First ligand-driven light-induced spin change *at room temperature* in a transition-metal molecular compound

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Applied to the new iron(II) compound Fe(t-msbpy)$_2$(NCS)$_2$ (t-msbpy = 4-methyl-4′-*trans*-styryl-2,2′-bipyridine), a novel strategy based on the so-called "ligand-driven light-induced spin change" (or LD-LISC) effect, which consists in triggering the metal ion electronic spin-state crossover in a complex by a photochemical modification of the ligand, allowed this photomagnetic effect to be observed for the first time at room temperature. The compound, studied in CH_3CN or CD_3CN, was found to be initially nearly diamagnetic ($S = 0$) by means of NMR experiments. Then, irradiation of a solution to the photostationary state with $\lambda_{exc} = 334$ nm was shown, by using UV-VIS spectrometry, to result in the *trans* → *cis* isomerization of the styryl substituent of msbpy and in the subsequent $S = 0$ (low spin) $\rightarrow S = 2$ (high spin) conversion of a significant fraction of the iron(II) ions.

The high-spin state (HS) ⇔ low-spin state (LS) crossover, chiefly observed in a number of molecular compounds containing a transition-metal ion (3d^4 to 3d^7) in octahedral symmetry, has been extensively documented.[1–4] The phenomenon can be thermo-, piezo- and photoinduced. In all cases, the transition is obtained through the change of the population of the HS and LS electronic levels. The resulting structural modifications at the molecular scale mainly concern the metal–ligand bond lengths, the ligands being only slightly affected.

Recently,[5–7] we reported a new way to get photoinduced spin-state crossovers. This strategy, called ligand-driven light-induced spin change (or LD-LISC), consists in triggering the crossovers from primary photoreactions on the ligands. It should enable photoinduced conversions between two long-lived spin states to be observed not only below 70 K (highest temperature for the observation of the light-induced spin transitions previously reported[1,8]), but over a wide temperature range (only restricted by the thermal stability of the compound). It is worth noticing that the bistable character and hence the memory effect exhibited by such compounds is of importance, for it may result in practical applications in optical information storage and display devices.

As discussed elsewhere,[6] a prerequisite for the light-induced spin change to be observed is that the two complexes formed with the ligand photoisomers exhibit different magnetic behaviors as a function of temperature. This condition is anticipated to be fulfilled, in particular, when at least one of these compounds undergoes a thermally induced spin crossover. In the temperature range over which the metal ion can be either in the HS or in the LS state, depending on the configuration of the photosensitive ligand in the complex, a spin-state change should result from ligand photoconversion. This photomagnetic effect was first shown to occur in Fe^{II}(stpy)$_4$(NCBPh$_3$)$_2$, stpy standing for the *trans*/*cis*-photoisomerizable ligand 4-styrylpyridine;[7] samples were in the form of cellulose acetate films. As the complex formed with *trans*-stpy (hereafter *t*-stpy) exhibits a thermal $S = 2$ (HS) ⇔ $S = 0$ (LS) crossover between ≈230 and ≈140 K, whereas that formed with *cis*-stpy is HS at any temperature, the light-induced spin change could be observed at $T_{obs} = 140$ K. In order to shift the thermal spin crossover, and hence T_{obs}, towards higher temperatures, our strategy was to look for another appropriate compound with a stronger ligand field than in Fe^{II}(t-stpy)$_4$(NCBPh$_3$)$_2$. As Fe^{II}(4,4′-dimethyl-2,2′-bipyridine)$_2$(NCS)$_2$ was found to undergo a thermal spin crossover at a rather high temperature, *viz* ≈ 270 K,[9] we decided to prepare the parent compound Fe^{II}(t-msbpy)$_2$(NCS)$_2$ (t-msbpy = 4-methyl-4′-*trans*-styryl-2,2′-bipyridine) where the *trans*/*cis* photoisomerizable styryl substituent is tethered on a bidentate ligand.

