sample space inside the cryostat, a final temperature (i.e., 80 K) was reached by cooling with helium vapors at 5 K/min. When collected, the ⁵⁷Fe Mössbauer spectra were fitted using the MossWinn software package;[55] when required, prior to fitting, the signal-to-noise ratio was adjusted by the filtering and line sharpening procedures built in the MossWinn software program and by statistically-based approach developed by Prochazka et al.^[56] The isomer shift values were referred to α-Fe at room temperature.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] W. Fujita, Awaga, Kunio, Science 1999, 286, 261-262.
- [2] T. Rueckes, K. Kim, E. Joselevich, G. Y. Tseng, C.-L. Cheung, C. M. Lieber, *Science* 2000, 289, 94-97.
- [3] T. K. Paraïso, M. Wouters, Y. Léger, F. Morier-Genoud, B. Deveaud-Plédran, *Nat. Mater.* 2010, 9, 655.
- [4] O. Sato, Nat. Chem. 2016, 8, 644-656.
- [5] O. Kahn, C. J. Martinez, Science 1998, 279, 44-48.
- [6] P. Gütlich, Y. Garcia, H. A. Goodwin, Chem. Soc. Rev. 2000, 29, 419-427.
- [7] A. Bousseksou, G. Molnar, L. Salmon, W. Nicolazzi, *Chem. Soc. Rev.* 2011, 40, 3313-3335.
- [8] D. J. Harding, P. Harding, W. Phonsri, *Coord. Chem. Rev.* 2016, 313, 38-61.
- [9] R. W. Hogue, S. Singh, S. Brooker, *Chem. Soc. Rev.* 2018, 47, 7303-7338.
- [10] S. Bonhommeau, T. Guillon, L. M. Lawson Daku, P. Demont, J. Sanchez Costa, J. F. Letard, G. Molnar, A. Bousseksou, *Angew. Chem. Int. Ed.* 2006, *45*, 1625-1629.
- [11] D. Aravena, E. Ruiz, J. Am. Chem. Soc. 2012, 134, 777-779.
- [12] N. Hoshino, F. Iijima, G. N. Newton, N. Yoshida, T. Shiga, H. Nojiri, A. Nakao, R. Kumai, Y. Murakami, H. Oshio, *Nat. Chem.* 2012, *4*, 921-926.
- [13] H. J. Shepherd, I. A. Gural'skiy, C. M. Quintero, S. Tricard, L. Salmon, G. Molnar, A. Bousseksou, *Nat. Commun.* **2013**, *4*, 2607.
- [14] S.-i. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nat. Photon.* **2014**, *8*, 65-71.
- [15] C.-F. Wang, R.-F. Li, X.-Y. Chen, R.-J. Wei, L.-S. Zheng, J. Tao, Angew. Chem. Int. Ed. 2015, 54, 1574-1577.
- [16] K. Senthil Kumar, M. Ruben, Coord. Chem. Rev. 2017, 346, 176-205.
- [17] H. Zheng, Y.-S. Meng, G.-L. Zhou, C.-Y. Duan, O. Sato, S. Hayami, Y. Luo, T. Liu, *Angew. Chem. Int. Ed.* 2018, 57, 8468-8472.
- [18] J. Yuan, S.-Q. Wu, M.-J. Liu, O. Sato, H.-Z. Kou, J. Am. Chem. Soc. 2018, 140, 9426-9433.

