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Pulsed-Laser Switching in the Bistability Domain of a Cooperative Spin Crossover Compound: A Critical Study through Calorimetry

M. Castro^{+,}, O. Roubeau⁺, L. Piñero-López[#], J. A. Real[#], J. A. Rodríguez-Velamazán^{+,§}*

⁺Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC and Universidad de Zaragoza, Spain; [#]Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, 46980 Paterna, Valencia, Spain; [§]Institut Laue-Langevin, 38042 Grenoble Cedex 9, France

AUTHOR INFORMATION

Corresponding Author

Tel: 00-34-976762528

Fax: 00-34-976761957

*E-mail: mcastro@unizar.es

1
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3 ABSTRACT
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6 The photo-switching from low spin (LS) to high spin (HS) state and the reverse process in the
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8 bistability domain of spin crossover compounds (SCO) is a promising function to be used in
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10 molecular electronic devices, evidenced mainly through spectroscopy. The phenomenon, and in
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12 particular its mechanism, is however still under debate since some controversial experimental
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14 results have been reported. Here we present a calorimetric experimental study of the photo-
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16 switching of the [Fe(pyrazine)Pt(CN)₄] SCO material by a nanosecond-pulsed green laser. Our
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18 results confirm single laser pulse of varying energies result in significant LS to HS
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20 transformations and show that calorimetry provides an accurate quantification of the overall
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22 conversion. Successive pulses allow increasing the conversion, achieving a maximum of 60%
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24 under our experimental conditions. The HS to LS transformation is on the other hand not induced
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26 at any laser fluences contrary to previous reports. The results are compared with those reported
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28 with Raman spectroscopy and critically discussed in terms of efficiency of the transformation
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30 and potential thermal effects.
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38 **KEYWORDS** Spin Transition; thermal analysis; photo-induced transitions; iron compounds;
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40 porous coordination polymers.
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3 INTRODUCTION
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5 The control of the magnetic properties of molecular compounds by external stimuli, including
6 temperature, light, pressure, electric or magnetic field is an important scientific topic spurred on
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8 by envisaged uses in molecular spintronics as memory storage, transistors and switching devices.
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12 ¹ Among these switchable magnetic materials, Fe^{II} spin crossover (SCO) compounds^{2,3} are one of
13 the most interesting systems, due the spin transition between a diamagnetic low spin state (LS, S
14 = 0) and a paramagnetic high spin state (HS, $S = 2$), associated with changes in various physical
15 properties (optical, electrical and structural), induced by an external perturbation. The well-
16 studied switching induced by light, so-called Light-Induced Excited Spin State Trapping
17 (LIESST),⁴ is however limited to low temperatures by the thermally-activated relaxation of the
18 metastable trapped HS state. Recently, a novel approach has been considered to obtain photo-
19 induced reversible spin state switching at higher temperature; it contemplates irradiation within
20 the bistability domain of SCO materials with a large thermal hysteresis loop, characteristic of the
21 presence of a first-order transition. In such conditions, the light-trapped species are expected to
22 be stable, as long as the system is maintained within the bistability conditions. A few promising
23 reports demonstrating the validity of the approach have already been published. The first
24 experimental result was obtained measuring the optical reflectivity of the [Fe(PM-BiA)₂(NCS)₂]
25 compound (PM-BiA = N-2'-pyridylmethylene-4-aminobiphenyl), for which a large stationary
26 photo-induced HS fraction ($\alpha = 0.6$) was produced within the thermal hysteresis loop from the
27 initial LS state by a single green laser nanosecond-pulse.⁵ Neither larger HS fractions, through
28 additional pulses, nor the reverse switching, attempted with various wavelengths and fluences,
29 could however be obtained. In the SCO complex [FeL(CN)₂] \cdot H₂O (L = N₃O₂ Schiff-base
30 macrocyclic ligand) the photo-excitation from a HS:LS (1:1, $\alpha = 0.5$) mixture state to $\alpha \approx 0.88$ of
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3 HS species was produced using a single-shot laser pulse and monitored through absorption
4 spectra.⁶ This work evidenced the existence of threshold values both in wavelength and in laser
5 fluence to trigger the photo-excitation. The mechanism in this specific system however likely
6 involves a change in coordination number and is thus not a simple SCO process. Several papers⁷⁻
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9 on the [Fe(pz)Pt(CN)₄] SCO compound (pz = pyrazine) used Raman spectroscopy to monitor the effect of the light excitation. In this case and for a polycrystalline powder sample, bidirectional photo-induced process (LS to HS and HS to LS) was obtained using the same nanosecond-pulsed green laser.⁷ Photo-switching from the LS state was probed at several temperatures within the hysteresis loop reaching a HS fraction of $\alpha = 0.2$ for a single laser pulse and 0.4 after a second pulse was applied. Surprisingly, no further increase in HS fraction was detected with additional pulses, while a quite large laser fluence of 250 mJ/cm² was used. In a later study⁹ a 100% conversion could be reached using a much lower laser fluence of at least 20 mJ/cm², with a threshold value of around 5 mJ/cm². On a polycrystalline powder sample, the reverse transformation could only be produced from a HS-LS mixture state (with an initial LS fraction of 0.3).⁷ On the other hand, a complete bidirectional photo-excitation was obtained on single-crystals, again using the same nanosecond-pulsed green laser.⁸ In this case, the HS to LS phase transformation was achieved from a full HS state and using a low laser fluence (≈ 5 mJ/cm²) that had no effect in the case of the polycrystalline sample. The photo-excitation within the hysteresis loop can also be performed using a continuous laser irradiation as shown by Raman spectroscopy with a complete LS to HS conversion of the [Fe(H₄L)₂](ClO₄)₂·H₂O·2(CH₃)₂CO SCO compound (H₄L = 2,6-bis(5-(2-hydroxyphenyl)pyrazol-3-yl)pyridine).¹⁰ Single-pulse photo-switching was also attempted in triazole-based 1D polymeric spin crossover compounds.¹¹ In [Fe^{II}(Htrz)₂(trz)](BF₄) (Htrz = 1-H-

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3 1,2,4-triazole) a bidirectional switching, i.e. LS to HS and HS to LS, was detected through
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5 Raman spectroscopy by pulsed green irradiation at the same wavelength but only when the
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7 excitation was done at temperatures close to the ascending (378 K) and descending (351 K)
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9 branches of its large thermal hysteresis loop.¹² No effect could however be detected when the
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11 excitation was performed at temperatures in the centre of the hysteresis loop.
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15 In all these experimental reports the sample heating due to the irradiation was considered to
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17 have no significant effect on the detected phenomenology, although some unexplained aspects
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19 such as the reversibility of the process using an identical wavelength for which drastically
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21 different absorption densities are detected in the HS and LS states or the necessity to be close to
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23 (or even within) the thermal phase transition for realizing the switching may originate in
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25 thermally-related effects. These would mostly result from a local (surface) over-heating, over a
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27 very short time-scale and thus difficult to detect, and include a thermally-induced LS to HS
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29 transformation due to sufficient heating or a thermally-induced HS to LS transformation
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31 resulting from the response of temperature control to local heating. The former has indeed more
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33 recently been proposed as the origin of the impossibility to perform the HS to LS phase
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35 transformation in $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$, whatever the wavelength and fluence used,¹³ as well as
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37 the main source of laser-induced switching in the SCO compounds $[\text{Fe}(\text{NH}_2\text{-trz})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$
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39 and $[\text{Fe}(\text{NH}_2\text{-trz})_3](\text{Br})_2 \cdot 3\text{H}_2\text{O}$.¹⁴⁻¹⁶ In these latter studies, the authors used time-resolved optical
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41 reflectivity data, thus accessing only the surface response, and considered huge local heating.
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43 Additionally, a large local temperature gradient will produce a heat transfer to the rest of the
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45 material increasing its temperature until a common temperature is reached when thermal
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47 equilibrium is obtained with the surrounding. This has in fact been directly observed with Raman
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49 microscopy with micro-scale spatial resolution, showing a LS to HS conversion outside the
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3 irradiated region in $[\text{Fe}^{\text{II}}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$.¹⁷ Although performed on a non cooperative Fe^{III} SCO
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5 compound, time resolved single-crystal optical and X-Ray diffraction studies actually revealed
6
7 for the first time a multistep process including photo, elastic and thermal-induced phenomena
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9 occurring at different timescales.^{18,19} Recently, the same research group has also detected these
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11 consecutive three steps on a cooperative Fe^{III} SCO compound^{20,21} (excitation was performed on
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13 the LS state but outside of the thermal hysteresis loop) and they conclude that a strong response
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15 in this case is mainly due to the temperature increase caused by the laser excitation which allows
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17 the sample to surpass its spin transition temperature where the abrupt conversion to HS state
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19 happens. Eventually, the dynamics of the growing or contraction of laser induced initial HS
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21 domains and the related accommodation strain is very likely to play a role.²²
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27 Altogether, and although there is no doubt single-laser pulse in the bistability domain of
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29 cooperative SCO materials does induce LS to HS phase transformations, the true mechanisms for
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31 both LS to HS and HS to LS transformations clearly remain disputable. In this respect, it should
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33 be noted that all reports so far have been based solely on (local) spectroscopic methods. Bulk
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35 structural, magnetic and thermal studies remain clearly necessary to understand, improve and
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37 apply the observed phenomena. In this work, we report the first calorimetric study of the laser-
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39 induced switching within the bistability domain of a SCO compound. We focus on the spin
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41 crossover $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ compound with its spin crossover around room temperature, and test
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43 both the LS to HS and HS to LS phase transformations, seeking confirmation of the pulsed-laser
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45 switching phenomena and additional insights towards their understanding.
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EXPERIMENTAL METHODS

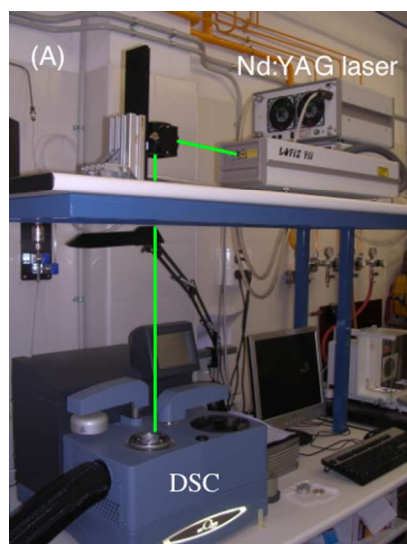
Synthesis and sample description

A microcrystalline powder (PP) and mono-crystalline (SC) (ca. 40-80 microns) samples of the dehydrated form of the spin crossover compound [Fe(pyrazine)(Pt(CN)₄)] were obtained as previously described.²³ Both samples show orange color at room temperature indicative of a HS state. An aged PP sample (APP) taken from the same batch but after one year stored in a plastic bag at room temperature has been also used in some calorimetric experiments.

Experimental calorimetric set up

A differential scanning calorimeter (DSC) model Q1000 from TA instruments equipped with a liquid nitrogen cooling system (LNCS) in order to reach low temperature has been used. The irradiation of the sample was performed keeping open the oven and using the photo-calorimetric commercial accessories (PCA) that allow illuminating the sample inside the oven while it is under the helium gas atmosphere. In order to remove traces of water molecules possibly absorbed from air moist, the sample was submitted to an initial thermal treatment at 140°C during 30 min inside the DSC oven and under Helium gas atmosphere before proceeding with the calorimetric measurements. Irradiation was done when the calorimeter was operating in the isothermal mode, that is, the instrument was set to maintain constant the selected temperature ($T_{\text{irradiation}}$). Thermograms (cooling and heating) were performed at a scan rate of 10 K/min. The sample masses were 1.10, 0.87 and 0.97 mg for PP, APP and SC samples respectively. The sample was spread on the aluminium pan (6 mm of diameter) and covered by a thin fused silica plate in order to avoid the loss of material. A pulsed Nd³⁺: YAG laser (LOTIS TII LS-2134U) operating at 532 nm with a pulse width of 7-8 ns was used as the excitation source. The spot size is 6 mm allowing the irradiation of the complete aluminium pan and therefore the whole sample.

