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Review

Multifunctionality in spin crossover materials

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Dedicated to Professor Rüdiger Kniep on the occasion of his 60th birthday.

Contents

Abstract

One of the most important trends in the spin crossover (SCO) field is focused on the synthesis of new molecule-based functional materials in which the SCO properties may be combined with other physical or chemical properties in a synergic fashion. The current stage of investigations regarding interplay and synergic effects between SCO, magnetic coupling, liquid crystalline properties, host–guest interactions, non-linear optical properties, electrical conductivity, and ligand isomerization is highlighted and discussed.

Keywords: Spin crossover (SCO); Synergy; Magnetic coupling; Liquid crystalline properties; Host–guest interactions; Non-linear optical properties; Electrical conductivity; Ligand isomerization

1. Introduction

Thermal spin transition (spin crossover (SCO)) is one of the most fascinating and most extensively explored dynamic electronic structure phenomena in coordination chemistry. It began about seven decades ago with the work of Cambi and his co-workers on the unusual magnetic behaviour of iron(III) dithiocarbamato complexes [1]. Later, with the introduction of ligand field theory into coordination chemistry by F.E. Ilse and H. Hartmann around 1950, an excellent theoretical model became available to understand quantitatively the optical and magnetic properties of open-shell coordination compounds [2]. Experimental observations could be interpreted using quantum chemical and group theoretical methods, and even fine effects like covalency, orbital contribution to the magnetic moment, zero-field splitting have been recognized as important factors in describing the electronic structure of transition metal ions and the chemical bonding of complex molecules, particularly in molecule-based magnetism.

Ligand field theory became widely accepted by coordination chemists, and the interest grew rapidly in searching for new coordination compounds exhibiting thermally induced

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spin transition, a phenomenon which has been well understood on the basis of the new model. The existence of such “bi-stable” compounds was, after all, predicted by Pauling [3] and Orgel [4].

More than three decades after Cambi et al. discovered thermal spin crossover in iron (III) complexes, the first examples of iron(II) and cobalt(II) exhibiting drastic changes of their magnetic moments as a function of temperature became known [5–8]. Particularly the class of iron(II) spin crossover systems has grown rapidly, mainly stimulated by the coinciding development of Mössbauer spectroscopy, a hyperfine interaction technique which proved to be extremely well suited to characterize the electronic and molecular structure and magnetic properties of iron compounds. The change of spin states by temperature variation is clearly reflected by typical high spin (HS) and low spin (LS) resonance signals in the Mössbauer spectrum. Together with other physical techniques the spin transition properties of many compounds, particularly those of iron(II), have been extensively studied. Spin crossover research of the last three decades was mainly devoted to investigating the spin transition properties under the influence of chemical modifications (ligand substitution, change of anions and solvent molecules, metal dilution) and physical perturbation such as irradiation (LIESST effect), pressure and magnetic field.

The primary focus has been the nature of the cooperative interactions between the spin state changing complex molecules; these have been recognized as being responsible for special features of the spin transition characteristics such as temperature and abruptness of the transition and hysteresis effects. The vast amount of detailed knowledge covering a broad range of material preparation as well as physical characterisation has been accumulated in many review articles [9].

Having arrived at a reasonable understanding of how to control the spin transition processes in solid material and, furthermore, with the recognition that spin crossover compounds bear the potential for practical applications in switching and display devices, recent activities in this field have been mostly devoted to the design of new SCO compounds in which SCO properties may be combined with other physical or chemical properties in a synergic fashion, e.g. magnetic exchange, liquid crystalline properties, host–guest chemistry, non-linear optics, electrical conductivity and ligand isomerization.

Synergic systems with two or more phase transitions of different physical nature may lead to a number of advantages in practical applications, e.g. enhancement of spin transition signals, switching and sensing in different temperature regimes. Although the efforts in this area have commenced only recently, and much of the work is in progress, it is worth reviewing the current activities in the following account.

2. Spin crossover and magnetic interactions

In the last decade, it was realised that the interplay between SCO and magnetic coupling could be exploited to govern the magnetic properties of molecular compounds. It was foreseen that the intramolecular ferromagnetic or antiferromagnetic coupling in such systems could be suppressed or enhanced alternating the spin state of the metal centres. Extension of this approach to 2D and 3D coordination polymers would enable one to combine two different kinds of phase transitions in the same solid, namely magnetic order and SCO. The synthesis of hybrid materials made of magnetically ordered 2D and 3D anionic networks and SCO cations held between or within networks has been a pursued strategy as well. The goal is to investigate how the magnetic order can influence the spin crossover process. However, apart from synthetic challenges which involve the tailoring of these hybrid materials, the most difficult point is to synchronize both electronic phenomena. Indeed, magnetic order was still not reported for such a kind of networks above 70 K, while the SCO process is usually frozen below this temperature due to kinetic effects.

Currently, only few examples could be related to this particular class of materials in which an interplay between magnetic exchange and SCO has been achieved. In fact, this interplay has only been observed in Fe(II) bpym-based dinuclear complexes [10] and in pyridazine-bridged macrocyclic cobalt(II) dinuclear compounds [11]. Herchel and co-workers have reported the heterometallic cyanide-bridged $\{Cr[CNFe^5L]_3(CN)_3\}$ (L: N, N′-bis(1-hydroxy-2-benzylidene)-1,7-diamino-4-azaheptane) compound exhibiting a thermally induced SCO along with exchange coupling. The SCO behaviour is less pronounced in this heterometallic complex; a considerable amount of iron(III) centres stays high spin still at 6 K [12]. The magnetic susceptibility as a function of temperature could be reproduced with a model taking into account spin crossover and magnetic interactions among all metal centres. Many efforts have been invested in order to achieve an interplay between magnetic interactions and SCO in magnetic porous networks based on oxalato [13] and dicyanamide [14] type and in magnetically ordered $MnPS_3$ layers [15].

Interplay between intramolecular antiferromagnetic coupling and SCO has been reported in iron(II) complexes of the type $\{[Fe(L)(NCX)_2]_2bpym\}$, where L: 2,2′-bipyrimidine(bpym) [16–21], 2,2′-bithiazoline(bt) [17,22], 6-methyl-2,2′-bipyridine(CH_3-bipy) [23] and X: S, Se (Fig. 1). Along with temperature variation, the effects of hydrostatic pressure and light irradiation (LIESST effect) [10] on these compounds have been extensively explored. These experiments enabled us to identify the occurrence of different dinuclear species during the spin conversion process, namely [HS–HS], [HS–LS] and [LS–LS]. A distinctive feature in these compounds is the presence of a plateau in the middle of the two-step spin transition curve indicating about 50% of conversion. The spin transition does not set in simultaneously in both iron centres of the pair despite their identical surroundings and therefore equal ligand field strengths. Mössbauer spectroscopy in applied magnetic field has confirmed that the plateau of the spin transition curve consists mainly of [HS–LS] pairs [18,19,22,24]. This result

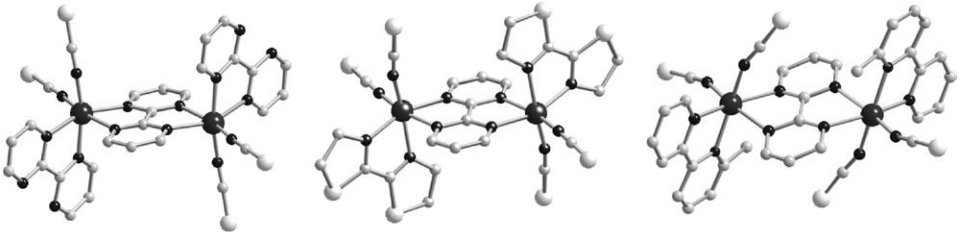


Fig. 1. Molecular structure of $\{[Fe(bpym)(NCS)_2]_2(bpym)]\}$ (a), $\{[Fe(bt)(NCS)_2]_2(bpym)]\}$ (b) and $\{[Fe(CH_3\text{-}bipy)(NCS)_2]_2(bpym)]\}$ (c) (adapted from [10,23]).

evidences that the spin conversion in these dinuclear Fe(II) systems proceeds through [HS–HS] ↔ [HS–LS] ↔ [LS–LS] transformation. The energetic stabilization of mixed [HS–LS] species has been interpreted in terms of synergy between intra- and intermolecular cooperative interactions (short- and long range), which stabilize energetically the mixed pairs. It leads to the plateau region of a two-step transition and determines its width.

The magnetic behaviour at ambient pressure of the derivatives $\{[Fe(L)(NCX)_2]_2bpym\}$ (L: bpym, bt and X: S, Se) is depicted in Fig. 2. The complex $\{[Fe(bpym)(NCS)_2]_2bpym\}$ does not display thermally induced spin conversion, but exhibits intramolecular antiferromagnetic coupling between the two iron(II) ions through the bpym bridge (coupling constant $J = -4.1\,cm^{-1}$). When thiocyanate is replaced by selenocyanate the resulting $\{[Fe(bpym)(NCSe)_2]_2bpym\}$ derivative shows an abrupt spin transition in the 115–125 K temperature region with a small hysteresis loop of 2.5 K width. Only 50% of the iron(II) atoms undergo spin transition. The decrease of the $\chi_M T$ values at lower temperatures is due to zero-field splitting of the $S = 2$ state of the remaining ions in the HS configuration. The magnetic properties of $\{[Fe(bt)(NCS)_2]_2bpym\}$ and $\{[Fe(bt)(NCSe)_2]_2bpym\}$ are similar. These compounds undergo a complete spin transition in a similar remarkable two-step fashion with two steps centred at 197 and 163 K for $\{[Fe(bt)(NCS)_2]_2bpym\}$ and at 265 and 223 K for $\{[Fe(bt)(NCSe)_2]_2bpym\}$. In both cases, the plateau corresponds approximately to 50% spin conversion. The thermal dependence of $\chi_M T$ at different pressures for $\{[Fe(bpym)(NCS)_2]_2bpym\}$ and $\{[Fe(bpym)(NCSe)_2]_2bpym\}$ have been investigated [18] (Fig. 3). Coexistence of antiferromagnetic coupling and spin crossover in $\{[Fe(bpym)(NCS)_2]_2bpym\}$ clearly follows from magnetic susceptibility measurements at $P = 0.63$ GPa. A partial conversion from 100% [HS–HS] to 55% [HS–LS] species takes place. At $P = 0.89$ GPa the total conversion to [HS–LS] pairs is accomplished. It means, that at this

