Ligand-Driven Light-Induced Spin Change in Transition-Metal Complexes: Selection of an Appropriate System and First Evidence of the Effect, in Fe^{II}(4-styrylpyridine)$_4$(NCBPh$_3$)$_2$

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The first observation of a ligand-driven light-induced spin-state change (LD-LISC effect) in a transition-metal complex is reported. The compounds under investigation are of the type Fe^{II}L$_4$X$_2$, where L is a *cis/trans* photoisomerizable ligand. For an iron(II) spin-state change to result from ligand *cis* ↔ *trans* conversion, the Fe^{II}(*trans*-L)$_4$X$_2$ species had to exhibit a thermally-induced high-spin state ↔ low-spin state crossover. This property was checked by variable-temperature magnetic susceptibility measurements, for compounds with X$^-$ = NCBPh$_3^-$ or NCBH$_3^-$ and L = 1-phenyl-2-(4-pyridyl)ethene (or 4-styrylpyridine, abbreviated as Stpy), 1-(4-R-phenyl)-2-(4-pyridyl)ethene (R = CH$_3$, COOCH$_3$), or 1-(1-naphthyl)-2-(4-pyridyl)ethene. The results are comparatively discussed. The best candidate for the LD-LISC effect to be observed is found to be Fe(Stpy)$_4$-(NCBPh$_3$)$_2$: the complex (C$_t$) formed with *trans*-Stpy undergoes a thermally-induced spin crossover centered around 190 K; the one (C$_c$) formed with *cis*-Stpy retains the high-spin state at any temperature. Photoisomerization of the Stpy ligand, at 140 K, in the complex embedded within a cellulose acetate matrix, is effectively shown, on the basis of UV−vis absorption measurements, to trigger the spin-state change of the iron(II) ions.

Introduction

In transition-metal molecular compounds, the so-called "ligand-driven light-induced spin change" (or LD-LISC) effect, recently reported,[1−3] should lead to the occurrence of photochemically-triggered electronic spin-state crossovers *at relatively high temperatures*, compared to the well-known "light-induced excited spin state trapping" (or LIESST) process which is quantitative only below ∼50 K.[4−6] Moreover, this effect may be observed with complexes including any d^4 to d^7 transition metal ions. The strategy consists of using molecules that include at least one photosensitive ligand and in triggering the metal ion spin change by varying the ligand-field strength under the effect of an electromagnetic radiation. The photochemical process we first adopted is the ligand *cis/trans* photoisomerization. However, any other photoreaction capable of changing the ligand field significantly might also be appropriate.

A prerequisite for the observation of the LD-LISC effect is that the two complexes C$_c$ and C$_t$ formed with the ligand *cis* and *trans* isomers present different magnetic behaviors as a function of temperature. In the temperature range where the spin states of C$_c$ and C$_t$ differ, it should be possible to induce the spin change of the metal ion by photoisomerizing the ligand. A convenient procedure to achieve this purpose is to design the metal environment in order that at least one of the two complexes exhibits a thermally-induced high-spin (HS) state ↔ low-spin (LS) state crossover. If so, a slight variation of the ligand-field strength is expected to alter the temperature

dependence of the magnetic properties significantly. Of course, C$_c$−C$_t$ couples where the metal ion retains the HS state at any temperature in one of the components and the LS state in the other should also be appropriate. However such couples, if existing, should not be easily obtained, for the relevant ligand-field strength values must now lie on both sides of the spin-crossover range, which is hardly predictable and requires the ligand-field change resulting from the C$_c$ ↔ C$_t$ photoconversion to be much larger than in the former case.

The first system found to be adapted to the observation of the LD-LISC effect was of the type Fe^{II}(Stpy)$_4$(NCS)$_2$,[3] where Stpy stands for 4-styrylpyridine, i.e. 1-phenyl-2-(4-pyridyl)-ethene (see **1**, with R = H), and the two NCS$^-$ groups are in

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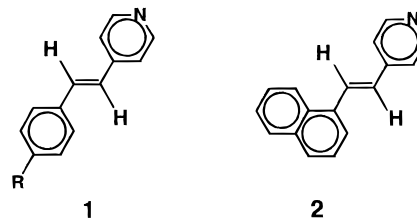
trans positions. Fe(*trans*-Stpy)$_4$(NCS)$_2$ does exhibit a thermally-induced spin conversion centered around 108 K, while Fe(*cis*-Stpy)$_4$(NCS)$_2$ is in the HS state at any temperature. It follows that the highest temperature at which the light-induced spin change might be observed is as low as 90 K and that the photoisomerization quantum yield should therefore be rather weak. So, we decided to modify the metal environment in order to increase this temperature.

