PO 01

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High spin metastable state induced by rapid cooling in Fe(Imidazo[1,2-A]pyrazine)[M(CN)$_2$]$_2$ series with M = Ag and Au spin crossover complexes.

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For an iron (II) spin crossover complex, the singlet state of Fe^{+2}, low spin (LS) state with spin S=0, is usually the stable state at low temperatures. Nevertheless, a metastable quintet state with a high spin (HS) of S=2 can also occurs, when it is induced by an external perturbation such LIESST [1](light induced excited spin state) or SOXIESST [2](soft x-ray induced excited spin state trapping). Although it is possible to induce such a HS metastable state at low temperatures by rapid cooling[3] without using external stimuli. Such phenomenon has only been successfully demonstrated in a few reported systems [4] different to the ones here presented.

In this contribution, we are reporting a study on the thermally-induced spin crossover in the Fe(Imidazo[1,2-A]pyrazine)[M(CN)$_2$]$_2$ series with M = Ag, Au to shed light on how the spin transition is observed with changes in the temperature. The spin transition was studied from magnetic, IR, and Raman data. In addition, structural studies from XRD powder patterns complemented that information.

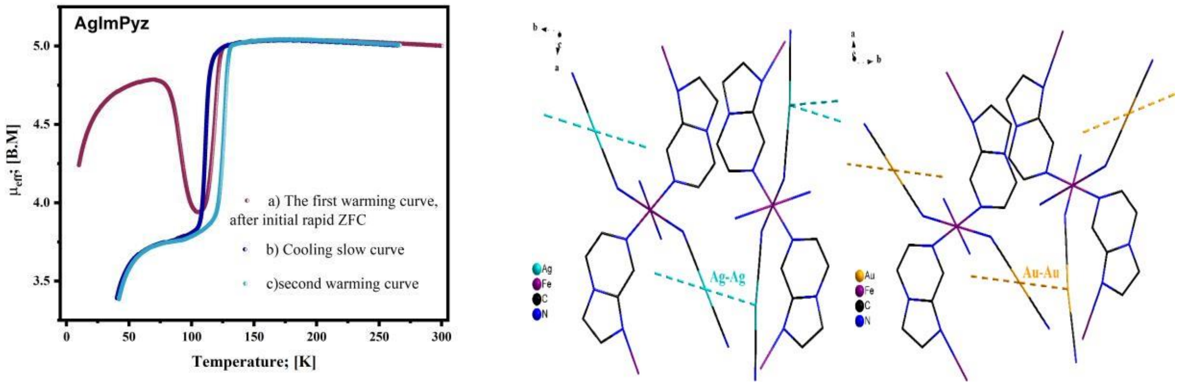

Figure 1. a) Magnetization Vs temperature curves after rapid cooling (metastable state), cooling slow and warming modes for Ag sample, **b)** Atom packing within the framework for Fe(L)[M(CN)$_2$]$_2$ with M = Ag, Au; L = ImPyz.

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Spin-Crossover and Supramolecular Interactions: Modulating Structural Changes

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Structure and function are intimately associated and nowhere is this more true than in the field of spin crossover (SCO).[1] SCO complexes are versatile materials capable of switching between two electronic configurations: low spin (LS) and high spin (HS), triggered by various external stimuli such as temperature, light, and pressure. In this study, we explore the interplay between spin-crossover behavior and supramolecular interactions. Specifically, we investigate how these properties can be precisely tuned by manipulating weak non-covalent interactions among their molecular components. This is carried out through a crystallographic study of mononuclear Fe(II) complexes, wherein either the ligand or the anion bears H-donor and H-acceptor groups.[2] Furthermore, we explore the impact of modifying the position of these groups within the ligand (*ortho*, *meta*, *para*) on the spin-crossover behavior (Figure 1).

