



Cite this: *Dalton Trans.*, 2016, **45**, 14008

Received 4th May 2016,
Accepted 1st August 2016

DOI: 10.1039/c6dt01745b

www.rsc.org/dalton

Spin state switching of metal complexes by visible light or hard X-rays

Daniel Unruh,^a Patrick Homenya,^a Manish Kumar,^b Ralf Sindelar,^b Yann Garcia*^c and Franz Renz*^a

Electromagnetic stimuli of spin crossover compounds restricted to UV-vis light irradiation for many years could be recently extended to X-ray excitation. This review covers a large variety of light-induced effects, as well as recent analogues stimulated by X-ray irradiation which have not yet been reviewed. The focus is also on multistable multinuclear spin crossover compounds which are the subject of lively discussions within the spin crossover community. Their spin transition often occurs incompletely and with different switching mechanisms. In this review, we recall a predicted sequential switching induced thermally as well as a concerted stimulation mechanism by light irradiation for these interesting multifunctional materials.

Introduction

More and more systems bearing high-density and high speed data transfer with low power consumption are currently considered in the communication market for the design of future spintronic devices.^{1,2} In this context, coordination compounds

presenting spin crossover (SCO) phenomena are currently considered to be potential materials of choice. These compounds are reversibly convertible between a low-spin (LS) state and a high-spin (HS) state by an external stimulus. The stimuli-responsive transition can be triggered chemically (*e.g.* by solvent, ligand exchange, pH, *etc.*) as well as physically (*e.g.* by temperature, pressure or electromagnetic radiation *etc.*).^{3,4}

The spin states of these materials can be monitored by a large panel of physical techniques to follow changes in their structural, magnetic, vibrational and most often optical properties. Mössbauer spectroscopy is popularly used for the study of iron compounds since it gives much information on the spin and oxidation states and on the structural features and lifetimes of excited states including relaxation phenom-

^aInstitute of Inorganic Chemistry, Leibniz Universität Hannover, 30167 Hannover, Germany. E-mail: franz.renz@acd.uni-hannover.de

^bFaculty II, University of Applied Science and Arts, Ricklinger Stadtweg 120, 30459 Hannover, Germany

^cInstitute of Condensed Matter and Nanosciences, Molecules, Solids and Reactivity (IMCN/MOST), Université catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. E-mail: yann.garcia@uclouvain.be



Daniel Unruh

Daniel Unruh was born in Dinslaken, Germany, in 1989. After finishing his master's degree in material- and nanochemistry at Leibniz University Hannover, Germany, in 2013 he started his PhD studies at the Institute of Inorganic Chemistry in Hannover. His research interests are spin transition materials as well as polymer fibers. In detail, his current focus is on the adaption of stimuli-responsive coordination compounds in polymer

fiber composites for sensor applications. He has been a member of the Hannover School for Nanotechnology (HSN) since 2013.



Patrick Homenya

Patrick Homenya was born in Northeim, Germany, in 1983. After graduate school he started studying Chemistry at Leibniz University Hannover where he received his diploma degree in 2009. In 2014, he completed his PhD studies in the field of spin transition compounds. Currently, Patrick Homenya is working as a scientific expert on material analyses at the Landeskriminalamt Niedersachsen (State Office of Criminal Investigation of Lower Saxony). His current research interests include the forensic examination of paints, plastics, glass, gunshot residues and explosives.

ena.^{5,6} Since the spin state switching of coordination complexes is accompanied by modification of the macroscopic properties of the material (*e.g.* magnetism, colour, size, *etc.*), these compounds have gained a lot of interest due to their potential for applications in spintronics, display devices and sensors.^{7–12} Despite their great potential, very few technical applications including such materials are known at present – possibly limited by problems in handling such complexes on a molecular level (*e.g.* addressing single molecules, chemical instability, *etc.*).^{7–9} Solving these issues is currently an important topic in the field of nanoscience with the aim to customize future spintronic devices.^{13–16}

In this respect, electromagnetic or even electric excitations are considered the most promising stimuli, compared to thermally induced SCO.³ In this review, we provide a brief survey of the different SCO stimuli, in particular those induced by visible light and hard-X-rays.^{4,17} We then outline different switching mechanisms of recently discovered multinuclear SCO compounds.¹⁸ The status on ligand induced isomerizations leading to spin state transitions including Ligand Driven Light Induced Spin Change (LD-LISC)¹⁹ and Light Driven Coordination Induced Spin State Switching (LD-CISS)²⁰ was covered in a recent comprehensive review.²¹

Stimuli of spin transitions – a brief overview

The story starts in 1931, when Cambi *et al.* observed for the first time an anomalous magnetic behaviour, which was ascribed to a spin conversion in an Fe^{III} mononuclear complex induced by thermal energy.²² Three years later, a spin transition stimulated by ligand exchange was reported by Pauling *et al.*²³ Several years later, a growing interest in iron SCO

compounds, stimulated by the discovery of the Mössbauer effect in 1958,²⁴ led to the discovery of several other methods to stimulate the spin transition (*e.g.* by pressure) in a further period of time (Scheme 1).²⁵ In 1970, Gülich *et al.* introduced an original approach to switch the spin state, using Mössbauer emission spectroscopy to investigate SCO analogues (⁵⁷Co-labelled compounds), *e.g.* [⁵⁷Co/Co(phen)₂(NCS)₂] (phen = 1,10-phenanthroline).²⁶ Besides other alterations (*e.g.* change of the inner coordination sphere or metal–ligand bond rupture), a change of spin states was observed as well. In particular, the [Fe(phen)₂(NCS)₂] (phen = 1,10-phenanthroline) model complex, which undergoes a thermally induced spin transition, could be trapped in its HS state despite falling below its typical transition temperature $T_{1/2}$ (~180 K).²⁷ This uncommon phenomenon, which was termed NIESST (Nuclear Induced Excited Spin State Trapping), was recently reviewed.²⁷ The discovery of the possibility to switch the spin state by light in the crystalline state, termed LIESST (Light Induced Excited Spin State Trapping), constituted a milestone, which is currently widely applied in current chemistry.¹⁷ Decurtins *et al.* identified the LIESST effect for the first time on the mononuclear Fe^{II} complex [Fe(ptz)₆](BF₄)₂ (ptz = 1-propyltetrazole) by green light irradiation ($\lambda = 514.5$ nm) at helium temperatures using diffuse reflectance and ⁵⁷Fe Mössbauer spectroscopies.²⁸ Later, Hauser reported on the back switching effect – termed reverse-LIESST – in which the spin transition from HS to LS was induced by red light irradiation ($\lambda = 820$ nm).²⁹ In both ways electronic excitation to singlet as well as MLCT states with very short lifetimes is followed by a decay to either HS or LS states *via* several intersystem crossing steps.²⁹ As the HS → LS transition is highly spin-forbidden and the tunnelling rate is very low, at low temperatures – described by the inverse energy gap law by Hauser *et al.* in 1991²⁹ – long lifetimes of the respective metastable states are observable. At raising



Manish Kumar

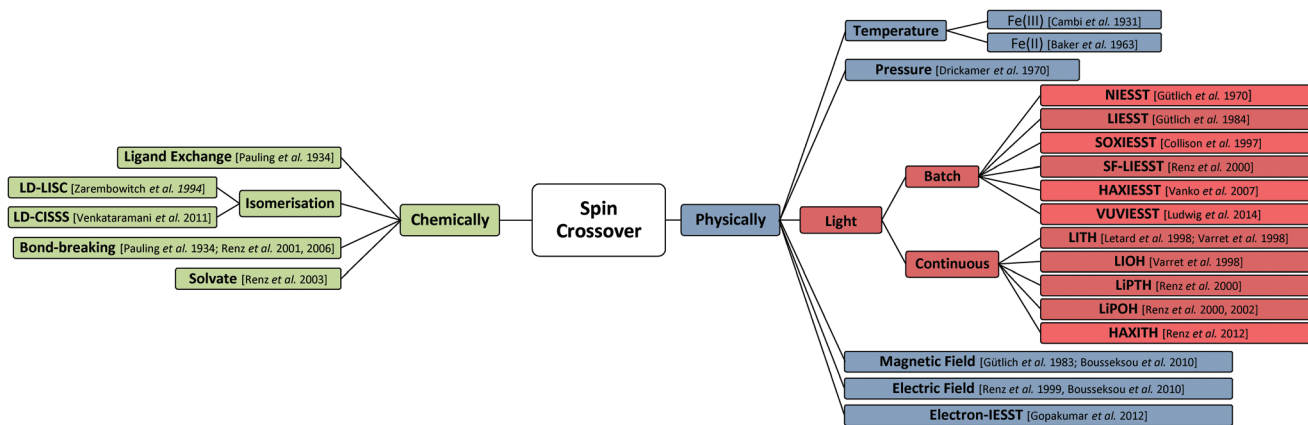
Manish Kumar is currently working on his PhD thesis at the Mechanical and Bioprocess Engineering at the University of Applied Science and Arts, Hannover, Germany. His work is focused on stimuli-responsive nano-bio-fibers for on-demand drug release. In 2011, he obtained a bachelor's degree in Electronic and Communication Engineering from RGPV, Bhopal, India. In 2013, he obtained a master's degree in Nanoscience

and Technology from Pondicherry University, Puducherry, India. He worked with Li-ion batteries as a Junior Researcher at Nanoscience and Energy Materials Laboratory, IISER-TVM, Kerala, India. His current research interests include the development and characterization of stimuli-responsive nanofibers.



