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Emerging trends in spin crossover (SCO) based functional materials and devices

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ABSTRACT

The design and synthesis of functional molecules with controllable properties are at the forefront of modern materials chemistry research due to their diverse applicability, especially in device miniaturization. Spin crossover (SCO) complexes can be switched between low (LS) and high spin (HS) magnetic states with the help of an external perturbation, and are promising candidates for the realization of molecule-based electronic and spintronic components, such as switching and memory elements. Although the area is relatively old and a multitude of SCO active transition metal complexes of d⁴-d⁷ electronic configuration have been reported, the field continues to grow, and several interesting research directions have emerged. In this context, the present review attempts to give a concise overview of recent trends in SCO research. Attempts devoted towards rendering multifunctionality to the SCO systems in order to bridge the gap between laboratory and reality, and efforts made to study spin state dependence of physical property modulation such as electrical conductance from single molecule level to bulk, prerequisite for the realization of SCO-based devices, are emphasized by discussing the most relevant past and recent literature.

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1. Introduction

The recent advent of molecular electronics [1–3] and spintronics [4–8] has enabled scientists to investigate the potential of molecules in transport experiments [9–11]. As a result, a number of devices using functional molecules, such as (molecular) – rectifiers [1,12,13], wires [12–14], logic gates [15,16], machines [17–19] and switches [20], have been reported in the literature, seeking to replace conventional silicon-based architectures via bottom-up methodology. Molecular switches, operated by differing mechanisms [21], are of great fundamental and technological importance, and play a pivotal role in the design of modern molecular electronic circuitry. Among them, the spin crossover (SCO) phenomena of metal-organic complexes exhibiting a low spin (LS)/high spin (HS) bistability [22–34] upon application of external stimuli such as temperature, pressure, light and electric field (Fig. 1) have garnered high interest within the construction of molecular devices. Abrupt LS to HS transition [35–37], wide thermal hysteresis loop ($\Delta T_{1/2}$) [38–42], laser pulse induced spin state switching inside thermal hysteresis loop [43–49], and room



Fig. 1. (a) Schematic representation of the SCO phenomena in a Fe^{II} complex with d⁶ electronic configuration: The dark red circle on the far-left side of the figure shows the LS state of the central Fe^{II} ion in an ideal octahedral (O_h) environment. The pale-yellow circle on the far-right side indicates the HS state of the Fe^{II} centre. Note the volume expansion of the complex octahedron upon SCO mediated by elongation of metal ligand Fe-N bonds. The terms T, P, L, and E represent, temperature, pressure, light and electric field used as an external perturbation to induce SCO and (b) An example of an SCO complex (inset) showing RT bistability and the corresponding $\chi_m T$ vs. T curve indicating abrupt first order transition with a thermal hysteresis ($\Delta T_{1/2}$) desirable for device applications, reproduced with permission from [35].



Fig. 2. The principle behind the luminescence tracking of an SCO event based on synergies coupling between SCO and luminescence. Energy transfer (ET) from the excited energy donor to the LS SCO complex leads to the quenching of donor emission. For the HS SCO complex, the luminescence of the donor is retained due to the reduced spectral overlap, $J(\lambda)$, between the donor emission and HS acceptor absorption.

temperature (RT) bi-stability [40,50–57] have rendered SCO materials suitable for the realization of molecular electronic and spintronic devices capable of operating at ambient conditions [58].

A common strategy in the design of molecular devices consists of the addition of a second functionality, e.g. luminescence, optical activity, or electronic transport, whose response to an external stimulus is synergistically dependent on the magnetic spin state of the SCO molecule [59,60]. However, by following the hybrid approach, the SCO molecules have to be attached to surfaces or electrodes; a situation that can strongly change the respective SCO parameters, and even lead to complete loss of the switching behaviour [61]. In this regard, SCO active nanostructures [62] and thin films of the monolayer to multilayer thickness [63–69] have been prepared to probe the effect of size reduction on the SCO characteristics; electrical addressing of these materials revealed the spin-state dependence of conductivity ideally suited for device fabrication.

Excellent reviews covering several aspects of SCO phenomenon have appeared in the past [23,26,70–78]. Recently, topics such as the role of ligand design in affecting SCO [79,80], phase transition and photo-switching dynamics of SCO complexes [81-83], SCO in Fe^{III} complexes [84], charge transport and electrical properties of SCO materials [85], guest effects on SCO in Hoffmann-type metal-organic frameworks (MOF) [86] and SCO characteristics of [Fe(phen)₂(NCS)₂] on metallic surfaces [61] have been reviewed. However, an account detailing recent progress made in the areas of SCO-based multifunctional materials and nanostructures, studied to boost the application potential of SCO systems is lacking. Furthermore, several emerging, technologically-important avenues of SCO research have not been reviewed. This review intends to fill this gap by evoking a concise discussion, with selective coverage of recent results, on emerging recent trends in SCO-based functional materials and devices. Therefore, we would like to put emphasis on cutting-edge fundamental developments and advances made towards building functional SCO entities tailor-made for various applications.

2. SCO and multifunctionality

2.1. SCO and luminescence

2.1.1. Introductory remarks

The development of an optical method that can interact with the spin switching event upon thermal SCO may expand the horizon of SCO-based applications, particularly as magneto-optical switches [87]. A two-component (dyad) bi-functional system comprising of an SCO active element capable of existing in two different spin states, and with a signalling unit that has an emission which can be affected upon spin state switching (Fig. 2) could function as an SCO-based magneto-optical switch.

A donor-acceptor (D-A)/donor-bridge-acceptor (D-B-A) dyad system, operating via an energy transfer (ET) mechanism, featuring luminescent (fluorescence or phosphorescence) moieties as an energy donor and SCO Fe^{II}-complex skeleton as an energy acceptor are suitable candidates to read the spin state by luminescence. The rationale behind the design of such a molecular system is the absorption change of the SCO unit upon thermal SCO, LS \rightarrow HS and vice versa. The spin state switching modulates the emission characteristics of the luminophore, depending upon the expanse of spectral overlap between the donor-luminophore emission and acceptor-SCO entity centred absorption originating from ¹(MLCT) and d-d electronic transitions.

The LS state of an SCO complex is a better energy acceptor due to its relatively high absorption coefficient in the visible region of the electronic spectrum, and its close energetic proximity with the common luminophores emitting in the ultra violet (UV) and visible regions. This facilitates an efficient spectral overlap between the donor (luminophore) emission and acceptor (LS state) absorbance and subsequent quenching of donor luminescence (Fig. 2). Whereas the HS state featuring very weak absorption in the near-IR (NIR) region is energetically not matched, i.e. less spectral overlap, to quench the emission of the energy donor via an ET mechanism, hence the donor luminescence may remain unquenched. From a design point of view, an SCO active system featuring an abrupt first order transition is desired, given the temperature-dependent emission characteristics of the luminophores.

The applied strategies developed so far can be classified into two different categories:

- (i) complexation of SCO active metal ions either with intrinsically luminescent chelating ligands or employing charge balancing luminescent counter anions, and
- (ii) covalent-grafting or physical-doping of a luminophore with an SCO active molecular complex, nanocomposite and 1D coordination network as elaborated below.



Fig. 3. Structure of the luminescent ligands **1** [88], **2** [89], and **3** [36] utilized to study coupling between SCO and luminescence. λ_{exc} and λ_{em} are excitation and emission wavelengths, respectively.

2.1.2. Luminescent SCO systems based on intrinsically luminescent ligands or anions

In this category, intrinsically luminescent chelating ligands (Fig. 3) are employed to probe spin state and luminescence. A direct energy transfer pathway is envisioned to operate between the ligand and metal centre in a specific spin state as observed in a mononuclear Fe^{II} SCO complex featuring 2,6-bi's (benzimida-zolyl) pyridine ligand (**1**, Fig. 3) [88].

Nevertheless, finding a correlation between spin state and luminescence in complexes featuring intrinsically luminescent chelating ligands has been proven to be rather difficult, because the resulting complexes exhibited incomplete SCO transition, or were even SCO inactive. For cases where SCO is persistent, no quenching or modulation of the ligand-centred luminescence is observed due to *"electronic uncoupling*" between the ligand (**2** and **3**, Fig. 3) and SCO centre [36,89]. In a subclass of this category, Fe^{II}-1,2,4triazole complexes featuring 9,10-dimethoxyanthracene-2-sulfo nate and 1-pyrenesulfonate non-coordinating luminescent counter anions are utilized to probe spin state via luminescence modulation, and photo-relaxation processes of 1-pyrenesulfonate anions were spin state dependent [90].

2.1.3. Luminescent spin systems based on SCO entities grafted/doped with luminophores

In this category, the luminescent fragment is covalently linked to the chelating ligands (Fig. 4), leading to the formation of donor-bridge-acceptor (D-B-A) type luminescent spin systems. In this way, spin state switching in molecular complexes, 1D coordination polymer networks, and nanoparticles are probed employing luminescence as an internal reporter. In an initial attempt, Fabbrizzi and co-workers demonstrated a solution phase fluorescent molecular thermometer based on temperature dependant modulation of fluorescence mediated by spin state interconversion in a D-B-A type complex system featuring Ni^{II}-cyclam spin system, methylene (-CH₂-) spacer and naphthalene fluorophore [91]. In a recent report, a Fe^{II}-(naphth-1-yl) -N-(3,5-di (pyridin-2-yl) -4H-1,2,4-triazol-4-yl) methanimine) complex system featuring the naphthalene fluorophore (**5**, Fig. 4)



Fig. 4. Structure of the ligands functionalized with luminescent antennas (highlighted in blue), **4** [91], **5** [92], **6** [93], **7** [94], and **8** [95], utilized to probe coupling between SCO and luminescence. λ_{exc} and λ_{em} are excitation and emission wavelengths, respectively.



Fig. 5. (a) Schematic of SCO active nanoparticles grafted with luminescent pyrene probe, (b) monomer and excimer based PL from pyrene moieties at lower and higher grafting ratio of the luminophore and (c) temperature dependence of magnetic property and (d) its reproduction from PL measurements, reproduced with permission from [100].

has been reported to show luminescence modulation upon spin state interconversion [92].

Following a similar approach, Ruben and co-workers grafted a pyrene luminophore (**6**, Fig. 4) to a bpp-Fe^{II} (bpp = 2, 6-bis (pyrazol-1-yl) pyridine) SCO active unit via a butyl (-(CH₂)₄-) bridging group, but observed no correlation between the fluorescence of the pyrene group and the spin state of the Fe^{II} ion in the bulk [93]. See also a recent report detailing no correlation between spin-state switching and ligand (donor) centred luminescence in a heterotrinuclear [Pt₂Fe] SCO complex [94].

In a set of hetero-dinuclear triple helicate Fe^{II} complexes of the formula (HHH)-[LnFe(L_n)₃]⁵⁺ (n = 1 or 3 and Ln = Eu³⁺), the Europium complex part (**8**, Fig. 4) acted as an energy donor. In LS (HHH) -[LnFe (L₁) ₃]⁵⁺, the Eu³⁺ based emission is quenched due to the efficient spectral overlap between the Eu³⁺ centred emission and an LS absorption band of (HHH) -[LnFe (L₁) ₃]⁵⁺. By contrast, the lack of such spectral overlap led to incomplete quenching of the Eu³⁺ based emission in the pure HS (HHH) -[LnFe (L₃) ₃]⁵⁺ complex [95].