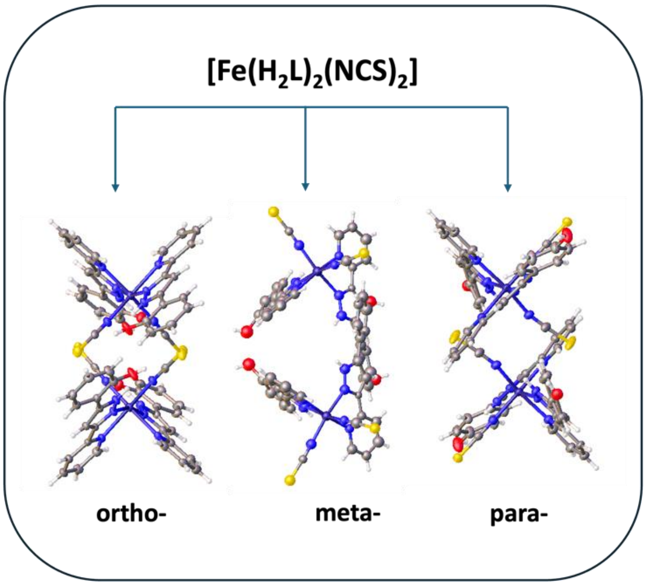

Figure 1. Cross-section view of the 1D chain for the *ortho*-, *meta*-, and *para*- complexes

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Penetrated cyano-bridged CPs using 4-methylpyrimidine ligand

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Coordination polymers (CPs) are widely investigated by many researcher due to its easily tunable properties. Soma-Iwamoto type structure is one of Hofman-type cyano-bridged CPs, which contains center metal ion and bridging liner dicyanide monovalent metal complex which form 2D cyano-bridged layer, and another ligands are coordinated to perpendicular to this layer. The spin-crossover (SCO) phenomenon is a reversible spin transition between high-spin (HS) and low-spin (LS) states. This phenomenon is also widely investigated by many researcher since this phenomenon is expected to using for functional materials such as data storage, sensor or switching devices.

We previously synthesized cyano-bridged CPs with pyrimidine-type Fe(4-methylpyrimidine)$_2$[Au(CN)$_2$]$_2$[1)] and Fe(4-methylpyrimidine)$_2$[Ag(CN)$_2$]$_2$[2)], these complexes show SCO phenomenon. Now we synthesized Fe(4-methylpyrimidine)$_2$[Au(CN)$_2$]$_2$·Fe(H$_2$O)$_2$(4-methylpyrimidine)$_2$[Au(CN)$_2$]·[Au(CN)$_4$], This complex shows consist of 2D coordination polymer Fe(4-methylpyrimidine)$_2$[Au(CN)$_2$]$_2$, cationic 1D coordination chain polymer Fe(H$_2$O)$_2$(4-methylpyrimidine)$_2$[Au(CN)$_2$] and [Au(CN)$_4$]$^-$ 0D anion (Figure 1). Crystal structure of this complex suggests 2D coordination polymer part Fe(4-methylpyrimidine)$_2$[Au(CN)$_2$]$_2$ in this complex shows spin transiton above RT due to change of bond length, Even this part is is identical to previously reported complex[2] which shows HS state in room temperature. Poor data quality at 373 K due to instability of crystal of this complex at 373 K.

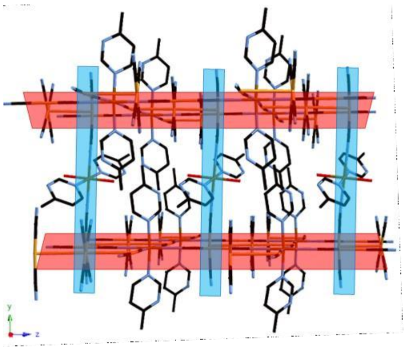

Figure 1. Structure of complex

Table 1. Bond length of complex

	373(2) K	298(2) K	88(2) K
Fe-N(2D, L)	2.14(2) Å	2.008(5) Å	1.997(4) Å
Fe-N(2D, CN)	2.07(5) Å	1.933(7) Å	1.920(8) Å
Fe spin state	HS	LS	LS
Fe-N(1D, L)	2.26(2)	2.239(6) Å	2.231(5) Å
Fe-N(1D, CN)	2.16(2)	2.159(5) Å	2.145(5) Å
Fe spin state	HS	HS	HS

