Spin-crossover in iron(II)-Schiff base complexes

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The spin-crossover (SCO) phenomenon is one of the most prominent examples of bi-stability in molecular chemistry, and the SCO complexes are proposed for nanotechnological applications such as memory units, sensors, and displays. Since the discovery of the SCO phenomenon in tris(N,N-dialkyl-dithiocarbamato)iron(III) complexes, numerous investigations have been made to obtain bi-stable SCO complexes undergoing spin-state switching at or around room temperature (RT). Valiant efforts have also been made to elucidate the structure–property relationship in SCO complexes to understand the factors—such as ligand-field strength, molecular geometry, and intermolecular interactions—governing the SCO. Schiff base ligands are an important class of nitrogen-rich chelating ligands used to prepare SCO complexes, because the Schiff base ligands are easy to synthesize and tailor with additional functionalities. Iron(II)-Schiff base complexes are a well-studied class of SCO active complexes due to the propensity of the complexes to undergo bi-stable SCO. In this context, this perspective attempts to elucidate the structure–SCO property relationships governing SCO in selected mono-, bi-, and multi-nuclear iron(II)-Schiff base complexes.

1. Introduction

1.1. General introduction to spin-crossover (SCO)

Spin-crossover is a reversible transition between low-spin (LS) and high-spin (HS) states mediated by external stimuli: examples include temperature, light, pressure, and electric field.1–16 The LS to HS switching or vice versa causes changes in the magnetic moment of the SCO complexes; some of the SCO complexes also show thermochromism.17–20 Temperature is the most commonly used stimulus to induce SCO at the bulk scale. Light is employed as a stimulus to effect LS to HS switching at low-temperatures (T < 10 K), which is termed light-induced excited spin-state trapping (LIESST). Note, a reverse-LIESST is also possible, that is, HS to LS switching.21–28 Pressure is a unique stimulus applied to cause SCO in bulk samples,29,30 whereas an electric field is used to switch spin-states at the single molecule level, for example, an SCO complex embedded in a molecular junction or surface bound thin SCO films.31,32

SCO could be observed for a transition metal complex with a 3dⁿ (n = 4–7) electronic configuration. The SCO is most commonly encountered in 3d⁶ octahedral or pseudo-octahedral iron(II) complexes featuring ligands of moderate field-strength. Note, the LS and HS state of an SCO active iron(II) complex is diamagnetic and paramagnetic, respectively. Depending on the ligand field splitting (Δo) and the pairing energy (P), there are two ways that electrons can populate in the t₂g and e₅ set of orbitals of an iron(II) complex (Fig. 1(top)). For strong field ligands Δo > P, hence a LS state is preferred due to the paring of electrons in the t₂g set of orbitals. In the case of weak field ligands Δo < P and a HS state are favoured. For an intermediate field strength Δo = P and it is possible to induce the SCO by the application of an external stimulus as mentioned before.33

SCO in molecular complexes is classified as: (a) gradual (b) abrupt (c) hysteretic (d) stepwise, and (d) incomplete (Fig. 1(bottom)).4 Much interest has been focused on SCO complexes exhibiting the cooperative first-order spin-state switching with hysteresis, and such complexes are termed bi-stable complexes,3,10,12,18,34–38 because the complexes can exist in two different stable electronic states depending on the history.39 Bi-stable SCO complexes showing a relatively large thermal hysteresis (ΔT ≥ 45 K) centered around room temperature (RT) are desired for applications, especially to obtain molecule-based switching and memory devices.12

Factors such as the ligand-field strength, counter anions, co-crystallized lattice solvent molecules, and intermolecular interactions influence the SCO properties, especially the SCO
temperature $T_{1/2}$ ($T_{1/2}$ is a temperature where equal proportions of LS and HS states exist), steepness/abruptness of the curve (that is, the $\gamma M T$ versus $T$ plot, where $\gamma M = \text{molar magnetic susceptibility and } T = \text{temperature}$), and thermal hysteresis width ($\Delta T$). The abruptness of solid SCO complexes depends on the nature of cooperative interactions between the switching units, that is, on the efficiency of the crystal lattice to transmit the geometry changes and electronic spin-state change that occur during the spin transition. Most SCO-active iron(II) complexes are mono-nuclear, and reports on the discrete bi- or multi-nuclear iron(II) complexes are relatively rare. Schiff base ligands are versatile platforms to produce mono-, bi-, and multi-nuclear iron(II)-SCO complexes with remarkable properties such as abrupt, hysteretic, and RT spin-state switching.

1.2. Schiff base ligand systems

Schiff bases are condensation products of primary amines and carbonyl compounds. Structurally, a Schiff base (also known as an imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (−C=O) is converted by a primary amine into an imine or azomethine (−HC=NR) functionality. An N₆-coordination environment around the central metal ion is the most commonly employed coordination mode to prepare SCO complexes. Schiff base ligands can form the desired N₆-iron(II) complexes along with N₄O₂-iron(II) complexes. Remarkably, some of the N₄O₂-iron(II) Schiff base complexes are reported to show abrupt and hysteric RT SCO as discussed in the following sections. By tailoring the Schiff-base ligands with appropriate functional groups, the SCO behaviour of the iron (II) complexes can be tuned. Usually, a range of precursor aldehydes and amines featuring desired functional groups are used to synthesize and design Schiff base ligands.

This possibility of synthesizing Schiff base ligands tailored with functional entities such as luminescent and self-assemble, directing groups is an added advantage towards the realization of application oriented multifunctional SCO materials. The following sections will focus on factors governing SCO in mono-, bi- and multi-nuclear iron(II)-Schiff base SCO complexes.

2. SCO in mononuclear iron(II)-Schiff base complexes

2.1. $[\text{FeN}_4\text{O}_2]$ complexes composed of tetradentate Jäger-type $\text{N}_4\text{O}_2$ and imidazole/N-heterocyclic ligands

Detailed structure–SCO property relationships in iron(II) complexes composed of Schiff base-like ligands and imidazole have been reported by Weber and co-workers. Two different modifications of a mixed ligand iron(II)-complex—$[\text{FeL}1(\text{HIm})_3][\text{I}]$—were synthesized by treating the precursor Schiff base complex—$[\text{FeL}1(\text{MeOH})_3]$—with an excess of HIm in MeOH (Scheme 1). During the reaction, two of the MeOH molecules from the precursor complex were replaced by the imidazole ligands leading to the formation of 1. The precipitation of 1 from the boiling reaction mixture yielded $1^{\text{HT}}$, which exhibited a 70 K thermal hysteresis width. Powder or microcrystalline forms of another modification of 1—$1^{\text{LT}}$—was obtained by cooling the reaction mixture and allowing it to
stand at RT or 4 °C. Crystallographic analyses of 1HT and 1LT revealed a distorted octahedral coordination geometry around iron(II) with equatorially and axially coordinated tetradentate L1 and imidazole ligands, respectively.

Both 1HT and 1LT showed first order SCO with thermal hysteresis (bi-stable SCO). A 70 K wide thermal hysteresis loop with \( T_{1/2} = 279 \) K was reported for 1HT, whereas, 1LT showed above RT SCO with \( T_{1/2} = 329 \) K and \( \Delta T = 5 \) K as depicted in Fig. 2.

Two different intermolecular hydrogen-bonding interactions between the neighbouring complex moieties constituted a 2D network structure in the crystal lattice of 1HT as shown in Fig. 2a. On the other hand, a 3D network structure composed of three different H-bonding interactions was observed in the crystal lattice of 1LT, see Fig. 2b. These intermolecular hydrogen-bonding interactions caused abrupt SCO by mediating cooperative interactions between the switching entities and contributed to the opening of the hysteresis loop upon LS to HS switching or vice versa.

