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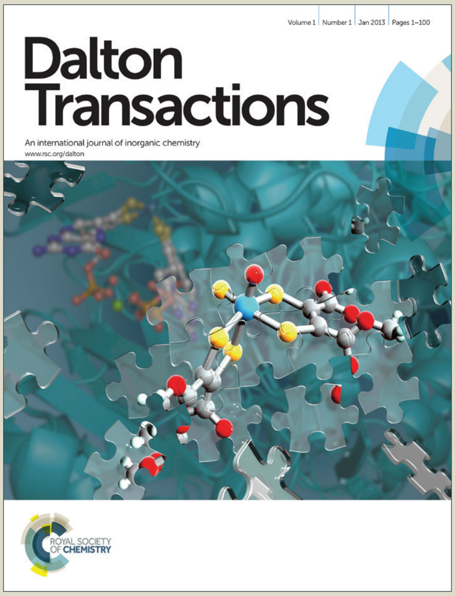

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Communication

Polymorphism Dependent Light Induced Spin Transition

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Photomagnetic study of orthorhombic and tetragonal low spin polymorphs of compound [Fe(L)$_2$](BF$_4$)$_2$ revealed different properties and thermal stability of their metastable high spin states. Furthermore, the reversible thermally induced phase/spin transition between low spin and high spin orthorhombic phases was studied by variable temperature UV/VIS spectroscopy.

Materials with tuneable magnetic properties have attracted interest of the investigation during last several decades.[1] Among the various external triggers like temperature, pressure or electric current control, the light irradiation presents convenient and cheap tool which can be easily used for the tuning of not only magnetic properties of materials.[1c] Upon light irradiation various interesting phenomena were found so far, like photoinduced metal to metal charge transfer and valence tautomerism,[2a,b] magnetic coupling, ordering and pole inversion[2c] or single molecule magnetism.[2d] Photoinduced magnetisation was also observed in the case of ST compounds. This important finding concerns switches where low spin (LS) ↔ high spin (HS) phototransformation is performed through spin-orbital mechanism. The LIESST effect (Light Induced Excited Spin State Trapping)[3] has been described in many examples of iron(II) spin transition (ST) compounds and occasionally also in the case of ferric complexes.[4] But, the photoexcitation and existence of metastable HS state at cryogenic temperatures denote several issues for the possible application of photoactive ST materials.[5] Therefore the development of new photoactive ST materials and better understanding of structural, magnetic and spectral properties of photoexcited states are pivotal subjects of investigation with respect to the implementation into memory devices or in display technology.

Thermally controlled ST is very sensitive upon miscellaneous chemical effects like ligand substitution, counter anion exchange or presence of solvents in the structure. However, their variation is usually accompanied by dramatic changes in the crystal structure and symmetry. Thus, beside intramolecular parameters like ligand field strength of donor ligands, the different molecular packing in the crystal lattice result in a different kind of internal pressure, which can affect the presence, cooperativeness and completeness of ST. Such influence of polymorphism has been already reported and proved that different crystal symmetry created different spin states and different ST behaviour.[6] On the other hand, only few polymorphic ST systems have been studied by photoexcitation experiments so far.[7-9] Significantly different low temperature LS→HS photoconversion, light induced thermal hysteresis (LITH) under the permanent light irradiation and time dependent isothermal relaxation of photoinduced HS state were observed in the investigation of two polymorphic forms of mononuclear complex [Fe(PM-BiA)$_2$(NCS)$_2$] (PM-BiA=(N-2'-0-pyridylmethylene)-4-(aminobiphenyl)).[7] Relationships between structural and thermal and photoinduced ST was also reported for four phases of trans-[Fe(abpt)$_2$(NCS)$_2$] (abpt=1 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole), where after long term exposition to laser light even a fifth polymorph with different magnetic properties was observed.[8] Recently has been shown, that polymorphic variability in [{Fe(NCBH$_3$)(py)}$_2$(μ-L1)$_2$] (L1=3,5-bis(2-pyridyl)-1,2,4-triazolate; py=pyridine) has strong impact on thermal and photoinduced switching of inequivalent iron(II) sides of dinuclear system.[9]