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3 All this photo-calorimetric system is shown in Figure 1. In order to estimate the laser fluence
4 (mJ/cm²), graphite powder (mass around 0.1 mg) was used as a good absorbing sample so the
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6 whole pulse energy is converted into heat. It was also spread on the pan as a thin film and
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8 covered by the fused silica plate, and the DSC heat flow peak, required for keeping constant the
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10 temperature after the laser pulse, was determined. Results are shown in Figure S1 included in the
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12 Supporting information.
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36 **Figure 1.** Experimental photo-calorimetric set up.

37 38 39 **Additional magnetic, spectroscopic and structural characterization**

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41 Magnetic measurements on SC sample were performed with an MPMS-XL SQUID
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43 magnetometer from Quantum design in the 200 - 340 K temperature range and under 1 Tesla
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45 applied field. The SC sample was warmed to 140°C for 30 min in a desiccator, before performing
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47 magnetic measurements.
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51 Single-crystal X-Ray diffraction was performed at 310 and 240 K on the SC sample using an
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53 Oxford Diffraction Xcalibur diffractometer with enhanced Mo K α radiation ($\lambda = 0.71071 \text{ \AA}$) at
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55 the X-ray and Fluorescence Analysis Service of the Servicio General de Apoyo a la
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3 Investigación-SAI, Universidad de Zaragoza. Cell refinement, data reduction and absorption
4 corrections were performed with the CrysAlisPro suite.²⁴ The structure was solved with SIR97²⁵
5 and refined on F^2 with the SHELXTL suite.^{26, 27}
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10 The visible absorption spectra of a powder sample near room temperature has been obtained for
11 both LS and HS state by diffuse reflectance and using a Jasco V-60 UV/Vis/NIR
12 spectrophotometer equipped with PIV-756/PIN 757 horizontal sampling integrating sphere
13 system.
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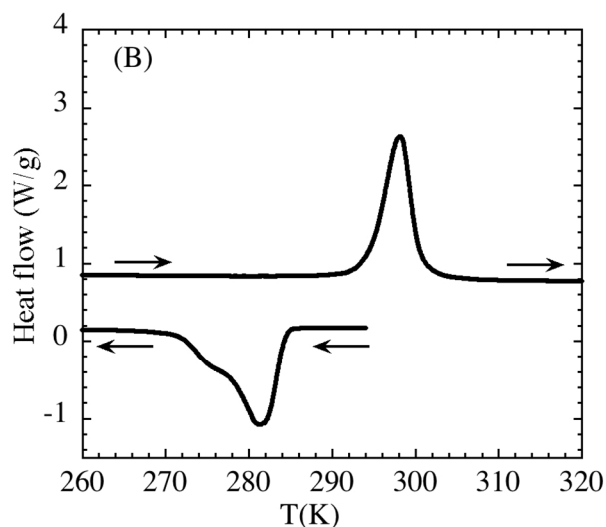
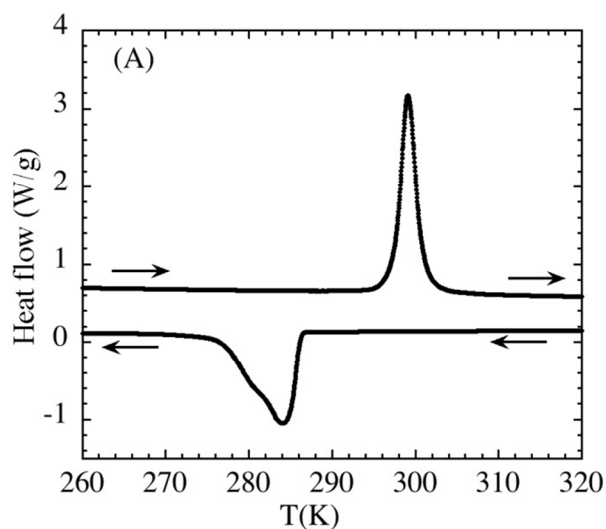
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18 The corresponding results provided in the supporting information, are in agreement with
19 previously reported data, and support the spin transition as detected through DSC.
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23 24 25 26 27 RESULTS AND DISCUSSION

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29 The three-dimensional porous coordination network [Fe(pz)Pt(CN)₄] was first reported in 2001
30 in its hydrated form²³, that exhibits a hysteretic SCO with $T_{1/2, \text{cooling}} = 220$ K and $T_{1/2, \text{heating}} = 240$
31 K. ($T_{1/2}$ being the temperature at which HS and LS states have equal populations). Removal of
32 the lattice solvent water molecules by heating to 120-130 °C for 30 min results in dehydrated
33 [Fe(pz)Pt(CN)₄] (**1**), which is stable when kept in a dry atmosphere, and only slowly reabsorbs
34 water from air moist. Dehydration can be done on single crystals without loss of crystallinity,
35 and results in a shift of the hysteresis towards higher temperature. Polycrystalline powders and
36 single-crystals of **1** or partially re-hydrated **1** have very similar SCO properties with a large and
37 rather abrupt hysteresis centred on room temperature; only slight variations of the transition
38 temperatures have been reported, values of $T_{1/2, \text{cooling}}$ ranging 283-291 K and $T_{1/2, \text{heating}}$ ranging
39 305-311 K, with an hysteresis width of 24 to 28 K.^{7,8,23,28} This compound has been extensively
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3 studied and a collection of interesting properties has been reported like the chemoswitching²⁹
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5 between HS and LS states and molecular rotation correlated with the change of the spin state.³⁰
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8 The thermograms, i.e. heat flow vs. temperature scans, obtained at 10 K/min are represented in
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10 Figure 2 for the studied PP (Figure 2A), APP (Figure 2B) and SC (Figure 2C) samples of
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12 [Fe(pyrazine)(Pt(CN)₄)] respectively. These measurements are fully reproducible and depict the
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14 first order spin transition exhibited by this compound. Temperatures corresponding to the
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16 maximum of the peaks together with their enthalpy and entropy contents are gathered in Table 1.
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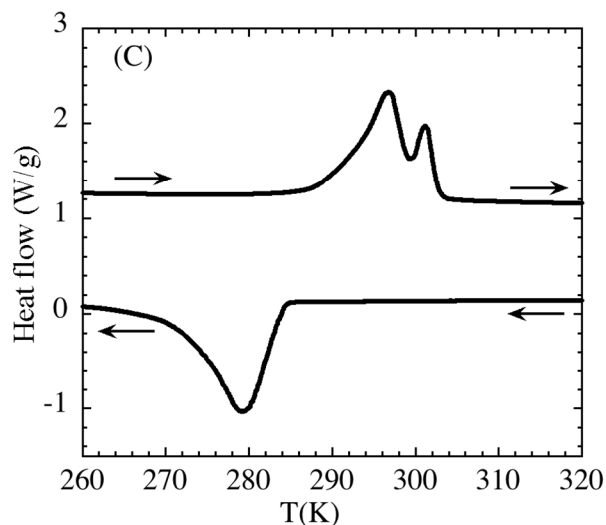


Figure 2. Heating and cooling thermograms for: (A) Microcrystalline powder (PP) sample, (B) aged microcrystalline powder (APP) sample and (C) Mono-crystalline (SC) sample.

Table 1. Characteristic temperatures and thermodynamic contents for the three studied samples of **1**, as determined from calorimetric measurements.

Sample	T_{heating} (K)	$\Delta H_{\text{heating}}$ (kJ/mol)	$\Delta S_{\text{heating}}$ (J/mol K)	T_{cooling} (K)	$\Delta H_{\text{cooling}}$ (kJ/mol)	$\Delta S_{\text{cooling}}$ (J/mol K)	$T_{1/2, \text{heating}}$ (K)	$T_{1/2, \text{cooling}}$ (K)
PP	299.1	19.3	66	283.9	20.5	75	299.2	282.4
APP	298.1	21.3	72	281.3	22.8	82	297.6	279.8
SC	296.2/301.2	21	72	279.2	23	84	296	277.8

The three samples show strong but rather broad anomalies on cooling, corresponding to the HS to LS transition, while on heating, for the LS to HS transition, a sharper peak is detected for the PP sample and the SC sample presents two sharp overlapped peaks. The peaks for the APP sample are broader and shifted to slightly lower temperatures. The hysteresis width of SC sample is around 20 K, similar to that for the polycrystalline samples (15-17 K). Critical temperatures are in the low temperature range of the previously reported temperatures on **1**. Magnetic

measurements (see supporting information, Figures S2 and S3) performed on the SC sample are in agreement with the calorimetric data. Additionally, single-crystal X-Ray diffraction on the SC sample confirmed the previously reported structure, with no significant trace of re-absorbed lattice water molecules (see supporting information, Table S1 and Figure S5), and Fe-N bond lengths characteristic of HS and LS state respectively at 310 and 240 K. For the three samples, the presence of significant amounts of re-absorbed water can be discarded since the spin transition occurs at higher temperature than the fully hydrated sample.^{7,16}

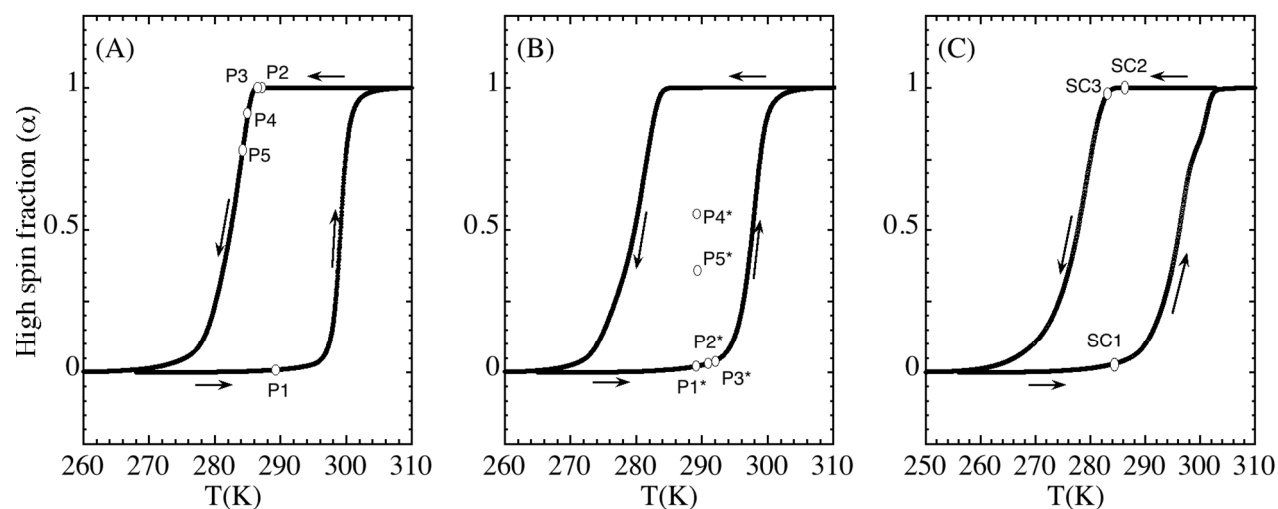


Figure 3. Thermal hysteresis loops for: (A) PP sample, (B) Aged PP sample (APP) and (C) SC sample. Irradiation temperatures ($T_{\text{irradiation}}$) for each sample are marked in the respective hysteresis loop and correspond to: 289.15 K (P1, P1*), 291.15 K (P2*), 293.15 K (P3*) and 284.15 K (SC1) for the case of LS to HS excitation while excitation at 287.15 K (P2), 286.65 K (P3), 285.15 K (P4), 284.15 K (P5), 286.15 K (SC2) and 283.15 K (SC3) was done for the HS to LS one. For APP sample, excitation was also performed at 289.15 K (P4* from heating branch, P5* from cooling branch) when starting from a mixed HS/LS state.

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Figures 3A, 3B and 3C show the thermal hysteresis loops determined from our calorimetric measurements after subtracting the appropriate baselines for the PP, APP and SC samples respectively. The HS fraction, $\alpha(T)$, has been obtained as the ratio between the enthalpy content of the anomaly, $\Delta H(T)$, calculated by integration of the excess heat flow as temperature increases and the enthalpy content of the complete transformation, that is $\Delta H_{\text{heating}}$ for the LS \rightarrow HS case and $\Delta H_{\text{cooling}}$ for the HS \rightarrow LS one. Critical temperatures, $T_{1/2, \text{heating}}$ and $T_{1/2, \text{cooling}}$ determined from these hysteresis loops for the three samples are collected in Table 1.

