

# Carboxylic acid-functionalized spin-crossover iron(II) grids for tunable switching and hybrid electrode fabrication

Takuya Shiga,<sup>\*,†</sup> Yamato Sato,<sup>†</sup> Minami Tachibana,<sup>†</sup> Hiroki Sato,<sup>†</sup> Takuto Matsumoto,<sup>†</sup> Hajime Sagayama,<sup>‡</sup> Reiji Kumai,<sup>‡</sup> Youichi Murakami,<sup>‡</sup> Graham N. Newton<sup>§</sup> and Hiroki Oshio<sup>\*,†</sup>

<sup>†</sup> Graduate School of Pure and Applied Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

<sup>‡</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>§</sup> GSK Carbon Neutral Laboratories for Sustainable Chemistry, The University of Nottingham, Nottingham NG7 2GA, U.K.

*Spin crossover, Magnetism, Switchable molecules, Iron, Polynuclear complex.*

## Supporting Information Placeholder

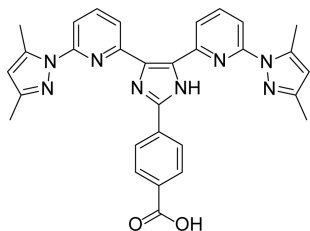
**ABSTRACT:** Two carboxyl-substituted iron(II) grids, one protonated,  $[\text{Fe}_4(\text{HL})_4](\text{BF}_4)_4 \cdot 4\text{MeCN} \cdot \text{AcOEt}$  (**1**), and the other deprotonated,  $[\text{Fe}_4(\text{L})_4] \cdot \text{DMSO} \cdot \text{EtOH}$  (**2**) ( $\text{H}_2\text{L} = 4\text{-}[4,5\text{-bis}\{6\text{-}(3,5\text{-dimethylpyrazol-1-yl})\text{pyrid-2-yl}\}\text{-1H-imidazol-2-yl}]\text{benzoic acid}$ ), were synthesized. Single crystal X-ray structure analyses reveal both complexes have a tetranuclear  $[2 \times 2]$  grid structure. **1** formed one-dimensional chains through intermolecular hydrogen bonds between the carboxylic acid units of neighboring grids, while **2** formed two-dimensional layers stabilized by  $\pi\text{-}\pi$  stacking interactions. **1** showed spin transition between  $3\text{HS-1LS}$  and  $1.5\text{HS-2.5LS}$  states around 200 K, while **2** showed spin crossover between  $4\text{LS}$  and  $2\text{LS-2HS}$  states above 300 K. A modified ITO electrode was fabricated by soaking the ITO in a solution of **1**. The resultant electrode showed reversible redox waves attributed to original redox processes of Fe(II)/Fe(III).

The rational design of bistable molecules for use in molecular devices is a key target in modern science.<sup>1</sup> Such materials have been investigated both for their fundamental chemistry and as components in nanoscale molecular switching technologies.<sup>2</sup> Spin-crossover (SCO) complexes are bistable molecules, the spin-state of which can be switched upon the application of external stimuli (temperature, light, pressure, etc.), rendering them desirable candidates as the active components of molecular-based devices.<sup>3</sup> SCO complexes can be designed by tuning the nature of the ligand field, and transition metal clusters with a wide variety of sizes and topologies have been reported to exhibit the phenomenon.<sup>4</sup> In order to develop new functional spin crossover materials, the supramolecular arrangement of the molecular species should be controlled.<sup>5</sup> Extension and functionalization of complex capping ligands can allow this, and simultaneously influence the electronic structure of the system, affecting the SCO properties of the molecular cluster. The spatial assembly of SCO molecules in