In the present paper we report (*i*) the synthesis of the complex; (*ii*) the temperature dependence of its magnetic properties in the solid state (obtained on a Faraday-type susceptometer) and in CH_3CN or CD_3CN solutions (determined from NMR experiments); (*iii*) the detection by UV-VIS spectrometry of the *trans* → *cis* photoisomerization of the styryl groups of the complex in solution and (*iv*) the subsequent spin change of the iron(II) ions, this being qualitatively supported by magnetic measurements carried out on a SQUID magnetometer. We shall see that for this compound the LD-LISC effect can be observed at room temperature.

Experimental

Syntheses

All compounds were prepared, handled and maintained either in darkness or under inactive (red) light, in order to prevent any photoisomerization process, and the syntheses of the iron(II) complexes were accomplished under an argon atmosphere, using previously degassed solvents.

***t*-msbpy.** The preparation of this ligand was guided by the procedures described for some related compounds.[10] It consisted in refluxing for 40 h a mixture of 4-4′-dimethyl-2,2′-bipyridine (9.7 mg, 53 mmol), benzaldehyde (8 mL, 72 mmol) and potassium acetate (5.2 mg, 53 mmol) in acetic anhydride (7.4 mL, 67 mmol), in the presence of a small amount (≈3 mg) of iodine. Before complete cooling, the resulting viscous solution was poured into chilled water (300 mL) made alkaline (pH = 8–9) with triethylamine. The precipitate that formed was isolated by filtration, washed with water, and treated with CH_2Cl_2 in order to eliminate the insoluble 4,4′-distyryl-2,2′-bipyridine impurity. The solid compound resulting from solvent removal was then sublimed under vacuum at 120 °C. ^1H NMR data (δ) in CH_3CN: 8.62 (d, 1H); 8.54 (d, s, 2H); 8.28 (s, 1H); 7.66 (dd, 2H); 7.54 (d, 16.4 Hz, 1H); 7.54–7.38 (m, 5H); 7.30 (d, 16.4 Hz, 1H). The coupling constant $J = 16.4$ Hz was ascribed to the *trans* ethylenic group. Anal. calcd (%) for $C_{19}H_{16}N_2$: C 83.79, H 5.92, N 10.29. Found: C 83.21, H 6.30, N 10.13.

[Fe^{II}(*t*-msbpy)$_3$](NCS)$_2$. This complex, used as the starting material for synthesizing Fe^{II}(*t*-msbpy)$_2$(NCS)$_2$, was obtained as follows. A solution of $Fe(SO_4)_2(NH_4)_2 \cdot 6H_2O$ (101 mg, 0.26 mmol) in water (2 mL) was added dropwise to a 206.8 mg (0.77 mmol) sample of *t*-msbpy dissolved in EtOH (10 mL). The red solution was heated at 65 °C for 1 h, then cooled to room temperature. After addition to a saturated KNCS aqueous solution ($\approx$10 mL), which caused a red precipitate to form, the mixture was further stirred for 20 min and decanted. The solid was separated by filtration and dried under vacuum in a desiccator. Anal. calcd (%) for $FeC_{59}H_{48}N_8S_2 \cdot 3.5H_2O$: C 67.36; H 5.27; N 10.65; S 6.09. Found: C 66.56; H 5.21; N 10.83; S 6.91. Complete removal of the water molecules was obtained by heating the compound at 60 °C overnight under an argon stream.

Fe^{II}(*t*-msbpy)$_2$(NCS)$_2$. Fe^{II}(*t*-msbpy)$_2$(NCS)$_2$ was isolated in the form of a violet or a black microcrystalline powder according to the procedure adapted for extracting one msbpy ligand from [Fe^{II}(*t*-msbpy)$_3$](NCS)$_2$. Addition of hexane (25 mL) to a solution of [Fe^{II}(*t*-msbpy)$_3$](NCS)$_2$ (100 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (10 mL) led to the violet complex ($C_{t,v}$). This complex was isolated by filtration, washed with ethyl ether and then dried at 80 °C overnight under an argon stream. Anal. calcd (%) for $FeC_{40}H_{32}N_6S_2$: C 67.03; H 4.50; N 11.73; S 8.93. Found: C 66.71; H 4.62; N 11.86; S 8.21.