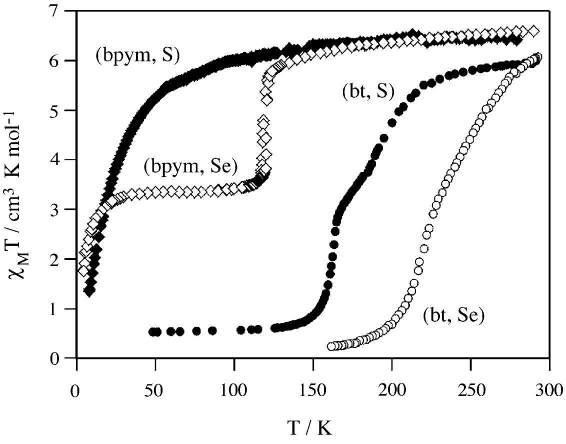


Fig. 2. Magnetic behaviour of $\{[Fe(L)(NCX)_2]_2bpym\}$ (L = bpym, bt, and X = S, Se) complexes (adapted from [10]).

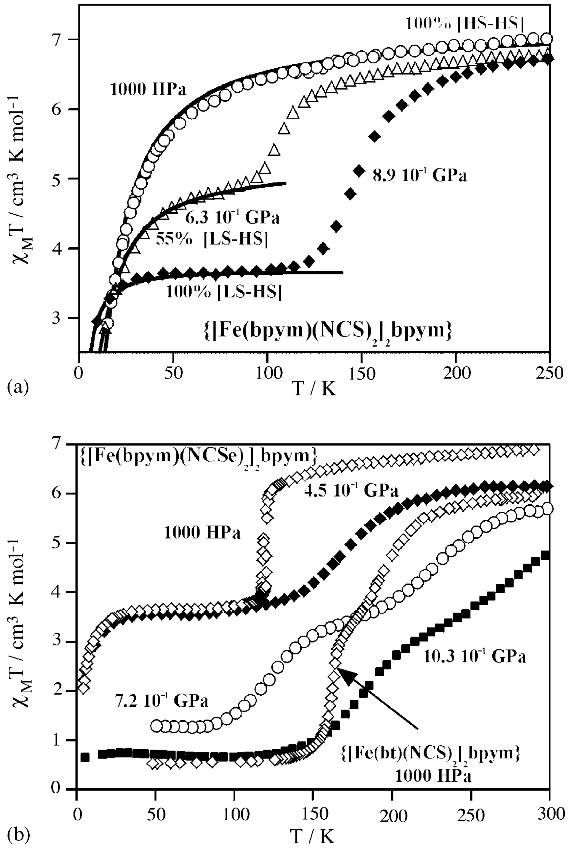


Fig. 3. Temperature dependence of $\chi_M T$ for $\{[Fe(bpym)(NCS)_2]_2(bpym)\}$ at different pressures (a). The solid lines, together with estimated concentrations of [HS–LS] and [HS–HS] species correspond to calculations using the appropriate Hamiltonian. Temperature dependence of $\chi_M T$ for $\{[Fe(bpym)(NCSe)_2]_2(bpym)\}$ at different pressures (b). The magnetic behaviour of $\{[Fe(bt)(NCS)_2]_2(bpym)\}$ at ambient pressure has been also included for comparison (adapted from [10,18]).

pressure, $\{[Fe(bpym)(NCS)_2]_2bpym\}$ undergoes a similar [HS–HS] ↔ [HS–LS] spin transition with $T_{1/2} \approx 150$ K as $\{[Fe(bpym)(NCSe)_2]_2bpym\}$ does at ambient pressure. Seemingly, the effect of pressure lower than 0.45 GPa on the thermal transformation of the spin state of $\{[Fe(bpym)(NCSe)_2]_2bpym\}$ is a shift of $T_{1/2}$ towards higher temperatures. For higher pressures, a second transition appears in addition to the former one, due to the onset of thermal spin transition in the second metal centre. Between 0.72 and 1.03 GPa a two-step spin transition is observed.

As can be seen, by appropriate choice of the peripheral ligands the antiferromagnetic coupling can be suppressed due to the occurrence of LS species caused by thermal SCO in one or both iron centres of the pair. These studies have demonstrated that the ligand field strength in these compounds can be tuned by pressure in an effective way.

Recently, a method of direct monitoring of spin state and magnetic coupling in dinuclear iron(II) compounds was developed [19,20]. This method involves Mössbauer spectroscopy carried out in an external magnetic field and allows a quantitative determination of spin states of Fe(II) dinuclear pairs. It has been demonstrated in the $\{[Fe(L)(NCX)_2]_2bpym\}$ series [10,19,20] and in $\{[Fe(phdia)(NCS)_2]_2phdia\}$ (phdia: 4,7-phenanthroline-5,6-diamine) [24] compounds. Photomagnetic experiments on $\{[Fe(bt)(NCS)_2]_2bpym\}$ [22] and $\{[Fe(bpym)(NCSe)_2]_2bpym\}$ [19] have been performed using this method. One of the issues has been the elucidation of the nature of metastable pairs which are generated at low temperatures by light irradiation of a ground [LS–LS] state. As is illustrated in Fig. 4(a), at 4.2 K before irradiation the Mössbauer spectrum of a sample of $\{[Fe(bt)(NCS)_2]_2bpym\}$, which was enriched to 20% of ^{57}Fe, reflects the presence of mainly LS species. The Mössbauer parameters obtained from the fitting of the spectrum are: $\delta_{LS} = 0.357(1)\,mm\,s^{-1}$ (related to α-iron), $\Delta E_{Q(LS)} = 0.452(2)\,mms^{-1}$. After irradiation of the sample for one hour ($\lambda = 514$ nm) at 4.2 K, the Mössbauer spectrum of $\{[Fe(bt)(NCS)_2]_2bpym\}$ shows a decrease in the intensity of the LS species (62.0%) in favour of an increase of the HS species (38.0%) (Fig. 4(b)). The Mössbauer measurements in a magnetic field of 50 kOe at 4.2 K allows the identification of the nature of the metastable states. As is shown in Fig. 4(c) the total spectrum measured after irradiation consists of three components. One of them with isomer shift and quadrupole splitting values being equal to δ_{LS}(bt, S) and $\Delta E_{Q(LS)}$(bt, S) is identified as the “fingerprint” of the LS state with the local effective magnetic field being nearly the same as the applied field, $H_{eff} \approx H_{ext}$. The second low-intensity broadened doublet with parameter values δ_{HS}(bpym, S) and $\Delta E_{Q(HS)}$(bpym, S) and $H_{eff} = 14$ kOe, corresponds to iron(II) ions in antiferromagnetically coupled [HS–HS] pairs. The third component with parameter values close to δ_{HS}(bpym, S) and $\Delta E_{Q(HS)}$(bpym, S) is unambiguously assigned to the HS state in [HS–LS] pairs, because the measured effective magnetic field at the iron nuclei of 85 kOe clearly originates from a spin quintet ground state of iron(II) ($S = 2$). LIESST experiments in $\{[Fe(bt)(NCS)_2]_2bpym\}$ have shown that the photoinduced species are not only [HS–LS] but also [HS–HS] pairs. The appearance of the [HS–LS] state has its origin in the above discussed synergy between intra- and intermolecular interactions. In contrast, the photoinduced species correspond to [HS–HS] pairs in $\{[Fe(bpym)(NCSe)_2]_2bpym\}$.

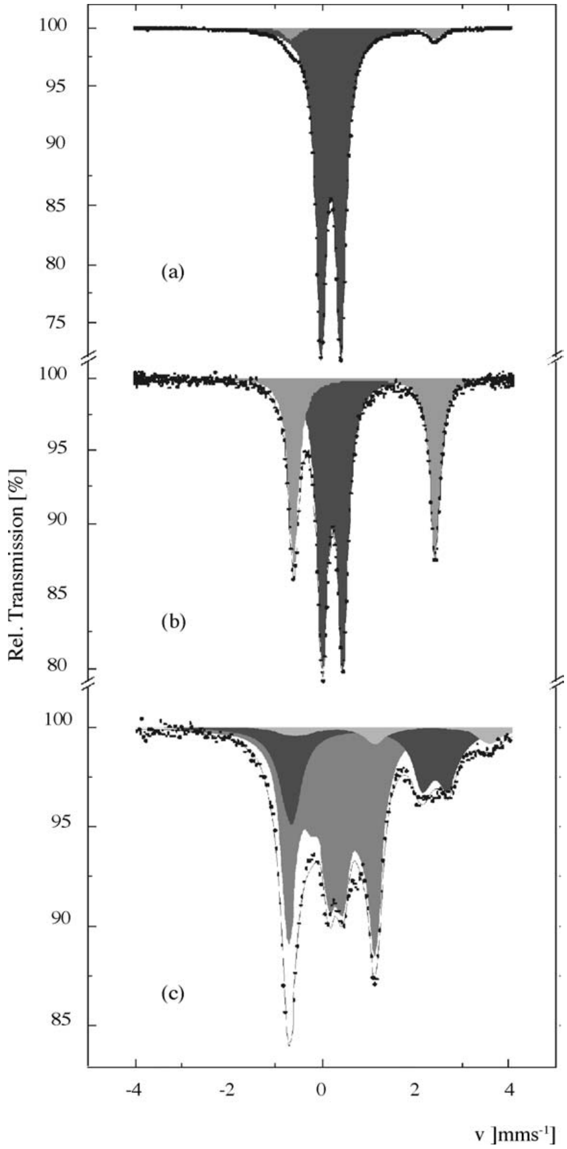


Fig. 4. ^{57}Fe Mössbauer spectra of $\{[Fe(bt)(NCS)_2]_2bpym\}$ recorded at 4.2 K in zero-field before irradiation (a), immediately after irradiation (b). Mössbauer subspectra correspond to: HS species (grey), LS species (dark grey). ^{57}Fe Mössbauer spectra of (bt, S) at 4.2 K in a magnetic field of 50 kOe recorded after 1 day after light irradiation (c). LS in [HS–LS] and [LS–LS] pairs (grey), HS in [HS–LS] pairs (light grey), HS in [HS–HS] pairs (dark grey) (adapted from [10]).