The present work is mainly related to the species Fe^{II}(Stpy)$_4$-(X)$_2$ where X$^-$ = NCBPh$_3^-$ and NCBH$_3^-$. With both anionic ligands, the thermal spin crossover of the C$_t$ complex Fe(*trans*-Stpy)$_4$(X)$_2$ was expected to be significantly shifted toward higher temperatures, compared to that observed for X$^-$ = NCS$^-$; such a trend had been previously reported for the homologous species

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Fe(phen)$_2$(X)$_2$ (phen = 1,10-phenanthroline).[7–9] Moreover, in order to possibly increase still more the spin-conversion temperature and/or to reduce the residual HS fraction at low temperature, we have also investigated compounds of the type Fe^{II}(*trans*-L)$_4$(X)$_2$, where X$^-$ = NCBPh$_3$$^-$ or NCBH$_3$$^-$ and L is a 4-styrylpyridine derivative whose phenyl ring is either para-substituted with R = CH$_3$ or COOCH$_3$ (see **1**) or replaced by a 1-naphthyl group (see **2**).

The LD-LISC effect has been demonstrated for the first time, at 140 K, by UV−visible absorption spectrometry, on the species Fe(Stpy)$_4$(NCBPh$_3$)$_2$ embedded in polymeric films of cellulose acetate.

Experimental Section

Preparation of the Ligands. All these compounds were synthesized out of light so as to exclude any photoisomerization process.

***trans*-4-Styrylpyridine (or *trans*-Stpy).** This was prepared as described recently,[11] by using the method first outlined by Shaw et al.[10] and generally adopted afterward,[12–14] which consists of reacting equimolar amounts of 4-methylpyridine and benzaldehyde in acetic anhydride at reflux. However, the procedures utilized[11] for treating this mixture and purifying the resulting brown precipitate as white needles were different from those reported formerly.

***trans*-1-(4-Methylphenyl)-2-(4-pyridyl)ethene (or *trans*-MeStpy).** The synthesis of this ligand was derived from the previous one. A 0.1 mol (9.70 mL) sample of 4-methylpyridine and 0.1 mol (12 g) of 4-tolualdehyde were dissolved in 17 mL of acetic anhydride. The solution was refluxed with stirring for 24 h, then cooled to room temperature, and poured into 70 mL of ice-cold water to hydrolyze the excess of acetic anhydride. The mixture was made alkaline (pH 8−9) with an aqueous solution of NaOH. The precipitate that formed was filtered off, washed repeatedly with water, dried under vacuum, and recrystallized from a 1:1 ethanol/water mixture in the form of cream-colored needles. Yield: ∼70%. Anal. Calcd for C$_{14}$H$_{13}$N: C, 86.11; H, 6.71; N, 7.17. Found: C, 85.78; H, 6.72; N, 7.27. ^{1}H NMR chemical shifts (ppm) and coupling constants (Hz) in CDCl$_3$: dd, 8.56, J = 6 (2H); d, 7.44, J = 8 (2H); dd, 7.36, J = 6 (2H); d, 7.28, J = 17 (1H); d, 7.21, J = 8 (2H); d, 6.97, J = 17 (1H); s, 2.4 (3H).

***trans*-1-(4-(Methylcarboxy)phenyl)-2-(4-pyridyl)ethene (or *trans*-COOMeStpy).** The first stage of the synthesis consisted in preparing the *trans*-Stpy derivative whose phenyl ring is para-substituted with −COOH. A 0.1 mol (10 mL) sample of 4-methylpyridine and 0.1 mol (16.9 g) of 4-carboxybenzaldehyde were refluxed in acetic anhydride (40 mL) for 16 h. The mixture was then cooled to room temperature and poured into 100 mL of ice-cold water. The resulting white precipitate was filtered off and washed repeatedly with water, ethanol, and ethyl ether. The acid function was characterized from the ^{1}H NMR and IR spectra. Yield: ∼72%. Part of this compound (2.5 g) was then allowed to react with 20 mL of thionyl chloride in order to obtain the corresponding acid chloride. The mixture was stirred for 12 h at room temperature, and the excess thionyl chloride was removed by distillation under atmospheric pressure. The yellow-white residue of acid chloride was dried under vacuum and then immediately treated with 20 mL of neat methanol in order to be converted into ester. The mixture was stirred for 1.30 h at 0 °C and the excess methanol removed under vacuum. In the final product, the pyridine ring was protonated, as shown by the existence of a large band near 2700 cm^{-1} in the IR spectrum. Its deprotonation was achieved by dissolving the ester in dichloromethane and making the solution alkaline with

triethylamine. After extraction of this solution with water, the dichloromethane of the organic phase was removed by distillation under reduced pressure and the residue was recrystallized from a 1:1 ethanol/water mixture. The white precipitate of ester was isolated and dried under vacuum. Yield: ∼30% with regard to the starting acid. Anal. Calcd for C$_{15}$H$_{13}$NO$_2$·0.14CH$_2$Cl$_2$: C, 72.43; H, 5.34; N, 5.58; O, 12.76. Found: C, 72.80; H, 5.25; N, 4.93; O, 13.22. ^{1}H NMR chemical shifts (ppm) and coupling constants (Hz) in CDCl$_3$: dd, 8.62, J = 6 (2H); d, 8.07, J = 8.5 (2H); d, 7.61, J = 8.5 (2H); dd, 7.40, J = 6 (2H); d, 7.33, J = 16 (1H); d, 7.13, J = 16 (1H); s, 3.95 (3H).