Treatment of a sample of [Fe^{II}(*t*-msbpy)$_3$](NCS)$_2$ with anhydrous acetone for 3 weeks in a Soxhlet apparatus gave the black complex ($C_{t,b}$). Anal. calcd (%) for $FeC_{40}H_{32}N_6S_2$: C 67.03; H 4.50; N 11.73; S 8.93; Fe 7.79. Found: C 66.19; H 4.88; N 11.59; S 8.76; Fe 7.73.

Physical measurements

For compounds in the solid state, magnetic susceptibility data were determined at both decreasing and increasing temperatures (in order to look for the possible existence of a thermal hysteresis effect) using a Faraday-type susceptometer equipped with an Oxford Instruments helium continuous-flow cryostat or a Quantum Design SQUID Magnetometer (MPMS5S Model). Samples of [$HgCo(NCS)_4$] and palladium were used as the calibrants, respectively. The independence of the susceptibility value with regard to the applied magnetic field was checked at room temperature. Diamagnetic corrections were estimated from Pascal's tables at -432×10^{-6} cm^3 mol^{-1}.

For compounds in solution (solvent CD_3CN), magnetic susceptibility measurements were carried out either using the technique of Evans[3,11–13] on a Bruker AM (400 MHZ) NMR spectrometer equipped with an Oxford Instruments cryogenic set-up or on a SQUID magnetometer. In the former case, chemical shifts in ^1H NMR spectra were referenced to TMS as an internal standard. For SQUID experiments, the quasi-symmetrical sample holder was realized by connecting two EPR quartz tubes together (outer diameter: 5 mm). The two compartments were thus separated by a layer of quartz. The top part contained a very small amount of solution ($\approx$0.06 mL) and the lower part was sealed under high vacuum.

UV-visible absorption spectra (solvent CH_3CN) were obtained on a Varian Cary 5E double-beam spectrophotometer equipped with Cary temperature controller and temperature probe accessories. Spectra were corrected for the solvent thermal expansion.[14]

Irradiations of the solutions were performed at 334 nm with Oriel equipment including a 1/8 m grating monochromator optically coupled with a 200 W Hg (Xe) lamp. The solutions were handled under inactive light. The reactors were 10 mm path length quartz cells. The sample holder for the SQUID measurements was rotated in the light beam ($\lambda = 340$ nm, standard bandpass filter 340FS25-25).

Results and discussion

Magnetic properties

The magnetic properties of $C_{t,v}$ and $C_{t,b}$, first determined on microcrystalline samples, are depicted in Fig. 1 in the form of $\chi_M T$ *vs.* T plots (χ_M = molar magnetic susceptibility, T = temperature). As required, they are typical of a $S = 2 \leftrightarrow S = 0$ crossover of iron(II) ions.

For $C_{t,v}$, the transformation is centered around 264 K. The $\chi_M T$ values are found to increase smoothly from 0.42 cm^3 mol^{-1} K below 80 K to 3.15 cm^3 mol^{-1} K at 400 K and are easily extrapolated to 3.20 cm^3 mol^{-1} K for the upper plateau. It follows that the molecules are mostly in the LS state only below $\approx$150 K and that, at room temperature, $\approx$35% of the molecules are in the LS state and $\approx$65% in the HS state.

Regarding $C_{t,b}$, the quasi-totality of the spin conversion takes place above 300 K. The $\chi_M T$ product retains the same value, *viz.* 0.30 cm^3 mol^{-1} K, from 100 to 240 K. Above this it increases, first very slightly up to about 300 K and then more rapidly. At 450 K, the highest temperature experimentally allowed, $\chi_M T = 2.81$ cm^3 mol^{-1} K. The upper plateau should correspond to a value of $\approx$3.17 cm^3 mol^{-1} K. So, the transition is found to be centered around 380 K. At room temperature, this complex is nearly all in the LS form.