Ralf Sindelar

Ralf Sindelar (1963) received his doctorate from RWTH Aachen. After some years in industry he worked at the University of Erlangen-Nürnberg and then at Fraunhofer-Gesellschaft in Freiburg and Darmstadt before he accepted a position as professor of primary shaping and materials science at Hochschule Hannover in 2007. In this organization he is the head of the cost centre materials-lab and he is running a laboratory for electro-spinning.



Scheme 1 Historic time line of various spin crossover stimuli. Adapted from ref. 4.

temperatures, the system returns back to the LS state due to higher tunnelling rates.^{29,30} First limited to 57 K for the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ complex,³¹ the relaxation temperature could be increased up to 135 K for the macrocyclic mononuclear complex $[\text{FeL}_{222}\text{N}_3\text{O}_2(\text{CN})_2]\cdot\text{H}_2\text{O}$ ($\text{L}_{222}\text{N}_3\text{O}_2 = 3,12,18\text{-triazol-6,6-dioxabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene}$).³²

Similarly, the relaxation temperature after thermal trapping is as high as 156 K for the same complex,³² and even reaches 250 K for an Fe^{II} trinuclear 1,2,4-triazole complex discovered recently.³³ Although bidirectional switching by pulsed laser irradiation and temperature jump effects with a thermal hysteresis loop of a 3D coordination polymer were discovered by Bousseksou *et al.*,³⁴ partial bidirectional optical switching was demonstrated in Fe^{II} mononuclear tetrazole complexes, with memory effects up to ~ 70 K.³⁵ More recently, Hauser *et al.* discovered a persistent bidirectional optical switching of the HS 2D coordination polymer $[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2$ ($\text{bbtr} = 1,4\text{-di}(1,2,3\text{-triazol-1-yl})\text{butane}$) with a light-induced stability below 100 K.³⁶ The stabilization of the LS state and the persistent

bistability were explained by strong cooperative effects resulting in the presence of a large hysteresis loop with $T_c^{\uparrow} = 100$ K and T_c^{\downarrow} near or formally even below 0 K.³⁶

The strong field (SF)-LIESST – discovered by Renz, Gütlich *et al.* – opened up a new door in the SCO area because of the totally unexpected spin switching in SF complexes in which no thermal SCO is observable.³⁷

SF-LIESST was detected in a metal-diluted coordination compound, $[\text{Fe}_{0.02}\text{Mn}_{0.98}(\text{tpy})_2](\text{ClO}_4)_2$ ($\text{tpy} = 2,2':6',2''\text{-terpyridine}$), although $[\text{Fe}(\text{tpy})_2](\text{ClO}_4)_2$ is known to be LS. It proved to be a single-molecule mechanism and could be explained by a stabilization of the excited spin state by the host lattice (in this case $[\text{Mn}(\text{tpy})_2]^{2+}$) (Scheme 2).³⁷ The SF-LIESST was also found on a nondiluted mononuclear Fe^{II} complex $[\text{Fe}(\text{L}_{222}\text{N}_5)(\text{CN})_2]\cdot\text{H}_2\text{O}$ ($\text{L}_{222}\text{N}_5 = 2,13\text{-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene}$).³⁸

Yet, LIESST and NIESST are initiated at cryogenic temperatures due to low tunneling rates, which led to the thermal



Yann Garcia

Yann Garcia is a professor of inorganic and analytical chemistry at the Université catholique de Louvain, Belgium. After a doctorate with Prof. Olivier Kahn at CNRS Bordeaux, he moved to Mainz for a postdoc with Prof. Philipp Gütlich in 1999, before being appointed in Louvain in 2001. He is a specialist in materials chemistry, Mössbauer spectroscopy and spin crossover. He has co-authored more than 200 papers with several cover

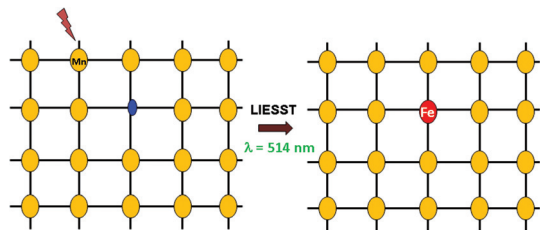
pages of recognized chemistry journals, including 10 book chapters on inorganic chemistry, several guest editorials and two patent applications.



Franz Renz

Franz Renz is a professor of Inorganic Chemistry at Leibniz Universität Hannover, Germany. His research focuses on coordination chemistry, sequential and concerted stimuli-responsive mono- and multinuclear iron spin crossover materials as well as Mössbauer spectroscopy, e.g. as a member of the NASA MER mission since 2004 on Mars. In 1997, he finished his doctorate at the Technical University in Vienna and in 2005 his habilitation at the Johannes Gutenberg-University of Mainz. He is known for his contributions to the discovery of the SF-LIESST and HAXIESST effects.

He is known for his contributions to the discovery of the SF-LIESST and HAXIESST effects.



Scheme 2 SF-LIESST mechanism in a schematic view of the $^{57}\text{Fe}_{0.02}\text{Mn}_{0.98}(\text{tpy})_2^{2+}$ crystal lattice. The LS Fe ion is blue and the HS one is red.

decay of metastable states at higher temperatures, preventing potential room temperature photo-induced spin state switching. Over the last two decades more spin transition effects induced by visible light have emerged, differentiating between light irradiation as a “single” excitation pulse and a continuous exposure. At continuous irradiation all these effects described below are based on the LIESST phenomenon. Whereas stimulation in LITH (Light Induced Thermal Hysteresis)^{39,40} and LIOH (Light Induced Optical Hysteresis)³⁹ are induced at cryogenic temperatures, LiPTH (Light Induced Perturbed Thermal Hysteresis) and LiPOH (Light Induced Perturbed Optical Hysteresis) could occur at much higher temperatures,^{41,42} thus foreseeing potential applications.

In LITH, after LIESST population of the metastable HS state at low temperature, green light irradiation was maintained in both warming and cooling modes. Indeed, while reversibly varying the temperature at constant irradiation, Létard *et al.* and Varret *et al.* independently observed a hysteresis loop on an Fe^{II} mononuclear complex⁴⁰ and a coordination polymer,³⁹ respectively. This phenomenon could be explained by an interplay between HS state light excitation and its increasing thermal decay at higher temperatures.^{41,42} Intermolecular interactions of single molecule switching centres were also identified, thus allowing to ascribe the presence of a LITH to cooperative effects.³⁹ The LITH thus found its usefulness for the study of noncooperative thermally induced spin conversions of a gradual nature, which were expected to be cooperative. This was nicely exemplified in the $[2 \times 2]$ Fe₄ SCO grid by Lehn, Gülich *et al.* who evidenced a LITH loop using ⁵⁷Fe Mössbauer spectroscopy, despite the very smooth character of the SCO curve as concluded from bulk magnetic measurements, which was not expected for a tetranuclear SCO complex (Fig. 1).⁴³

A similar cooperative behaviour was observed by Varret *et al.* by changing the intensity of the irradiated light at a constant temperature. Also similar to LIESST, this hysteresis effect was called LIOH.³⁹ In comparison with the abovementioned hysteresis effects at cryogenic temperatures, LiPTH and LiPOH^{41,42} are spin transition stimuli at higher temperatures. Based on the same interplay between HS state excitations by light and thermal decay, the hysteresis behaviour could be manipulated. For instance, the coordination compound $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ (phy = 1,10 phenanthroline-2-carbaldehyde-phenylhydrazone) shows a thermal hysteresis between 270 K and

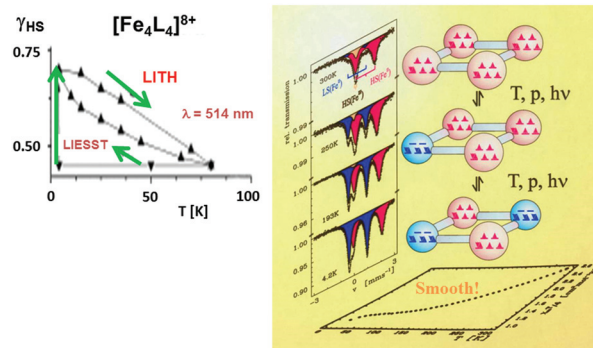


Fig. 1 Identification of cooperative effects in a grid like Fe^{II} SCO complex $[\text{Fe}_4\text{L}_4]^{8+}$ thanks to LITH below 100 K (left side) despite the gradual character of the thermally induced spin conversion (right side, bottom).