***trans*-1-(1-Naphthyl)-2-(4-pyridyl)ethene (or *trans*-NPE).** The synthesis of this compound was initiated similarly to that described by Galiazzo et al.,[15] i.e. by refluxing 4-methylpyridine (0.1 mol, ∼10 mL) and 1-naphthaldehyde (0.1 mol, 15.6 g) in acetic anhydride (10 mL) for 12 h with stirring. However the treatment of this mixture differed from that reported previously. The excess acetic anhydride was removed, first by distillation under reduced pressure and then by dissolving the tarry residue into dichloromethane, making the solution alkaline with triethylamine, and extracting it three times with 5 mL of water. The brown residue obtained on removing the solvent of the organic phase was dissolved into HCl-containing water. After one extraction with toluene to eliminate the unchanged aldehyde, this solution was made alkaline with an aqueous solution of NaOH and then extracted with cyclohexane. The beige precipitate that appeared on removing this solvent was recrystallized from cyclohexane. Yield: ∼50%. Anal. Calcd for C$_{17}$H$_{13}$N: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.00; H, 5.15; N, 6.03. ^{1}H NMR chemical shifts (ppm) and coupling constants (Hz) in CDCl$_3$: dd, 8.61, J = 6 (2H); m, 8.2−7.5 (8H); dd, 7.43, J = 6 (2H); d, 7.04, J = 16 (1H).

***cis*-4-Styrylpyridine (or *cis*-Stpy).** This was obtained from a Wittig reaction, as described by Williams et al.,[13] except that benzyltriphenylphosphonium chloride was used in place of the corresponding bromide. Bp: 103−104 °C (0.4 mmHg). ^{1}H NMR chemical shifts (ppm) and coupling constants (Hz) in CD$_3$CN: dd, 8.45, J = 6 (2H); m, 7.26 (5H); dd, 7.13, J = 6 (2H); d, 6.85, J = 12 (1H); d, 6.60, J = 12 (1H). Gas chromatography showed that the product was composed of 99% *cis*-Stpy and 1% *trans*-Stpy.

Preparation of the Metal Complexes. These compounds were synthesized under argon, and out of light in order to prevent ligand photoisomerization. The solvent (anhydrous methanol) was distilled over CaCl$_2$, dried over 3 Å molecular sieves, and degassed just before use. All complexes were obtained in a similar manner. The procedure will be detailed solely for one of them. It consists of preparing a Fe-(NCBPh$_3$)$_2$- or Fe(NCBH$_3$)$_2$-containing solution and in reacting it upon one of the above photoisomerizable ligands.

Fe(*trans*-Stpy)$_4$(NCBPh$_3$)$_2$. A 185.6 mg sample of FeSO$_4$·7H$_2$O (0.67 mmol) in anhydrous methanol (4.5 mL) was added dropwise to 414.2 mg of sodium cyanotriphenylborate hydrate (1.34 mmol) in the same solvent (9 mL). The mixture was stirred at room temperature for 10 min, allowed to settle for 10 min, and then decanted. The precipitate of Na$_2$SO$_4$ was filtered off and washed with anhydrous methanol (2 mL). The Fe(NCBPh$_3$)$_2$-containing methanolic fractions were combined, degassed again, and then added dropwise to a suspension of 362.5 mg of *trans*-4-styrylpyridine (2.0 mmol) in a degassed water−methanol mixture (9 mL−9 mL). A yellow-orange precipitate formed. The mixture was stirred further for 2 h, and the precipitate was isolated by filtration and dried under an argon stream. Anal. Calcd for C$_{90}$H$_{74}$N$_6$B$_2$Fe: C, 82.03; H, 5.66; N, 6.38; B, 1.67; Fe, 4.25. Found: C, 81.82; H, 5.59; N, 6.40; B, 1.59; Fe, 4.11.

Fe(*cis*-Stpy)$_4$(NCBPh$_3$)$_2$. The compound is a yellow powder. Anal. Calcd for C$_{90}$H$_{74}$N$_6$B$_2$Fe: see the above values. Found: C, 81.96; H, 5.56; N, 6.36; B, 1.57; Fe, 3.93.

