

## COMMUNICATION

## A Ring of Grids: A Giant Spin-Crossover Cluster

Takuya Shiga,<sup>\*a</sup> Minami Tachibana,<sup>a</sup> Hajime Sagayama,<sup>b</sup> Reiji Kumai,<sup>b</sup> Graham N. Newton,<sup>c</sup> Hiroki Oshio<sup>a,d</sup> and Masayuki Nihei<sup>a</sup>Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

**Mononuclear and icosanuclear complexes, [Fe<sup>II</sup>(HL)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**1**) and [Fe<sup>II</sup><sub>20</sub>(L)<sub>24</sub>](BF<sub>4</sub>)<sub>16</sub> (**2**), were synthesized using an asymmetric multidentate ligand (HL). **1** has a bis-chelate structure with two protonated ligands, while **2** has a ring-shape structure comprised of four [2x2] grid moieties and four mononuclear units. Both were found to exhibit spin-crossover behavior.**

Spin-crossover (SCO) complexes are materials in which a transition metal ion can exist in (at least) two discrete, interchangeable magnetic states: high-spin (HS) and low-spin (LS). Such systems have inevitably drawn significant attention for their potential application as single-molecule switches, and they are extensively studied from both fundamental and application-focused perspectives.<sup>1</sup> The SCO behavior of a complex can be tuned by modifying the ligand field strength or by inducing cooperativity via directed supramolecular interactions between neighboring SCO-active species. This can be a particularly fruitful approach, and network compounds with extended (1D to 3D) structures have been shown to exhibit hysteretic SCO behavior thanks to strong cooperativity between neighbors, giving them significant scope as potential components in future molecular memory devices.<sup>2</sup> Many discrete SCO systems have been studied, with the majority based on mononuclear Fe(II) complexes in which the transition metal ion sites in an N<sub>6</sub> coordination environment. On the other hand, multi-nuclear SCO complexes have characteristic properties such as multi-step SCO behavior and dual response

to the external stimuli originating from the coexistence of more than two unique SCO sites with different coordination environments. However, several examples of SCO-active clusters with nuclearities of two to eight metal ions have been reported so far.<sup>3</sup> Dinuclear SCO complexes offer the benefit of relatively simple molecular design with the potential for multistep spin transition behavior associating with symmetry breaking, which is originating from the intramolecular impact of structural distortions and electronic effects during spin crossover to yield two unique SCO sites.<sup>4</sup> Tetranuclear and octanuclear cage-type complexes in which Fe(II) ions occupy the apices have also been prepared and shown to exhibit guest-dependent SCO properties.<sup>5</sup> Such systems are interesting not only due to their capacity to show multi-step SCO, but also due to their host-guest chemistry based on their specific structural features. However, there are no examples of the multi-nuclear SCO-active complex with the nuclearity higher than eight.

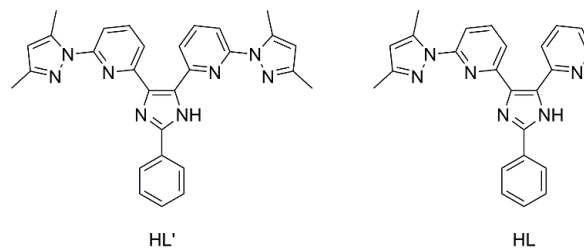


Chart 1 Symmetric and asymmetric ligands HL' and HL.

In recent years, there have been a number of reports of tetranuclear [2x2] grid-type complexes, which can be synthesized by using rigid and planar multidentate ligands.<sup>6</sup> A few of SCO active [2x2] grid-type complexes such as [Fe<sup>II</sup><sub>4</sub>(L<sup>A</sup>)<sub>4</sub>](ClO<sub>4</sub>)<sub>8</sub> (L<sup>A</sup> = 4,6-bis(2',2''-bipyrid-6'-yl)-2-phenylpyrimidine),<sup>7a</sup> [Fe<sup>II</sup><sub>4</sub>(HL<sup>B</sup>)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub>·CH<sub>3</sub>OH (H<sub>2</sub>L<sup>B</sup> = 2,2'-bis(phenyl-2-pyridylmethylene)carbonic dihydrazide),<sup>7b</sup> [Fe<sup>II</sup><sub>4</sub>(L<sup>C</sup>)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub>, (L<sup>C</sup> = 3,5-Bis{6(2,2'-dipyridyl)}pyrazole),<sup>7c</sup> [Fe<sup>II</sup><sub>4</sub>(HL<sup>D</sup>)<sub>4</sub>]Cl<sub>4</sub>·9H<sub>2</sub>O, [Fe<sup>II</sup><sub>4</sub>(L<sup>D</sup>)<sub>2</sub>(H<sub>2</sub>L<sup>D</sup>)<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub>·6H<sub>2</sub>O (H<sub>2</sub>L<sup>D</sup> = 4,6-bis(2-((6-bromopyridin-2-yl)methylene)hydrazinyl)pyrimidine),<sup>7d</sup> [Fe<sup>II</sup><sub>4</sub>(L<sup>E</sup>)<sub>4</sub>](OTf)<sub>8</sub>·14H<sub>2</sub>O

