Dalton Transactions

PAPER

Check for updates

Cite this: *Dalton Trans.*, 2019, **48**, 17014

Received 13th August 2019, Accepted 22nd October 2019 DOI: 10.1039/c9dt03285a

rsc.li/dalton

Introduction

Responsive switchable materials have always been given widespread attention in the search for new advanced materials with potential applications. One outstanding example of molecular switching is featured by the SCO behaviour displayed by coordination complexes centred on transition metals with $3d^4-3d^7$ electronic configurations. Among these, the most investigated molecular materials are pseudo-octahedral iron(π)

^bInstituto de Ciencia Molecular (ICMol), Universitat de València, C/Catedrático José Beltrán Martínez 2, 46980 Paterna, Valencia, Spain. E-mail: jose.a.real@uv.es

^cDepartamento de Física Aplicada, Universitat Politècnica de València, Camino de Vera s/n, E-46022 Valencia, Spain

^dCollege of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266510, PR China



Wenlong Lan, () ‡^a Francisco Javier Valverde-Muñoz, ‡^b Yong Dou,^a Xiaoyun Hao,^a M. Carmen Muñoz, () ^c Zhen Zhou,^a Hui Liu,^a Qingyun Liu,^d José Antonio Real () *^b and Daopeng Zhang () *^a

Rare loop-like isostructural one-dimensional coordination polymer (1D-CP) systems formulated as $\{Fe(DPIP)_2(NCSe)_2\}_n \cdot 4DMF$ (1) and $\{Fe(DPIP)_2(NCSe)_2\}_n \cdot 4DMF$ (2) were obtained by self-assembling Fe^{II} and pseudohalide NCX⁻(X = S, Se) ions in presence of the V-shaped bidentate bridging ligand, namely, *N,N'*-dipyridin-4-ylisophthalamide (DPIP), and were characterized by elemental analysis, IR spectroscopy, TGA, single crystal X-ray diffraction and powder X-ray diffraction. The magnetic studies show that complex 2 undergoes a complete thermally induced spin crossover (SCO) behavior centered at $T_{1/2}$ = 120 K with *ca.* 5 K thermal hysteresis loop and light-induced excited spin state trapping effect (LIESST) with T_{LIESST} = 65 K. However, either the homologous X = S (1) or the desolvated form of complex 2 is high spin at all temperatures, proving further the concerted synergy for the SCO of 2 between the intrinsic ligand field and that indirectly induced *via* hydrogen bond interaction. The current results provide valuable information for the design of new 1D SCO systems *via* the rational control of the cooperated effects derived from the intramolecular coordination bond and the intermolecular supramolecular interactions.

complexes, because they offer a reversible drastic change between the paramagnetic high spin S = 2 (HS, $t_{2g}{}^4e_g{}^2$) and the diamagnetic low-spin S = 0 (LS, $t_{2g}{}^6e_g{}^0$) electronic states. The transformation between the two types of the spin states can be driven by external stimuli (temperature, pressure, light, and analytes), accompanied by concomitant drastic changes of magnetic, optical (colour) and electrical properties as well as drastic responses in structure, which provide an important set of useful outputs.¹

Since the seminal work on the iconic mononuclear complexes $[Fe(phen)_2(NCS)_2]$ and $[Fe(2,2'-bipy)_2(NCS)_2]$,^{2,3} a great deal of $[Fe^{II}(L)_p(NCX)_2]$ -based (X = S, Se) SCO materials have been reported during the past sixty years.^{1d} The most prolific series corresponds to mononuclear complexes derived from [phen/2,2'-bipy]-type α -diimine chelate ligands, which often favour the *cis* conformation of the ligands.⁴ Inspired by the same idea, relevant series of related bipyrimidine-,^{5,6} pyrazolate-,^{7–9} triazolate-,¹⁰ pyridine-¹¹ and 4,4'-bipyridinebridged¹²⁻¹⁴ Fe^{II} dinuclear SCO complexes containing ancillary imine ligands and NCX⁻ groups have also been reported.¹⁵⁻¹⁷ The use of bis-monodentate pyridine-like bridging-ligands has afforded a much more reduced but relevant series of trans- $[Fe^{II}(\mu-L)_2(NCX)_2]_n$ 2D-SCO compounds,^{18–23} some of which constitute excellent examples of porous coordination polymers



View Article Online

^aCollege of Chemical and Chemical Engineering, Shandong University of Technology, Zibo 255049, PR China. E-mail: dpzhang73@126.com

[†]Electronic supplementary information (ESI) available: Some important structural parameters for complex 1. The representative cell packing diagram for complexes 1 and 2. The magnetic property for complex 1. The TGA analysis for complex 2. The calculated and measured pattern of PXRD and the IR spectra for complexes 1 and 2. Perspective views of the packing of complex 2. CCDC 1897988–1897990. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt03285a

[‡]These two authors contributed equally.



Scheme 1 The formula of the bridging ligand DPIP.