Fe(*trans*-Stpy)$_4$(NCBH$_3$)$_2$. The compound is a red-orange powder. Anal. Calcd for C$_{54}$H$_{50}$N$_6$B$_2$Fe: C, 75.32; H, 5.86; N, 9.77; B, 2.56; Fe, 6.49. Found: C, 74.90; H, 5.90; N, 9.72; B, 2.46; Fe, 6.90.

Fe(*cis*-Stpy)$_4$(NCBH$_3$)$_2$. The compound is a yellow crystalline powder. Anal. Calcd for C$_{54}$H$_{50}$N$_6$B$_2$Fe: see the above values. Found: C, 75.13; H, 5.82; N, 9.78; B, 2.28; Fe, 6.10.

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Fe(*trans*-MeStpy)₄(NCBPh₃)₂. The compound is an orange powder. Anal. Calcd for $C_{94}H_{82}N_6B_2Fe$: C, 82.18; H, 6.02; N, 6.12; B, 1.60; Fe, 4.07. Found: C, 81.86; H, 6.03; N, 5.92; B, 1.58; Fe, 3.85.

Fe(*trans*-COOMeStpy)₄(NCBH₃)₂·4H₂O. The compound is an orange powder. Anal. Calcd for $C_{62}H_{66}N_6O_{12}B_2Fe$: C, 63.89; H, 5.71; N, 7.22; B, 1.89; O, 16.49; Fe, 4.79. Found: C, 63.15; H, 5.50; N, 7.10; B, 1.83; Fe, 4.68; O (calculated by difference), 17.77.

Removal of water molecules could be obtained by heating the solid under reduced pressure at 80 °C for 1.5 h. The color of the resulting product, contrary to that of the hydrated species, changes (from orange to dark purple) on passing from room temperature to 77 K, which shows that iron(II) ions exhibit a thermally-induced spin crossover. It should be noted that this compound tends to recover its water molecules rapidly.

Fe(*trans*-NPE)₄(NCBPh₃)₂. The compound is a yellow-orange crystalline powder. Anal. Calcd for $C_{106}H_{82}N_6B_2Fe$: C, 83.92; H, 5.45; N, 5.54; B, 1.41; Fe, 3.68. Found: C, 83.63; H, 5.52; N, 5.52; B, 1.26; Fe, 3.74.

Preparation of the Polymeric Films. A number of cellulose acetate films including Fe(*trans*-Stpy)₄(NCBPh₃)₂ or Fe(*cis*-Stpy)₄(NCBPh₃)₂ at different concentrations were prepared using the following procedure. To a filtered solution of cellulose acetate (0.70 g) in acetone (15 mL) was added a given volume of a solution containing the C_t (2.25 mg) or the C_c (4.52 mg) complex in acetone (5 mL). The mixture was stirred, poured into an 8 cm diameter flat-bottomed glass vessel (Petri box), and then allowed to stand in darkness or under inactive light until the solvent was completely evaporated. To make this evaporation very slow (~1 week), the vessel was covered with finely-bored laboratory film. All these films were later kept in darkness.

Physical Measurements. Variable-temperature magnetic susceptibility data were determined for bulky samples, using a Faraday-type magnetometer equipped with an Oxford Instruments helium continuous-flow cryostat. HgCo(NCS)₄ was used as the calibrant. The independence of the susceptibility with regard to the applied magnetic field was checked, for each complex, at room temperature. Diamagnetic corrections were estimated from Pascal's tables. The temperature was varied at a rate of 1 K min⁻¹.

UV−visible absorption measurements were carried out on polymeric films, using a Varian Cary 5E double-beam spectrophotometer, equipped with an APD Cryogenics closed-cycle helium cryogenic system including a DMX-1E cryostat and a DE-202 expander. Film irradiations were performed *in situ*, at 260 and 322 nm, with a Jobin-Yvon xenon 150 W stabilized lamp, coupled with a Jobin-Yvon H-10 concave holographic grating monochromator.

¹H NMR spectra were recorded on a Bruker 200 MHz spectrometer.

Results and Discussion

In the room-temperature IR spectra of all the above complexes, the ν_{CN} absorption of the anionic ligands is observed between 2178 and 2195 cm⁻¹. As the band is single and sharp, it is to be expected that the two NCBH₃ or NCBPh₃ entities of each molecule are *trans*-located with regard to the set of the four Fe−N(pyridine ring) bonds. Similar characteristics were observed for ν_{CN} absorption in the IR spectra of Fe(*trans*-Stpy)₄(NCS)₂ and Fe(*cis*-Stpy)₄(NCS)₂, and the X-ray crystal structures of these compounds[3] corroborated the *trans* positions of the NCS groups. It should be noted that the ν_{CN} wavenumber was found to increase on passing from NCS (2067 ± 4 cm⁻¹) to NCBH₃ (2183 ± 5 cm⁻¹) and then to NCBPh₃ (2192 ± 3 cm⁻¹), while the corresponding absorption decreases, being successively very strong, strong, and medium.