<sup>a</sup> Graduate School of Pure and Applied Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan.  
E-mail: shiga@chem.tsukuba.ac.jp

<sup>b</sup> Photon Factory and Condensed Matter Research Center, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Oho 1-1, Tsukuba, Ibaraki 305-0801, Japan.

<sup>c</sup> GSK Carbon Neutral Laboratories for Sustainable Chemistry, University of Nottingham, Nottingham, NG7 2TU, U.K.

<sup>d</sup> State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Rd., 116024 Dalian, China

† Electronic Supplementary Information (ESI) available: Experimental procedures and characterisation data; crystallographic figures and tables; X-ray powder diffraction, TGA analyses. CCDC 2013374-2013377. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

( $L^E = 2,6$ -bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole)<sup>7e</sup> have been reported. In the course of developing our research into the functional SCO systems,<sup>8</sup> we recently reported two tetranuclear [2x2] grid-type SCO complexes,  $[Fe^{II}_4(L')_4](BF_4)_4$  and  $[Fe^{III}_2Fe^{II}_2(L')_4](BF_4)_6$ , stabilized by the symmetric multidentate ligand  $HL'$  (= 2-phenyl-4,5-bis{6-(3,5-dimethylpyrazol-1-yl)pyrid-2-yl}-1*H*-imidazole, Chart 1(left)). In  $[Fe^{II}_4(L')_4](BF_4)_4$ , structural distortion of the grid structure afforded four unique SCO sites, leading to multistep thermal SCO, while partial oxidations of Fe(II) ions gave the  $[Fe^{III}_2Fe^{II}_2(L')_4](BF_4)_6$  mixed-valence grid exhibiting wavelength-selective light-induced excited spin state trapping (LIESST) of Fe(II) and Fe(III) ions.<sup>8f</sup>

In this paper, a new asymmetric ditopic multidentate ligand  $HL$  (= 2-phenyl-5-pyrid-2-yl-4-{6-(3,5-dimethylpyrazol-1-yl)pyrid-2-yl}-1*H*-imidazole, Chart 1(right)) was synthesized and its complexation reactions with iron(II) ions were studied. In contrast to symmetric  $L'$ , asymmetric  $L$  has two different chelating sites, bi- and tri-dentate chelates, which may afford more than two unique SCO sites in the [2x2] grid. In addition, the [2x2] grid constructed by asymmetric  $L$  may introduce vacant coordination sites, and the extension of the molecular structure can be expected by further coordination of the bridging  $L$  to the vacant sites. As a result, the protonated ligand  $HL$  acted as a simple tridentate ligand to yield a mononuclear complex,  $[Fe^{II}(HL)_2](BF_4)_2$  (**1**). On the other hand, the deprotonated ligand  $L$  gave an unprecedented giant icosanuclear complex,  $[Fe^{II}_{20}(L)_{24}](BF_4)_{16}$  (**2**), in which sixteen  $L$  groups supported four [2x2] grids with coordinatively unsaturated sites and the additional eight  $L$  ligands and four Fe(II) ions bridged the grids to form a giant ring of grids exhibiting unique electronic states.