280 K, which was shifted to lower temperatures (~ 10 K) by continuous irradiation with green light and shifted to higher temperatures by red light.⁴¹

Apart from UV-vis light irradiation, X-ray excitation experiments on SCO materials experienced recently a renaissance. The first excitation effects induced by X-rays were discovered by Collison *et al.* in 1997,⁴⁴ although different kinds of X-ray spectroscopy like XPS or XAFS were earlier used to monitor spin transition in coordination compounds.^{45,46} Collison *et al.* have shown that L-edge absorption of X-rays with relatively low energy could be used to stimulate a spin transition at low temperatures. In the so-called SOXIESST (Soft X-ray Induced Excited Spin State Trapping) the HS state could be trapped below a certain temperature by irradiation with soft X-rays, similar to the LIESST effect. Unfortunately the SOXIESST effect is accompanied by SOXPC (Soft X-ray Photochemistry) which causes chemical changes in the investigated SCO compound, $[\text{Fe}(\text{phen})_2(\text{NCX})_2]$ (X = S, Se). Over time the compound gets degenerate to an irreversible LS state form which seems to be chemically different from the initial LS ground state. This phase transition, which has not yet been explained fully, is temperature-independent.⁴⁴

A SOXIESST effect has also been recently reported for the mononuclear complex $[\text{Fe}(\text{bpbz})_2(\text{phen})]$ (bpbz = dihydrobis(pyrazolyl)borate) either adsorbed on Au(111)⁴⁷ or in direct contact with a highly oriented pyrolytic graphite surface.⁴⁸ Apart from soft X-rays, Vankó *et al.* were able to stimulate a spin transition in an Fe^{II} compound using high energy X-rays.⁴⁹ The so-called HAXIESST (Hard X-ray Induced Spin State Trapping) effect is comparable to the abovementioned effects (LIESST, NIESST and SOXIESST). Although the mechanism has not been evaluated so far, a similar trapping mechanism was discussed. In contrast to NIESST and SOXIESST, a K-shell excitation causes almost no significant structural or chemical transition of the complexes, which gives the HAXIESST effect an enormous advantage for using it in potential applications. The idea of using the large penetration power and spatial resolution of hard X-rays enhances this potential because hard X-rays could theoretically be used to address single molecules or a small

number of complexes individually.⁴⁹ The HAXIESST effect was discovered in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ at low temperatures, the very same compound which was investigated for the SOXIESST effect. A maximum amount of 72% of the complex could be converted to the HS state at 10 K by hard X-ray irradiation (Fig. 2). In this case absorption of high energy photons creates 1s holes, causing following processes to fill these vacancies. Consequently the iron compound gets trapped in the metastable HS state. Triggers for this excitation could be several secondary processes following the electron capture in the 1s orbital (e.g. secondary electrons, scattered electrons, X-ray emission, etc.) but the exact mechanism has not been elucidated so far. Increasing temperature lowers the HS state fraction to 42% at 45 K, while the HS state completely disappears at 55 K (Fig. 2).⁴⁹ The existence of thermal decay at higher temperatures is in accordance with observations in comparable effects like LIESST, NIESST or SOXIESST. In line with LIESST but in contrast to NIESST and SOXIESST, almost no significant chemical changes in the samples were observed, making the effect completely reversible.⁴⁹

The preserved integrity of the sample after irradiation with hard X-rays suggests that a hysteresis effect – compared to LITH induced by visible light – could, in principle, exist. The first evidence of a HAXITH, i.e. the determination of a thermal hysteresis loop at continuous irradiation of a SCO compound with hard X-rays at cryogenic temperatures, was discovered by Renz *et al.* in 2012.⁵⁰ By reversibly changing the temperature between 40 K and 50 K with constant heating and cooling rates, respectively, increasing amounts of the HS state fraction of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ with every cycle up to a maximum were observed.⁴⁴ Similarly, vacuum UV photons can populate the metastable HS state leading to the Vacuum UV Induced Excited Spin State Trapping (VUVIESST) effect discovered by Ludvig *et al.* in 2014.⁵¹

Compared to the large variety of effects to stimulate a SCO by visible light (e.g. LITH, LIOH, LiPTH, LiPOH) only a few analogues excited by hard X-ray irradiation have been found

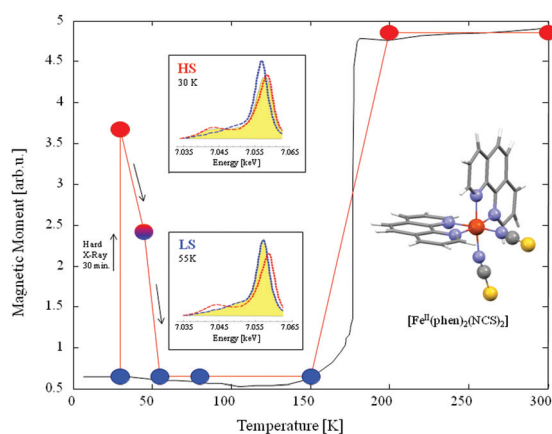


Fig. 2 HAXIESST effect evidenced at 30 K on $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. The red lines are a guide for the eyes. The black line represents magnetic measurements. A HAXITH is evidenced below 50 K.

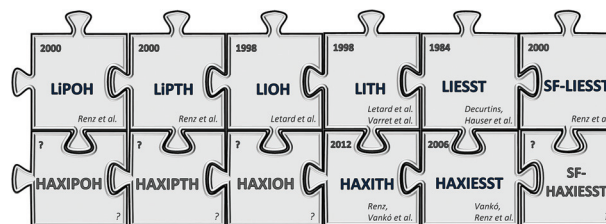


Fig. 3 Illustration of established SCO effects stimulated by visible light or hard X-rays including the publication year, author and predicted effects which have not yet been found.⁵²

up to now. Considering the similarity between visible light and hard X-rays as a stimulus, one should be able to observe other spin transition effects induced by hard X-rays (Fig. 3). For example, a strong field effect similar to SF-LIESST is conceivable and first results of investigations on this phenomenon will be published anytime soon.

Finally, it is worth mentioning the possibility to switch the spin state using electrons, studied by Ruben *et al.* on an iron(II) mononuclear complex,⁵³ followed by other examples of electrical switching of the 1D chain $[\text{Fe}(\text{Htrz})_2\text{trz}]\text{BF}_4$,^{54,55} including the Electron Induced Excited Spin State Trapping (EIESST) first described by Gopakumar *et al.*^{47,56}

Concerted or sequential switching in multinuclear spin crossover complexes

In contrast to electromagnetic induced spin transitions which were discussed in the first part of this review mostly on mononuclear SCO systems, the second part focuses on multinuclear complexes showing thermal SCO as well as some interesting photomagnetic effects. Multinuclear SCO complexes have been investigated intensively within the last 15 years, exhibiting promising SCO behaviours for possible applications, in particular binuclear complexes.^{57–76} Compared to spin state switching in mononuclear compounds, multinuclear complexes promise more drastic changes of the macroscopic material properties. For instance, the total amount of unpaired electrons – and therefore the magnetic moment – as well as their coupling could accumulate over all metallic centres, increasing interactions compared to those in mononuclear complexes (e.g. $\text{Fe}^{\text{III}}\text{-d}^5$ in HS: $S = 5/2$; dinuclear $\text{Fe}^{\text{III}}\text{-d}^5$ in HS: $S = 10/2$; up to $S = 60/2$ in a dodecanuclear complex).^{64,77} In addition, some intermediate states can be populated, leading to various switching processes and intramolecular interactions between metal centres. For instance, dinuclear Fe^{II} complexes assumed the existence of spin pairs being in either a [LS–LS] state at lower temperatures or a [HS–HS] state at higher temperatures, leading to sequential switching or direct spin transitions. Furthermore a mixed spin state situation of [HS–LS] nature could be identified.^{57,60,78} Therefore a one- or two-step spin transition could be evidenced in such oligomers. Ksenofontov *et al.* were the first to prove the existence of such intermediate states by running applied magnetic field