(CPs) made up of interpenetrated 2D layers.^{24–29} Even less common is the family of 1D-SCO CPs generically formulated as $[Fe^{II}(L)_p(NCX)_2]_n$ (p = 1, 2). The use of chelate bis-bidentate bridging ligands based on 4,6-bis(dipyridylamino)-3,4,5triazine^{30–32} and tris-bidentate α -diimine ligand 1,4,5,8,9,12hexaazatriphenylene (HAT)³³ has provided a series of SCO chains (p = 1) with NCX⁻ *trans*- and *cis*-coordinated Fe^{II} centres, respectively. Interestingly, the HAT derivative is an uncommon example of the chiral 1D-SCO complex. A rare example of 1D-SCO [Fe^{II}(L)(NCX)_2]_n, exhibiting the [FeN₅S] coordination sphere and based on the tridentate ligand L tris-(2-pyridyl)metoxymethane has recently been reported.³⁴

To the best of our knowledge, only two 1D systems with formula *trans*-[Fe^{II}(μ -L)₂(NCX)₂]_n, showing SCO described so far, have been reported by Tao *et al.* One is based on the bridging ligand L = 5,6-di(pyridin-4-yl)-1,2,3,4-tetrahydropyrazine formed *in situ*. Its thiocyanate derivative (X = S) displays an incomplete (*ca.* 50%) thermally induced SCO behavior.^{35a} The second example is afforded by the bridging ligand 4,4'-dipyridyl disulfide (dpds). In this recent study, Tao *et al.* investigated NCX⁻ anions with X = C(CN)₂, BH₃ and Se. The two former derivatives display complete SCO, while the selenocianate compound is HS at all temperatures.^{35b}

As a further step in this line, herein, we report a new rare loop-like 1D system formulated as $\{Fe(DPIP)_2(NCX)_2\}_n \cdot 4DMF$ (X = S (1), Se(2)), where DPIP is the V-shaped bridging ligand L = N,N'-dipyridin-4-ylisophthalamide (Scheme 1). Interestingly, while 1 and the desolvated form of 2 (2*) are fully paramagnetic in the whole temperature range, the parent solvated form 2 displays a complete thermal- and photo-induced SCO behavior, showing the concerted synergy between the intrinsic ligand field stemming from the DPIP/NCSe and that indirectly induced through interactions such as intermolecular interactions from the guest solvent molecules.

Experimental section

Elemental analyses of carbon, hydrogen, and nitrogen were performed using an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000–400 cm⁻¹ region. Variabletemperature magnetic susceptibility data were recorded for single crystals of **1** and **2** (10–20 mg) at the scanning rate of 0.5 K min⁻¹ using a Quantum Design MPMS2 SQUID susceptometer equipped with a 5.5 T magnet, operating at 1 T and temperatures in the range 300–10 K. Experimental susceptibilities were corrected from diamagnetism of the constituent atoms by the use of Pascal's constants. Powder X-ray measurements were performed on a PANalytical Empyrean X-ray powder diffractometer (monochromatic MoK α radiation). Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851e instrument in the 298–1290 K temperature range under a nitrogen atmosphere at a rate of 10 K min⁻¹.

General procedures and materials

All the reactions were performed at room temperature under an air atmosphere and all the chemicals and solvents used were of reagent grade without further purification. FeCl₂, KSCN and KSeCN were purchased from commercial sources. The ligand N,N'-dipyridin-4-ylisophthalamide (DPIP) was prepared according to the reported method.³⁶

Synthesis of complexes 1 and 2. These two complexes were prepared using a three-layer diffusion method. The ligand DPIP (0.2 mmol, 63.6 mg) dissolved in 5 mL DMF was laid in the bottom of a tube, to which a mixture solvent of DMF and MeOH in a ratio of 1:1 was carefully added. Then, the methanol solution containing Fe(SCN)₂ (0.1 mmol) or Fe(SeCN)₂ (0.1 mmol), which was freshly prepared by filtering the mixture of KSCN (0.2 mmol, 19.4 mg) or KSeCN (0.2 mmol, 28.8 mg) and FeCl₂ (0.1 mmol, 12.6 mg) in methanol, was carefully added to the top of the mixed solvent layer. Single crystals suitable for X-ray diffraction were obtained about two weeks later, which were then collected by filtration and dried in air giving the yield about 50%.

Anal. calcd for $C_{50}H_{56}FeN_{14}O_8S_2$ (1). C, 54.54; H, 5.13; N, 17.81. Found: C, 54.48; H, 5.01; N, 17.95. Main IR bands (cm⁻¹): 2056 (s, ν_{SCN}), 1680 (s, $\nu_{C=O}$), 3074 (m, ν_{N-H}).

Anal. calcd for $C_{50}H_{56}FeN_{14}O_8Se_2$ (2). C, 50.26; H, 4.72; N, 16.41. Found: C, 50.12; H, 4.61; N, 16.56. Main IR bands (cm⁻¹): 2056 (s, ν_{SCN}), 1680 (s, $\nu_{C=O}$), 3075 (m, ν_{N-H}).

