

Editorial

# Synthesis and Applications of New Spin Crossover Compounds

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The spin crossover (SCO) between multi-stable states in transition metal material is one of the attractive molecular switching phenomena which is responsive to various external stimuli such as temperature, pressure, light, electromagnetic field, radiation, nuclear decay, soft-X-ray, guest molecule inclusion, chemical environments and so forth. The light induced excited spin state trapping (LIESST) effect, the nuclear decay induced excited spin state trapping (NIESST) effect and the soft X-ray induced excited spin state trapping (SOXIESST) effect are associated with the SCO phenomena.

The crystal chemistry of SCO behavior in inorganic crystal materials might be able to be potentially associated with smart materials and promising materials for applications as components of memory devices, displays, sensors and mechanical devices and, especially, actuators such as artificial muscles. This is possible after Cambi and colleagues' pioneering research on the anomalous magnetic behaviors of mononuclear.

The Fe(III) coordination complexes [1] was first demonstrated as SCO phenomena in the early 1930s. Further, significant and fundamental scientific attention has been focused on the SCO phenomena in a wide research range of fields of fundamental chemical and physical and related sciences [2]. The interdisciplinary regions of chemical and physical sciences related to the SCO phenomena are also important.

The Special Issue is devoted to various aspects of the SCO and related research containing 18 interesting original papers on valuable and important SCO topics.

Regarding the interdisciplinary regions related to SCO research, impurity-induced spin-state crossover in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-x}\text{Al}_x\text{O}$  was reported. However, the spin-state crossover also semi-quantitatively explained the enhanced thermopower and the anomalously large coercive field induced by the substituted Al ion [3]. The classic SCO is impossible in Cu(II) complexes with diamagnetic ligands, including the diamagnetic structural analogs to nitroxides which link to solid SCO-like phenomena of heterospin coordination compounds based on copper hexafluoroacetylacetonate  $[\text{Cu}(\text{hfac})_2]$  with nitronyl nitroxide radicals. This was described because they can undergo structural transformations accompanied by spin transitions induced by external effects [4]. The SCO behavior of cobalt(II) terpyridin-4'-yl nitroxide complex as an exchange-coupled SCO material was reported as a successful example of multifunctional SCO materials with combining magnetic exchange coupling interactions [5]. A charge-transfer phase transition (CTPT) accompanied by an electron transfer between adjacent  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  sites was also reported in relation to the dithioxalato-bridged iron mixed-valence complex [6].

The octahedral Fe(II) SCO systems with  $3d^6$ , which can be transitioned between the diamagnetic  $(t_{2g})^6$  and the paramagnetic  $(t_{2g})^4(e_g)^2$  configuration, are able to be widely and deeply investigated as potentially smart materials. The temperature dependence of the mosaicity for 5 thermo-induced iron(II) SCO compounds were investigated using X-ray diffraction, as the volume of high-spin (HS) and low-spin (LS) crystal packings are known to be very different [7]. Regarding the solvent effects of the SCO, the effects of lattice solvent on the solid-state SCO of a dinuclear Fe(II) triple helicate

complex series [8] and SCO Fe(II) imidazolyimine complexes [9] were reported in supramolecular crystal systems with delicate and subtle host-guest interactions. The synthesis, crystal chemistry, and photomagnetic properties of the SCO complexes with  $[\text{Fe}(\text{bpp})_2]^{2+}$  were researched in a 3D supramolecular architecture, including hydrogen bonds between iron(II) complexes, nicotinate anions, and water molecules [10]. The 1,2,3-triazole-containing polydentate ligand iron(II) SCO family into a linear pentadentate ligand system was reported. This was shown in an abrupt and incomplete HT SCO at approximately 400 K while the SCO transition was irreversible due to the crystal-to-amorphous transformation in association with the loss of the lattice MeCN solvent molecules [11]. A series of SCO Fe(II) complexes based on dipyridyl-*N*-alkylamine and thiocyanate ligands were investigated, and the higher SCO transition temperature explained the more pronounced linearity of the Fe–N–C angles in the crystal recently indicated by experimental and theoretical magneto-structural research [12].

