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Enhancement of spin-crossover cooperativity mediated by lone pair–π interactions and halogen bonding†

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Rational ligand design has allowed the generation of a highly cooperative spin-transition iron(II) complex, an unprecedented result in the family of (2,2′-dipyridylamino/s-triazine)-based SCO materials.

The remarkable switching properties of spin crossover (SCO) materials have driven their utilization in several areas, namely for the development of display and memory devices,[1] electrical and electroluminescent devices,[2] MRI contrast agents,[3] switchable liquid crystals,[4] nanoparticles,[5] and thin films.[6] In most applications, highly cooperative systems, *i.e.* abrupt low-spin (LS) ↔ high-spin (HS) transitions, are required.[6,7]

For about seven years, our group and that of Murray have been concurrently developing a family of dipyridylamino-substituted-triazine that are designed to generate iron(II) SCO compounds.[8–17] The iron(II) systems obtained so far from such ligands solely exhibit gradual spin transition behaviours,[18] indicative of poor cooperativity between the metal centres. Recently, we have discovered that the incorporation of pentafluorophenyl rings on the triazine unit allows the occurrence of very particular supramolecular interactions, *viz.* lone pair–π contacts and halogen bonding, which apparently enhance the cooperative properties of the corresponding SCO complex, *i.e.* $[\mathrm{Fe}(\mathbf{L1}^{\mathbf{F}})_2(\mathrm{NCS})_2]\cdot 2\mathrm{CH_3CN}$ ($\mathbf{L1}^{\mathbf{F}}$ = 2-(*N*,*N*-bis(2-pyridyl)-amino)-4,6-bis(pentafluorophenoxy)-(1,3,5)triazine).[18]

Stimulated by these findings, we have now prepared a new member of this family of ligands, *i.e.* 2-chloro-4-(*N*,*N*-(2-pyridyl)-amino)-6-(pentafluorophenoxy)-(1,3,5)triazine (**L1**, Scheme S1, ESI†), specifically designed to favour various types of intermolecular interactions (*viz.* π–π, lone pair–π and halogen bonding contacts), to promote the cooperative character of its ensuing iron(II) SCO complex. Actually, the compound $[\mathrm{Fe}(\mathbf{L1})_2(\mathrm{NCS})_2]\cdot 2\mathrm{CH_3OH}$ (**1**) herein described shows the highest cooperative comportment achieved to date with a dipyridylamino-substituted-triazine ligand.

Ligand **L1** is easily obtained in two steps by reaction of 2,4,6-trichloro-1,3,5-triazine with 2,2′-dipyridylamine and pentafluorophenol (ESI†). Reaction of two equivalents of **L1** with one equivalent of $\mathrm{Fe(NCS)_2}$ in $\mathrm{MeOH{-}CH_2Cl_2}$ produces $[\mathrm{Fe}(\mathbf{L1})_2(\mathrm{NCS})_2]\cdot 2\mathrm{CH_3OH}$ (**1**) with a yield of 77% (ESI†). **1** crystallizes in the triclinic space group $P\bar{1}$, both at 100 K (LS state, purple crystal) and 200 K (HS state, yellow crystal) (Table S1, ESI†). A representation of the molecular structure of **1** at 100 K (LS **1**) is shown in Fig. 1a. Selected bond distances and angles for LS and HS **1** are listed in Table S2 (ESI†). The octahedral coordination environment of the iron(II) ion in **1** is typical for this type of SCO compounds,[16,17] with two **L1** ligands at the equatorial plane of the octahedron and two *trans* isothiocyanates at the apical positions. At 100 K, the $\mathrm{Fe{-}N_{L1}}$ distances in the range 2.005(3)–2.012(2) Å and $\mathrm{Fe{-}N_{NCS}}$ bond lengths of 1.953(3) Å are typical of a LS iron(II) ion (Table S2, ESI†). At 200 K, these coordination bond lengths increase by *ca.* 0.22 Å for $\mathrm{Fe{-}N_{L1}}$ and *ca.* 0.12 Å for $\mathrm{Fe{-}N_{NCS}}$ (Table S2, ESI†), thus describing a full spin transition as also observed by variable-temperature magnetometry. Indeed, the temperature dependencies of the χT product for bulk **1** (Fig. 2a, χ being the molar paramagnetic susceptibility), evidence an abrupt thermal SCO, from 3.17 $\mathrm{cm^3\ mol^{-1}\ K}$ above 200 K, a typical value for an Fe(II) ion in a HS $S = 2$ state, to *ca.* 0.22–0.20 $\mathrm{cm^3\ mol^{-1}\ K}$ below 50 K, which is indicative of a mostly LS $S = 0$ state.[19] In addition to its abruptness, the process of thermal SCO in **1** exhibits a small but reproducible hysteretic behaviour, the transition being centred at 123 K and 124 K respectively upon cooling and warming (Fig. S1, ESI†). Such strong cooperative behaviour is unique among the family of (2,2′-dipyridylamino/s-triazine)-based SCO compounds reported so far. Hence the SCO properties of **1** are compared to