SCO nanocomposites of the type $[Fe(H-trz)_2(trz)]BF_4@SiO_2$ chemically grafted with luminescent markers such as Tb^{3+} complexes [96], dansyl derivatives [97], and cadmium telluride (CdTe) nanocrystals [98] on the outer SiO₂ shell are reported to show coupling between SCO and luminescence. In a post-synthetic approach, Tao and co-workers grafted pyrene and Rhodamine B luminophores onto the back-bone of the 1D complex $[Fe(C_2H_4N_4)_3]$ (ClO₄)₂ (C₂H₄N₄ = 4-NH₂-1,2,4-triazole), reporting luminescence modulation upon SCO [99].

Bousseksou and co-workers have achieved remarkable "mechanically induced structural means of luminescence modulation", taking advantage of the cooperative nature of SCO. The bi-stable $[Fe(H-trz)_2(trz)]BF_4$ nanoparticles core, protected by a silica shell hybrid, was grafted with a pyrene luminophore (Fig. 5a). Upon SCO, an increase of the excimer lifetime and luminescence inten-

sity, and bathochromic shifting of the emission maximum were observed (Fig. 5b), while the monomer emission exhibited negligible spin-state dependence [100].

The observed strong coupling between the pyrene excimer emission and SCO was attributed to spin transition induced mechanical strain, which means volume expansion of the complex originating from the SCO LS \rightarrow HS transition (Fig. 5d). This "*indirect*" strategy is rather interesting and may be extrapolated to molecular systems featuring cooperative and abrupt SCO.

Correlation between spin state and luminescence has been observed in nanoparticles (NP) of $[Fe(NH_2Trz)_3]$ (OTs)₂ (NH₂Trz = 4-amino-1,2,4-triazole; OTs = tosylate) 1D polymeric complex doped with Rhodamine 110. This system was reported to be useful in fluorescence thermometry application due to the bi-functional, SCO and luminescence nature of the hybrids [101]. Similarly, Bousseksou and co-workers studied spin state changes in thin films and nanoparticles of the $[Fe(hptrz)_3]$ (OTs)₂ (hptrz = 4-heptyl-1,2,4-triazole and OTs = tosylate) 1D polymer by doping it with the acridine orange luminophore and showed spin state detection down to a single particle level of size 150 nm based on luminescence modulation upon spin state switching [102].

2.1.4. Ligand structure mediated coupling between spin state and luminescence

Apart from the so-far discussed categories, structural means to elucidate the correlation between SCO and luminescence are reported. In a special scenario, Garcia and co-workers reported an SCO active bi-nuclear { $[Fe_2(L)_5(NCS)_4]_3(MeOH)_4$ } complex featuring a 1,2,4-triazole-based ligand (**9**, Fig. 6) that was capable of undergoing inter-conversion between enol and keto forms by varying the temperature, the corresponding variation in luminescence enabled spin state tracking of the Fe^{II} centres [103].



Fig. 6. Structure of the ligands, 9 [103] and 10 [104], reported to show coupling between spin state and luminescence upon structural modifications.

In a remarkable solution phase study, Weber and co-workers reported the realization of luminescence modulation upon SCO, wherein the addition of pyridine ligand to the solution of a Ni²⁺ SCO complex featuring Schiff base-like ligands bearing a heteroaromatic fluorophore (**10**, Fig. 6) altered the geometry of the complex, and led to remarkable variation in fluorescent intensity enabling spin state tracking in the system [104].

From a device perspective, Matsuda and co-workers reported an ITO/chlorophyll-[Fe(dpp)₂](BF₄)₂/Al (dpp = 2,6-di(pyrazol-1-yl) pyridine) electroluminescent device featuring spin state dependent ON-OFF switching of electroluminescence. The room temperature emission from the device was quenched when cooled to 260 K, attributed to HS (RT) \rightarrow LS (260 K) transition of the complex [105].

2.1.5. Summary and perspectives

Although there are reports detailing the synergy between SCO and luminescence, in most cases mechanistic attributes based on the difference in volume of the LS and HS states are made. Among the materials reported, the 1D systems coupled with a range of luminophores, either by chemical grafting or doping, showed the most consistent results. The results obtained for the 1D-luminescent spin systems are interesting due to their near RT abrupt SCO characteristics associated with a large hysteresis loop. On the other hand, efforts to probe the synergy between SCO and luminescence in molecular complexes either with intrinsically luminescent ligands or ligands tethered with a luminescent entity led to mixed results, wherein the majority of the systems showed no correlation between spin state and luminescence (Figs. 3 and 4). Molecular systems showing SCO-mediated abrupt first order phase transition [35,36] are good candidates in view of the design of molecular bi-functional spin-photon systems given their narrow $T_{1/2}$ temperature range (±10 °C), which may be beneficial in terms of applicability.

2.2. Chiral SCO materials

Strong redistribution of electronic states upon spin crossover renders SCO-based materials with magneto-optical device applicability [106–108]. However, the potential of achiral photochromic SCO complexes to undergo destructive read-out, i.e. erasing of the stored data due to high-energy light exposure and conformational modifications, proves a huge bottle-neck towards the development of realistic memory devices based on SCO complexes [109]. It is proposed that combining SCO with chirality will facilitate non-destructive read-out of spin states due to the use of low-energy irradiation, thus avoiding photoinduced data destruction during reading-out of the stored information [110]. In this regard, a range of chiral-SCO hybrids of molecular/polymeric nature has been reported as detailed below.

2.2.1. One-dimensional (1D) chiral SCO systems

A one-dimensional (1D) cyanide bridged chiral coordination $[Co^{III}((R)-pabn)][Fe^{II}(tp)(CN)_3](BF_4)\cdot 1H_2O$ polymer (hereafter CoFe 1H₂O, where both Co^{III} and Fe^{II} centres were in their low spin ground states) featuring three-way (optical, thermal and electrical) switching characteristics is a unique example of multifunctional SCO active material [111]. The CoFe·1H₂O system (Fig. 7a) showed thermal SCO with 23 K hysteresis loop (Fig. 7c and d), and the final phase has been identified as a mix of HS-Co^{II} and LS-Fe^{III}. The occurrence of intra-chain $Fe^{II} \rightarrow Co^{III}$ inter valence electron transfer (IVT) facilitated thermal and light induced charge transfer induced spin transition (CTIST), or electron transfer coupled spin transition (ETCST) in the CoFe₁H₂O validated by temperature-dependent Mössbauer experiments. Cooling the system to 5 K followed by laser irradiation at a wavelength of 808 nm led to a huge jump in the $\chi_m T$ value (300 e.m.u mol⁻¹ K), which was attributed to the formation of a metastable HS state with a T_{ETCST} value of 78 K (Fig. 7c). Irradiation of the system with a green or red laser light failed to induce the HS state formation, confirming the role of IVT in facilitating SCO. The photo-generated HT phase of the CoFe 1H₂O upon alternating current (ac) magnetic susceptibility measurements showed frequency dependence of in and out of phase (χ'_m and χ''_m , respectively) susceptibility values that are indicative of single chain magnet (SCM) behaviour (Fig. 7c inset).

Direct current (dc) conductivity (σ_{dc}) measurements revealed the semiconducting and insulating nature of the HS and LS states, respectively. Interestingly, the resultant T vs. σ_{dc} experiments reasonably reproduced the χ_m T vs. T profile (Fig. 7d) which implies a synergy between spin state and electrical conductivity, thus enabling electrical readout of the spin state. The chiral characteristics of the CoFe-1H₂O system were not exploited to address the spin states. Moreover, a 1D homo chiral complex [Fe(HAT)(NCS)₂]- ∞ -(n MeOH) (n = 1.5, 0; HAT = 1,4,5,8,9,12-hexaazatriphenylene) showed, upon loss of MeOH solvent, two-step SCO, but no further experiments were carried out to relate chirality with SCO [112].

2.2.2. Two-dimensional (2D) chiral SCO systems

One of the earliest attempts to realize a chiral-SCO hybrid resulted in a homo chiral two-dimensional (2D) Fe^{II} - Fe^{III} mixed-valence SCO system. The Fe^{II} - Fe^{III} hybrid has been synthesized employing a two step strategy. In the first step, a chiral $[Fe^{II}H_3L]^{2+}$ (H_3L = tris{[2-{(imidazole-4-yl)methylidene}amino] ethyl}amine) has been synthesized by complexing Fe^{II} ion with an achiral H_3L ligand. The chiral nature of the $[Fe^{II}H_3L]^{2+}$ is attributed to the screw type coordination of the ligand with Fe^{II} . A one-pot self-assembly of $[Fe^{II}H_3L]^{2+}$ with *in situ* generated $[Fe^{III}L]$ (L being the deprotonated H_3L) under aerobic conditions resulted in the chiral mixed valence Fe^{II} - Fe^{III} compound (Fig. 8).

The spontaneously resolved Fe^{II}-Fe^{III} chiral conglomerate structure exhibits interesting features, namely, mixed valence states of iron metal centres (Fe^{II}/Fe^{III}), spin-crossover of the Fe^{II} and Fe^{III} electronic structures, and optical activity. Temperature driven SCO associated with the Fe^{II} and Fe^{III} centres of the chiral supramolecular system enabled the observation of three accessible electronic states, LS Fe^{II}-LSFe^{III}, HS Fe^{II}-LSFe^{III}, and HS Fe^{II}-HSFe^{III}. Although the proposed use of optical activity facilitating nondestructive read-out of electronic states was not experimentally validated, this work sets the base for the future development of memory elements based on chiral SCO systems [110].

2.2.3. Three-dimensional (3D) chiral SCO systems

A first breakthrough in the synthesis of three-dimensional (3D) chiral SCO assemblies was achieved by Ohkoshi and co-workers by obtaining the compound ((+) $Fe_2[Nb(CN)_8]$ (4-bromopyridine)_8:2H_2O). The cyano-bridged SCO active bimetallic assembly (+)-Fe_2[Nb(CN)_8] (4-bromopyridine)_8:2H_2O exhibited



Fig. 7. (a) The asymmetric unit of $[Co^{II}((R)-pabn)][Fe^{III}(tp)(CN)_3](BF_4)\cdot 1H_2O$ (CoFe- $1H_2O$), (b) Square-wave type packing of (CoFe- $1H_2O$), (c) Light-induced magnetic susceptibility data of CoFe- $1H_2O$ Thermal magnetic susceptibility measurements (blue) and the susceptibility after light irradiation (red) as a function of temperature. Inset: Low-temperature frequency dependence of the out-of-phase magnetic response, indicative of a slow magnetic relaxation and (d) Temperature dependences of the d.c. conductivity (red) and magnetic susceptibility (blue) of CoFe- $1H_2O$ in the thermal ETCST region, reproduced with permission from [111].



Fig. 8. a) Synthesis of the mononuclear chiral molecule $[Fe^{II}H_3L]^{2^+}$ in Δ and Λ forms from the achiral H₃L ligand and a Fe^{II} ion, b) synthesis of neutral $[Fe^{III}L]$ by deprotonation of the imidazole molecules of the $[Fe^{II}H_3L]^{2^+}$ in air, and c) formation of a 2D homochiral Fe^{II}-Fe^{III} hexamer, intermolecular imidazole-imidazolate hydrogen bonds led to a 2D sheet like self-organization, reproduced with permission from [110].