The observation of hydrogen bonding interaction mediated bistable SCO in 1 prompted the synthesis of structurally similar [FeLn(Him)\(_2\)] \( n = 2 \text{–} 5 \) complexes (Scheme 1). Attempts were made to obtain the complexes by substituting the methanol molecules of the precursor complex, [FeLn(MeOH)\(_2\)] \( n = 2 \text{–} 5 \), by imidazole. The product of the complex formation reaction is highly influenced by the nature of the solvent, concentration of the precursor complex, and the ratio of the iron(II) complex to imidazole.

Successful syntheses of hexacoordinate [FeLn(Him)\(_2\)] \( n = 2 \text{–} 5 \), complexes were not realized in all cases. For L5, only penta-coordinate complex 5 was obtained; the use of a large excess of imidazole and various solvents as the reaction medium failed to push the equilibrium more towards the desired hexa-coordinated complex. Remarkably, octahedral complexes with the composition [FeLn(Him)\(_2\)] (L2 (2), L3 (3), and L4 (4)), were obtained for the three remaining ligands L2–L4. The spin-state switching characteristics of the powder complexes depend on the precipitation temperature. Complexes 2 and 3 showed gradual SCO with \( T_{1/2} = 344 \) K and \( T_{1/2} = 170 \) K, respectively. For 3, the coexistence of equal proportions of LS and HS iron(II) states was observed at 37 K indicating incomplete SCO.

To probe the role of the extended π-system and N-heterocycles of varying structures in tuning the SCO behaviour, a family of iron(II) complexes (Fig. 3) featuring equatorially coordinated tetradentate dianiminoanthraquinone-based Schiff base-like ligands and axially coordinated N-heterocycle ligands were synthesized.

Complex 6 (L6: R = Ph, \( \text{Lax} = \text{Py} \)) crystallized with a pyridine solvent and showed a stable and reversible first-order SCO \( (T_{1/2} = 175 \) K) with a small hysteresis as depicted in Fig. 3b.

Complex 7 (L7: R = OMe, \( \text{Lax} = \text{Py} \)) also contained a lattice pyridine molecule. The complex showed a gradual and two-step SCO with \( T_{1/2} = 150 \) K and \( T_{2/3} = 80 \) K; the SCO is incomplete with a residual HS fraction of 0.29 at 60 K \( (\chi_MT = 0.84 \text{ cm}^3 \text{ kmol}^{-1}) \). Annealing of the complex at 400 K led to the loss of pyridine from the lattice as indicated by thermo-

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**Scheme 1** Synthesis of charge-neutral [FeN\(_4\)O\(_2\)] complexes 1–5.
Tridentate pyridylmethene-aminophenol (pap: L9) and quinolyl-napthaldimine (qsal: L10) ligands used to prepare iron(II) complexes (Chart 2) were used to prepare charge-neutral iron(II) complexes composed of equatorially coordinated Schiff base like ligands tethered with alkyl chains and axially coordinated N-heterocycle ligands.

In brief, first order SCO with or without hysteresis and stepwise spin-state switching behaviour are observed in [FeN₄O₂] type complexes (1–10) composed of Schiff base like ligands—L₁–L₈—and a range of axially coordinated heterocycles. The nature and occurrence of SCO in the complexes is governed by preparation conditions, intermolecular interactions, and the presence or absence of lattice solvent molecules.

2.2. [FeN₄O₂] complexes composed of tridentate N₂O⁻ ligands

Tridentate pyridylmethene-aminophenol (pap: L9) quinolyl-salicyaldimine (qsal: L10–L15), and quinolyl-naphthalidine (qnal: L16 and L17) ligand systems featuring a N₂O⁻ donor set (Chart 2) were used to prepare charge-neutral iron(II) complexes. The absence of anions in the lattice of charge-neutral complexes may allow the switching entities to have larger interactions, which in turn could facilitate cooperative spin-state switching.

The role of intermolecular elastic and electrostatic interactions contributing to the occurrence of cooperative spin-state switching is demonstrated for the charge-neutral [Fe(L₉)₂] complex (11). The complex showed an abrupt SCO around RT with T₁/₂ = 299 K and ΔT = 17 K as depicted in Fig. 4(a). The complex is also LIESST active, and T_LIESST = 58 K was reported. In the crystal lattice of 11, hydrogen-bonding interactions among the molecules formed infinite chains, which are interconnected via a 3D-network of intermolecular van der Waals contacts and π–π interactions. Synergetic influence of such elastic and electrostatic interactions caused cooperative SCO in 11. The related water solvated qsal-complex—[Fe(L₁₀)₂]·2H₂O (12·2H₂O)—showed a gradual and incomplete SCO with T₁/₂ centred above 300 K; the de-solvated 12 showed a similar SCO behaviour to that of 12·2H₂O except for a slight shift above 200 K as shown in Fig. 4(a).

The spin-state switching behaviour of qsal-complexes—13–17—composed of −COOH (L₁₁) or halogen (X = Br, L₁₄, and I (L₁₅)) substituted ligands was investigated to understand the role of intermolecular interactions and halogen substitution effects on the SCO properties. The −COOH substituted complex (13) showed hysteretic SCO (T₁/₂ = 140 K) with a 21 K thermal hysteresis width (Fig. 4b), which is attributed to the hydrogen bond network structure originating from the COOH groups. In the halogen substituted series, complex 14 tethered with fluorine showed a temperature invariant HS state. The rest of the complexes—15 (X = Cl), 16 (X = Br), and 17 (X = I)—underwent temperature and light-induced SCO as depicted in Fig. 4(c). Complex 15 showed two-step SCO (T₁/₂ = 308 K and T₃/₂ = 316 K), first of its kind for (N₂O⁻) qsal iron(II) complexes, accompanied by symmetry breaking.

The complexes 16 and 17 exhibited T₁/₂ = 342 K, and 295 K, respectively. Density functional theory (DFT) calculations revealed the role of π-donor halogen substituents in influencing the T₁/₂ values of complexes 15–17. However, inter-

![Chart 2](image-url)
molecular interactions seem to overshadow the electronic effects. In the crystal lattice of 15 and 16, Cl and Br substituents formed C–H⋯X interactions, whereas the I⋯π interaction is observed in the I substituted complex 17. The I⋯π interaction prevented the occurrence of a set of π–π interactions observed in the crystal lattice of 15 and 16; these missing interactions shifted the $T_{1/2}$ of 17 to lower temperatures relative to 15 and 16.

