

First Evidence of a Photoinduced Spin Change in an Fe^{III} Complex Using Visible Light at Room Temperature

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An iron(III) complex [Fe(salten)(Mepepy)]BPh₄ containing only one photoisomerizable ligand (Mepepy) has been synthesized, it exhibits a thermally-induced spin crossover in the solid state and in solution {H₂salten = 4-azaheptamethylene-1,7-bis(salicylideneimineate); Mepepy = 1-(pyridin-4-yl)-2-(*N*-methylpyrrol-2-yl)ethene}. The photoisomerizations of both the free and coordinated Mepepy

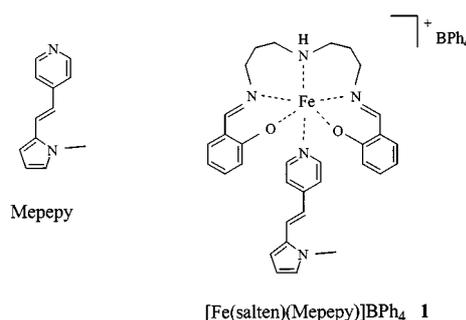
ligand have been observed at room temperature with visible-light irradiation and monitored by UV/Vis and ¹H NMR spectrometries. *trans-to-cis* isomerization of only one photosensitive ligand in the iron(III) complex is sufficient to detect a partial spin change of the iron(III) ion. This photoinduced spin change is seen for the first time from a high-spin state to a low-spin state.

Spin crossover phenomena exhibited by transition metal complexes are the subject of intensive studies.^{[1][2]} In this field, the ligand-driven light-induced spin change (LD-LISC) concept first described by our group^[3] has opened up new perspectives for the purpose of optical information storage on the molecular scale. For this it is necessary to synthesize complexes in which a photoinduced modification of one or several ligands would result in a ligand field change and trigger the metal ion spin conversion.

The feasibility of the LD-LISC process was first demonstrated^{[3][4]} at 140 K on an iron(II) complex containing four photosensitive ligands. Ultra-violet irradiation of this compound induced a *trans* ↔ *cis* isomerization of the four ligands and a subsequent low-spin (LS) ↔ high-spin (HS) conversion. More recently, the LD-LISC effect has been observed at room temperature^[5] on an iron(II) complex containing two photoisomerizable ligands. A *trans* to *cis* photoconversion in this compound induced a low-spin towards high-spin change. We now want to show that the isomerization of only one photosensitive ligand is sufficient to induce a spin change. We will also show that the LD-LISC effect can be observed in an iron(III) compound. For this purpose, we present a study of an iron(III) complex containing only one photoisomerizable ligand which has the distinctive feature of absorbing visible light.

Our strategy was to coordinate an iron(III) ion to a pentadentate salten²⁻ ligand {H₂salten = 4-azaheptamethylene-1,7-bis(salicylideneimineate)}, the sixth position being occupied by a potentially photosensitive Mepepy ligand {Mepepy = 1-(pyridin-4-yl)-2-(*N*-methylpyrrol-2-yl)ethene}.^[6] The H₂salten ligand has been employed because several complexes based on this ligand are known to exhibit thermally-induced spin crossovers.^{[7][8]} The behavior under

irradiation of the Mepepy ligand has not yet been explored but the *trans* and *cis* isomers are expected to be stable and interconvertible by visible light. We report here the synthesis of [Fe(salten)(Mepepy)]BPh₄ (**1**), its electronic and magnetic properties, and the observation of the LD-LISC effect at room temperature by suitable NMR spectroscopic experiments.



