3020 *Inorg. Chem.* **1999,** *38,* 3020−3021

First Evidence of the LIESST Effect in a Langmuir−Blodgett Film

Jean François Létard,[*,†] Olivier Nguyen,[†] Hélène Soyer,[‡] Christophe Mingotaud,[*,‡] Pierre Delhaès,[‡] and Olivier Kahn[†]

Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS No. 9048, 33608 Pessac, France, and Centre de Recherche Paul Pascal, UPR CNRS No. 8641, 33600 Pessac, France

Received March 3, 1999

It is well established that for some iron(II) compounds in octahedral environments a spin crossover occurs between a low-spin (LS, $S = 0$) and a high-spin (HS, $S = 2$) state. The process can be induced by a change in temperature or pressure or by a light irradiation.[1] The spin-state conversion may occur gradually or with some abruptness. When the intersite interactions are sufficiently strong, a thermal hysteresis may be observed. The system is then bistable; it possesses a memory effect. The factors governing the occurrence of a thermal hysteresis are not fully understood yet. To obtain new insights on this problem, two complementary strategies are being developed. The former one is based on carefully controlled modifications in the molecular structures (polymeric[2] and/or supramolecular[3]). The latter strategy is related to the control of the supramolecular architecture inside the material. Along this line, the Langmuir−Blodgett (LB) technique is very attractive because of its ability to pack and orient molecules in a controlled fashion along a surface. Recently, the problem of the chemical instability of iron(II) compounds at the gas−water interface has been solved by changing either the subphase or the chemical structure of the hydrophobic part.[4] Well-defined LB films of spin-crossover iron(II) compounds have then been obtained.[5]

In this Communication, we report on the first evidence of the light induced excited spin state trapping[6] (LIESST) effect in a LB film incorporating iron(II) spin-crossover sites. This observation allowed us to study the influence of the surroundings on the lifetime of the metastable HS state generated by light irradiation. Let us recall that the LIESST process is limited to the low-temperature range, typically below 50 K.

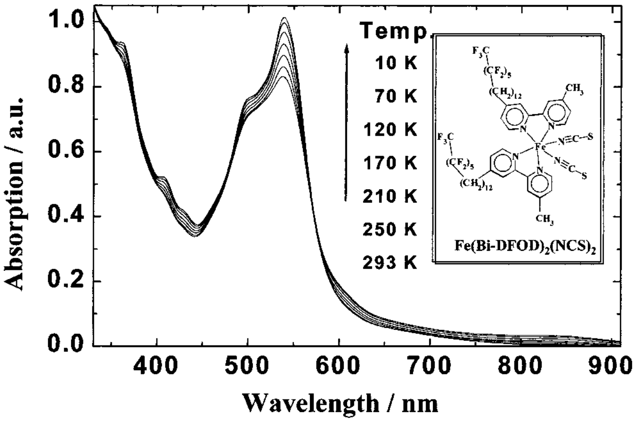

Figure 1. Temperature dependence of the UV−visible electronic absorption spectra for $Fe(Bi\text{-}DFOD)_2(NCS)_2$ in a LB film of 300 deposited layers. Inset: Molecular structure of $Fe(Bi\text{-}DFOD)_2(NCS)_2$.

The compound *cis*-bis(thiocyanato)bis(4-(13,13,14,14,15,15,16,16,17,17,18,18,18-tridecafluorooctadecyl)-4′-methyl-2,2′-bipyridine) iron(II), denoted $Fe(Bi\text{-}DFOD)_2(NCS)_2$ (structure in Figure 1), was prepared as recently described.[5b] The LB film was obtained by spreading a chloroform solution of $Fe(Bi\text{-}DFOD)_2(NCS)_2$ (concentration 1 mM) on a 10^{-2} M KNCS aqueous solution. The compression isotherm yields a molecular area of ca. 63 Å^2 at the collapse pressure, indicating that the packing contact is assured not by the alkyl chains but by the metal cores, which is the ideal situation for achieving strong intersite interactions along the surface. The LB film was deposited with a transfer ratio close to 0.95 onto a Mylar substrate with a transfer speed of 1 cm min^{-1} and at a pressure of 35 mN m^{-1}. X-ray diffraction experiments showed a periodicity of 40.6 Å for the layer structure. Magnetic measurements versus temperature revealed a nearly complete spin conversion when the LB film was preheated above 370 K, while only 10% of spin conversion occurs if the upper temperature reached was 340 K, i.e., below the melting of the semifluorinated chains.[5c] All of the experiments were performed on LB films which were not preheated.

The temperature dependence of the UV−visible absorption spectra for a LB film consisting of 300 layers of $Fe(Bi\text{-}DFOD)_2(NCS)_2$ is presented in Figure 1. The HS → LS transition results in a strong enhancement of the MLCT band around 538 nm. The color of the compound remains unchanged, in contrast with what happens for tetrazole and triazole iron(II) derivatives.[2,7,8] An irradiation at 10 K with a red light ($\lambda = 630{-}670$ nm, power =

[†] Institut de Chimie de la Matière Condensée de Bordeaux.