The mononuclear complex,  $[Fe^{II}(HL)_2](BF_4)_2$  (**1**), was synthesized by the reaction of  $Fe(BF_4)_2 \cdot 6H_2O$  and the asymmetric ligand  $HL$  in the absence of base. The molecular structure of **1** was determined by single crystal X-ray diffraction (Figure S1, Table S1). **1** crystallizes in the monoclinic space group  $P2_1/c$ . The complex consists of two (still protonated)  $HL$  ligands and one Fe(II) ion, forming a bis-chelate mononuclear structure. The Fe(II) ion exists in an octahedral coordination geometry, coordinated by six nitrogen atoms from the tridentate coordination sites of the two ligands. In the crystal lattice, there are two  $BF_4^-$  anions, one ethyl acetate, and two water molecules per one complex cation. At 300 K, the average coordination bond length and  $\Sigma$  value (the sum of the deviation of each of the 12 *cis* N-Fe-N angles from 90°) of the Fe(II) ion are 2.172 Å and 148.7°, respectively, which are typical of HS Fe(II) ions. In contrast, the average coordination bond length and  $\Sigma$  value of the Fe(II) ion at 20 K are 2.077 Å and 134.2°, respectively, suggesting positional disorder of LS and HS Fe(II) ions. This change is indicative of SCO behavior. The spin states were confirmed by Mössbauer spectra at 300 K and 50 K (Figure S2) and cryomagnetic data for a fresh sample of **1**. Magnetic susceptibilities of **1** were collected in the temperature range of 5 K – 300 K (Figure S3). The  $\chi_m T$  value for **1** at 300 K was 3.16 emu mol<sup>-1</sup> K, which is close to the expected value (3.00 emu mol<sup>-1</sup> K) of one magnetically isolated HS iron(II) ion ( $g = 2.00$ ). As the temperature was lowered, the  $\chi_m T$  values gradually decreased from around 170 K, reaching 1.42 emu mol<sup>-1</sup> K at 70

K, which corresponds to a 1:1 ratio of HS and LS iron(II) ions. In the crystal structure, **1** showed hydrogen-bonded interactions between the imidazole and pyridine moieties to form 1D chain structure along the crystallographic *c* axis (Figure S1c), which may contribute the stabilization of HS/LS species with 1:1 ratio.<sup>9–10</sup> To confirm the 1:1 spin state ratio, X-ray structural measurements were performed using a synchrotron radiation source. Despite this, superlattice diffraction peaks, which are indicative of regular alternating HS and LS species, were not observed.

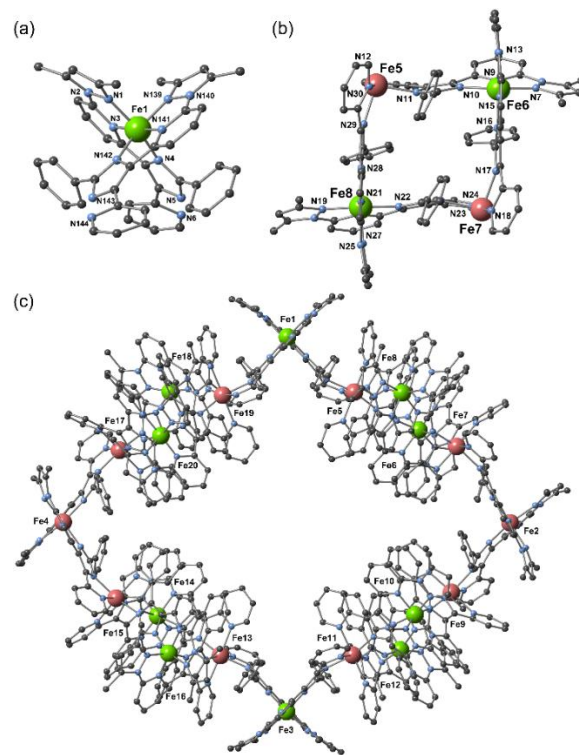


Fig. 1 Molecular structure of **2**. (a) mononuclear bridging unit, (b) tetranuclear [2x2] grid moiety, (c) overall structure of **2**. Lattice solvents and  $BF_4^-$  anions were omitted for clarity. Colour code: C, grey; N, light blue; high-spin Fe(II), pink; low-spin Fe(II), light green.