Scheme 1. The photosensitive ligand and complex made and studied

The elemental analysis, IR characterizations and the magnetic behavior allow us to propose the structure presented in Scheme 1 for [Fe(salten)(Mepepy)]BPh₄. The magnetic susceptibility of a powdered sample of **1** was measured in the temperature range 10–320 K. The temperature dependence of the $\chi_M T$ product (χ_M = molar magnetic susceptibility) shows a gradual $S = 1/2 \leftrightarrow S = 5/2$ crossover of iron(III) ions (Figure 1) as expected for complexes of this family.^{[7][8]} No thermal hysteresis was observed. The crossover taking place between 150 K and 320 K is obviously incomplete at 320 K however, due to the low thermal stability under partial vacuum, measurements at higher temperatures were not possible. The low temperature plateau around $\chi_M T = 0.53 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ indicates that nearly all molecules are in the low-spin state. In contrast, the $\chi_M T$ value at 320 K ($2.68 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$) indicates that about 55% of the molecules are in the high-spin state (assuming that $\chi_M T = S(S+1)/2 = 4.4 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ for $S = 5/2$).

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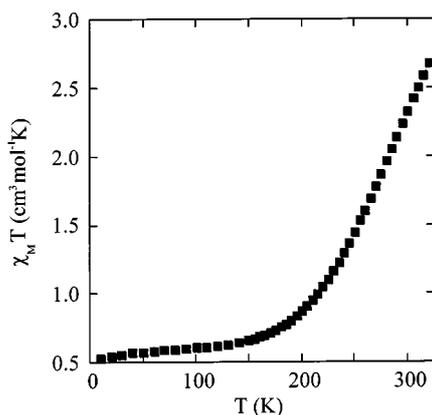


Figure 1. Temperature dependence of $\chi_M T$ of $[\text{Fe}(\text{salten})(\text{Mepepy})]\text{BPh}_4$ as a powder

Irradiation of the uncoordinated Mepepy ligand was carried out first. The experiments were performed at $\lambda = 405 \pm 5$ nm on acetonitrile solutions at room temperature and monitored by UV/Vis and NMR spectrometry. The UV/Vis spectrum of the free Mepepy ligand shows two $\pi-\pi^*$ transition bands (Figure 2a). Upon irradiation, the strongest effect is observed on the band at $\lambda_{\text{max}} = 353$ nm ($\epsilon = 22800 \text{ M}^{-1}\cdot\text{cm}^{-1}$) which is slightly blue-shifted and decreases to about half its intensity. The band at $\lambda_{\text{max}} = 241$ nm ($\epsilon = 7800 \text{ M}^{-1}\cdot\text{cm}^{-1}$) is less affected. An isosbestic point is observed at 300 nm. Irradiation of the ligand in an NMR tube in deuterated acetonitrile (10^{-3} M) leads to a photostationary state which is composed of 66% of the *cis* isomer and 34% of the *trans* isomer.^[9] From these results it is possible to compute the absorption band for the pure *cis* isomer, which is represented in Figure 2a.

We then studied the effect of light on the complex $[\text{Fe}(\text{salten})(\text{Mepepy})]\text{BPh}_4$ under the same conditions of solvent and temperature. Irradiation of solutions at wavelengths in the range 320–405 nm leads to very similar evolutions of the UV spectra and the photostationary states are reached within a few minutes. We chose to investigate the effect of visible light at $\lambda = 405 \pm 5$ nm, as for Mepepy. The UV/Vis absorption spectrum of **1** in a $1.87 \times 10^{-5} \text{ M}$ acetonitrile solution (Figure 2b) shows a strong band ($\lambda_{\text{max}} = 351$ nm, $\epsilon = 62000 \text{ M}^{-1}\cdot\text{cm}^{-1}$) which can be assigned to a “Mepepy”-centered $\pi-\pi^*$ transition and a weaker band ($\lambda_{\text{max}} = 480$ nm, $\epsilon = 6900 \text{ M}^{-1}\cdot\text{cm}^{-1}$) arising from a ligand-to-metal charge transfer (LMCT). Irradiation of this solution (Figure 2b) leads both to a slight blue-shift of the Mepepy-centered $\pi-\pi^*$ band (from 351 to 345 nm) and to a pronounced decrease of its intensity (from $\epsilon = 62000$ to $\epsilon = 39000 \text{ M}^{-1}\cdot\text{cm}^{-1}$ at 351 nm). In contrast, the LMCT band at 480 nm is essentially unaffected. The presence of a well defined isosbestic point at 301 nm shows the coexistence of only two molecular species upon irradiation. The parallel evolution upon irradiation of the $\pi-\pi^*$ band of uncoordinated and coordinated Mepepy strongly suggests that irradiation of **1** also causes a *trans* to *cis* photoisomerization of the coordinated Mepepy.