X-ray data collection and structure refinement. Single crystals of the two complexes for the X-ray diffraction analysis with suitable dimensions, which were selected from the mother liquor for direct measurement, were mounted on a glass rod, and the crystal data were collected on a Bruker SMART CCD diffractometer using a MoK α sealed tube (λ = 0.71073 Å) at 293 K and 100 K, using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-2014 program package. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All non-hydrogen atoms were refined with anisotropic displacement coefficients, assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C) and their coordinates were allowed to ride on their respective carbons. CCDC 1897988-1897990 for complexes 1, 2-HS (293 K) and 2-LS (100 K) are included in the supplementary crystallographic data for this paper.[†] Details of the crystal para-

Table 1	Details of the crysta	parameters,	data collection,	and refinement fo	r complexes 1	and 2
---------	-----------------------	-------------	------------------	-------------------	----------------------	-------

	1 (293 K)	2- HS (293 K)	2-LS(100 K)
Formula	C ₅₀ H ₅₆ FeN ₁₄ O ₈ S ₂	C ₅₀ H ₅₆ FeN ₁₄ O ₈ Se ₂	C ₅₀ H ₅₆ FeN ₁₄ O ₈ Se ₂
FW	1101.06	1194.86	1194.86
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
a(A)	25.3667(12)	25.240(2)	25.1307(14)
$b(\dot{A})$	14.6482(5)	14.5659(8)	14.3256(8)
$c(\dot{A})$	17.1303(9)	17.2422(14)	17.0759(11)
α (Å)	90	90	90
β (Å)	118.455(6)	117.624(10)	118.119(8)
γ (Å)	90	90	90
$V(Å^3)$	5596.2(4)	5616.3(7)	5421.9(6)
Z	4	4	4
$\rho_{\rm calcd} ({\rm g}{\rm cm}^{-3})$	1.307	1.413	1.464
$\mu (\text{mm}^{-1})$	0.407	1.628	1.686
F(000)	2304	2448	2448
$\theta(\circ)$	3.07 to 25.01	3.07 to 25.01	3.10 to 25.01
Unique reflections	4860	4935	4758
Reflections $(I > 2\sigma)$	3116	3497	3836
GOF on F^2	1.035	1.048	1.050
$R_1[I > 2\sigma(I)]$	0.0783	0.0629	0.0569
wR_2 (all data)	0.2336	0.1845	0.1463
$\rho_{\rm max}/\rho_{\rm min}$ (e Å ⁻³)	0.848/-0.659	1.521 / -0.751	1.615 / -0.976

meters, data collection, and refinement are summarized in Table 2 Selected bond lengths (Å) and angles (°) for complex 2 Table 1.

Synthesis and general characterization

The title compounds $\{Fe(DPIP)_2(NCX)_2\}_n \cdot 4DMF X = S(1)$ and Se (2) were synthesized by a three-layer slow diffusion method using a DMF solution of DPIP (bottom layer) and a methanol solution of Fe(NCX)₂ (top layer) in stoichiometric molar ratio 2:1, for which the two solutions were separated by a 1:1 mixture of DMF/Methanol. Single crystal X-ray analysis for both complexes was performed at 293 K. Furthermore, for the sake of fully disclosing its LS state, the crystal structure analysis for 2 was also performed at 100 K (based-on the magnetic property). Both complexes were characterized by IR spectroscopy and X-ray Powder diffraction (XRPD). The IR spectra (Fig. S1, ESI[†]) display the presence of a sharp peak characteristic of the stretching mode $C \equiv N$ at about 2056 cm⁻¹ characteristic of the NCX⁻ (X = S, and Se) groups. The peak at about 1680 cm⁻¹ can be assigned to the stretching vibrations of the C=O amide group. XRPD (Fig. S2 and S3[†]) confirmed that the obtained single crystals and the bulk materials correspond to the same crystalline phase. Furthermore, the thermal analysis confirmed the loss of the four DMF in one sharp step at about 450 K (Fig. S4†).

Crystal structure

Selected bond lengths and angles for complexes 1 and 2 are given in Table S1 (ESI)[†] and Table 2, respectively. Compounds 1 and 2 are isostructural and crystallize in the monoclinic C2/cspace group. Fig. 1 displays the coordination environment of the crystallographically unique Fe^{II} centre together with the corresponding atom numbering. The Fe^{II} site is situated at the centre of a slightly distorted [FeN₆] octahedron, in which the four equatorial positions are occupied by four N atoms from

	2(HS 293 K)		2*(LS 100 K)
Fe(1)-N(1)	2.132(4)	Fe(1)-N(1)	1.960(4)
Fe(1)-N(2)	2.215(4)	Fe(1) - N(2)	2.013(4)
Fe(1)-N(1)#1	2.132(4)	Fe(1)-N(1)#1	1.960(4)
Fe(1)-N(2)#1	2.215(4)	Fe(1)-N(2)#1	2.013(4)
Fe(1)-N(5)#2	2.196(4)	Fe(1)-N(5)#2	2.024(4)
Fe(1)–N(5)#3	2.196(4)	Fe(1)–N(5)#3	2.024(4)
N(1)-Fe(1)-N(5)#2	89.39(15)	N(1)-Fe(1)-N(5)#2	88.09(15)
N(1)#1-Fe(1)-N(5)#2	94.45(15)	N(1)#1-Fe(1)-N(5)#2	89.40(15)
N(1) - Fe(1) - N(5)#3	94.45(15)	N(1) - Fe(1) - N(5)#3	89.40(15)
N(1)#1-Fe(1)-N(5)#3	89.39(15)	N(1)#1-Fe(1)-N(5)#3	88.09(15)
N(5)#2-Fe(1)-N(5)#3	90.2(2)	N(5)#2-Fe(1)-N(5)#3	89.9(2)
N(1) - Fe(1) - N(2) # 1	87.04(15)	N(1) - Fe(1) - N(2) # 1	92.83(15)
N(1)#1-Fe(1)-N(2)#1	89.08(16)	N(1)#1-Fe(1)-N(2)#1	89.69(15)
N(5)#3-Fe(1)-N(2)#1	90.58(14)	N(5)#3-Fe(1)-N(2)#1	89.9(2)
N(1) - Fe(1) - N(2)	89.08(16)	N(1) - Fe(1) - N(2)	89.69(15)
N(1)#1-Fe(1)-N(2)	87.04(15)	N(1)#1-Fe(1)-N(2)	92.83(15)
N(5)#2-Fe(1)-N(2)	90.58(14)	N(5)#2-Fe(1)-N(2)	90.46(14)
N(2)#1-Fe(1)-N(2)	88.9(2)	N(2)#1-Fe(1)-N(2)	89.3(2)
Symmetry codes: 2: # 1/2: #4 r y = 1 z 2*:	(1 - x, y, -z + y)	$\frac{1}{2}; \frac{\#2}{2}x, y + 1, z; \frac{\#3}{2} - \frac{\pi}{2}$	-x, y + 1, -z +