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† Electronic supplementary information (ESI) available: Experimental procedures, crystallographic data and figures showing the different supramolecular bonds present in the solid-state structure of **1**. CCDC 968835 (LS **1**) and 968836 (HS **1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc48334g

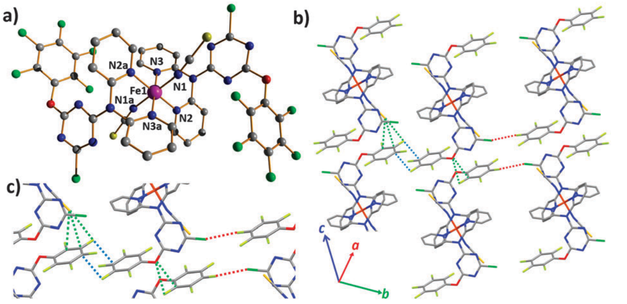

Fig. 1 (a) Molecular structure of **1** (LS state, determined at 100 K) with partial atom-numbering scheme. The H atoms and the lattice methanol molecules are not shown for clarity. Symmetry operation: a, $1 - x$, $1 - y$, $1 - z$. (b and c) Supramolecular framework observed in the solid-state structure of **1**, generated by π–π, lone pair–π and halogen bonding interactions (blue, green and red dotted lines, respectively), all involving the pentafluorophenyl ring.

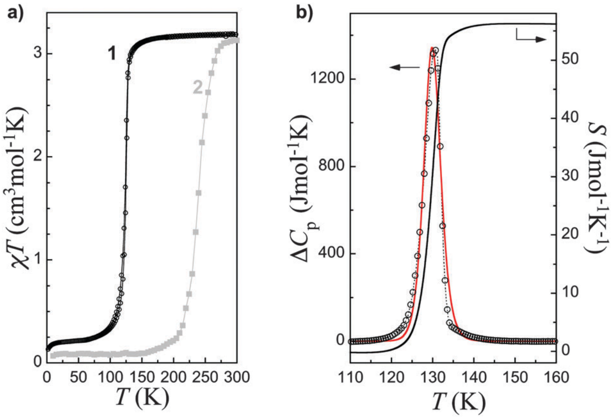

Fig. 2 (a) χT *vs.* T plot for **1** (empty black circles) and **2** (full grey squares).[18] Lines are only guides to the eye. (b) Excess molar heat capacities and the excess entropy associated with the SCO in **1**. The full red line is a fit to the domain model of Sorai (see ESI† and ref. 21) with $n = 14.2$.