Fig. 9. (a) Crystal structure of (+)-Fe₂[Nb(CN)₈](4-bromopyridine)8-2H₂O, viewed along the c-axis, (b) Coordination environments around Fe and Nb. Red, blue, green, yellow and light green balls represent Fe, Nb, Br, C and N, respectively, (c) Temperature dependence of $\chi_m T vs. T$ plot of (+)-Fe₂[Nb(CN)₈](4-bromopyridine)8-2H₂O upon temperature decrease (red) and increase (blue), (d) Temperature dependence of the SH intensity of a single crystal. Red and blue squares represent the SH intensities as the temperature decreases and increases, respectively, and (e and f) SH intensity vs. θ plots of the LT phase at 80 K and the HT phase at 200 K, reproduced with permission from [113].

SCO induced second-harmonic generation (SHG), light induced reversible SCO with long-range magnetic ordering, and photo-reversible switching of the magnetization induced second-harmonic generation (MSHG) effect. The system underwent thermal SCO ($T_{1/2} = 118$ K) with a 12 K hysteresis loop. The SHG intensity of the LS state of the system has been reported to be much higher than that of the corresponding HS state (Fig. 9e and f). A thermal hysteresis of the SHG intensity has also been observed (Fig. 9c) analogous to the thermal hysteresis loop obtained upon thermal SCO [113].

Recently, another example 3D chiral metal–organic framework $[Fe^{II}(Hmptpy)_2]$. EtOH. 0.2DMF, (Hmptpy = 3-methyl-2-(5-(4-

(pyridin-4-yl) phenyl)-4H-1,2,4-triazol-3-yl)-pyridine) demonstrates that SCO has been obtained via crystallization-induced spontaneous resolution into Λ and Δ isomers. The [Fe^{II}(Hmptpy)₂]. EtOH. 0.2DMF complex exhibited a two-step SCO with T_{C1} and T_{C2} at 200 and 357 K, respectively [114].

2.2.4. Molecular chiral SCO complexes

While preparation of 1-3D chiral SCO entities is realized via spontaneous resolution, chiral SCO active mononuclear complexes have been prepared by employing chiral ligands. Variation of the SCO parameters has been observed clearly discriminating between the chiral and racemic complexes [115]. Pilkington and co-workers



Fig. 10. (a) Schematic representation of a 1D-chain like structure of $[Fe(NH_2trz)_3](L-CSA)_2$ complex, the L-CSA anions are situated in the inter-chain channels and (b) CD spectra of a colloidal solution of $[Fe(NH_2trz)_3](L-CSA)_2$ nanoparticles (c = 0.1 mmol/L) recorded at different temperatures (298–327 K) in heating mode. Individual CD bands are detected for each spin state: 344 (negative), 317 (positive), 293 (negative), 247 (positive) and 278 (negative) nm for the LS state and 301 (positive) and 255 (negative) nm for the HS state, reproduced with permission from [60].

synthesized a chiral macrocyclic complex [Fe(dpN₃O₂) (CN)₂] (dp = diphenyl) in (R, R), (S, S) and racemic forms by employing the chiral dpN₃O₂ ligand. The complex structure comprised of 1:1 mixture of 6-coordinate LS and 7-coordinate HS Fe^{II} centres. The (R, R) and (S, S) forms of the complex have undergone an incomplete thermal SCO with a $T_{1/2}$ = 250 K and showed LIESST effect, whereas their racemic counterpart remained mostly LS and LIESST inactive [116].

Following a totally different approach, chiral anions are utilized to create a chiral coordination framework. The 1D complex $[Fe(NH_2trz)_3](L-CSA)_2$ (NH₂trz = 4-amino-1,2,4-triazole, L-CSA = L-camphorsulfonate) (Fig. 10a) is prepared as homochiral coordination NPs taking advantage of the L-CSA anion.

The NPs displayed abrupt switching of chiral properties upon cooperative spin transition, i.e., specific chiro-optical (circular dichroism) properties that are different in their HS and LS states (Fig. 10b) thus allowing the complex system to function as a "chiral memory", also aided by the hysteretic SCO characteristics of the system. A bi-stable, supramolecular chiral composite gel of composition [Fe(NH₂trz)₃](L-CSA)₂–CHCl₃ has also been obtained, indicating the possibility of preparing soft chiral SCO active functional materials [60].

Apart from the electronic applications, the utility of chiral SCO complexes in the detection [117] and resolution [118] of chiral solvent guests has also been demonstrated.

2.2.5. Summary and perspectives

The afore-discussed reports clearly reveal the important role of chiral-SCO materials in developing SCO-based electronic/ spintronic elements. From a synthesis point of view, most of the reports rely on the crystallization-induced resolution of the chiral SCO entities into specific enantiomers. However, it would be highly desirable to design and synthesise chiral SCO complexes of predefined chirality. This can be achieved by using chiral ligands to build optically active SCO complexes as reported by Pilkington and co-workers. More efforts in this direction are necessary to realize the true potential of chiral SCO materials. Furthermore, it would be interesting to build helical 1D SCO materials by employing peptide based ligands with pre-defined handedness; such materials may be useful to realize spin polarized transport in spintronic junctions, e.g. by attaching an SCO active head group on a peptide backbone gating of the chiral induced spin, selectivity (CISS) effect could be observed [119].

3. Hybrid SCO materials

3.1. SCO-Graphene hybrid materials

3.1.1. Introductory remarks

Graphene is a highly researched 2D material due to its attractive electrical and mechanical properties; applications in electronics, spintronics, and nanomechanics have been proposed based on graphene [120,121]. Importantly, graphene could be manipulated by external means; this opens the possibility of functionalizing it especially via non-covalent strategies [122,123] and exploring interfacial proximity effects, i.e., the role of molecule-surface interface in altering SCO characteristics [124-126,65,127,128,67,129]. By combining an advantageous molecular property such as switchable SCO magnetism with alluring electrical characteristics of graphene in the form of a supramolecular molecule-graphene hybrid, novel magneto-electronic effects could be expected. Such hybrid architectures combining carbon-based structures and the class of magnetic molecules called single molecule magnets (SMM) have been reported in the literature with the aim of building molecular spintronic devices [130,131], and remarkable breakthroughs have already been achieved. But not much has been reported in terms of graphene-SCO hybrids yet.

3.1.2. Bulk SCO-graphene/reduced graphene oxide hybrids

As a first step, it is customary to probe the persistence of SCO in the hybrid material at the bulk scale, and to study the interfacial proximity effect of the graphene surface in altering the spin states. Gu and co-workers prepared SCO-graphene nanocomposites by non-covalently anchoring nanoparticles (NPs) of the well-studied 1D SCO coordination polymer [Fe(Htrz)₂(trz)]_n(BF₄)]_n (Htrz = 1H-1,2,4-triazole) on graphene, and observed alteration of the SCO parameters, T_{1/2} and thermal hysteresis width (Fig. 11), due to the graphene surface proximity [132].

Hayami and co-workers reported SCO-reduced graphene oxide (rGO) hybrid materials exhibiting both electrical conductivity and SCO behaviour. Electrostatic interactions between the negatively charged GO and Fe^{III} complex cations of $[Fe(qnal)_2]^+CI^-$ and $[Fe(qsal)_2]^+CI^-$ resulted in the formation of non-conductive $[Fe(qnal)_2]_nGO$ and $[Fe(qsal)_2]_nGO$ hybrids which upon thermal reduction yielded conductive $[Fe(qnal)_2]n$ -rGO and $[Fe(qsal)_2]n$ -rGO was reported to exhibit both thermal and light induced spin crossover



Fig. 11. (a) Schematic representation of non-covalent functionalization of graphene with $[Fe(Htrz)_2(trz)]_n(BF_4)]_n$ NPs and the (b) corresponding $\chi_m T$ vs. T plots showing graphene surface proximity induced alteration of (labels b and c) SCO characteristics of $[Fe(Htrz)_2(trz)]_n(BF_4)]_n$ NPs, reproduced with permission from [132].



Fig. 12. (a) Molecular structure of $[Fe(bpz)_2phen]$, (b) AFM topography image of 0.2 ML of $[Fe(bpz)_2phen]$ on HOPG, (c) Temperature-dependent Fe L_{2,3} X-ray absorption spectra of 0.4 ML of $[Fe(bpz)_2phen]$ on HOPG. Spectra before and after illuminating the sample with green light at T = 6 K are shown in blue and green, respectively and (d) Fraction of HS molecules as a function of temperature during cooling the sample without illumination (black solid symbols) and after saturation of the light-induced HS state during heating the sample (green solid symbols), reproduced with permission from [135].

characteristics; this coexistence of SCO and electrical conductivity of rGO in [Fe(qnal)₂]_n-rGO might be of importance regarding SCO-based electronic applications [133].

3.1.3. SCO on highly oriented pyrolytic graphite (HOPG) surface

Attempts have also been made to study SCO complexes on a highly oriented pyrolytic graphite (HOPG) surface to probe self-assembly and SCO characteristics of absorbed complexes on 2D surfaces. The complex $[Fe^{II}(bpp)_2](BF_4)_2$ self-assembled on HOPG surfaces as 1D chains composed of oligonuclear beads and single molecules [134]. Cooperativity on the surface has been observed for the chains composed of oligonuclear beads. This result is rather interesting given the efforts devoted to probing SCO in reduced dimensions (cf. section 4 of this review), whereas the chains composed of single molecules exhibited random spin states. Current

induced tunnelling spectroscopy (CITS) studies performed at the single molecule level revealed the LS complex to be three times more conductive than the HS complex, in contrast to most of the studies associating high conductance with the HS state, *vide infra*.

In a remarkable study, Bernien and co-workers probed SCO characteristics of vacuum sublimed [Fe(bpz)₂phen] ((bpz = dihydrobis(pyrazolyl)borate) and (phen = 1,10-phenanthroline)) molecules (Fig. 12a) of submonolayer coverage on HOPG surface (Fig. 12b), employing X-ray absorption spectroscopy, and reported the thermal SCO and light-induced excited spin state trapping effect (LIESST) active nature (Fig. 12c and d) of the [Fe(bpz)₂phen] in direct contact with the HOPG surface [135].

These results are promising in the context of building graphene-SCO hybrids at molecular scale, since switching may well translate on graphene surface (cf. 3.1.4) analogues to HOPG in-line with the



Fig. 13. (a) schematic of the device with CVD graphene μ-contact printed with a bistable SCO nanoparticle thin film and (b) Temperature dependence of graphene electrical properties after the deposition of SCO nanoparticles, reproduced with permission from [137].

literature reports detailing *"invariance of self-assembly characteristics"* associated with the same molecule on HOPG and graphene substrates [136].

3.1.4. Graphene-SCO hybrid based device architectures

Two recent studies elucidated the coupling between spin state and electrical conductivity in graphene-SCO hybrid based device architectures (Fig. 13). A graphene substrate has been used to probe SCO in NP thin films of the $[Fe(trz)(H-trz)_2]_n(BF_4)_n$. Electrical transport measurements revealed spin-state dependence of the resistivity of graphene thus making it possible to monitor the SCO (Fig. 13b) [137].

Direct transport measurements of a single-layer graphene sheet functionalized with a silica shell coated SCO $[Fe(trz)(H-trz)_2]_n(BF_4)_n$ NPs showed SCO mediated above RT thermal hysteresis loop in the conductance spectrum, implying synergy between spin state of the NPs and electrical characteristics of graphene [138].