Cooperative and lattice solvent dependent SCO is observed in a set of quinal based complexes. The complex—[Fe(L16)$_2$]·CH$_2$Cl$_2$ (18·CH$_2$Cl$_2$)—featuring a π-extended aromatic ligand crystallized as a dichloromethane solvate. An abrupt SCO ($T_{1/2} = 220$ K and $\Delta T = 2$ K) was observed for 18·CH$_2$Cl$_2$. The corresponding solvent-free complex (18) showed a similar abrupt SCO with $T_{1/2} = 265$ K. The complexes are LIEST active, and a $T_{LIEST} = 71$ K and 57 K is reported for 18·CH$_2$Cl$_2$ and its solvent-free counterpart, respectively. A structurally related complex—[Fe(L17)$_2$](19)—composed of a differently oriented naphthalene group remained HS throughout the investigated temperature range demonstrating the sensitive nature of SCO to the alignment of intermolecular π–π interactions.$^{70}$

Pyridyl-benzyohydrazonate type ligands (Chart 3) are another important class of Schiff-base ligands used to prepare iron(II) complexes that can undergo SCO. The methanol solvated complex showed abrupt and hysteretic SCO with $T_{1/2} = 310$ K and $\Delta T = 60$ K in the first heat-cool cycle. Subsequent cycles resulted in the loss of solvent inside the SQUID cavity, and the solvent free complex (20) showed $T_{1/2} = 282$ K, $\Delta T = 7$ K (Fig. 5(a)), and $T_{LIEST} = 74$ K.$^{71}$

Alkyl chain tethered amphiphilic-SCO complexes with self-assembly propensity are of interest to prepare micro- or nano-structured SCO architectures.$^{72}$ Although SCO is observed in alkyl-tethered iron(II) complexes,$^{73,74}$ the occurrence of hysteretic SCO in such complexes is hindered due to the, alkyl chain mediated, less-efficient propagation of structural deformations...
of the switching core. In a rare scenario, bent-shaped iron(II) complex—[Fe(L19)]2+ (21)—tethered with C_{10} alkyl chains showed symmetry breaking LS (monoclinic; P2_1/n) → HS (orthorhombic; P2_1_2_1_2) switching with T_{1/2} = 286 K and ΔT = 35 K at a scan rate of 0.2 K min\(^{-1}\) (Fig. 5b). The SCO is incomplete and at 400 K a 1:1 mixture of isolated HS and LS fractions (χM\(\Delta T\) = 1.67 cm\(^3\) mol\(^{-1}\) K) is observed. A magnetic anomaly due to the conformational change of the alkyl chains accompanied SCO in the 300 K to 295 K range (Fig. 5(b)-inset). The concomitant occurrence of magnetic anomaly and hysteresis width with decreasing particle size was observed owing to the increasing surface area with decreasing particle size.77

An amino-group substituted SCO complex—[Fe(L20)]2+ (22)—responsive to chemical stimuli showed a gradual SCO with T_{1/2} = 320 K. Exposing the complex to HCl vapour induced the partial dissociation of the complex and consequent loss of SCO; the protonated complex remained HS throughout the partial disassociation of the complex and consequent loss of SCO, whereas the solvent-free complex (24) showed bi-stable SCO with T_{1/2} = 323 K and ΔT = 40 K indicating lattice guest(s) dependent SCO as depicted in Fig. 6(c).

Variable temperature luminescence studies of the solvent-free complex revealed a discontinuity in the luminescence intensity (Fig. 6(d)) in the 200 K–400 K temperature range evidencing the synergistic coupling between luminescence and the spin-state. A subsequent study demonstrated substituent dependent SCO and luminescence-SCO correlation in related complexes.82

2.3. [FeN\(_6\)]\(^{2+}\) complexes composed of bidentate imidazolylmine and tripodal tris-bidentate imidazolylamine or thiazolylmine ligands

A range of Fe\(_n\) type mononuclear iron(n) complexes composed of bi-, tri-, and hexadentate Schiff base ligands are reported. Imidazol-2-ylimine- and imidazol-4-ylimine-based iron(n) complexes are a well investigated class of [FeN\(_6\)]\(^{2+}\) SCO complexes. In general, iron(n)-imadazol imine complexes are prepared employing two different strategies, namely by treating bidentate imidazolylmine (Charts 4 and 5) and tripodal tris-bidentate ligands (Chart 6) with iron(n) to form [Fe(L)\(_2\)]\(^{2+}\) and [Fe(L)]\(^{2+}\) complexes, respectively.

In a recent review, Scott and others45 discussed the SCO behavior of [FeN\(_6\)]\(^{2+}\) iron(n) complexes prepared from a range of imidazolyl imine ligands and established structure–SCO property relationships. In the light of this, the discussion in this contribution is restricted to complexes showing remarkable SCO behavior such as abrupt and hysteresic SCO and stepwise spin-state switching. A discussion on chiral iron(n)-imidazolylmine complexes is also presented to exemplify the...
usefulness of imidazolylimine ligands to obtain functional SCO complexes.

Anion-dependent SCO behavior in a series of $[\text{M}(L)\text{Cl}]^2+$ type iron(n)-imidazolylimine complexes—$[\text{Fe}(L23)\text{Cl}]X$ ($X = \text{AsF}_6$, 25 and $\text{BF}_4$ 26)—is reported. The octahedral complexes composed of three bi-dentate L23 ligands (Chart 4) are obtained as facial isomers $\text{fac-[Fe(H L23)]}^{2+}$ with equal proportions of $\Delta$ and $\Lambda$ enantiomers (Fig. 7a) in the crystal lattice. Hydrogen-bonding interactions between the imidazole and chloride ions (NH⋯Cl−) generated 1D ladder and 2D network assembly structures for 25 and 26, respectively. The complex 25 featuring a larger AsF$_6^-$ anion showed one-step SCO ($T_{1/2} = 128$ K) with 4 K thermal hysteresis width as depicted in Fig. 7(c), whereas complex 26 with a relatively small BF$_4^-$ anion remained in the HS state across the 300 K–5 K scan range. The AsF$_6^-$ and BF$_4^-$ anions, accommodated in the cavities of the hydrogen bonded network, are not involved in the formation of the network structure. However, the size of the counter anions governed the direction of the hydrogen bonds (Fig. 7(b)), which in turn affected the network propagation. Such variations in the supramolecular organization manifested as anion dependent SCO behaviour in 25 and 26.

A similar complex—$[\text{Fe}(L23)\text{Cl}]\text{PF}_6$ (27)—was obtained as two different polymorphs. Polymorph 27-1, prepared employing MeOH as the solvent, showed scan-rate dependent two-step hysteretic SCO. At a scan rate of 0.5 K min$^{-1}$, $T_1^1 = 122$ K and $T_{1/2} = 105$ K were observed. The steps $T_1^1$ and $T_2^1$ are associated with $\Delta T = 11.3$ K and 18.6 K, respectively (Fig. 7(d)). The NH⋯Cl− hydrogen-bond mediated 1D-ladder-like self-assembled structure of polymorph 27-1 is maintained during the SCO as per the crystallographic analysis. The SCO is governed by the structural changes associated with the FeN$_6$ coordination sphere, anion disorder, and the conformation change of $n$-propyl groups. A structurally related complex; $\text{fac-[Fe(L24)Cl]}\text{Cl}\text{PF}_6$ (28) showed three-step SCO. At a scan rate of 0.5 K, $T_1^1 = 124$ K ($\Delta T = 14.4$ K), $T_{1/2} = 141$ K ($\Delta T = 6.3$ K), and $T_2^1 = 153$ K ($\Delta T = 2.4$ K) were obtained. In the crystal lattice, the complex entities self-organized as a tetrameric cubane-like structure—$\text{fac-[Fe(L24)Cl]}^{2+}$—constructed from twelve NH⋯Cl hydrogen bonds. The three-step SCO observed in the complex is tentatively attributed to the stepwise switching of the iron(n) centers residing in the cubane-like structures.

Anion-dependent SCO is demonstrated in another series of complexes—$[\text{Fe}(L25)\text{Cl}]X$ ($X = \text{PF}_6$ 29, ClO$_4$ 30, and $\text{BF}_4$ 31). Steeper SCO profiles were obtained with decreasing anion size—$\text{PF}_6^- > \text{ClO}_4^- > \text{BF}_4^-$. However, a linear anion size dependence of $T_{1/2}$ is not observed for the complexes: 29 ($T_{1/2} = 154$ K, $\Delta T = 3.5$ K), 30 ($T_{1/2} = 185$ K, $\Delta T = 1.5$ K), and 31 ($T_{1/2} = 147$ K, $\Delta T = 1.8$ K).