1, z; #4 x, y + 1, z.

two independent pyridinecarboxamido ligands and the two axial trans N atoms belong to the N atoms of the XCN groups. At 293 K, the Fe-Naxial bond lengths of 2.121(6) and 2.132(4) Å for 1 and 2, respectively, are slightly shorter than the Fe-N_{equatorial} bond lengths, 2.207(5), 2.234(5) (1) and 2.215(4), 2.196(4) (2) Å, indicating a slightly compressed octahedral geometry for the Fe^{II} ion. At 100 K, the average Fe-N bond length for complex 2, equal to 1.999(4) Å, is 0.182 Å shorter than that at 293 K (2.181(4) Å). This significant change (over 9% reduction in bond lengths), consistent with the magnetic behaviour of 2 (vide infra), is attributed to the occurrence of a



Fig. 1 ORTEP representation of the coordination environment of complex 2 (100 K). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

practically complete spin conversion from HS to LS of the Fe^{II}. This spin conversion also affects the coordination bond angles around the Fe^{II} centre. Indeed, the parameter \sum Fe, corresponding to deviations from the ideal octahedron of the 12 "*cis*" bond angles $(\sum_{i=1}^{12} |\theta i - 90^\circ|)$, is 20.34°at 293 K and decreases significantly down to 12.66° at 100 K, which is consistent with the more regular octahedral geometry typically observed for the LS state of the Fe^{II}.

In complexes **1** and **2**, the two independent V-shaped equatorial DPIP ligands act as bridges connecting the Fe^{II} centres, thus generating a loop-like 1D chain running along the *b* axis (Fig. 2a and b). For **2**, the intra-chain Fe–Fe distance is



Fig. 2 Side (a) and top (b) views of the looped-like 1D chain structure of 1 and 2. (c) Hydrogen bonds (red-white broken lines) between the four DMF molecules and the corresponding amido groups. The DMF molecules have been highlighted with black bonds.

14.326(2) Å in the LS state and slightly increases until 14.566(1) Å in the HS sate. The chains superpose perfectly along the *a* axis, defining layers that stack along the *c* axis. The shortest Fe…Fe distances between adjacent layers are 9.035(1), 12.40(6), 14.464(1) and 18.70(4) Å in the LS structure and change, serially, to 9.039(1), 12.39(8), 14.571(1) and 18.85(5) Å in the HS state (see Fig. S5[†]). In both complexes, the pseudosquare grids are stabilized by 4 strong hydrogen bond interactions established between the amido N atoms and the O atoms of the 4 DMF molecules, which block the windows of the grids (Fig. 2c). The comparative strong intermolecular N-H…O hydrogen bond interactions are with the D…A distances 2.911 and 2.879 Å and the <DHA angles 164.1 and 164.08° (Fig. 2c). In addition, there also exists weak intermolecular C-H…N interactions between the benzene moiety and the N atom of the XCN group, especially in LS state of 2 (Fig. S6[†]).

Magnetic and photomagnetic properties

The thermal dependence of $\chi_{\rm M}$ T product, $\chi_{\rm M}$ being the magnetic susceptibility per mole of the compound and *T* the temperature, for samples of **1** and **2** constituted of single crystals were measured under an external magnetic field of 2000 Oe in the range of 10–300 K at the scan temperature rate 1 K min⁻¹ (Fig. 3). For complex **1**, the room temperature $\chi_{\rm M}T$ value is 3.75 cm³ K mol⁻¹, consistent with the typical value of Fe^{II} in the HS state characterised by relevant orbital contribution. (Fig. S7†) Upon cooling, the $\chi_{\rm M}T$ value remains almost constant until about 30 K, indicating that the Fe^{II} centres are HS in the whole range of temperatures.

Similarly, the $\chi_M T$ value is 3.72 cm³ K mol⁻¹ in the temperature range 300–150 K for 2 (Fig. 3). However, below this temperature, $\chi_M T$ drops sharply down to 0.15 cm³ K mol⁻¹ at 50 K, showing the occurrence of a complete SCO from the HS state to the LS state. In the heating mode, $\chi_M T$ vs. T plot does not



Fig. 3 Magnetic and photomagnetic properties of **2**. (inset) Pictures of one single crystal of **2** in the HS state (yellow) and LS state (dark red-violet).