Magnetic Behavior. In the five C_t complexes under investigation, the iron ion exhibits a thermally-induced $S = 2 \leftrightarrow S = 0$ spin crossover, as shown by the $\chi_M T$ vs T plots reproduced in Figure 1 (χ_M = molar magnetic susceptibility); let us mention that the curve related to Fe(*trans*-COOMeStpy)₄(NCBH₃)₂ was obtained after correction of the experimental data for the presence of a certain amount of the HS species Fe(*trans*-COOMeStpy)₄(NCBH₃)₂·4H₂O (see the synthesis section). The
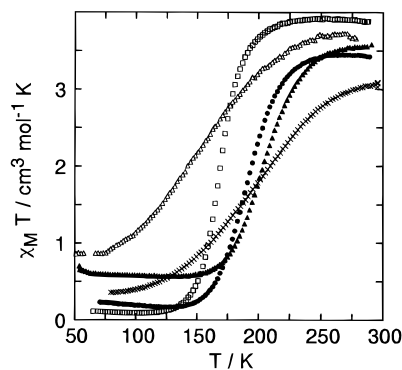

Figure 1. Temperature dependence of $\chi_M T$ for the C_t complexes Fe-(*trans*-Stpy)₄(NCBPh₃)₂ (full circles), Fe(*trans*-Stpy)₄(NCBH₃)₂ (full triangles), Fe(*trans-Me*Stpy)₄ (NCBPh₃)₂ (open squares), Fe(*trans*-COOMeStpy)₄(NCBH₃)₂ (open triangles), and Fe(*trans*-NPE)₄(NCBPh₃)₂ (crosses).
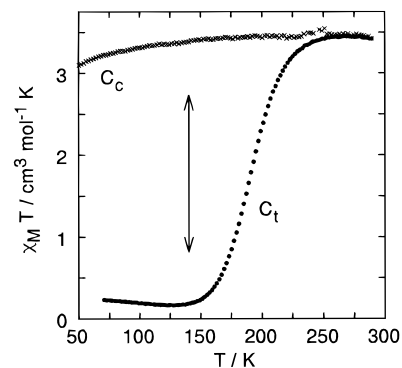

Figure 2. Temperature dependence of $\chi_M T$ for the C_t and C_c forms of Fe(Stpy)₄(NCBPh₃)₂. At 140 K, photoinduced $C_c \leftrightarrow C_t$ interconversion is expected to result in iron(II) HS-state $\leftrightarrow$ LS-state crossover.

magnetic behaviors of these compounds appear to be widely different. In particular, the cooperative character of the spin conversion is much weaker for Fe(*trans*-COOMeStpy)₄-(NCBH₃)₂ and Fe(*trans*-NPE)₄(NCBPh₃)₂ than for the other species.

In contrast, both C_c complexes are in the HS state at any temperature: the $\chi_M T$ product retains a nearly constant value on cooling, passing from 3.42 (3.58) cm³ mol⁻¹ K at room temperature to 3.00 (3.19) cm³ mol⁻¹ K at 30 K for Fe(*cis*-Stpy)₄(NCBPh₃)₂ (see Figure 2) and Fe(*cis*-Stpy)₄(NCBH₃)₂, respectively.

In Table 1 are collected the characteristic data related to the C_t complexes, viz. the highest and lowest $\chi_M T$ values (referred to as $(\chi_M T)_{max}$ and $(\chi_M T)_{min}$, respectively), an estimate of the residual HS fraction in the lowest temperature range, and the temperatures at which the HS-to-LS transformation is half-accomplished ($T_{1/2}$) or just completed (T_0). The rather low $(\chi_M T)_{max}$ value found for Fe(*trans*-NPE)₄(NCBPh₃)₂ as well as the shape of the relevant $\chi_M T$ vs T plot (see Figure 1) shows that, for this compound, the spin conversion is already in progress at room temperature. Moreover, the relatively high $(\chi_M T)_{min}$ values obtained for Fe(*trans*-Stpy)₄(NCBH₃)₂, Fe(*trans*-COOMeStpy)₄(NCBH₃)₂, and Fe(*trans*-NPE)₄(NCBPh₃)₂ are indicative of the existence of significant amounts of residual HS species (going from ~11 to 22%) in the lowest temperature range.

