A Spin Transition System with a Thermal Hysteresis at Room Temperature

Jonas Kröber,† Epiphane Codjovi,† Olivier Kahn,*,†
Françoise Grolière,‡ and Charlotte Jay‡

Laboratoire de Chimie Inorganique
URA No. 420, Université de Paris-Sud
91405 Orsay, France
Laboratoires d'Electronique Philips
22 avenue Descartes
94453 Limeil Brevannes, France

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One of the challenging issues in molecular chemistry deals with the use of molecular compounds in electronic devices and systems.[1] The molecular treatment and storage of information are some of the important facets of molecular electronics. Among the possible applications, our group is more particularly concerned with the display as a first step toward signal processing. Devices for such purposes must incorporate compounds exhibiting the phenomenon of bistability. In the context of molecular chemistry, bistability may be defined as the property of a molecular assembly existing under two stable (or metastable) electronic states in a given range of external environmental parameters (temperature, pressure, etc.).[2] In other words, the variation of an electronic property versus one of these parameters must exhibit a hysteresis effect. For most of the applications, the bistability must occur around room temperature. We found a method to tune the temperature range of a thermal hysteresis loop and obtained a system capable of existing under two stable states at room temperature.

Probably the most spectacular example of molecular bistability is provided by the phenomenon of spin transition, in particular in iron(II) chemistry.[3-5] Some sixfold coordinated iron(II) compounds show a transition between a diamagnetic state (spin $S = 0$) below a critical temperature T_c and a paramagnetic state ($S = 2$) above T_c. When the iron(II) ions are linked together within the crystal lattice by bridges (or molecular wires), the $S = 0 \leftrightarrow S = 2$ transition may become cooperative.[6,7] It then occurs in a very abrupt fashion, with a thermal hysteresis; there are two critical temperatures, $T_c\uparrow$ and $T_c\downarrow$, in the warming and the cooling mode, respectively, which confer a memory effect on the system. Furthermore, in some cases, the transition is accompanied by a dramatic change of color.[8-10]

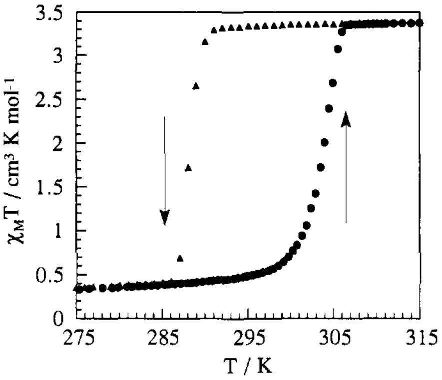
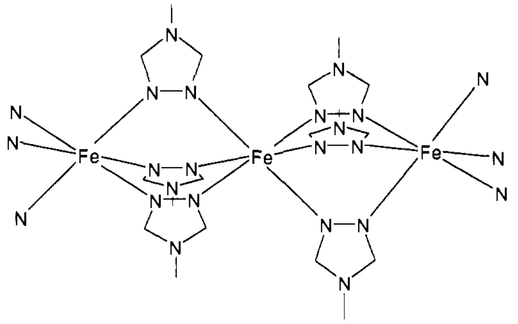


Figure 1. $\chi_M T$ versus T plot for $[Fe(Htrz)_{3-3x}(4\text{-}NH_2trz)_{3x}](ClO_4)_2{\cdot}nH_2O$ with $x = 0.05$ in both the warming (●) and the cooling (▲) modes. The temperature dependence of the molar fraction of high-spin sites, ρ, may be deduced from the magnetic susceptibility data, assuming that the magnetic susceptibility of the compound follows a Curie law in the $S = 2$ state; ρ is then proportional to $\chi_M T$. The magnetic susceptibility data reveal a residual paramagnetism below $T_c\downarrow$, which may be due, at least in part, to a small proportion of Fe(III) sites in spite of the use of ascorbic acid.