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Accessing the magnetic bistability of substituted Jäger-type iron(II) N_2O_2 platforms

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Molecular bistability, especially the spin crossover phenomena is predominant in $3d^{4-7}$ metal complexes in an octahedral coordination environment. Two electronic states, that is high spin and low spin, can be accessed via external chemical/physical perturbation. Accompanied with that are changes in physical properties e.g. bond lenghts and magnetic properties.[1] Temperature-dependent X-ray diffraction, magnetochemical measurements and Mössbauer studies allow to track variations in bond lengths and magnetic variations, respectively, since in iron(II) complexes a complete change of occupation of antibonding orbitals upon spin transition is present. Cooperativity between the spin centers is crucial to redirect structural changes upon spin transition.[2] Besides short range interactions via π-π-stacking or hydrogen bonding, long range interactions can be realized via the synthesis of coordination polymers.[3] We herein present remote-substituted Jäger-type iron(II) N_2O_2-coordinating platforms that reversibly undergo spin transition with thermal hysteresis close to room temperature.

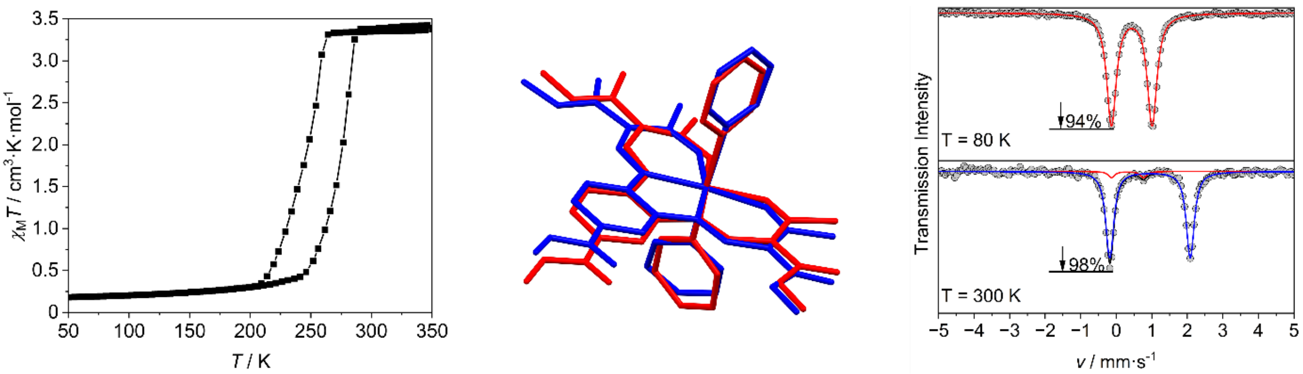

Figure 1. $\chi_M T$ vs T curve showing a thermal hysteresis loop (left). Comparison of the crystal structures of a high spin (blue) and low spin (red) iron(II) compound (middle). Mössbauer spectra at 80 K and 300 K showing high and low spin quadrupolar doublets.

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PO 05

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Assembling Smallest Prussian Blue Analogs Using Chiral Hydrogen Bond Donor

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Flexible tuning of electronic and spin states in molecular materials is promising and challenging in the field of materials science. In the case of the cyanide-bridged CoFe complexes, when the energy difference between the iron and cobalt ions is extremely small, a change in electronic state can be induced by external stimuli such as heat, light, or pressure; this is due to the occurrence of the electron transfer coupled spin transition (ETCST). The ETCST-active CoFe complexes can exhibit electronic state variation between the low-temperature (LT) phase ($[\mathrm{Co}^{\mathrm{III}}_{\mathrm{LS}}\text{-}\mathrm{Fe}^{\mathrm{II}}_{\mathrm{LS}}]$) and the high-temperature (HT) phase ($[\mathrm{Co}^{\mathrm{II}}_{\mathrm{HS}}\mathrm{Fe}^{\mathrm{III}}_{\mathrm{LS}}]$).[1-2] In previous works, the occurrence of ETCST has been controlled by the tuning of the redox potentials for Co/Fe sites by chemical modifications.[3] However, there are no examples that the ETCST behavior was promoted through self-assembling. In this presentation, we demonstrate a new approach to constructing functional metal complexes based on ETCST behavior.

