Spin Crossover in Gels

Thermoreversible Gels as Magneto-Optical Switches[**]

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The discovery of solid materials with appealing physical properties is mostly stimulated by their "potential" applications in nanotechnologies, molecular electronics, or quantum computing.[1] To achieve these objectives, the limiting step is often the transfer of bulk properties to technologically convenient systems (films, nanocomposites, fibers, gels).[2] In the past 20 years, spin-crossover (SC) materials have attracted considerable interest for their applicability as information storage, sensors, or display devices.[3] In particular, polymeric chains of iron(II) bridged by triazole ligands display abrupt spin-crossovers making of these materials optical and magnetic switches.[4] Moreover, their SC temperature can be adjusted to around ambient temperature by choosing suitable counteranions and triazole substituents.[4] Nevertheless, only a few prototypes using films of solid particles embedded in polymer matrices have been developed, but none has ever been used industrially. An alternative to these films consists in incorporating SC entities into soft-matter phases, such as gels. Herein, we describe physical gels exhibiting magnetic and optical properties originating from SC precursors. This system illustrates a route for processing SC solids into physical gels as carried out, for example with photofunctional[5] and biocompatible organogels.[6]

Among the spin-crossover Fe^{II}/triazole materials, we have focused on the solid precursor of formula $[Fe^{II}(C_{18}trz)_3](ptol)_2\cdot 2H_2O$ (**1**, ptol = *para*-tolylsulfonate; $C_{18}trz$ = 4-octadecyl-1,2,4-triazole). This SC material presents two interesting features: it contains ptol anions inducing a spin-crossover around room temperature[7] and it contains triazole ligands functionalized by long alkyl chains which are typically introduced to obtain gelator or mesogenic molecules.[8] Compound **1** can be easily obtained by reaction of aqueous solutions of $[Fe(ptol)_2]\cdot 6H_2O$ with ethanolic solutions of $C_{18}trz$ (Scheme 1).[9] As shown in Scheme 2 (top), the

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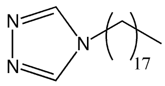
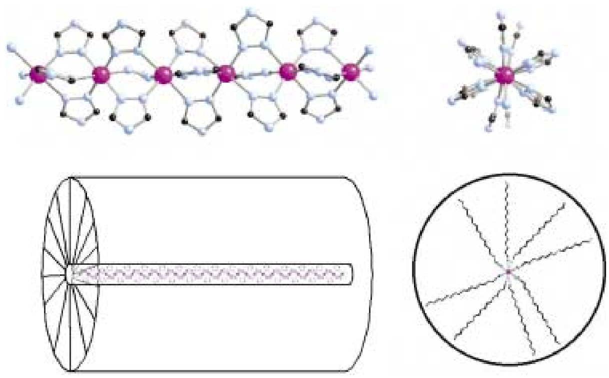


Scheme 1. 4-octadecyl-1,2,4-triazole ligand (C_{18}trz).

obtained material has a linear polymeric structure, with triazole units or substituted triazole rings in an eclipsed arrangement around the Fe^{II} metal ions.[10] The Fe chains in **1** can thus be viewed as anisotropic rodlike species with organic pendent arms (see Scheme 2, bottom). In the solid state, this polymeric material has a thermal magnetic and thermochromic crossover from a purple diamagnetic solid (low-spin, $S=0$, absorption band at about 550 nm) at room temperature to a colorless paramagnetic solid (high-spin, $S=2$, absorption band at about 820 nm) at higher temperature. The crossover temperature, T_{SC}, depends on whether the sample is hydrated ($T_{SC}=47\,°C$) or dehydrated ($T_{SC}=7\,°C$). This difference is usually attributed to a solvent effect on the ligand-field strength around the Fe^{II} centers.[11] A small fraction of the iron ions remains in the high-spin state over the whole temperature range. It is accepted that these ions are the Fe^{II} units at chain ends, and amount here to 2 % of the sample (based on the residual magnetism observed below 200 K), thus indicating an average mean chain length of approximately 33 nm in the solid (taking a value of 3.3 Å as an approximate Fe–Fe separation[10]).



Scheme 2. Top: schematic representation of the polymeric structure of $[Fe^{II}(Rtrz)_3]_n^{2n+}$ chains (R groups have been removed for clarity; purple Fe, cyan N, and black C). Bottom: schematic view of the cylindrical anisotropic rod formed by polymeric chains bearing long alkyl groups.