The control of the magnetic and optical properties by light remains a challenging topic in materials science in view of the possible implementation in magneto-optical devices. Certainly, spin crossover or valence tautomerism [25,26] systems are examples of photoswitching coordination complexes together with Prussian Blue analogues,

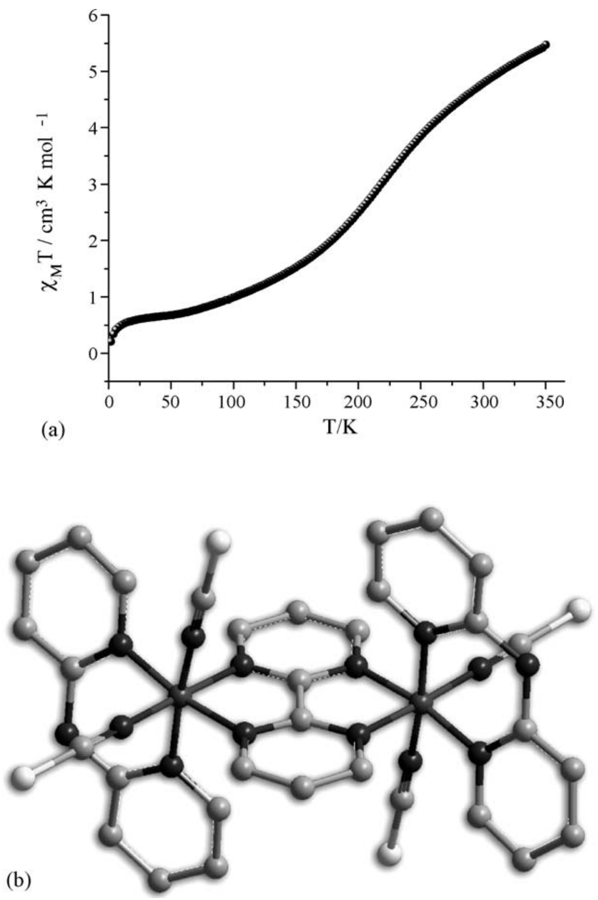


Fig. 5. Temperature dependence of $\chi_M T$ and proposed molecular structure for $[Fe(dpa)(NCS)_2]_2$bpym (adapted from [29]).

particularly in which long-range magnetic ordering is modified by photons [27,28]. In $\{[Fe(bt)(NCS)_2]_2bpym\}$ and $\{[Fe(bpym)(NCSe)_2]_2bpym\}$complexes irradiation with light of different wavelengths induces the switching between diamagnetic, paramagnetic and magnetically coupled states, however, below liquid nitrogen temperature. The next step along this research line concerns the synthesis and design of materials exhibiting such synergic properties at more accessible temperatures, which is a requirement for practical applications.

Presently, the question is posed as to whether all dinuclear compounds will exhibit this two-step SCO behaviour. In this respect, a gradual transition curve without a plateau has been observed in the $\{[Fe(dpa)(NCS)_2]_2bpym\}$ (dpa: 2,2′-dipyridylamine) derivative (Fig. 5); the lack of such a plateau has been ascribed to weak inter-dimer interactions [29]. Murray [30], Brooker [31], Kaizaki [32,33] and co-workers have recently reported on new dinuclear iron(II) SCO systems based on pyrazolate and triazolate bridges, which have added new interesting results to this topic. The spin conversion in these complexes takes place via [HS–HS] ↔ [LS–LS] transformation (Fig. 6), however, in the case of [33] a two-step transition with %50 [HS–HS] and 50% [LS–LS] pairs at the plateau region have been demonstrated by X-ray structural determination. In bpym or phdia-bridge dinuclear Fe(II) compounds, the predominant factor that determines the existence of the [HS–LS] species is the strength of intermolecular interactions in the solid. Indeed, weak intermolecular interactions are responsible for the direct [HS–HS] ↔ [LS–LS] transformation observed in the $\{[Fe(dpa)(NCS)_2]_2bpym\}$ complex [29]. In fact, one cannot exclude that similar principles govern the spin crossover process in dinuclear Fe(II) compounds with different types of bridging ligands. Recently Murray et al. have found a one-step SCO [HS–HS] ↔ [HS–LS] for the dinuclear complex $[Fe_2(PMAT)_2](BF_4)_4 \cdot DMF$ with triazolate-bridge [34]. Further experiments in this new kind of dinuclear systems are necessary to explore the importance of the bridging ligand in this context.

Regarding Co(II) dinuclear systems Brooker, Murray and co-workers [35] have synthetized the unique examples up to date exhibiting spin crossover ($S = 3/2 \leftrightarrow S = 1/2$) at high temperatures and antiferromagnetic exchange of the low-spin d^7–d^7 ions at low temperatures ($2J = -10$ to $14\,cm^{-1}$). The complexes are doubly pyridazine-bridged dicobalt(II) macrocycles with molecular formulae $[Co_2L(MeCN)_4](ClO_4)_4 \cdot 4MeCN$ and $[Co_2L(NCS)_2(SCN)_2]$ (L: piridazine-containing Schiff-base ligand). The spin transition in these complexes are more smooth as compared to many mononuclear Co(II) compounds [36].

As mentioned above, the synthesis of hybrid materials composed of magnetically ordered anionic networks and spin crossover cations has been subject to research during the past decade. Investigations have been promoted in order to study the electronic and structural influences which a magnetically ordered network might impart upon the SCO process of the cations hosted within. A first step along this research line has been done by Decurtins et al. who have reported on the spin transition of cations encapsulated into the 3D oxalate net $[Co(2,2'\text{-bipy})_3][LiCr(C_2O_4)_3]$ (2,2′-bipy: 2,2′-bipyridmidine). The cations undergo a very gradual spin transition over the range 50–300 K, while the net is not magnetically ordered [13]. In parallel, Murray and co-workers have investigated the encapsulation of Fe(II) and Fe(III) SCO cations into magnetically ordered metal-dicyanamide anionic networks of the 2D $\{[Fe(2,2'\text{-bipy})_3][Fe(dca)_3]_2\}$ [37] and 3D $\{[Fe(pz_3CH)_2][Mn(dca)_2(MeOH)_2]_3Cl_2\}$ (pz_3CH: tri(1*H*-pyrazol-1-yl)methane) systems [14]. In both compounds the cation is in the LS state and the iron(II) and Mn(II) ions of the anionic net show weak antiferromagnetic interactions. Recently, the same research group has found that in the network $\{[Fe(L)_3][Fe(dca)_3]Cl_2\}$ L: being 2,2′-bi-1,4,5,6-tetrahydropyrimidine the Fe(III) cations held in cavities retain their SCO behaviour [14]. Floquet and co-workers have reported a system in which Fe(III) SCO cations are inserted in the semiconducting host lattice of $MnPS_3$ capable of acquiring spontaneous magnetization. The spin transition in this system occurs above 100 K whereas the ferromagnetic ordering of the host lattice takes place around 35 K [15]. At this stage, further developments become necessary

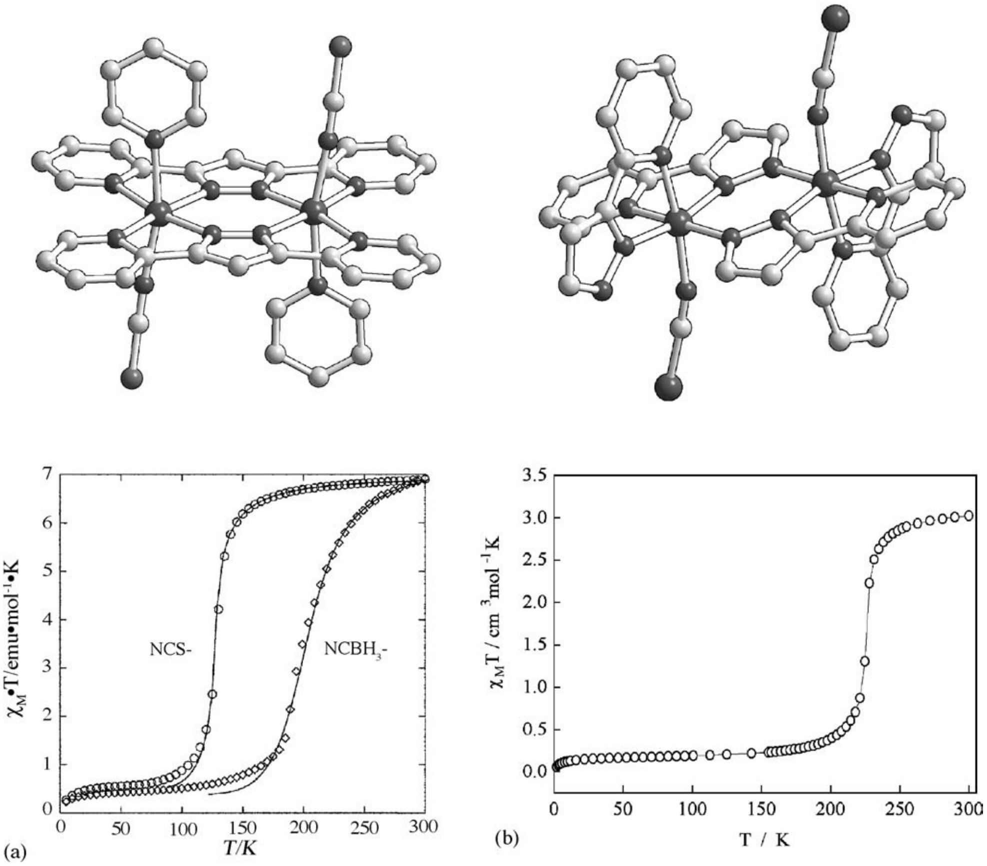


Fig. 6. $\chi_M T$ vs. T and molecular structure for [{Fe(NCBH$_3$)(py)}$_2$(μ-bpypz)$_2$] and [{Fe(NCS)(py)}$_2$(μ-bpypz)$_2$] (a). $\chi_M T$ vs. T and molecular structure for [(pypzH)(NCSe)Fe(μ-pypz)$_2$Fe(NCSe)(pypzH)]·2H$_2$O (b) (adapted with permission from [30,32]).

in order to implement an interplay between the magnetic ordering and the SCO process in such hybrid materials.