To facilitate the observation of the LD-LISC effect, the following conditions are required: (i) T_0 (and therefore $T_{1/2}$) must be high enough for the ligand *cis/trans* isomerization not to be hindered as a consequence of the matrix rigidity; (ii) the thermally-induced spin conversion has to be rather complete at

Table 1. Characteristic Magnetic Data for the C_t Complexes

compound	$(\chi_M T)_{max}$ (cm³ mol⁻¹ K)	$(\chi_M T)_{min}$ (cm³ mol⁻¹ K)	HS fraction at low T (%)	$T_{1/2}$ (K)	T_0 (K)
Fe(*trans*-Stpy)₄(NCBPh₃)₂	3.42	0.17	2	190	140
Fe(*trans*-Stpy)₄(NCBH₃)₂	3.58	0.58	16	200	155
Fe(*trans*-MeStpy)₄(NCBPh₃)₂	3.87	0.09	1	166	120
Fe(*trans*-COOMeStpy)₄(NCBH₃)₂	3.70	0.80	22	155	75
Fe(*trans*-NPE)₄(NCBPh₃)₂	3.07	0.39	~11	186	90
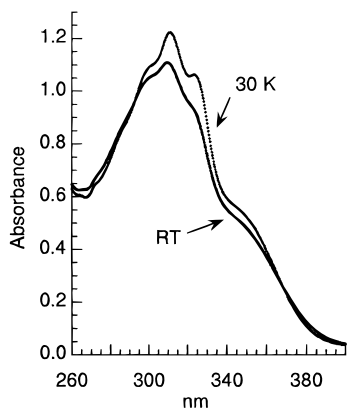
Figure 3. Absorption spectra, at room temperature and 30 K, of Fe-(*trans*-Stpy)₄ (NCBPh₃)₂ embedded in a cellulose acetate film.

Figure 4. Absorption spectra, at room temperature and 100 K, of Fe-(*cis*-Stpy)₄ (NCBPh₃)₂ embedded in a cellulose acetate film.

Figure 5. Temperature dependence of the relative absorbance variation $(A_T - A_{RT})/A_{RT}$, at 342 nm, for the C_t and C_c forms of Fe(Stpy)₄-(NCBPh₃)₂ embedded in cellulose acetate films. The straight line for C_c was drawn for clarity.

this temperature, in order that the spin-change-detecting signal may be as large as possible. So, it clearly appears that the best candidates for this observation are Fe(*trans*-Stpy)₄(NCBPh₃)₂ and Fe(*trans*-MeStpy)₄(NCBPh₃)₂. Favoring the temperature criterion led us to choose the former compound. The magnetic behaviors of this species and of the homologous C_c form are presented in Figure 2. They show that, at 140 K, according to whether Stpy is in the *trans* or the *cis* configuration, the iron-(II) ion is in the LS or the HS state, respectively. So, the LD-LISC effect should very likely be observed at this temperature.

LD-LISC Effect. To provide evidence for the occurrence of the LD-LISC effect in compounds embedded within polymeric matrices, three points have to be confirmed: (i) that the magnetic behaviors of the C_t and C_c complexes as a function of temperature are comparable with those of the corresponding bulky polycrystalline samples; (ii) that the ligand *cis/trans* photoisomerization can take place with a nonnegligible quantum yield at the temperature chosen for the observation of the effect; (iii) that this photoisomerization results in a change of the metal ion spin state. The experiments (variable-temperature UV−visible absorption measurements) were carried out on both Fe-(Stpy)₄(NCBPh₃)₂ isomers included in cellulose acetate films.

(a) Variable-Temperature Spin-State Behavior of Fe(II) in the C_t and C_c Complexes. The spectra of C_t and C_c were recorded at room temperature (RT) and 30 K (Figure 3) and at RT and 100 K (Figure 4), respectively.