This solid precursor is only slightly soluble in alkane solvents, for example, decane, dodecane or cyclohexane. However, heating heterogeneous mixtures of various compositions (1.9 to 35, 1 to 30, and 1 to 20 wt % of **1** to decane, dodecane, and cyclohexane, respectively) above 140 °C yields monophasic viscous liquids. At these temperatures, the liquid phases are colorless and transparent. Cooling the system back to room temperature does not produce any solid precipitation and a homogeneous purple gel is obtained (see Supporting Information).[12] We have studied the temperature/composition pseudo-phase diagram of the system **1**/decane in more detail. At any concentration, the starting mixture is heterogeneous (e.g. solid + decane) at room temperature. Upon heating, jelly domains start to appear around 50–60 °C, and an isotropic viscous liquid is obtained above T_{melt}. Upon cooling, a homogeneous gel forms at T_{gel} below T_{melt}. This hysteresis feature at the gel–liquid transition is commonly observed for gels of low-molecular-mass gelators.[13] Below a threshold concentration of solid (1.9 wt % of **1** in decane), biphasic mixtures of gel-like aggregates and decane are obtained. Above 35 wt % of **1** in decane, the mixture remains in the form of a heterogeneous "pasty solid". The characteristic temperatures, T_{melt} and T_{gel} are given on the pseudo-phase diagram of Figure 1. The gel/liquid phase transition can be considered as a dissolution process.[8] For an ideal solution, the molar concentration C can be expressed as follows Equation (1).

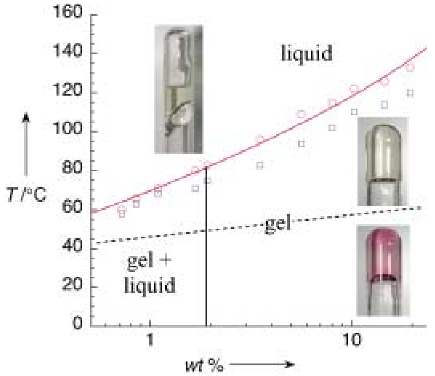


Figure 1. Temperature–composition pseudo-phase diagram for the binary **1**/decane system. Red points are data obtained upon warming, blue points are data obtained on cooling and determined by the inverted tube test. The red full line is the fit obtained with the ideal solution model (see text). The dashed line represents the spin-crossover temperature T_{SC} of the gels and the black vertical line represents the frontier between the homogeneous gel domain and the biphasic region.

$$\ln C(T_{melt}) = -\Delta H_{melt}/R\,T_{melt} + constant \tag{1}$$

Experimentally, fitting of the T versus $wt\,\%$ semi-log plot displayed in Figure 1 confirms this typical behavior. Hence the exothermic heat of association or melting enthalpy, ΔH_{melt}, has been estimated as approximately 55 kJ mol^{-1}, in good agreement with melting enthalpies of organogels with interactions between long alkyl chains.[13] By analogy with these organogels, the gel formation may result from a precipitation of small aggregates.[14] Indeed atomic force microscopy (AFM) reveals the presence of anisotropic aggregates in the gels with an average size of 150 nm in length and about 10 nm in diameter (Figure 2). This result indicates that the gels are not formed from individual chains of the solid precursor but from bundles of them. To probe the solvent–aggregates interaction, thermogravimetric experiments (see Supporting Information) have been performed. The solvent loss from the hybrid gels occurs at the boiling temperature of the pure solvents. Therefore, the interaction between solvent and gelator aggregates is weak. This feature and the thermoreversibility of the gel–liquid transition are characteristic of the physical nature of the formed gels.

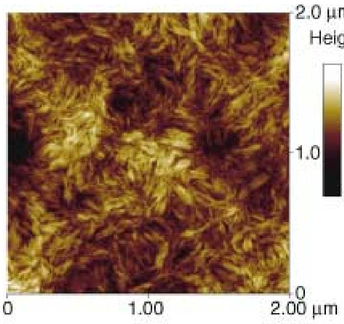


Figure 2. Tapping mode AFM image of a **1**/decane gel (3.5 wt%) on highly oriented pyrolytic graphite measured with a multimode Nanoscope III from Digital Instruments.

By analogy with the precursor material, the purple color of the transparent gels indicates that at least some of the Fe^{II} ions are in their low-spin state at room temperature. As observed during the gelation, the gels turn colorless above about 45 °C indicative that only iron(II) centers in the high-spin configuration are present. This optical signature of a spin crossover and the detection of typical IR bands[15] confirm the presence of the Fe^{II}/triazole polymeric chains in the gel. The spin-crossover process has been monitored and yields a reproducible peak in differential scanning calorimetry (DSC) and a sharp increase of the magnetization at this temperature (corresponding to the dashed line in Figure 1). Typical behavior of a **1**/decane gel (5 wt%) is depicted in Figure 3.

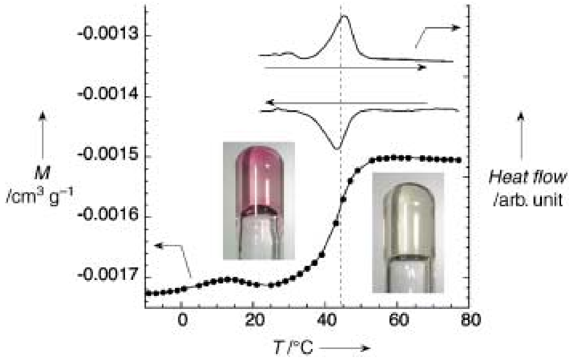


Figure 3. Temperature dependence of the massic magnetic moment (M) at 1000 Oe and DSC thermograms (inset; 5 °C min^{-1}) of a 5 wt% **1**/decane gel. The dotted line corresponds to the spin-crossover temperature ($T_{SC} = 44$ °C) deduced from DSC and magnetic measurements. The anomalies observed on the magnetic moment curve below 25 °C correspond to the solid–liquid first-order transition in pure decane.