Mössbauer measurements,⁷⁹ although later Mössbauer experiments showed that the application of a magnetic field was not always necessary.⁸⁰ Besides thermal spin transition, LIESST occurs in Fe dinuclear SCO compounds as well.⁸¹ In comparison with LIESST in mononuclear complexes, Létard *et al.* observed an unexpected increase of the [HS–HS] state at increasing temperatures, which was explained by strong antiferromagnetic interactions of the Fe(II) centers.⁸¹ In this context, Moussa *et al.* used different wavelengths to excite either [HS–LS] or [HS–HS] states. While irradiation with infrared light ($\lambda = 1342$ nm) populates [HS–LS] states, red light ($\lambda = 647.1$ nm) stimulates [HS–HS] states.⁸² In the meantime a large number of multinuclear spin transition compounds have been published containing three to twelve metal centres, including or not including iron,⁸³ as well as for coordination polymers.⁸⁴ The list includes trimers,^{33,64,85,86} tetramers,^{43,86–94} pentanuclear assemblies,^{95–97} tetradecanuclear assemblies,⁹⁸ heptamers,⁹⁹ as well as a pentadecanuclear spherical cluster $\{\text{Fe}_9[\text{Re}(\text{CN})_8]_6\}$ showing an incomplete spin conversion of only one iron center.¹⁰⁰ The LIESST effect was also encountered in iron(II) coordination polymers,^{36,39,101} in particular in 1D chains.^{10a,102} The first example of a LIESST effect in a 1D chain was discovered by Koningsbruggen *et al.* on $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ (btzp = 1,2-bis(tetrazol-1-yl)propane).¹⁰³ The thermal relaxation after LIESST was found to proceed in two steps, presumably due to different chain lengths in the 1D material.¹⁰³ Interestingly, chain length distributions were also taken to be responsible for the two step character of the thermally induced spin transition of $[\text{Fe}(\beta\text{Alatr}_z)_3](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\beta\text{Alatr}_z = 1,2,4$ -triazol-4-yl-propionate), the first of its kind for a 1D iron(II) chain with 1,2,4-triazole ligands.¹⁰⁴ The topic was recently reviewed with the focus centred on the LIESST effect on 1D iron(II) 1,2,4-triazole SCO chains.¹⁰⁵

We highlight below some examples of multinuclear SCO systems. Gembický *et al.* initially described an Fe(II)/Fe(III) mixed valence heptanuclear system, consisting of six Fe(III) pentadentate precursor building blocks and a $[\text{Fe}(\text{CN})_6]^{4-}$ centre unit,¹⁰⁶ which could be tuned to a SCO system by Boca *et al.* (Fig. 4).^{99b}

Renz *et al.* investigated multinuclear compounds using Co and Mo surrounded by either six or eight Fe(III) pentadentate complex precursors.¹⁰⁷ Surprisingly, SCO was observable in those systems although single Fe(III) building blocks are typical weak-field complexes, populating exclusively the HS state.¹⁰⁷ Especially the nonanuclear Mo complex $[[^3,3,3\text{ LFeNC}]_8\text{Mo}]\text{Cl}_4$ (Fig. 5) could see its peripheral iron units be thermally switched to LS on cooling as shown by Mössbauer spectroscopy (Fig. 6a and b).¹⁰⁷ Interestingly, green light irradiation ($\lambda = 514$ nm) induced a partial population of the HS state at 20 K (Fig. 6d).¹⁷ Despite the similarity to LIESST in mononuclear coordination compounds, the mechanism of multinuclear photonic-stimulated transitions could differ completely. Saadat *et al.* postulated the existence of a small fraction of Fe^{II} ions in the LS state. Considering the mechanism to achieve such a Fe^{II} LS, they suggested a concerted switching mechanism by light irradiation, which is shown in Fig. 6c.¹⁸ In this particular case they assumed that all Fe^{III}

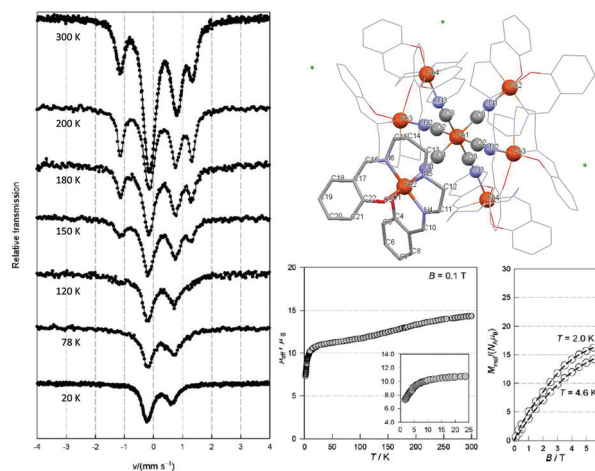


Fig. 4 Mössbauer spectra (left), crystal structure (top, right) and magnetic measurements (bottom, right) of the mixed Fe(II)/Fe(III) heptanuclear complex $[\text{Fe}^{\text{II}}\{(\text{CN})\text{Fe}^{\text{III}}\text{L}^5\}_6]\text{Cl}_2$.⁹⁹

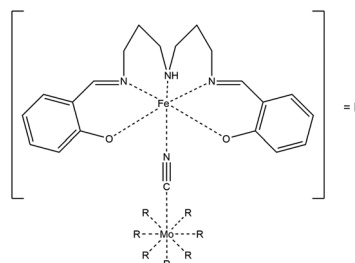


Fig. 5 Schematic view of the nonanuclear Mo complex $[[^3,3,3\text{ LFeNC}]_8\text{Mo}]\text{Cl}_4$.

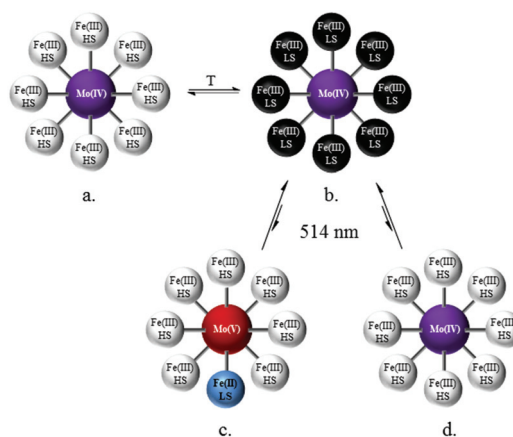


Fig. 6 Schematic illustration of the presumable switching mechanisms in $[[^3,3,3\text{ LFeNC}]_8\text{Mo}]\text{Cl}_4$. Thermal-induced SCO occurs sequentially between HS (a) and LS (b) Fe^{III} ions while a complete transition to the LS state could not be observed. Green light irradiation at low temperatures could lead to either a concerted switching to (c) or a sequential transition to (d) similar to LIESST.¹⁸

centres of the nonanuclear complex are in their LS state at 20 K. Green light irradiation switches seven of those centres to their HS state. Simultaneously an electron transfer from the Mo centre to one Fe^{III} centre, which remains in its LS state, would take place (Fig. 6c).¹⁸

Light Induced Electron Transfer Coupled Spin Transition (LIETCST) was first observed on Prussian blue analogues.^{27a,108}

More recently, several photoswitchable polymetallic complexes containing also [Mo(CN)₈]⁴⁻ building blocks and Mn, Cu or Zn centres were communicated by Marvaud, Mathoniere *et al.*^{109–116} Their switching mechanism is under discussion and could be related to the Fe₈Mo system described above, given the fact that in addition to electron transfer from the Mo to Cu atoms, a LS to HS transition centred on the Mo atom was postulated thanks to X-ray magnetic dichroism.¹¹⁷ More precise investigations of the suggested mechanisms in such multinuclear systems are needed to verify different switching mechanisms stimulated by light (concerted) or thermally (sequential). Further examples of electron-transfer-coupled spin transition (ETCST) can be found for cyanide bridged molecular systems.^{118,119} Even more exciting are the important application perspectives provided by bimetallic metal organic frameworks regarding room temperature magnetic bistability,¹²⁰ and magnets based on the LIESST effect.^{121,122}

Concluding remarks

In this review article, we have covered different kinds of stimuli to induce spin crossover in iron compounds, focusing on electromagnetic irradiation-induced spin state switching phenomena in mono- as well as multinuclear coordination compounds. In particular, we have outlined well known effects such as LIESST or LITH occurring in mononuclear complexes as well as their new analogues HAXIESST and HAXITH. In addition, we have predicted other effects such as HAXIOH, HAXIPTH, and HAXIPOH which have not yet been described. Furthermore, we have outlined thermal and light induced spin crossover occurring in multinuclear coordination compounds containing two to twelve metal centres. While the LIESST effect was found in several dinuclear complexes, light stimuli in higher nuclearity complexes often follow an intramolecular electron transfer mechanism. We anticipate that the present report could stimulate investigations on the abovementioned light and X-ray induced phenomena in mononuclear as well as multinuclear switchable coordination compounds. The recent communication that the LS spin state of Mo^{IV} complexes can be photo-induced leading to a long-lived HS state (stable on warming up to 90 K) after a structural rearrangement¹²³ could indeed stimulate future studies on numerous unexplored systems.