3. Liquid crystalline and spin crossover properties

Liquid crystals were discovered more than a century ago and remained primarily the object of scientific curiosity until the discovery of the twisted nematic effect in 1971 [38] which launched the era of liquid crystal applications. The development of liquid crystal displays (LCD) has revolutionized the portable computer industry, and LCDs are now found in many electronic devices.

Liquid crystals [39–43] are an ordered fluid that is intermediate between the three-dimensionally ordered crystal phase and the disordered liquid phase; it is often referred to as mesophase and its constituent molecules as mesogens. Materials that can form a mesophase in the absence of a solvent are thermotropic liquid crystals, and phase transitions are observed as a function of temperature. By virtue of their fluid nature, liquid crystals are easily processed into films, yet retain the optical properties of crystalline materials such as the ability to rotate plane-polarized light. In addition, the orientation of polar molecules in liquid crystal films can be modulated on a relatively short time scale using a weak electric field. Most liquid crystal applications are based on this simple concept of an ON/OFF light shutter. The vast majority of thermotropic mesogens are rod-shape compounds composed of a rigid aromatic core and alkyl side chains (calamitic liquid crystals).

In recent years, the design of metal-containing liquid crystals (metallomesogens) has attracted much attention because of the possibility to align paramagnetic liquid crystals by weak magnetic fields. Classic rodlike organic liquid crystals are diagmagnetic and can be easily oriented by an electric field while they require relatively strong magnetic fields in order to be aligned, and this is not suitable with small devices such as displays. Indeed, it has promoted investigations that afforded liquid crystals containing rare-earth ions [44], nickel(II) [45] or copper(II) [46] among others [41]. The actual switching rate is slow due to the high viscosity of the complexes.

The individual peculiarities of SCO and LC compounds have stimulated the idea of combining both properties in a single material. A first step in this direction was done by Galyametdinov and co-workers, which reported an iron(III) complex gathering both properties [47]. The complex consists of an Fe(III) metal coordinated to Schiff based ligands with elongated substituents employed to provide the rod-like geometry and hence the LC properties of the system

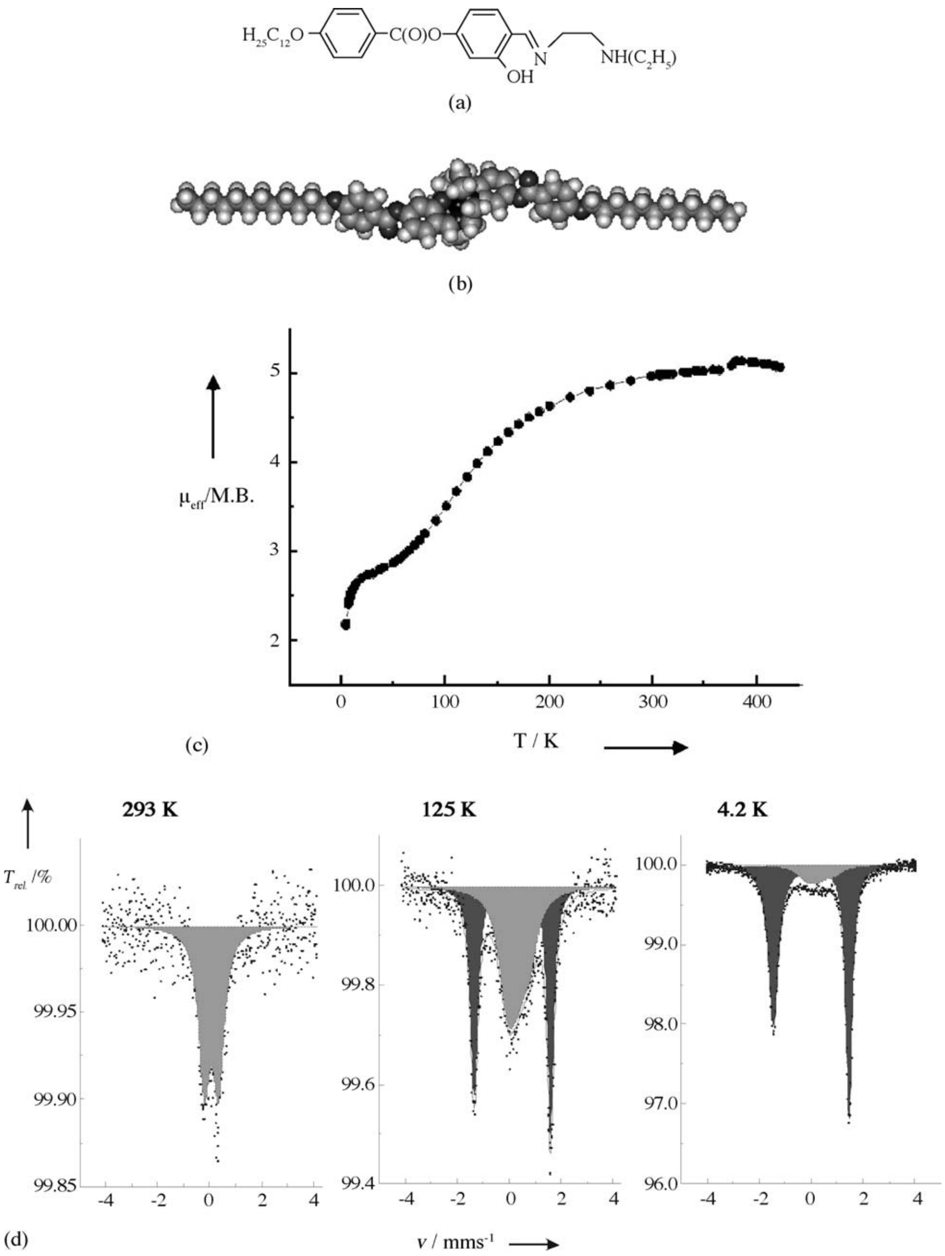


Fig. 7. LC Schiff base ligand: *N*-alkyloxy-salicylidenyl-*N*′-ethylenediamine (a). Computer simulation of the molecular structure of $[Fe(L)_2](PF_6)$ L: *N*-alkyloxy-salicylidenyl-*N*′-ethylenediamine (b). Temperature dependence of the effective magnetic moment, μ_{eff}, for $[Fe(L)_2](PF_6)$ (c). Mössbauer spectra for $[Fe(L)_2](PF_6)$ at room temperature, 125 K and 4.2 K (d). Fe(III)HS: light grey and Fe(III)LS: dark grey (adapted from [47]).

(Fig. 7(a)). Both events are not synchronous in this material but appear in different temperature regimes. The spin transition is continuous and takes place in the temperature range of 300–370 K while the fan-shaped texture usually attributed to the smectic A mesophase is observed between 388 and 419 K. The result of temperature dependent magnetic measurements are shown in Fig. 7(c), and ^{57}Fe Mössbauer spectra recorded at different temperatures are displayed in Fig. 7(d). Interestingly, due to the presence of paramagnetic ions, the material exhibits enhanced magnetic anisotropy and can be aligned by a magnetic field in the mesophase of the liquid crystal.

Fujigaya et al. have reported on the coexistence of both phenomena, SCO and LC, apparently in the same temperature region. The iron(II) complexes are one-dimensional systems based on triazole derivatives [48]. However, the supposed mesomorphism of the complexes have not been confirmed neither by optical polarizing microscopy nor by DSC measurements. Hayami and co-workers [49] have recently observed the spin transition around 230 K in the mononuclear iron(II) complex $[Fe(3C16\text{-}L)_2(NCS)_2]$ (3C16-L: 3,4,5-tris(hexadecyloxy)-*N*-((pyridin-2-yl)methylene)benzenamine), which subsequently revealed the smetic phase above 350 K.