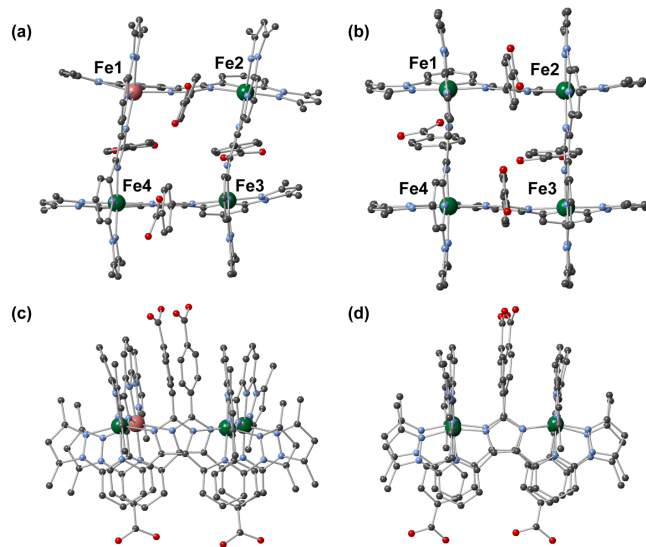
a bulk system can lead to cooperativity in their switching response. For example, large magnetic hysteresis loops have been observed in network systems in which strong intermolecular interactions such as covalent-bonds,  $\pi\text{-}\pi$  stacking and hydrogen bonds mediate the cooperative SCO response.<sup>6</sup> Such materials may have applications in future memory storage technologies. SCO complex ligand modification can enable a range of phenomena such as LISC (Ligand Induced Spin Crossover),<sup>7</sup> and facilitate surface fixation and patterning.<sup>8</sup> The vast majority of research into SCO materials focusses on mononuclear complexes, however an increasing number of polynuclear SCO compounds have been reported, and found to exhibit complex switching behavior derived from intramolecular metal-metal interactions.<sup>9</sup> We recently reported two tetranuclear grid type SCO complexes,  $[\text{Fe}^{\text{II}}_4(\text{L}')_4](\text{BF}_4)_4$  and  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_2(\text{L}')_4](\text{BF}_4)_6$ , stabilized by the multidentate ligand  $\text{HL}' (= 2\text{-phenyl-4,5-bis}\{6\text{-}(3,5\text{-dimethylpyrazol-1-yl})\text{pyrid-2-yl}\}\text{-1H-imidazole})$ . The clusters exhibited multistep thermal SCO and wavelength-selective Light-induced excited spin state trapping (LIESST) properties.<sup>10</sup> In order to develop polynuclear SCO complexes for applications in future technologies there are two key areas that must be addressed: fine-tuning the multi-step SCO behavior by molecular design, and organization of the molecular species into electronically addressable surface arrays. To this end, functionalization of SCO complexes with carboxylate groups allows us to explore the effects of the ligands' electronic state on the switching properties, allows us to generate extended hydrogen-bonded arrays of clusters, and facilitates the fabrication of surface-modified electrodes. Here we report the synthesis and characterization of carboxylic acid-modified  $[\text{Fe}_4]$  grids, their SCO properties, and their use in the modification of ITO electrodes. In order to evaluate possibilities of the molecules for molecular devices, electronic state in solid and solution states were investigated by magnetic and electrochemical measurements. Two carboxylic acid functionalized tetranuclear  $[\text{Fe}_4]$  grid compounds, one protonated  $[\text{Fe}_4(\text{HL})_4](\text{BF}_4)_4 \cdot 4\text{MeCN} \cdot \text{AcOEt}$  (**1**) and the other deprotonated  $[\text{Fe}_4(\text{L})_4] \cdot \text{DMSO} \cdot \text{EtOH}$  (**2**)

( $H_2L = 4$ -[4,5-bis(6-(3,5-dimethylpyrazol-1-yl)pyrid-2-yl)-1*H*-imidazol-2-yl]benzoic acid), were synthesized and structurally characterized by X-ray analyses. Both compounds showed thermal and light-induced SCO behavior, and **1** shows pseudo reversible four step redox processes. In addition ITO- $[Fe_4]$  composite electrodes were fabricated and electrochemically characterized.

### Chart 1. Structure of ligand $H_2L$



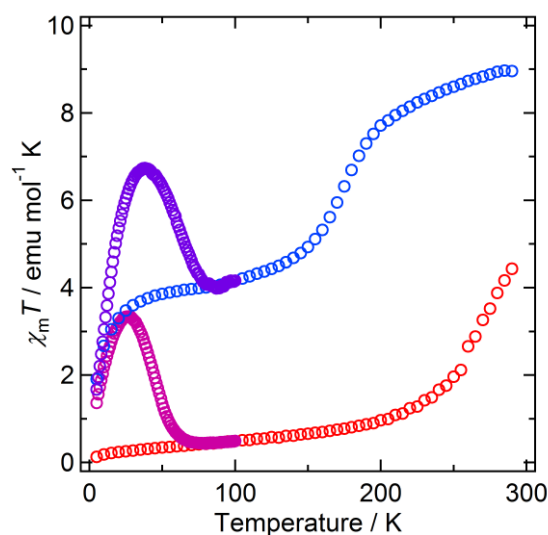
The polypyridyl, carboxylic acid-bearing, multidentate ligand,  $H_2L$  (4-[4,5-bis(6-(3,5-dimethylpyrazol-1-yl)pyrid-2-yl)-1*H*-imidazol-2-yl]benzoic acid), was synthesized following a protocol adapted from our previous study.<sup>10</sup> The tetranuclear iron grid,  $[Fe_4(HL)_4](BF_4)_4 \cdot 4MeCN \cdot AcOEt$  (**1**), was synthesized by the reaction of  $H_2L$  with  $Fe(BF_4)_2 \cdot 6H_2O$  in acetonitrile. The deprotonated analogue,  $[Fe_4(L)_4] \cdot DMSO \cdot EtOH$  (**2**), was synthesized by reaction of **1** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).



**Figure 1.** Molecular structures of (a) **1** and (b) **2**. Side view for (c) **1** and (d) **2** at 100 K. Colour code: C, grey; N, light blue;  $Fe^{II}(HS)$ , pink;  $Fe^{II}(LS)$ , green.