From a theoretical point of view, an electric-field-induced SCO effect in a graphene - 5d transition metal (metal = Os) hybrid has been predicted. The SCO is accompanied by a massive magnetic



Fig. 14. (a) Electronic isomers involved in the VT equilibrium of Co^{III} complex, upon temperature variation, ligand centred single unpaired electron (shown as a red dot) is transferred to the Co^{III} (Is) facilitating the reduction of Co^{III} (Is) to Co^{II} (hs) and (b) Photographs of a 2% wt. PMMA thin film of the complex at different temperatures. The magenta-like colour found at room temperature (middle image) changes to cyan in a reversible manner when heated below Tg (left image) and irreversibly if heated above Tg (right image), reproduced with permission from [141].

anisotropy change due to the planar symmetry of the system, which may be useful for the realization of single-ion magnetic switches operable at RT [139].

3.1.5. Summary and perspectives

Results are abundant in the literature detailing surface-induced suppression and blocking of SCO due to strong molecule-surface interactions especially at the interface [124–126,65,127,128,67,12 9]. Employing graphene as a weekly interacting surface seems to work well in preserving switching characteristics of SCO active molecules, nanostructures and thin films as elucidated via aforediscussed examples and resulted in SCO-based devices. Albeit the remarkable advancements made in this direction, several avenues remain to be explored, e.g. by synthesizing SCO complexes substituted with appropriate anchoring/functional groups, the graphene surface could be non-covalently functionalized in a defined way. Also, by utilizing (i) the templating nature of graphene and (ii) weak intermolecular interactions among the appropriately functionalized SCO molecules, rationally controlled 2D self-assembly and dimension-specific aggregates of SCO molecules could be obtained. This may result in dependance of SCO behaviour on the nature of self-assembly and molecular aggregates on the graphene; however, such experiments have still to be carried out in future.

3.2. SCO-conducting polymer hybrid materials

A problematic aspect of molecule-based electronic materials, including SCO complexes, is their insulating or large band gap semi-conducting nature, which needs to be addressed to render them suitable for device applications. Anchoring of the SCO complexes by conducting polymers featuring superior electronic properties may yield a hybrid material with interesting electronic and magnetic properties and spin state dependant conduction tuning of the host polymer matrix.

A poly pyrrole-[Fe(trz)(H-trz)₂]_n (BF₄)_n NP composite showing SCO-induced modulation of polymer electrical conductivity (σ) from 50–300% and conductance hysteresis was reported being suited for technological applications [140]. A Co^{III} (LS) complex exhibiting valence tautomerism mediated temperature dependant LS \rightarrow HS switching (Fig. 14a) has been used to fabricate a poly (methyl methacrylate) (PMMA)-SCO composite in three different forms, namely, (i) PMMA-SCO films of μ M thickness (Fig. 14), (ii) micro/nano structured particles and (iii) lithographically fabricated nanosized objects on a Si substrate.

A non-volatile memory effect was conferred to the system upon heating the composite above the glass-transition temperature (Tg) of the PMMA, which was attributed to the slow crystallization of the SCO complexes embedded in the PMMA matrix [141].



Fig. 15. (a) The asymmetric unit of the crystal structure of [Co(terpy)₂](TCNQ)₃].CH₃CN. and (b) Temperature dependence of the electrical conductivity of [Co(terpy)₂] (TCNQ)₃]CH₃CN, reproduced with permission from [142].

3.3. Other SCO active hybrids

Apart from this, Dunbar and co-workers reported an inorganic-organic radical bifunctional SCO conducting material, $[Co(terpy)_2]$ (TCNQ)₃]CH₃CN (terpy = 2,2';6,2''-terpyridine, TCNQ = 7,7,8,8- tetracyanoquino-dimethane), exhibiting high electrical conductivity with an anomaly at 190 K (Fig. 15) attributed to structural variations effected by the HS \rightarrow LS transition of Co^{II} [142].

Moreover, Saha-Dasgupta and co-workers reported pressureinduced SCO in perovskite MOFs of formula [CH₃NH₂CH₃][Fe (HCOO)₃] and [NH₃OH][Fe(HCOO)₃]. Both compounds are predicted to undergo SCO with large hysteresis; a prerequisite for the design of an SCO-multiferroic hybrid material [143]. In the quest to realize a hybrid material with long-range magnetic ordering and showing SCO simultaneously, Pardo and co-workers synthesized an MOF-SCO hybrid by post-synthetic incorporation of an SCO complex, [Fe^{III}(sal₂-trien)]NO₃·H₂O (H₂sal₂-trien = N,N'-Dis alicylidenetriethylenetetramine, inside the porous sites of the MOF, Na₄{Mn₄[Cu₂(Me₃mpba)₂]₃}.60H₂O [Me₃mpba⁴⁻ = N,N-2,4,6trimethyl-1,3-phenylenebis(oxamate)]. Unlike the parent SCO complex, the encapsulated SCO complex showed SCO behaviour. A relatively strong ferrimagnetic ordering and increased magnetic ordering temperature for the MOF has been observed due to the encapsulation of the SCO complex [144]. Recently, Weber and co-workers realized SCO-zeolite composites by encapsulating Fe^{II} SCO complexes inside zeolite supercages and reported significant impact of zeolite environment on SCO characteristics of the complexes [145].

4. SCO-based micro and nanoarchitectures

4.1. Introductory remarks

Preparation and characterization of SCO active materials at micro and nanometre regime and studying of their SCO characteristics, to probe whether they can retain their magnetic and cooperative behaviour analogous to their bulk counterpart, is a subject of paramount importance given their application potential in nanoelectronics and spintronics [62,146]. Theoretical considerations predicted strong modulation of SCO behaviour, including shifts of transition temperature, changes in nature of transition (abrupt or continuous), and increase or decrease of hysteretic behaviour upon size reduction, attributed to reduced intermolecular interactions and evolution of the effective crystal field strength around the metal centre with the particle size.

Most experimental descriptions of nanostructured SCO materials have been reported for a series of triazole-based 1D coordination polymers $[Fe(trz)(H-trz)_2]_n$ (BF₄)_n (Htrz = 1H-1,2,4-triazole and trz = triazolato ligand) (T_{1/2} = 340 K and $\Delta T_{1/2} = 40-45$ K), $[Fe(NH_2trz)_3]_n(2X)_n$ (X = counter anion), and $[Fe(R-trz)_3]_n.(2X)_n$ (R = 1,2,4-triazole derivative). Nanostructured 2 and 3-dimensional (2D and 3D) polymeric complexes including Hoffman-type MOFs, $[Fe(pyz)Pt(CN)_4]_n$ (pyz = pyrazine) as well as molecular complexes, for e.g. $[Fe(phen)_2](NCS)_2$, have also been studied to address the important question of how the SCO parameters evolve with size in the low-nanometer regime.

Micro-heterogeneous water-in-oil emulsions, or the *reverse micelle technique*, has so far been a predominantly employed method to prepare SCO NPs (Fig. 16).

Synthetic parameters such as the nature of the surfactant (anionic or non-ionic), the surfactant ratio, time, temperature, and the concentration of the metal ion are reported to influence the morphology, size and magnetic properties of the resultant particles [147]. SCO nanostructures are also prepared in homogeneous media employing surfactants and polymers such as poly (vinvlpvrrolidone) (PVP). In some cases, these two methods are employed in tandem to investigate the hysteresis characteristics of the resultant nanostructures. This is nicely exemplified by Salmon and co-workers, wherein nanoparticles of [Fe(hptrz)₃](OTs)₂ complex (hptrz = 4- heptyl-1,2,4-triazole, OTs = tosylate) have been prepared both in heterogenous microemulsion [148] and homogeneous [149] media using different surfactants and polymeric stabilizers. This led to significant alterations in the SCO properties of the resultant NPs. Recently, spray drying (SD) was used to obtain nanostructures of polymeric and molecular SCO complexes [150]. Often, the NPs are also embedded in a matrix, for e.g. glycerol, to study matrix effects on the SCO characteristics [151].

4.2. SCO nanostructures based on polymeric 1D complexes

In general, the size reduction of triazole-based 1D polymeric SCO complexes resulted in reduced thermal hysteresis width, abrupt to gradual SCO, and shifting of transition temperature to lower values in comparison to the respective bulk.

Interestingly, one of the seminal studies in this field reported comparable SCO characteristics between the spherical NPs of average size 14.6 nm and a bulk sample of $[Fe(trz)(H-trz)_2]_n(BF_4)_n$ com-



Fig. 16. Steps involved in the synthesis of SCO NPs employing reverse micelle technique, adopted with permission from [147].

plex [52]. Another study reported 40 and 29 K hysteresis width for 11.5 nm and 6 nm sized particles of $[Fe(trz)(H-trz)_2]_n (BF_4)_n$ complex, respectively [152]. This observation of a $\Delta T_{1/2}$ even in 6 nm sized NPs of $[Fe(trz)(H-trz)_2]_n(BF_4)_n$ complex is a real breakhrough towards realizing SCO-based applications. Interestingly, the only observation of spherical $[Fe(trz)(H-trz)_2]_n(BF_4)_n$ complex NPs reported in the previous studies [52,152] (Fig. 17a) was refuted in a recent investigation which described, upon employing the same synthetic method, isolation of rod shaped NPs of various sizes (Fig 17c). Moreover, a linear relationship between the size and hysteresis width of the rods has been inferred. A 16 K reduction in hysteresis width has been observed upon removal of surfactant layer (matrix) surrounding the nanorods (Fig 17d), tentatively attributed

to the reduced cooperative interactions mediated by surfactant coating in 3D space. This emphasizes the role of a matrix in tuning the thermal hysteresis width and the need for proper removal of it to discern true structure property relationships in SCO NPs synthesized in micro-heterogenous media [153].

The important role of the surrounding medium in tuning the SCO characteristics of $[Fe(trz)(H-trz)_2]_n$ (BF₄)_n NPs (ca. 3.2 nm) was further exemplified by embedding them in a mesoporous silica monolith matrix. Remarkably, the embedded NPs showed room temperature bi-stability and 65 K wide hysteresis larger than the bulk complex featuring $\Delta T_{1/2}$ = 40–45 K [154].

From a synthesis point of view, a few different synthetic approaches other than the microemulsion and surfactant based



Fig. 17. (a) TEM image and (b) $\chi_m T$ vs T plot of as-prepared [Fe(Htrz)₂(trz)](BF₄) NPs, (c) TEM image and (d) $\chi_m T$ vs T plot of raw (green circles and line) and washed (dark grey squares and line) NPs, note the reduced hysteresis width after removal of surfactant layer by repeated washing, reproduced with permission from [153].



Fig. 18. (a) Environment of the Fe^{II} SCO centre in the $[Fe(3-Fpy)_2M(CN)_4]$ (M^{II} = Ni, Pd, Pt) compounds and (b) $\chi_m T$ vs. T dependences for bulk microcrystalline, $400 \times 400 \times 30$ nm nanocrystals, and 70×30 nm nanoparticles of $[Fe(3-Fpy)_2Ni(CN)_4]$, reproduced with permission from [160].

methods have also been employed to prepare nanostructured materials of $[Fe(trz)(H-trz)_2]_n$ (BF₄)_n. Rod-shaped polymer or surfactant coating free particles have been synthesized in a homogeneous acid media, obtaining the $[Fe(trz)(H-trz)_2]_n$ (BF₄)_n complex in various sizes, and different chemical compositions with differing SCO characteristics. The smaller rods corresponding to the [Fe(trz)(H-trz)₂]_n $(BF_4)_n$ complex showed SCO at high temperature $(T_{1/2} \approx 375 \text{ K})$ with а 45 K thermal hysteresis. On the other hand, longer rods corresponding to the fully protonated $[Fe(Htrz)_3]_n((BF_4)_2)_n: 3H_2O$ derivative showed SCO just below room temperature ($T_{1/2} \approx 272$ K) with a 13 K thermal hysteresis, showing the primordial importance of the chemical nature of the complex rather than the size of the rods in determining SCO characteristics [155]. In a recent work, SCO active nanorod arrays of $[Fe(trz)(H-trz)_2]_n (BF_4)_n$ have been prepared using heterogeneous cation-exchange polymer resins as a matrix [156], and the resultant nanorod arrays showed much less abrupt SCO characteristics with large thermal hysteresis in comparison with the bulk compound.