Irradiation experiments were performed using 532 nm laser pulses of varying fluences at temperatures $T_{\text{irradiation}}$, depicted in Figures 3A, 3B and 3C, chosen to have similar temperature differences with respect to the characteristic temperatures ($\Delta T = T_{1/2}^{\text{heating}} - T_{\text{irradiation}}$ or $T_{\text{irradiation}} - T_{1/2}^{\text{cooling}}$) as in the relevant reported works⁷⁻⁹ in order to allow comparison.

Let us first describe, following the example for the PP sample shown in Figure 4A, the experimental procedure for the photo-excitation of the LS species in order to induce the HS state. After cooling down from room temperature to a low enough temperature (253 K for PP and APP samples and 243 K for the SC sample) to reach a complete transformation to the LS state (a), the sample is heated up to $T_{\text{irradiation}}$ inside the hysteresis loop (b) (for example P1, P1* and SC1 point in Figure 3A, 3B and 3C respectively, then the sample is still fully LS) and this temperature is maintained constant (c). During this isotherm, a single laser pulse (or several of them) is applied to the sample. Figure 4A shows the case of a single laser pulse applied at 8 min with a laser fluence of 27 mJ/cm². A peak on the heat flow is clearly detected corresponding to the response of the calorimeter in order to keep a constant temperature against the effect of the laser pulse that disturbs this isothermal step (see rectangular box in Figure 4A). Finally, the thermogram is recorded on cooling (d) and an anomaly, centred at around T_{cooling} , is detected corresponding to

the conversion of HS species to LS state (see circle in Figure 4A and thick line in Figure 4B) thus providing direct evidence that HS species have been produced by the laser pulse.

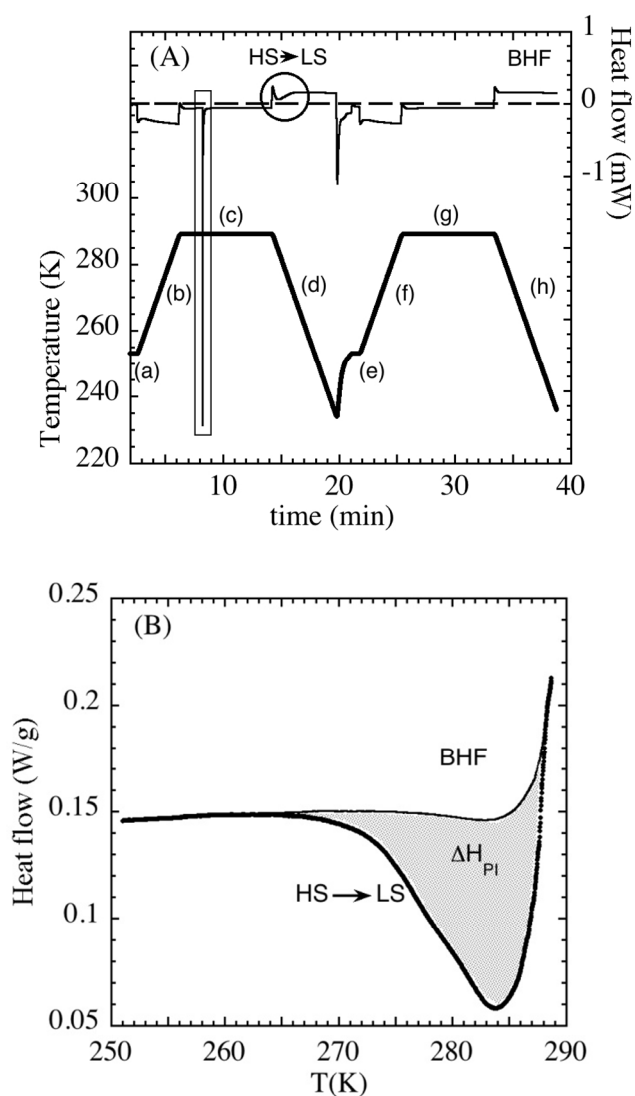


Figure 4. (A) Example of the programmed temperature profile (thick line) and heat flow (thin line) during the experimental procedure, as explained in the text, in order to perform photo-excitation of the LS state. The dashed line represents heat flow equal to zero. Rectangular box: Peak on the heat flow corresponding to the response of the calorimeter in order to keep the sample temperature constant when the laser pulse is applied. Circle: Calorimetric anomaly corresponding to the conversion of the photo-induced HS species to LS state. (B) Process

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3 followed (see text) to deduce the enthalpy content of the anomaly, ΔH_{PI} , needed to estimate the
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5 HS fraction induced by the irradiation. The thick line is the calorimetric anomaly corresponding
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7 to the conversion of the photo-induced HS species to LS state and the thin line is the background
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9 heat flow (BHF).
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13 To determine the HS fraction produced by the irradiation, α , defined here as the ratio between
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15 the enthalpy content of the anomaly, ΔH_{PI} , and the enthalpy content of the complete HS \rightarrow LS
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17 transformation $\Delta H_{cooling}$ (Table 1), a baseline must be subtracted. This background heat flow,
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19 BHF, indicated in Figure 4A and shown in Figure 4B (as a thin line) together with the anomaly
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21 for the case of a laser fluence of 27 mJ/cm^2 , is obtained subjecting the sample to the exact same
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23 thermal history (see Figure 4A: e-f-g-h) but without the application of the laser pulse. The excess
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25 heat flow (Δ Heat flow) after subtracting the corresponding baseline and for the different
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27 irradiation experiments performed at 289.15 K (100% LS state corresponding to point P1 in
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29 Figure 3A) is shown in Figure 5A for the PP sample together with their enthalpy contents.
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31 Similarly, excess heat flow for the case of the APP (for P1* in Figure 3B) and SC (for SC1 in
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33 Figure 3C) samples are shown in Figure S6 and S7 respectively.
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40 The results for the three samples are summarized in Figure 5B where α versus the laser fluence
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42 is represented and $\Delta T = 10 \text{ K}$, 8.5 K and 12 K for the PP, APP and SC samples respectively. The
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44 available data from previous studies on **1** using Raman spectroscopy are gathered on the same
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46 scale to allow proper comparison.
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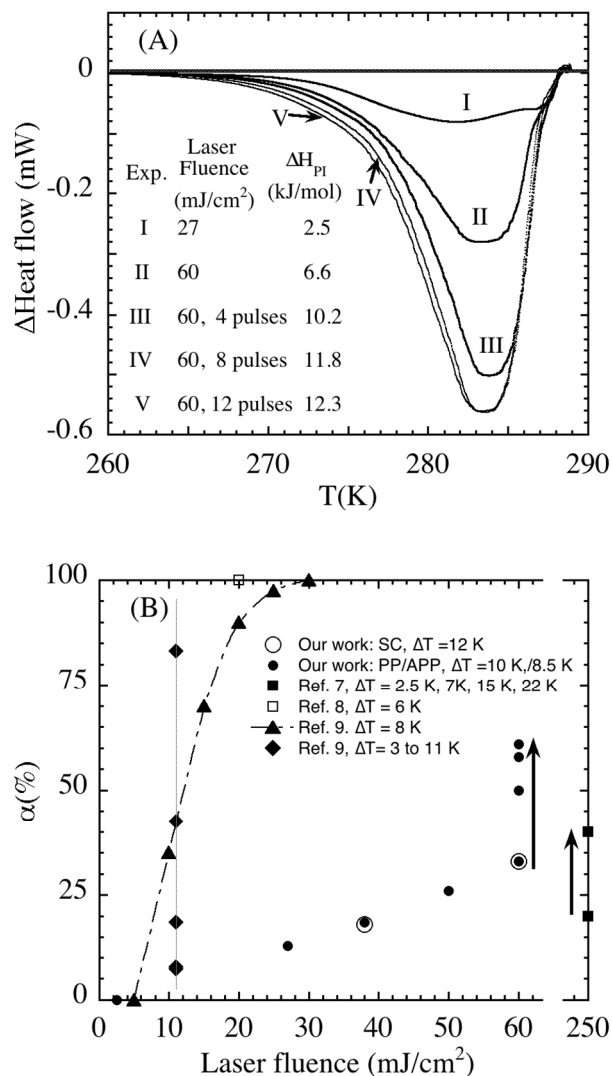


Figure 5. (A) Calorimetric anomalies for the PP sample after irradiation at 289.15 K (P1, 100% LS state). Excess heat flow ($\Delta\text{Heat flow}$) after subtracting the corresponding background heat flow (BHF) for two laser fluencies (27 (I) and 60 (II) mJ/cm²) and also for the case of 4(III), 8(IV) and 12 (V) consecutive pulses of 60 mJ/cm². (B) HS fraction induced by irradiation versus laser fluence on the compound 1. Experimental results from literature are also represented for comparison (see text). Arrows indicate the HS fraction increase when several laser pulses are applied consecutively.