Those of C_t clearly depend on the temperature. The broad band with a maximum at 311 nm and the two shoulders at ∼300 and ∼323 nm correspond to Stpy $\pi \rightarrow \pi^*$ absorption. The unresolved band at ∼350 nm, which does not appear in the spectrum of the uncoordinated ligand, is likely to correspond to a charge-transfer process: consequently, it is expected to be noticeably sensitive to the metal ion spin state. Moreover, around this wavelength, the absorption arising from cellulose acetate can be considered negligible. Following the temperature dependence of the absorbance (A_T) at 342 nm did allow us to obtain evidence for the expected thermally-induced spin crossover. This is represented in Figure 5, in the form of the (A_T − A_{RT})/A_{RT} vs T plot. The $T_{1/2}$ value (∼185 K) is close to that obtained for the bulky sample (190 K). However the spin-conversion process is less cooperative (see Figure 2 for
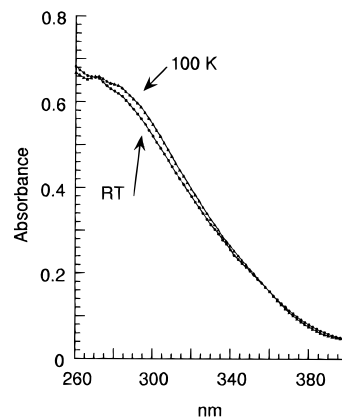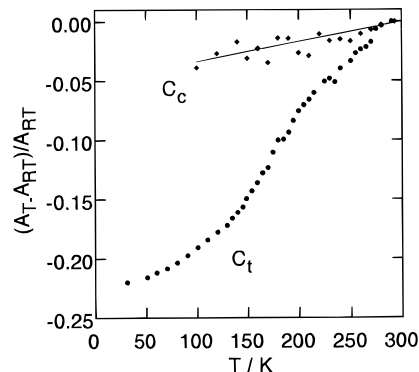
comparison), presumably as a consequence of the dilution of the compound in the polymeric matrix and/or its interaction with this matrix through hydrogen-bonding. It should be noted that, for the most concentrated samples studied, the phenomenon could be visually observed, for it is accompanied by a yellow-orange-to-red color change on passing from RT to 77 K.

The absorption curves of C_c (Figure 4) are quite different from those of C_t. As already reported in the case of the free Stpy ligands, the maximum absorbance, of $\pi \rightarrow \pi^*$ nature, is shifted toward lower wavelengths ($\lambda_{max} \approx 285$ nm) and is found to be reduced in intensity upon comparison with similarly concentrated samples. However, the charge-transfer band, though hardly detectable, appears again as a shoulder (at ∼340 nm) of the previous broad absorption. At 342 nm, the absorbances at RT and 100 K only slightly differ. Though the (A_T − A_{RT})/A_{RT} vs T plot (Figure 5) cannot be accurately defined at this wavelength, it shows unambiguously that the complex is in the same spin state (known to be the HS state) at both temperatures. This conclusion is corroborated by the absence of thermochromism, the concentrated samples under study retaining the same yellow color on passing from RT to 77 K. We note that the slight slope of the curve might be associated with the polymeric film contraction on cooling.

Thus it clearly appears that, in Fe(*trans*-Stpy)$_4$(NCBPh$_3$)$_2$ as well as in Fe(*cis*-Stpy)$_4$(NCBPh$_3$)$_2$, the spin-state behavior of iron(II) as a function of temperature is similar whether the complex is examined in the form of a polymeric film (cf. Figure 5, derived from the UV−visible absorption data) or of a bulky polycrystalline sample (cf. Figure 2, derived from the magnetic susceptibility data).

(b) Ligand *cis/trans* Photoisomerization at 140 K. The *cis/trans* photoisomerization of uncomplexed 4-styrylpyridine in solution has been widely investigated (see, e.g., refs 16−19). At room temperature, *trans*-Stpy was shown to convert into *cis*-Stpy through the singlet pathway which consists of ^{1}*trans* → ^{1}*perp* internal rotation about the central double bond. At lower temperatures, the triplet alternative mechanism, which implies ^{1}*trans* → ^{3}*trans* intersystem crossing followed by ^{3}*trans* → ^{3}*perp* twisting, takes place. It becomes predominant only below ca. 100 K, when isomerization is practically hindered by the viscosity of the medium. The $\Phi_{t\rightarrow c}$ quantum yield at room temperature, with $\lambda_{exc} = 313$ nm, was found to vary from 0.37 to 0.46 according to the solvent and to be zero at 77 K in a 3-methylpentane rigid matrix.[17b] The main deactivation path competing with *trans* → *cis* photoconversion is fluorescence emission. Regarding *cis*-Stpy, the singlet excited state is not fluorescent. For this species, the only ^{1}*cis* deactivation process besides *cis* → *trans* isomerization is the cyclization to a dihydropolycyclic compound.[16b,19a] However this reaction, which is reversible in the absence of oxidants, takes place with a low rate and, consequently, gives a very poor photostationary concentration of cyclized species. At room temperature, $\Phi_{c\rightarrow t}$ and Φ_{cycl} quantum yields in *n*-hexane are 0.34 and 0.015, respectively, for $\lambda_{exc} = 254$ nm.[16b]

For coordinated 4-styrylpyridine, whose photochemical behavior was investigated in a number of complexes in solution (see, e.g., refs 20−22), *cis/trans* isomerization was found to be the only detectable photoreaction and to lead to photostationary states very rich in converted isomer.