Abbreviations

EIESST	Electron induced excited spin state trapping
ETCST	Electron transfer coupled spin transition

HAXIESST	Hard X-ray induced excited spin state trapping
HAXITH	Hard X-ray induced thermal hysteresis
HAXIOH	Hard X-ray induced optical hysteresis
HAXIPOH	Hard X-ray induced perturbed optical hysteresis
HAXIPTH	Hard X-ray induced perturbed thermal hysteresis
LD-CISS	Light driven coordination induced spin state switching
LD-LISC	Ligand driven light induced spin change
LIESST	Light induced excited spin state trapping
LIETCST	Light induced electron transfer coupled spin transition
LIOH	Light induced optical hysteresis
LIPOH	Light induced perturbed optical hysteresis
LIPTH	Light induced perturbed thermal hysteresis
LITH	Light induced thermal hysteresis
NIESST	Nuclear induced excited spin state trapping
SF-HAXIESST	Strong field hard X-ray induced excited spin state trapping
SF-LIESST	Strong field light induced excited spin state trapping
SOXIESST	Soft X-ray induced excited spin state trapping
SOXPC	Soft X-ray photochemistry
VUVIESST	Vacuum UV induced excited spin state trapping

Acknowledgements

We acknowledge financial support from the Hannover School of Nanotechnology (HSN), Leibniz Universität Hannover (LUH), Hochschule Hannover (HsH) and DFG (Re1627/1-3), FNRS (PDR T.0102.15) and COST actions CM1305 and CA15128. We dedicate this contribution to Prof. Dr Dr h. c. em. P. Gütllich on the occasion of his 82nd birthday.

References

- J. Tang and K. L. Wang, *Nanoscale*, 2015, 7, 4325–4337.
- J. Huang, R. Xie, W. Wang, Q. Li and J. Yang, *Nanoscale*, 2016, 8, 609–616.
- (a) P. Gütllich, A. B. Gaspar and Y. Garcia, *Beilstein J. Org. Chem.*, 2013, 9, 342–391; (b) P. Gütllich and Y. Garcia, Spin crossover systems, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, 2015, p. 1.
- F. Renz, *J. Phys.: Conf. Ser.*, 2010, 217, 012022.
- P. Gütllich and Y. Garcia, *J. Phys.: Conf. Ser.*, 2010, 217, 012001.
- P. Gütllich and Y. Garcia, in *Mössbauer spectroscopy - Tutorials Book*, ed. Y. Yoshida and G. Langouche, Springer, 2013, pp. 23–89.
- M. C. Muñoz and J. A. Real, in *Spin-crossover materials*, ed. M. A. Halcrow, John Wiley and Sons, Chichester, UK, 2013, pp. 121–146.
- G. Molnar, L. Salmon, W. Nicolazzi, F. Terki and A. Bousseksou, *J. Mater. Chem. C*, 2014, 2, 1360–1366.

- 9 P. Gamez, J. S. Costa, M. Quesada and G. Aromi, *Dalton Trans.*, 2009, 7845–7853.
- 10 (a) Y. Garcia, V. Ksenofontov and P. Gütllich, *Hyperfine Interact.*, 2002, **139**, 543–551; (b) J. Linares, E. Codjovi and Y. Garcia, *Sensors*, 2012, **12**, 4479–4192; (c) C. M. Jureschi, J. Linares, A. Rotaru, M. H. Ritti, M. Parlier, M. M. Dîrtu, M. Wolff and Y. Garcia, *Sensors*, 2015, **15**, 2388–2398; (d) C.-M. Jureschi, J. Linares, A. Boulmaali, P. R. Dahoo, A. Rotaru and Y. Garcia, *Sensors*, 2016, **16**, 187.
- 11 (a) C. Lefter, R. Ran, S. Tricard, J. Dugay, G. Molnar, L. Salmon, J. Carrey, A. Rotaru and A. Bousseksou, *Polyhedron*, 2015, **102**, 434–440; (b) C. Lefter, V. Davesne, L. Salmon, G. Molnár, P. Demont, A. Rotaru and A. Bousseksou, *Magnetochemistry*, 2016, **2**, 18, DOI: 10.3390/magnetochemistry2010018.
- 12 Y. Garcia, P. J. Van Koningsbruggen, E. Codjovi, R. Lapouyade, O. Kahn and L. Rabardel, *J. Mater. Chem.*, 1997, **7**, 857–858.
- 13 A. Bousseksou, G. Molnar, P. Demont and J. Menegotto, *J. Mater. Chem.*, 2003, **13**, 2069–2071.
- 14 M. Mikolasek, G. Felix, W. Nicolazzi, G. Molnar, L. Salmon and A. Bousseksou, *New J. Chem.*, 2014, **38**, 1834–1839.
- 15 G. Molnar, L. Salmon, W. Nicolazzi, F. Terki and A. Bousseksou, *J. Mater. Chem. C*, 2014, **2**, 1360–1366.
- 16 E. J. Devid, P. N. Martinho, M. V. Kamalakar, I. Šalitroš, U. Prendergast, J.-F. Dayen, V. Meded, T. Lemma, R. González-Prieto, F. Evers, T. E. Keyes, M. Ruben, B. Doudin and S. J. Van der Molen, *ACS Nano*, 2015, **9**, 4496–4507.
- 17 P. Homenya, L. Heyer and F. Renz, *Pure Appl. Chem.*, 2015, **87**, 293–300.
- 18 R. Saadat and F. Renz, *Moessbauer Eff. Ref. Data J.*, 2012, **35**, 216–237.
- 19 M.-L. Boillot, J. Zarembowitch and A. Sour, *Top. Curr. Chem.*, 2004, **234**, 261–276.
- 20 S. Venkataramani, U. Jana, M. Dommaschk, F. D. Sönnichsen, F. Tuzcek and R. Herges, *Science*, 2011, **331**, 445–448.
- 21 M. M. Khusniyarov, Light-induced spin crossover, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, 2015, p. 1.
- 22 L. Cambi and L. Szegö, *Ber. Dtsch. Chem. Ges.*, 1931, **64**, 2591–2598.
- 23 L. Pauling and C. D. Corvell, *Proc. Natl. Acad. Sci. U. S. A.*, 1936, **22**, 159–163.
- 24 R. L. Mössbauer, *Hyperfine Interact.*, 2000, **126**, 1–12.
- 25 H. G. Drickamer and C. W. Frank, *Electronic Transitions and the High Pressure Chemistry and Physics of Solids*, Chapman and Hall, London, 1973.
- 26 H. Sano and P. Gütllich, *Hot atom chemistry in relation to Mössbauer emission spectroscopy*, ed. T. Matsuura, Hot Atom Chemistry, Tokyo, Kodanski, 1984, pp. 265–302.
- 27 (a) P. Gütllich, Y. Garcia and Th. Woike, *Coord. Chem. Rev.*, 2001, **219–221**, 839–879; P. Gütllich, *Top. Curr. Chem.*, 2004, **234**, 231–260; (b) P. Gütllich and Y. Garcia, Photo-magnetism in molecular systems, in *Reference Module in Materials Science and Materials Engineering*, 2015, DOI: 10.1016/B978-0-12-803581-8.03095-2.
- 28 (a) S. Decurtins, P. Gütllich, C. P. Köhler, H. Spiering and A. Hauser, *Chem. Phys. Lett.*, 1984, **13**, 1; (b) S. Decurtins, P. Gütllich, K. M. Hasselbach, A. Hauser and H. Spiering, *Inorg. Chem.*, 1985, **24**, 2174–2178.
- 29 A. Hauser, A. Vef and P. Adler, *J. Chem. Phys.*, 1991, **85**, 8710–8717.
- 30 A. Hauser, *Comments Inorg. Chem.*, 1995, **17**, 17–40.
- 31 J. Jeftić, M. Matsarski, A. Hauser, A. Goujon, E. Codjovi, J. Linares and F. Varret, *Polyhedron*, 2001, **20**, 1599–1606.
- 32 H. Wang, C. Sinito, A. Kaiba, J. Sanchez Costa, C. Desplanches, P. Dagault, P. Guionneau, J. F. Létard, P. Negrier and D. Mondieig, *Eur. J. Inorg. Chem.*, 2014, 4927–4933.
- 33 (a) V. Gómez, C. Sáenz de Pipaón, P. Maldonado-Illescas, J. C. Waerenborgh, E. Martin, J. Benet-Buchholz and J. R. Galán-Mascarós, *J. Am. Chem. Soc.*, 2015, **137**, 11924–11927; (b) C. Sáenz de Pipaón, P. Maldonado-Illescas, V. Gómez and J. R. Galán-Mascarós, *Magnetochemistry*, 2016, **2**, 20, DOI: 10.3390/magnetochemistry2020020.
- 34 (a) S. Cobo, D. Ostrovski, S. Bonhommeau, L. Vendier, G. Molnár, L. Salmon, K. Tanaka and A. Bousseksou, *J. Am. Chem. Soc.*, 2008, **130**, 9019–9024; (b) S. Bonhommeau, G. Molnár, S. Cobo, D. Ostrovskii and A. Bousseksou, *Polyhedron*, 2009, **28**, 1610–1613; (c) E. Collet, L. Henry, L. Piñeiro-López, L. Toupet and J. A. Real, *Curr. Inorg. Chem.*, 2016, **6**, 61–66.
- 35 (a) P. Poganiuch, S. Decurtins and P. Gütllich, *J. Am. Chem. Soc.*, 1990, **112**, 3270; (b) R. Hinek, H. Spiering, P. Gütllich and A. Hauser, *Chem. – Eur. J.*, 1996, **2**, 1435–1439.
- 36 (a) P. Chakraborty, R. Bronisz, C. Besnard, L. Guénée, P. Pattison and A. Hauser, *J. Am. Chem. Soc.*, 2012, **134**, 4049–4052; (b) P. Chakraborty, S. Pillet, E.-E. Benedeif, C. Enachescu, R. Bronisz and A. Hauser, *Chem. – Eur. J.*, 2013, **19**, 11418–11428.
- 37 F. Renz, H. Oshio, V. Ksenofontov, M. Waldeck, H. Spiering and P. Gütllich, *Angew. Chem., Int. Ed.*, 2000, **112**, 3832–3834.
- 38 J. Sánchez Costa, C. Balde, C. Carbonera, D. Denux, A. Wattiaux, C. Desplanches, J.-P. Ader, P. Gütllich and J. F. Létard, *Inorg. Chem.*, 2007, **46**, 4114–4119.
- 39 A. Desaix, O. Roubeau, J. Jeftic, J. G. Haasnoot, K. Boukheddaden, E. Codjovi, J. Linares, M. Nogues and F. Varret, *Eur. Phys. J. B*, 1998, **6**, 183–193.
- 40 J. F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau and O. Kahn, *Inorg. Chem.*, 1998, **37**, 4432–4441.
- 41 F. Renz, H. Spiering, H. A. Goodwin and P. Gütllich, *Hyperfine Interact.*, 2000, **126**, 155–158.
- 42 F. Renz, H. Spiering, P. Gütllich, K. H. Sugiyarto and H. A. Goodwin, In: TOSS-Meeting, Seeheim, Germany, 2002.
- 43 E. Breuning, M. Ruben, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gütllich, E. Wegelius and K. Rissanen, *Angew. Chem., Int. Ed.*, 2000, **39**, 2504–2507.