When  $Fe(BF_4)_2 \cdot 6H_2O$  was reacted with  $HL$  in the presence of the strong base DBU a self-assembled icosanuclear iron complex **2**,  $[Fe_{20}(L)_{24}](BF_4)_{16}$ , was obtained. **2** crystallized in the triclinic space group  $P\bar{1}$  and consists of twenty iron ions and twenty-four deprotonated ligands, forming a giant discrete complex with a ring-shape structure comprised of four [2x2] grid moieties and four mononuclear bridging units (Figure 1 and Figure S5). The iron ions in the icosanuclear complex can be categorized into three distinct environments; type A, B, and C. In each [2x2] grid moiety, two of the four iron ions (type A: bis-coordinated Fe in the grid) have bis-tridentate coordination geometries at the  $N_3$  sites of two deprotonated ligands, while the others (type B: tris-coordinated Fe in the grid) have tris-bidentate environments. Type B ions interact with three deprotonated ligands, in which two belong to grid moieties and one is from the bridging unit. As for the mononuclear bridging unit, the iron ion of type C (Fe in the mononuclear unit) exists in a bis-tridentate coordination environment, bound by the tridentate sites of two deprotonated ligands. The available bidentate sites of these

two ligands connect to two grid moieties, such that the mononuclear unit acts as a rigid right-angle bridge between grids. All in all, four mononuclear bridging units connect four [2x2] tetranuclear units alternately, forming a giant ring-shaped molecule. The average coordination bond lengths and  $\Sigma$  values at 100 K are summarized in Table S2. The structural features at 100 K suggest that half of the iron ions are in their HS state and the others are in their LS state at 100 K. More specifically, the iron ions of type A (Fe6, Fe8, Fe10, Fe12, Fe14, Fe16, Fe18, and Fe20) and type B (Fe5, Fe7, Fe9, Fe11, Fe13, Fe15, Fe17, and Fe19) are LS and HS, respectively. While two (Fe2, Fe4) of the bridging ions (type C) are HS and two (Fe1, Fe3) are LS. Although all type C ions have the same coordination environments, the structure of the ring is distorted from an ideal square to form a diamond shape causing the disparity in spin states. The Fe2 and Fe4 ions at opposite corners have large  $\Sigma$  values, while Fe1 and Fe3 ions have relatively small  $\Sigma$  values, indicating HS and LS states, respectively. Consequently, **2** has four types of iron ions caused by the unique coordination moieties (type A-C) and different degree of distortion in type C ions. The spin states were checked by Mössbauer spectra at 300 K and 20 K (Figure S6). To date, a few giant complexes composed of multiple [2x2] grids have been reported.<sup>11</sup> For example, a {Cu<sub>16</sub>} complex with a 4x[2x2] core stabilised by rigid multidentate ligands,<sup>11b</sup> and a dodecanuclear 3x[2x2] nickel cluster based on the hydrazine ligand, 2-(hydroxyamino)-N'-[1-(2-pyridyl)ethylidene]propanohydrazine.<sup>11c</sup> In the present work, the structure of the icosanuclear complex can be described as having a 4x[2x2]+4 core, rendering it the first example of a new class of giant oligonuclear complex based on grid-type structure motifs.

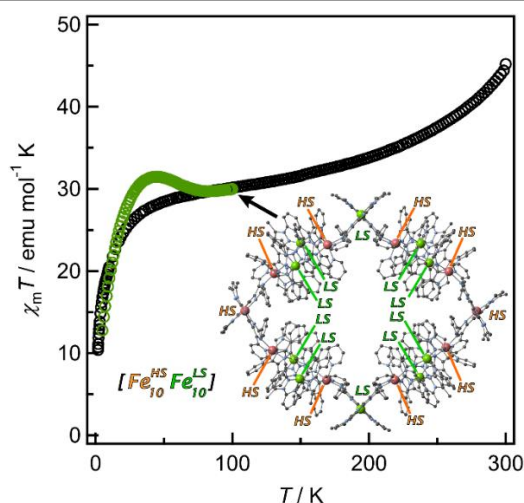


Fig. 2 Plots of  $\chi_m T$  versus  $T$  for **2**. The  $\chi_m T$  values in the LIESST state for **2** are shown in green. Inset: schematic representation of the spin states at 100 K.