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3 For the PP sample, no excitation is detected for a laser pulse of around 2.5 mJ/cm^2 , but α
4 reaches 0.13 and 0.33 for 27 and 60 mJ/cm^2 respectively with a good reproducibility.
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6 Consecutive pulses of 60 mJ/cm^2 allow increasing the photo-induced fraction up to a saturation
7 value of 0.60, for 12 successive pulses. Irradiation of the APP sample with pulses of 38, 50 and
8
9 60 mJ/cm^2 resulted in slightly less efficient transformations than for the PP sample (ca. 30%, see
10 Figure S6), but these data, scaled to the PP values at 60 mJ/cm^2 , actually follow the exact same
11 trend as shown in Figure 5B where scaled data are depicted. The results for the SC sample are
12 comparable since for 38 and 60 mJ/cm^2 , α is 0.18 and 0.33 respectively (see supporting
13 information, Figure S7). In order to check the consistency of our results, α has been additionally
14 determined, for the latter case, by measuring a heating thermogram instead of a cooling one,
15 since the calorimetric anomaly due to the transition from LS to HS after the irradiation must be
16 smaller than the case without light excitation (see supporting information, Figure S8). In this
17 case, α gives 0.28, in agreement with the value obtained using the cooling procedure, 0.33.
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22 The photo-induced HS fractions obtained here are comparable to the first reported results with
23 a polycrystalline sample⁷ where from the LS state and after irradiation with one single laser pulse
24 with very large fluence of 250 mJ/cm^2 ($\Delta T = 2.5 \text{ K}$), a HS fraction of 0.2 has been reached, 0.4
25 after a second pulse is applied. In our case, a laser fluence of only $40\text{-}60 \text{ mJ/cm}^2$ is required to
26 reach a converted HS fraction of 0.2-0.3, and successive pulses improve the overall conversion
27 to 0.60. On the contrary, in the original work, no further increment of the HS fraction was
28 produced by additional pulses, but similar results were obtained with $\Delta T = 7, 15$ and 22 K
29 performing the excitation with 10 successive pulses.⁷ However, the same group later reported a
30 complete photo-conversion^{8,9} for both polycrystalline ($\Delta T = 8 \text{ K}$) and single crystal ($\Delta T = 6 \text{ K}$)
31 samples from the LS to the HS states using a single pulse and with only laser fluences above 20
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3 mJ/cm² and with a threshold value of 5 mJ/cm². Our experiments performed at 2.5 mJ/cm² agree
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5 with the presence of a threshold but do not reproduce this complete photo-conversion. A possible
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7 explanation may lie in the larger thickness of our polycrystalline sample since the radiation may
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9 not reach the whole sample and therefore cannot completely excite it.¹⁸ Another source of
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11 discrepancy may come from the determination of the laser fluences, which we determined here
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13 in-situ using the calorimeter (see Supplementary Information), while it is not described in the
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15 related reports.⁷⁻⁹
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20 Another aspect relevant to the efficiency of the transformation lies in possible heating effects
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22 associated with the laser pulse and the energy deposited in the sample, as well as the thermal
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24 control of the used set-up during the photo-irradiation experiments. In fact, a large transient
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26 temperature jump, ΔT_h , may occur, at least locally, and some authors have estimated it to be of
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28 some tens of degrees, therefore allowing to claim that heating mechanism plays a key role in the
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30 LS to HS conversion.^{16,18,19,21} Even in the case of a bistable system, such a transient temperature
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32 incursion may be large enough to allow the sample to reach or surpass the ascending branch of
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34 the hysteresis. To assess this possibility in our case, let us roughly evaluate the maximal
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36 transformed fraction, i.e. considering the minimal necessary ΔT_h , assuming the photo-induced
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38 effect is solely thermal and the whole pulse energy is invested to increase the temperature of the
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40 sample. Of course, this also has to involve the energy required to convert the LS species into HS
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42 ones and thus the total enthalpy associated with the transformation, $\Delta H_{\text{heating}}$, (see Table 1) a term
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44 particularly important due to the first order character of the spin transition. This contribution has
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46 not been considered by some authors^{16,21} for the estimation of the temperature jump for first
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48 order spin transition and only the heat capacity term, enough in the case of second order
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50 transition^{18,19,21}, has been used. In our case, for a single pulse with a laser fluence of 60 mJ/cm²
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3 applied at 289.15 K, the total amount of energy reaching the sample is $E = 17$ mJ, assuming that
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5 the sample is spread uniformly on the aluminium capsule (area = $\pi \cdot 0.3^2 = 0.283$ cm²). For the PP
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7 sample, a ΔT_h of 11 K would be sufficient to result in a full LS to HS transformation and
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9 $\Delta H_{\text{heating}} = 44.34$ J/g (see Table 1 and using 435.3 g/mol as molecular mass). Then considering a
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11 mean value of the heat capacity for this compound³¹ in the 270-320 K temperature range
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13 (excluding the transition temperature range) as $C_p = 0.378$ J/gK and the simple relation $E =$
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15 $m^* \cdot C_p \cdot \Delta T_h + m^* \cdot \Delta H_{\text{heating}}$ gives $m^* = 0.35$ mg, that is at most 32% of the total PP sample mass
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17 ($m = 1.10$ mg) would be transformed with one laser pulse. At first the fact this estimated
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19 transformed fraction is close to the observed one, 33%, seems to indicate a dominant role played
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21 by thermal effects. However, the calculation is made, neglecting optical transformation, and most
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23 of all without considering any heat transfer to the thermal bath, nor to the rest of the sample. A
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25 detailed evaluation of these effects requires analysing a complex thermal model, a task that is
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27 beyond this study. In our case, the heat transfer to the thermal bath is particularly relevant since
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29 the sample is in relatively good thermal contact with large masses of metallic parts (mainly the
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31 aluminium pan and also the sample support of the DSC oven), in addition maintained at constant
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33 temperature by the set-up. Actually, due to the laser pulse, only a small perturbation of the
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35 measured temperature well below 0.5 K is detected by the thermocouple located in the sample
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37 support and in contact with the bottom of the aluminium pan. This means that a significant
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39 fraction of the energy deposited in the sample by the laser pulse will not be invested in
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41 increasing the sample temperature. The typically low thermal conductivity of coordination
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43 compounds³² also means that the propagation of the temperature increase within the sample will
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45 be slow, and thus allow for heat losses to the environment. Eventually, any portion of the sample
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47 suffering a smaller ΔT_h will either transform only partially (if reaching the warming branch of
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3 the hysteresis loop) or not at all. Altogether, it therefore appears evident that the observed
4 transformation of 33% can by no means be solely due to heating effect. This statement is also
5 supported by the fact that similar transformed fractions are obtained when irradiating with a laser
6 pulse of 60 mJ/cm² the APP sample at different temperatures (P1*, P2* and P3*, that is $\Delta T =$
7 8.5, 6.5 and 4.5 K respectively), while an increase would be expected upon reducing ΔT (i.e.
8 performing the excitation closer to $T_{1/2, \text{heating}}$) if the heating-induced mechanism would be
9 dominant. Additionally, the saturation effect obtained using several pulses can be also explained
10 by absorption and not only by thermal effects.¹⁵ Due to the fact the LS state has a higher
11 absorption than the HS state for the excitation wavelength (see Figure S4), and as the LS species
12 at the particle/sample surface decrease, the penetration increases and more HS species could be
13 photo-induced until a saturation is reached when the intensity is reduced by the HS state
14 absorption and no further excitation of LS can be induced. Therefore, while there is for sure
15 some heating effect involved, it appears that the LS to HS conversion within the thermal
16 hysteresis of [Fe(pyrazine)Pt(CN)₄] is not the (sole) result of a local heating due to the laser
17 pulses used, in line with previous affirmations.⁷⁻⁹ Altogether our results are in agreement with the
18 original data of ref 7, but differ with the later reported results by the same authors (see Figure
19 5B) on the same compound⁹ and with those on [Fe(PM-BiA)₂(NCS)₂] and [Fe(NH₂-
20 trz)₃](NO₃)₂·H₂O compounds^{5,15} where an increase of the high spin fraction as the excitation
21 temperature increases has been determined. These discrepancies are striking, although a number
22 of experimental conditions, some difficult to control or compare, may have a non-negligible
23 effect, such as the material composition and properties, sample characteristics (crystallinity,
24 crystallite size) or the thermal contacts and temperature controls.
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3 We have also investigated the excitation inside the hysteresis loop from the HS state using the
4 same type of irradiation. In this case, the sample was cooled from room temperature (HS state)
5 down to a temperature (P2-P5 in Figure 3A for PP sample, and SC2, SC3 for SC sample in
6 Figure 3C) where the compound is still in the HS state or presents a HS-LS mixture state. Once
7 the temperature is stable and controlled by the calorimeter, a laser pulse is applied to induce LS
8 species. Subsequently, a heating thermogram is performed in order to detect a calorimetric
9 anomaly due to the conversion of these LS species to a HS state. Because the energy of the pulse
10 seems to be crucial in order to induce LS species, i.e high energetic pulses were not suitable to
11 photo-induce them from the HS state because heating of the sample competes against the photo-
12 excitation,⁸ we first performed the experiments using a low laser fluence of around 2.5 mJ/cm².
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14 As an example, Figure 6 shows one of these experiments performed in the PP sample. After the
15 irradiation at P2 (see Figure 3A), only a very small anomaly is detected in the subsequent heating
16 thermogram at around 300 K in agreement with the expected temperature range if some amount
17 of LS species was induced and these were converted into HS species. However when the same
18 experiment is performed without the application of the laser pulse, the calorimetric anomaly also
19 appears with comparable enthalpy content, indicating that the LS photo-induced fraction is
20 negligible. Similar result has been obtained for the SC sample when irradiation was performed at
21 SC2 (see Figure 3C and supporting information Figures S9-S10).
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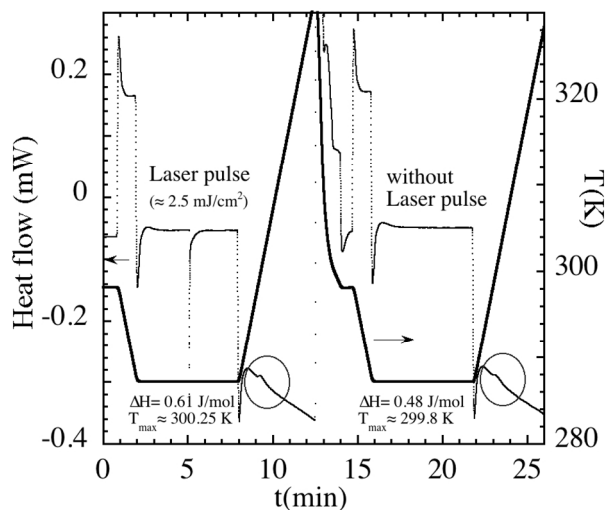


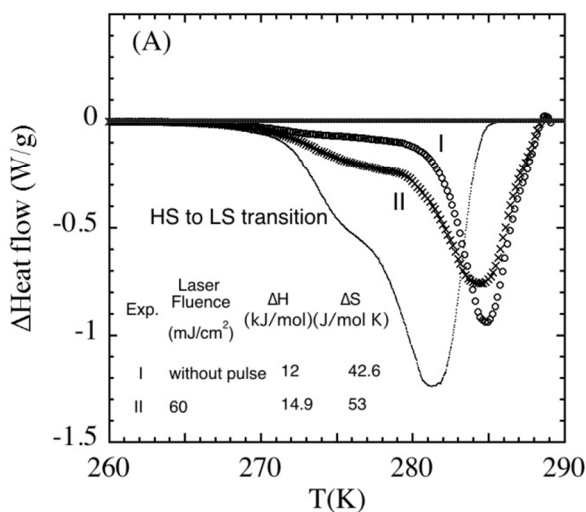
Figure 6. Calorimetric experiments corresponding to the irradiation at 287.15 K (P2) on PP sample using a low laser fluence (2.5 mJ/cm^2). Sample has been subjected to the same thermal history with and without irradiation. Similar anomaly is obtained in the subsequent heating indicating that no photo-induced LS species are produced.

This behaviour is in disagreement with ref. 8 where a complete HS to LS switch was induced. On the other hand, our results do agree with those reported in ref. 7 (our experimental conditions are similar to the experiment corresponding to point H of Figure 5 in this reference) where no excitation of LS species has been obtained from the HS state. The same behaviour has been obtained for the irradiation at P3, P4, P5 and SC3 (see supporting information, Figures S11-S15) where the excitation is performed in a LS-HS mixture state. This result also disagrees with ref 8, since when the irradiated state is a mixture of LS and HS species and a low power laser pulse is used some amount of photo-induced LS species is obtained. The fact that the enthalpy content of the detected calorimetric anomalies (equal with and without laser pulse) are larger as the temperature of irradiation is lower supports the thermal origin for these anomalies and reflects the conversion of the pre-existing LS species at the irradiation temperature to the HS state. The

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3 use of large energetic pulses (16, 27 and 60 mJ/cm² at P3, P4 and SC2 respectively) was also
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5 tested but does not allow inducing a detectable amount of LS species. The present calorimetric
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7 study therefore evidences that no HS to LS optical conversion can be obtained as the result of
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9 nanosecond-pulsed green laser irradiation, in agreement with the absence of absorption band in
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11 this range of wavelengths. The previously detected presence of LS species under similar
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13 conditions most likely arises from thermally converted centres due to the closeness of the
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15 experiment temperature to the thermal conversion. Here, it is interesting to note that Hauser et al
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17 have recently produced an efficient HS to LS switching (reverse-LIESST) in in the vicinity of
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19 the thermal transition of the [Fe(ptz)₆](BF₄)₂ spin crossover compound (ptz = 1-propyl-tetrazole)
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21 using an adequate wavelength of 830 nm, and unravelling the role of ligand-field states in the
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23 ultrafast photophysical cycle of this specific compound.³³
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29 In order to evaluate the influence of the initial state on the LS to HS excitation process,
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31 experiments were repeated starting from a thermally induced HS/LS mixed state instead of a full
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33 LS state. For this, the APP sample is first heated from the LS state up to 298.15 K reaching a
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35 HS/LS mixed state with $\alpha = 0.6$ according to the hysteresis loop (Figure 3B). After the sample
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37 temperature is decreased down to 289.15 K (P4* in Figure 3B), a pulse of 60 mJ/cm² is applied,
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39 and a thermogram is performed on cooling, allowing the corresponding anomaly to be recorded.
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41 The experiment following the same thermal history, but without the application of the pulse, has
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43 also been performed for comparison. The results are shown in Figure 7A together with the peak
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45 corresponding to the complete HS → LS transition. Without pulse, an anomaly centred at 285 K
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47 is obtained with a low temperature tail down to 270 K. The peak is significantly shifted to higher
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49 temperature than the peak corresponding to the complete HS → LS transition in agreement with
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51 the expected behaviour when a minor loop is followed, and thus consistent with the formation of
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independent domains.³⁴ Additionally, considering the enthalpy content we can estimate a high spin fraction of 0.56 in agreement with the expected value at 298.15 K from the heating branch of the hysteresis loop. The excitation changes the profile of the peak increasing the tail and decreasing the contribution at higher temperature. In this case, we can evaluate $\alpha = 0.69$, then an increase of 0.13 has been induced by the irradiation which is lower than the value obtained by the same pulse performed on the 100% LS state and at the same temperature. The same experiment was repeated with 4 pulses and again the profile of the peak was modified showing a larger tail at low temperature corresponding to a prominent peak and a decrease of the peak at high temperature with a maximum temperature shifted to lower temperature. The HS fraction increase was only 18 % smaller than the 50% achieved from the 100% LS state.