The jump in magnetization of 2.3×10^{-4} emu g^{-1}, centered around 44 °C, corresponds well to what is expected for 72% of the Fe^{II} centers going from a diamagnetic to a paramagnetic state. Taking into account that the terminal iron ions remain in the high-spin state, a comparison with the solid (in which 98% of Fe^{II} undergoes a spin-crossover) suggests that the chain length may be reduced in the gel. Nevertheless, polymeric chains of **1** have been incorporated into gels and still present SC properties, which makes these gels thermochromic and magnetic switches.

All the gels can be cut into pieces and present a jelly-like behavior. Preliminary rheological measurements on **1**/decane gels, in the linear regime at low stress (0.1 to 5 Pa), show a visco-elastic behavior dominated by the elastic component, as expected for a gel (G' about one order of magnitude higher than G''). G' was found to increase slightly with the frequency, in particular below 1 Hz, while two broad modes of relaxation were observed for G'', one centered around 10^{-4} Hz, and one at frequencies higher than 10 Hz (not shown). This behavior is reproducible in homogenous gels of various compositions, either freshly prepared or after several months. The order of magnitude of G' depends on the concentration of precursor material and ranges from about 30 Pa (2 wt%) to around 900 Pa (15 wt%). Moreover, flow experiments show that the gel is shear-thinning, which suggests an orientation of the anisotropic aggregates under controlled shears. In addition, after applying such high shears, recovery of the original visco-elastic behavior would indicate a thixotropic nature for these gels.

Studying these SC gels, one main drawback has been found. As shown in Figure 4, large solid particles of a few hundreds of micrometers slowly form within the gel (over days to weeks depending on the preparation conditions). These particles can take the form of starlike aggregates, cross-linked fibers, and even cubic crystals (depending of the conditions). The homogeneous gel can be regenerated easily as the particles disappear upon warming above T_{melt} and cooling down below T_{gel}. Such a demixion-crystallization process is the sign of the gel metastability at room temperature and results from the weak solubility of the precursor solids in alkanes. Since chloroform is a good solvent for these precursors, we have used $CHCl_3$/alkane mixtures (10/90 to 30/70 wt%) in which the gelation occurs spontaneously at room temperature. The resulting gels are homogeneous and stable for at least over five months. In addition, the use of solvent mixtures has allowed tuning of the T_{gel} and T_{melt} temperatures between 20 and 120 °C. This ability to tune the gel–liquid transition temperatures also makes the formulation processes of this system easier.

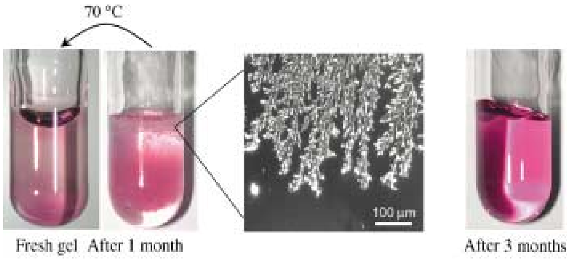


Figure 4. Demixion-crystallization process in gel of **1**/decane (left), with the observation of the large crystallites through crossed analyzers-polarizers (center). Typical stable homogeneous **1**/$CHCl_3$/decane gel (solvent mixture: 28/72 wt%; right).

In conclusion, the known polymeric Fe^{II}/triazole system has been modified by functionalizing the triazole ligands with long alkyl chains. Dissolving these new SC materials in organic solvents, we have been able to obtain hybrid gels and to study their thermo-reversible magnetic (at T_{SC} diamagnetic metal ions become paramagnetic), optical (at T_{SC} the transparent purple gel becomes colorless), and rheological (at T_{melt} the thixotropic gel converts into liquid) properties. We have shown that T_{melt} can be tuned using mixtures of solvents. Moreover, preliminary results indicate that T_{SC} is also adjustable by changing the counteranions of the SC precursor.[16] These gels illustrate successfully the strategy of transferring the unusual physical properties of solids into a soft-matter phase and open a new route to design polyfunctional materials.

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[12] Note that the pure ligand 4-octadecyl-1,2,4-triazole does not gelify alkane solvents, while gels are also obtained starting from SC solids having other lengths of alkyl substituents (C_{13} and C_{16}) on the triazole rings.

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[15] When the triazole ligand is in a local C_{2v} symmetry (case of a 1,2-bridging coordination mode), the intensity of ring torsion vibration modes is weak compared to their intensities in a non-C_{2v} case, as for example, in the pure 1*H*-1,2,4-triazole. In our case in the gel spectra, these vibration bands at approximately 670 cm^{-1} are very weak confirming the local C_{2v} symmetry.

[16] 5 wt % of $[\mathrm{Fe^{II}(C_{18}trz)_3](X)_2{\cdot}2\,H_2O}$ in decane forms upon warming purple and colorless gels in which $\mathrm{X^- = Cl^-}$ or $[\mathrm{BF_4}]^-$. Their T_{SC} values are above and below room temperature, approximately 80 °C and −20 °C, respectively.