Unravelling of a [High Spin – Low Spin] ↔ [Low Spin – High Spin] Equilibrium in Spin-Crossover Iron(II) Dinuclear Helicates Using Paramagnetic NMR Spectroscopy

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Abstract: Spin-crossover between high-spin (HS) and low-spin (LS) states of selected transition metal ions in polynuclear and polymeric compounds is behind their use as multistep switchable materials in breakthrough electronic and spintronic devices. Here we report the first successful attempt to observe the dynamics of a rarely found broken-symmetry spin state in binuclear complexes, which mixes the states [HS-LS] and [LS-HS] on a millisecond timescale. The slow exchange between these two states identified by paramagnetic NMR spectroscopy in solutions of two spin-crossover iron(II) binuclear helicates, which are amenable to molecular design, opens the way for them to emerge as double quantum dot cellular automata for information storage and processing.

Spin-crossover (SCO) coordination complexes and frameworks are switchable materials that use the ability of transition metal ions to switch between two spin states with a different number of unpaired electrons under an applied stimulus, such as temperature, pressure or light irradiation.[1] In discrete compounds, this behaviour is most often observed for molecular complexes with a single metal ion, which is usually iron(II) ion.[2] However, a multistep thermal SCO is sometimes found in bi-[3–5], tri-nuclear[6–8] and grid[9,10] complexes thus making them suitable switching elements in molecular devices for electronics[11–13], spintronics[14,15] and information processing applications.[16,17].

For a binuclear complex, at least three different states are possible; those include fully high-spin [HS-HS] or low-spin [LS-LS] states that are commonly encountered in SCO compounds and an intermediate broken-symmetry state [HS-LS] that was previously accessed[18] only in a few solids.[19] In such rare cases,[20,21] the latter is almost[22] always induced by crystallographic symmetry breaking. In an even more unlikely event,[23] the spin state switching by one metal ion may cause large structural rearrangements of the molecule that modulate the ligand-field strength at the other metal ion so as to stabilize the broken-symmetry state[23] in a solution. In a binuclear complex with a two-fold symmetry, the two metal ions can switch their spin state with an equal probability to produce either of both [HS-LS] or [LS-HS] equivalent species, rendering an observation of any transformations between them so difficult that it has not been achieved yet.

In this communication, we report the first successful attempt to identify temperature-dependent dynamics of the broken-symmetry state that results in the exchange between the two states [HS-LS] and [LS-HS] on the millisecond timescale in solutions of SCO-active binuclear iron(II) helicates $X@[Fe_2L_3]X\cdot(PF_6)_2$ (**$X@[Fe_2L_3]$**, X = Cl or Br, Fig. 1). As earlier shown by some of us,[24] the complexes exist as [HS-LS] species stable over a wide range of temperatures in the solid state, thus representing a unique case of detection of a truly [HS-LS] state with unambiguous observation of the state of each iron(II) ion within the molecule.[25]

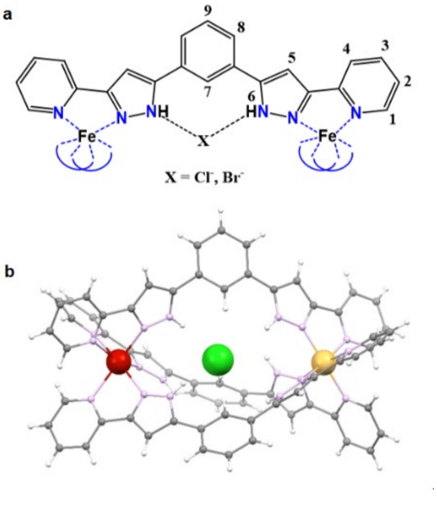

Figure 1. Coordination mode of the ligand **L** in **X@[Fe$_2$L$_3$]** (a) and representation of the cationic supramolecular helicate (Cl@[Fe$_2$L$_3$])$^{+3}$ (b) as obtained by single-crystal X-ray diffraction. [24]

Interestingly, the possible equilibrium [HS-LS] ⇔ [LS-HS] between the two equivalent species has never been observed before. The latter can be hypothetically probed by paramagnetic NMR spectroscopy, which is routinely used in SCO research to follow the spin state of molecular compounds,[26] such as the above iron(II) helicates with the two-fold symmetry broken by paramagnetism of one of the metal ions.[27]

As is the common wisdom in molecular magnetism,[28] chemical shifts in the NMR spectra of a mononuclear complex with a HS ion that does not show strong spin-orbit coupling, e.g. HS iron(II) ion, depend linearly on the inverse temperature (Fig. 1a) with the slope being specific for each nucleus as a direct consequence of the Curie Law. For a SCO-active compound, the same linear dependence is observed at high temperatures but a gradual population of the LS state upon cooling causes deviations from the linearity. If the switching between the two spin states is fast in the NMR timescale, which is almost always the case,[29,30] the chemical shifts become weighted averages of those for the HS and LS species.[31,32] Below a certain temperature, only the diamagnetic LS state of the ion(II) ion is populated in a solution, as corroborated by temperature-independent NMR spectra.