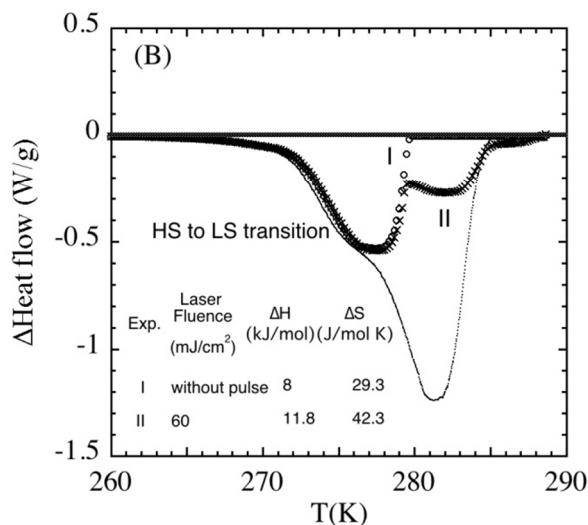


Figure 7: Anomalies (crosses) obtained on cooling after excitation with a laser pulse of 60 mJ/cm² at 289.15 K from a HS/LS mixed state reached, as it is explained in the text, from the 100% LS (A) and 100% HS (B) state. The complete HS to LS transition (small dots) and the anomalies obtained following the same thermal history but without laser pulse (open circles) are also shown for comparison (see text).

We have then performed the same type of experiment but creating the HS/LS mixed state from the pure HS, i.e. by cooling the sample from the HS state down to 280.15 K ($\alpha = 0.55$ from the cooling branch of the hysteresis loop in figure 3B), then heating up to 289.15 K (P5* in Figure 3B), irradiating with a laser pulse of 60 mJ/cm², and recording a thermogram on cooling. The same thermal process was repeated but without the application of the pulse in order to have a reference baseline. The latter, shown in Figure 7B, presents an anomaly starting at around 280 K as expected and matches perfectly the low temperature part of the peak corresponding to the complete HS to LS transition. This anomaly corresponds to the final conversion of the remaining HS species. Considering its enthalpy content (Figure 7B), the converted HS fraction was 0.35, lower than the expected value of 0.55. This can be due to a relaxation process of the HS centres

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3 to the ground LS state, similar to the case of the $[\text{Fe}(\text{H}_4\text{L})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot 2(\text{CH}_3)_2\text{CO}$ SCO
4 compound.¹⁰ Irradiation modifies this anomaly, shown also in Figure 7B, and a new peak appears
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6 at the high temperature side and also reproduces the peak obtained without the application of the
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8 pulse. Both anomalies are perfectly delimited by the peak corresponding to the 100% HS to LS
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10 transition. The mixed HS/LS state reached corresponds to $\alpha = 0.52$, then the increase due to the
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12 irradiation is 0.17 which is slightly higher than the HS fraction increase from the HS/LS mixed
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14 state reached through the heating branch but still significantly lower than the value reached from
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16 the full LS state corresponding to $\alpha = 0.26$. However, when the excitation is performed at the
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18 same temperature on a similar HS/LS mixed state obtained previously by irradiation (P1 in
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20 Figure 3A and after four pulses a HS fraction of 0.5 is reached from the 100%LS state close to
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22 the previous thermally induced mixed HS/LS state) the increase of the HS fraction by four
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24 additional consecutive pulses was only 0.08. It thus appears that irradiation from a thermally
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26 induced mixed HS/LS state from either HS and LS state is less efficient than from a pure LS
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28 state but more efficient than from a similar mixed HS/LS state reached by irradiation.
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39 CONCLUSIONS

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41 In summary, the optical switching from LS to HS state of the $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ SCO material
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43 through single and multiple green ($\lambda = 532$ nm) nanosecond-laser pulse(s) has been confirmed
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45 and accurately evaluated using calorimetry, a complement to the Raman spectroscopy only
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47 results previously reported. A maximum conversion of 60% has been obtained by successive
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49 pulses, likely limited by the penetration depth of light within the sample/crystallites. Besides, the
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51 results seem to indicate that, although thermal effects may be present, the LS to HS
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53 transformation is not the sole consequence of such effects. On the other hand, the reverse
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3 transformation, HS to LS, previously reported to be induced at the same wavelength, has not
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5 been observed, and evidence is given here that such transformation is likely the result of thermal
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7 effects and/or relaxation of the HS species, due to the closeness of the temperature experiments
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9 to the cooling branch of the thermal SCO hysteresis. Finally, conversion starting from a
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11 thermally induced LS/HS mixed state is found to be less efficient than from a pure LS state,
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13 however the mixed LS/HS state is created, i.e. either from the pure HS or LS state although more
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15 efficient than from a similar mixed LS/HS state obtained by irradiation. This work highlights the
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17 great potential of photo-calorimetry to study switching of cooperative SCO materials within their
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19 bistability domain.
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33 AUTHOR INFORMATION

34 35 **Corresponding Author**

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41 **Notes**

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43 LPL and JAR synthesized the materials. JARV, OR and MC realized the experiments. The
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45 manuscript was written by OR and MC with contributions from all authors. All authors have
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47 given approval to the final version of the manuscript. The authors declare no competing financial
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49 interests.
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52 53 54 **ACKNOWLEDGMENT**

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20 calorimetría del Instituto de Ciencia de Materiales de Aragón (ICMA).
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34 ASSOCIATED CONTENT

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37 **Supporting Information Available:** Determination of the laser fluences. Temperature
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39 dependence of the magnetic properties of the SC sample of **1**. Visible absorption spectra of
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41 powder sample for the LS and HS state. Crystallographic data and refinement details of **1** at 310
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43 and 240 K. Selected calorimetric experiments with irradiation. This material is available free of
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45 charge via the Internet <http://pubs.acs.org>.
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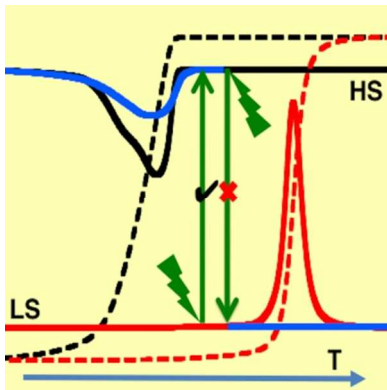
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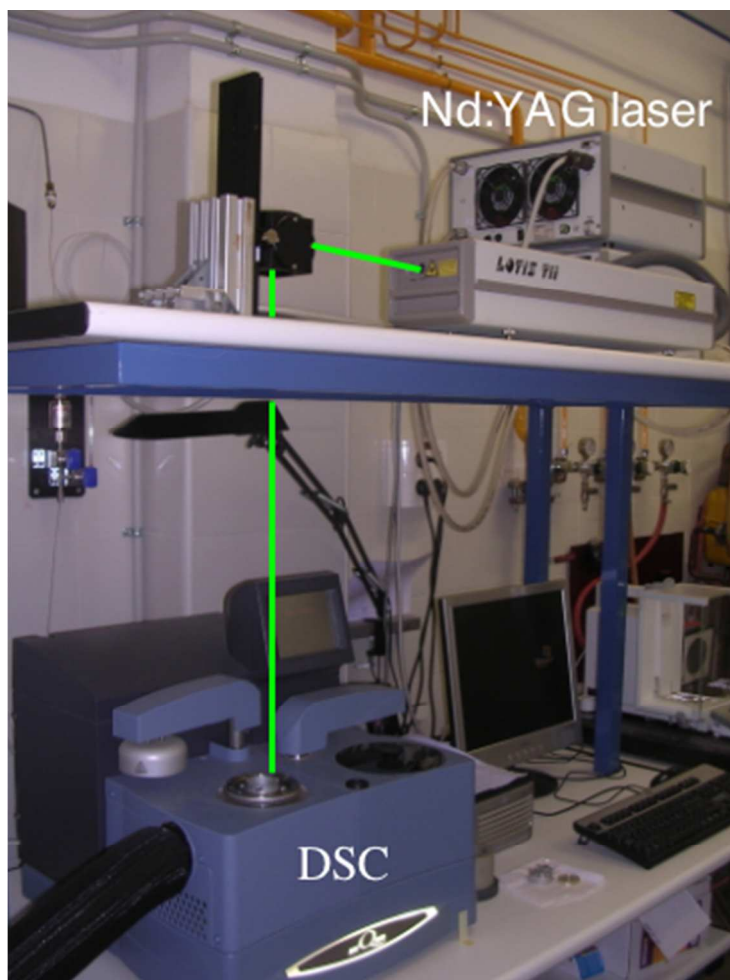
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TOC GRAPHICS