those of [Fe(**L1**^{F})$_2$(NCS)$_2$]·2CH$_3$CN (**2**) (whose ligand **L1**^{F} includes two pentafluoro rings instead of one for **L1**), which already displayed an improved cooperative behaviour with respect to other similar compounds;[18] the significantly smaller ΔT_{80} value (the temperature range within which 80% of the transition occurs) of *ca.* 8 K for **1** ($\Delta T_{80} \approx 50$ K for **2**[18]) is a rough measure of its increased cooperative character (Fig. 2). This higher cooperativity is confirmed by Differential Scanning Calorimetry (DSC). The derived molar heat capacity of **1** at constant pressure, *i.e.* C_p, exhibits a sharp anomaly between 117 and 145 K, culminating at 130 K and with an onset at 125 K. This feature is in perfect agreement with the magnetic data (Fig. S2, ESI†), and is thus due to the SCO process in **1**. Both the associated excess enthalpy and entropy of respectively 7.29 kJ mol^{-1} and 56.3 J mol^{-1} K^{-1} are large for a SCO at these relatively low temperatures (Fig. 2b and Fig. S3, ESI†), and are ascribed to its cooperative character.[20] Fitting the excess heat capacity of **1** to Sorai's domain model[21] actually results in a high number of interacting molecules per domain, *i.e.* $n = 14.2$ (red line in Fig. 2b, see ESI† for details), which is characteristic of a cooperative SCO. This value is more than twice that of **2**, namely $n = 6.2$.[18] Importantly, the excess entropy is well above the purely electronic component, $R\ln 5$, indicating an important role played by the coupling of the electronic transition with lattice phonons. This enhanced cooperative behaviour of **1** most likely arises from packing features involving intermolecular interactions.

The octahedral distortion parameters Σ and Φ gauge the magnitude of the deformation of the coordination geometry relative to a perfect octahedron (for which $\Sigma = \Phi = 0$).[7,22,23] For LS **1**, $\Sigma = 32$ and $\Phi = 42$, and their values increase to respectively 39 and 64 upon LS → HS transition (Table S3, ESI†). The corresponding $\Delta\Sigma$ and $\Delta\Phi$ values of respectively 7 and 22 thus reflect a distortion of the O_h geometry, although they are smaller than those of the less cooperative compound **2** (respectively 11 and 36).[18] This observation disagrees with literature suggestions that associate a large distortion with a high cooperativity between the transiting centres.[7] The $\Delta\Sigma$ and $\Delta\Phi$ data observed for **1** and **2** rather indicate that low distortion values may also be associated with a cooperative behaviour, as in other *trans*-[Fe(L)$_2$(NCS)$_2$] compounds (where L is an alpha-diimine ligand) with strong intermolecular interactions.[24] This can be explained by the way the local distortion of the coordination sphere is affected by its environment; accordingly, other structural aspects such as intra- and intermolecular interactions can play an important role regarding cooperativity. Indeed, low $\Delta\Sigma$ and $\Delta\Phi$ values can indicate a lack of freedom for the iron(II) centres to undergo the geometry distortion that takes place upon the t_{2g}^6 (LS) → $e_g^2t_{2g}^4$ (HS) transition, possibly as the result of steric constraints arising from a more "rigid" solid-state packing of the molecules. In fact, such a situation is expected to allow an efficient communication of the SCO distortion to adjacent iron(II) ions, giving rise to an abrupt transition (with possibly hysteresis).

The crystal packing of **1** corroborates the above assumptions. Ligand **L1** has been designed on the basis of the earlier results achieved with ligand **L1**^{F},[18] with the objective to favour a better interaction between the iron(II) ions in the solid state (and thus increase the cooperativity). Therefore, one of the two pentafluoro units of **L1**^{F} has not been introduced in **L1**. Consequently, **L1** is less bulky than **L1**^{F} (which, in principle, will endorse a closer packing of the metal complexes) but still possesses a fluorinated phenyl ring, which is of paramount importance for the generation of supramolecular interactions (that may enhance cooperativity).[18] Careful analysis of the crystal structure of **1** reveals that, as anticipated, the pentafluorophenyl unit plays a crucial role in the close association of the molecules in the lattice (as observed for **2**,[18] but to a lesser extent). Indeed, this fluorinated arene is involved in an intricate network of noncovalent bonds that produces a 3D framework (Fig. 1b).