In the presented article relationships between structural variability, spectral properties and photoinduced ST properties are studied in detail. The structural and magnetic study of [Fe(L)$_2$](BF$_4$)$_2$ (L = 4-ethynyl-2,6-bis(pyrazol-1-yl)pyridine)) revealed exciting impact of polymorphism on the spin states and magnetic switching of related phases.[10] The room temperature crystallization from acetonitrile solution results in **1A** orthorhombic ($P2_12_12_1$) and **1B** tetragonal ($I4_1/a$) polymorphs. Both obey crystallographic phase reorganization into the third orthorhombic (*Pbcn*) polymorph **1C** at elevated temperature (see ESI, Fig. S1). Above 330 K, the LS polymorph **1A** undergoes reversible phase and spin transition into the HS **1C** phase, accompanied by an abrupt hysteresis loop of 8 K width. On the contrary, the tetragonal **1B** phase remains LS up to 420 K and it is converted into the HS **1C** phase irreversibly. The complete temperature variable structural relation between three polymorphic phases of the compound [Fe(L)$_2$](BF$_4$)$_2$ can be expressed by a **1B**→**1C**↔**1A** pathway.

The reversible **1A**↔**1C** phase/spin transition was investigated also by solid state temperature dependent UV/VIS spectroscopy in the thermal range 298 – 379 K. Measurements performed in the heating as well as in the cooling mode, revealed significant differences in the spectral region 13000 – 25000 cm^{-1} (770 – 400 nm), where pronounced d-d transitions and LMCT bands of the LS **1A** polymorph decreased upon heating (see ESI, Fig. S2). Another significant signal of the ST was identified in the near IR region around 10000 cm^{-1} (1000 nm), where the HS $^5T_2 \rightarrow {}^5E$ band started to rise with temperature. The subtraction of the HS spectrum recorded at 373 K from all other spectra resulted in the appearance of LS $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$ bands centred at

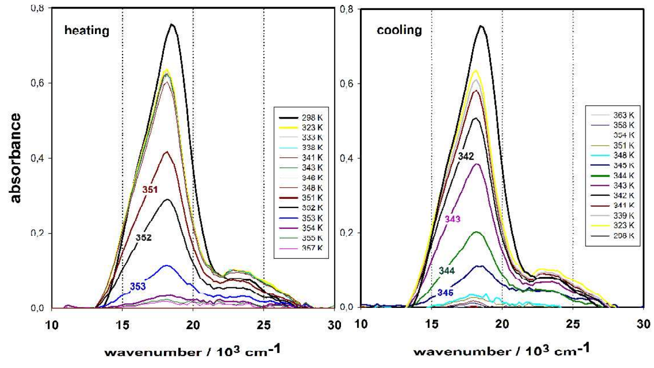

Figure 1 Temperature dependent solid state VIS absorption spectra of polymorph **1A** recorded in heating (left) and then in cooling (right) mode.

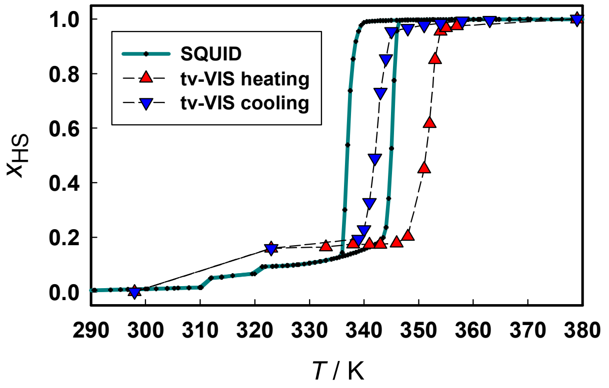

Figure 2 Comparison of the thermal hysteresis loops reconstructed from magnetic (solid line, sweeping rate = 1 K/min) and from VIS absorption spectroscopy measurements (sweeping rate = 1 K/min) of the phase/spin transition **1A↔1C**

