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Editor's Choice

Unidirectional electric field-induced spin-state switching in spin crossover based microelectronic devices

Constantin Lefter[a,b], Reasmey Tan[c], Julien Dugay[c], Simon Tricard[a], Gábor Molnár[a], Lionel Salmon[a], Julian Carrey[c], William Nicolazzi[a], Aurelian Rotaru[b,*], Azzedine Bousseksou[a,*]

[a] Laboratoire de Chimie de Coordination, CNRS & Université de Toulouse (UPS, INP), 205 route de Narbonne, 31077 Toulouse, France
[b] Faculty of Electrical Engineering and Computer Science & Research Center MANSiD, Stefan cel Mare University, 13 University Street, 720229 Suceava, Romania
[c] LPCNO, CNRS & Université de Toulouse (INSA, UPS), 135 ave Rangueil, 31077 Toulouse, France

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ABSTRACT

We report on a molecular spin-state switching phenomenon induced by an electric field in micrometric objects of the $[Fe(Htrz)_2(trz)](BF_4)$ spin crossover complex, organized between interdigitated electrodes. By applying an electric field step of 40 kV/cm at temperatures within the thermal hysteresis region of the first-order spin transition, the iron(II) ions are switched from the metastable high spin to the stable low spin state obtaining a rather incomplete transition but perfectly reversible by heating. A model based on the interaction between the electric field and the electric dipolar moment of spin crossover complexes, grasps the main features of the experimental data.

1. Introduction

Spin crossover (SCO) materials are made of (pseudo-)octahedral coordination complexes of transition-metal ions with four to seven electrons in the 3d orbitals. Depending on the ligand field strength, the electrons can occupy the 3d orbitals in two different ways giving rise to the so-called low spin (LS) and high spin (HS) electronic configurations, which can be interconverted in a controllable and reversible manner [1–3]. The electronic spin-state switching phenomenon is accompanied by drastic changes in magnetic, optical, electrical and mechanical properties of the materials, providing a very attractive scope for potential applications in different technological fields, such as memories, actuators, sensors and displays [4–6]. Up to now, it has been shown that the switching between the two spin-states can be triggered by various external stimuli such as temperature change, light irradiation, application of an external pressure or intense magnetic fields as well as chemical adsorption/desorption phenomena [1–3]. However, these external stimuli are rather difficult to implement in micro/nano-electronic devices where the control of the SCO phenomenon by electric fields or currents would be desirable.

The interest of using SCO materials as active elements in electronic devices increased after discovering the thermal bistability in the (quasi-static) dielectric constant for SCO compounds [6] followed by the observation of spin state dependence of the electrical conductivity in a few bulk materials [7–10] and micro- or nanoelectronic devices [11–15]. Another important progress was the development of hybrid materials containing both conducting and SCO moieties, either at the molecular [16–18] or at the material scale [19]. Charge transport in single SCO molecules was also investigated using both planar nanoelectronic devices ('nanogaps') [20–23] as well as scanning tunneling microscope [24–27]. Switching from one spin-state to another using an electrical stimulus has also been reported in nanometric tunnel junctions [12,23–25].

In this letter we present the experimental observation of switching the spin-state of micrometric particles of $[Fe(Htrz)_2(trz)](BF_4)$ (Htrz = 1H-1,2,4-triazole, trz = 1,2,4-triazolato) (**1**) from the HS to the LS state by the application of an electric field.

2. Experimental

Micrometric rod-shaped particles of **1** were synthesized as described in ref. [10]. The insets in Figure 1 show the transmission electron microscopy (TEM) image of the particles and the

* Corresponding authors.
E-mail addresses: rotaru@eed.usv.ro (A. Rotaru), azzedine.bousseksou@lcc-toulouse.fr (A. Bousseksou).

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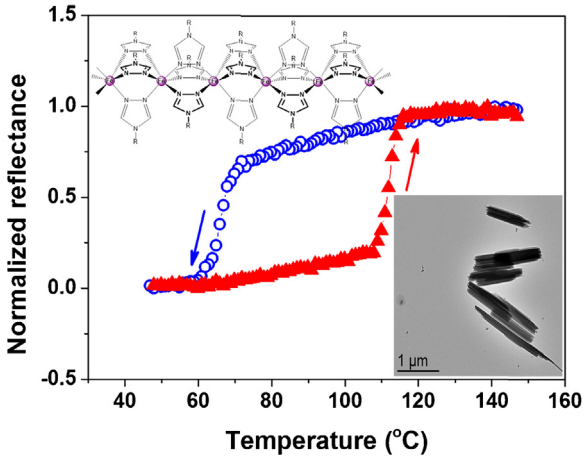

Figure 1. Temperature dependence of the normalized optical reflectance recorded at 550 nm in the heating and cooling modes for $[Fe(Htrz)_2(trz)](BF_4)$ microparticles. The insets show the TEM image of the particles (bottom) and the schematic representation of the chemical structure (top).

schematic chain structure of our compound. The spin transition properties of the powder of **1** were controlled through variable-temperature optical reflectivity (550 nm) measurements at a rate of 2 °C/min. Interdigitated Au microelectrodes on Si/SiO_2 substrates (with Ti anchoring layer) were fabricated by conventional photolithography and lift-off process with an inter-electrode gap of 4 μm. The powder of **1** was dispersed in ethanol and the particles were deposited between the electrodes from this suspension by dielectrophoresis similarly as described in ref. [14]. For variable temperature electrical measurements we used a Linkam HFS600E-PB4 cryostat equipped with gold tipped tungsten electric probes. A Keithley 6430 sub-femtoamp remote source-meter was used to apply the bias and to measure the current in the device. All thermal cycles were registered at a rate of 5 °C/min.