A new cyanide-bridged CoFe complex (**1**) was synthesized. Temperature-dependent structural and magnetic data revealed that **1** was paramagnetic in whole temperature ranges. After the self-assembling of **1** with hydrogen-bonding donor molecules (HBD), the supramolecular assembly of **2** showed an abrupt change between paramagnetic and diamagnetic with thermal hysteresis, suggesting the complete magnetic phase transition after hydrogen-bonding formation. Crystal engineering of hydrogen-bonded architecture can influence their packing motif and electronic state variation, yielded in the fine-tuning of the spin state.

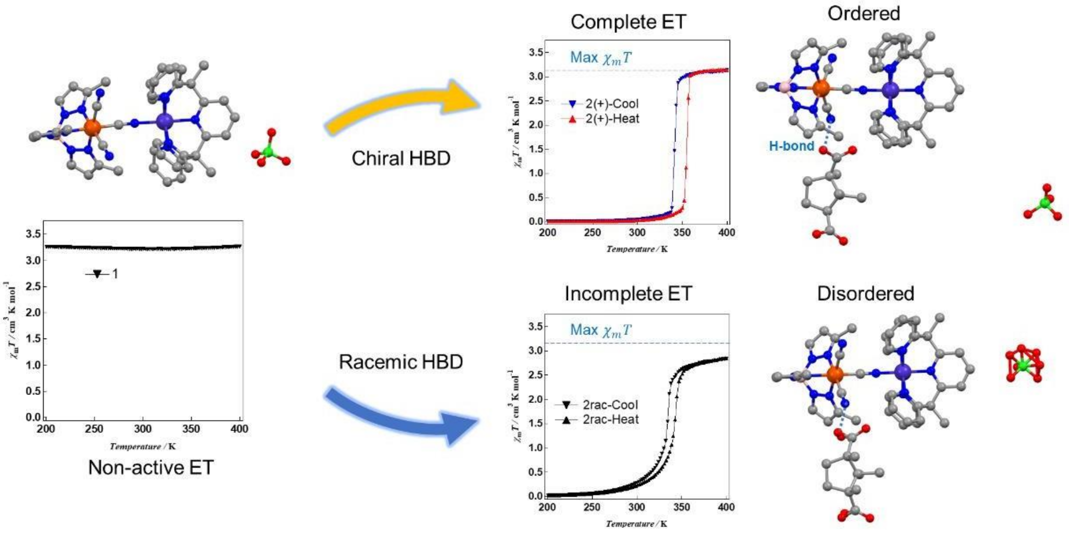

Figure 1. Structure and magnetic properties of CoFe complexes.

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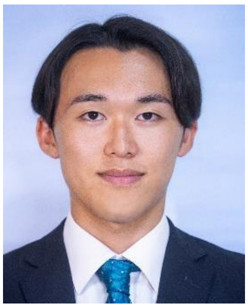
Mononuclear Fe(III) complexes showing slow magnetic relaxation and spin crossover



