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**Photocurrent phenomena across the bistability region in
[Fe(Htrz)2(trz)](BF4) spin crossover micro-rods †**

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Complete List of Authors:	<p>Lefter, Constantin; CNRS, Laboratoire de Chimie de Coordination / UPR8241; Stefan cel Mare University, Faculty of Electrical Engineering and Computer Science</p> <p>Tan, Reasmey; Universite de Toulouse, INSA, UPS, LPCNO, Dugay, Julien; Universite de Toulouse, INSA, UPS, LPCNO Toulouse, France,</p> <p>Tricard, Simon; CNRS, Laboratoire de Chimie de Coordination / UPR8241</p> <p>Molnár, Gábor; CNRS, Laboratoire de Chimie de Coordination / UPR8241</p> <p>Salmon, Lionel; CNRS, Laboratoire de Chimie de Coordination / UPR8241</p> <p>Carrey, Prof. J.; Universite de Toulouse, INSA, UPS, LPCNO, Rotaru, Aurelian; Stefan cel Mare University, Department of Electrical Engineering and Computer Science</p> <p>Bousseksou, Azzedine; CNRS, Laboratoire de Chimie de Coordination / UPR8241</p>

ARTICLE

Light induced modulation of charge transport phenomena across the bistability region in $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ spin crossover micro-rods †

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Constantin Lefter ^{a,b}, Reasmey Tan ^c, Julien Dugay ^c, Simon Tricard ^a, Gábor Molnár ^a, Lionel Salmon ^a, Julian Carrey ^c, Aurelian Rotaru ^{b*}, Azzedine Bousseksou ^{a*}

We studied the effect of light irradiation on the electrical conductance of micro-rods of the spin crossover $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ network, organized between interdigitated gold electrodes. By irradiating the sample with different wavelengths (between 295 and 655 nm) either in air or under a nitrogen atmosphere we observed both a reversible and an irreversible change of the current flowing in the device. The reversible process consists of an abrupt decrease of the current intensity (ca. 10 – 50 %) upon light irradiation, while the irreversible process is characterized by a slow, but continuous increase in time of the current, which persists also in the dark. These photo-induced processes were only detected in the high conductance low-spin (LS) state of the complex. On switching the rods to the high spin (HS) state the conductance decreases two orders of magnitude (at the same temperature) and - as a consequence - the photo-effect vanishes.

Introduction

Spin crossover (SCO) molecular complexes or extended coordination networks are constituted of $3d^4$ - $3d^7$ transition-metal ions in a pseudo-octahedral coordination sphere. These compounds are known to exhibit bistability of their physical properties (magnetic, optical, mechanical or electric) by the application of different external stimuli (light, pressure, temperature, magnetic field).^{1, 2} The possibility of synthesizing these compounds in a variety of shapes and sizes ranging from nanoparticles to micro-rods, as well as thin films or other nanostructures makes them interesting for a wide variety of applications.³⁻⁵

Investigating the electrical properties of spin crossover molecular materials is of utmost importance for the further development of these systems as bistable molecular micro/nanoelectronic devices. Indeed, since the first reports on the spin-state dependence of the dielectric permittivity⁶ and DC electrical conductivity^{7, 8} of SCO compounds the interest in both theoretical and experimental studies of their electrical properties significantly increased^{9-25, 27-29}

Since the optical properties (absorption and refractive index) are also strongly modified upon the spin transition one can anticipate also very interesting photocurrent phenomena in these materials. Here we report the observation of a photo-

activated process in micrometric rods of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ through the hysteresis region of the thermal spin transition. We observed both a reversible and irreversible effect of light on the current intensity, but only in the high conductance (low spin) state of the complex, apparently because of the very low current intensity in the high spin state.

Results and discussions

Micro-rods of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ SCO compound of ca. 1 μm length and ca. 200 nm width were obtained as previously reported⁸. It is worth to note that we did not use any surfactant for the synthesis of the particles in order to have access directly to the electrical properties of the pure SCO material. The spin transition properties of the powder sample have been verified using variable temperature (5 K/min heating and cooling rates) diffuse reflectivity measurements around 540 nm, since the LS state has significantly higher absorbance in this spectral region. As shown in figure 1a the LS to HS and the HS to LS transitions occur around 110 °C and 66 °C, respectively. These values are in good agreement with previous reports on this compound^{8, 25-28}. (See the Electronic Supporting Information, ESI for sample characterization details, including powder X-ray diffractogram, Raman scattering and infrared absorption spectra).