- 44 D. Collison, C. D. Garner, C. M. McGrath, J. F. W. Mosselmans, M. D. Roper, J. M. W. Seddon, E. Sinn and N. A. Young, *J. Chem. Soc., Dalton Trans.*, 1997, 4371–4376.
- 45 S. Vasudevan, H. N. Vasan and C. N. R. Rao, *Chem. Phys. Lett.*, 1979, **65**, 444–451.
- 46 C. Cartier, P. Thuéry, M. Verdaguer, J. Zarembowitch and A. Michalowicz, *J. Phys. Colloq.*, 1986, **47-C8**, 563–569.
- 47 T. G. Gopakumar, M. Bernien, H. Naggert, F. Matino, C. F. Hermanns, A. Bannwarth, S. Mühlenberend, A. Krüger, D. Krüger, F. Nickel, W. Walter, R. Berndt, W. Kuch and F. Tuczek, *Chem. – Eur. J.*, 2013, **19**, 15702–15709.
- 48 M. Bernien, H. Naggert, L. M. Arruda, L. Kipgen, F. Nickel, J. Miguel, C. F. Hermanns, A. Krüger, D. Krüger, E. Schierle, E. Weschke, F. Tuczek and W. Kuch, *ACS Nano*, 2015, **9**, 8960–8966.
- 49 G. Vankó, F. Renz, G. Molnar, T. Neisius and S. Karpatis, *Angew. Chem., Int. Ed.*, 2007, **46**, 5306–5309.
- 50 F. Renz, G. Vankó, P. Homenya, R. Saadat, Z. Németh and S. Huotari, *Eur. J. Inorg. Chem.*, 2012, 2653–2655.
- 51 E. Ludwig, H. Naggert, M. Kalläne, S. Rohlf, E. Kröger, A. Bannwarth, A. Quer, K. Rosnagel, L. Kipp and F. Tuczek, *Angew. Chem., Int. Ed.*, 2014, **53**, 3019–3023.
- 52 P. Homenya, *PhD Thesis*, Leibniz University Hannover, 2014.
- 53 V. Meded, A. Bagrets, K. Fink, R. Chandrasekar, M. Ruben, F. Evers, A. Bernand-Mantel, J. S. Seldenthuis, A. Beukman and H. S. J. Van der Zant, *Phys. Rev. B: Condens. Matter*, 2011, **83**, 245415.
- 54 T. Miyamachi, M. Gruber, V. Davesne, M. Bowen, S. Boukari, L. Joly, F. Scheurer, G. Rogez, T. K. Yamada, P. Ohresser, E. Beaurepaire and W. Wulfhekel, *Nat. Commun.*, 2013, **3**, 938.
- 55 (a) F. Prins, M. Monrabal Capilla, E. A. Osorio, E. Coronado and H. J. Van der Zant, *Adv. Mater.*, 2011, **23**, 1545–1549; (b) A. Rotaru, J. Dugay, R. P. Tan, I. A. Guralskiy, L. Salmon, P. Demont, J. Carrey, G. Molnar, M. Raspaud and A. Bousseksou, *Adv. Mater.*, 2013, **25**, 1745–1749.
- 56 T. G. Gopakumar, F. Matino, H. Naggert, A. Bannwarth, F. Tuczek and R. Berndt, *Angew. Chem., Int. Ed.*, 2012, **51**, 6262–6266.
- 57 (a) J. A. Real, J. Zarembowitch, O. Kahn and X. Solans, *Inorg. Chem.*, 1987, **26**, 2939–2943; (b) J. A. Real, A. Bolvon, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret and J. Zarembowitch, *J. Am. Chem. Soc.*, 1992, **114**, 4650–4658; (c) J. A. Real, I. Castro, A. Bousseksou, M. Verdaguer, R. Burriel, M. Castro, J. Linares and F. Varret, *Inorg. Chem.*, 1997, **36**, 455–464; (d) V. Ksenofontov, A. B. Gaspar, J. A. Real and P. Gütllich, *J. Phys. Chem. B*, 2001, **105**, 12266–12271.
- 58 (a) F. Tuna, M. R. Lees, G. J. Clarkson and M. J. Hannon, *Chem. – Eur. J.*, 2004, **10**, 5737–5750; (b) R. J. Archer, C. S. Hawes, G. N. L. Jameson, V. McKee, B. Moubaraki, N. F. Chilton, K. S. Murray, W. Schmitt and P. E. Kruger, *Dalton Trans.*, 2011, **40**, 12368–12373.
- 59 (a) M. H. Klingele, B. Moubaraki, J. D. Cashion, K. S. Murray and S. Brooker, *Chem. Commun.*, 2005, 987–989; (b) J. A. Kitchen, N. G. White, G. N. L. Jameson, J. L. Tallon and S. Brooker, *Inorg. Chem.*, 2011, **50**, 4586–4597.
- 60 (a) A. B. Gaspar, M. C. Muñoz and J. A. Real, *J. Mater. Chem.*, 2006, **16**, 2522–2533; (b) A. Bousseksou, G. Molnár, J. A. Real and K. Tanaka, *Coord. Chem. Rev.*, 2007, **251**, 1822–1833.
- 61 K. S. Min, K. Szwierczek, A. G. DiPasquale, A. L. Rheingold, W. M. Reiff, A. M. Arif and J. S. Miller, *Chem. Commun.*, 2008, 317–319.
- 62 K. S. Murray, *Eur. J. Inorg. Chem.*, 2008, 3101–3121.
- 63 (a) 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; (b) G. S. Matouzenko, E. Jeanneau, A. Y. Verat and A. Bousseksou, *Dalton Trans.*, 2011, **40**, 9608–9618; (c) G. S. Matouzenko, E. Jeanneau, A. Verat and Y. de Gaetano, *Eur. J. Inorg. Chem.*, 2012, **6**, 969–977.
- 64 I. Salitros, R. Boca, L. Dlhán, M. Gembicky, J. Kozisek, J. Linares, J. Moncol, I. Nemeč, L. Perasinova, F. Renz, I. Svoboda and H. Fuss, *Eur. J. Inorg. Chem.*, 2009, 3141–3154.
- 65 J. M. Jarrod, S. M. Neville, B. Moubaraki, S. J. Iremonger, K. S. Murray, J. F. Létard and C. J. Kepert, *Chem. – Eur. J.*, 2010, **16**, 1973–1982.
- 66 (a) Y. Garcia, F. Robert, A. D. Naik, G. Zhou, B. Tinant, K. Robeyns, S. Michotte and L. Piraux, *J. Am. Chem. Soc.*, 2011, **133**, 15850–15853; (b) J. A. Wolny, Y. Garcia, I. Fauss, S. Rackwitz, K. Schlage, H.-C. Wille and V. Schuenemann, *Hyperfine Interact.*, 2016, **237**, 65; (c) X. Cheng, Q. Yang, C. Gao, B.-W. Wang, T. Shiga, H. Oshio, Z.-M. Wang and S. Gao, *Dalton Trans.*, 2015, **44**, 11282–11285.
- 67 O. Roubeau, P. Gamez and S. J. Teat, *Eur. J. Inorg. Chem.*, 2013, 934–942.
- 68 B. Ding, Y. Y. Liu, Y. Wang, J.-G. Ma, Z. Niu, W. Shi and P. Cheng, *Inorg. Chem. Commun.*, 2013, **31**, 44–48.
- 69 C. J. Schneider, J. D. Cashion, N. F. Chilton, C. Etrillard, M. Fuentealba, J. A. K. Howard, J.-F. Létard, C. Milsmann, B. Moubaraki, H. A. Sparkes, S. R. Batten and K. S. Murray, *Eur. J. Inorg. Chem.*, 2013, 5–6, 850–864.
- 70 S. Kanegawa, S. Kang and O. Sato, *Eur. J. Inorg. Chem.*, 2013, 5–6, 725–729.
- 71 (a) J. A. Kitchen, J. Olguin, R. Kulmaczewski, N. G. White, V. A. Milway, G. N. L. Jameson, J. L. Tallon and S. Brooker, *Inorg. Chem.*, 2013, **52**, 11185–11199; (b) R. Kulmaczewski, J. Olguin, J. A. Kitchen, H. L. C. Feltham, G. N. L. Jameson, J. L. Tallon and S. Brooker, *J. Am. Chem. Soc.*, 2014, **136**, 878–881.
- 72 X. Cheng, Q. Yang, C. Gao, B.-W. Wang, T. Shiga, H. Oshio, Z.-M. Wang and S. Gao, *Dalton Trans.*, 2015, **44**, 11282–11285.
- 73 M. Yamasaki and T. Ishida, *Chem. Lett.*, 2015, **44**, 920–921.