Structural isomers—$\text{fac-}[\text{Fe}(L26)\text{Cl}]\text{ClO}_4$ 32 and $\text{fac-}[\text{Fe}(L27)\text{Cl}]\text{ClO}_4$ 33—featuring methyl groups at the 4- and 5-positions, respectively, of the imidazole ring were prepared employing ligands L26 and L27. The complexes crystallized as solvent-free $\text{fac-}$enantiomers, and a similar crystal packing is observed. Complex 33 showed partial SCO ($T_{1/2} = 390$ K), whereas 32 remained HS and no SCO is observed. A sterically crowded coordination environment around iron(n) due to the close proximity of the methyl group to the coordinating imid-
azole nitrogen trapped in the HS state. On the other hand, the placement of the methyl group at the 5-position of the imidazole ring in produced a relatively less crowded coordination environment around iron(II) thereby stabilizing the LS state. Thus, the role of steric crowding in influencing the spin-state in isomeric coordination complexes was demonstrated.

The synthesis, structural investigation, and SCO behavior of iron(II) complexes — — — derived from a tridentate imidazolylimine-based ligand were reported by Huang and others. Each mer- coordinates to the iron(II) equatorially through imidazole nitrogen donors and axially by the imine nitrogen donors. The Fe–N bond-length in is smaller than the Fe–N bond-length of 2.15 Å observed for a HS iron(II) complex. But this value is larger than that expected for LS iron(II), indicating the co-existence of LS- and HS-states. Complex showed a gradual and incomplete SCO with and was observed. The second heating and cooling cycles produced a small hysteresis loop, which is attributed to a partial removal of the Et₂O solvent. Complex showed gradual, hysteresis and complete above-RT SCO with and . The complexes were also LIESST active at 5 K and showed , respectively due to the short life-time of the light-induced excited HS states.

Recently, multifunctional SCO complexes have attracted much interest due to their utility to obtain SCO-based device architectures. Chirality is an important molecular property, and by combining the SCO property with chirality, novel hybrid materials displaying magneto-chiral dichroism and ferroelectricity could be realized. Furthermore, chirality dependent SCO behaviour in molecular complexes could be obtained considering the sensitive nature of SCO to intermolecular interactions. Thus, its desirable to have chiral SCO complexes both in terms of applications and from a fundamental scientific point of view.

The fac-bidentate helical coordination mode of imidazolylimine ligands produces Δ and Λ isomers of complexes as discussed above. However, equal proportions of Δ and Λ isomers were observed in the crystal lattice of most of the complexes discussed above. Notable exceptions are complexes and , whose crystal lattice is composed exclusively of Λ-enantiomers. The use of chiral imidazolylimine ligands induced selective crystallization of either Δ or Λ enantiomers of complexes as detailed below.

The spin-state switching behaviour of enantiomers, co-enantiomers, racemates, and co-racemates of chiral imidazolylimine-based iron(II) complexes is reported. First, two sets of enantiomeric complexes — (i) Δ-[Fe(R-L29)](ClO₄)₂ (35) and Δ-[Fe(S-L30)](ClO₄)₂ (36) (Fig. 8a); (ii) Δ-[Fe(R-L31)](ClO₄)₂ (37) and Δ-[Fe(S-L32)](ClO₄)₂ (38) (Fig. 8b)— were prepared by performing a multi-component self-assembly reac-

Fig. 7 (a) Δ and Λ isomers of 25, (b) hydrogen bonding modes in 25 and 26, and versus T plots of (c) 25 and (d) 27-1, and (e) scan rate dependent SCO of 27-2. (d) Reprinted with permission from ref. 84. Copyright (2015) American Chemical Society. (a) and (e) Reprinted with permission from ref. 85. Copyright (2017) Elsevier.
tion by treating together chiral phenylethylamine (R or S), 1-alkyl-2-imidazolecarboxaldehyde, and Fe(ClO$_4$)$_2$·6H$_2$O. Subsequent co-crystallization of the enantiomers resulted in the formation of co-enantiomers: 35R37R (AA) and 36S38S (ΔΔ); racemates: 35R36S (ΔΔ) and 37R38S (ΔΔ); and co-racemate: 35R36S37R38S (ΔΔΔΔ).

Enantiomers 35 and 36 remained HS throughout the measurement temperature range of 2 K–400 K. A gradual and complete SCO ($T_{1/2} = 291$ K) is observed for enantiomers 37 and 38, respectively. The co-enantiomeric complex 35R37R also showed a gradual, reversible, and complete SCO around room temperature but with $T_{1/2}$ shifted upward to 301 K. The racemate 35R36S showed a gradual and incomplete SCO with $T_{1/2} = 336$ K, and the racemate 37R38S exhibited a 46 K wide hysteresis loop as depicted in Fig. 8(e). The co-racemate 35R36S37R38S showed an incomplete and above RT SCO ($T_{1/2} = 330$ K) with a hysteresis loop of 11 K (Fig. 8(f)).

In an interesting scenario, the chiral iron(n) complex—fac-Δ-[Fe(S-L30)$_3$]$_2$(BF$_4$)$_2$ (39)—was obtained as two solvent free polymorphs. In the dark purple polymorph 39-I, the edge-to-face C–H⋯π interactions between the phenyl C–H and the neighbouring phenyl ring involve the H-atom located at the meta position of the phenyl ring. Such edge-to-face C–H⋯π interactions in polymorph 39-II involve the H-atom located at the para-position of the phenyl ring. Polymorph 39-I underwent gradual SCO with $T_{1/2} = 294$ K, and 39-II was trapped in the HS state in the 400 K–5 K temperature range. Remarkably, the HS polymorph 39-II showed ferroelectric behaviour due to the polar (C$_3$) point group associated with it.

Four homochiral-iron(n) SCO complexes, 40–43, were obtained from in situ generated chiral ligands—{(R)-Ln (n = 33–36). The complexes 40, 42, and 43 were obtained as fac-Δ isomers, whereas 41 was obtained as a fac-Λ isomer. Complexes 40 and 43 showed a reversible, gradual and, complete SCO with $T_{1/2} = 257$ K and 282 K, respectively. An incomplete and gradual SCO is observed for 41 and 42 with $T_{1/2} = 375$ K and 137 K, respectively. However, 41 showed steeper SCO than 42. Complexes 41 and 43 with a lower symmetry exhibited one-step SCO at a relatively higher temperature range than that of 40 and 42. The different SCO behaviour of complexes 40–43 was attributed to the substitution effect, packing mode, and intermolecular interactions. The electronic substitution effect arises due to the varying nature of functional groups (R$^2 =$ -H (40), -Cl (41), and -OCH$_3$ (42)) placed on the amine moiety, which modified the ligand-field strength around the iron(n) affecting the nature of SCO. Apart from the electronic effect, packing modes certainly exerted an obvious influence on the SCO behaviour. Significant differences in the crystal packing of complexes 40–43 were observed due to the differing substitution pattern of the complexes. Various intermolecular C–H⋯π interactions between the imidazole and phenyl rings in 40 and 43 are observed. Remarkably, 41 exhibited a relatively stronger C–Cl⋯π intermolecular interaction, which raised the $T_{1/2}$ value of 42 relative to other complexes. In the series 40–43, the strength of the intermolecular interaction seems to be a dominating factor in deciding the $T_{1/2}$ value.