SCO in NPs of compounds $[Fe(NH_2-trz)_3]_n(2X)_n$ is reported to be size-dependent similar to $[Fe(trz)(H-trz)_2]_n$ (BF₄)_n, but comparing different studies is not that straightforward due to the differing nature of counter anions associated with the $[Fe(NH_2-trz)_3]_n(2X)_n$ nanostructures reported so far. For instance, Létard and co-workers studied the size dependence of SCO in NPs of [Fe $(NH_2-trz)_3]_n(2Br)_n\cdot 3H_2O$, prepared via the reverse micelle technique using non-ionic surfactant Lauropal [157]. Below the critical size of 50 nm, gradual SCO with severe reduction of hysteresis (2 K against the 15 K reported for the bulk complex) was reported, indicating the loss of cooperativity. This is corroborated by an experimental study detailing the disappearance of hysteresis characteristic below a critical size of \sim 45–50 nm of surfactant coated $[Fe(NH_2-trz)_3]_n(2Br)_n\cdot 3H_2O$ $(NH_2-Trz = 4-amino-1,2,4-triazole)$ [158]. A cooperative and weak size-dependent SCO in 4-40 nm sized $[Fe(NH_2-trz)_3]_n(2Tos)_n$ (Tos = *p*-toluene sulfonate) complex NPs has been reported [159]. Monodispersed NPs (200-300 nm) of $[Fe(NH_2-trz)_3]_n(2doe)_n$ (doe = dodecyl sulfonate) prepared from a precipitation method showed first order abrupt SCO with a $\Delta T_{1/2}$ of 13 K. From the above studies, it can be concluded that the preservation of first-order hysteric SCO for the [Fe(NH₂-trz)₃] $n(2X)_n$ series of complexes is possible above a critical particle size, which is still in the few nm region. For compounds $[Fe(R-trz)_3]_n(2X)_n$, the critical temperature of the SCO is shifted downwards as the particle size diminishes, and the hysteresis width vanishes below a critical particle size of around 6 nm.

4.3. SCO nanostructures based on 2 and 3D complexes

The size-dependent evolution of SCO characteristics of prototype 2D and 3D polymer NP of the formula $[Fe(L)_2M(CN)_4]_n$ and [Fe(L)M(CN)₄]_n, respectively, have also been probed. Real and co-workers prepared nanocrystals and nanoparticles of 2D SCO polymers [Fe(3-Fpy)₂M(CN)₄]_n (3-Fpy = 3-Fluoropyridine, M^{II} = Ni, Pd, Pt) (Fig. 18a) by employing a microemulsion technique and a PVP coating. Square-like nanocrystals of [Fe(3-Fpy)₂M(CN)₄]_n with dimensions 400x400x30 nm were obtained from the microemulsion technique undergoing a hysteric first order spin transition in the temperature range of 200–225 K. NPs of average size $200 \times 100, 100 \times 60, \text{ and } 70 \times 30 \text{ nm}$ obtained from the PVP coating method exhibited an incomplete and continuous second-order spin transition around 160 K with drastically reduced hysteresis widths and higher residual HS fraction (Fig. 18b), elucidating the role of synthesis methods in determining SCO characteristics of [Fe(3-Fpy)₂M(CN)₄]_n NPs [160].

Nanostructures of cyanide-bridged 3D SCO coordination polymer $[Fe(pyz)Pt(CN)_4]_n$, (pz = pyrazine) have also shown sizedependent SCO behaviour. Bulk samples of [Fe(pyz)Pt(CN)₄]_n undergo very cooperative spin transition with cooling and heating critical temperatures at 285 and 309 K with ($\Delta T_{1/2}$ = 25 K), respectively. Mallah and co-workers first prepared NPs of [Fe(pyz)Pt $(CN)_4]_n$ in three different sizes using a microemulsion technique, and the particles showed magnetic behaviour different from the bulk complex. A gradual SCO and a downward shift in the transition temperature was observed for 7 and 14 nm particles. The hysteresis width almost vanished for the 7 nm particles, while the 14 nm particles showed $\Delta T_{1/2}$ of 1.4 K. Apart from size, the surrounding matrix is reported to again play an important role in determining SCO characteristics of [Fe(pyz)Pt(CN)₄]_n polymers. A large hysteresis of (size) 15 K was observed when particles were coated with a thin silica shell, whereas softer Calixarene matrix destroyed the cooperativity [161].

Size variation has proven to influence the ultrafast SCO dynamics in $[Fe(pyz)Pt(CN)_4]_n$ nanocrystals. A femtosecond time resolved spectroscopic study on size and temperature dependence of photoinduced SCO transition in nanocrystals (NCs) of [Fe(pyz)Pt $(CN)_4]_n$ showed faster and efficient SCO with a 5–10 ps time constant for the smaller NCs with the size of 123 or 78 nm and 25 nm thickness attributed to the presence of higher residual LS fraction. On the other hand, the larger 375 nm NCs with 45 nm thickness showed relatively weaker SCO in comparison with their small size counterparts and underwent SCO in 20 ps, emphasizing the role of surface energy in altering the thermodynamics of the SCO phase transition [162].

4.4. SCO nanostructures based on [Fe(L)(bipy)]_n polymeric SCO complex

Size-dependant SCO characteristics have also been observed in NPs prepared from other families of coordination polymers. Weber



Fig. 19. (a) Structure of $[Fe^{III}(3-MeO-SalEen)_2](PF_6)$ and (b) Response to femtosecond laser excitation of LS crystals of different sizes. Response of samples, expressed in high spin fraction X_{HS} , in the form of nanocrystals (top), microcrystals (middle) and, a single crystal (bottom). hv, El and Th denote, respectively, the photoinduced, elastic and thermal steps. The green arrow indicates the shift of the elastic step towards shorter times as the size of the system is reduced, reproduced with permission from [167].

and co-workers prepared microcrystals of the SCO coordination polymer $[FeL(bipy)]_n$ (L = [3,3']-[1,2-phenylenebis(iminoethyli dyne)] bis-(2,4-pentanedionato)(2-), bipy = 4,4'-bipyridine) in a poly(4-vinylpyridine) (P4VP) matrix. The synthesis performed by sequentially adding the precursor complex [FeL]_n and bipyridine bridging ligand resulted in particles of varying size ranging from sub-micrometre to micrometre regime, depending on the number of cycles. The smaller sized particles showed incomplete SCO profile because of trapping of differently coordinated Fe^{II} in either LS or HS state. The bigger particles produced showed SCO characteristics like the bulk material $(T_{1/2} = 219 \text{ K} \text{ and } T_{1/2} = 237 \text{ K},$ $\Delta T_{1/2}$ = 17 K), indicating the disappearance of size effects beyond a critical particle size. It is noteworthy that particles of varying size showed abrupt first-order SCO characteristics analogous to the bulk complex irrespective of their size [163]. In continuation of this work, NPs of the $[Fe(L)(bipy)]_n$ have been synthesized using PVPbased block-copolymer micelle as a template. The NPs with a core size of 49 nm showed $\Delta T_{1/2}$ of 8 K. In both cases, the better crystallinity of the bigger sized particles resulted in the observation of SCO characteristics like bulk [164].

4.5. SCO nanostructures based on molecular complexes

Probing of SCO in micro and nanostructured materials made from discrete SCO molecules is a less explored topic compared to studies detailing nanostructures of coordination polymers of 1-3D in nature. In a remarkable study, Boillot and co-workers prepared micro- and nanometer-sized particles of $[Fe^{III}(3-MeO-SalEen)_2]$ (PF₆) (H-3-MeOSalEen being the condensation product of 3-methoxy-substituted salicylaldehyde and *n*-ethylethylenediamine) (Fig. 19a) [165] and reported partial loss of the cooperative character and first order to gradual SCO with decreasing size, whereas the transition temperature and the completeness of the transition remain unaltered upon size reduction [166].

Recently, Collet and co-workers studied dynamics of LS to HS transition in single $[(300 \pm 50) \times (200 \pm 50) \times (15 \pm 5) \,\mu\text{m}^3]$, micro- $[(7.5 \pm 2.1) \times (0.64 \pm 0.15) \times (0.21 \pm 0.03) \,\mu\text{m}^3]$, and nano $[(950 \pm 150) \times (270 \pm 40) \times (35 \pm 7) \,\mu\text{m}^3]$ crystals of $[Fe^{III}(3\text{-MeO-SalEen})_2]$ (PF₆) complex upon femtosecond laser excitation, and

observed a size-dependent three step response (Fig. 19b); note the dispersion of micro- and nanocrystals in polymer matrix [167]. In step one, a fraction of the molecules photoswitched from LS to HS state, with size swelling, in a femtosecond time scale through ultrafast intersystem crossing (ISC). The HS fraction (X_{hs}^{hv}) is more prevalent in the micro- and nanocrystals (Fig. 19b top and middle) due to their smaller nature in comparison with the penetration length of the laser pulse (5 µm at 800 nm), leading to a homogeneous excitation. In step two, the HS fraction further increased (X_{hs}^{EI}) via intermolecular elastic interactions with 20 ns, 1 ns and 300 ps time scales for single, micro-, and nanocrystals respectively. Note the 150 fs time scale associated with the single molecule spin state switching [168].

Thermal effects resulted in the population of HS states (X_{hs}) in the third step. The dynamics of this step are not size dependent. An increased fraction of HS states (X_{hs}Th) has been observed for the single crystals as it due to efficient thermal energy distribution within the crystal lattice. By contrast, the surrounding polymer matrix acted as a heat sink and quenched such thermal energy dissipation within the micro and nanocrystals and limited thermal polulation of the HS states, a matrix effect. Note also a report detailing the reverse process; spin state switching via laser heating of the matrix wherein thermal energy is transferred from the surrounding matrix to the SCO complex dispersed in it [169]. In a nutshell, the spin state switching in nanocrystals is predominantly elastic interaction mediated against the thermally activated switching in large single crystals. Remarkably, such elastic interactions induced switching of more than five molecules per photon, four times faster than the thermal pathway.

