Spin Transition in a Langmuir–Blodgett Film

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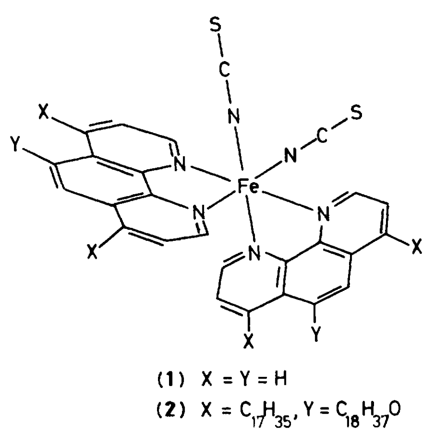
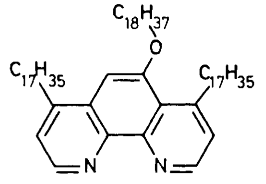
$Fe(X_2Yphen)_2(NCS)_2$ (X_2Yphen is a trisubstituted 1,10-phenanthroline with X = $C_{17}H_{35}$ and Y = $C_{18}H_{37}O$) incorporated in a Langmuir–Blodgett film shows a spin transition which has been studied by i.r. spectrometry.

One of the most exciting perspectives in molecular chemistry is the use of isolated molecules or of assemblies of molecules in electronic circuits and devices. Some preliminary results have already been obtained in this respect, concerning switching, information storage, or signal processing. Irrespective of the different final goals one concept is relevant in most of these fields, that of molecular bistability.[1] A spectacular example of bistability for an assembly of molecules is provided by the spin transition phenomenon.[2,3] In some cases, the thermally induced transition between high-spin and low-spin states is very abrupt with an hysteresis effect.[2,3] Such a situation is particularly interesting since it opens the door to passive information storage. The Langmuir–Blodgett (LB) method appears particularly well suited to give tailored molecular assemblies exhibiting electronic properties.[4] We report here on the first example of a spin transition in a Langmuir–Blodgett film.

The archetypal compound exhibiting an abrupt spin transition (at T_c = 176 K) is $Fe(phen)_2(NCS)_2$ (**1**) (phen = 1,10-phenanthroline).[2] We have synthesized $Fe(X_2Yphen)_2(NCS)_2$ (**2**) where X_2Yphen is the trisubstituted 1,10-phenanthroline (**3**). Compound (**2**) is amphiphilic, with a hydrophilic core and three hydrophobic chains, and was prepared by reaction (1) in refluxing pyridine (py). The synthesis of the precursor (**3**) is a tedious, four-step process.



(**1**) X = Y = H
(**2**) X = $C_{17}H_{35}$, Y = $C_{18}H_{37}O$



(**3**)

From (**2**), we have transferred 200 layers onto calcium fluoride and quartz substrates, using the Langmuir–Blodgett technique.[5]

$$Fe(py)_4(NCS)_2 + 2\ X_2Yphen\ (\mathbf{3}) \longrightarrow Fe(X_3Yphen)_2(NCS)_2\ (\mathbf{2}) + 4py \qquad (1)$$

The spin transition in the LB film was studied by variable temperature i.r. spectrometry on CaF_2 slides, focusing on the 2000—2150 cm^{-1} frequency range which corresponds to the C–N stretching vibration of the thiocyanate ligands.[6] Representative spectra are shown in Figure 1. At room temperature, we observed a doublet corresponding to the high-spin species (2065 and 2075 cm^{-1}) and, with a much weaker intensity, a doublet at higher frequency corresponding to low-spin species (2108 and 2116 cm^{-1}). Upon cooling to about 200 K, the intensity of the former doublet continuously decreases in favour of the latter. Below 200 K, the transition

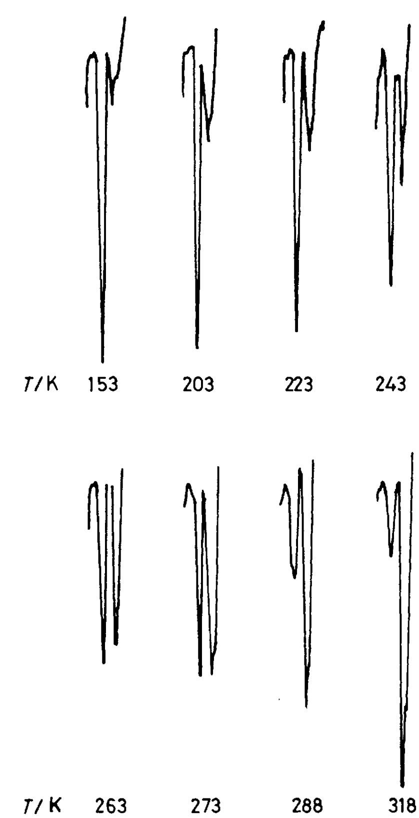


Figure 1. Temperature dependence of the i.r. spectra for the LB film in the 2000—2150 cm^{-1} wavenumber range.

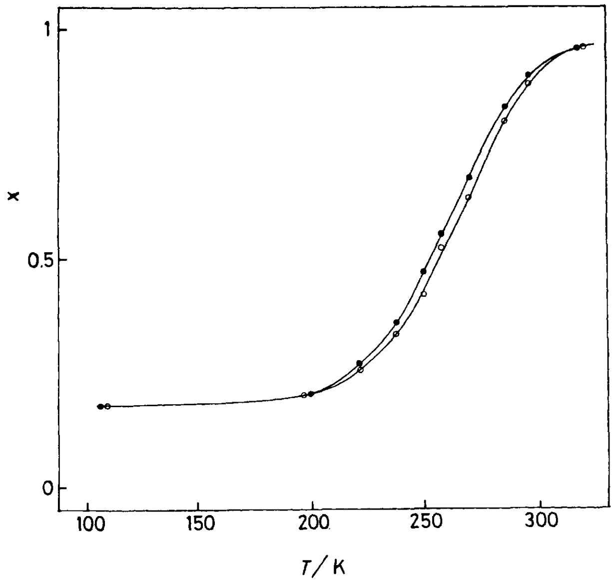


Figure 2. Temperature dependence of the molar fraction of high-spin species x for the LB film in both the cooling mode (●) and the warming mode (○). The full lines are for guidance only.

seems to terminate although it is incomplete. These i.r. data lead to the x (molar fraction of high-spin species) = $f(T)$ plot of Figure 2 from the relative intensities of the two doublets. Experiments were performed in both the cooling and warming modes. The transition is far from being abrupt; it takes place over a temperature interval of *ca.* 75 K. Nevertheless, it is definitely less smooth than a simple Boltzmann distribution law between a spin singlet and a spin quintet separated by a Δ energy gap would suggest. Moreover, a weak hysteresis of *ca.* 4 K seems to be present. Some co-operativity is clearly retained in the LB film. This co-operativity is two-dimensional instead of three-dimensional. Indeed, whatever the total number of deposited monolayers, the polar heads of the molecules in a LB film are decoupled from plane to plane. X-Ray diffraction pattern exhibits nine orders of diffraction and the measured long spacing is 28 Å. The critical temperature T_c for (**2**), defined as the temperature at which x is 0.5, is 260 K, *i.e.* much higher than for (**1**). About 18% of high-spin molecules are still present below 200 K, possibly because the film may contain another species, *e.g.* $Fe(py)_2(X_2$-$Yphen)(NCS)_2$.

The results unambiguously show that a spin transition may be observed in a LB film and that some co-operativity is retained in the two-dimensional network.

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