The ligand chirality mediated selective preparation of fac-Λ and fac-Δ enantiomers was reported. Ligands R-L37 and S-L38 favoured the selective formation of fac-Λ-44 and fac-Δ-45 enantiomers, respectively. The crystalline fac-A-44 with a co-crystallized EtOH showed complete and cooperative SCO with $T_{1/2} =$
195 K; the SCO behaviour of \textit{fac-\Delta-45} is not reported. Thus, it is not possible to discern the enantiomer dependence of SCO.\textsuperscript{93}

The chiral resolution of racemic lactonitrile (LN) and methylglutaronitrile (MGN) by a homochiral SCO complex—\textit{fac-\Delta-[Fe(RL3)3][ClO4]2-MeCN} (46)—was demonstrated. The complex cations are stacked into a left-handed double helix supramolecular structure with MeCN solvent guests filling the helical channel. Complex 46 showed gradual SCO with \(T_{1/2} = 355\) K in the first heating mode. In the subsequent cycles, \(T_{1/2} = 217\) K is observed due to the loss of lattice MeCN. Dissolution of 46-MeCN in racemic LN or MGN led to the formation of triple helical 46-1/3(R)-LN and 46-1/3(S)-MGN crystals with R-LN and S-MGN located in the helical channel. The 46-1/3(R)-LN and 46-1/3(S)-MGN showed incomplete SCO behaviour with \(T_{1/2} = 363\) K, and no solvent loss is observed. The space group difference between 46-MeCN (P2\(_1\)) and 46-1/3(R)-LN/46-1/3(S)-MGN (P2\(_12_12_1\)) complexes is attributed as the reason behind the different spin-state switching behaviour of the complexes.\textsuperscript{94}

2.4. \([\text{FeN}_6]^{2+}\) complexes composed of tripodal tris-bidentate imidazolylamine and thiazolylamine ligands

Iron(II) complexes based on tripodal tris-bidentate-imidazolylamine and -thiazolylamine ligands (Chart 6) showing remarkable SCO behaviour were reported. A correlation between the SCO behaviour and relative size of the anions is established in a series of complexes: \([\text{Fe(\text{L40})]}\text{Cl-X (X} = \text{PF}_6 (47), \text{AsF}_6 (48), \text{SbF}_6 (49), \text{and CF}_3\text{SO}_3 (50)]\). In each complex, the NH⋯Cl hydrogen bonding interactions between the chloride ion and NH groups of imidazole corresponding to three neighbouring complex cations resulted in the formation of a 2D-extended network structure. The anion occupied the space between the 2D-sheets, whose structure is affected by the size and shape of the anion, causing modifications of the spin-state switching behaviour. One-step incomplete and two-step complete SCO behaviour were observed for 47 (\(T_{1/2} = 122\) K) and 48 (\(T_{1/2} = 82\) K), respectively. On the other hand, complexes 49 (\(T_{1/2} = 117\) K) and 50 (\(T_{1/2} = 82\) K) showed a gradual and steep one-step SCO behaviour, respectively. A small 4 K thermal hysteresis loop was observed for 50 at a scan rate of 1 K min\(^{-1}\). The \(T_{1/2}\) values of the complexes decreased with increasing anion size, that is, from PF\(_6^-\) to CF\(_3\)SO\(_3^-\).

In an interesting study, two separate cooperative SCO behaviours mediated by kinetically controlled phase transition involving the conformational change of the \(n\)-butyl chains and the associated reorganization of the intermolecular interactions were demonstrated. The complex, \([\text{Fe(\text{L41})]}[\text{PF}_6]_2 (51)\) showed abrupt and hysteretic SCO at 122 K and \(\Delta T = 14\) K at a scan rate of 4 K min\(^{-1}\). On the other hand, \(T_{1/2} = 156\) K and \(\Delta T = 41\) K were observed at a scan rate of 0.1 K min\(^{-1}\).

The occurrence of a temperature lag due to the freezing-in of the HS state during the HS to LS (LS1) switching caused the lower \(T_{1/2}\) value observed for the faster scan. At a scan rate of 0.1 K min\(^{-1}\), spin-state switching involves an additional LS state (LS2), and SCO at 0.1 K min\(^{-1}\) scan rate is best described as the one involving the same HS state and two different LS states, namely LS1 and LS2 as depicted in Fig. 9(c). Crystal structure analysis of 51 at LS1 (110 K) and LS2 (130 K) states revealed marked differences in the conformations of the alkyl chains (Fig. 9(d)) as well as the relative positions of the counter-ions. These remarkable variations in the conformation of alkyl chains induced different intermolecular interactions, which facilitated the access of the LS2 state at the lower scan rate thereby a larger hysteresis width is obtained at 0.1 K min\(^{-1}\).\textsuperscript{61}

SCO in \([\text{FeL}]^{2+}\) type complexes featuring tripodal tris-bidentate thiazolylamine ligands was also studied. The commonly observed NH⋯Cl hydrogen-bonding interactions in the above-discussed imidazolylamine-based complexes are absent in thiazolylamine complexes due to the absence of the N–H hydrogen bond donor in the thiazolylamine ligand. However, SCO is no less spectacular in thiazolylamine-based complexes. Anion dependent SCO in a series of solvent-free \([\text{Fe(\text{L42})]}][\text{X}]_2 (\text{X} = \text{BF}_4 (52), \text{SbF}_6 (53), \text{and CF}_3\text{SO}_3 (54)]\) complexes was reported. Complexes 53 (SbF\(_6^-\)) and 54 (CF\(_3\)SO\(_3^-\)) having relatively larger anions showed gradual and incomplete SCO, respectively. On the other hand, an abrupt and hysteretic SCO was observed for complex 52 with a relatively smaller charge balancing BF\(_4^-\) anion; \(T_{1/2} = 270\) K and \(\Delta T = 3\) K were obtained at a scan rate of 1 K min\(^{-1}\). More intermolecular interactions between \([\text{Fe(\text{L42})]}^{2+}\) entities in 52, relative to the complex cations of 53 and 54, inferred from the crystallographic analysis of the complexes, explains the abrupt SCO of 52. Low-spin six-coordinate complexes 53 and 54 crystallized as enantiomerically pure \(\Lambda\) and \(\Delta\) enantiomers, respectively from an acetonitrile-ether solvent system; a chiral space group \(\text{Pbc}_{2}_1 (53)\) and \(\text{P6}_5 (54)\) was observed. However, the six-coordinate LS-52 crystallized in the achiral space group—\(P2_1/c\) from the acetonitrile-tert-butylmethyl ether solvent system. Remarkably, the HS-52 crystallized as a seven-coordinate complex involving a new Fe–N (bridgehead) bond: a change in the coordination number—from six to seven—upon LS → HS switching was revealed.\textsuperscript{95} A similar complex \([\text{Fe(\text{L43})]}[\text{BF}_4]_2 (55)\) crystallized as a racemate.
from the ethanol–ether solvent mixture. Complex 55 showed a re-entrant symmetry-breaking gradual SCO with \( T_{1/2} = 208 \) K.\(^9^6\)

2.5. \([\text{FeN}_6]\) complexes composed of triazole-based bidentate and tripodal tris-bidentate ligands

Schiff base ligands composed of the 1,2,3-triazole ring offer suitable ligand field strength to obtain SCO active iron(II) complexes. Some examples of iron(II) SCO complexes composed of 1,2,3-triazole-based tetradentate and tripodal tris-bidentate ligands are discussed as follows (Chart 7).