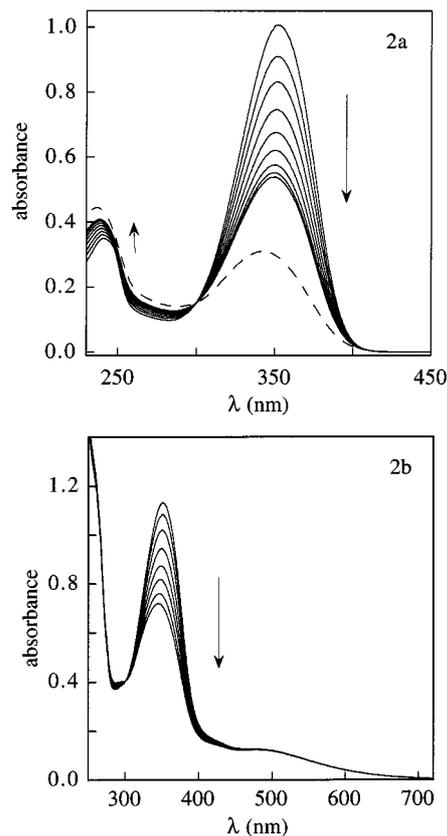


Figure 2. UV/Visible absorption spectra and evolutions upon irradiation at 405 nm of acetonitrile solutions of Mepepy (10^{-5} M) (2a) and of $[\text{Fe}(\text{salten})(\text{Mepepy})]\text{BPh}_4$ ($1.87 \times 10^{-5} \text{ M}$) (2b); the spectrum in dashed lines in 2a represents the calculated spectrum of pure *cis*-Mepepy

The magnetic susceptibility, and its variation under irradiation, of acetonitrile solutions of **1** were measured by the Evans method (^1H NMR spectrometry).^{[10][11]} The temperature dependence of $\chi_M T$ has been obtained between 243 K and 333 K for a 10^{-2} M CD_3CN solution of **1** before irradiation. Figure 3 reveals a thermal spin-crossover behavior with $\chi_M T$ increasing from $1.48 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ at 243 K to $3.61 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ at 333 K.

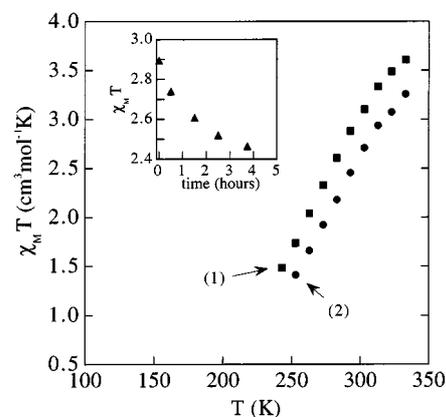


Figure 3. Temperature dependence of $\chi_M T$ of a CD_3CN solution (10^{-2} M) of $[\text{Fe}(\text{salten})(\text{Mepepy})]\text{BPh}_4$ before irradiation (1) and of a 10^{-3} M CD_3CN solution of the steady state (2); inset: time dependence of $\chi_M T$ of a 10^{-3} M CD_3CN solution of $[\text{Fe}(\text{salten})(\text{Mepepy})]\text{BPh}_4$

A 10⁻³ M CD₃CN solution of **1** in a capillary has been irradiated at room temperature. The irradiation induces a small decrease (inset of Figure 3) of $\chi_M T$ at 294 K from 2.89 to 2.46 cm³·mol⁻¹·K. This allows us to infer that **1** undergoes a partial HS \leftrightarrow LS change under irradiation. The temperature dependence of $\chi_M T$ of the steady state (Figure 3) reveals a thermal spin-crossover behavior with $\chi_M T$ increasing from 1.41 cm³·mol⁻¹·K at 253 K to 3.26 cm³·mol⁻¹·K at 333 K. The thermal spin crossovers before as well as after irradiation are reversible. Furthermore, it should be noted that solutions before and after irradiation are stable in the dark.