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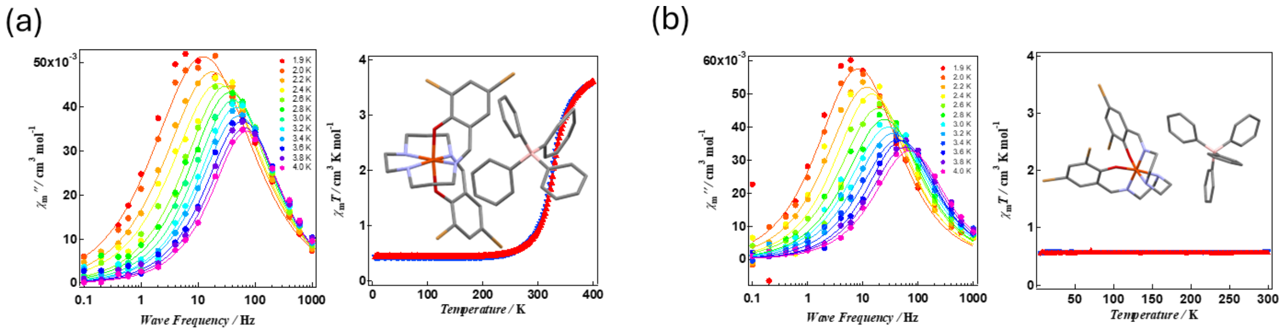
The development of magnetic functional compounds is attractive theme in the field of materials science. In spin crossover materials, which are bistable as molecular devices, the phenomenon is strongly influenced by the coordination environment of the central metal. Meanwhile, slow magnetic relaxation is important for applications such as quantum computation and high-density data storage. In recent years, in particular, molecules with spin quantum number S = 1/2 have attracted much attention as candidates for spin cubits, but the examples for the coexistence of spin crossover and slow magnetic relaxation in Fe(III) are quite limited. In this presentation, we demonstrate a series of mononuclear complex that exhibits slow magnetic relaxation attributed to the low spin S = 1/2 Fe(III). In this study, we systematically synthesize Fe(III) complexes and clarify the influence of the coordination environment on spin crossover, as well as the occurrence and effect of magnetic relaxation behavior in Fe(III).

A series of $[\mathrm{Fe^{III}}(3,5\text{-diX-R}_2\text{nml})](\mathrm{BPh}_4)$ (R = salicylaldehyde (sal), 2'-Hydroxyacetophenone (hap), nml = 222, 232, 323, 333) are prepared and characterized.[1] Magnetic susceptibility measurements showed that **1** exhibits a spin crossover at 330 K, whereas **2** is stable at LS over the entire temperature range. AC susceptibility measurements showed a frequency dependence in both **1** and **2**.



1 $[\mathrm{Fe^{III}}(3,5\text{-diX-sal}_2 323)](\mathrm{BPh}_4)$ **2** $[\mathrm{Fe^{III}}(3,5\text{-diX-hap}_2 222)](\mathrm{BPh}_4)$

Figure. (a) Chemical structure of **1** and magnetic behavior. (b) Chemical structure of **2** and magnetic behavior.

Figure 1. Structures of **1** and **2**

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Chiral induced spin selectivity (CISS) effect in one-dimensional metal string complexes and chiral separation

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Interplay between the chirality and spin remains the frontier of modern physical science, especially in term of the chiral-induced spin selectivity (CISS) that intrinsically hooks the structural chirality and the polarization of spins in a material. Such phenomena are expected to play an important role in spintronic devices and magnetic field responsing phenomena in biological processes.[1] In most studies, chiral molecules used in the experiments are diamagnetic organic molecules such as DNA and helicenes to avoid the debate between CISS and spin-orbital coupling (SOC), however, combining these two factors may lead to materials with multiple tunable conducting states and acting as a single component multilevel computational unit.

Herein, we target on the series of extended metal atom chain complexes, namely $[M_3(dpa)_4(NCS)_2]$ (Fig. 1, dpa^- = di(2-pyridyl)amide anion, M = Cu, Co, Ni) with natural helicity, molecular conductivity from metal-wire like structure, tunable spin states and ease of device fabrication. Our efforts include the enantioseparation of monohelical metal-wire molecules by introducing a chiral anion and forming enantioselective 1D coordination polymer $[\Delta\text{-}M_3(dpa)_4\Lambda\text{-}(As_2(tartrate)_2)]$ (M= Co(II), Ni(II)) and convert it back to enantiopure $[M_3(dpa)_4(NCS)_2]$.[3] On the other hand, the formation of SAMs using racemic complexes were also achieved by immersing gold substrate into a high concerntration solution of the complexes. Future endeavors fall on the conductive-AFM (c-AFM) measurements and c-AFM with magnetically polarized tips under ultralow temperature to evaluate the potential CISS effect. The relationship between spin stats, molecular helicity and molecular conductance will be elucidated.