Polyomorphism-dependent hysteretic SCO is demonstrated in \([\text{FeL44(NCS)}]_2\) (56). The tetradentate \( \text{L44} \) coordinates the iron(II) at equatorial positions, and anionic NCS\(^-\)ligands coordinate via nitrogen donors and occupy the axial positions to produce a charge-neutral complex. Remarkably, two solvent-free polymorphs of 56—I and 56—II—were obtained. Treating methanol solutions of \( \text{L44} \) and Fe(NCS)\(_2\) together simultaneously yielded 56—I and 56—II. Exclusive crystallization of 56—II was achieved by treating a CHCl\(_3\) solution of \( \text{L44} \) with a MeOH solution of Fe(NCS)\(_2\). The orange polymorph 56—I is HS at RT and showed abrupt and hysteretic SCO with \( T_{1/2} = 270 \) K and \( \Delta T = 2 \) K. The dark purple-red polymorph 56—II is LS at RT and showed similar abrupt and hysteretic SCO (\( \Delta T = 2 \) K) as 56—I. However, a 101 K upward shift of the switching temperature (\( T_{1/2} = 371 \) K) is observed for 56—II relative to 56—I (Fig. 10(a)). Crystallographic analysis of the polymorphs 56—I and 56—II revealed significant differences in the packing modes. In 56—I, C–H⋯S hydrogen-bonding interactions produced an extended 3D-network structure (Fig. 10(b)). On the other hand, the 3D-network of 56—II is constituted of C–H⋯S and C–H⋯N hydrogen-bonding interactions. The existence of the additional C–H⋯N and differently organized C–H⋯S hydrogen-bonding interactions in 56—II relative to 56—I caused the observed 100 K increase in \( T_{1/2} \) of 56—II.\(^9^7\)

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**Fig. 10** (a) \( \chi_M T \) versus \( T \) plots of 56—I (red) and 56—II (blue), (b) packing arrangement in the crystal lattice of 56—I (left) and 56—II (right), (c) structural features contributing to the crystal engineering approach used to design bi-stable SCO complexes: 57—59, and (d) \( \chi_M T \) versus \( T \) plots of complexes 57 (black), 58 (orange), 59a (purple), and 59b (green). Reprinted with permission from ref. 37. Copyright (2017) American Chemical Society.

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A crystal engineering approach based on concerted molecular motions of the ligand backbone (Fig. 10(c)) was employed to prepare 1,2,3-triazole-based bi-stable iron(n) SCO complexes: \([\text{Fe}L_{45}(\text{NCS})_{2}]\) (57), \([\text{Fe}L_{46}(\text{NCS})_{2}]\) (58), \([\text{Fe}L_{47}(\text{NCS})_{2}]0.5\text{H}_{2}\text{O}\) (59a), and \([\text{Fe}L_{47}(\text{NCS})_{2}]0.5\text{CH}_{3}\text{CN}-0.5\text{CH}_{3}\text{OH}-\text{H}_{2}\text{O}\) (59b). All the complexes showed stable bi-stable SCO behavior upon repeated cycling. The solvent free complexes 57 (\(T_{1/2} = 399\) K and \(\Delta T = 20\) K) and 58 (\(T_{1/2} = 240\) K and \(\Delta T = 1\) K) showed abrupt and hysteretic SCO at above and below RT, respectively (Fig. 10(d)). The solvated complexes 59a and 59b showed SCO at RT and above RT, respectively, with \(T_{1/2} = 338\) K (59a) and 309 K (59b); \(\Delta T = 26\) K (59a) and 31 K (59b) as shown in Fig. 10(d). In all the complexes, weak C–H…π hydrogen-bonding interactions facilitated the formation of 3D-network structures incorporating additional C–H…π and π–π interactions. Such intermolecular interactions and flexible nature of ligand backbones \(\text{L}_{45}–\text{L}_{47}\) promoted bi-stable SCO behaviour in complexes 57–59. Complex \(\text{[FeL}_{48}\) (NTf)\(_2\) (60) composed of tripodal tris-bidentate ligand \(\text{L}_{48}\) showed a gradual SCO with \(T_{1/2} = 280\) K.\(^{28}\)

2.6. Other remarkable examples

Reversible spin-state dependent rupture and formation of an Fe–N bond was demonstrated in some families of iron(n) complexes composed of macrocyclic Schiff base ligands. Such a process increases the lifetime of the LIESST generated HS state and renders the complexes suitable for applications. Complex \([\text{FeL}_{49}(\text{CN})_{2}]\cdot\text{MeOH}\) \((\text{61-MeOH})\) derived from the macrocyclic Schiff base ligand \(\text{L}_{49}\) (Fig. 11(a)) and axially coordinating CN\(^{–}\) via carbon donors is LS in the 300 K to 5 K temperature range. Upon excitation with white or green light at low temperatures, LIESST mediated population of the metastable HS state showing a HS \(\rightarrow\) LS relaxation rate of 0.3 K min\(^{−1}\) was observed. The observed \(T_{\text{LIESST}} = 140\) K is remarkably higher than the usual 50 K–80 K range observed for iron(n) SCO complexes. An explanation based on coordination number change in concert with HS \(\rightarrow\) LS switching/relaxation was proposed to account for the high \(T_{\text{LIESST}}\) observed in \(\text{61-MeOH}\). A recent crystallographic study confirmed the above attribution by characterising the HS \(\text{61-MeOH}\) as a seven-coordinate complex as depicted in Fig. 11(b). In essence, the coordination number change, from seven (HS) to six (LS), associated with thermal relaxation of the LIESST produced HS state to the thermodynamic LS state increased the lifetime of the metastable HS state of \(\text{61-MeOH}\).\(^{99}\)

A recently reported charge neutral complex—\([\text{Fe(L}_{50}\) (NCS)\(_2\)]\)\(_2\) (62)—showed stable and hysteretic SCO behaviour with \(T_{1/2} = 286\) K and \(\Delta T = 41\) K at a scan rate of 2 K min\(^{−1}\) (Fig. 11(d)). Crystallographic studies of the complex at 300 K (HS) and 230 K (LS) revealed a structural transition from monoclinic \(P2_{1}/c\) (HS) to \(Pccn\) (LS).\(^{100}\) The analogous complex \([\text{Fe(L}_{50}\) (NCS)\(_2\)]\) \((\text{63})\) showed SCO with \(T_{1/2} = 211\) K and \(\Delta T = 41\) K. Complex \(\text{62}\) is not LIESST active, whereas a small effect was observed for \(\text{63}\).

3. An outlook on the SCO behaviour of multinuclear and 1D-polymeric SCO complexes based on Schiff base ligands

Apart from the above discussed mononuclear complexes, SCO in multinuclear iron(n) complexes composed of Schiff base ligands is also studied. Supramolecular interactions such as hydrogen bonding and π–π interactions contribute to abrupt and hysteretic SCO in mononuclear complexes. On the other hand, the nature of spin-state switching in multinuclear iron(n) complexes is governed by intramolecular interactions mediated by ligand backbones connecting switching iron(n) centres and intermolecular contacts between discrete switching entities.

3.1. Multinuclear complexes

Among multinuclear iron(n) complexes, dinuclear systems are a well-studied class, especially to obtain stepped [LS–LS] \(\rightarrow\) [LS–HS] \(\rightarrow\) [HS–HS] spin-state switching. Some examples belonging to two major classes of binuclear SCO systems—triply- and doubly stranded iron(n) helicates—showing abrupt and hysteretic SCO are discussed as follows.