- 74 R. W. Hogue, H. L. C. Feltham, R. G. Miller and S. Brooker, *Inorg. Chem.*, 2016, **55**, 4152–4165.
- 75 M. Darawsheh, L. A. Barrios, O. Roubeau, S. J. Teat and G. Aromi, *Chem. – Eur. J.*, 2016, **22**, 8635–8645.
- 76 C. Koehler and E. Rentschler, *Eur. J. Inorg. Chem.*, 2016, **13–14**, 1955–1960.
- 77 F. Renz, D. Hill, M. Klein and J. Hefner, *Polyhedron*, 2007, **26**, 2325–2329.
- 78 Y. Garcia, C. M. Grunert, S. Reiman, O. van Campenhoudt and P. Gütllich, *Eur. J. Inorg. Chem.*, 2006, 3333–3339.
- 79 V. Ksenofontov, H. Spiering, S. Reiman, Y. Garcia, A. B. Gaspar, N. Moliner, J. A. Real and P. Gütllich, *Chem. Phys. Lett.*, 2001, **348**, 381–386.
- 80 C. M. Grunert, S. Reiman, H. Spiering, J. A. Kitchen, S. Brooker and P. Gütllich, *Angew. Chem., Int. Ed.*, 2008, **47**, 2997–2999.
- 81 (a) G. Chastanet, A. B. Gaspar, J. A. Real and J. F. Létard, *Chem. Commun.*, 2001, 819–820; (b) J. F. Létard, J. A. Real, N. Moliner, A. B. Gaspar, L. Capes, O. Cador and O. Kahn, *J. Am. Chem. Soc.*, 1999, **121**, 10630–10631.
- 82 N. O. Moussa, G. Molnar, S. Bonhommeau, A. Zwick, S. Mouri, K. Tanaka, J. A. Real and A. Bousseksou, *Phys. Rev. Lett.*, 2005, **94**, 107205.
- 83 D. J. Harding, P. Harding and W. Phonsri, *Coord. Chem. Rev.*, 2016, **313**, 38.
- 84 (a) Y. Garcia, V. Niel, M. C. Muñoz and J. A. Real, *Top. Curr. Chem.*, 2004, **233**, 229–257; (b) C. Genre, G. S. Matouzenko, E. Jeanneau and D. Luneau, *New J. Chem.*, 2006, **30**, 1669–1674.
- 85 (a) G. Vos, R. A. Le Fèvre, R. A. G. De Graaff, J. G. Haasnoot and J. Reedijk, *J. Am. Chem. Soc.*, 1983, **105**, 1682–1683; (b) G. Vos, R. A. G. De Graaf, J. G. Haasnoot, A. M. Van der Kraan, P. de Vaal and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 2905–2910; (c) M. Thomann, O. Kahn, J. Guilhem and F. Varret, *Inorg. Chem.*, 1994, **33**, 6029–6037; (d) J. J. A. Kolnaar, G. van Dijk, H. Kooijman, A. L. Spek, V. G. Ksenofontov, P. Gütllich, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1997, **36**, 2433–2440; (e) Y. Garcia, P. Guionneau, G. Bravic, D. Chasseau, J. A. K. Howard, O. Kahn, V. Ksenofontov, S. Reiman and P. Gütllich, *Eur. J. Inorg. Chem.*, 2000, 1531; (f) C. Chong, B. Berini, K. Boukheddaden, E. Codjovi, J. Linares, Y. Garcia, A. D. Naik and F. Varret, *Phys. Status Solidi A*, 2010, **207**, 1227–1231; (g) J. A. Wolny, S. Rackwitz, K. Achterhold, Y. Garcia, K. Muffler, A. D. Naik and V. Schünemann, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14782–14788; D. Savard, C. Cook, G. D. Enright, I. Korobkov, T. J. Burchell and M. Murugesu, *CrystEngComm*, 2011, **13**, 5190–5197.
- 86 M. Nihei, M. Ui and H. Oshio, *Polyhedron*, 2009, **28**, 1718–1721.
- 87 T. Matsumoto, G. N. Newton, T. Shiga, S. Hayami, Y. Matsui, H. Okamoto, R. Kumai, Y. Murakami and H. Oshio, *Nat. Commun.*, 2014, **5**, 3865.
- 88 M. Nihei, M. Ui, M. Yokota, L. Han, A. Maeda, H. Kishida, H. Okamoto and H. Oshio, *Angew. Chem., Int. Ed.*, 2005, **44**, 6484.
- 89 D. Y. Wu, O. Sato, Y. Einaga and C.-Y. Duan, *Angew. Chem., Int. Ed.*, 2009, **48**, 1475–1478.
- 90 T. Nishihara, M. Nihei, H. Oshio and K. J. Tanaka, *J. Phys.: Conf. Ser.*, 2009, **148**, 012033.
- 91 B. Schneider, S. Demeshko, S. Dechert and F. Meyer, *Angew. Chem., Int. Ed.*, 2010, **49**, 9274–9277.
- 92 A. Ferguson, M. A. Squire, D. Siretanu, D. Mitcov, C. Mathonière, R. Clérac and P. E. Kruger, *Chem. Commun.*, 2013, **49**, 1597.
- 93 R. A. Bilbeisi, S. Zarra, H. L. C. Feltham, G. N. L. Jameson, J. K. Clegg, S. Brooker and J. R. Nitschke, *Chem. – Eur. J.*, 2013, **19**, 8058.
- 94 L. Li, N. Saigo, Y. Zhang, D. J. Fanna, N. D. Shepherd, J. K. Clegg, R. Zheng, S. Hayami, L. F. Lindoy, J. R. Aldrich-Wright, C.-G. Li, J. K. Reynolds, D. G. Harman and F. Li, *J. Mater. Chem. C*, 2015, **3**, 7878–7882.
- 95 J. J. A. Kolnaar, M. I. De Heer, H. Kooijman, A. L. Spek, G. Schmitt, V. Ksenofontov, P. Gütllich, J. G. Haasnoot and J. Reedijk, *Eur. J. Inorg. Chem.*, 1999, 881.
- 96 M. Shatruk, A. Dragulescu-Andrasi, K. E. Chambers, S. A. Stoian, E. L. Bominaar, C. Achim and K. R. Dunbar, *J. Am. Chem. Soc.*, 2007, **129**, 6104–6116.
- 97 Z. Yan, W. Liu, Y.-Y. Peng, Y.-C. Chen, Q.-W. Li, Z.-P. Ni and M.-L. Tong, *Inorg. Chem.*, 2016, **55**, 4891–4896.
- 98 (a) M. B. Duriska, S. M. Neville, B. Moubaraki, J. D. Cashion, G. Halder, K. W. Chapman, C. Balde, J. F. Létard, K. S. Murray, C. J. Kepert and S. R. Batten, *Angew. Chem., Int. Ed.*, 2009, **48**, 2549–2552; (b) M. B. Duriska, S. M. Neville, B. Moubaraki, K. S. Murray, C. Balde, J. F. Létard, C. Kepert and S. R. Batten, *ChemPlusChem*, 2012, **77**, 616.
- 99 (a) F. Renz, C. Zaba, L. Roßberg, S. Jung, M. Klein, G. Klingelhöfer, A. Wünsche, S. Reinhardt and M. Menzel, *Polyhedron*, 2009, **28**, 2036–2038; (b) R. Boca, I. Salitros, J. Kozisek, J. Linares, J. Moncol and F. Renz, *Dalton Trans.*, 2010, **39**, 2198–2200.
- 100 S. Chorazy, R. Podgajny, K. Nakabayashi, J. Stanek, M. Rams, B. Sieklucka and S. Ohkoshi, *Angew. Chem., Int. Ed.*, 2015, **54**, 5093–5097.
- 101 (a) Y. Garcia, V. Ksenofontov, G. Levchenko, G. Schmitt and P. Gütllich, *J. Phys. Chem. B*, 2000, **21**, 5045; (b) V. Niel, A. Galet, A. B. Gaspar, M. C. Munoz and J. A. Real, *Chem. Commun.*, 2003, **11**, 1248–1249; (c) M. Seredyuk, A. B. Gaspar, V. Ksenofontov, M. Verdager, F. Villain and P. Gütllich, *Inorg. Chem.*, 2009, **48**, 6130–6141; (d) V. Martinez, Z. Arcis Castillo, M. C. Munoz, A. B. Gaspar, C. Etrillard, J. F. Letard, S. A. Terekhov, G. V. Bukin, G. Levchenko and J. A. Real, *Eur. J. Inorg. Chem.*, 2013, **5–6**, 813–818; (e) N. F. Sciortino, Q. M. Neville, J. F. Létard, B. Moubaraki, K. S. Murray and C. J. Kepert, *Inorg. Chem.*, 2014, **53**, 7886–7893; (f) M. Seredyuk, L. Pineiro-Lopez, M. C. Munoz,