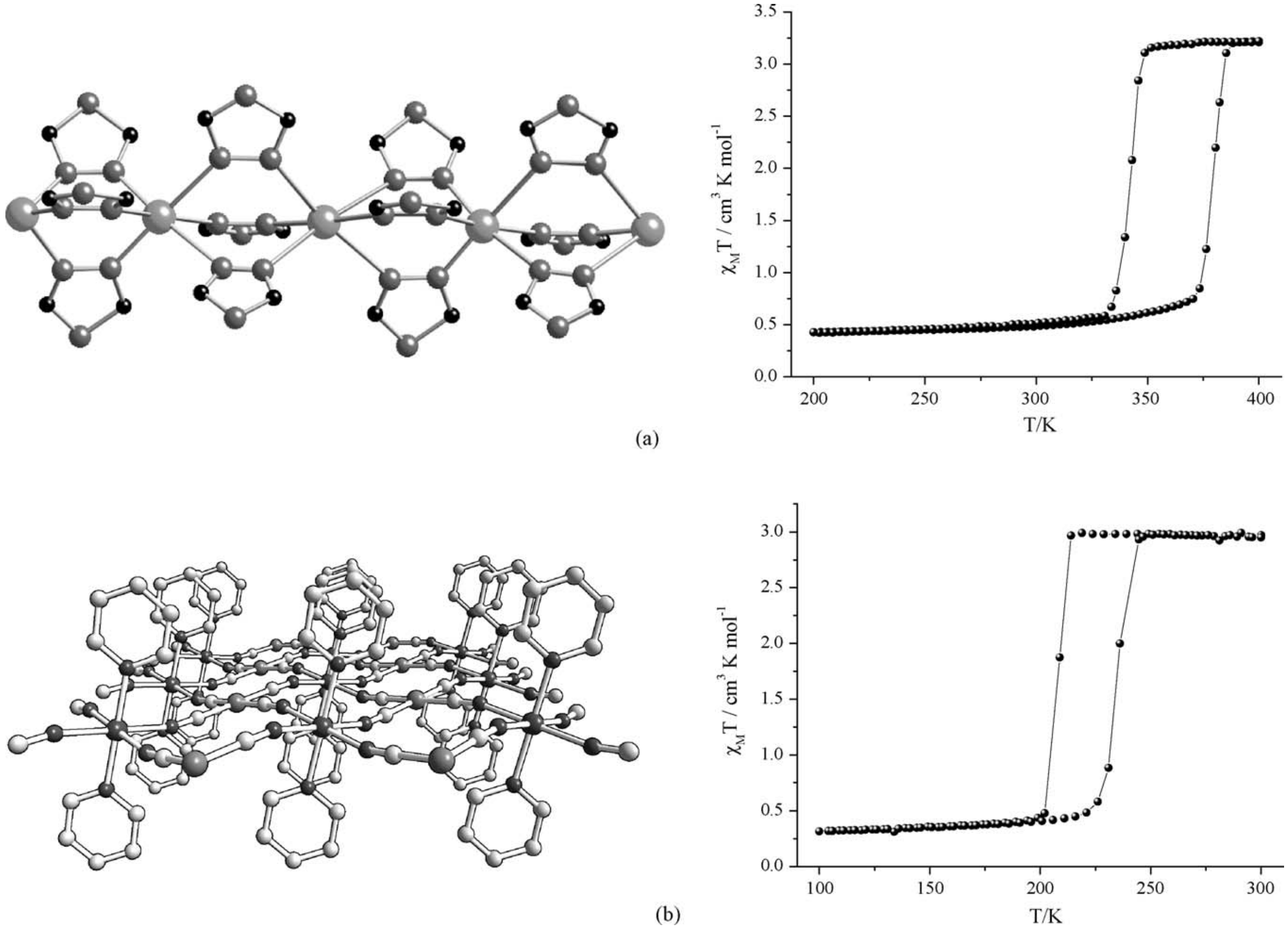


Fig. 8. Magnetic properties and molecular structures of $[Fe(H\text{-}trz)_2(trz)](BF_4)$ (a) and $[Fe(py)_2Pt(CN_4)]$ (b) (adapted from [74,77]).

Gaspar et al. [50] have also been investigating the possibility to synchronize both transitions in Fe(II) complexes. The first step in the tailoring of these hybrid materials has been the choice of SCO systems showing abrupt spin transition near or above room temperature. This is the range of temperatures at which usually the LC phase transition is observed. In this respect, the polymeric compounds based on the ligand triazole and Hofmann type clathrates are among the best candidates, showing abrupt spin transition above or near to room temperature accompanied by a pronounced change of color (Fig. 8). The second step in this approach concerns the incorporation of the LC moiety to the SCO system, which implies the attachment of the aromatic core with the alkyl chains to the triazole or pyridine ligands (Fig. 9). Self-assembly of 3,5-dihydroxy-*N*-4*H*-1,2,4-triazol-4-ylbenzamide and $Fe(BF_4)_2 \cdot 6H_2O$, $Fe(CF_3SO_3)_2$ or $Fe(p\text{-tol})_2$ have afforded a family of complexes with general formula $[Fe(C_n\text{-trz})_3](A)_2$, n being the number of carbon atoms of the alkyl chain (4, 6, 8, 10, 12) and $A = BF_4^-$, $CF_3SO_3^-$, *p*-tol$^-$ (Fig. 10). The complexes with the anions BF_4^- and $CF_3SO_3^-$ undergo SCO around room temperature. The LC properties are being investigated at present. Particularly interesting are the *p*-toluenesulphonate (*p*-tol) derivatives. These complexes have LS behaviour at room temperature. Upon heating they show an abrupt and complete spin transition accompanied by a pronounced change of colour (Fig. 11). DSC measurements,

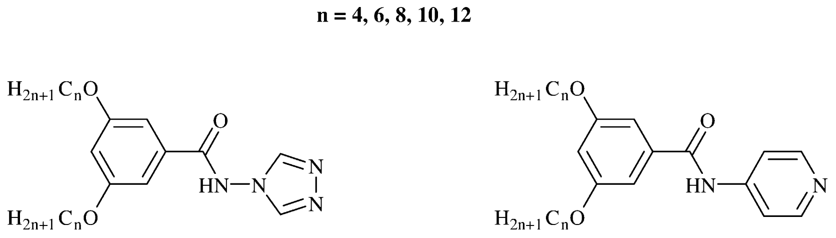


Fig. 9. 3,5-dialcoxy-*N*-4*H*-1,2,4-triazol-4-ylbenzamide (rigth) and 3,5-dialcoxy-*N*-pyridine-4-ylbenzamide (left) ligands (adapted from [50]).

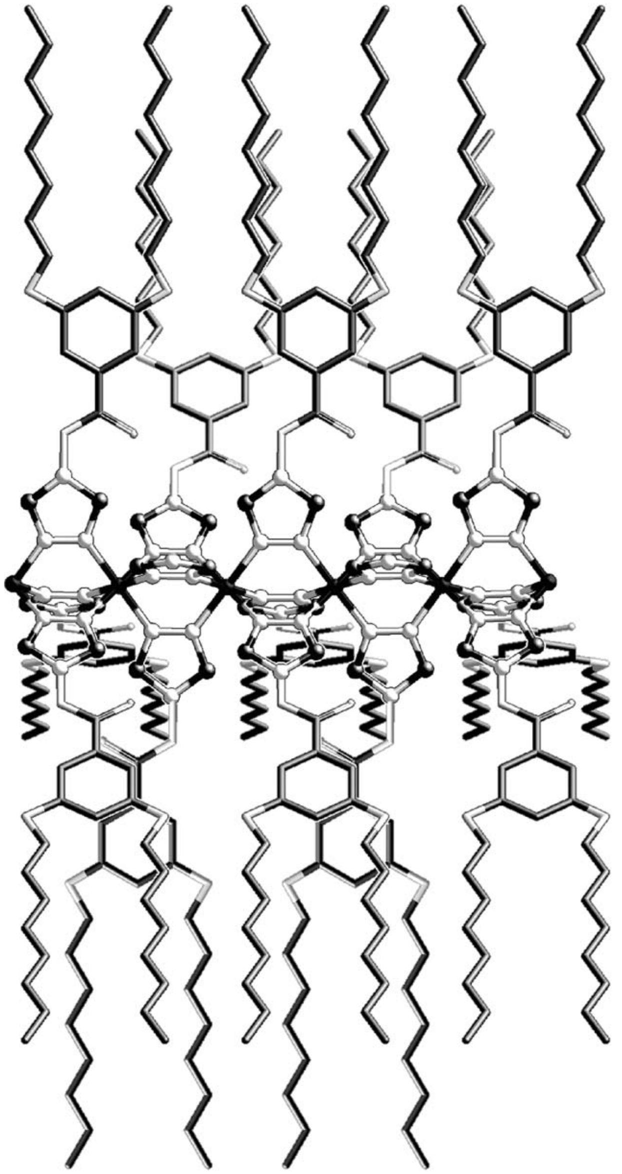


Fig. 10. Schematic drawing of the molecular structure of [Fe(C_n-trz)$_3$](A)$_2$ (adapted from [50]).

X-ray powder diffraction analysis and optical microscopy studies have proved that the transition from the crystalline state to the mesophase (discotic columnar) takes place synchronuously with the spin transition.

4. Functional porous spin crossover polymers

Porous molecular compounds have recently attracted the attention of researchers because of physico-chemical properties of nanoscale-sized cavities and the novel phenomena accociated with them. Besides, there is growing practical interest in their application in analytical separation, storage and heterogeneous catalysis. Two decades ago basically two classes of porous materials were known, inorganic and carbon-based materials. Regarding microporous inorganic solids, the largest two subclasses comprises alumosilicates and alumophosphates. Zeolites are 3D crystalline, hydrated alkaline or alkaline-earth alumosilicates in which the porosity is created through the elimination of water molecules, whereas the framework usually remains unaltered. The cavities have originally been exploited as molecular-sieves in gas separation and catalytic processes.

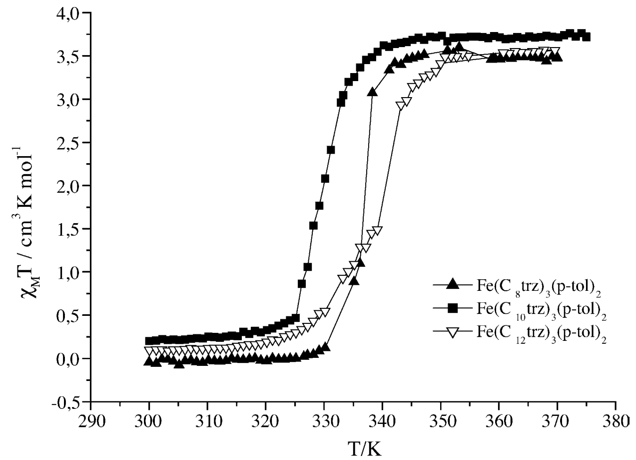


Fig. 11. Magnetic behaviour of [Fe(C_n-trz)$_3$](*p*-tol)$_2$ *n*: 8, 10, 12 (adapted from [50]).