Boillot and co-workers reported the evolution of SCO on size reduction of charge neutral prototype SCO complex $Fe(phen)_2(NCS)_2(phen = 1,10-phenanthroline)$, exhibiting a cooperative first-order phase transition induced SCO with $T_{1/2} = 176$ K and ca. 1 K thermal hysteresis [170]. A solvent-assisted precipitation technique was used to prepare crystalline objects of size ranging from 15 to 1400 nm from the diamagnetic [Fe(phen)_3](NCS)_2 ionic precursor. The nano sized crystallites of Fe(phen)_2(NCS)_2 showed disappearance of cooperativity, more gradual SCO, and downshifting of the transition



Fig. 20. (a) SCO characteristics of PEG dispersed particles of Fe(phen)₂(NCS)₂: 20 nm (2d), 29 nm (2c), [650(260)] × 175(80) nm³) (2b) and micro-[1.4(0.4)] × 0.35(0.14) μ m³ (2a) and pure polycrystalline sample of Fe(phen)₂(NCS)₂ and (b) hysteretic χ_m T vs. T plot of the nanocrystal of Fe(phen)₂(NCS)₂, inset shows scanning electronic microscope (SEM) Image of the nanocrystals, reproduced with permission from [170,171].

temperature in contrast to the micrometre sized particles and bulk Fe(phen)₂(NCS)₂ complex exhibiting abrupt first-order SCO. Surfactant-free rhombohedric nanocrystals of Fe(phen)₂(NCS)₂ complexes with dimensions of $203 \times 203 \times 106$ nm to $142 \times 142 \times 74$ nm have been synthesized employing the reverse micelle technique. Interestingly, the nanocrystals underwent an abrupt and more cooperative spin transition with an 8K thermal hysteresis (Fig. 20b) when compared with the bulk Fe (phen)₂(NCS)₂ possessing, for both polymorphs, ca. 1 K thermal hysteresis. In this case, the better quality of the crystallites was responsible for the increased cooperativity, a point further proven by the reduced thermal hysteresis exhibited by the defective crystallites. The particles were dispersed in matrices such as polyethylene glycol, Nujol, glycerol, and triton to infer the effect of polymeric coating on SCO characteristics. The polymer coating of nanocrystallites effected more continuous SCO and a reduced thermal hysteresis width (Fig. 20a): attributed to chemical pressure asserted by the organic polymers on the Fe^{II} centres [171].

Strong modulation of SCO characteristics has been observed upon dispersing microparticles of [Fe(phen)₂(NCS)₂] in glassy or semi-crystalline matrices [172]. Enachescu and co-workers also studied the influence of the embedding matrix on the relaxation of Fe(phen)₂(NCS)₂ microparticles and found strong change of the HS to LS relaxation curve when the compound was dispersed in a glycerol matrix. This is attributed to an initial positive local pressure acting on the edge spin-crossover molecules from the matrix side, inducing faster start of the relaxation [173].

Boillot and co-workers studied SCO characteristics of nano- and microparticles of its analogous Fe(Me₂-bpy)₂(NCSe)₂ complex prepared from its diamagnetic precursor [Fe(Me₂-bpy)₃] (NCSe)₂·S $(S = H_2O \text{ or } MeOH)$ by employing either thermolysis or precipitation in an anti-solvent, leading to a polycrystalline or particulate powder of Fe(Me₂-bpy)₂(NCSe)₂ with sizes 56, 460 and 1200 nm. $Fe(Me_2-bpy)_2(NCSe)_2$ showed The bulk incomplete SCO $(\chi_m T = 2.57 \text{ cm}^3 \text{ mol}^{-1} \text{ K} \text{ at } 371 \text{ K})$ with ca. 5% residual HS fraction below 250 K. Interestingly, the nano sized objects of Fe(Me₂bpy)₂(NCSe)₂ showed no size dependence to SCO characteristics and their magnetic properties are like the bulk Fe(Me2bpy)₂(NCSe)₂ partially attributed to the molecular nature of particles [174]. Morgan and co-workers reported a rare example of 1D nanostructures prepared from an SCO active Fe^{III} complex [Fe^{III}L] $(BF_4)_{0.8}Br_{0.2}$. The nanowires have been prepared employing an alumina-based template method. The 1D structures showed incomplete SCO characteristics with more residual HS fraction in comparison with their bulk counterpart [175].

Sun and co-workers prepared SCO vesicular nanospheres based on series charge neutral SCO complexes, $[Fe(H_2Bpz_2)_2(dialkyl-bipy)]^0$ $(H_2Bpz_2 = dihydrobis(1-pyrazolyl)$ borate, dialkyl-bipy = N4, N4'-dialkyl-(2,2'- bipyridine)-4,4'-dicarboxamide, alkyl = propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and cetyl) (Fig. 21a), with single-external diameters of approximately 100 nm using a binary CHCl₃-H₂O solvent mixture. The spin transition temperatures for the bulk materials are found at around 160 K (Fig. 21b), whereas the vesicular nanospheres in the solid state showed above RT SCO (Fig. 21c) [176].

4.6. SCO nanostructures via grafting of SCO active Fe^{ll} complexes on pre-formed NPs

Following a totally different approach, hybrid SCO active nanometric switchable units have been prepared by anchoring SCO complexes on pre-formed NPs such as SiO₂ and gold (Au). This strategy involves the rational design of SCO complexes featuring anchoring groups to connect with the nanostructures via surface functionalization. Fleury and co-workers reported a hybrid SCO active nanostructure made from a SiO₂ core and a Fe^{II} coordination complex prepared via a three step synthetic protocol. A SiO₂ core functionalized with a bis(1-methylimidazolyl)-type ligand was coordinated with the octahedral Fe^{II} complex, leading to the precipitation of the SCO active hybrids. The particles showed SCO characteristics reminiscent of similar molecular complexes [177]. Van der Molen and co-workers prepared Au NP arrays incorporating spin crossover molecules by grafting an SCO active molecular complex (Fig. 22a) featuring a thioacetate anchoring group onto Au NPs, and studied the magnetic and electrical properties of the resultant hybrid. Raman spectroscopy and magnetization measurements provided evidence for SCO in these arrays [178]. Electrical measurements of these arrays (Fig. 22b) showed a minimum in the resistance vs. temperature curves (Fig. 22c), a result absent in analogous networks containing the non-switching ligand molecules. A percolation mechanism assuming a higher resistive HS state, rationalized by transport calculations, has been evoked to explain the resistance minimum.

4.7. Summary and perspectives

The efforts so far devoted towards the understanding of structure-magnetic properties relating to nanosized SCO entities have demonstrated the preservation of SCO at the nanometre scale with significant alterations in transition temperatures, the size of



Fig. 21. (a) Illustration of the self-assembly of the Fe^{II} complexes into vesicular nanospheres. Temperature dependence of χ_m T vs. T plots of (b) the bulk materials (1–9) in the temperature range of 305–100 K, and (c) the lyophilized vesicular nano-spheres (NS-4–NS-9) in the temperature range of 400–200 K, under an applied magnetic field of 2000 Oe, reproduced with permission from [176].



Fig. 22. (a) Schematic representation of SCO molecule, (b) Schematic representation of SCO molecule-Au nanoparticle junction, (c) R vs T plot of SCO molecule-Au nanoparticle junction, (d) R vs T plot calculated by percolation model, and (e) calculated R vs T curves showing the relation between resistance minimum and percentage of spin transition, reproduced with permission from [178].



Fig. 23. (a) Crystal structure of $Fe_2[Nb(CN)_8](4$ -pyridinealdoxime)_8·2H₂O, (b) magnetic hysteresis curves at 2 K. Note the appearance of a magnetic hysteresis loop with a coercive field of 240 Oe after irradiation with 473 nm light (red curve) and (c) Schematic of ferrimagnetic ordering between Nb^{IV} (S = 1/2) and Fe^{II} HS (S = 2) due to light-induced spin-crossover, reproduced with permission from [180].

the hysteresis loop, the nature of SCO (abrupt/continuous), and the degree of LS or HS fraction. The surrounding media significantly alter the magnetic properties of nano sized SCO materials by the so-called matrix effect. Despite extensive work, establishing a clear correlation between SCO characteristics and particle size has proved to be difficult, especially for 1D polymeric complexes, and comparison of results obtained from various studies often leads to confusing trends. On the other hand, a clear picture emerged for 2D and 3D polymeric materials. Upon miniaturization, the transition became more gradual, with a clear reduction in hysteresis width compared to their bulk counterparts. The surface termination of NPs of the polymeric SCO materials is not well defined an incomplete coordination shell around the metal ion or solvent coordination of the vacant sites are often attributed to the presence of remnant HS or LS fraction, leading to incomplete SCO. This problem could be avoided by building SCO NPs composed of molecular complexes. A problematic aspect of this approach would be found in the case of ionic complexes, where the relative location of counterions near the surface may differ from that which is observed in the core of the particle. This may render molecules on surfaces with different SCO properties compared to the inner molecules. By employing charge-neutral complexes in a bottom-up synthetic strategy, the counter anion problem could be alleviated. Understandably, a few other important aspects such as mode of preparation, the role of solvent molecules, and the phase difference between the bulk and NPs may also play a significant role in determining SCO characteristics molecule based SCO nanostructures.

5. SCO and photomagnetism

The discovery of photoinduced magnetization in a Prussian blue analogue, $K_{0.2}Co_{1.4}$ [Fe(CN)₆]·6.9H₂O, led to a new class of photomagnets [179]. In a similar approach, SCO and charge-transfer



Fig. 24. Two states of a four-dot QCA cell, reproduced with permission from [190].

(CT) based photomagnets have been reported. SCOphotomagnetism arises from the magnetic ordering of paramagnetic HS states populated by light-induced excited spin state trapping effect (LIESST) at low temperatures; an intra-atomic phenomenon involving LS and HS states. By contrast, CT-induced photomagnetism involves metal-to-metal charge transfer (MMCT) between two metal centres, and bi-stability originates from two different states of the metal-metal bond.

Ohkoshi and co-workers reported an elegant example of an LIFSST induced SCO magnet, $Fe_2[Nb(CN)_8](4$ pyridinealdoxime)₈·2H₂O (Fig. 23a) [180]. The Fe–Nb 3D cyanide bridged metal-organic framework (MOF) showed gradual thermal SCO from $HS \rightarrow LS$ upon cooling and remained paramagnetic at low temperatures, due to the presence of Nb^{IV} with S = 1/2. Light irradiation of this system at 473 nm led to the population of HS Fe^{II} states with (S = 2). These two centres are antiferromagnetically coupled via a super exchange pathway by the non-magnetic cyanide bridging ligand. This led to spontaneous magnetization and light-induced long-range ferrimagnetic ordering (T_c) at 20 K with a coercive field (H_c) of 240 Oe (Fig. 23b).

A similar cyano-bridged Fe-Nb bimetal assembly, Fe₂[Nb(CN)₈]-(4-methylpyridine)₈·2H₂O, exhibited two-step SCO and photomag-



Fig. 25. Molecular structure and $\chi_m T$ vs. T plot of the [MeL₄Fe^{II}₄](BF₄)₄ complex indicating a spin transition from 4 HS state to 2 HS-2 LS state suitable for QCA application, reproduced with permission from [190].



Fig. 26. (a) Structure of the bridging ligand, 2-phenyl-4,5-bis[6-(3,5-dimethyl-1H-pyrazol-1-yl)pyrid-2-yl]-1H-imidazole, utilized to build the grid complexes, (b) and (c) crystal structures of $[Fe_4^{II}]$ and mixed valent $[Fe_2^{II}Fe_2^{II}]$ grids (key: green = HS-Fe^{II}, sky-blue = LS-Fe^{II} and orange = LS-Fe^{III}) and (d) Thermal and light-induced magnetic susceptibility $[Fe_4^{II}]$ (empty markers) and $[Fe_2^{II}Fe_2^{II}]$ (filled markers). The $[Fe_2^{II}Fe_2^{II}]$ grid is thermally inactive but LIEEST active (filled green and orange curves), reproduced with permission from [192].

netic behaviour ($T_c = 14$ K and $H_c = 2300$ Oe) upon irradiation with 532 nm light at 2 K. Irradiation with 785 nm light reduced magnetization due to the reverse LIESST effect, i.e. population of LS states from HS state, implying excitation wavelength dependence of photomagnetism [181]. The presence of residual HS sites at low temperatures led to the observation of SMM behaviour of [Fe(mtz)₆] (CF₃SO₃)₂(mtz = 1-methyltetrazole) complex. The Fe^{II} HS sites possessing significant magnetic anisotropy showed field-induced slow relaxation of their magnetization, and the SMM properties could be reversibly switched OFF upon visible light irradiation [182].