Magnetic susceptibilities of **2** were collected in the temperature range of 5 K – 300 K (Figure 2). Below 150 K, the  $\chi_m T$  values are almost constant and are close to the theoretical value for ten high spin and ten low spin iron ions (30.0 emu mol<sup>-1</sup> K). These spin states are consistent with the structural analyses at 100 K, and type B and half of the type C ions remain

in the HS state across the entire measured temperature range. The  $\chi_m T$  value of **2** at 300 K was 45.2 emu mol<sup>-1</sup> K, which corresponds to 75 % of the iron(II) ions being in their HS state (theoretical  $\chi_m T$  value of twenty HS iron(II) ions: 60.0 emu mol<sup>-1</sup> K), which is also supported by Mössbauer data at 300 K (Figure S5). Unfortunately, the crystal structure of **2** with all iron(II) ions being in their HS states was not determined due to the high transition temperature. Considering the coordination environments of each iron ion, those in the bis-chelate coordination sites (type A and half of type C) are expected to show spin transition. In this magnetic measurement, fresh solvated sample was used to limit desolvation effects. Note that the magnetic behaviour of the dried sample shows different gradual SCO due to structural changes based on solvent loss (Figure S4).

In order to further elucidate the SCO behaviour, LIESST experiments were performed for **1** and **2**. The magnetic susceptibilities of both compounds were monitored upon irradiation with 808 nm red and 532 nm green lasers at 5 K (Figures S3 and Figure 2). In **1**, a distinct increase in the  $\chi_m T$  value was observed upon green light irradiation reaching a saturation value of 2.11 emu mol<sup>-1</sup> K. As the temperature was increased after initial irradiation, the  $\chi_m T$  values decreased to 1.50 emu mol<sup>-1</sup> K at 73 K due to thermal relaxation. This magnetic behaviour is typical for SCO-active complexes, in spite of the fact that the LIESST was not completed. Furthermore, the light-excited metastable structure of **1** was determined by single crystal X-ray structural analysis. Changes of coordination bond length and  $\Sigma$  value from the mixed HS/LS state to the complete HS state were observed (Table S3). The metastable structure obtained after light irradiation has similar bond lengths and angles to those observed in the HS state, which is a common feature in previously reported LIESST systems.<sup>8a, 8b, 8c, 8e, 8f</sup> In **2**, a change in  $\chi_m T$  values at 5 K was observed upon green laser irradiation. The  $\chi_m T$  value at 5 K was 12.78 emu mol<sup>-1</sup> K, which was slightly smaller than the value of the original  $\chi_m T$  value (16.81 emu mol<sup>-1</sup> K) due to antiferromagnetic interactions between paramagnetic centers. After irradiation, the  $\chi_m T$  value reached a maximum value of 31.48 emu mol<sup>-1</sup> K at 44 K before thermal relaxation to the ground state with the  $\chi_m T$  values of 29.79 emu mol<sup>-1</sup> K at 76 K. It should be noted that the LIESST behaviour was similar under both green and red laser irradiation.

In summary, a new asymmetric ligand and its mononuclear and icosanuclear iron complexes were synthesized. The structures and magnetic properties of the mononuclear and icosanuclear iron complexes were investigated, and both were found to exhibit gradual spin crossover behavior. To the best of our knowledge, the icosanuclear complex **2** is the largest discrete SCO complex observed to date, although several high nuclearity iron complexes have been reported in the field of SMM research.<sup>13</sup> In general, discrete polynuclear iron clusters of 10 or more iron ions are very rare, thus this result will shed fundamental light on the 'bottom-up' chemistry of nanoscale magnetic materials.<sup>14</sup> In setting out to modify a ligand we knew to favor the formation of SCO-active clusters, we aimed to extend our recent studies on the preparation of grid-type

clusters and were lucky to serendipitously obtain the 'giant' icosanuclear cluster. This combination of design and 'luck' helps us to understand how the introduction of vacant coordination sites and enhanced ligand bridging capacity can allow us to link pre-designed fragments together into more complex, highly organized, cooperative nanoscale switchable systems and may be a key building block in the development of true molecular switching technologies.

This work was supported by a Grant-in-Aid for Scientific Research (C) (no. 20K05537), a Grant-in-Aid for Challenging Exploratory Research (no. 18K19088), a Grant-in-Aid for Fostering Joint International Research (no. 19KK0358), and a Grant-in-Aid for Scientific Research on Innovative Areas 'Coordination Asymmetry' (no. JP16H06523) from the Japan Society for the Promotion of Science (JSPS). This work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2018G102). GNN thanks the Leverhulme Trust (RPG-2016-442) and the University of Nottingham Propulsion Futures Beacon of Excellence.

## Conflicts of interest

There are no conflicts to declare.

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