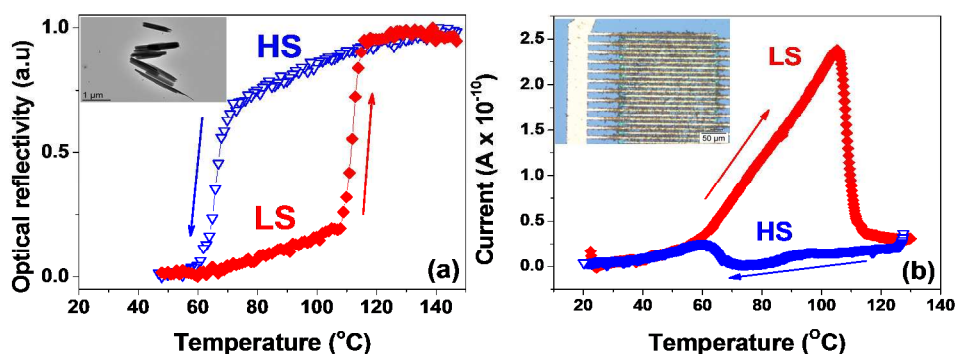


Figure 1. (a) Temperature dependence of the optical reflectivity ($\lambda = 540$ nm) of the powder sample in the heating and cooling modes. The inset shows a TEM image of the micro-rods. (b) Temperature dependence of the current intensity ($U = 20$ V) in the device in the heating and cooling modes. The inset shows the photo of the interdigitated electrode device with the particles.

For electrical measurements the particles were organized between interdigitated gold electrodes using dielectrophoresis as described by Rotaru et al.²⁹. Current-temperature measurements were performed using a Linkam cryostat equipped with two gold-tipped tungsten probes connected to a Keithley 6430 source-meter. The thermal dependence of the current was recorded at a heating/cooling rate of 5 K/min by applying a constant bias (20 V) across the electrodes.

In agreement with our previous results^{8, 28, 29} the conductivity is strongly thermally activated and the LS state is significantly more conductive (figure 1b). The spin transition temperatures (65 °C and 108 °C) inferred from the electrical measurement are in good agreement with the optical data.

The experimental setup used to study the light irradiation effect on our devices is presented in figure 2. It consists of a 100 W Xe lamp, an IR filter, in order to prevent the heating of the sample, and an optical fibre. At the end of the optical fibre we have mounted various optical filters with different wavelengths and a mechanical shutter. The sample was irradiated through the fused silica window of the cryostat and the current was recorded before, during and after the light irradiation at a fixed temperature and a fixed bias.

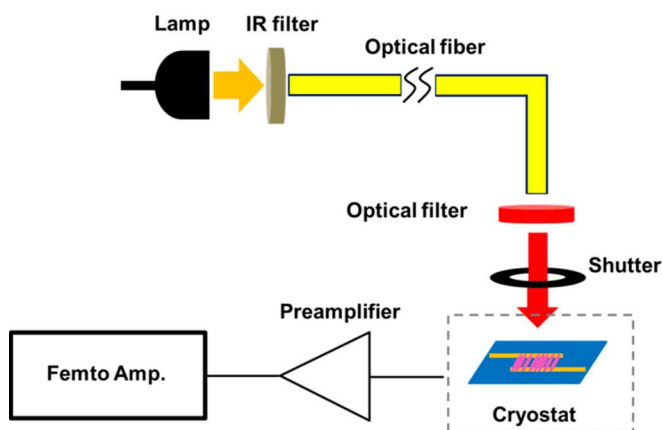


Figure 2. Schematic representation of the experimental setup used for the variable temperature photocurrent measurements.

Typical current-voltage characteristics of the device are reported in figure 3. The I-V curves have been recorded in the LS state at 95 °C both in the dark and under light exposure. In both cases we observe an ohmic response and a lower current intensity (higher resistance) under light irradiation.

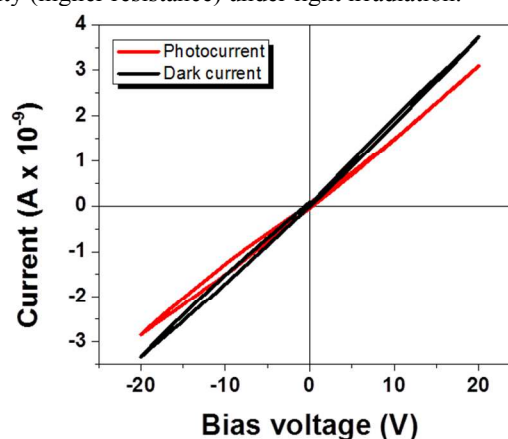


Figure 3. I-V characteristics of the device in dark and under light irradiation (full spectrum) recorded in air at 95 °C in the LS state.