Few years ago synthetic methods for porous coordination polymers have been developed. Research on the structure of porous coordination polymers has increased rapidly, and examples with functional microporous framework soon started to appear [51–55]. Microporosity can be defined as the ability of the framework to maintain an extensive net of micropores [56–59] with high degree of selectivity and reversibility in their guest-exchange chemistry [60–62] and heterogeneous catalytic activity [63,64]. Indeed, these particular properties have prompted the belief that coordination frameworks may find an application in molecular separations of gases such as H_2, O_2, CO, NO, CO_2 and CH_4 which are related with actual environmental and energy issues [65]. The implementation of microporosity in coordination frameworks has offered the opportunity to capitalize on the unique electronic aspects of molecular chemistry to impart specific electronic functionality. In fact, “molecular sponges” [66–67] and transition metal hydroxide layers [68–70] for which reversible dehydration/rehydration provokes significant changes in the magnetic properties have been reported. Likewise, the guest dependent properties of porous luminescent frameworks and conducting molecular charge-transfer salts have recently been explored [71–73].

The search for alternative approaches to obtain cooperative SCO polymers has led to functional frameworks in which the magnetic properties change on inclusion and removal of guest molecules as a consequence of the modifications in the electronic environment of the metal centres. The assembly of molecular SCO building blocks by rigid linkers such as bis-monodentate ligands has yielded 1D [74–76], 2D [77–84]

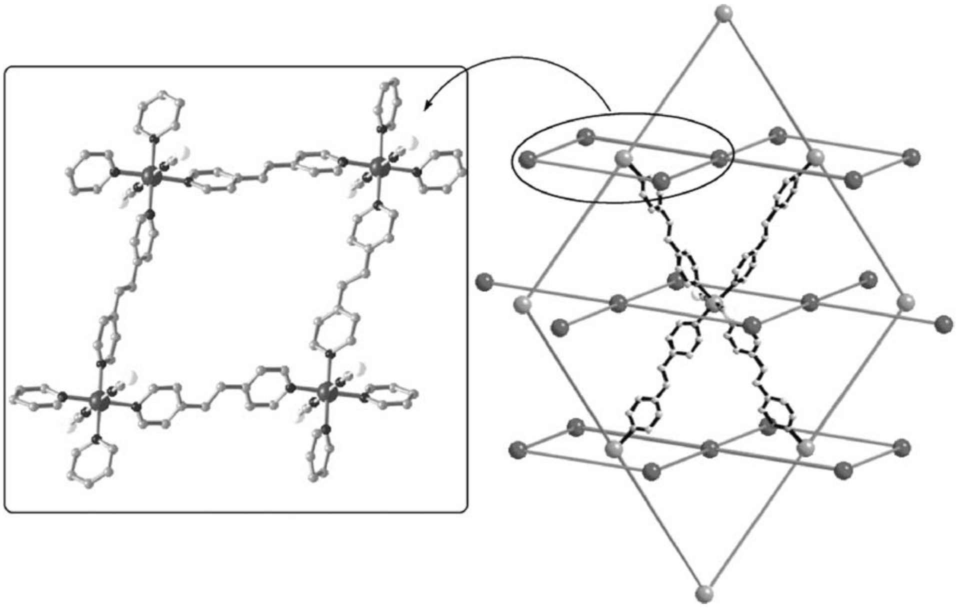
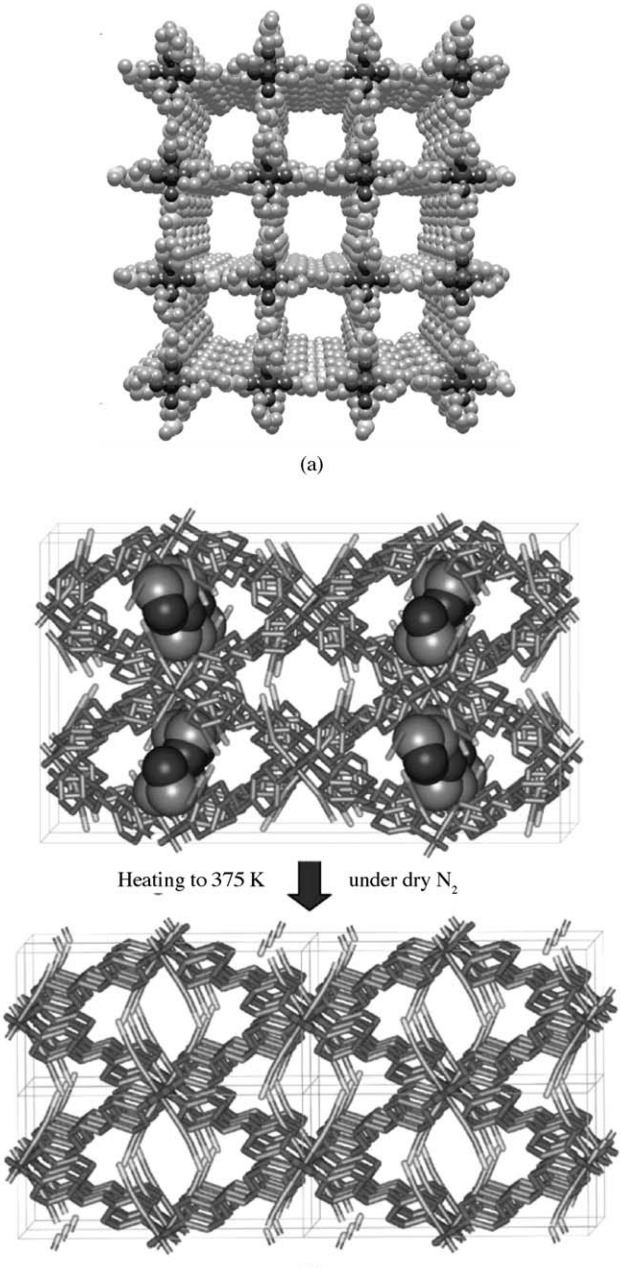


Fig. 12. Molecular structure of [Fe(bpe)$_2$(NCS)$_2$]·CH$_3$OH. Schematic views of the two independent interlocked mutually perpendicular sets of [Fe(bpe)$_2$(NCS)$_2$]$_n$ planes. The rods represent the bpe ligands connecting two iron atoms (adapted with permission from [82]).

and 3D [85–88] systems with many of them containing solvent of crystallization within the lattice. In several of these complexes the effect of desolvation/resolvation on the SCO properties has been studied. The assembling of iron(II) ions and bridging molecules such as bis-monodentate pyridine-like ligands has afforded a series of frameworks with general formula [FeL$_2$(NCS)$_2$]·*n*S, L being bispyridylethylene (bpe, $n = 1$, Solv = MeOH) [82], *trans*-4,4′-azopyridine (azpy, Solv = MeOH, EtOH and PrOH) [83] and 1,4-bis(4-pyridyl-butadiyne) (bpb, $n = 0.5$, Solv = MeOH) [84]. The compound [Fe(bpe)$_2$(NCS)$_2$]·MeOH is unusual in that it is made up of interlocking 2D networks constituted by parallel layers (Fig. 12). A compressed octahedron comprises a central iron atom with two *trans*-thiocyanato ligands filling the axial positions and four pyridine nitrogen atoms building the basal plane. Each bpe ligand connects two iron atoms defining the edges of a [Fe]4 rhombus. The edge-shared rhombuses define the grid-layered structures mentioned above with all the iron atoms in a coplanar sheet. Parallel sheets are displaced so that the iron centres of the first sheet are vertically above the third, fifth and further odd-numbered sheets, while vertically above the mid-points of [Fe]4 rhombuses of the even-numbered sheets. An equivalent stack of sheets is found in planes perpendicular to the first set defining large square channels where MeOH molecules are located (Fig. 13(a)). [Fe(bpe)$_2$(NCS)$_2$]·MeOH shows SCO behaviour whose extent and steepness are very sensitive to sample preparation revealing different HS and LS residual fractions at low and high temperature, respectively. This behaviour was associated with the particular nature of the extended porous framework with large channels where crystalline defects and molecular inclusions exert, most likely, subtle structural and electronic effects which influences the SCO process. This feature has been clarified by Halder et al. who have reported the compound [Fe(4,4′-azpy)$_2$(NCS)$_2$]·*x*S [83], a system having a similar structure as [Fe(bpe)$_2$(NCS)$_2$]·MeOH [82].

The compound [Fe(4,4′-azpy)$_2$(NCS)$_2$]·*x*S consists of the double interpenetrating 2D square grids formed by linking Fe(II) ions by 4,4′-azpy ligands. The grids interpenetrate each other in a diagonal fashion to give 1D guest-filled channels which occupy ca. 12% of the crystal volume (Fig. 13(b)). The system is made out of two unequivalent kinds of iron(II) centres with similar ligand binding geometries but different second coordination spheres due to a hydrogen-bonding interaction which involves the guests and the coordinating thiocyanate ligands of one Fe(II) centre. The dehydration of the framework occurs without destruction of the single crystallinity and is a reversible process. The desorbed material (host) can absorb a range of different guest molecules either through the vapour or liquid phase. After guest removal the general structural motif of interpenetrating grids remains unaltered although the structure sustains a number of changes: the grids display both a hinging motion and a slippage with respect to each other. The framework evidences guest-dependent SCO properties. The fully desorbed material does not undergo spin transition whereas the guest-loaded systems display continuous incomplete transitions (Fig. 14). Structural studies performed on [Fe(4,4′-azpy)$_2$(NCS)$_2$]·EtOH at low temperatures have shown that the iron centres involved in H-bonding to the guest molecules undergoes SCO. Moreover, structural studies on partially solvated materials suggest that it is principally the local interaction of the guest molecules rather than their influence on the overall framework geometry that influences the SCO properties.