- [19] M. Mikolasek, M. D. Manrique-Juarez, H. J. Shepherd, K. Ridier, S. Rat, V. Shalabaeva, A. C. Bas, I. E. Collings, F. Mathieu, J. Cacheux, T. Leichle, L. Nicu, W. Nicolazzi, L. Salmon, G. Molnar, A. Bousseksou, J. Am. Chem. Soc. 2018, 140, 8970-8979.
- [20] P. Gutlich, H. A. Goodwin, in *Spin Crossover in Transition Metal Compounds I, Vol.* 233 (Eds.: P. Gutlich, H. A. Goodwin), Springer-Verlag Berlin, Berlin, **2004**, pp. 1-47.
- [21] G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, 298, 1762-1765.
- [22] A. Galet, A. B. Gaspar, M. C. Muñoz, G. V. Bukin, G. Levchenko, J. A. Real, Adv. Mater. 2005, 17, 2949-2953.
- [23] J. E. Clements, J. R. Price, S. M. Neville, C. J. Kepert, Angew. Chem. Int. Ed. 2014, 53, 10164-10168.
- [24] B. Rosner, M. Milek, A. Witt, B. Gobaut, P. Torelli, R. H. Fink, M. M. Khusniyarov, Angew. Chem. Int. Ed. 2015, 54, 12976-12980.
- [25] D. Pinkowicz, M. Rams, M. Misek, K. V. Kamenev, H. Tomkowiak, A. Katrusiak, B. Sieklucka, J. Am. Chem. Soc. 2015, 137, 8795-8802.
- [26] Z.-P. Ni, J.-L. Liu, M. N. Hoque, W. Liu, J.-Y. Li, Y.-C. Chen, M.-L. Tong, Coord. Chem. Rev. 2017, 335, 28-43.
- [27] M. Estrader, J. Salinas Uber, L. A. Barrios, J. Garcia, P. Lloyd-Williams, O. Roubeau, S. J. Teat, G. Aromi, *Angew. Chem. Int. Ed.* **2017**, *56*, 15622-15627.
- [28] S. Brooker, Chem. Soc. Rev. 2015, 44, 2880-2892.
- [29] R. Kulmaczewski, J. Olguin, J. A. Kitchen, H. L. Feltham, G. N. Jameson, J. L. Tallon, S. Brooker, *J. Am. Chem. Soc.* **2014**, *136*, 878-881.
- [30] S. Cobo, D. Ostrovskii, S. Bonhommeau, L. Vendier, G. Molnar, L. Salmon, K. Tanaka, A. Bousseksou, J. Am. Chem. Soc. 2008, 130, 9019-9024.
- [31] M. Paez-Espejo, M. Sy, K. Boukheddaden, J. Am. Chem. Soc. 2016, 138, 3202-3210.
- [32] E. Trzop, D. Zhang, L. Pineiro-Lopez, F. J. Valverde-Munoz, M. Carmen Munoz, L. Palatinus, L. Guerin, H. Cailleau, J. A. Real, E. Collet, Angew. Chem. Int. Ed. 2016, 55, 8675-8679.
- [33] Z.-Y. Li, H. Ohtsu, T. Kojima, J.-W. Dai, T. Yoshida, B. K. Breedlove, W.-X. Zhang, H. Iguchi, O. Sato, M. Kawano, M. Yamashita, *Angew. Chem. Int. Ed.* 2016, 55, 5184-5189.
- [34] M. Nihei, Y. Yanai, I. J. Hsu, Y. Sekine, H. Oshio, Angew. Chem. Int. Ed. 2017, 56, 591-594.
- [35] J. E. Clements, J. R. Price, S. M. Neville, C. J. Kepert, Angew. Chem. Int. Ed. 2016, 55, 15105-15109.
- [36] W. Liu, Y.-Y. Peng, S.-G. Wu, Y.-C. Chen, M. N. Hoque, Z.-P. Ni, X.-M. Chen, M.-L. Tong, *Angew. Chem. Int. Ed.* 2017, *56*, 14982-14986.
- [37] N. F. Sciortino, K. A. Zenere, M. E. Corrigan, G. J. Halder, G. Chastanet, J. F. Letard, C. J. Kepert, S. M. Neville, *Chem. Sci.* 2017, *8*, 701-707.
- [38] N. F. Sciortino, K. R. Scherl-Gruenwald, G. Chastanet, G. J. Halder, K. W. Chapman, J.-F. Letard, C. J. Kepert, *Angew. Chem. Int. Ed.* 2012, 51, 10154-10158.
- [39] M. J. Murphy, K. A. Zenere, F. Ragon, P. D. Southon, C. J. Kepert, S. M. Neville, J. Am. Chem. Soc. 2017, 139, 1330-1335.
- [40] M. Shatruk, H. Phan, B. A. Chrisostomo, A. Suleimenova, *Coord. Chem. Rev.* 2015, 289-290, 62-73.
- [41] A. Hauser, in Spin Crossover in Transition Metal Compounds II, Springer Berlin Heidelberg, Berlin, Heidelberg, 2004, pp. 155-198.
- [42] M. Nihei, H. Tahira, N. Takahashi, Y. Otake, Y. Yamamura, K. Saito, H. Oshio, J. Am. Chem. Soc. 2010, 132, 3553-3560.
- [43] M. Nihei, Y. Suzuki, N. Kimura, Y. Kera, H. Oshio, Chem. Eur. J. 2013, 19, 6946-6949.
- [44] E. Milin, V. Patinec, S. Triki, E.-E. Bendeif, S. Pillet, M. Marchivie, G. Chastanet, K. Boukheddaden, *Inorg. Chem.* 2016, 55, 11652-11661.
- [45] J.-X. Hu, L. Luo, X.-J. Lv, L. Liu, Q. Liu, Y.-K. Yang, C.-Y. Duan, Y. Luo, T. Liu, Angew. Chem. Int. Ed. 2017, 56, 7663-7668.
- [46] E. Milin, V. Patinec, S. Triki, E.-E. Bendeif, S. Pillet, M. Marchivie, G. Chastanet, K. Boukheddaden, *Inorg. Chem.* 2016, *55*, 11652-11661.

ARTICLE

- [47] T. Boonprab, S. J. Lee, S. G. Telfer, K. S. Murray, W. Phonsri, G. Chastanet, E. Collet, E. Trzop, G. N. L. Jameson, P. Harding, D. J. Harding, *Angew. Chem. Int. Ed.* **2019**, *58*, 11811-11815.
- [48] S. Ohkoshi, K. Imoto, Y. Tsunobuchi, S. Takano, H. Tokoro, *Nat. Chem.* 2011, 3, 564-569.
- [49] X. Feng, C. Mathoniere, I.-R. Jeon, M. Rouzieres, A. Ozarowski, M. L. Aubrey, M. I. Gonzalez, R. Clerac, J. R. Long, *J. Am. Chem. Soc.* 2013, 135, 15880-15884.
- [50] M. Seredyuk, M. C. Muñoz, M. Castro, T. Romero-Morcillo, A. B. Gaspar, J. A. Real, *Chem. Eur. J.* **2013**, *19*, 6591-6596.
- [51] V. A. Money, C. Carbonera, J. Elhaïk, M. A. Halcrow, J. A. K. Howard, J.-F. Létard, *Chem. Eur. J.* 2007, *13*, 5503-5514.
- [52] N. Paradis, G. Chastanet, J.-F. Létard, Eur. J. Inorg. Chem. 2012, 2012, 3618-3624.
- [53] J. J. McKinnon, D. Jayatilaka, M. A. Spackman, *Chem. Commun.* 2007, 3814-3816.
- [54] G. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112-122.
- [55] Z. Klencsár, E. Kuzmann, A. Vértes, J. Radioanal. Nucl. Chem. 1996, 210, 105-118.
- [56] R. Prochazka, P. Tucek, J. Tucek, J. Marek, M. Mashlan, J. Pechousek, Meas. Sci. Technol. 2010, 21, 025107.