- F. J. Martinez-Casado, G. Molnar, J. A. Rodriguez-Velamazan, A. Bousseksou and J. A. Real, *Inorg. Chem.*, 2015, **54**, 7424–7432.
- 102 (a) M. Quesada, F. Prins, E. Bill, H. Kooijman, P. Gamez, O. Roubeau, A. L. Spek, J. G. Haasnoot and J. Reedijk, *Chem. – Eur. J.*, 2008, **14**, 8486–8499; (b) G. Dupouy, S. Triki, M. Marchivie, N. Cosquer, C. J. Gomez-Garcia, S. Pillet, E.-E. Bendeif, C. Lecomte, S. Asthana and J. F. Létard, *Inorg. Chem.*, 2010, **49**, 9358–9368; (c) C. Balde, W. Bauer, E. Kaps, S. Neville, C. Desplanches, G. Chastanet, B. Weber and J. F. Létard, *Eur. J. Inorg. Chem.*, 2013, **15**, 2744–2750; (d) S.-L. Zhang, X.-H. Zhao, Y.-M. Wang, D. Shao and X.-Y. Wang, *Dalton Trans.*, 2015, **44**, 9682–9690.
- 103 P. J. Van Koningsbruggen, Y. Garcia, O. Kahn, L. Fournès, H. Kooijman, A. L. Spek, J. G. Haasnoot, J. Moscovic, K. Provost, A. Michalowicz, F. Renz and P. Gülich, *Inorg. Chem.*, 2000, **39**, 1891–1900.
- 104 M. M. Dîrtu, F. Schmidt, A. D. Naik, A. Rotaru, I. Rusu, S. Rackwitz, J. A. Wolny, V. Schünemann and Y. Garcia, *Chem. – Eur. J.*, 2015, **21**, 5843–5855.
- 105 Y. Garcia, F. Renz and P. Gülich, *Curr. Inorg. Chem.*, 2016, **6**, 4.
- 106 M. Gembický, R. Boca and F. Renz, *Inorg. Chem. Commun.*, 2000, **3**, 662–665.
- 107 F. Renz and P. Kerep, *Polyhedron*, 2005, **24**, 2849–2851.
- 108 O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **272**, 704–705.
- 109 J. M. Herrera, V. Marvaud, M. Verdaguer, J. Marrot, M. Kalisz and C. Mathoniere, *Angew. Chem., Int. Ed.*, 2004, **43**, 5468–5471.
- 110 L. Catala, C. Mathoniere, A. Gloter, O. Stephan, T. Gacoin, J.-P. Boilot and T. Mallah, *Chem. Commun.*, 2005, 746–748.
- 111 S.-I. Ohkoshi, H. Tokoro, T. Hozumi, Y. Zhang, K. Hashimoto, C. Mathoniere, I. Bord, G. Rombaut, M. Verelst, C. Cartier Dit Moulin and F. Villain, *J. Am. Chem. Soc.*, 2006, **128**, 270–277.
- 112 J. Long, L.-M. Chamoreau, C. Mathoniere and V. Marvaud, *Inorg. Chem.*, 2009, **48**, 22–24.
- 113 M.-A. Arrio, J. Long, C. Dit Moulin, A. Bachschmidt, V. Marvaud, A. Rogalev, C. Mathoniere, F. Wilhelm and P. Sainctavit, *J. Phys. Chem. C*, 2010, **114**, 593–600.
- 114 (a) O. Stefanczyk, A. M. Majcher, M. Rams, W. Nitek, C. Mathoniere and B. Sieklucka, *J. Mater. Chem. C*, 2015, **3**, 8712–8719; (b) O. Stefanczyk, C. Mathoniere and B. Sieklucka, *Curr. Inorg. Chem.*, 2016, **6**, 26–33.
- 115 Y. Umetsu, S. Chorazy, K. Nakabayashi and S.-I. Ohkoshi, *Eur. J. Inorg. Chem.*, 2016, **13–14**, 1980–1988.
- 116 N. Bridonneau, L.-M. Chamoreau, G. Gontard, J.-L. Cantin, J. Von Bardeleben and V. Marvaud, *Dalton Trans.*, 2016, **45**, 9412–9418.
- 117 O. Bunau, M.-A. Arrio, Ph. Sainctavit, L. Paulatto, M. Calandra, A. Juhin, V. Marvaud and C. Cartier dit Moulin, *J. Phys. Chem. A*, 2012, **116**, 8678–8683.
- 118 G. N. Newton, K. Mitsumoto, R.-J. Wei, F. Iijima, T. Shiga, H. Nishikawa and H. Oshio, *Angew. Chem., Int. Ed.*, 2014, **53**, 2941–2944.
- 119 T. Shiga, T. Tetsuka, K. Sakai, Y. Sekine, M. Nihei, G. N. Newton and H. Oshio, *Inorg. Chem.*, 2014, **53**, 5899–5901.
- 120 H. Tokoro, S. Miyashita, K. Hashimoto and S.-I. Ohkoshi, *Phys. Rev. B: Condens. Matter*, 2006, **73**, 172415.
- 121 S.-I. Ohkoshi, K. Imoto, Y. Tsunobuchi, S. Takano and H. Tokoro, *Nat. Chem.*, 2011, **1**.
- 122 S.-I. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai and H. Tokoro, *Nat. Photonics*, 2014, **8**, 65–71.
- 123 N. Bridonneau, J. Long, J.-L. Cantin, J. Von Bardeleben, S. Pillet, E.-E. Bendeif, D. Aravena, E. Ruiz and V. Marvaud, *Chem. Commun.*, 2015, **51**, 8229–8232.