It is worth pointing out that the photoisomerization of a *trans* to *cis* styryl-pyridine group in an iron(II) complex^{[4][5]} results in a spin change from a low-spin state to a high-spin state. We report here the first example where light irradiation leads to a spin change in the opposite direction. This apparent discrepancy can be explained: as the methylpyrrole moiety of the Mepepy ligand is a strong π -donor group,^[6] the conversion of the *trans* isomer into the *cis* isomer results in a decrease of the π -donor character of the ligand and thus increases the ligand field strength and induces the HS \leftrightarrow LS change.

In conclusion, we have described the first Fe^{III} complex able to present a "Ligand-Driven Light-Induced Spin Change" behavior at room temperature. The complex contains only one photosensitive ligand which can be effectively photoisomerized by visible light. We have characterized the *trans* to *cis* photoisomerizations of the uncoordinated and coordinated Mepepy ligand and demonstrated that the *trans* to *cis* isomerization in complex **1** is accompanied by a small, but significant, decrease of $\chi_M T$, which shows an unusual high-spin to low-spin change.

Attempts are currently underway to cast thin films of **1** in order to study the effect of light in the solid state.

Experimental Section

General: Starting materials were purchased from Acros. Solvents were purchased from Merck. Acetonitrile was distilled from CaH₂. The photosensitive ligand and its complexes were prepared and handled under darkness to prevent photoisomerization. Magnetic Measurements: Quantum Design SQUID Magnetometer (MPMS5S model). UV/Vis: Varian Cary 5E or Cary 300. IR: Perkin-Elmer Spectrum 1000. NMR: Bruker AM 400 (400 MHz). Evans NMR: the NMR tube is equipped with a special stem coaxial insert (Wilma, WGS - 5BL). Irradiation: 200 W Hg (Xe) lamp (Oriol) with a standard bandpass filter 405 FS10-25 (Andover Corporation).

The ligand Mepepy^[6] was prepared according to the published procedure. - ¹H NMR (CD₃CN, 400 MHz): δ = 8.47 (d, J = 5.9 Hz, 2 H), 7.40 (d, J = 5.9 Hz, 2 H), 7.35 (d, J = 16.2 Hz, 1 H), 6.84 (d, J = 16.2 Hz, 1 H), 6.76 (m, 1 H), 6.59 (m, 1 H), 6.11 (m, 1 H), 3.72 (s, 3 H). - IR (KBr): $\tilde{\nu}$ = 955, 965 (C=C *trans*), 1590 (pyridine) cm⁻¹.

[Fe(salten)Cl]^[7] was prepared according to the published procedure.

[Fe(salten)(Mepepy)][BPh₄ 1: To a solution of [Fe(salten)Cl] (360 mg, 0.84 mmol) in MeOH (16 mL) was added a solution of Mepepy (201 mg, 1.09 mmol) in MeOH (2 mL). The mixture was warmed at 60°C for 1 hour, then filtered. To the filtrate was added a solution of sodium tetraphenylborate (288 mg, 0.84 mmol) in MeOH (4 mL). The mixture was then warmed for a further 5 minutes at 60°C and allowed to stand overnight. The precipitate was filtered off, washed with cold MeOH (3 mL), water (3 \times 10 mL), Et₂O (2 \times 15 mL) and dried in vacuo for 2 hours to give 466 mg of a black microcrystalline powder (yield 62%). - C₅₆H₅₅BFeN₅O₂ (896.7): calcd. C 74.97, H 6.18, N 7.81, Fe 6.24; found C 75.01, H 6.27, N 7.82, Fe 6.00. - IR (KBr): $\tilde{\nu}$ = 3231, 3214 (N-H), 1600 (pyridine), 950 (C=C *trans*), 732, 706, 611 (BPh₄) cm⁻¹.

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 [9] For *cis*-Mepepy: ¹H NMR (400 MHz, CD₃CN): δ = 6.61 (d, J = 12.2 Hz, 1 H, C=C *cis*), 6.36 (d, J = 12.2 Hz, 1 H, C=C *cis*), 3.57 (s, 3 H, CH₃).
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