A binuclear helicate **X@[Fe$_2$L$_3$]** with two iron(II) ions, however, may adopt three different spin states, [LS-LS], [LS-HS] and [HS-HS]. As the temperature range accessible by solution NMR spectroscopy is limited by the solidification of the solvent, only two of them – [HS-HS] and [HS-LS] – have to be considered for the iron(II) helicate that becomes [LS-LS] at temperatures below 100 K.[24] Both these states are paramagnetic, so one would expect the chemical shifts in each state to follow the linear dependence on the inverse temperature with different slopes for the species [HS-HS] and [HS-LS]. In the temperature region of a SCO between them, the NMR spectra of **X@[Fe$_2$L$_3$]** would feature a weighted average of the chemical shifts for the two states (Fig. 2b).

For the helicate **X@[Fe$_2$L$_3$]** in the state [HS-HS], eight signals are expected in the ^{1}H NMR spectrum owing to the two-fold symmetry of the molecule in this state. When one of its two iron(II) ions switches to the LS state (Fig. S1), this symmetry breaks and therefore should produce 14 new signals; those would exclude the protons of the NH groups, as they are located close to the metal center and may exchange with the protons of the solvent, such as methanol-d$_4$, thus becoming silent. Of them, the signals of the pyridine-pyrazole moiety coordinated to the HS iron(II) ion should have large paramagnetic shifts, while the one coordinated to the LS iron(II) ion might experience only a minor influence from the distant paramagnetic center, thus showing almost diamagnetic chemical shifts that are insensitive to the temperature changes[27] (Fig.3).

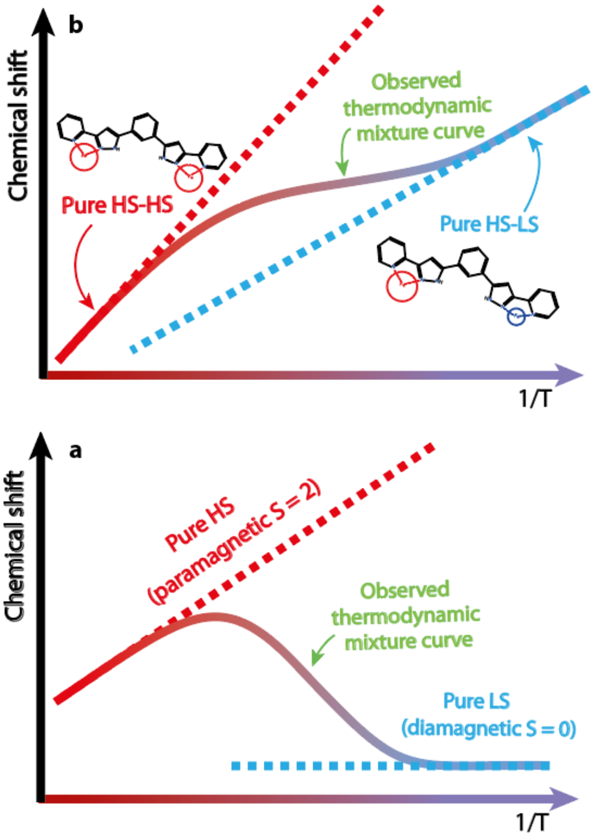

Figure 2. Coordination mode of the ligand **L** in **X@[Fe$_2$L$_3$]** (a) and representation of the cationic supramolecular helicate (Cl@[Fe$_2$L$_3$])$^{+3}$ (b) as obtained by single-crystal X-ray diffraction. [24]