The light effect was studied inside the hysteresis loop at various temperatures, where we exposed the device at different wavelengths for a period of time. Figure 4 shows the typical response of the device at 95 °C both in the heating (LS state) and cooling (HS state) modes. (These experiments have been repeated on several different electrode arrays and for several times on the same electrode array. Similar results were obtained in each case.) Light irradiation in the LS state leads to two distinct effects. On one hand, we observed a reversible photoeffect, which consists in the decrease of the electrical current only while the sample is exposed to light. The percentage of variation depends on the wavelength (see below) and is around 15%. The switching time is relatively long (ca. 15 s). On the other hand, an irreversible photoeffect was also observed wherein the overall current intensity increased with time and persisted also in the dark. Actually, when the light is turned off the current continues to increase for a long period (several tens of minutes). We verified that this slow evolution of the sample is not related to the applied bias, because the same tendency was observed even if the bias was set to zero.

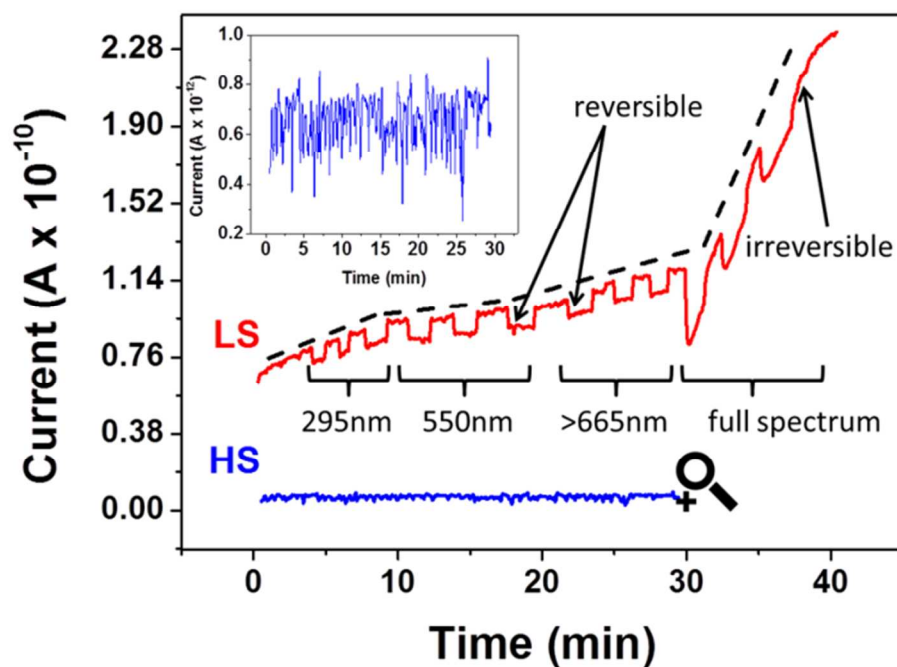


Figure 4. Current flowing in the device under light irradiation (20 V bias voltage). Light was successively turned on and off at different wavelengths - indicated in the figure. All data were recorded at 95 °C in air both in the HS and LS states. The inset shows a zoom of the current in the HS state. In the LS state both reversible and irreversible photoconductivity phenomena are observed. The dashed line is an “eye guide” of the irreversible behavior

We verified also that such current drift does not occur when the sample is kept in dark (see Figure S2 in the ESI). We have repeated these experiments in the same conditions (temperature, light exposure and applied bias) in the HS state as well, but we observed no effect of light (see figure 4). However, the current intensity in the HS state (7 pA) is very low when compared to that in the LS state (~100 pA). Taking into account the measurement noise (~1 pA) we cannot detect reliably small (< 40 %) current intensity variations in the HS state (see Figure S3 the ESI for further explanations). In other words even if there is a light-induced effect in the HS state it might be masked by the noise. We have also investigated the current drop in the LS state under light exposure at other temperatures. Under full spectrum irradiation we obtained 0 %, 4.4 %, 7.5 % and 4.0 % current decrease at 20, 70, 90 and 110 °C respectively (in the LS state). As shown in figure 1b the current in the device is the highest around 95 °C, hence this temperature dependence of the photoeffect indicates its possible correlation with the current intensity. Since the carrier density does not vary much with temperature in this system⁸ this result suggests that the photoeffect is correlated with the mobility of the charge carriers. Figure 4 shows also the influence of the wavelength of the light on the photoeffect (see also Table 1 and Figure S4 in ESI). These wavelengths were selected since the SCO [Fe(Htrz)₂(trz)](BF₄) compound has a strong charge transfer absorption band in the LS state around 280 nm and a ligand-field absorption band around 550 nm, while it has a weak absorption in the near IR (700 – 800 nm) in the HS state. Nevertheless, we could not observe any clear correlation between the current response and the absorption spectra of the complex (figure 4): Apparently in the LS state photoeffects can be generated through the entire UV-visible-NIR spectral range.