As the observation of the LD-LISC effect requires diluted samples, we also investigated the magnetic properties of Fe(*t*-msbpy)$_2$(NCS)$_2$ in solution, between 293 and 333 K (highest temperature compatible with the use of CD_3CN as the solvent), using the Evans NMR method[3,11–13] The experiments were carried out on solutions of $C_{t,v}$. The choice of this species, in spite of the more appropriate magnetic behavior of $C_{t,b}$ in the solid state, was dictated by two observations: the solutions of $C_{t,b}$, contrary to those of $C_{t,v}$ change only slowly with time—which may be due, at least partly, to the very low solubility of this complex in acetonitrile—and, as will be seen hereafter, the UV spectrum obtained after stabilization closely resembles that of $C_{t,v}$. Despite the very low accuracy of χ_M

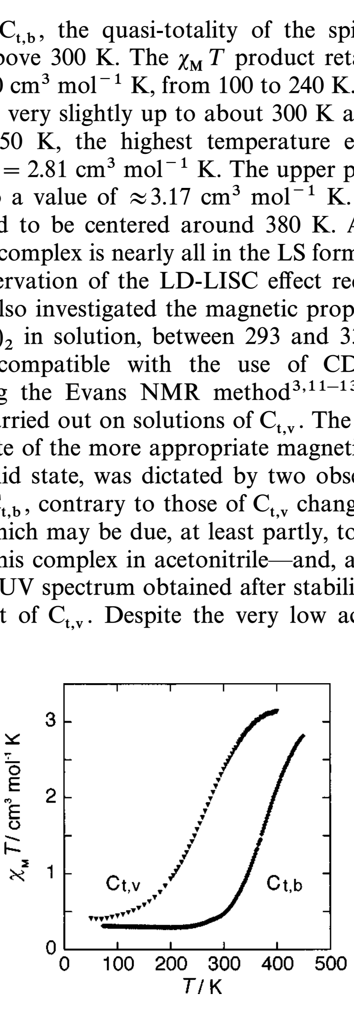

Fig. 1 Temperature dependence of $\chi_M T$ for $C_{t,b}$ and $C_{t,v}$ in the solid state.

values in the present conditions (where large corrections with regard to weak experimental values are required) the complex was clearly shown to be nearly diamagnetic at 293 K ($\chi_M T = 0.170 \pm 0.006$ cm^3 mol^{-1} K) and was found to probably exhibit the very beginning of a LS-to-HS conversion on heating ($\chi_M T$/cm^3 mol^{-1}K $= 0.197 \pm 0.006$ at 303 K, 0.197 ± 0.006 at 313 K, 0.219 ± 0.006 at 323 K and 0.221 ± 0.006 at 333 K). It should be noted that such a behavior is close to that found for $C_{t,b}$ in the solid state (see Fig. 1).

These NMR data were corroborated by the temperature dependence of the UV-VIS spectra. Fig. 2 shows the room temperature spectra of acetonitrile solutions of $C_{t,v}$ and, for comparison, *t*-msbpy. The most prominent band, with a maximum at 331 nm for $C_{t,v}$ and at 291 nm for *t*-msbpy, corresponds to the π–π^* absorption of *t*-msbpy. The weaker band at 550 nm, which only appears in the former spectrum, is assigned to a metal-to-ligand charge-transfer process. The evolution of this spectrum on increasing temperature from 293 to 330 K is shown on Fig. 3(*a*). Two isosbestic points appear at 236 and 313 nm, which nearly guarantees that only two species are present. The absorbance is lowered over a wide span of wavelength and the MLCT band is shifted toward higher energies (by ≈3 nm ≈60 cm^{-1}). This behavior parallels the trend usually observed upon the LS → HS transformation in some spin-crossover compounds of the type Fe^{II}L$_2$X$_2$ (see Table 1 for the MLCT bands). Furthermore, the recovery of the room temperature spectrum after a thermal cycle shows the reversibility of the process. Consequently, the above set of observations can be ascribed to the decrease of the LS/HS ratio upon a spin-equilibrium process. Moreover, as the difference in absorbance $A_{RT} - A_T$ (RT = room temperature) at a given wavelength is easily shown to vary with temperature like the HS fraction of Fe^{II} ions, the $A_{RT} - A_T$ *vs.* T plot (depicted below as plot 1 in Fig. 6) drawn for $\lambda = 345$ nm, which corresponds to the largest variation, corroborates that an increasing number of metal ions undergoes a LS-to-HS crossover on heating.