Ligand \(\text{L}_{51}\) (Chart 8) was used to prepare dinuclear triple helicate iron(n) complexes—\([\text{Fe}_{2}L_{51}]_{3}\) \((\text{ClO}_{4})_{4}·5\text{CH}_{3}\text{NO}_{2}\) \((\text{64})\) and \([\text{Fe}_{2}L_{51}]_{3}[\text{BF}_{4}]_{4}·6.5\text{CH}_{3}\text{NO}_{2}·0.5\text{H}_{2}\text{O}\) \((\text{65})\). Complex \(\text{64}\) crys-
tallized in the centrosymmetric space group $P2_1/C$ and the crystal lattice was composed of equal proportions of homo-
chiral $A$-$A$ and $A$-$A$ pairs indicating the absence of sponta-
nous chiral resolution. A zigzag 1D-self-organization along the 
crystallographic $c$-axis was observed due to the hydrogen 
bonding interactions between the neighbouring dinuclear 
units, which also placed the iron(n) centres in the helicate at a 
slightly different crystallographic environment. The triple heli-
cate complex (65) featuring BF$_4^-$ anions crystallized as needle 
and block polymorphs, and the crystal structure of the block 
polymorph, crystallized in the centrosymmetric space group 
$P1$, was reported. As in the case of 64, a heterochiral/racemic 
architecture was observed for 65. However, hydrogen bonding 
interactions in the crystal lattice of 65 produced a 2D-sheet like 
self-organization along the crystallographic $c$-axis. Complexes 
64 and 65 showed incomplete/half SCO behaviour, that is, the 
expected complete [LS-LS] $\rightarrow$ [LS-HS] $\rightarrow$ [HS-HS] switching is 
not observed. Instead, a stable mixed [LS-HS] phase associated 
with a distinct dinuclear helicate was reported below 220 K 
and 180 K for 64 ($\gamma_M^T = 3.3$ cm$^3$ K mol$^{-1}$) and 65 ($\gamma_M^T = 
3.7$ cm$^3$ K mol$^{-1}$), respectively. Complex 64 underwent the [LS-
HS] $\rightarrow$ [HS-HS] switching with $T_{1/2} = 240$ K. Remarkably, 
complex 65 showed the [LS-HS] $\rightarrow$ [HS-HS] switching ($T_{1/2} = 
187$ K) with a 7 K thermal hysteresis loop at a scan rate of 2 K 
min$^{-1}$. The 2D-sheet like self-organization involving stronger 
hydrogen bonding interactions in 65 compared to the 1D-
organization observed in 64 is a contributing factor promoting 
abrupt and hysteretic SCO in 65.$^{101}$

Craze and others reported a series of binuclear iron(n)- 
Schiff base SCO complexes—[Fe$_2$(L52)$_3$][BF$_4$]$_2$ (66), [Fe$_2$(L53)$_3$] 
([BF$_4$])$_2$ (67), and [Fe$_2$(L54)$_3$][BF$_4$]$_2$ (68)—based on ligands L52-
L54 (Chart 8). The effects of the steric properties of three 
different central ligand atoms ($X$ = $-$CH$_2$-$,$ $-$S$-$, or $-$O$-$) on 
the structure and SCO of their respective helicate architectures 
were investigated. All the three helicates displayed a gradual 
and incomplete SCO from the mixed [LS-HS] state to [HS-HS] 
state. The heating and cooling modes resulted in a small hys-
teresis for all the three helicates as shown in Fig. 12(b). For 66, 
the $\chi_M^T$ versus $T$ plot in the cooling mode is in accordance 
with the occurrence of half [HS-HS] $\rightarrow$ [LS-HS] SCO with a 
broad transition happening between 60 K to 250 K. The $\chi_M^T$ 
value of 7.71 cm$^3$ K mol$^{-1}$ observed at RT corresponds to two 
magnetically uncoupled octahedral iron(n) centres in the heli-
cate. As the temperature is lowered, $\chi_M^T$ remained constant 
until 250 K and then dropped in a single step with a $T_{1/2}$ of 
155 K ($\gamma_M^T = 4.41$ cm$^3$ K mol$^{-1}$ at 50 K). This indicates incom-
plete SCO with around 40% of the iron(n) centres in the LS 
state. In the heating mode $T_{1/2} = 170$ K is observed resulting 
in a thermal hysteresis of 15 K. The compound 68 also showed 
gradiual SCO with $T_{1/2} = 150$ K and 165 K for the cooling and 
heating cycles, respectively, with a 15 K hysteresis loop. The RT 
$\chi_M^T$ value of 7.67 cm$^3$ K mol$^{-1}$ is in accordance with the com-
plete HS-HS state of the iron(n) centres; the $\gamma_M^T = 3.92$ cm$^3$ K 
 mol$^{-1}$ at 50 K indicates approximately half-completed SCO. Complex 67 ($X = S$) showed abrupt SCO from the mixed [LS-
HS] state (Fig. 12(a)) to [HS-HS] state. The complex is HS at RT 
($\gamma_M^T = 7.65$ cm$^3$ K mol$^{-1}$) and showed an abrupt one-step SCO 
behaviour with $T_{1/2} = 123$ K and $\Delta T = 15$ K.$^{102}$

Remarkably, a complete [LS-LS] $\rightarrow$ [HS-HS] switching is 
observed in the methylated analogue of 66: [Fe$_2$(L55)$_3$][ClO$_4$]$_2$ 
(69). The dehydrated complex 69 showed complete [HS-HS] to 
[LS-LS] switching, upon cooling from 300 K with $T_{1/2} = 140$ K. 
Complex 69 also showed complete LIESST mediated [LS-LS] to 
[HS-HS] switching at low-temperature. The hydrated complex 
$-[Fe_2(L53)_3][ClO_4]_2$·$4H_2O$ (69·$4H_2O$)—showed a half complete 
[HS-HS] to [LS-LS] SCO.$^{103}$

High temperature hysteretic SCO in triazole-based dinuclear 
double-helicate complexes—[Fe$_2$(L54)$_3$][PF$_6$]$_2$·$5H_2O$·CH$_3$CN 
(70) and [Fe$_2$(L57)$_3$][ASF$_6$]$_2$·$3H_2O$·CH$_3$CN (71)—was reported. 
Complex 70 showed stable two-step SCO behaviour upon 
repeated cycling. The first gradual SCO step is observed until 
432 K followed by the second abrupt step with $T_{1/2} = 432$ K and 
$\Delta T = 11$ K at a scan rate of 1 K min$^{-1}$. The structurally 
analogous complex 71 (Fig. 12(c)) showed an unsymmetrical and 
hysteretic [LS-LS] $\rightarrow$ [HS-HS] SCO in the first heat cool-cycle; 
$T_{1/2} = 443$ K and $\Delta T = 82$ K (Fig. 12(d)) were observed at a scan 
rate of 0.5 K min$^{-1}$. Subsequent scanning resulted in the modi-
fication of the SCO behaviour due to lattice solvent loss. A het-
erochiral crystal lattice is observed for both the complexes, and 
the molecular organization in the lattice is governed by $\pi$-$\pi$ 
and C-C-H-$\pi$ interactions in 70 and by $\pi$-$\pi$ interactions in 71. 
Such intermolecular interactions promoted hysteretic SCO 
profiles in 70 and 71. The $\Delta T = 82$ K reported for 71 is the widest 
hysteresis loop reported so far for a dinuclear-helicate as 
claimed by the authors of the original study.$^{18}$

A range of tetrnuclear tetrahedral cages, tetrnuclear [2 $\times$ 2] 
grids, and octanuclear iron(n) complexes based on Schiff 
base ligands were reported.$^{15,46}$ SCO in these systems is 
gradual most probably due to the lack of cooperativity associ-
ated with the intra cage/grid iron(n) switching centres placed
in a slightly different crystallographic environment as observed in dinuclear complex 64. Due to the lack of abrupt and hysteric SCO in the multinuclear complexes, a further discussion on them is not presented in this perspective. The interested reader may consult recent reviews by Kruger and co-workers and Brooker and co-workers for more details on the SCO behaviour of multinuclear iron(II) complexes.