For most of the potential applications, the room temperature must fall in the middle of the hysteresis loop. We succeeded in designing a molecular system of this kind. The basic compound is $[Fe(Htrz)_3](ClO_4)_2$, where Htrz is the unsubstituted 1,2,4-1*H*-triazole.[11] Htrz is known to bridge metal ions through either the 1,2 or, more exceptionally, the 2,4 nitrogen positions,[12] leading to polymeric structures, as shown below: which favor the cooperativity.[13,14] The compound, when perfectly dry, shows a rather smooth spin transition around 265 K with a weak thermal hysteresis, about 5 K. When one drop of water is added to ca. 50 mg of $[Fe(Htrz)_3](ClO_4)_2$, the transition becomes very abrupt, both in the warming and cooling mode, with $T_c\uparrow$ = 313 K and $T_c\downarrow$ = 296 K. The role of water[15] is most likely to create hydrogen bonds which favor further the cooperativity, as already observed in quite a few compounds, for instance $[Fe(NCS)_2(4,4'\text{-bis-}1,2,4\text{-triazole})_2](H_2O)$.[13] This transition is accompanied by a purple–white color change. Indeed, the absorption spectrum shows a broad band at 520 nm corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transition in the $S = 0$ state, while it does not show any band in the visible region in the $S = 2$ state, the $^5T_{2g} \rightarrow {}^5E_g$ transition being located around 850 nm. The hysteresis loop is just above room temperature. $T_c\uparrow$ and $T_c\downarrow$ can be shifted

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† Université de Paris-Sud.

‡ Laboratoires d'Electronique Philips.

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[11] The pure compound was prepared as follows: a solution of 6×10^{-3} mol of 1,2,4-1*H*-triazole (414.4 mg) in 100 mL of methanol was added at room temperature into a solution of 2×10^{-3} mol of iron(II) perchlorate hexahydrate (725.6 mg) and about 10 mg of ascorbic acid in 100 mL of methanol. The resulting mixture remained limpid, even after stirring. The methanol was evaporated to dryness with a rotary evaporator at about 60 °C, and the compound precipitated as a white powder which turned purple on cooling. Ascorbic acid was used to prevent the partial oxidation of iron(II) in iron(III). Anal. Calcd for $C_6H_9N_9O_{12}Cl_3Fe$: C, 12.84; H, 1.62; N, 22.46; Cl, 18.95; Fe, 9.95. Found: C, 12.96; H, 2.01; N, 21.94; Cl, 18.19; Fe, 9.76. The doped samples were obtained in the same way by using the appropriate mixtures of 1,2,4-1*H*-triazole and 4-amino-1,2,4-triazole.

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[15] To allow observation of the abrupt transition, the compound must be kept in a humid atmosphere. At room temperature, under 1 atm, the noncoordinated water molecules favoring the cooperativity go away.

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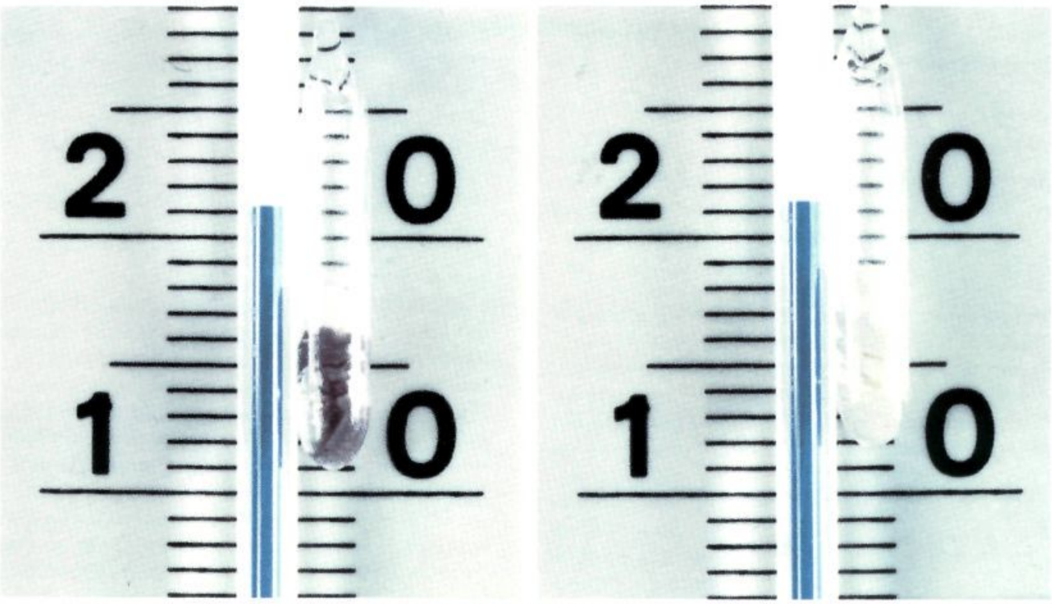