3. Results and discussion

The thermal behavior of the optical reflectance recorded on **1** is shown in Figure 1, presenting the onset of switching from the LS to HS state at 107 °C and the reverse switching from the HS to LS state around 71 °C. This wide, abrupt and reproducible thermal hysteresis loop observed above room temperature is a well-known feature of this triazole based coordination network [28–30]. We have previously shown that the spin transition in this compound can be observed not only by optical and magnetic measurements, but also through various electrical parameters, such as conductivity, dielectric constant and loss modulus, making compound **1** an attractive candidate for electronic and spintronic devices [8–10,13–15]. For the experiments described in this letter particles of **1** were aligned between interdigitated microelectrodes using dielectrophoresis. Figure 2a shows the temperature dependence of the current flowing in this device under a 40 kV/cm electric field. The overall current vs temperature (*I*–*T*) characteristics of the device were found basically the same as the ones we reported for similar devices in ref. [14]. Upon heating the device from 30 to 130 °C (red symbols) a strong thermal activation of the current was observed up to 111 °C, where a sharp current decrease from 0.45 nA to 1.8 pA, characteristic of the LS to HS transition, was registered. When cooling the device (blue symbols), the latter remains in the HS state until 71 °C where the current increases from 2.3 pA to 35 pA closing the hysteresis loop (characteristic to the HS to LS transition). The thermal cycle was recorded several times to ensure the reliability of the device. While the current intensity showed some evolution the transition temperatures were found well reproducible in all

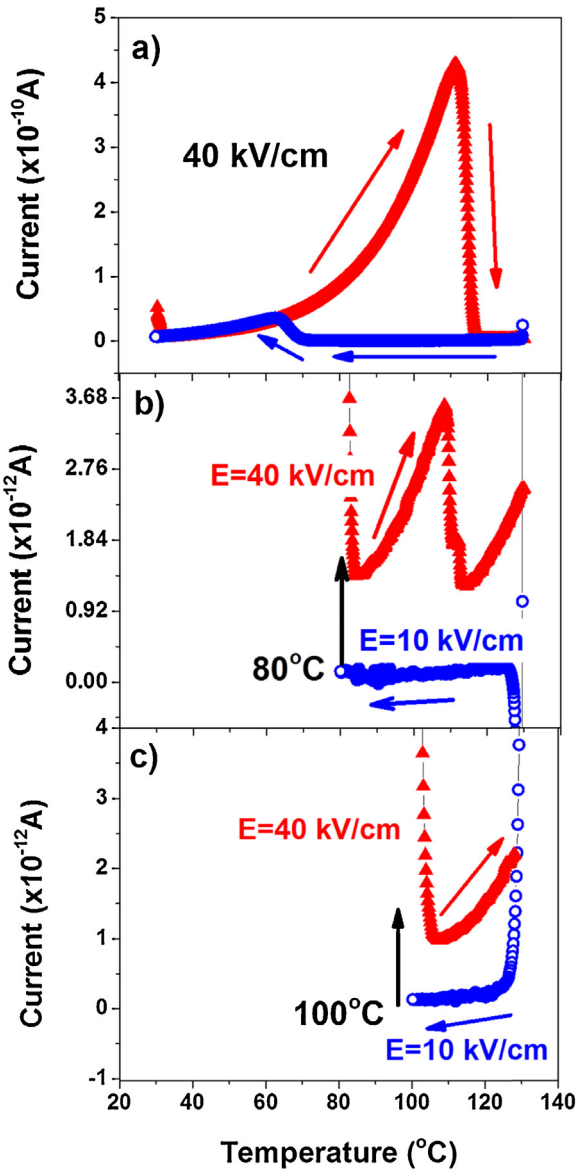

Figure 2. Current vs temperature characteristics of the interdigitated electrode device connected with particles of 1. Heating (red symbol) and cooling (blue symbol) rates are 5 °C/min. (a) Full heating-cooling cycle between 30 and 130 °C under 40 kV/cm electric field. (b, c) Incomplete thermal cycles: cooling from 130 to 80 °C (b) or to 100 °C (c) under 10 kV/cm bias followed by heating back to 130 °C under an electric field of 40 kV/cm. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

registered curves, before, between and after the switches were performed (see Figure S1 in the Supplementary Information, SI). The cycle measured between electrical switches was recorded with a 10 kV/cm electric field, which is sufficient to reveal the SCO phenomena. This aspect will be exploited later. It may be worth to note also that the optical reflectivity signal from the device cannot be used to detect the SCO (for its very weak change), hence only electrical means were used to this aim.

In order to explore the possibility of spin-state switching by an applied electrical field we have stopped the thermal cycling at different temperatures within the hysteresis loop and applied isothermally a voltage bias. In the heating mode we could not observe any significant effect, i.e. we could not induce any LS to HS transition by the electric field. This fact will be treated further in the letter. On the contrary, a clear response to the applied electric field was systematically observed in the cooling mode near