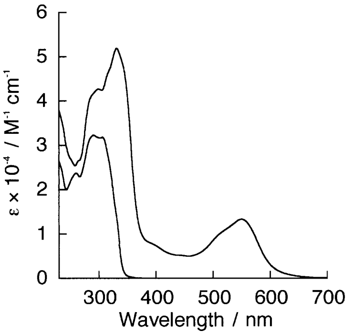

Fig. 2 UV-VIS spectra of acetonitrile solutions of $C_{t,v}$ (upper trace) and *t*-msbpy (lower trace) at 293 K.

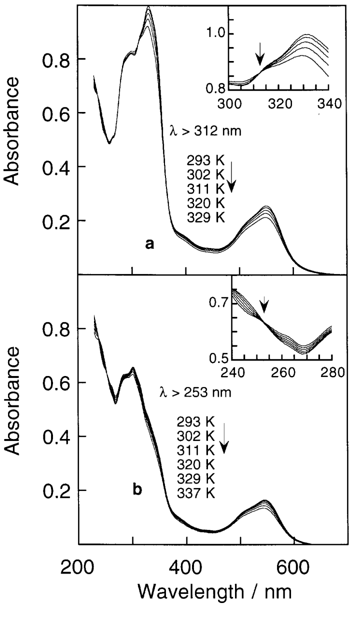

Fig. 3 Temperature dependence of the UV-VIS spectrum of a 1.9×10^{-5} M acetonitrile solution of $C_{t,v}$: (*a*) before irradiation, (*b*) after irradiation to the photostationary state with $\lambda_{exc} = 334$ nm. Insets: isosbestic points are indicated with arrows.

Table 1 MLCT absorption frequencies of iron(II) ions in some spin-crossover complexes of the type FeL$_2$X$_2$ (with L = bidentate ligand)

Compound^a	Spin state	ν/cm^{-1} MLCT^{LS}	ν/cm^{-1} MLCT^{HS}	Ref.
Fe(phen)$_2$(NCS)$_2$	$^1A_1 \leftrightarrow {}^5T_2$	17200	18000	15
Fe(phen)$_2$(NCSe)$_2$	$^1A_1 \leftrightarrow {}^5T_2$	17550	18200	15
Fe(bpy)$_2$(NCS)$_2$	$^1A_1 \leftrightarrow {}^5T_2$	17000	18400	16

^{a} phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine.

So, it can be concluded that the $S = 0 \leftrightarrow S = 2$ spin crossover exhibited by the complex Fe(*t*-msbpy)$_2$(NCS)$_2$ in the solid state is retained in solution and that, with this complex, the investigation of the LD-LISC effect is workable *at room temperature* in acetonitrile solution.

The above results do not allow one to specify the differences between the two forms of Fe(*t*-msbpy)$_2$(NCS)$_2$ in the solid state. $C_{t,b}$ and $C_{t,v}$ are likely to correspond to various diastereoisomeric compositions[15] and/or crystalline structures.[17] Since in all the mononuclear spin-crossover complexes of the type FeL$_2$(NCS)$_2$ (where L is a bidentate ligand) the thiocyanate groups are always in a *cis* configuration,[18] such a configuration certainly holds in the present compound. So, the only structural characteristic in question, regarding the molecule, is related to the diastereoisomerism that may exist, depending on the relative arrangement of the four substituents of the msbpy ligands. Two diastereoisomers with a pseudo-C_2 symmetry should be favored by the relative positions of the NCS groups in the coordination core, but a mixture of these isomers cannot be completely ruled out. However, the observation of specific infrared frequencies at 1012 cm^{-1} for $C_{t,v}$ and 792 cm^{-1} for $C_{t,b}$ might be indicative of the presence of only one isomer. As for the polymorphism hypothesis, suggested besides the formation of diastereoisomers, it can be neither corroborated nor ruled out because of the amorphous state of $C_{t,v}$.