18500 cm^{-1} (540 nm) and 23000 cm^{-1} (435 nm) respectively. Their intensity decreased with heating in favour of the HS state and completely vanished above 363 K (Fig. 1). The HS molar fraction, calculated from maximum absorbance values of $^1A_1 - {}^1T_1$ bands (Fig. 2), confirmed the presence of thermal hysteresis loop with $T_{1/2\downarrow}$ = 342 K and $T_{1/2\uparrow}$ = 351 K transition temperatures (SQUID-DC data: $T_{1/2\downarrow}$ = 337 K, $T_{1/2\uparrow}$ = 345 K). Small elevation of hysteresis loop and $T_{1/2}$ temperatures can be explained by fact that spectroscopic measurements were carried out at atmospheric pressure, while magnetic investigation was performed in vacuum. Moreover, magnetic studies revealed a small increase of the HS fraction before its own phase/spin transition becomes visible (region of 310 K – 330 K). This can also be detected by spectroscopy. Taking into the account diffraction data recorded at 350 K,[10] where average Fe-N bond distances for Fe1 and Fe2 centres (1.968 Å and 1.969 Å; ΣFe1=93.3°[11] and ΣFe2=100.7°) presents about 3% increase relative to the purely LS structure **1A** at 180 K (1.939 Å and 1.901 Å; ΣFe1=86.2° ΣFe2=87.9°), one can conclude that the onset in the x_{HS} vs T curve might be related to a first small step of ST in the polymorph **1A** before the **1A↔1B** phase/spin transition. The photoexcitation of both **1A** and **1B** LS polymorphs was carried out at 10 K (Fig. 3). As a light source a green laser (λ = 532 nm) was used with intensity adjusted to 10 mW cm^{-2}. When light was applied on **1A**, a significant increase of magnetic moment was observed immediately. After 80 min of irradiation the χT product function reached saturation at 2.7 cm^3 K mol^{-1}. Subsequent heating in the dark revealed a further increase in χT, which is related to the zero field splitting. At 39 K, χT reached 3.33 cm^3 K mol^{-1}, which is comparable with the HS value observed by the thermally induced phase/spin conversion above 350 K (3.35 cm^3 K mol^{-1}). Thus one can conclude that photoexcitation of orthorhombic **1A** polymorph was quantitative, and all LS Fe(II) atoms were converted to the HS state. Further heating caused a decrease of the magnetic moment due to the thermal relaxation of metastable HS state and above T(LIESST) = 90 K (Fig. 3a) the compound becomes diamagnetic again. The photoexcitation of **1B** was carried out in the same manner as in the case of orthorhombic **1A** phase. When laser light was applied at 10 K, magnetic moment started to increase up slowly to saturated value χT = 0.92 cm^3 K mol^{-1} (after ca 110 min). Then, the magnetic investigation in the dark revealed presence of photoexcited state up to T(LIESST) = 23 K (Fig. S3b). The maximum of χT reached 1.26 cm^3 K mol^{-1}, which indicates that only about 40 % of Fe(II) atoms were photoconverted into the HS state.

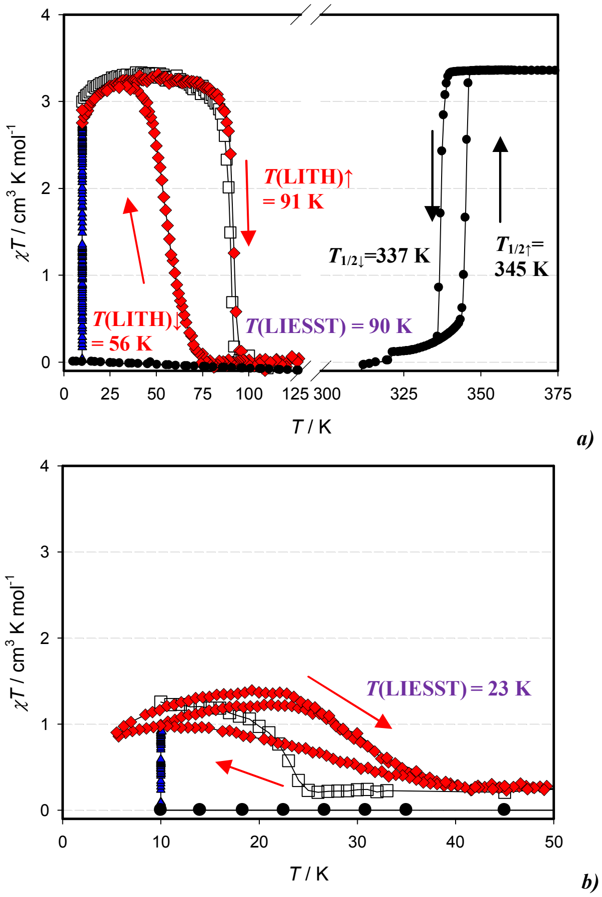

Figure 3 Magnetic properties of polymorphs **1A** (*a*) and **1B** (*b*). Circles – *χT vs T* in dark, triangles – laser photoexcitation (532 nm) at 10 K; squares – temperature dependence of photoexcited high spin state in the dark (LIESST curve); red rhombus - temperature dependence of photoexcited high spin state under permanent laser light irradiation (LITH curve). All measurements were recorded at B_{DC} = 0.1 T.