First, molecules of **1** are connected *via* parallel-displaced π–π interactions characterized by short F···C contact distances of 3.076(6) Å for LS **1** and 3.205(6) Å for HS **1** (Fig. S4, ESI†). Since the sum of the van der Waals radii (vdW) of F and C is 3.17 Å, the distances above are illustrative of a strong interaction. The pentafluorophenyl ring strongly interacts with a neighbouring isothiocyanate sulfur atom (Fig. S5, ESI†). This lone pair–π interaction is defined by S···C and S···F contact distances of respectively 3.347(6)–3.382(5) Å and 3.269(4) Å (for LS **1**), which are below the corresponding sums of vdW radii, namely 3.5 Å and 3.27 Å. An additional lone pair–π interaction is observed between the pentafluorophenyl ring and the ligand oxygen atom from an adjacent complex (Fig. S6, ESI†). The consequent O···F and O···C contact distances of respectively 2.922(4) Å and 3.085(6) Å (for LS **1**), describing this supramolecular bond, again are clearly below the corresponding sums of vdW radii (namely 2.99 and 3.22 Å), thus characterizing a strong interaction. Lastly, the pentafluorophenyl group is involved in a very strong halogen bond (Fig. S7, ESI†), as evidenced by the short F···Cl distances of 2.969(4) Å (LS **1**) and 3.013(4) Å (HS **1**), which are notably below the sum of vdW of F and Cl (*i.e.* 3.22 Å). This network of noncovalent bonds generated by the pentafluorophenyl ring produces a compact and rigid molecular packing, which creates efficient paths for the propagation of the local distortion due to the SCO process at the iron(II) ions, resulting in a strongly cooperative spin crossover (abrupt transition with hysteresis loop).

The origin of the different cooperative behaviours observed for **1** and **2**,[18] despite the similar crystal packings and supramolecular interactions, can be clarified *via* examination of the distinct Fe···Fe separation distances in the lattice, their variation upon spin transition and the dimensionality of the strong noncovalent interactions (Fig. S8 and S9, Tables S4 and S5, ESI†). For **1**, the distinct Fe···Fe separation distances found along the three crystallographic axes equal to 9.084 (*a* axis), 10.766 (*b* axis) and 12.658 Å (*c* axis) for the LS state, and the highest variation (*i.e.* distance increase by 3.7%) upon LS → HS transition is observed in the *b* direction (Table S4, ESI†). For **2**, the corresponding values are 8.350, 11.358 and 15.689 Å (LS **2**), with the greatest variation (*i.e.* 3.5%) in the *a* direction (Table S5, ESI†), for which the Fe···Fe separation distance is the shortest. Accordingly, a good cooperativity is likely effective within the iron(II) supramolecular chain formed along the crystallographic *a* axis in **2**,[18] but the communication between these chains is comparatively poorer, which can justify the limited cooperativity exhibited by **2**. Indeed, the importance of interchain interactions for the occurrence of highly cooperative SCO systems has been highlighted in triazole-based coordination chains.[4,25] In contrast, the corresponding chains in **1** are clearly interacting with each other in the *b* direction (Fig. S8c, ESI†), while the Fe···Fe separation in the *c* direction is significantly shorter for **1**, compared to **2** (12.658 *vs.* 15.689 Å in the LS state, Tables S4 and S5, ESI†). Overall, the denser packing of the transiting centres (for instance, the sum of the three Fe···Fe separation distances is 32.508 Å for LS **1** while it is 35.397 Å for LS **2**; Tables S4 and S5, ESI†), and the multidimensional set of supramolecular interactions in **1** justifies its greater cooperative behaviour.

In conclusion, the judicious (apparently minor) modification of a ligand (*i.e.* from **L1^F** to **L1**) has allowed the preparation of a SCO iron(II) compound with a strongly enhanced cooperativity. Indeed, while the earlier compound **2** exhibits a gradual SCO (ΔT_{80} = 50 K), **1** displays an abrupt spin transition (ΔT_{80} = 8 K), with a small hysteresis loop of 1 K. This drastically distinct behaviour is ascribed to a better communication between the transiting metal centres; for instance, the 1D chains of Fe(II) ions observed in the crystal packing (*a* direction) of both complexes are strongly interacting with each other in **1** in the *b* direction (particularly *via* strong Cl···F halogen bonds), in contrast to **2**. Current investigation is aimed at designing a new ligand that would favour the interaction of the Fe(II) chains (along *a*) both in the *b* and *c* directions, which would further improve the strength and multidirectionality of the supramolecular interactions.

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