Paper

match that of the cooling mode, thereby defining a narrow hysteresis *ca.* 5 K wide. The characteristic equilibrium temperatures, $T_{1/2}$, at which the molar fraction of HS and LS centres is equal to 0.5 are *ca.* 118.0 K and 123.0 K for the cooling and heating modes, respectively. This relative low equilibrium temperature (average 120 K) for the SeCN⁻ derivative justifies the lack of SCO for the SCN⁻ counterpart, since it is wellknown that $T_{1/2}$ values are usually 50–100 K higher for homologous SeCN⁻ derivatives corroborating the stronger ligand-field strength induced by the latter. Interestingly, the crystals change from light yellow in the HS state to deep red in the LS state (see inset in Fig. 3).

The SCO behaviour of **2** has been simulated reasonably well (Fig. 4) using the regular solution model expressed in eqn (1):³⁷

$$\ln\left[\frac{1-\gamma_{\rm HS}}{\gamma_{\rm HS}-\gamma_{\rm HS}^{\rm R}}\right] = \frac{\Delta H + \Gamma(1+\gamma_{\rm HS}^{\rm R}-2\gamma_{\rm HS})}{RT} - \frac{\Delta S}{R} \tag{1}$$

where ΔH , ΔS and Γ are the enthalpy, the entropy variations and the parameter accounting for the cooperative nature of the spin conversion, respectively. The molar HS fraction, γ_{HS} , is determined from the magnetic susceptibility through eqn (2):

$$\gamma_{\rm HS} = [(\chi_{\rm M}T) - (\chi_{\rm M}T)_{\rm LS}] / [(\chi_{\rm MT})_{\rm HS} - (\chi_{\rm MT})_{\rm LS}]$$
(2)

The molar fraction $(\gamma_{HS})^{R}$ accounts for the inactive species that remain HS at low temperatures and is calculated as follows (eqn (3)):

$$(\gamma_{\rm HS})^{\rm R} = (\chi_{\rm M}T)^{\rm R} / [(\chi_{\rm M}T)_{\rm HS}]$$
(3)

 $(\chi_{\rm M}T)$ is the value of $\chi_{\rm M}T$ at any temperature, $(\chi_{\rm M}T)_{\rm HS}$ is the $\chi_{\rm M}T$ value of the pure HS state $(T \to \infty)$, $(\chi_{\rm M}T)_{\rm LS} \approx 0$ is the $\chi_{\rm M}T$ value of the pure LS state and $(\chi_{\rm M}T)^{\rm R}$ represents the residual $\chi_{\rm M}T$ value due to HS species blocked at low temperatures. The simulation of the SCO curve gives the typical thermodynamic parameters $\Delta H = 7.92$ kJ mol⁻¹, $\Gamma = 2.4$ kJ mol⁻¹ and $\Delta S = 66$ J K⁻¹ mol⁻¹, using the values $(\chi_{\rm M}T)^{\rm R} = 0.26$ cm³ K mol⁻¹ (at 80 K) and $(\chi_{\rm M}T)_{\rm HS} = 3.72$ cm³ K mol⁻¹ extracted from the magnetic data.



Fig. 4 The simulation for the magnetic property of complex 2.

In addition to strong thermochromism (inset Fig. 3), compound 2 displays a light-induced excited spin state trapping effect (LIESST) at a low temperature.³⁸ The photo-generation of the metastable HS* state was performed at 10 K, irradiating the red light (λ = 633 nm) with a microcrystalline sample of 2 (ca.3 mg) (Fig. 3). At 10 K, $\chi_{\rm M}T$ is ca. 0.08 cm³ K mol⁻¹ and increases sharply upon irradiation and reaches a $\chi_{M}T$ saturation value of about 3.00 cm³ K mol⁻¹ in less than one hour. Then, the temperature was increased at a rate of 0.3 K min⁻¹ after the light irradiation was switched off. The $\chi_M T$ value continued to slowly increase to a maximum value of *ca.* 3.56 cm³ K mol⁻¹ up to a temperature of about 57 K, showing that the light-induced population of the HS* state is complete. As the temperatures increased further from 57 K, the $\chi_{M}T$ value dropped sharply, attaining a value of about 0.26 cm³ K mol⁻¹ at ca. 75 K, indicative of a practically complete relaxation from the metastable HS* to LS. The characteristic T_{LIESST} temperature obtained from $\partial \chi_{\rm M} T / \partial T$ in the 10–100 K interval is *ca*. 67.5 K, perfectly agreeing with the correlation line $T_{\text{LIESST}} = T_0$ $-0.3T_{1/2}$ with $T_0 = 100$ K, being typical for the less rigid coordination center [Fe^{II}N₆] constituted of monodentate ligands with small geometrical constraints, as it is the present case.³⁹

The strong H-bonding interactions between the loop-like 1D host entity and the co-crystallized DMF guest solvent molecules is denoted by the relatively high temperature, ca. 450 K, from which the DMF molecules are released in a sharp step giving 2^{desolv} (see TGA in Fig. S4[†]). The desolvated phase partly loses crystallinity, which is clearly observed when comparing the respective X-ray powder diffraction patterns (see Fig. S8[†]), which prevented the structural analysis of 2^{desolv}. The perfect consistency of the elemental analysis, IR spectra and magnetic data support the idea that the chains remain despite the loss of the DMF molecules. However, it seems obvious that in 2^{desolv}, the packing of the chains must change drastically with respect to that of 2 since the thermal dependence of $\chi_{M}T$ for 2^{desolv} (Fig. 3) corresponds to a typical HS behavior at any temperature, thereby showing the essential role played by the DMF molecules in the stabilization of the LS state of 2 and, consequently, in the observation of SCO.