[‡] Centre de Recherche Paul Pascal.

(1) (a) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293. (b) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83. (c) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527. (d) Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1. (e) König, E. *Struct. Bonding (Berlin)* **1991**, *76*, 51. (f) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024 and references therein. (g) Gütlich, P.; Jung, J.; Goodwin, H. *Molecular Magnetism: From Molecular Assemblies to the Devices*; Coronado, et al., Eds.; NATO ASI Series E, Applied Sciences; Kluwer: Dordrecht, 1996; Vol. 321, p 327.

(2) (a) Vreugdenhil, W.; van Diemen, J. H.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedgijk, J.; van der Kraan, A. M.; Kahn, O.; Zarembowitch, J. *Polyhedron* **1990**, *9*, 2971. (b) Kahn, O.; Kröber, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718. (c) Lavrenova, L G.; Ikorskii, V. N.; Varnek, V. A.; Oglezneva, I. M.; Larionov, S. V. *Polyhedron* **1995**, *14*, 1333. (d) Kahn, O.; Codjovi, E.; Garcia, Y.; van Koningsbruggen P. J.; Lapouyade, R.; Sommier, L. In *Molecule-Based Magnetic Materials*; Turnbull, M. M., Sugimoto, T., Thompson, L. K., Eds.; ACS Symposium Series 644; American Chemical Society: Washington, DC, 1996.

(3) (a) Létard, J.-F.; Guionneau, P.; Codjovi, E.; Lavastre, O.; Bravic, G.; Chasseau, D.; Kahn, O. *J. Am. Chem. Soc.* **1997**, *119*, 10861. (b) Létard, J.-F.; Guionneau, P.; Rabardel, L.; Howard, J. A. K.; Goeta, A. E.; Chasseau, D.; Kahn, O. *Inorg. Chem.* **1998**, *37*, 4432. (c) Guionneau, P.; Létard, J.-F.; Yufit, D. S.; Chasseau, D.; Bravic, G.; Goeta, A. E.; Howard, J. A. K.; Kahn, O. *J. Mater Chem.* **1999**, *9*, 985. (d) Létard, J.-F.; Daubric, H.; Cantin, C.; Kliava, J.; Bouhedja, Y. A.; Nguyen, O.; Kahn, O. *Mol. Cryst. Liq. Cryst.*, in press.

(4) (a) Armand, F.; Badoux, C.; Bonville, P.; Ruaudel-Teixier, A.; Kahn, O. *Langmuir* **1995**, *11*, 3467. (b) Ruaudel-Teixier, A.; Barraud, A.; Coronel, P. *Thin Solid Films* **1998**, *160*, 107.

(5) (a) Soyer, H.; Mingotaud, C.; Boilot, M.-L.; Delhaès, P. *Langmuir* **1998**, *14*, 5890. (b) Soyer, H.; Mingotaud, C.; Boilot, M.-L.; Delhaès, P. *Thin Solid Films* **1998**, *327−329*, 435. (c) Soyer, H.; Dupart, E.; Gomez-Garcia, C.; Mingotaud, C.; Delhaès, P. *Adv. Mater.* **1999**, *11*, 382.

(6) (a) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A *Chem. Phys. Lett.* **1984**, *105*, 1. (b) Decurtins, S.; Gütlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. *Inorg. Chem.* **1985**, *24*, 2174.

10.1021/ic990259m CCC: $18.00

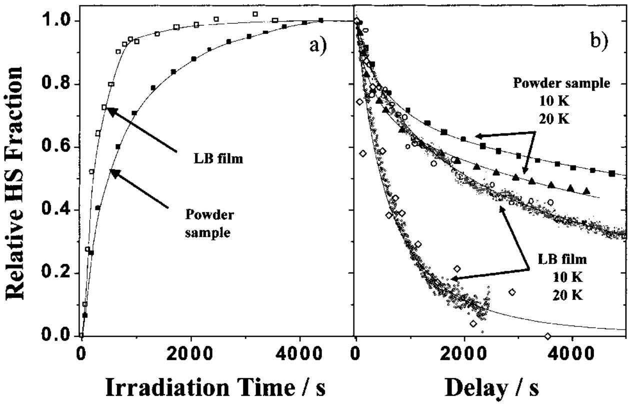

Figure 2. (a) Relative HS molar fraction deduced from magnetic measurements under light irradiation as a function of time at 10 K. (b) Decay of the metastable HS state. Data obtained for a powder sample at (■) 10 K and (▲) 20 K from magnetic measurements. Data obtained for a LB film at (○) 10 K and (◇) 20 K from magnetic measurements, and (●) from UV−visible spectroscopy.