Real and co-workers have reported on a 2D spin crossover system formulated as [Fe(bpb)$_2$(NCS)$_2$]·0.5MeOH



(a)

(b)

Fig. 13. Schematic view of the porous frameworks $[Fe(bpe)_2(NCS)_2]\cdot$MeOH showing the large channels (a). Structures of (b) $\{Fe_2(4,4'\text{-azpy})_4(NCS)_4\}$ (EtOH) and (c) $\{Fe(4,4'\text{-azpy})_2(NCS)_2\}$emphasising the 1D guest-filled channels (adapted with permission from [82,83]).

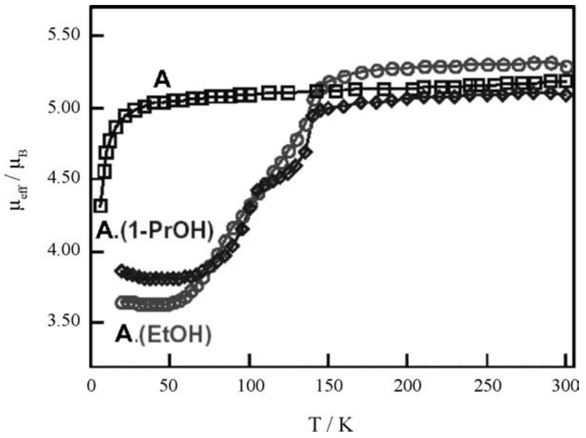
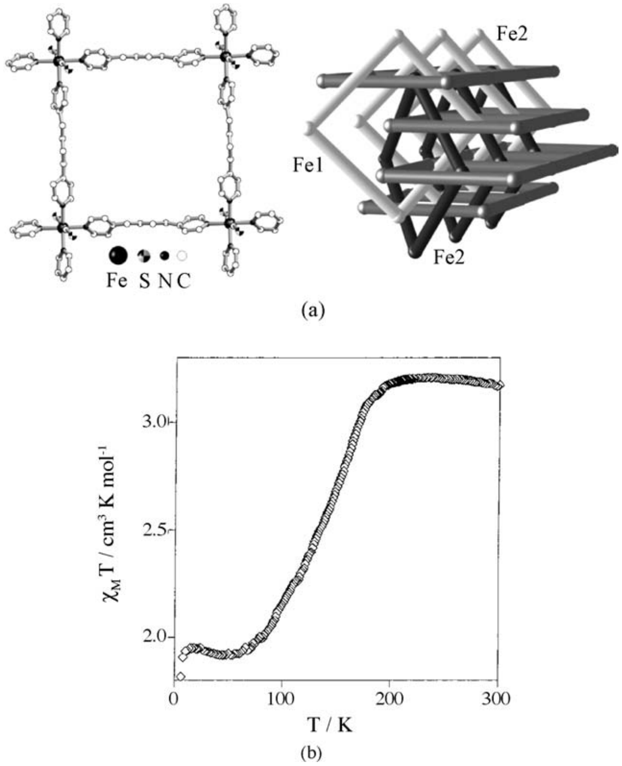


Fig. 14. Magnetic moment, μ_{eff}, vs. temperature for $\{Fe_2(4,4'\text{-azpy})_4(NCS)_4\}\cdot x$(guest) (denoted A {guest}), showing 50% SCO for the fully loaded systems and no SCO for the fully desorbed phase. The ethanol and methanol loaded phases undergo a single-step spin crossover whereas the 1-propanol adduct shows a two-step transition with a plateau (adapted from [82]).

(bpb = 1,4-bis(4-piridyl)butadiyne) which consists of two different arrays of nets (Fig. 15) [84]. Two crystallographically independent iron sites (Fe1 and Fe2) define the nodes of the nets. The iron atoms have similar coordination surroundings in both sites, which consist of compressed octahedra with two *trans*-thiocianato ligands in the axial positions and four pyridine N-atoms in the basal plane. Each bpb ligand connects two iron atoms defining large [Fe4] squares (Fig. 15a). The edge-shared squares define the net structures with all the iron atoms, either coplanar (A set, Fe1) or slightly corrugated (B set, Fe2). The iron-to-iron separation through the bpb ligand is 16.628 and 16.393 Å for the A and B nets, respectively. B consists of two mutually perpendicular stacks of inter-locked squared grids organised along [1 1 0] and [−1 1 0] directions.



(a)

(b)

Fig. 15. Molecular structure of $[Fe(bpb)_2(NCS)_2]\cdot0.5$ MeOH (a). Schematic view of the triple interpenetration of the $[Fe(bpb)_2(NCS)_2]_n$ grids. The parallel A set of planes, defined by iron atoms of the type Fe1, is interpenetrated by the mutually interpenetrated B and C sets of planes, which are defined by the iron atom of the type Fe2 (see text) (a). $\chi_M T$ vs. T for $[Fe(bpb)_2(NCS)_2]\cdot0.5$ MeOH (b) (adapted with permission from [84]).

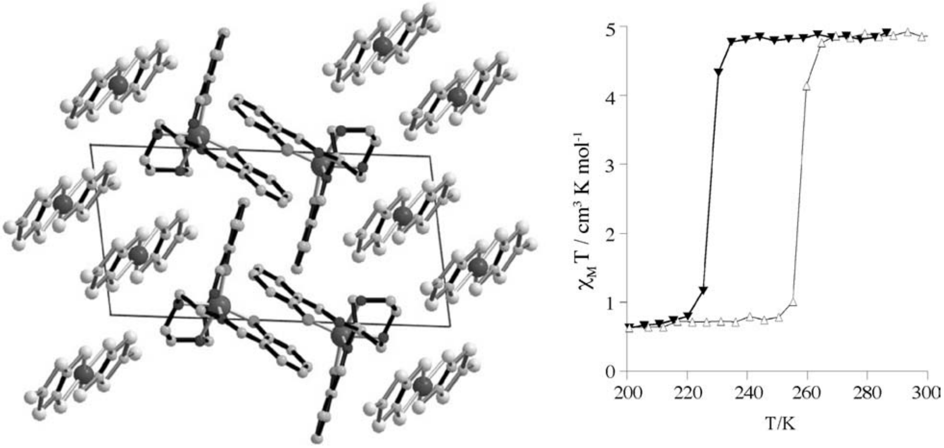


Fig. 16. Schematic view of the crystal structure and magnetic properties of $\{[Fe(sal_2\text{-trien})][Ni(dmit)_2]\}$ (adapted with permission from [92]).

$[Fe(bpb)_2(NCS)_2]\cdot 0.5MeOH$ undergoes a continuous 50% spin conversion. The occurrence of 50% conversion (see Fig. 15b) has been ascribed to the presence of two different iron sites. In this respect, it is remarkable that for site Fe1 is more probable than for site Fe2 to undergo spin transition as the former displays shorter average Fe—N bond distances. In addition, a strong interaction between solvent molecules and site Fe1 is observed. As in the previous examples, interaction of the solvent molecules with the Fe(II) centres directly influence the ligand field splitting at the metal sites.

The suitability of cyano-metallate complexes as connectors between iron(II) SCO centres to build highly cooperative thermo-, pressure- and photo-switchable two- and three-dimensional coordination polymers have been demonstrated [78]. Noteworthy is the rich inclusion chemistry of these Hofmann-like polymers which accounts as well for reversible guest-exchange processes. The porous nature of these polymers does open new opportunities for implementing synergy between inclusion chemistry and the SCO phenomenon which is currently being explored in our group.

Nowadays, the properties of functional guests and those of porous frameworks (non-linear optical activity, conductivity, spin crossover, magnetism, chromism, fluorescence) have been investigated separately. The research of the cooperative properties of functional frameworks incorporating functional guest molecules is a current challenge.

5. Spin crossover properties and electrical conductivity

Electrical conductivity is a fundamental property of matter currently being investigated in the realm of molecular compounds. Since the discovery of the electrical conductivity in perylene bromine [89], many efforts have been invested in order to obtain high T_c superconductors based on organic and organometallic charge transfer complexes and radical ion salts [90,91]. Actually, the trend in the field of organic conductors aims towards the design of hybrid materials combining organic cationic radicals and functional molecular anions able to add a second physical property of interest. Following this approach ferromagnetic metals, magnetic superconductors, chiral conductors and switchable conductors have been synthesized [92]. Despite many intrinsic benefits such as the possibility of switching the electronic conductivity, up to now, molecular superconductors cannot compete with inorganic superconductors in terms of processing, stability and particularly critical temperatures.

Switchable molecular SCO building blocks have recently been proposed to be combined with radical ionic salts with the aim of tuning the conducting properties by acting on the bi-stable cation [93]. This strategy has already led to some interesting results, e.g. the salt $\{[Fe(sal_2\text{-trien})][Ni(dmit)_2]_3\}$ (sal_2-trien: bissalicylideneaminotriethylenetetramine and dmit: 4,5-dimercapto-1,3-dithiole-2-thione), obtained from electrolysed solutions of $\{[Fe(sal_2\text{-trien})][Ni(dmit)_2]\}$. This material exhibits a structural arrangement typical of $[Ni(dmit)_2]^{\delta-}$ fractional oxidation state compounds; layers of $[Ni(dmit)_2]^{\delta-}$ units separated from each other by layers of disordered $[Fe(sal_2\text{-trien})]^+$ cations (Fig. 16). The cationic units undergo cooperative SCO behaviour with a hysteresis loop of 30 K and the layers of $[Ni(dmit)_2]^{\delta-}$ favours the occurrence of electronic transport. At room temperature the electrical conductivity of this hybrid complex is 0.20 S 9cm^{-1}. Preliminary electrocrystallization experiments of $\{[Fe(sal_2\text{-trien})][Ni(dmit)_2]\}$ have afforded small amounts of crystalline material $\{[Fe(sal_2\text{-trien})][Ni(dmit)_2]_x\}$ whose magnetic and conductivity properties demonstrate that $\{[Fe(sal_2\text{-trien})][Ni(dmit)_2]\}$ is a suitable precursor for the synthesis of switchable SCO molecular conductors.