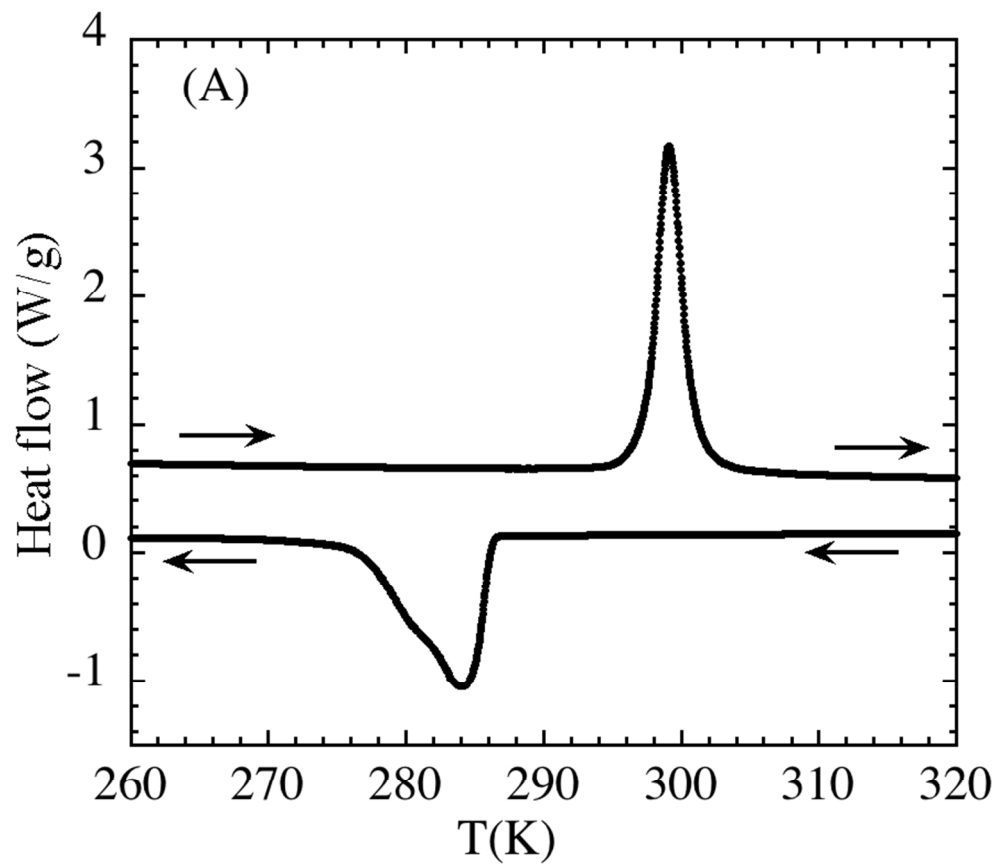


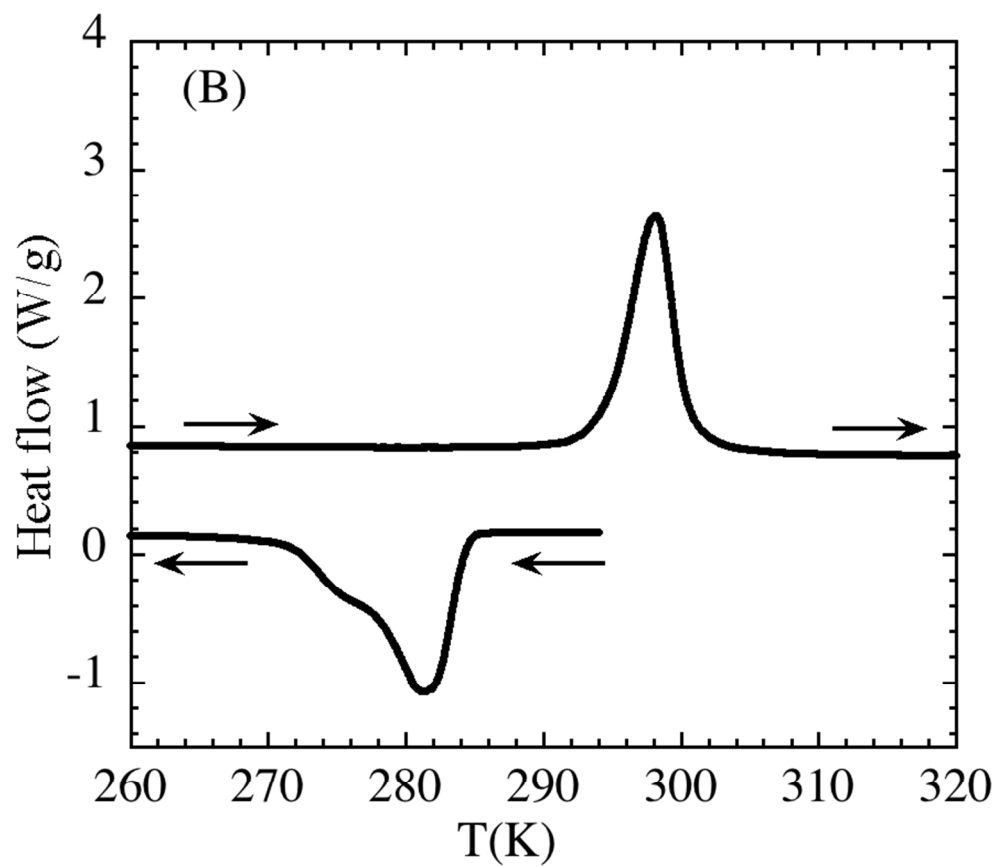
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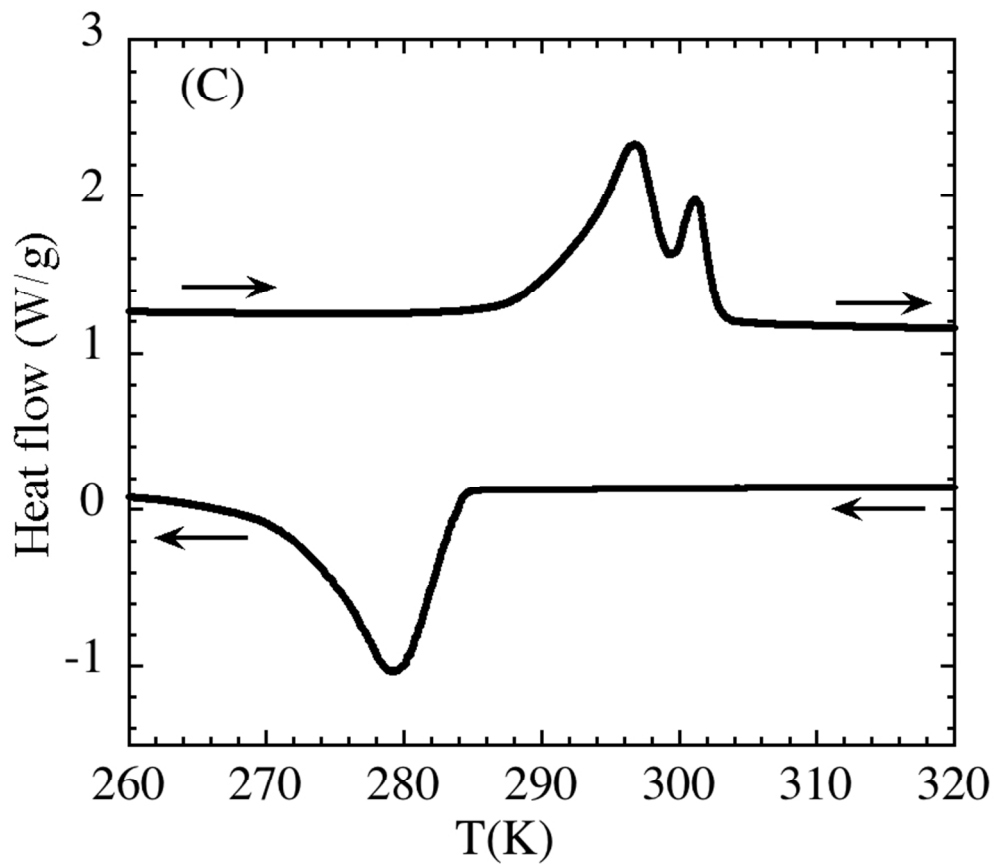


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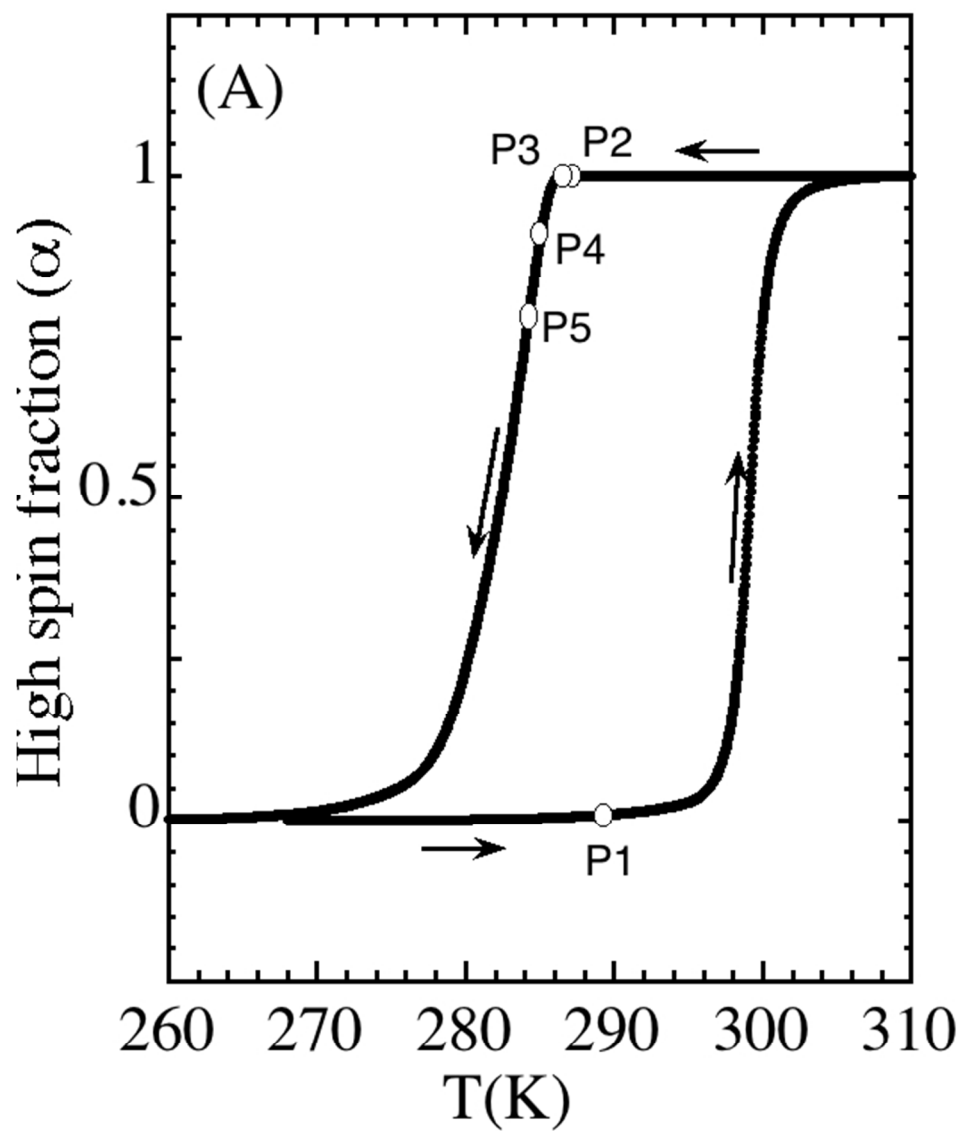




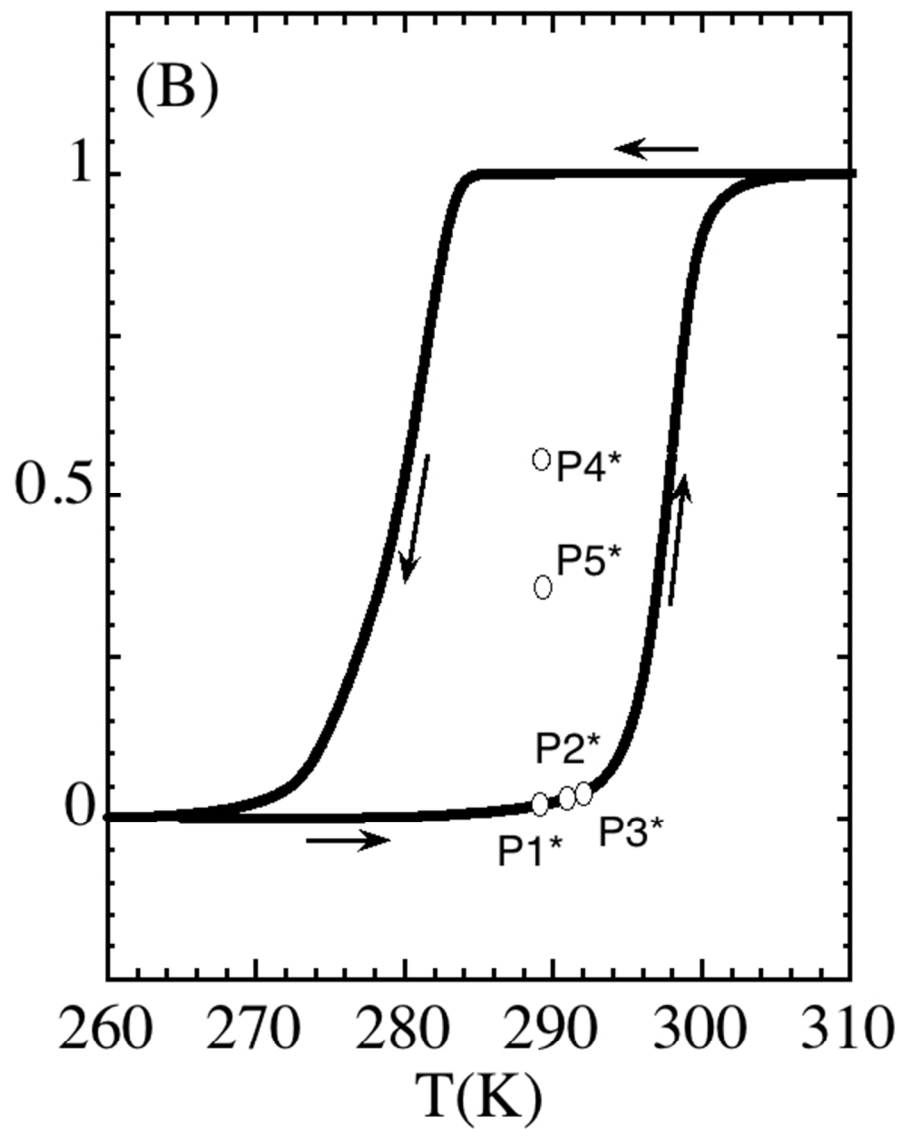
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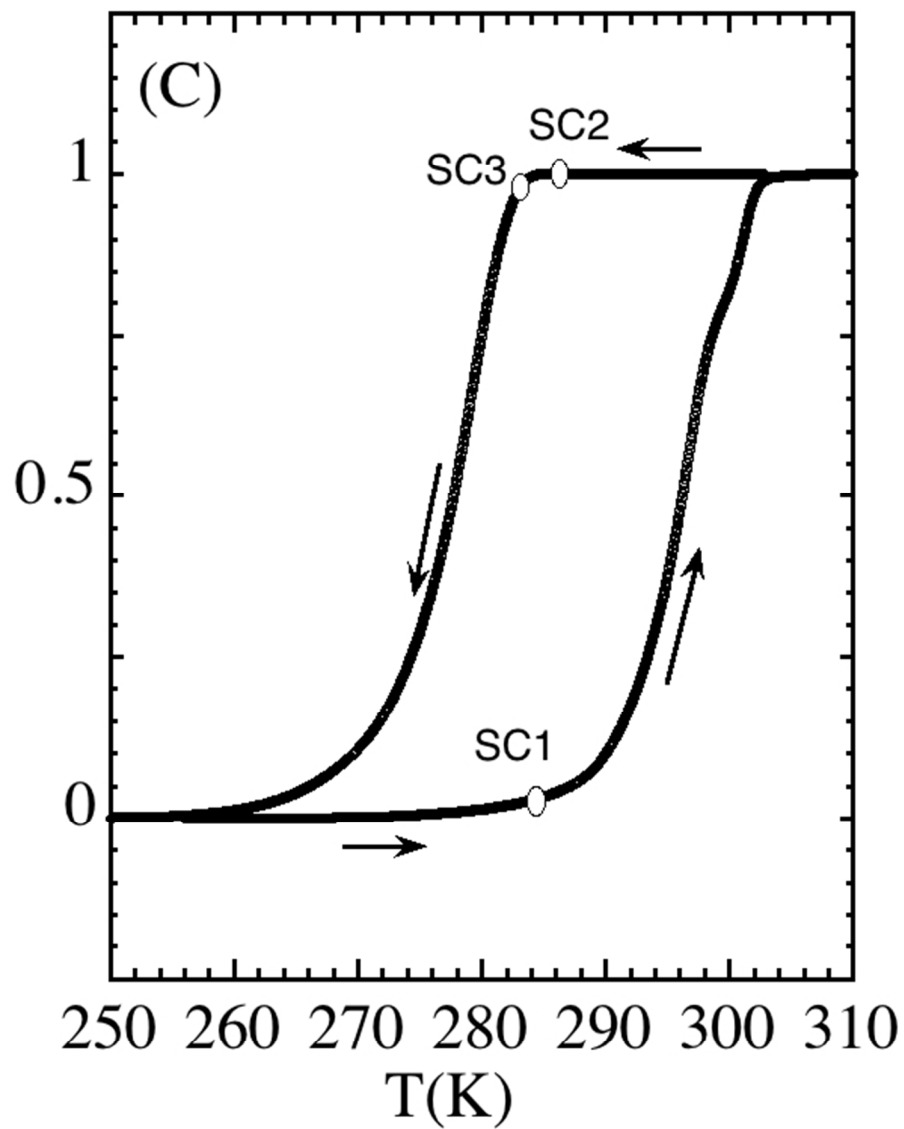