Discussion on the cooperative character in the CP

As described above, the Fe^{II} centres remain HS in the S derivative (1) irrespective of the temperature, while the Se counterpart (2) displays a 5 K wide hysteretic SCO behaviour centred at 120.5 K and complete LIESST effect. The paramagnetic nature of 1 and the relatively low $T_{1/2}$ values of 2 are related to the relatively weak ligand field induced by the bridging ligand DPIP. Indeed, although in general the ligand strength felt by the Fe^{II} centres depend to some extent on the crystal packing, it is safe to infer that the amide moieties of DPIP have a marked electron withdrawing effect on the pyridine groups, thereby decreasing their σ -donor character, and thus stabilising the HS state of 1. This effect is partially mitigated in 2 owing to the stronger ligand field induced by the NCSe⁻ anions. These results are consistent with those reported by Tao *et al.* for the 1D-SCO CP based on the bridging ligand L = 5,6-di(pyridine-4-yl)-1,2,3,4-tetrahydropyrazine (X = S), where the pyridine groups, coupled by a C=C bond, lack of electron withdrawing groups. This thiocyanate derivative undergoes a gradual incomplete (*ca.* 50%) SCO centred at $T_{1/2}$ \approx 160 K, which is ascribed to the rigidity of the bridging ligand.^{35*a*} The same group has investigated for a series of 1D CPs formulated as [Fe^{II}(dpds)₂(NCX)₂]_{*n*}'S with X = Se (S = 3.5 H₂O), BH₃ and C(CN)₂ and dpds = 4,4'-dipyridyl disulphide. In this system, the pyridine moieties of dpds seem to generate weaker ligand strength than DPIP, in contrast to 2, where the NCSe⁻ derivative is HS at any temperature. However, this weak ligand field was compensated using the much stronger pseudo-halide coordinating anions [C(CN)₃]⁻ and NCBH₃⁻, which induce rather gradual SCO behaviours to the corresponding complexes.

As mentioned in the introduction, alternative approaches to $[Fe^{II}(L)(NCX)_2]_n$ related 1D-SCO CPs were proposed by Neville, Murray and Real et al. using polydentate chelating ligands, which were able to induce stronger ligand fields and hence higher $T_{1/2}$ characteristic temperatures.^{30–33} Despite the apparent more robust and rigid nature of the reported chains, the SCO behaviours are rather gradual compared with the title compound 2. In general, it can safely be stated that the thermo- and photo-induced SCO properties of 2 are unique in the series of related compounds $[Fe^{II}(L)_p(NCX)_2]_p$ (p = 1, 2). We believe that the cooperative nature of the SCO observed for 2 is due to the effective hydrogen bonds O···H-N defined between the DMF and the H-N moieties of DPIP (Fig. 2c). These interactions act as strips hampering the potential rotation of the DPIP's amide arms. Indeed, a superposition of the HS and LS structures clearly show that the $[Fe_2(DPIP)_4]$ loops perfectly match in both states (see Fig. 5), a fact that proves our hypothesis about the rigidity of the structure as the principal cause of the cooperative nature of the SCO of 2. The rotational degree of freedom in related bridging ligands has also been considered as a shockabsorber mechanism of the elastic interactions between the SCO centres in a distinct series of 1D-SCO CPs with tetrazole or triazole donor groups generically formulated as $[Fe(L)_3](X)_2$ and $[Fe(L)_2(L')_2](X)_2$ (X = ClO₄⁻, BF₄⁻) where the SCO behaviour is usually gradual.^{40,41} A representative number of studies dealing with this and other aspects influencing the cooperativity in the latter series of triple- and double-bridged chains is gathered from ref. 42 and 43.



Fig. 5 Orthogonal perspectives of the superposition of the LS (red) and HS (blue)[Fe₂(DPIP)₄] loops for 2.

Coming back again to complex 2, the structural rigidity conferred by the O···H–N hydrogen bonds to the chains vanishes after removing the included DMF molecules. This fact obviously provokes profound modifications in the crystal packing, which must include the torsion angles of the $[Fe_2(DPIP)_4]$ loops, thereby stabilising the HS of 2^{desolv}.

Conclusion

This report was undertaken to investigate new loop-like 1D-SCO CPs of the type $[Fe^{II}(L)_2(NCX)_2]_n$ based-on the V-shaped bis-monodentate bridging ligand DPIP (DPIP = N,N'-dipyridin-4-ylisophthalamide). The solvated SeCN⁻ derivative presents complete spin crossover behaviour with an obvious thermal hysteresis loop and the complete photo-switchable LIESST effect. In contrast, either the solvated NCS⁻ derivative or the desolvated SeCN⁻ derivative keeps the high spin state of Fe^{II} in the whole temperature range, providing clear information that both the coordination field of XCN⁻ and the guest solvent put cooperative influence on the SCO behaviour. The $\{Fe(DPIP)_2(NCX)_2\}_n$ complex is an excellent platform to further investigate the role of other guests with different polarities, steric effects and donor/acceptor abilities. This work is underway in our lab.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are very thankful for the support from the National Nature Science Foundation of China (21671121, 21173006), the Spanish Ministerio de Economíay Competitividad (MINECO), CTQ2016-78341-P, Unidad de Excelencia María de Maeztu (MDM-2015-0538), and Generalitat Valenciana (PROMETEO/2016/ 147). F. J. V. M. thanks MINECO for a predoctoral FPI grant.