A particularly successful and potentially developing synthetic kingdom for SCO iron(II) polymeric complexes with valuable and sophisticated functional crystal properties are the SCO Hofmann-type coordination polymers. The first compound of this type  $\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4$  reported in 1996 [13], opened various roads to a number of Hofmann-like SCO compounds with a large display of functional properties. The special issue contains 4 original research articles which are devoted to the synthesis and characterizations of various Hofmann-like polymeric systems. The optical microscopy technique to investigate the thermal and the spatio-temporal properties of the Hofmann-related SCO single crystal  $[\text{Fe}(2\text{-pytrz})_2(\text{Pt}(\text{CN})_4)]_n \cdot 3\text{H}_2\text{O}$  was described to show a first-order SCO behavior from a full high-spin (HS) state at high temperatures to intermediate, high-spin low-spin (HS-LS) states [14]. The precise crystallographic investigation on the polymeric SCO Hofmann-like compound  $\text{Fe}(3,4\text{-dimethyl-pyridine})_2[\text{Ag}(\text{CN})_2]_2$  was reported, and its temperature dependence was followed by the means of a single-crystal and powder X-ray diffraction [15]. These very important article reported in the special issue demonstrate a soft X-ray-induced excited spin state trapping (SOXEISST) effect in Hofmann-like SCO coordination polymers of  $\text{Fe}^{\text{II}}(4\text{-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$  and  $\text{Fe}^{\text{II}}(\text{pyridine})_2[\text{Ni}(\text{CN})_4]$  [16]. The emission Mossbauer spectra of  $^{57}\text{Co}$ -labelled  $\text{Co}(\text{pyridine})_2\text{Ni}(\text{CN})_4$  indicated that  $^{57}\text{Fe}$  atoms were assumed to be trapped in the excited electronic state ( $^5T$ ) by the nuclear decay induced excited spin state trapping (NIESST) effect [17]. The two SCO coordination polymers built up by the Hofmann-like frameworks combining  $\text{Fe}^{\text{II}}$  octahedral ions, 4-cyanopyridine and  $[\text{Au}(\text{CN})_2]^-$  linear units were described exhibiting ferromagnetic interaction [18]. A single crystal X-ray structural analysis showed that polymeric  $[[\text{Fe}(\text{NCS})_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$  and  $[[\text{Co}(\text{NCS})_2(\text{bpa})_2] \cdot \text{biphenyl}]_n$  had a chiral propeller structure of pyridines around the central metal, which was associated with crystal chemistry and their SCO phenomena for the  $[[\text{Fe}(\text{NCX})_2(\text{bpa})_2] \cdot (\text{guest})]_n$  family [19].

The Fe(III) SCO compounds are also important and attractive compounds as smart materials with multifunctional properties. The influence of geometry and counterion effects in determining the spin states in an iron (III) complex  $[\text{Fe}(\text{5F-sal}_2\text{333})]\text{X}$  was investigated using a crystal analysis, UV-Vis spectroscopy, SQUID and EPR spectroscopy. The R-sal<sub>2</sub>333 ligands promoting SCO in Fe(III) sites both in the solid state and in solution was established [20]. The hybrid ion-pair crystals containing hexadentate  $[\text{Fe}(\text{III})(3\text{-OMesal}_2\text{-trien})]^+$  SCO cationic coordination units and anionic gold complex units  $[\text{Au}(\text{dmit})_2]^-$  and  $[\text{Au}(\text{dddt})_2]^-$  were investigated by a single-crystal X-ray diffraction method, P-XRD, and SQUID measurements [21]. Fe(III) SCO compounds from qsal ligand (Hqsal = *N*-(8-quinolyl)salicylaldimine) were described. The optical conductivity spectra were calculated from the single-crystal reflection spectra, which were, to the best of their knowledge, the first optical conductivity spectra of SCO complexes [22].

Finally, the contribution of all the authors for sending their works is greatly appreciated. The Special Issue, "Synthesis and Applications of New Spin Crossover Compounds" presents a comprehensive report on the current work on SCO materials and will be interesting for the readers. The author is also deeply grateful to all the anonymous reviewers for their valuable suggestions and very dedicated evaluations, which have been very helpful for improving the quality of the Special Issue. The author

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In addition, the readers' submission of their valuable papers to the Special Issue "Synthesis and Applications of New Spin Crossover Compounds (Volume II)" would be further appreciated.

**Conflicts of Interest:** The author declares no conflict of interest.

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