A magnetic response to a light stimulus has been enforced in a non-photomagnetic cyano-bridged coordination polymer { $[Fe^{II}(-pyrazole)_4]_2[Nb^{IV}(CN)_8].4H_2O$ }n (FeNb), which showed unique

light induced photomagnetic behaviour upon application of high external pressure [183].

6. Recent advances in SCO active grid complexes

Supramolecular co-ordination frameworks comprising multiple bistable units capable of existing in more than two states in response to the external stimuli, heat or light, are proposed to be suitable candidates to build nanoscale multiresponsive switching elements [111,184]. Grid-type metal-organic complexes [185– 187] are an elegant example of multiple bistable units in view of their cooperative multi-step thermal SCO, wherein geometric and electronic changes associated with an individual SCO event are propagated to the neighbouring metal atoms, and their electronic states are altered synergistically [188,189].

This tunable and cooperative nature of electronic states of grid complexes is utilized to build molecular logic devices such as quantum cellular automata (QCA), an integral part of the quantum information processing (QIP) scheme [189]. In QCA, binary information (0,1) is encoded in cells that can interconvert between two different stable, degenerate but distinguishable states [190]. To realize SCO-based QCA, a tetra-metallic SCO grid featuring dimixed (2LS-2HS) spin states arranged trans to each other at the opposite corners of the cell with an ability to switch between spin-states is required (Fig. 24).

Meyer and co-workers reported one such thermally active pyrazolate-bridged Fe₄ [2 × 2] grid complex [$^{Me}L_4Fe_4^{II}$](BF₄)₄-·2MeCN (^{Me}L = 4-methyl-3,5-bis{6-(2,2'-bipyridyl)}pyrazole), featuring two HS and two LS ferrous ions located at the diagonally opposite corners of the grid (Fig. 25), a configuration required for the building of QCA devices based on molecular systems [190].

A similar Fe₄ grid complex constructed using a 4-bromo-3,5-bis $\{6-(2,2'-bipyridyl)\}$ pyrazole (^{Br}LH) ligand suitable to be implemented in a QCA architecture has also been reported recently. The [^{Br}L₄Fe^{II}₄](X)₄ complex showed spin-state switching between 4HS to 2HS-2LS states analogues to its predecessor, [^{Me}L₄Fe^{II}₄](BF₄)₄ [191].

Photo-active grid complexes with facile addressing of multiple discrete spin states are better suited for applications due to the facile optical addressing of spin states in comparison with the thermal SCO active grids [192]. Oshio and co-workers made the first breakthrough in this direction, by reporting a mixed valence tetranuclear grid-like complex ([Fe^{III}₂Fe^{II}₂]) (Fig. 26c), and elucidated the accessing of multiple electronic sites at identical conditions via site selective photo-excitation.

The $[Fe_2^{II}Fe_2^{II}]$ grid, in contrast to the monovalent $[Fe_4^{II}]$ grid (Fig 25b), is thermally inactive. Irradiation of $[Fe_2^{II}Fe_2^{II}]$ at low temperatures with green (Fe^{II}) and red (Fe^{III}) lasers induced sitespecific LIESST, rendering the molecule into existence in three discrete phases (Fig. 26c); this may enable the development of light-programmable nanoscale QCA devices and molecular memories with high data storage density [192].

A few other grid type systems featuring interesting structural and magnetic properties have appeared recently [193–195]. Ruben and co-workers reported the synthesis of isomeric tetra and trimeric grid complexes by the coordination of Fe^{II} ions with a tautomeric homo-ditopic ligand L. The structures of the two dominant tetrameric [Fe^{II}₄(L)₄]⁸⁺ complexes showed contrasting magnetic properties, Fe^{II} SCO vs. a blocked Fe^{II} HS state, demonstrating tautomeric-structure dependant magnetic properties [196].

7. Solvent sensors

Guest entities, especially gas or solvent molecules either cocrystallized or trapped inside porous networks of SCO materials, exert significant alterations in SCO properties [86,197–207], thus enabling the realization of SCO-based gas and solvent sensing devices. A few recent reports detailing this utility are described as follows.

Bousseksou and co-workers reported a reversible and RT operable sensor device based on micro-patterned gratings of a [Fe (bpac)]_n[Pt(CN)₄]_n SCO molecular organic framework. The SCO characteristics of the complex were altered in the presence of vapours of various organic compounds. This led to the variation of the refractive index which was *in situ* monitored by optical diffraction on a grating of $[Fe(bpac)]_n[Pt(CN)_4]_n$. A thermal annealing procedure was used to desorb the analyte, leading to selective



Fig. 27. (a) Crystal structure of $[Fe^{II}(tolpzph)_2(NCS)_2]$ -THF at 100 K, (b) magnetic moment of $[Fe^{II}(tolpzph)_2(NCS)_2]$. n(THF) (where $0 \le n \le 1$) as a function of temperature for 300 \rightarrow 50 K and then repeated cycles of 50 \rightarrow 400 K showing the solvent dependence of SCO, (c) the $T_{1/2}$ as monitored over ten consecutive cycles of interconversions $Fe^{II}(tolpzph)_2(NCS)_2$ -THF (green points) \rightarrow $Fe^{II}(tolpzph)_2(NCS)_2$ (purple points) and (d) plot of mole fraction of THF, n(THF) as mol(THF)/mol(Fe), as a function of the $T_{1/2}$ [210].

reuse of the sensor [208]. Cavallini and co-workers reported multimodal sensing of methanol and ethanol solvents by a solvatochromic charge neutral Fe^{II} SCO complex, $[Fe(L)_2]^0$ (LH: (2-(pyra zol-1-yl)-6-(1H-tetrazol-5-yl) pyridine)) [209]. The sensing capability of the complex was attributed to the inclusion of methanol or ethanol molecules into the crystalline structure, which altered the transition temperature, colour, birefringence and vibrational modes. By integrating the complex with a micrometric TAG sensor sensitive to the colour and birefringence, and separately exposing with ethanol and methanol, the solvents can be sensed by analysing the temperature dependence of the colour component of the CCD image of the SCO crystallite on the TAG sensor. The decrease in CCD counts and break points associated with the green component of the image at 270 and 256 K were utilized to discern methanol and ethanol solvent vapours respectively.

In a nice study, Miller and Brooker reported a multi-use, quantitative tetrahydrofuran (THF) solvent-sensing ability of the complex $Fe^{II}(tolpzph)_2(NCS)_2$. THF, (tolpzph = 4-p-tolyl-3-(phenyl)-5-(2-pyrazinyl)-1,2,4-triazole) (Fig. 27a), which can be reversibly desolvated to give $Fe^{II}(tolpzph)_2(NCS)_2$. Both the solvated and desolvated complexes are reported to be SCO-active with a 43 K variation of $T_{1/2}$ value (Fig. 27b). This characteristic, along with the help of thermogravimetric analysis (TGA), was utilized to quantitatively sense the even fractional amount of THF present in the lattice. The SCO characteristic of the complex is also reported to be sensitive to chloroform (CHCl₃) solvent [210].

8. Recent advances in electrical and spin transport characteristics of SCO-based materials

8.1. Introductory remarks

SCO complexes are actively pursued for the development of electronic and spintronic devices due to their attractive magnetic,

optical and electronic properties. Although translating and preserving switching behaviour of an SCO complex at single molecular level or in thin film architecture is challenging, mainly due to the cooperative nature of the SCO phenomenon in bulk or 3D solid state mediated by intermolecular interactions, relentless efforts have been made to probe the spin state dependence of electrical conductivity modulation of SCO materials, by integrating them in device architectures in the form of bulk powders [211,212] and composite materials [140,213,214], thin films [105,215-217], nanoparticles [184,218-220], and single molecules [221,222]. From a fabrication point of view, many techniques including Langmuir-Blodgett deposition, dip coating, drop casting and vacuum sublimation are utilized. Sublimation of an SCO complex on a suitable surface is highly desirable due to the pure nature of the resultant films, ranging from sub monolayer to multilayer coverage. Charge-neutral SCO complexes are suitable for this purpose as the absence of counter anions will greatly reduce scattering of charge carriers by the charged molecules, which is a hindrance to electron transfer across molecular junctions. In the following sections, recent breakthroughs achieved in the realm of charge and spin transport characteristics of device architectures featuring SCO entities are described.

8.2. Transport characteristics of single SCO molecules

8.2.1. Theoretical predictions

To realize molecular electronic/spintronic devices based on an SCO molecule, probing of spin state dependent transport characteristics of a single SCO molecule is predicted [85,223]. Aravena and Ruiz performed coherent transport calculations for a mononuclear *trans*-bis(3-(2-pyridyl)(1,2,3)triazolo(1,5)pyridine)bis(iso thiocyanato)-Fe^{II} complex ([Fe(tzpy)₂(NCS)₂]) (Fig. 28a) [224], by placing it between gold electrodes (Fig. 28b). The HS complex was predicted to be more conductive than the LS complex (Fig. 28c).



Fig. 28. (a) Structure of $[Fe(tzpy)_2(NCS)_2]$, (b) the device used in the calculations with the gold electrodes and the $[Fe(tzpy)_2(NCS)_2]$ and (c) I – V characteristics for the high-spin (red) and low-spin (blue) states. The inset shows the α (green) and β (orange) contributions to the current in the high-spin system, reproduced with permission from [224] and [225].



Fig. 29. (a) Conductance of the paramagnetic $[Fe(tzpy)_2(NCS)_2]$ under ambient conditions, (b) temperature-dependent conductance histograms for the paramagnetic $[Fe(tzpy)_2(NCS)_2]$ compound in vacuum under β -down and (c) α -up Ni magnetic polarizations and (d) schematic representation of the single-molecule junctions studied under two opposite Ni magnetic polarizations (labeled α and β). The paramagnetic $[Fe(tzpy)_2(NCS)_2]$ complex shows a high conductance switching which depends on the Ni tip spin polarizations (see arrows), while the transport in the diamagnetic $[FeL^A(NCS)_2]$ complex remains invariable, reproduced with permission from [229].

The closeness of the β -spin down electrons residing in the t_{2g} orbital lying energetically close to Fermi level (E_f) affected the HS complex to act as a spin filter, wherein β electrons were transmitted more efficiently in comparison with α -spin-up electrons [225]. Unprecedented ways to induce spin state switching have also been reported, for e.g. Sanvito and co-workers proposed the possibility of using the electrostatic field as a stimulus to induce SCO in molecular junctions comprising of polar molecules [226].

8.2.2. Three terminal devices

From the experimental front, efforts to prove the spin switching based on the afore-predicted mechanism gained much attention. Electrical triggering of SCO has been demonstrated for a [Mn (terpy-O-(CH₂)₆-SAC)₂)]²⁺ complex in a single-molecule three-terminal device. Reduction of the ligand upon variation of gate voltage induced HS to LS switching as a result of increased crystal field felt by the central metal ion; the resultant LS state was less conductive [227]. Through combined density functional theory and first principles calculations, Ruben and co-workers demonstrated the possibility of electron induced spin state triggering in a [Fe^{II}(bpp)₂]²⁺ (bpp = 2, 6-bis(pyrazol-1-yl) pyridine) complex and experimentally validated its viability by performing single molecule conductance studies in a three-terminal device [221].