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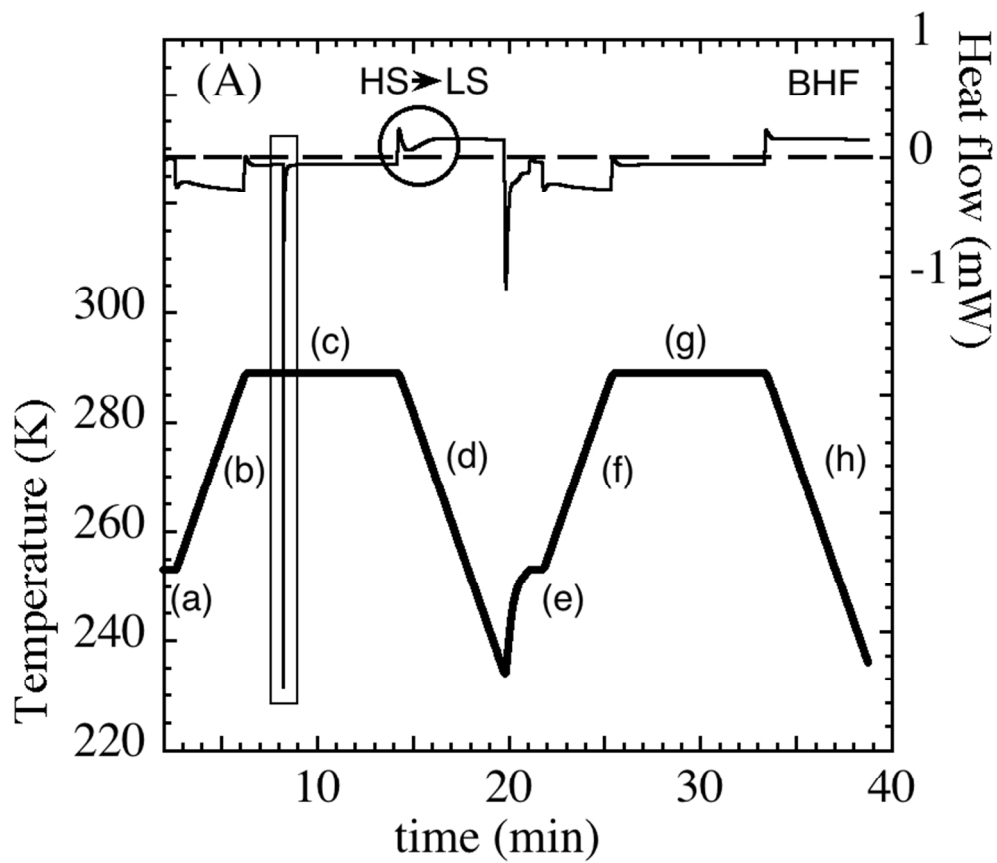


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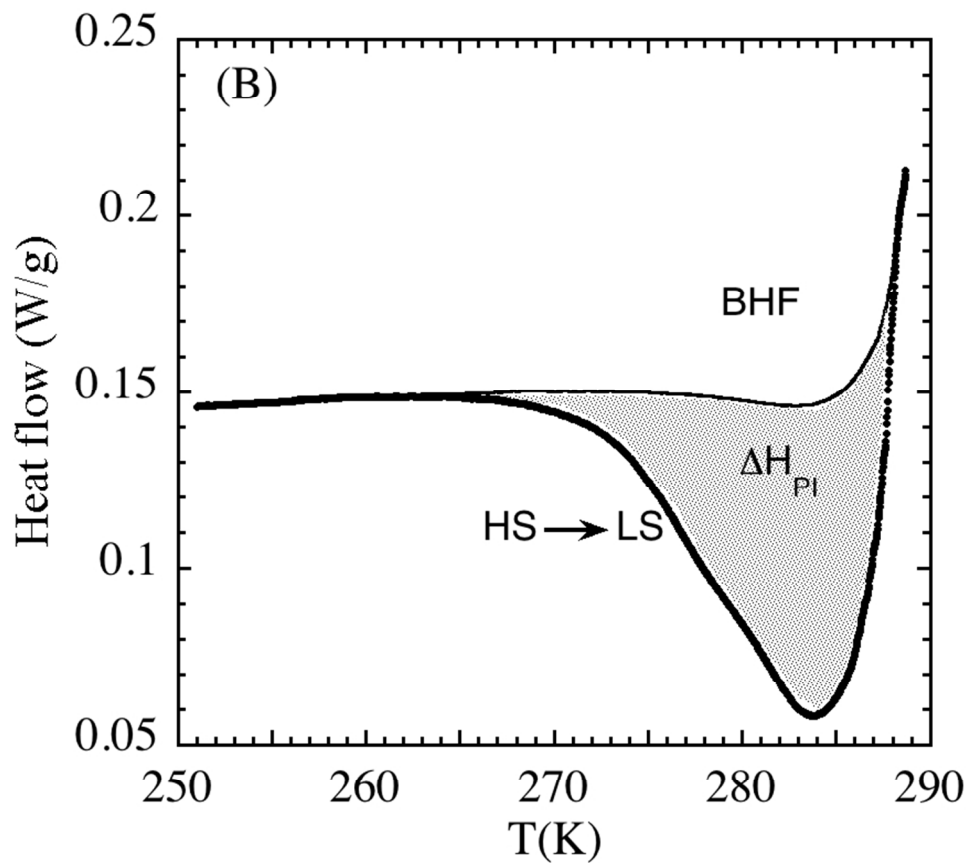




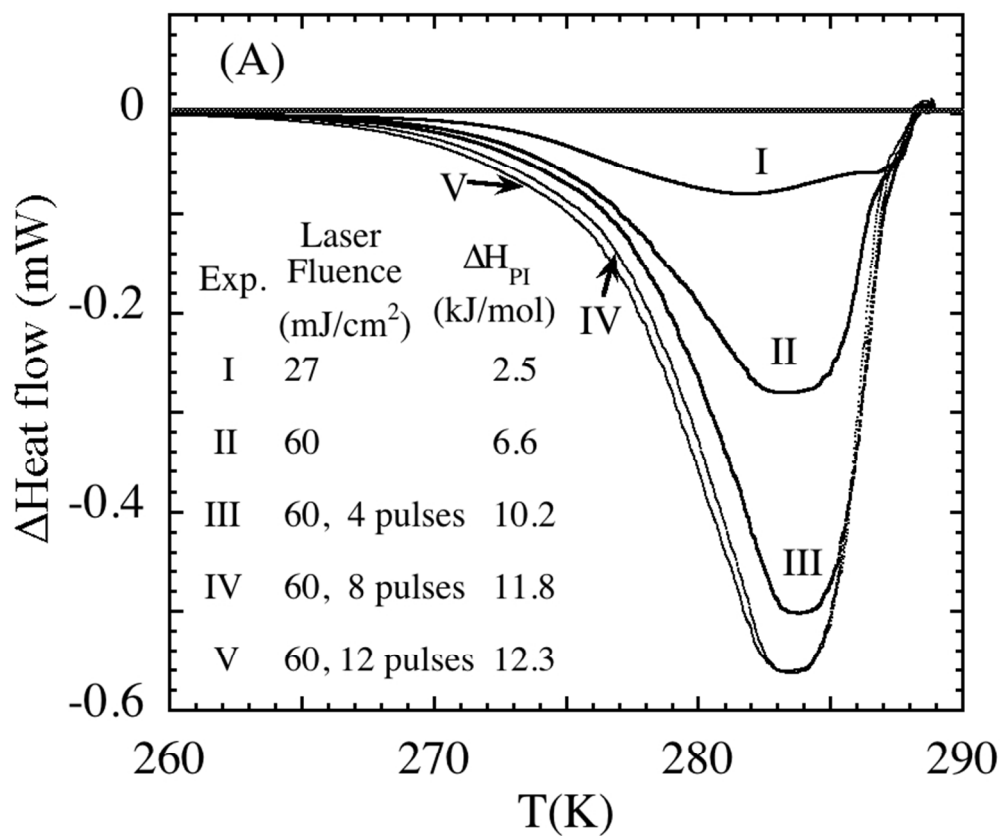
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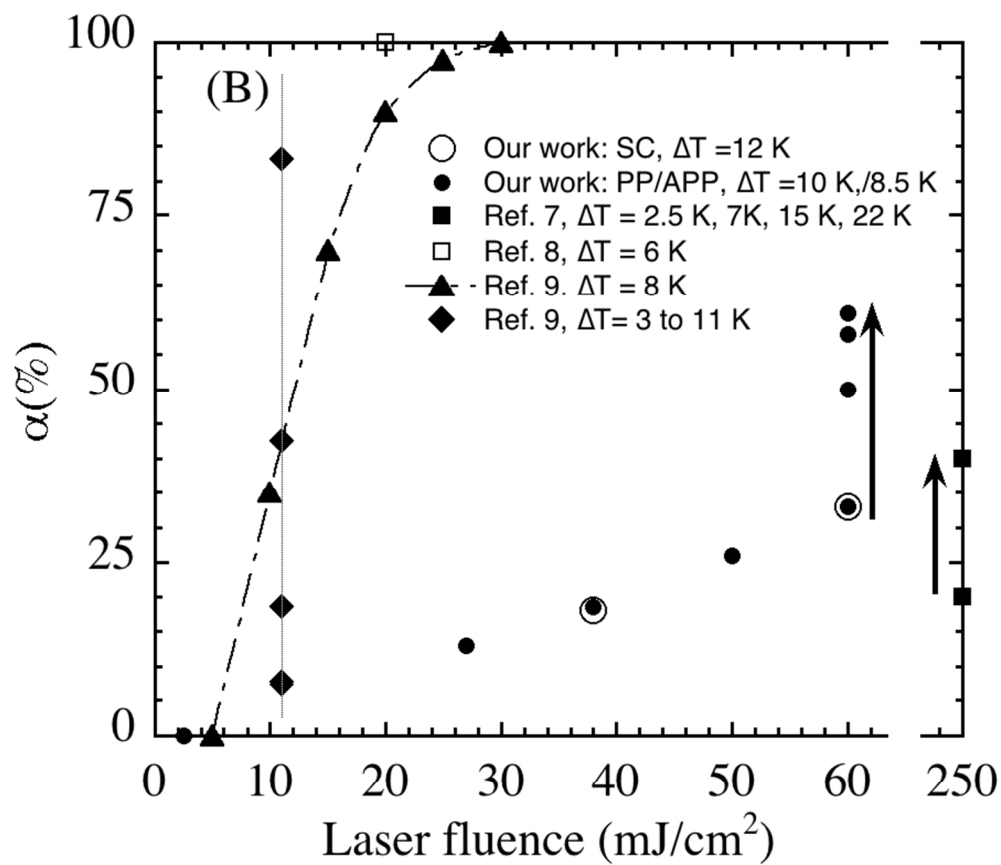