3.2. 1D-complexes

A series of 1D-coordination polymers composed of equatorially coordinated tetradentate Jäger-type ligands and axially coordinated ditopic-bidentate ligands such as 4,4′-azopyridine (azpy) (Chart 9) were reported by Weber and co-workers. The nature of self-organization of 1D-chain like architectures, flexibility of the axial ligands, and presence or absence of lattice solvent(s) governed the nature of SCO in 1D-coordination polymers. A few prominent examples showing bistable, abrupt, or stepwise SCO behaviour are detailed as follows.

Complexes [Fe(L1)(azpy)]_n (72) and [Fe(L2)(azpy)]_n (73) showed two-step SCO (T^1_1/2 = 326 K and T^2_1/2 = 156 K; 73: T^1_1/2 = 365 K and T^2_1/2 = 214 K) with intermediate plateaus comprising equal proportions of LS and HS states; the second switching step of 72 involves a 7 K thermal hysteresis loop. The widths of the intermediate plateaus were estimated to be 110 K and 75 K for 72 and 73, respectively.

The toluene solvated complex 72·tol showed gradual one-step SCO with T_{1/2} = 222 K. Heating 72·tol above 390 K led to the loss of the solvent, and the solvent free complex showed two-step SCO like 72 with T^1_1/2 = 320 K and T^2_1/2 = 150 K. X-ray structure analysis of 72 at 200 K (plateau region) revealed a layered arrangement. In each layer, a parallel arrangement of 1D-chain like architectures composed of alternating HS and HS iron(II) centres was observed. The layers are interlocked perpendicular to each other leading to a crosslinked arrangement, which caused stepwise SCO in 72 by promoting the formation of an intermediate plateau. A similar hysteretic stepwise SCO behaviour with an intermediate LS/HS plateau region was reported for [Fe(L5)(bpea)]_n (74), [Fe(L5)(bpea)]_n·0.25MeOH (75) [Fe(L5)(bpea)]_n·MeOH (76), [Fe(L1)(bipy)]_n·MeOH (77), and [Fe(L1)(bpey)]_n (78). X-ray structure analysis of complexes 74–78 revealed the formation of 1D-chains with linear (bipy), step-like (bpea), and zigzag (bppa) organization. While zigzag chains supported stepwise transitions, stiffness of the axial ligands and number of intermolecular contacts (see below) governed the size of the hysteresis width. Remarkably, [Fe(L1)(bpea)·MeOH] (79) showed stable one-step bi-stable SCO (T_{1/2} = 169 K and ΔT = 27 K) due to the step like organization of the 1D-chains.

A complete and incomplete cooperative SCO was reported for [Fe(L3)(bpy)]_n (80) and [Fe(L4)(bibmm)]_n (81), respectively. Upon cooling, 81 underwent a gradual SCO from the HS state until 180 K (30% conversion). Further cooling resulted in abrupt spin-state switching of the HS/LS (70:30) mixture with T_{1/2} = 174 K and ΔT = 5 K. The incomplete SCO observed for 81 is accompanied by a 4 K (T_{1/2} = 136 K and T_{2/3} = 140 K) thermal hysteresis loop; below 150 K, a mixed spin-state plateau with χ_nT = 1.58 cm³ K mol⁻¹ was observed. X-ray structure analyses of 80 revealed an increased number of short intermolecular contacts in the abrupt SCO region compared to the gradual region: the role of short intermolecular contacts in causing gradual to abrupt SCO was demonstrated. On the other hand, a zigzag molecular organization was observed in the X-ray structure of 81. Although such an organization favours stepwise SCO as discussed above, the spin-state switching from the mixed intermediate state to LS state is prohibited in 81 due to restraining interactions associated with the zigzag arrangement.

To get insight into the role of extended aromatic systems in promoting cooperative spin-state switching, a series of iron(II) complexes based on L6, L7, and L58 were synthesized. Complexes [Fe(L6)(bpea)·MeOH (82·MeOH) and [Fe(L6)(bpee)·MeOH (83·MeOH) showed abrupt and hysteretic SCO; T_{1/2} = 209 K (82·MeOH), 230 K (83·MeOH) and ΔT = 28 K (82·MeOH), and 40 K (83·MeOH) were observed. Annealing the complexes at 400 K produced solvent-free complexes 82 and 83, and the de-solvated complexes showed stable and hysteretic SCO with reduced ΔT relative to their solvated counterparts. Complex [Fe(L7)(bpee)] (84) showed abrupt SCO with T_{1/2} = 149 K.

The 1D-coordination polymer [Fe(L58)(bipy)] (85) shown in Fig. 13(a) underwent stable and above room temperature bistable SCO. In the first heat-cool cycle, the complex showed SCO with T_{1/2} = 352 K and ΔT = 57 K. A reduced hysteresis width (ΔT = 48 K) and switching temperature (T_{1/2} = 347 K) were observed in the second heat-cool cycle; no changes in the SCO behaviour were observed in the subsequent scans (Fig. 13(b)). The SCO is in concert with structural phase transition as revealed by the variable temperature powder X-ray diffraction and differential scanning calorimetry studies. Variable temperature photoluminescence studies evidenced spin-state dependent evolution of PL peaks located at 550 nm and 673 nm (Fig. 13(c)). The intensity of the 550 nm peak

![Chart 9 Structures of N₅O₃⁺ equatorially coordinating and ditopic bidentate axially coordinating ligands used to prepare iron(II) 1D-coordination polymers.](image-url)
decreased with increasing temperature in the 300 K to 400 K range, whereas the intensity of the 673 nm peak varied only slightly with respect to temperature. A plot of the intensity ratio of 550 nm and 673 nm peaks at many temperature points produced a profile like the one obtained from temperature dependent magnetic measurements (Fig. 13(d)). Thus, the luminescence readout of SCO in 85 is demonstrated.58

4. Conclusions

This perspective summarizes various classes of structurally characterized SCO-active mono-, multi-nuclear and 1D-polymeric iron(II)-Schiff base complexes. Some of the complexes showed SCO around RT with or without hysteresis. The SCO properties of the complexes are tuned by varying the precipitant temperature, tailoring a ligand with an appropriate chemical substituent, varying the counter-anion, and employing different solvents of crystallization. However, custom tuning of the SCO properties remains as a big challenge. Although most of the iron(II)-SCO compounds reported in the literature have an all nitrogen (N6) coordination environment, many examples of iron(n)-Schiff base complexes covered in this perspective feature N4O2 coordination. Remarkably, some of the N4O2-type complexes exhibited abrupt and hysteretic SCO suitable for device applications. The SCO properties of mixed ligand iron(n)-Schiff base complexes are also presented, and the complexes showed spin-state switching characteristics, promising toward device applications. On the other hand, the facile synthesis of functional Schiff base ligands facilitated the selective synthesis of SCO active enantiomeric iron(n) complexes and luminescence read-out of spin-states.

Majority of the SCO complexes presented in this perspective are mononuclear complexes. The realization of abrupt and hysteretic SCO in multi-nuclear iron(n) complexes remains a difficult problem to be tackled. Emphasis should be on obtaining multi-nuclear SCO active iron(n)-Schiff base complexes as these complexes may bring in cooperative effects causing wide hysteresis loops suitable for potential application purposes.

Conflicts of interest

The authors declare no conflicts of interest regarding the publication of this paper.

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