Cellulose acetate films containing Fe(*trans*-Stpy)$_4$(NCBPh$_3$)$_2$ were irradiated at 140 K, with $\lambda_{exc} = 322$ nm, until the photostationary state was reached. The initial and final spectra are depicted in Figure 6. Similar experiments were carried out on Fe(*cis*-Stpy)$_4$(NCBPh$_3$)$_2$, with $\lambda_{exc} = 260$ nm (Figure 7). In both cases, the alteration of the starting material spectrum under the effect of irradiation provides evidence for a *cis/trans* isomerization of 4-styrylpyridine. However, it clearly appears that the conversion ratio is rather low, compared to the results of previous studies on complexes, which is very likely to result from the rigidity of the polymeric matrix at 140 K. Assuming that both photostationary states only contain C$_c$ and C$_t$ complexes, their composition can be approximated from the simulation of their spectra with a linear combination of C$_c$ and C$_t$ spectra. C$_c$ irradiation is found to lead to about 67% C$_t$ and

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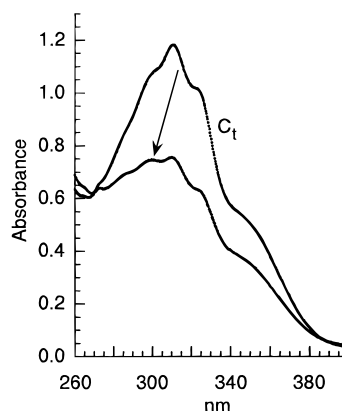

Figure 6. Absorption spectra of C$_t$ in a cellulose acetate film and of the photostationary state obtained after irradiation of the sample at 140 K with $\lambda_{exc} = 322$ nm.
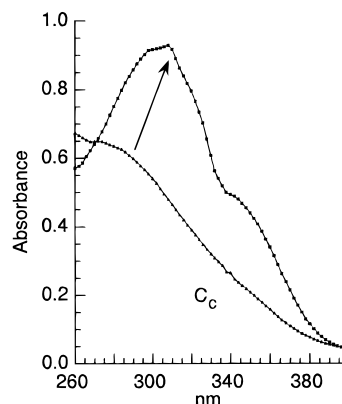

Figure 7. Absorption spectra of C$_c$ in a cellulose acetate film (at a concentration very close to that of C$_t$ in Figure 6) and of the photostationary state obtained after irradiation of the sample at 140 K with $\lambda_{exc} = 260$ nm.
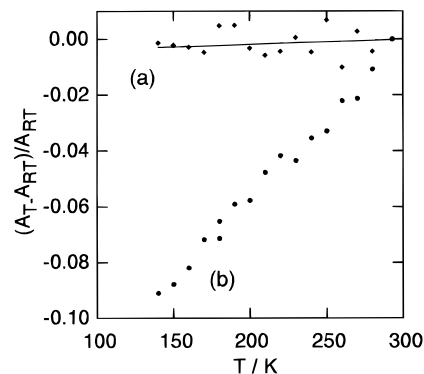

Figure 8. Temperature dependence of the relative absorbance variation $(A_T - A_{RT})/A_{RT}$, at 344 nm, for a C$_c$-containing cellulose acetate film, before (a) and after (b) irradiation with $\lambda_{exc} = 260$ nm at 140 K. The straight line (a) was drawn for clarity.

33% C$_c$, and the photostationary state arising from C$_t$ irradiation should be composed of about 67% C$_c$ and 33% C$_t$.

(c) Spin-State Change Resulting from Ligand Photoisomerization at 140 K. As seen above (Figure 5), iron(II) ions, at 140 K, are at least partly LS in the C$_t$ form of Fe(Stpy)$_4$-(NCBPh$_3$)$_2$, while they are HS in the C$_c$ form. Consequently, the photoinduced C$_c$ → C$_t$ and C$_t$ → C$_c$ conversions are very likely to result in iron(II) spin change. This conclusion was corroborated by following the variation of the $(A_T - A_{RT})/A_T$ ratio at 344 nm as a function of temperature (from 140 to 293 K) for a C$_c$ sample and for the same sample after irradiation with $\lambda_{exc} = 260$ nm at 140 K. The curves are represented in

Figure 8. Their comparison clearly shows that the C_t molecules resulting from the photoconversion of the HS C_c species exhibit a thermally-induced spin-state crossover and hence that they were effectively in the LS state at 140 K.

Conclusion

The above data provide evidence for the expected LD-LISC effect in $Fe(Stpy)_4(NCBPh_3)_2$. To complete this work, a thorough investigation of the photochemical properties of this complex, in solution or in cellulose acetate films, is in progress.[22]

The next step will consist of developing new systems where the LD-LISC effect might be observed under more favorable conditions, in particular at higher temperatures. This requires the iron(II) ions to be subjected to stronger ligand fields than in the complexes herein examined. Preliminary results obtained with a complex of the type $Fe(L)_2(NCS)_2$, where L is a bidentate ligand substituted with one photoisomerizable chain, should permit the photoinduced spin change to be observed in the vicinity of room temperature.