8.2.3. Electrical and spin transport characteristics of SCO complexes in scanning tunnelling microscopy (STM) junctions

The feasibility of effecting spin state switching via electrical fields has also been elaborated in scanning tunnelling microscopy (STM) junctions. Gopakumar and co-workers reported switching in junctions comprising of STM-tip/vacuum sublimed two-layer thin film of [Fe(bpz)2phen] (phen = 1,10-phenanthroline, bpz = di hydrobis(pyrazolyl)borate)/Au (111). Upon application of a

positive voltage around 1.8 V, the LS to HS switching was observed for molecules located in the second layer, whereas HS states produced for molecules in the first layer were effectively quenched by the substrate [228]. In a similar study, Miyamachi and coworkers reported the memristive behaviour of a single [Fe (phen)₂(NCS)₂] molecule deposited on a CuN surface. The chemisorption of Fe-phen on Cu (100) by thiocyanate groups caused quenching of the SCO, while adding an insulating CuN intermediate layer restored switching. This emphasises the role of subtle interfacial effects in controlling SCO characteristics at molecular level; [Fe(phen)₂(NCS)₂] in HS state is reported to be more conductive than its LS counterpart [222].

While the use of non-magnetic leads is prevalent in the electrical characterization of SCO complexes, Díez-Pérez and co-workers used a magnetically polarized Nickel (Ni) STM tip and demonstrated ambient temperature (298 K) spin sate dependent conduction modulation in a single molecule junction comprising of an Au/ SCO molecule $[Fe(tzpy)_2(NCS)_2]/magnetically polarized (\alpha or \beta) Ni$ electrode (Fig. 29) [229]. The HS paramagnetic [Fe(tzpy)₂(NCS)₂] complex (Fig. 29a) showed a 100-fold increase in conductance switching when contacted by the β-spin-polarized Ni tip compared to the α -spin-polarized Ni tip. The transport in the diamagnetic SCO inactive [FeL^A(NCS)₂] complex (note the use of two different complexes) remained invariable irrespective of the Ni tip polarization. Mechanistically, spin orbit coupling mediated spin filtering at the Au-S interface and its enhancement by the chemisorbed HS complex resulted in the production of β polarized electrons at the interface. This favourably coupled with the β -spin down electron of the complex in HS state, leading to the spin polarization at the metal-magnetic molecule spinterface. Upon contacting this spinterface with the appropriately polarized (β) Ni tip, a conductance switching is observed which is absent for an α -polarized Ni



Fig. 30. (a) Structure of polar heteroleptic $[Fe(tpy)_2]^{2+}(tpy = terpyridine)$ complex, Schematic of the voltage-triggered spin crossover switch in a single molecule junction, (b) LS Fe^{II} complex bridging the two electrodes at a small applied voltage and (c) HS Fe^{II} complex with distorted coordination sphere due to the alignment of the push-pull system in the applied electric field, reproduced with permission from [230].



Fig. 31. (a) Structure of a homoleptic mechanically triggerable $[Fe^{II}(tpy)_2]^{2^+}$ complex, (b) Schematic of the mechanical stretching (Δx) used to induced SCO in a molecular junction comprising Fe^{II} complex, (c) Three examples of conductance vs. electrode displacement measured in the presence of the Fe^{II} and Ru^{II} complexes and (d) Total transmission of the LS and HS geometries as shown in (b) in a metal–molecule–metal configuration calculated with self-consistent DFT-NEGF. The shaded areas correspond to spin polarized transmission for up (orange) or down (green) spin electrons, reproduced with permission from [231].

tip. Furthermore, experiments performed on the Cu surface showed no such spin polarized transport, emphasizing the role of the Au-S bond in producing polarized electrons mediated by spin orbit coupling.

Variable temperature conductance measurements of nanojunctions contacting the $[Fe(tzpy)_2(NCS)_2]$ molecule showed a peak in the conductance histogram at 298 K when the Ni tip is β -polarized. No such peak was observed for the junctions comprising a α polarized tip, indicating the spin polarized nature of conductance involving β electrons in line with the theoretical predictions [225].

8.2.4. Spin state dependent conductivity modulation in mechanically controlled break junction (MCBJ)

In a recent work, Mayor and co-workers demonstrated electric field induced switching of polar hetero-leptic $[Fe(tpy)_2]^{2+}$ (tpy = terpyridine) complex (Fig. 30a) embedded in a mechanically controlled break junction (MCBJ) set-up. One half of the complex featuring tpy ligand tailored with anchoring groups at 4 and 4' positions bridged the gap between the Au leads, while another di-polar half of the complex remained free to rotate (Fig. 30b and c). Upon application of the electric field, the free, di-polar part of the complex responded by distorting the complex geometry from the ideal O_h to a low symmetry configuration, thus enabling switching from LS to HS state, which caused conduction variation of the single molecule SCO junction [230].

Moreover, van der Zant and co-workers reported mechanical stretching induced SCO, leading to conductance switching at zero bias conditions for a homoleptic $[Fe^{II}(tpy)_2]^{2+}$ complex (Fig. 31a). The LS complex was chemically coupled between gold leads in an MCBJ set-up and mechanically pulled apart, leading to the stretching of the molecule facilitating SCO from LS \rightarrow HS (Fig. 31b).



Fig. 32. (a) Schematic representation of the ITO/SCO/AI junction, (b) *I*–V curves registered at room temperature, 100 and 5 K at a rate of 100 mV s⁻¹, (c) Visible light irradiation effect on the current flowing in the junction at 5 K through two successive ON/OFF cycles, followed by heating from 5 to 100 K in the dark. Dashed lines indicate current intensities in the HS and LS states and (d) Visible light irradiation effect on the current flowing in the junction at 100 K through two successive ON/OFF cycles. The applied bias in (b–d) was 1 V, reproduced with permission from [232].

The junctions featuring stretched configurations, i.e. HS complex, showed more conductance than their LS counterparts. This is attributed to the presence of higher density of states close to the E_f for the HS complex [231].

In an earlier study probing spin state dependence of electrical conductivity in single molecule junctions, Grohmann and coworkers reported, via current-imaging tunnelling spectroscopy (CITS), higher conducting nature of LS state for a $[Fe^{II}(bpp)_2]$ (BF₄)₂ complex cast on HOPG surface [134]. This result contrasts with most of the discussed studies elaborating high conductance of the HS state. This anomaly could be attributed to the differing nature of surfaces on which SCO molecules are deposited, Au or Cu vs. HOPG, leading to the varied alignment of molecular energy levels on the energy levels of metal or HOPG electrodes. In this context, a systematic study involving electrical characterization of an SCO complex on the varying surface is necessary to understand the underlying conductance switching completely.

Another interesting aspect is metal complexes studied in the STM junctions. Three terminal device architectures are SCO active in bulk scale, whereas the $[Fe(tpy)_2]^{2+}$ complexes studied by Mayor and co-workers and van der Zant and co-workers in MCBJ are LS at ambient conditions, and are not known to undergo thermal SCO due to the strong crystal field associated with the tpy ligands. This is quite interesting given the complexities associated with SCO phenomenon upon moving from bulk to molecular scale and interfacial effects quenching SCO. In this context, the observation of electric field and mechanical stretching induced switching in SCO inactive $[Fe(tpy)_2]^{2+}$ complexes is a new beginning in SCO research, and opens the door for the realization of switching elements without worrying about thermal SCO governed by many parameters, which is difficult even for a seasoned researcher in this field.

8.3. Electrical transport characteristics of thin film SCO junctions

Probing spin-state dependence of electrical characteristics of SCO active thin films is another important facet, due to the propen-

sity to build large area devices. Beaurepaire and co-workers investigated the current-voltage (I-V) characteristics of thin film devices based on $[Fe(phen)_2(NCS)_2]$ complex, and paved the way for the realization of bistable multifunctional SCO materials [216]. Bousseksou and co-workers reported non-volatile read-only memory effect based on the thin films of $[Fe(HB(pz)_3)_2]^0$ (pz = pyrazolyl) complex [215]. In a recent study, Bousseksou and co-workers fabricated optoelectronic devices with thin films of the [Fe(H₂B $(pz)_2(phen)$ ⁰ (Fig. 12a) SCO complex $(H_2B(pz)_2 = dihydrobis)$ (pyrazolyl)borate and phen = 1,10-phenanthroline) sandwiched between indium tin oxide (ITO) and Aluminium (Al) electrodes (Fig. 32a). Variable temperature current-voltage (I-V) characteristics of the devices with 10 nm thick SCO film displayed activationless tunnelling conductivity (Fig. 32b), whereas the thicker, 30 and 100 nm, junctions exhibited diode-like rectifying characteristics and bulk-limited thermally activated currents. Upon irradiation of the 10 nm thick device with white light at 5 K, a 7% reduction of current intensity was observed for the first irradiation, attributed to the population of HS state from LS state at 5 K via the LIESST mechanism. Successive irradiations resulted in no change in the current intensity (cf. Fig. 32c) due to the persistence of metastable HS state at 5 K. Heating the device to 100 K restored the high conductance state due to the population of LS state. Similar experiments performed by irradiating the junctions at 100 K resulted in a negligible change of the conductance (Fig. 32d). Note the more conducting nature of LS state of the film at this temperature, proving the SCO mediated (LS \rightarrow HS) conductance modulation at 5 K [232].

The results obtained for the thin film SCO devices are promising for the use of spin crossover compounds in nanoelectronic and spintronic devices. To further exploit in this direction, synthesis of sublimable SCO complexes with self-assembly propensity and molecular orbital (MO) engineering of SCO complexes for the interfacial alignment with the different substrate materials is warranted.

9. Conclusions

This review provided a collective overview of recent emerging trends in SCO research. The exciting results detailed in this review clearly demonstrate the utility of SCO materials in building optoelectronic, molecular electronic, and spintronic devices. Multifunctional SCO materials combining luminescence and chirality are investigated with the aim of building optoelectronic devices. While reports in the direction of SCO-luminescent hybrid materials are abundant, in most cases a proper understanding of the coupling between spin state-luminescence is not realized, and this needs to be systematically investigated in the future. In another direction, SCO molecules and nanostructures are coupled with graphene and conducting polymers to enhance the electrical properties of the otherwise insulating SCO complexes, and a synergic coupling between spin-state and electrical properties has been observed in the hybrids. Size reduction of SCO materials, especially polymeric complexes of 1-3D in nature, resulted in significant alterations of SCO characteristics, with some of the structures retaining SCO even at scales of a few nm. However, studies of nanostructured molecular complexes are relatively scarce, and several avenues remain to be explored For example, a systematic study of size reduction and the effect of the surrounding medium for an SCO active charge neutral complex would be an appropriate starting point; the absence of counteranion is a great advantage in this case. Probing of charge and electrical transport characteristics of SCO complexes ranging from bulk to single molecule level resulted in the observation of SCO-based switching and memory elements. The nature of the surface, interface and relative orientation of the molecules in mono and multilayer films are reported to be the important parameters in determining the switching capacity of SCO complexes. On the other hand, novel triggers, electric fields, and mechanical stretching are utilized to switch spin state at a single molecule level, which in our opinion is a significant advancement in SCO research. Overall, prospects in SCO research are high. However, several avenues still need to be explored to develop SCO materials that are applicable to magnetic and electronic devices.

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