6. Non-linear optics and spin crossover properties

During the last three decades multidisciplinary research on materials that exhibit non-linear optical properties (NLO) has increased rapidly [94–100]. The demand of materials with

NLO properties is caused mainly by advances in laser technology, which requires the compact frequency multiplicators capable effectively to generate the second (SHG) and third (THG) harmonics. Besides of widespread utilization in high power laser systems, NLO materials are of great importance for optoelectronic and photonic technologies relevant to optical computing.

NLO properties are found in a diverse kind of materials involving semiconductors, inorganic crystals [94,95], molecular organic materials [96–100] and metal–organic coordination compounds [101]. To date, only inorganic materials such as lithium niobate ($LiNbO_3$) and potassium dihydrogen phosphate (KH_2PO_4) are exclusively used in optoelectronic devices despite several molecular organic and metal–organic coordination compounds approach the efficiencies of that of $LiNbO_3$. However, molecular compounds have attracted great interest owing to their potential advantages over the conventional inorganics for advanced applications, among them the possibility of switching of quadratic NLO responses [101,102].

The technology of optoelectronics has made the need for photonic-electronic compatible materials pressing. Actually to combine the information processing capabilities of electronics and the speed of light it is necessary to integrate photonic devices with standard semiconductor electronics which appears to be a difficult technical task. For instance, linking magnetism or conductivity and NLO properties at the molecular level [103] is a challenging target pursued during the last decades, even if the possibility of using such materials in an operating electro-or magneto-optical device may still remain somewhat speculative. Several hybrid NLO-magnetic materials exhibiting spontaneous magnetization and SHG efficiencies have been reported [104]. However, to the best of our knowledge the observation of the interplay between these properties remains a challenging issue.

The possibility of a modulation of the cubic NLO response upon spin conversion has been suggested by Létard et al. [105] in the spin crossover compound $[FeL_2(NCS)_2]$ (L: *N*-(2-pyridylmethylene)aminobiphenyl) but the effect has not been observed yet. Recently, a theoretical investigation by Lacroix and co-workers [106] has revealed that the $S = 2 \leftrightarrow S = 0$ spin crossover process should result in an increase of the quadratic NLO response of about 25% of the initial value. The calculations have been made on the spin crossover complex $[Fe(5\text{-}NO_2\text{-sal-N}(1,4,7,10))]$ ($5\text{-}NO_2$-sal-N(1,4,7,10): $5\text{-}NO_2$-salicylaldehyd-N(1,4,7,10)). It is suggested that the enhancement of the molecular hyperpolarizability upon spin conversion is directly related to the structural changes which accompanies the process. The influence of the spin crossover process on the quadratic NLO response in molecular materials still awaits experimental confirmation.

At the macroscopic level the primary requirement for non-linear optical activity to occur is a noncentrosymmetric material featuring some degree of alignment of the dipolar molecular constituents. Lin have recently proved that noncentrosymmetric coordination networks with desired dimensionality (1D, 2D, 3D) can be rationally designed by taking advantage of well-defined metal coordination geometries in combination with carefully chosen rigid bridging ligands. We are actually investigating the suitability of asymmetric polypyridyl ligands and the metal-cyanide counterions $[M(CN)_2]^-$ M: Ag, Au and $[M(CN)_4]^{2-}$ M: Ni, Pt, Pd, Cd in order to assemble noncentrosymetric SCO networks.

7. Ligand isomerization and spin crossover

The control of magnetic and optical properties by light prompted the idea that the SCO materials could be used in magneto-optical devices. However, for all reported SCO compounds the possible optical recording using the LIESST effect [107] would be operative at low temperatures (below ca. 100 K). Zarembowitch and co-workers have reported an alternative strategy to achieve photoconversion of spin states called ligand-driven light-induced spin changes (LD-LISC) [108]. This approach concerns the synthesis of complexes in which a photo-induced modification of one or more ligands results in a ligand field change and triggers the metal ion spin conversion. The ligand isomerization enables photo-induced spin conversions between long-lived spin states at high temperature. These authors demonstrated the feasibility of this approach synthesising the two forms of the $[Fe(stpy)_4(NCS)_2]$ (stpy: 4-styrylpyridine) complex (Fig. 17(a)). $[Fe(\textit{trans}\text{-stpy})_4(NCS)_2]$ undergoes a thermally induced spin conversion centred at around 108 K, while

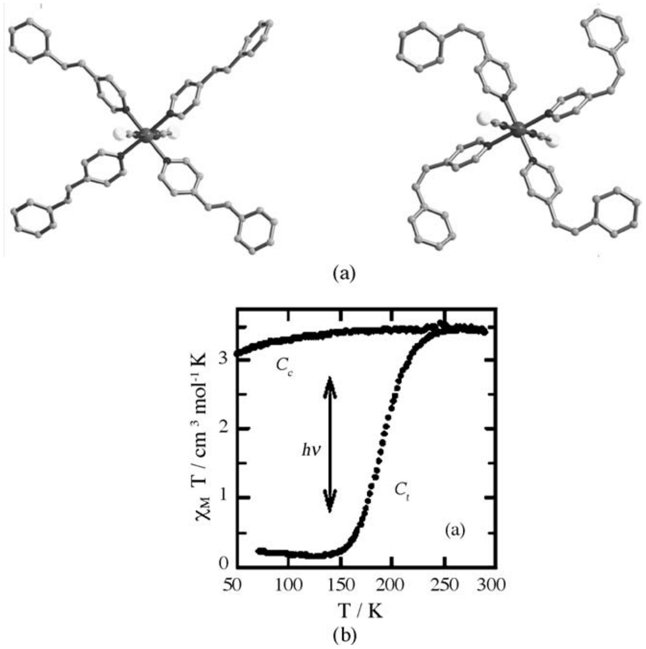


Fig. 17. Molecular structures of $[Fe(\textit{trans}\text{-stpy})_4(NCS)_2]$ (C_t) and $[Fe(\textit{cis}\text{-stpy})_4(NCS)_2]$ (C_c) (a). $\chi_M T$ vs. T for C_t and C_c. The photoexcitation of the 4-styrylpyridine ligands is performed irradiating the C_t and C_c samples at $\lambda = 322$ and 260 nm, respectively, resulting in a change of the spin state (adapted with permission from [109]).

[Fe(*cis*-stpy)$_4$(NCS)$_2$] is HS at any temperature (Fig. 17(b)). Irradiating the samples with light of appropriate wavelength, at temperatures just below T_c, provokes a spin change in the system as a result of the photoconversion of the ligand. This process has not been observed in the crystalline state because of the mechanical forces involved in the *cis–trans* conversion. However, Boillot and co-workers have observed the LD-LISC at 140 K in [Fe(stpy)$_4$(NCS)$_2$] embedded in cellulose acetate films and at room temperature in [Fe(*trans*-msbipy)$_4$(NCS)$_2$] (*trans*-msbipy: 4-methyl-4′-*trans*-styryl-2,2′-bipyridine) in acetonitrile solution [109].

8. Outlook and perspectives

The general advantage of SCO compounds is the flexibility and the versatility in molecular design. Due to their switching properties (colour, magnetism, dielectric constant, structure) the SCO materials are potentially useful for rewritable optical, thermal or pressure memories at a nanometric scale. To be useful in practice, a demanding set of material requirements must be met, such as room temperature operation, non-destructive writing and readout of the information. Nowadays, prototypes for thermal and pressure displays have already been described. However, for all reported SCO compounds the possible optical recording using the LIESST effect would be operative at low temperatures (below ca. 100 K). In order to overcome this limitation, one can explore new principles such as the coupling of SCO phenomena with other physical/chemical properties in a synergic fashion. It is expected that SCO materials with synergic properties will reveal additional functionalities suitable for practical applications. In the frame of this review we have discussed different approaches which are being explored in order to achieve multifunctionality in SCO materials. As far as synergy between SCO and magnetic exchange concerns, we do not envisage an easy way for its realization. In fact, static or pulsed magnetic fields (<30 T) have a negligible direct influence on the spin crossover process. Additionally, the possibility of magnetic ordering trivially disappears in the LS state. In this case, one can speak of an interplay between SCO and magnetic exchange as it has been shown for Fe(II) and Co(II) dinuclear systems. To reach synergy requires to combine crystal structural moieties with distinctive functional properties, e.g. chains or planes containing SCO centres and magnetically ordered networks. It is presumable that the magnetic ordering can influence directly the crystal field strength of SCO centres by means of magnetoelastic interactions. Reaching this goal is a matter of intelligent strategies of synthesis.

Porous SCO materials, liquid crystals with SCO properties and SCO complexes with isomerizable ligands can be considered as successful examples of multifunctional synergic materials. SCO liquid crystals comprise liquid-crystalline mesogens chemically bonded to thermo- and photo-chromic SCO centres. The physical variable influencing the spin state of complexes in porous materials is the amount of guest molecules, whereas the electrical field is expected to be effective in liquid crystals with SCO properties. The influence of an electrical field on the SCO process is currently pursued in our group, which has stimulated the development of these multifunctional materials. We have shown, that synergy between SCO and liquid crystalline properties has been achieved. Moreover, due to the ability of liquid crystals to form thin layers it has become possible to obtain SCO films.

The development of multifunctional SCO materials reflects a modern trend in molecular materials science. There is hope that multifunctional SCO systems will find applications as sensors, molecular separators of gases, in photonic devices, light modulators and filters, rewritable molecular memory devices and image processing. It is still a long way to go, but certainly exciting and attractive to chemists as well as physicists.

Acknowledgements

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