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Polymorphism dependent light induced spin transition†

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A 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 research interest during the last several decades.[1] Among the various external triggers like temperature, pressure or electric current control, light irradiation presents a convenient and cheap tool that can be easily used for the tuning of the 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) + 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, in the case of ferric complexes.[4] However, the photoexcitation and existence of metastable HS states at cryogenic temperatures indicates 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. Therefore, in addition to intramolecular parameters like ligand field strength of donor ligands, different molecular packing in the crystal lattice results in a different kind of internal pressure, which can affect the presence, cooperativeness and completeness of ST. Such an influence of polymorphism has been already reported and it has been proven that different crystal symmetries induce different spin states and different ST behaviours.[6] On the other hand, only few polymorphic ST systems have been studied by photoexcitation experiments to date.[7–9] Significantly different low temperature LS→HS photoconversion, light induced thermal hysteresis (LITH) under 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′-pyridylmethylene)-4-(aminobiphenyl)).[7] The relationships between structural and thermal and photoinduced ST were 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, it has been shown that the polymorphic variability in $[\{Fe(NCBH_3)(py)\}_2(\mu-L1)_2]$ (L1 = 3,5-bis(2-pyridyl)-1,2,4-triazolate; py = pyridine) has a strong impact on the thermal and photoinduced switching of inequivalent iron(II) sides of a dinuclear system.[9]

In the present article, the 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 an exciting impact of polymorphism on the spin states and magnetic switching of related phases.[10] The room temperature

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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 temperatures (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 irreversibly converted into the HS **1C** phase. The complete temperature variable structural relation between three polymorphic phases of the compound $[Fe(L)_2](BF_4)_2$ can be expressed by the **1B→1C↔1A** pathway.

The reversible **1A↔1C** phase/spin transition was also investigated by solid state temperature dependent UV/VIS spectroscopy in the thermal range of 298–379 K. Measurements performed in the heating as well as in the cooling modes revealed significant differences in the spectral region of 13 000–25 000 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 10 000 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 the other spectra resulted in the appearance of LS $^1A_1 \rightarrow ^1T_1$ and $^1A_1 \rightarrow ^1T_2$ bands centred at 18 500 cm^{-1} (540 nm) and 23 000 cm^{-1} (435 nm), respectively. Their intensities decreased with heating in favour of the HS state and completely vanished above 363 K (Fig. 1). The HS molar fraction, calculated from the maximum absorbance values of $^1A_1$–$^1T_1$ bands (Fig. 2), confirmed the presence of a thermal hysteresis loop with the transition temperatures of $T_{1/2\downarrow} = 342$ K and $T_{1/2\uparrow} = 351$ K (SQUID-DC data: $T_{1/2\downarrow} = 337$ K, $T_{1/2\uparrow} = 345$ K). A small elevation of the hysteresis loop and $T_{1/2}$ temperatures can be explained by the fact that the 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 310–330 K). This can also be detected by spectroscopy. Taking into account the diffraction
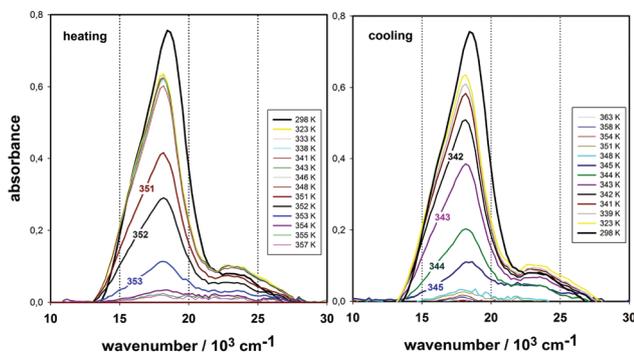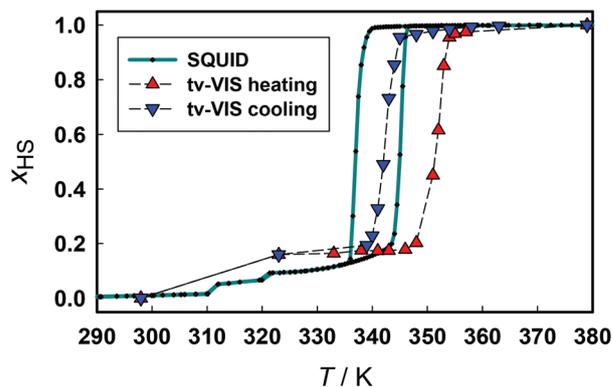

Fig. 2 Comparison of the thermal hysteresis loops reconstructed from magnetic (solid line, sweeping rate = 1 K min^{-1}) and from VIS absorption spectroscopy measurements (sweeping rate = 1 K min^{-1}) of the phase/spin transition **1A↔1C**.