trans → *cis* photoisomerization

The first step to demonstrate the occurrence of the LD-LISC effect is to provide evidence for the *trans* → *cis* photoisomerization of the styryl substituent of msbpy ligands in Fe^{II}(*t*-msbpy)$_2$(NCS)$_2$. The experiments were carried out on acetoni-

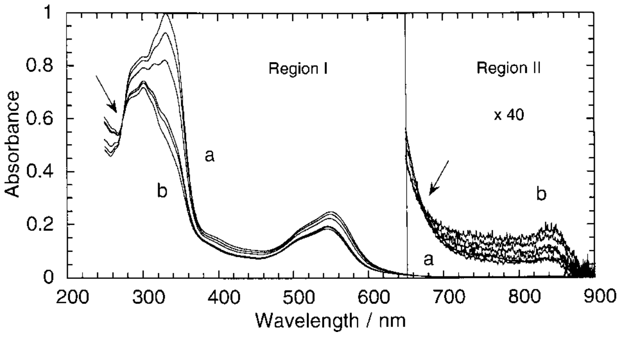

Fig. 4 Evolution of the UV-VIS spectrum of a 1.9×10^{-5} M acetonitrile solution of $C_{t,v}$ upon irradiation with $\lambda_{exc} = 334$ nm: (*a*) initial spectrum, (*b*) spectrum of the photostationary state. The features in the two regions have been scaled as indicated. Isosbestic points are indicated with arrows.

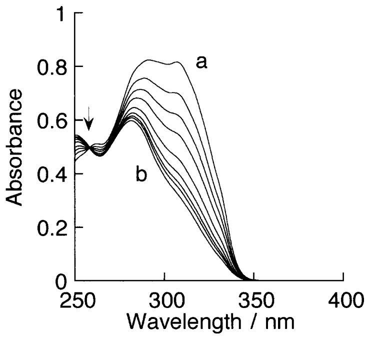

Fig. 5 Evolution of the UV-VIS spectrum of a 2.6×10^{-5} M acetonitrile solution of *t*-msbpy upon irradiation with $\lambda_{exc} = 312$ nm: (*a*) initial spectrum, (*b*) spectrum of the photostationary state.

trile solutions of $C_{t,v}$ and uncoordinated *t*-msbpy (for comparison), at room temperature, using UV-VIS spectrometry as the detecting technique.

Fig. 4 shows the evolution of the spectrum of $C_{t,v}$ upon irradiation of a solution with $\lambda_{exc} = 334$ nm, in the π–π* absorption region of *t*-msbpy. All the spectra intersect at 273 and 672 nm. Irradiation is found to result in a blue shift of the electronic transitions located in region I (from 331 to 301 nm for the π–π* band maximum and from 550 nm to 546 nm for the MLCT band maximum) and to reduced absorbance over a wide span of wavelengths. After each irradiation, the solutions are stable in the dark. As the 273 nm isosbestic point is located within the absorption range of the photosensitive ligand and the charge-transfer absorption is still observed in the visible region, the hypothesis of ligand dissociation can be ruled out.

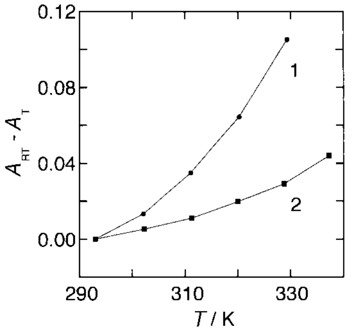

Fig. 6 $A_{RT} - A_T$ *vs.* T plots for $\lambda = 345$ nm of a 1.9×10^{-5} M acetonitrile solution of $C_{t,v}$: (curve 1) before irradiation and (curve 2) in the photostationary state.