1 mW, and time = 1 h) induces a decrease of the MLCT band on UV−visible absorption spectra. This likely reveals a roughly 20% conversion from the LS to the HS state through the LIESST process. To confirm this result, magnetic measurements were also carried out under light irradiation with a Kr^+ laser ($\lambda = 647.1-679.4$ nm, power = 50 mW, and time = 1 h) coupled through an optical fiber to the cavity of a MPMS-55 Quantum Design SQUID magnetometer. At 10 K, the magnetic response under irradiation was found to increase rapidly, as represented in Figure 2a. Let us notice here that the irradiation may locally heat the sample, whose temperature would then be higher than that indicated by the thermometer; this effect would tend to decrease the magnetic signal, in contrast to what is observed. Therefore, this behavior clearly demonstrates a partial conversion of the LS state into the HS state. A comparison of the relative HS populations between the LB film and a powder sample reveals that the LIESST process is more efficient for the LB film. Such an effect should be directly related to the small thickness and the high optical quality of the multilayer LB film compared to the diffusive powder.

The dynamics of the LIESST effect was studied with the SQUID setup for both the LB film and the powder sample, and with the UV−visible spectroscopy for the LB film. The decays of the HS molar fraction, γ_{HS}, versus time at 10 and 20 K are represented in Figure 2b. These data indicate a very good correlation between the kinetics obtained in UV−visible spectroscopy and SQUID technique for the LB film. The relaxation curves for both the LB film and the powder sample deviate from single exponentials. The time dependence of γ_{HS} is first rather fast; then it slows down. Similar behaviors were found for $[Fe(mephen)_3]^{2+}$ (2-mephen = 2-methyl-1,10-phenanthroline) embedded in polymer films[9a] and for a powder sample of $[Fe(otz)_6](BF_4)_2$ (otz = 1-*n*-octyltetrazole).[9b] This was attributed to local inhomogeneities in the polymer films and analyzed as a distribution of relaxation rates.[9] The relaxation curves for the LB film can be fitted satisfactorily with a Gaussian distribution[10] for the activation energy (E_a) with a standard deviation of 10 cm^{-1} and mean rate values, k_{HL}, of 3.0×10^{-4} s^{-1} and 1.4×10^{-3} s^{-1} at 10 and 20 K, respectively. For the powder sample, a standard deviation of 27(8) cm^{-1} and mean rate values of 1.2×10^{-4} s^{-1} and 2.1×10^{-4} s^{-1} were obtained at 10 and 20 K, respectively. These data demonstrate that the kinetics of the HS → LS relaxation is faster for the LB films than for the powder sample (Figure 2b). A possible explanation is that the internal pressure in the LB architecture is higher than in the powder sample, due to the packing contact of the metal centers.[10] A smaller activation energy occurs in LB films. In fact, Hauser demonstrated by studies of highly diluted single crystals, such as $[Fe_{0.1}Zn_{0.9}(ptz)_6](BF_4)_2$ with ptz = 1-*n*-propyltetrazole, and pure $[Fe(ptz)_6](BF_4)_2$ compound that both an internal and an external pressure affects the lifetime of the metastable HS state. For instance, at low temperature an external pressure of 1 kbar accelerates the HS → LS relaxation in $[Fe_{0.1}Zn_{0.9}(ptz)_6](BF_4)_2$ by 1 order of magnitude. This is due to the large difference in volume between the HS and LS states.[8c] It can also be noticed that the standard deviation of the LB film (10 cm^{-1}) is smaller than for the powder sample (27(8) cm^{-1}). This is in perfect agreement with the better defined architecture of the LB film with regard to the powder compound.

$Fe(Bi\text{-}DFOD)(NCS)_2$, to the best of our knowledge, is the first mononuclear spin-crossover species assembled in a LB film and presenting the LIESST effect. The lower standard deviation and the faster LIESST population observed in the LB film as compared to the powder was correlated to the better organization of the film. The faster dynamics of relaxation in the LB film was attributed to a pressure effect. Further investigations will be performed to confirm such a hypothesis, in particular by modulating the packing and the molecular density within the multilayer.

Acknowledgment. We acknowledge the financial support of the European Union in the frame of the TMR Network “Thermal and Optical Switching of Spin States (TOSS)”, Contract No. ERB-FMRX-CT98-0199.

IC990259M

---

(7) (a) Kahn, O.; Launay, J. P. *Chemtronics* **1988**, *3*, 140. (b) Zarembowitch, J.; Kahn, O. *New J. Chem.* **1991**, *15*, 181. (c) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

(8) (a) Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543. (b) Hauser, A. *Chem. Phys. Lett.* **1992**, *192*, 65. (b) Hauser, A. *J. Chem. Phys.* **1991**, *94*, 2741. (c) Jeftic, J.; Hauser, A. *Chem. Phys. Lett.* **1996**, *248*, 458.

(9) (a) Hauser, A.; Adler, J.; Gütlich, P. *Chem. Phys. Lett.* **1988**, *152*, 468. (b) Buchen, T.; Gütlich, P. *Chem. Phys. Lett.* **1994**, *220*, 262.

(10) Arrhenius equation: $k_{HL} = A \exp(-E_a/k_bT)$, with k_{HL} the relaxation rate (s^{-1}), A the preexponential factor, and E_a the activation energy (cm^{-1}) at a given temperature T (K).