data recorded at 350 K,[10] where the average Fe–N bond distances for Fe1 and Fe2 centres (1.968 Å and 1.969 Å; $\sum$Fe1 = 93.3°[11] and $\sum$Fe2 = 100.7°) presents about 3% increase relative to the purely LS structure **1A** at 180 K (1.939 Å and 1.901 Å; $\sum$Fe1 = 86.2° and $\sum$Fe2 = 87.9°), one can conclude that the onset in the x_{HS} vs. T curve might be related to the first small step of ST in 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 ($\lambda = 532$ nm) was used with the intensity adjusted to 10 mW cm^{-2}. When light was applied on **1A**, a significant increase of the 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}). Therefore, one can conclude that the photoexcitation of orthorhombic **1A** polymorph was quantitative, and all the 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 the metastable HS state; above T(LIESST) = 90 K (Fig. 3a), the compound becomes diamagnetic again. The photoexcitation of **1B** was carried out in the same manner as that in the case of orthorhombic **1A** phase. When laser light was applied at 10 K, the magnetic moment started to increase slowly to the saturated value of $\chi T = 0.92$ cm^3 K mol^{-1} (after *ca.* 110 min). Then, the magnetic investigation in the dark revealed the presence of the photoexcited state up to T(LIESST) = 23 K (Fig. S3b†). The maximum χT value reached 1.26 cm^3 K mol^{-1}, which indicates that only about 40% of Fe(II) atoms were photoconverted into the HS state.

The 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

Fig. 1 Temperature dependent solid state VIS absorption spectra of polymorph **1A** recorded in heating (left) and then in cooling (right) modes.
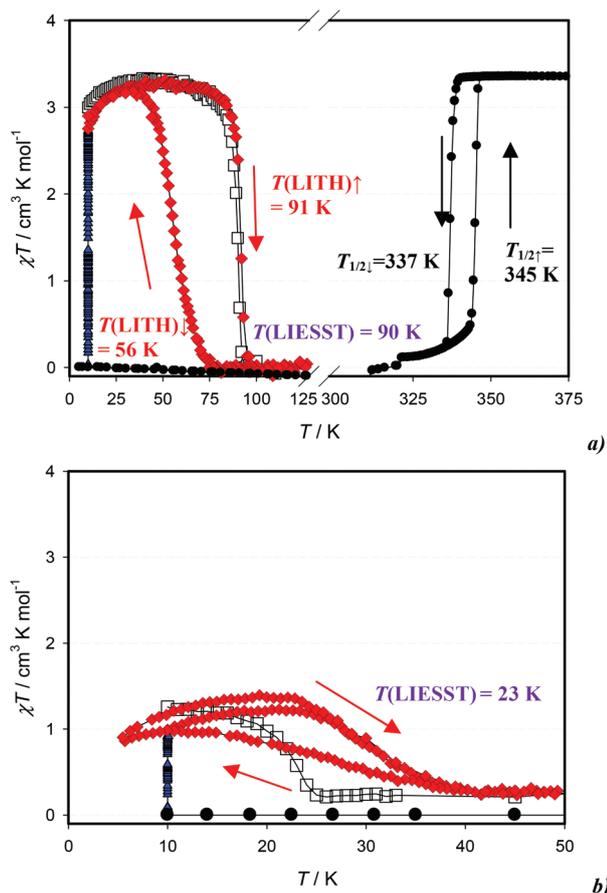
Fig. 3 Magnetic properties of polymorphs **1A** (*a*) and **1B** (*b*). Circles: χT *vs.* T in dark; triangles: laser photoexcitation (532 nm) at 10 K; squares: temperature dependence of photoexcited high spin state in the dark (LIESST curve); red rhombus: temperature dependence of photoexcited high spin state under permanent laser light irradiation (LITH curve). All the measurements were recorded at $B_{DC} = 0.1$ T.

in the dark. However, subsequent measurements in the cooling mode revealed the presence of light induced thermal hysteresis (LITH)[12] that is reproducible within two consecutive heating/cooling cycles. Such thermal hysteresis can be characterised by temperatures at which 50% of the photoexcited Fe(II) atoms are in the metastable HS state: $T(\text{LITH})\uparrow$ = 91 K, $T(\text{LITH})\downarrow$ = 56 K, and ΔT = 35 K. The LITH measurements of the tetragonal **1B** polymorph have again shown differing 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 complete relaxation to the LS state occurs. Afterwards, on cooling back to 10 K, hysteresis involving a few Kelvin degrees has been identified. Since the measurement during the cooling phase has touched the heating curve for the first time at a temperature of 10 K, we continued with cooling down to 5 K; thereafter, starting from this temperature, we measured the heating curve once again. The second heating curve exhibits marginally higher values than 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; consequently, the calculation of $T(\text{LITH})$ values would be meaningless.

In conclusion, by means of variable temperature absorption spectroscopy, a reversible phase/spin transition between two orthorhombic phases of the compound $[\text{Fe}(L)_2](\text{BF}_4)_2$ 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 the reversibility of the phase and spin transitions, abruptness and thermal hysteresis. The photoexcitation of the orthorhombic LS phase has revealed quantitative conversion to HS and expressive stability of the 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 the photoexcited polymorphs exhibit bistability of the metastable HS state under permanent irradiation. The thermal location and width of LITH again indicates interesting stability of the photoinduced HS state of polymorph **1A**. Polymorph **1B** exhibits a hysteresis loop involving only a few Kelvin degrees, the position of which is significantly moved towards the lower temperatures. We have described previously that the crystal structures of both polymorphs lack strong intermolecular interactions between the complex cations and there is no significant differences in the iron(II) coordination environment between them.[10] Therefore, such marked diversity in the 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 the 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.

Acknowledgements

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