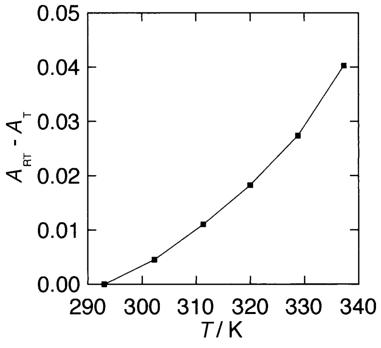

Fig. 7 $A_{RT} - A_T$ *vs.* T plots for $\lambda_{isosbestic} = 313$ nm in the photostationary state of a 1.9×10^{-5} M acetonirrile solution of $C_{t,v}$.

The *trans* → *cis* photoisomerization of the styryl substituent in uncoordinated *t*-msbpy, also carried out in acetonitrile with $\lambda_{exc} = 312$ nm, can be followed on Fig. 5. An isobestic point is observed at 253 nm. The photostationary state composition, analyzed from ^1H NMR data, is prevailingly *c*-msbpy[10] (estimated fractions: <30% *t*-msbpy and >70% *c*-msbpy, *c* = *cis*).

The similarity between the spectra obtained upon the irradiation of $C_{t,v}$ and uncoordinated msbpy solutions is clearly indicative of the occurrence of a photo-induced *trans* → *cis* conversion of the styryl substituents in $Fe^{II}(t\text{-msbpy})_2(NCS)_2$, which can be expressed in the form $C_t \rightarrow C_c$. The largest relative absorbance decrease being ≈55% at 345 nm, the C_c fraction in the photostationary state can be estimated to be higher, and may be very much higher, than ≈55% (this value corresonds to a hypothetical zero value of the C_c absorbance at the wavelength).

Light-induced spin change

Irradiation of an acetonitrile solution of $C_{t,v}$ was also found to result in the appearance and growth of a weak band at ≈840 nm, ≈11 900 cm^{-1} (Fig. 4, Region II), which was identified as a d–d absorption of Fe^{II} ions in the HS state (Table 2). Moreover, as seen above an isosbestic point appears at 673 nm. As the d–d band is expected to be of very weak intensity, its existence shows that a significant amount of C_c is in the HS state.

In order to support this statement, variable-temperature UV-VIS spectra of the same acetonitrile solution of $C_{t,v}$ in the photostationary state were then recorded from 293 to 337 K [Fig. 3(*b*)]. As previously mentioned for the non-irradiated solution, increasing temperature results in (*i*) the formation of an isosbestic point in the UV range (at 254 nm), (*ii*) a blue shift (of 3.7 nm, 125 cm^{-1}) in the MLCT absorption and (*iii*) a slight absorbance decrease above the isosbestic point wavelengths. Moreover, the process is found again to be reversible. These results are ascribed to the existence of a thermal spin equilibrium in the photostationary state, which is likely to be associated with the preponderant species, *viz.* C_c. The A_{RT}

Table 2 d–d absorption frequencies of iron(II) ions in some spin-crossover and HS complexes of the type FeL_2X_2 (with L = bidentate ligand)

Compound[a]	Spin state	ν/cm^{-1} $^1A_1 \rightarrow {}^3T_1$	ν/cm^{-1} $^5T_2 \rightarrow {}^5E$	
$Fe(phen)_2(NCS)_2$	$^1A_1 \leftrightarrow {}^5T_2$	$10400^{80\,K}$	$11900^{298\,K}$	15
$Fe(phen)_2(NCSe)_2$	$^1A_1 \leftrightarrow {}^5T_2$	$10400^{80\,K}$	$11900^{298\,K}$	15
$Fe(bpy)_2(NCS)_2$	$^1A_1 \leftrightarrow {}^5T_2$	unresolved$^{77\,K}$	$11200^{293\,K,\,b}$	16
$Fe(2\text{-}Mephen)_2Cl_2$	$^5T_2$		7900, 10300	20
$Fe(2\text{-}Mephen)_2Br_2$	$^5T_2$		8600, 10600	20
$Fe(2\text{-}Mephen)_2(NCS)_2$	$^5T_2$		9300, 11600	20
$Fe(phen)_2Cl_2$	$^5T_2$		8470, 10510	21
$Fe(phen)_2Br_2$	$^5T_2$		8470, 10750	21
$Fe(phen)_2(N_3)_2$	$^5T_2$		10200, 12200	21
$Fe(phen)_2(OCN)_2$	$^5T_2$		9250, 11350	20
$Fe(phen)_2(HCOO)_2$	$^5T_2$		10400, 12500	20