Table 1. Light-induced current intensity variation for three consecutive light exposures of different wavelengths and under full spectrum irradiation, recorded in air at 95 °C in the LS state.

Wavelength	295 nm	550 nm	665 nm	Full spectrum
1 st light exposure	12 %	15 %	14 %	55 %
2 nd light exposure	13 %	15 %	16 %	24 %
3 rd light exposure	13 %	15 %	15 %	24 %

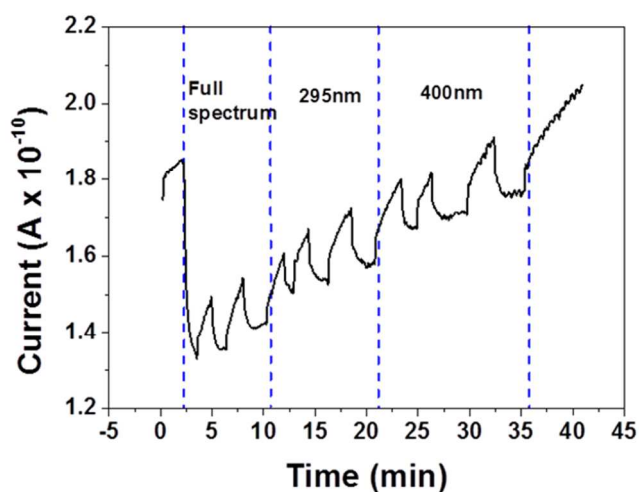


Figure 5. Current flowing in the device under light irradiation in nitrogen atmosphere (20 V bias voltage). Light was successively turned on and off at different wavelengths as indicated in the figure. All data were recorded at 95 °C in the LS state.

A similar behaviour has been observed in dry nitrogen atmosphere as in air, i.e. a reversible decrease of the current during the light irradiation and a continuous irreversible increase of the current (figure 5). However, the decrease in the current magnitude under light was always higher in air atmosphere. As shown in figure 5 the decrease of the current when the device is first exposed to light is significant (28 %) even in nitrogen, but the next on/off switches lead only to a change of about 7 %. These observations indicate that the reversible photoeffect phenomenon might be favoured by the adsorption/desorption of oxygen and/or humidity on the surface of the particles. Somewhat similar findings have been reported in the literature for other materials³⁰⁻³² and explained by oxygen-related surface charge traps. Such surface redox reactions may thus also play a role in the case of our device. We shall also mention that photo-current phenomena in the same SCO compound have been reported by Etrillard et al.²⁵. They investigated particles (ca. 500 nm length and 100 nm width) synthesized using surfactants and reported – in contrast to our results – a room temperature photo-conductance process with a significant increase in the electrical current during the light irradiation. However, no temperature (i.e. spin-state) dependence of the conductance has been reported.

Conclusions

In this work we report the first example of a spin crossover material based electrical device that can be preferential addressed by light stimulation according to its spin state. When [Fe(Htrz)₂(trz)](BF₄) particles in the low spin state are exposed to light we observed a reversible decrease in the current intensity as well as a slow irreversible increase of the current. In the high spin state no effect could be detected in otherwise identical conditions (bias, temperature, light irradiation). These photoeffects seem to be related simply to the mobility of the charge carriers, which increases with increasing temperature and which is significantly higher in the low spin state of the material when compared to the high spin state. The observed light-induced phenomena are also related to some extent to the sample environment as the effects are more pronounced in the presence of oxygen and humidity. Moreover no correlation could be made with the absorption spectrum of the spin crossover compound. These two latter observations point to a possible adsorbate mediated redox mechanism behind the photoeffects. While the underlying mechanism needs further investigations, it is clear that this possibility of turning on and off the photoeffect by switching the spin state of the system (within the hysteresis loop) is a new and promising property of spin crossover devices, which broadens the scope of their future applications.

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Notes

^aLCC, CNRS & Université de Toulouse (UPS, INP), Toulouse, France

^b Faculty of Electrical Engineering and Computer Science & AMNOL, Stefan cel Mare University, Suceava, Romania

^cLPCNO, INSA, CNRS, Université de Toulouse, Toulouse, France

* e-mail : rotaru@eed.usv.ro, azzedine.bousseksou@lcc-toulouse.fr

† Electronic Supplementary Information (ESI) available: sample characterization (Raman, FTIR and XRD spectra) and complementary photocurrent data analysis. See DOI: 10.1039/b000000x/

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