Figure 2. Photographs showing the same sample of $Fe(Htrz)_{3-3x}(4\text{-}NH_2)_{3x}](ClO_4)_2\cdot nH_2O$ with $x = 0.05$ in the $S = 0$ (left) and $S = 2$ (right) states, at 21 °C. This sample is the one used for the magnetic susceptibility measurements leading to the hysteresis loop of Figure 1. The compound within the tube is compressed with a small piece of white cotton to prevent the displacements of the crystallites when the magnetic field is applied.

toward lower temperatures by replacing Htrz by a mixture of Htrz and 4-NH_2trz, where 4-NH_2trz is 4-amino-1,2,4-triazole.

Let us define by $T_{1/2}$ the temperature for which the G versus ρ plot is symmetric with respect to $\rho = 0.5$, G being the Gibbs free energy of a spin transition system and ρ the molar fraction of high-spin sites. $T_{1/2}$ is equal to $\Delta H/\Delta S$, where ΔH and ΔS are the enthalpy and entropy variables, respectively, associated with the $S = 0 \leftrightarrow S = 2$ transition. For a cooperative spin transition, $T_c\uparrow$ and $T_c\downarrow$ are on either side of $T_{1/2}$, the $T_c\uparrow - T_c\downarrow$ hysteresis width depending on the cooperativity of the system. Due to the chemical analogy between $[Fe(Htrz)_3](ClO_4)_2$ and $[Fe(4\text{-}NH_2trz)_3](ClO_4)_2$, we may assume that the entropy variations ΔS are much the same. If it is so, then ΔH is weaker in the 4-NH_2trz derivative. Indeed, the pure $[Fe(4\text{-}NH_2trz)_3](ClO_4)_2$ material shows a smooth transition around $T_{1/2} = 130$ K. Doping $[Fe(Htrz)_3](ClO_4)_2$ with the 4-NH_2trz ligand results in a reduction of the enthalpy variation ΔH, hence in a lowering of the critical temperatures. The formula of the doped compound is $[Fe(Htrz)_{3-3x}(4\text{-}NH_2trz)_{3x}](ClO_4)_2\cdot nH_2O$. $T_c\uparrow$ and $T_c\downarrow$ decrease when x increases in the $0 \leq x \leq 0.1$ range according to $T_c\uparrow = 313 - 180x$ and $T_c\downarrow = 296 - 160x$. For $x = 0.05$, the transition occurs on either side of room temperature, with $T_c\uparrow = 304$ and $T_c\downarrow = 288$ K, as shown in Figure 1.[16] At 295 K, one may observe a purple compound in its $S = 0$ state or a white compound in its $S = 2$ state, depending on the history of the sample, as emphasized in Figure 2. Both states are stable at room temperature. A gentle cooling (by dipping the tube containing the compound in acetone and evaporating acetone) or a gentle warming (by the heat of the hand) of the sample is sufficient to induce the transition. It is worth mentioning that the color change has been reproduced many times without any detectable alteration of the phenomenon. The system apparently shows no fatigability.

The molecular system described in this communication seems to be the first one exhibiting such a bistability at room temperature. The method we used to tune the temperature range of the hysteresis loop seems to be of general applicability. We would like to emphasize the potentialities of the spin transition phenomenon in the context of molecular electronics. In the meantime, this phenomenon raises some fundamental questions concerning the microscopic origin of the cooperativity in a molecular lattice and opens quite appealing perspectives concerning the design of molecular-based memory devices and displays.

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[16] The magnetic susceptibility data were recorded with a Faraday-type magnetometer equipped with a new temperature-controlled device working in the 4.2–450 K temperature range. The temperature was varied at the rate of 1 K min^{-1} in both the cooling and the warming modes.