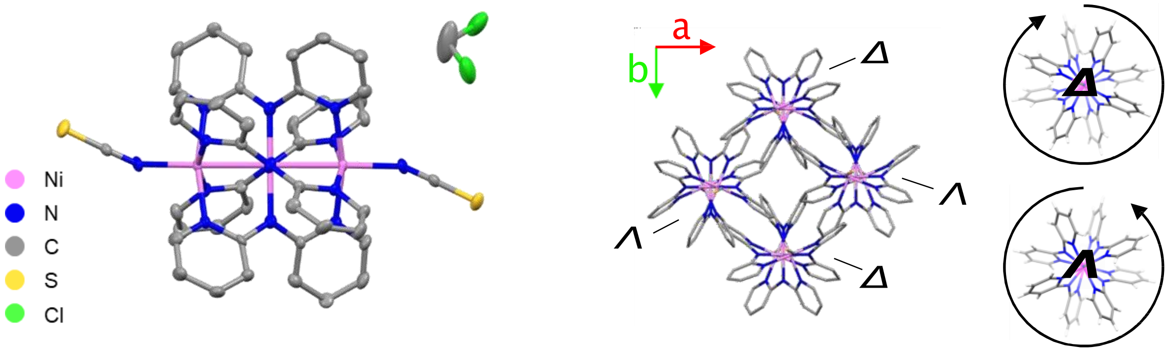

Fig. 1 Structure and packing of $[M_3(dpa)_4(NCS)_2]$

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PO 08

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Theoretical interpretation of intermolecular interactions of SCO complexes by metal dilution

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The development of functional materials based on magnetic switching behavior has potential for future molecule-based chemical sensors. The Spin crossover (SCO) behavior can be observed in first transition metal complexes with $3d^n$ (n = 4-7) electronic configuration, providing the two different spin states between high spin (HS) states and low spin (LS) states, by external perturbations (e.g., temperature, pressure, magnetic field, light). Although their intermolecular elastic interactions are known to determine the SCO behavior, the precise control of elastic interactions as well as crystal structures is quite difficult in the molecular materials. In order to solve the problem, solid solution approach is known as a method that can control the elastic interactions between metal centers. The main investigation was conducted in the series of Fe(II) complexes, but there are less examples for solid solution approach in Fe(III) SCO complexes. [1][2]

In this study, we dilute $[Fe(qsal)_2]NCSe$, which has a very strong cooperative effect,[3] by diamagnetic Ga^{3+} and Al^{3+} to clarify how the magnetic susceptibility can be controlled by metal dilution of iron(III) complexes. Temperature dependent HS fraction was estimated from the magnetic susceptibility data for a series of diluted samples. The energy shift and intermolecular interaction were calculated. As a result, the HS fraction increased at a low temperature when diluted with Ga^{3+} (**Figure**). This is due to the stabilization of the HS state by Ga^{3+}, which has almost the same ionic radius as that of the Fe3+ HS state. On the other hand, the HS fraction decreased at high temperatures when diluted with Al^{3+}(**Figure**). This is thought to be due to the stabilization of the LS state by dilution with Al^{3+}, which has a slightly smaller ionic radius than that of the LS state. By changing the dilution metal, we succeeded in switching the SCO behavior to the high and low temperature directions.

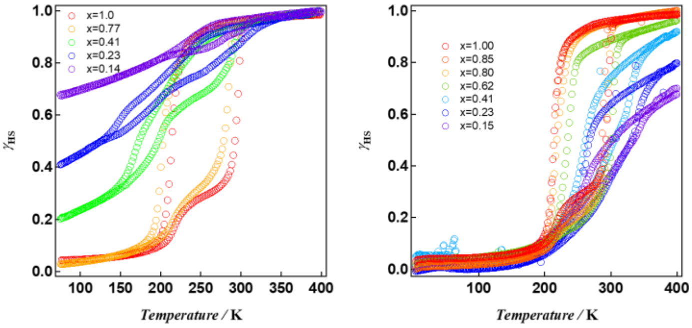

Figure. HS fraction of $[Fe_xGa_{1-x}(qsal)_2]NCSe$ (left) and $[Fe_xAl_{1-x}(qsal)_2]NCSe$ (right)

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