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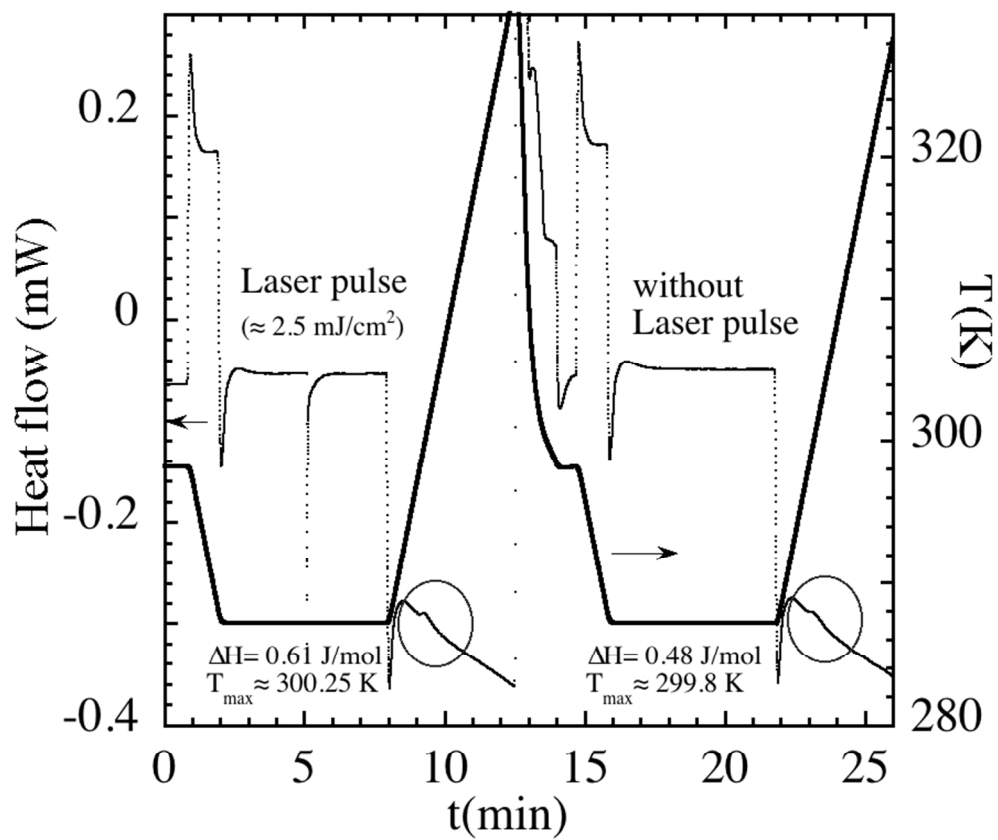


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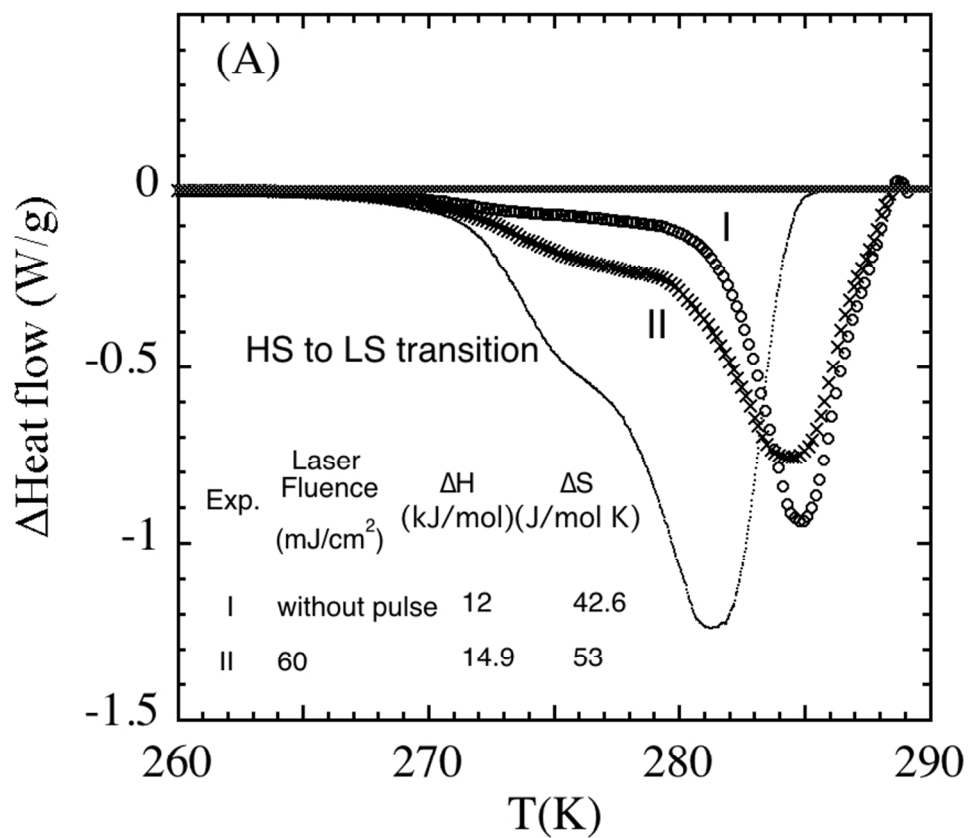




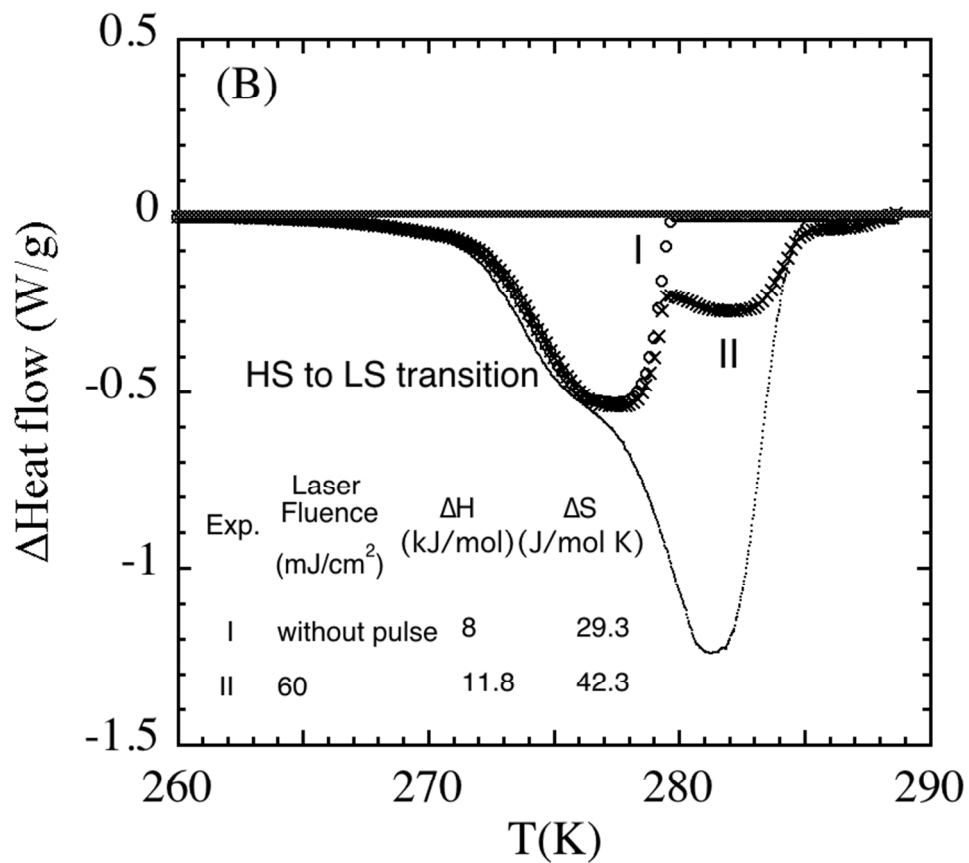
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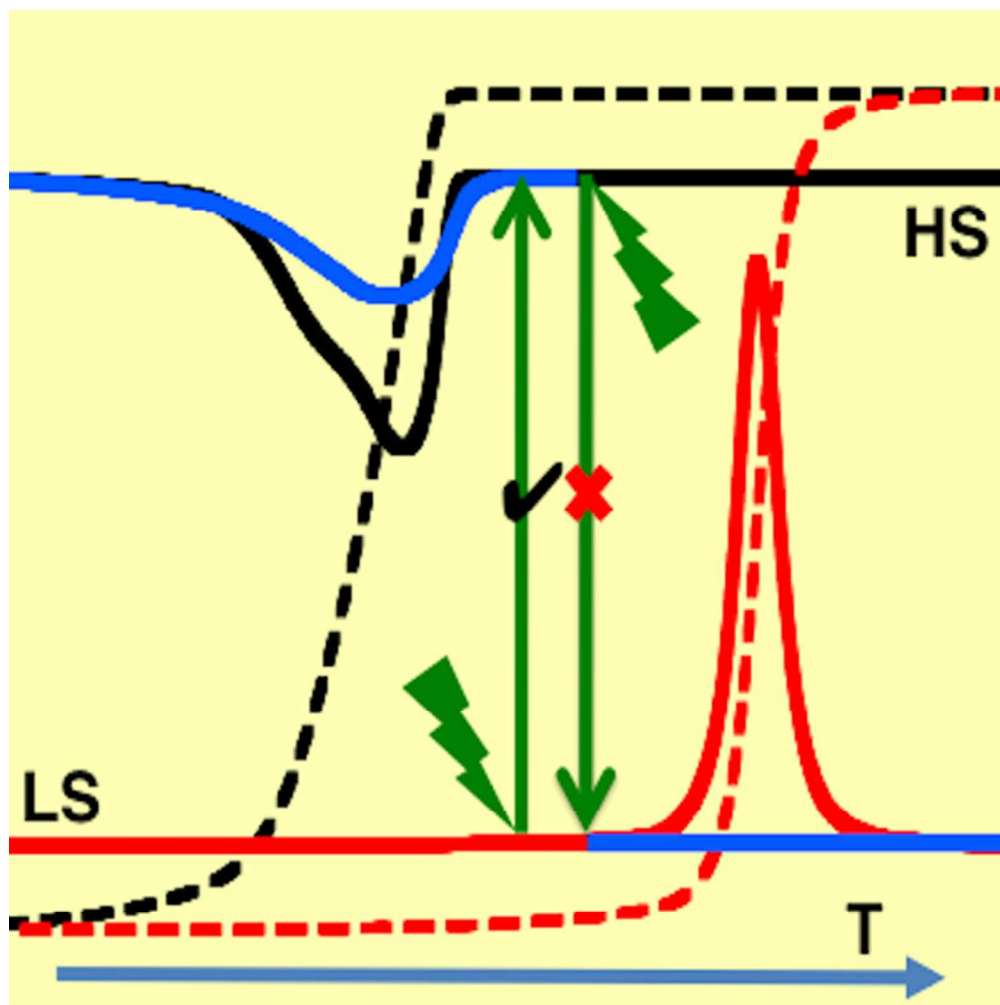
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80x70mm (288 x 288 DPI)



80x70mm (288 x 288 DPI)



50x50mm (300 x 300 DPI)