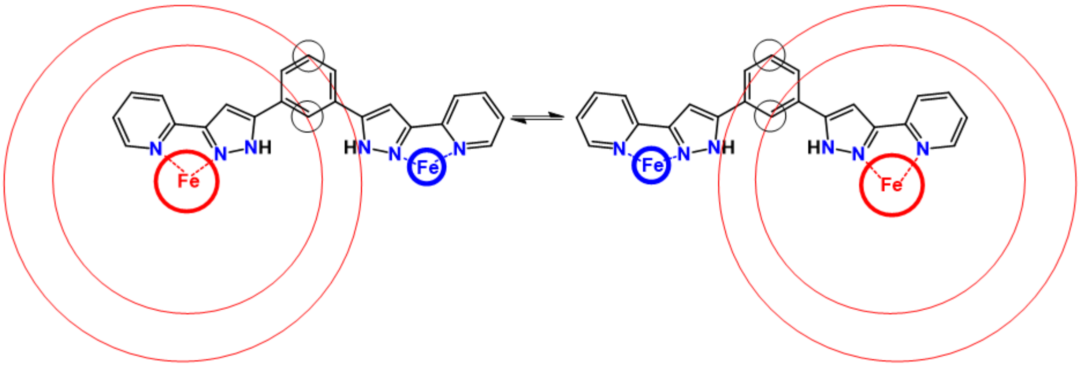

Figure 3. A schematic drawing of the effect of the paramagnetism (red concentric circles) of the HS iron(II) ions in two possible broken-symmetry states [HS-LS] and [LS-HS] of **X@[Fe$_2$L$_3$]**; only one ligand **L** is shown for clarity. The HS and LS iron(II) ions are highlighted by red and blue circles, respectively, and the protons that have the same chemical shifts in both these states, by black circles.

We, however, argue that the broken-symmetry state [HS-LS] in a solution participates in the dynamic exchange resulting in a simultaneous spin-state switching of the iron(II) ions in the helicates **X@[Fe$_2$L$_3$]** (Fig. S1). The process requires only the kinetic activation, as the states [HS-LS] and [LS-HS] are thermodynamically identical, and it should be accompanied by large structural rearrangements in contrast to the local exchange HS ⇔ LS that is usually fast in the NMR timescale. For **X@[Fe$_2$L$_3$]**, one may therefore expect to find eight signals that correspond to the state [HS-LS] if the exchange [HS-LS] ⇔ [LS-HS] is fast in the NMR timescale; otherwise, there should be 14 signals in the NMR spectrum. Note that two protons of the bridging phenyl group retain the same chemical shifts upon this exchange, as they are equidistant from the metal ions and thus should be unaffected by the exchange [HS-LS] ⇔ [LS-HS] dynamics (Fig. 3).

The temperature-dependent dynamics in the iron(II) helicates **X@[Fe$_2$L$_3$]** was thus studied in depth through variable-temperature NMR spectroscopy (Fig. 4) carried out on their solutions in methanol-d$_4$ and acetonitrile-d$_3$, allowing a wide temperature range for the experiment. The eight signals that are observed at temperatures of 260 – 320 K broaden significantly upon cooling and most of them disappear at 240 K (Fig. 4a). As the temperature reaches 220 K, however, some of these signals start to reappear but with much higher values of the chemical shifts. No such effects are found for the above two protons of the bridging phenyl group, so their behaviour can be followed over the entire temperature range accessed in the chosen solvents (Fig. 4b).

This behaviour can only be rationalized as follows. Starting from 320 K, the temperature decrease triggers the expected transition from [HS-HS] to [HS-LS], concomitant to the dynamic process [HS-LS] ⇔ [LS-HS] that is fast in the NMR timescale at the temperatures of 260 – 320 K. Consequently, the number of the signals in this temperature range obeys to the highest possible symmetry of the molecule and the chemical shifts adopt average values (Fig. 2b). As the state [HS-LS] with only one HS ion(II) ion (*i.e.* four unpaired electrons per molecule) is less paramagnetic than the state [HS-HS] with two such ions, the chemical shifts in the NMR spectra of the iron(II) helicates **X@[Fe$_2$L$_3$]** decrease with temperature in a different way than expected from the Curie law.[31] Further cooling causes the exchange [HS-LS] ⇔ [LS-HS] to enter an intermediate regime,[33] so the signals broaden till they disappear, owing to extremely large differences in chemical shifts between the protons close to the paramagnetic HS iron(II) ion and those near the diamagnetic LS iron(II) ion. Although it is difficult to identify the temperature at which the signals disappear, the coalescence temperature[33] is close to 210 K thus implying millisecond dynamics at a 600 MHz frequency. The protons of the bridging phenyl moiety have the same chemical shifts in both the states [HS-LS] and [LS-HS], and the corresponding temperature dependence (Fig. 4c) looks exactly like one predicted by Fig. 2b.