Notes and references

- (a) E. König, Struct. Bonding, 1991, 76, 51; (b) P. Gütlich, A. Hauser and H. Spiering, Angew. Chem., Int. Ed. Engl., 1994, 33, 2024; (c) J. A. Real, A. B. Gaspar, V. Niel and M. C. Muñoz, Coord. Chem. Rev., 2003, 236, 121; (d) Spin Crossover in Transition Metal Compounds I-III, Top. Curr. Chem, ed. P. Gütlich and H. A. Goodwin, 2004, vol. 233–235; (e) A. Bousseksou, G. Molnár, L. Salmon and W. Nicolazzi, Chem. Soc. Rev., 2011, 40, 3313.
- 2 W. A. Baker and H. M. Bobonich, *Inorg. Chem.*, 1964, 3, 1184–1188.
- 3 E. Koenig and K. Madeja, Inorg. Chem., 1967, 6, 48-55.
- 4 P. Guionneau, M. Marchivie, G. Bravic, J.-F. Letàrd and D. Chasseau, *Top. Curr. Chem.*, 2004, **234**, 97–128.

- J. A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn,
 F. Varret and J. Zarembowitch, *J. Am. Chem. Soc.*, 1992, 114, 4650–4658.
- 6 E. Trzop, M. Buron-Le Cointe, H. Cailleau, L. Toupet, G. Molnar, A. Bousseksou, A. B. Gaspar, J. A. Real and E. Collet, *J. Appl. Crystallogr.*, 2007, 40, 158–164.
- 7 K. Nakano, S. Kawata, K. Yoneda, A. Fuyuhiro, T. Yagi, S. Nasu, S. Morimoto and S. Kaizaki, *Chem. Commun.*, 2004, 2892–2893.
- 8 K. Nakano, N. Suemura, K. Yoneda, S. Kawata and S. Kaizaki, *Dalton Trans.*, 2005, 740–743.
- 9 B. A. Leita, B. Moubaraki, K. S. Murray, J. P. Smith and J. D. Cashion, *Chem. Commun.*, 2004, 156–157.
- 10 C. J. Schneider, J. D. Cashion, B. Moubaraki, S. M. Neville, S. R. Batten, D. R. Turner and K. S. Murray, *Polyhedron*, 2007, 26, 1764–1772.
- 11 J. J. M. Amoore, C. J. Kepert, J. D. Cashion, B. Moubaraki, S. M. Neville and K. S. Murray, *Chem. – Eur. J.*, 2006, **12**, 8220–8227.
- 12 D. Fedaoui, Y. Bouhadja, A. Kaiba, P. Guionneau, J.-F. Létard and P. Rosa, *Eur. J. Inorg. Chem.*, 2008, 1022– 1026.
- A. Y. Verat, N. Ould-Moussa, E. Jeanneau, B. Le Guennic,
 A. Bousseksou, S. A. Borshch and G. S. Matouzenko, *Chem. Eur. J.*, 2009, 15, 10070–10082.
- 14 G. S. Matouzenko, E. Jeanneau, A. Yu. Verat and A. Bousseksou, *Dalton Trans.*, 2011, 40, 9608–9618.
- 15 A. B. Gaspar, M. C. Muñoz and J. A. Real, *J. Mater. Chem.*, 2006, 16, 2522–2533.
- 16 K. S. Murray, in *Spin crossover materials: properties and applications*, ed. M. A. Halcrow, John Wiley & Sons, 2013, pp. 1–54.
- 17 J. J. Olguín and S. Brooker, in *Spin crossover materials: properties and applications*, ed. M. A. Halcrow, John Wiley & Sons, 2013, pp. 77–120.
- 18 W. Vreugdenhil, J. G. Haasnoot, O. Kahn, P. Thuery and J. Reedijk, J. Am. Chem. Soc., 1987, 109, 5272–5273.
- 19 A. Ozarowski, Y. Shunzhong, B. R. McGarvey, A. Mislankar and J. E. Drake, *Inorg. Chem.*, 1991, **30**, 3167–3174.
- 20 N. Moliner, C. Muñoz, S. Létard, X. Solans, N. Menéndez, A. Goujon, F. Varret and J. A. Real, *Inorg. Chem.*, 2000, 39, 5390–5393.
- M. Atsuchi, H. Higashikawa, Y. Yoshida, S. Nakashima and K. Inoue, *Chem. Lett.*, 2007, 36, 1064–1065.
- 22 C. J. Adams, M. C. Muñoz, R. E. Waddington and J. A. Real, *Inorg. Chem.*, 2011, **50**, 10633–10642.
- 23 Y.-C. Chuang, C.-T. Liu, C.-F. Sheu, W.-L. Ho, G.-H. Lee, C.-C. Wang and Y. Wang, *Inorg. Chem.*, 2012, **51**, 4663– 4671.
- 24 J. A. Real, E. Andrés, M. C. Muñoz, M. Julve, T. Granier,
 A. Bousseksou and F. Varret, *Science*, 1995, 268, 265–267.
- 25 T. Romero-Morcillo, N. De la Pinta, L. M. Callejo,
 L. Piñeiro-López, M. C. Muñoz, G. Madariaga, S. Ferrer,
 T. Breczewski, R. Cortés and J. A. Real, *Chem. Eur. J.*,
 2015, 21, 12112–12120.