[a] phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine, Me = methyl. [b] From a Gaussian analysis, two components can be distinguished in this band at ≈12 300 and ≈10 200 cm^{-1}. They correspond to the splitting of the upper ^5E term.[16]

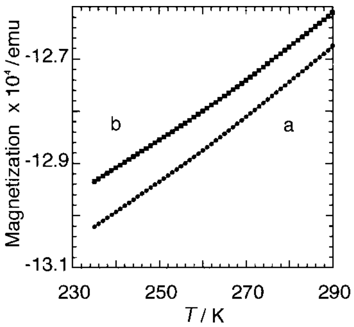

Fig. 8 Evolution of the magnetization of an CD_3CN solution of $C_{t,v}$ ($\approx 2 \times 10^{-4}$ M, volume 0.060 mL) upon irradiation with $\lambda_{exc} = 340$ nm: (*a*) before irradiation, (*b*) after irradiation. Measurements were performed from low to high temperature in a field of 40 kG.

— A_T *vs.* T variation for $\lambda = 345$ nm is depicted in Fig. 6, plot 2. This variation is found to be much lower than the previous one. As it results, at least partly, from the spin conversion of Fe^{II} ions in the residual fraction of $C_{t,v}$, the contribution of C_c appears to be either inexistent or very weak. The only explanation consistent with these experimental data is that, in the temperature range investigated, the compound C_c either retains the same spin state (*viz.* the HS state, as seen above), or is undergoing a very gradual LS-to-HS crossover where the amount of the resulting HS form is already significant. The same investigation, performed at $\lambda = 313$ nm [which corresponds to an isosbestic point in the UV spectra of $C_{t,v}$ at various temperatures, as shown in Fig. 3(*a*)] allows one to specify the C_c behavior. In this case the $A_{RT} - A_T$ *vs.* T variation (Fig. 7) is only due to C_c and shows effectively that this compound is at least partly exhibiting a LS → HS spin conversion. The formation of C_c(HS) upon irradiating $C_{t,v}$ solutions was corroborated by qualitative magnetic data obtained on a SQUID magnetometer. The variable temperature magnetization measurements were performed on dilute solutions in the 236–300 K temperature range (Fig. 8). The magnetization (M) slightly increases with temperature for all the studied samples as a consequence of some solvent vaporization in the SQUID sample holder. The very low M values are ascribed to the prevailing diamagnetic components of the sample holder and the solvent and also to weak paramagnetic components of the complexes. On irradiation of the solutions of $C_{t,v}$ a significant increase of the magnetization is observed over the whole temperature range, thus confirming the formation of paramagnetic species. Despite the accuracy of the measurements of the M values, they are spoiled by errors owing to experimental conditions (very small volumes of diluted solutions). Consequently, these measurements do not allow us to determine the corresponding $\chi_M T$ variation. SQUID measurements on irradiated solutions were followed by the recording of the UV spectra of these solutions after an additional dilution, which allowed us to check the formation and the persistence of a significant amount of C_c complex.

In the absence of additional magnetic or diamagnetic contributions, the observed increase of the magnetization, in irradiated solutions, is most likely to result from the LS → HS conversion of the iron(II) ions triggered by the *trans* → *cis* isomerization of the styryl substituent of msbpy.

Conclusion

We provide here evidence for the occurrence of a $C_t(LS) \rightarrow C_c(HS)$ photoconversion, and hence for the LD-LISC effect, for the first time *at room temperature*. The reversibility of the effect has now to be studied. Along this line the synthesis of the complex Fe(*c*-msbpy)$_2$(NCS)$_2$ is presently in progress.

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