At temperatures below 220 K, the exchange [HS-LS] ⇔ [LS-HS] becomes slow in the NMR timescale causing the signals from the protons near the HS iron(II) ion to reappear with strong paramagnetic shifts (Fig. 4a). Their typical Curie behaviour indicates that the transition from [HS-HS] to [HS-LS] is complete below 220 K and only two symmetry-broken states, [HS-LS] and [LS-HS], are populated at these temperatures. The signals of the protons near the LS iron(II) ion fall into a very crowded diamagnetic region of the spectrum thus precluding their detailed analysis owing to the additional broadening caused by low temperatures and to minor admixtures of the free ligand or, possibly, diamagnetic [X@FeL$_3$]-like species.[34]

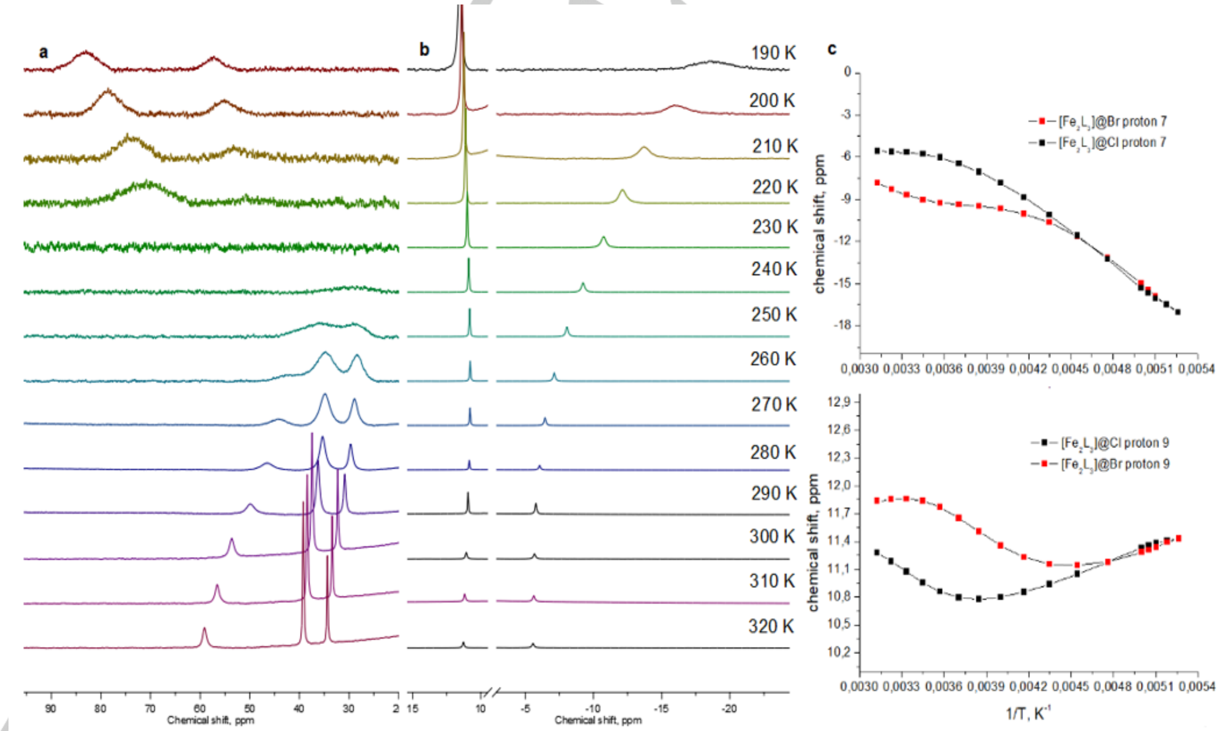

Figure 4. ^{1}H NMR spectra of **Cl@[Fe$_2$L$_3$]** in methanol-d$_4$ at selected temperatures in (a) weak- and (b) strong-field regions. (c) Chemical shifts *vs.* the inverse temperature for the symmetry-invariant protons of the bridging phenyl group (numbering scheme for protons is shown on Fig. 1). For the temperature dependence of other signals and ^{1}H NMR spectra for **Br@[Fe$_2$L$_3$]**, see Figs S2 – S9 of SI.