Magnetic properties of **1A** and **1B** polymorphs were also investigated under permanent laser irradiation. The measurement of **1A** performed in the heating mode is almost identical with the previously observed LIESST curve recorded in the dark. However, subsequent measurements in the cooling mode revealed presence of light induced thermal hysteresis (LITH)[12] that is reproducible within two consecutive heating/cooling cycles. Such a thermal hysteresis can be characterised by temperatures at witch 50 % of the photoexcited Fe(II) atoms are in the metastable HS state – T(LITH)↑ = 91 K, T(LITH)↓ = 56 K, and ΔT = 35 K. The LITH measurements of the tetragonal **1B** polymorph have again shown different photomagnetic behaviour in comparison with orthorhombic **1A**. Starting from 10 K, the photoexcited **1B** phase was measured in the heating mode up to 50 K where a complete relaxation to the LS state occurs. Afterwards on cooling back to 10 K a presence few Kelvin hysteresis has been identified. Since the measurement in the cooling has touched the heating curve for the first time at 10 K temperature, we continued with cooling down to 5 K and in the next starting from this temperature we measured the heating curve once again. The second heating curve has obeyed a bit higher values as the first one. Such disagreement between two heating LITH curves with different starting points suggests that the beginning of the complete LITH curve starts somewhere below the 5 K temperature; and consequently the calculation of T(LITH) values would be meaningless.

In conclusion, by variable temperature absorption spectroscopy a reversible phase/spin transition between two orthorhombic phases of the compound $[Fe(L)_2](BF_4)_2$ was identified. Upon heating, the decrease of LS d-d transition indicates solid state phase reorganisation from the diamagnetic LS phase to the HS polymorph. The consecutive cooling proved reversibility of the phase and spin transition, abruptness and thermal hysteresis. The photoexcitation of orthorhombic LS phase has revealed quantitative conversion to HS and expressive stability of metastable state above the temperatures of liquid nitrogen. On the contrary, the tetragonal **1B** polymorph exhibits only poor stability of the HS fraction accompanied by non-quantitative photoconversion. Both photoexcited polymorphs exhibit a bistability of the metastable HS state under the permanent irradiation. The thermal location and width of LITH again indicates interesting stability of photoinduced HS state of the polymorph **1A**. The polymorph **1B** exhibits only a few Kelvin hysteresis loop the position of which is significantly moved to lower temperatures. We described previously that crystal structures of both polyomorphs lack of strong intermolecular interactions between the complex cations and there is no significant differences in the iron(II) coordination environment between them.[10] Thus, such marked diversity in photomagnetism of **1A** and **1B** polymorphs has to be related to the different crystal symmetry, internal pressure and alignment of ST moieties within the crystal lattice. The structural investigation of both photoexcited phases present a task for our future investigation and we hope that it will bring more information and answers on the impact of polymorphism on the photomagnetic spin transition properties.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Synthesis, X-ray structure descriptions, experimental details about the magnetic, photomagnetic and Vis spectroscopy measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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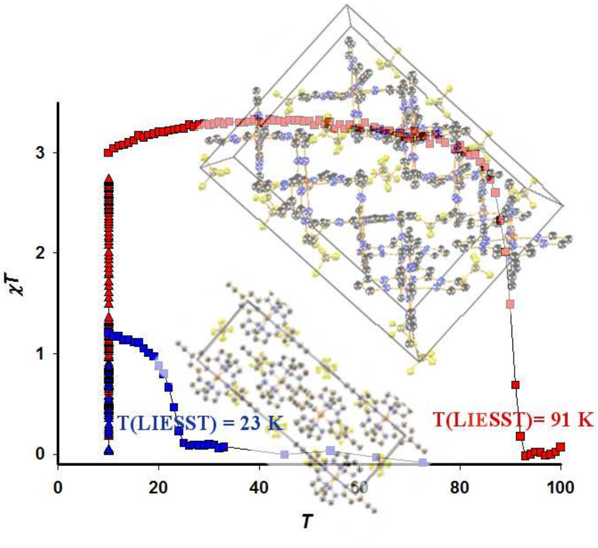
Graphical abstract



Polymorphism dependent photomagnetic behaviour was studied in the case of low spin 1A and 1B polymorphs of mononuclear iron(II) spin transition compound $[Fe(L)_2](BF_4)_2$.