- 26 G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762–1765.
- 27 S. M. Neville, B. Moubaraki, K. S. Murray and C. J. Kepert, Angew. Chem., Int. Ed., 2007, 46, 2059–2062.
- 28 S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, P. D. Southon, J. D. Cashion, J.-F. Létard, B. Moubaraki, K. S. Murray and C. J. Kepert, *J. Am. Chem. Soc.*, 2008, 130, 2869–2876.
- 29 G. J. Halder, K. W. Chapman, S. M. Neville, B. Moubaraki, K. S. Murray, J.-F. Létard and C. J. Kepert, *J. Am. Chem. Soc.*, 2008, **130**, 17552–17562.
- 30 S. M. Neville, B. A. Leita, D. A. Offermann, M. B. Duriska,
 B. Moubaraki, K. W. Chapman, G. J. Halder and
 K. S. Murray, *Eur. J. Inorg. Chem.*, 2007, 1073–1085.
- 31 S. M. Neville, B. A. Leita, G. J. Halder, C. J. Kepert, B. Moubaraki, J.-F. Létard and K. S. Murray, *Chem. – Eur. J.*, 2008, 14, 10123–10133.
- 32 T. M. Ross, B. Moubaraki, D. R. Turner, G. J. Halder, G. Chastanet, S. M. Neville, J. D. Cashion, J.-F. Létard, S. R. Batten and K. S. Murray, *Eur. J. Inorg. Chem.*, 2011, 1395–1417.
- 33 T. Romero-Morcillo, F. J. Valverde-Muñoz, M. C. Muñoz, J. M. Herrera, E. Colacio and J. A. Real, *RSC Adv.*, 2015, 5, 69782–69789.
- 34 K. Nebbali, C. D. Mekuimemba, C. Charles, S. Yefsah, G. Chastanet, A. J. Mota, E. Colacio and S. Triki, *Inorg. Chem.*, 2018, 57, 12338–12346.
- 35 (a) F.-L. Yang, J. Tao, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2011, **50**, 911–917; (b) X.-P. Sun, T. Liu, Z.-S. Yao and J. Tao, *Dalton Trans.*, 2019, **48**, 9243–9249.
- 36 N. N. Adarsh, D. K. Kumar and P. Dastidar, *CrystEngComm*, 2009, **11**, 796–802.
- 37 (a) C. P. Slichter and H. G. Drickamer, *J. Chem. Phys.*, 1972, 56, 2142–2160; (b) J.-P. Martin, J. Zarembowitch, A. Bousseksou, A. Dworkin, J. G. Haasnoot and F. Varret, *Inorg. Chem.*, 1994, 33, 6325–6333.
- 38 (a) S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering and A. Hauser, *Chem. Phys. Lett.*, 1984, **105**, 1–4; (b) A. Hauser, *Chem. Phys. Lett.*, 1986, **124**, 543–548.
- 39 G. Chastanet, C. Desplanches, C. Baldé, P. Rosa, M. Marchivie and P. Guionneau, *Chem. Sq.*, 2018, 1–18.
- 40 P. J. van Koningsbruggen, Y. Garcia, O. Kahn, L. Fournès, H. Kooijman, A. L. Spek, J. G. Haasnoot, J. Moscovici, K. Provost, A. Michalowicz, F. Renz and P. Gütlich, *Inorg. Chem.*, 2000, **39**, 1891–1900.
- J. Schweifer, P. Weinberger, K. Mereiter, M. Boca, C. Reichl, G. Wiesinger, G. Hilscher, P. J. van Koningsbruggen, H. Kooijman, M. Grunert and W. Linert, *Inorg. Chim. Acta*, 2002, 339, 297–306.
- 42 M. Quesada, H. Kooijman, P. Gamez, J. S. Costa,
 P. J. vanKoningsbruggen, P. Weinberger, M. Reissner,
 A. L. Spek, J. G. Haasnoot and J. Reedijk, *Dalton Trans.*,
 2007, 5434–5440.
- 43 (a) R. Bronisz, Inorg. Chim. Acta, 2002, 340, 215-220;
 - (b) R. Bronisz, Eur. J. Inorg. Chem., 2004, 3688-3695;
 - (c) R. Bronisz, Inorg. Chem., 2007, 46, 6733-6739;

(d) A. Białonska, R. Bronisz and M. Weselski, Inorg. Chem., 2008, 47, 4436-4438; (e) A. Białonska and R. Bronisz, Inorg. Chem., 2010, 51, 12630-12637; (f) A. Białonska, R. Bronisz and L. Baranowski, Eur. J. Inorg. Chem., 2013, 720-724;

Dalton Transactions