The signals of the two protons in the bridging phenyl group behave as expected for the process [HS-HS] ⇔ [HS-LS] (Fig. 4c), so they may be used to quantify the observed SCO in the iron(II) helicates **X@[Fe_2L_3]**. Of them, the 'external' proton 9 (Fig. 1) is most suitable for this purpose, as it is the farthest from the metal ions and thus experiences only little interference from different mechanisms of hyperfine interactions.[35] The simultaneous analysis of the temperature dependence of its chemical shift in the solutions of **Cl@[Fe_2L_3]** and **Br@[Fe_2L_3]** in methanol-d_4 and acetonitrile-d_3 under an assumption that the geometry of the complexes in the pure states [HS-HS] and [HS-LS] is rather insensitive to the choice of the halogen anion and the solvent (see SI for details) allowed obtaining the appropriate SCO curves from the variable-temperature NMR spectra (Fig. 5); the thermodynamic parameters (Table S1) being typical of a thermally-induced SCO in similar iron(II) complexes.[36,37] These SCO curves, however, show a strong anion- and solvent-dependence. The difference between the midpoint temperatures for **Cl@[Fe_2L_3]** and **Br@[Fe_2L_3]** in methanol-d_4 is close to the value of 40 K reported previously for the same complexes in the solid state,[24] thus confirming the influence of the encapsulated halogen anion on the SCO behaviour of the helicates to be of an intramolecular origin rather than a result of crystal packing effects. Switching to their acetonitrile solutions allows further modifying this behaviour by shifting the SCO curves by additional 20 to 40 K.

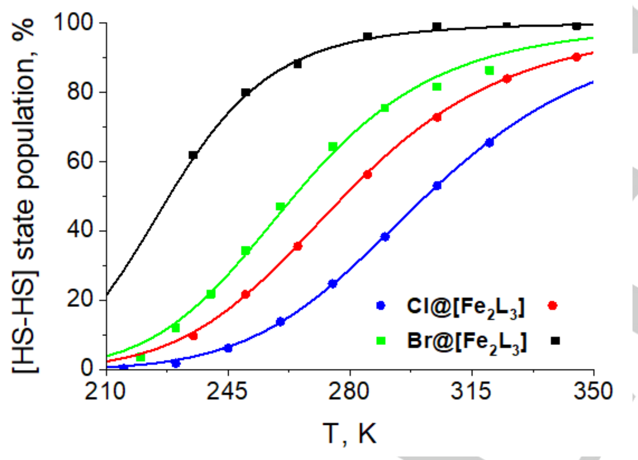

Figure 5. Population of the state [HS-HS] for **X@[Fe_2L_3]** in methanol-d_4 (blue and green dots) and acetonitrile-d_3 (black and red dots) at selected temperatures as obtained from the chemical shifts of the proton 9 of the bridging phenyl group. The lines correspond to the best fit by a regular solution model.[38]

The results obtained here for the iron(II) helicates **X@[Fe_2L_3]** by paramagnetic NMR spectroscopy are the first successful attempt to identify the dynamics of a broken-symmetry state that mixes the states [HS-LS] and [LS-HS] of a binuclear metal complex on a millisecond timescale, opening the way of exploiting two degenerate but distinct states within a molecule as "half-cell" double-dot quantum cellular automata (QCA).[16,17] The combination of two such molecules may result in a conventional class II QCA cell of Robin-Day classification[39] for signal transmission, inversion and logic operations.[40] In contrast to molecular mixed-valence compounds, which make use of Coulomb repulsion as the driving force of the QCA bistability,[41,42] SCO-active species would instead require a careful analysis of their vibronic structure[43] and magnetic interactions between the adjacent cells.[44] Regardless of the nature of individual states of metal ions, if they are envisaged for putative double-dot QCA for information storage and processing, a fast equilibrium [HS-LS] ⇔ [LS-HS] would result in their detrimental scrambling unless it can be slowed down by external factors, which is achievable in the solid state by crystal packing effects.[20,21][24] At the single-molecule level, however, one of the possibilities is to increase the rigidity of the ligand by proper chemical modifications that should increase the kinetic barrier between the states [HS-LS] and [LS-HS], thus resulting in the dynamics that is slow enough to use the SCO-active iron(II) helicates or similar binuclear complexes for data-processing applications.[45]

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Keywords: Spin crossover • Paramagnetic NMR • Broken symmetry • Magnetic properties • Helicates

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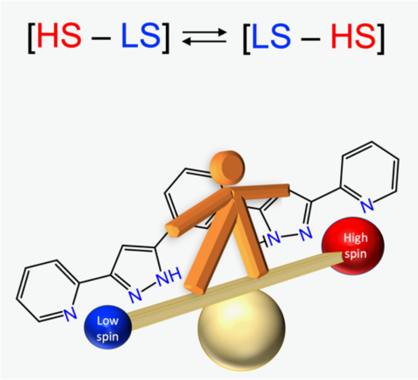

For a binuclear complex with two spin crossover active ions, at least three different states are possible; those include fully high-spin [HS-HS] or low-spin [LS-LS] states that are commonly encountered and a relatively unusual intermediate [HS-LS] state. The binuclear iron(II) helicates show the exchange dynamics [HS-LS] ⇔ [LS-HS] on a millisecond timescale in such a broken-symmetry state.