Single crystal X-ray structural analyses for **1** and **2** revealed that both complexes have similar  $[2 \times 2]$  type grid structure consisting of four iron(II) ions and four ligands (Figure 1). The carboxyl groups of **1** are protonated, while those of **2** are deprotonated. The valence states of all iron ions can be estimated as a divalent based on charge balance and coordination bond lengths (Table 1). In addition, structural data at different temperatures suggests spin transition behavior for both complexes. **1** formed one-dimensional chain through intermolecular hydrogen bonds between carboxylic acid units of neighboring grids, while **2** formed two-dimensional layers stabilized by  $\pi$ - $\pi$  stacking interactions (Figures S1 and S2).

Temperature dependent magnetic susceptibilities were measured between 5 and 290 K (Figure 3). For **1**, the  $\chi_m T$  value at 290 K was  $8.96 \text{ emu mol}^{-1} \text{ K}$ , which corresponds to the sum of the spin-only values expected for three magnetically isolated  $S = 2$  spins (3HS-1LS state). Lowering the temperature caused the  $\chi_m T$  value to decrease, initially gradually, then more abruptly at around 175 K, before reaching a plateau below 130 K with a  $\chi_m T$  value around  $4.5 \text{ emu mol}^{-1} \text{ K}$ , which is close to the value expected from 1.5 magnetically isolated  $Fe(II)$  ions suggesting a 1.5HS-2.5LS state. For **2**, the  $\chi_m T$  values plateau below 230 K reaching  $0.12 \text{ emu mol}^{-1} \text{ K}$  at 5 K, indicative of four low spin state  $Fe(II)$  ions. Above 230 K, the  $\chi_m T$  values increased, reaching  $4.43 \text{ emu mol}^{-1} \text{ K}$  at 290 K, indicating the occurrence of partial SCO behavior above 230 K. The gradual slope of the  $\chi_m T$  values of **1** and **2** across the whole temperature range might arise from the presence of a paramagnetic desolvated/annealed species, showing gradual SCO behavior (Figure S3).



**Figure 2.** Plots of  $\chi_m T$  versus  $T$  for **1** (blue) and **2** (red).  $\chi_m T$  values in LIESST state for **1** and **2** were shown in blue-purple and red-purple, respectively.

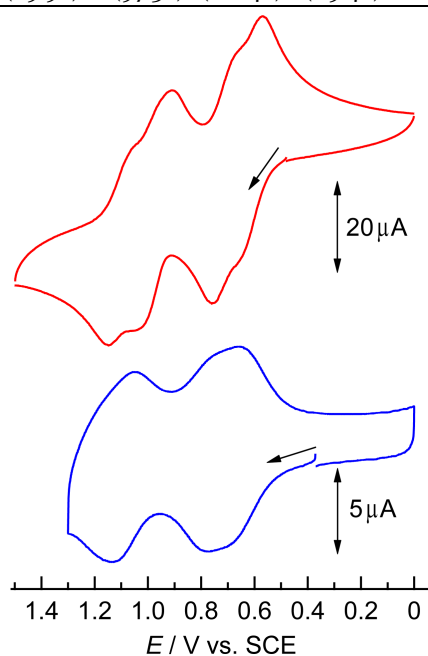
The electronic states accessed through the thermal spin crossover behavior were confirmed by variable temperature X-ray structural analyses and Mössbauer spectra (Figures S4 and S5). The average coordination bond lengths around the iron ions and the  $\Sigma$  values (corresponding to the sum of the deviation of each of the 12 *cis* N-Fe-N angles from  $90^\circ$ )<sup>11</sup> are summarized in Table 1. All measurement data supported one-step SCO behavior from 1.5HS-2.5LS to 3HS-1LS for **1** and from 4LS to 2HS-2LS for **2**. But 1.5HS-2.5LS state couldn't be observed in structural data due to averaged structure. Comparing the spin state of the previously reported grid molecule,  $[Fe_4(L)_4](BF_4)_4$ , which shows two-step SCO from 2HS-2LS to 4HS through a 3HS-1LS state, the present compounds were both found to stabilize low spin states. This difference is likely to arise from supramolecular packing effects derived from the existence of the pendant carboxyl groups.

LIESST experiments for performed for both complexes at 20 K. Both complexes were excited by green light (532 nm), resulting in an increase in  $\chi_m T$  values. As increasing temperature after light irradiation, the  $\chi_m T$  value increased rapidly to a maximum of  $6.74 \text{ emu mol}^{-1} \text{ K}$  for **1** at 38 K and  $3.35 \text{ emu mol}^{-1} \text{ K}$  for **2** at 38 K.

<sup>1</sup>K for **2** at 28 K. The relaxation temperatures were determined to be 82 K and 70 K for **1** and **2**, respectively. These light-induced spin states were assigned as 3HS-1LS and 2HS-2LS for **1** and **2** respectively, and were confirmed by X-ray structural analyses.

**Table 1.** Average bond lengths and  $\Sigma$  values (in parentheses) of comp. **1** and **2**.

	Fe1	Fe2	Fe3	Fe4	State
<b>1</b> (300 K)	2.169 (158.24)	1.972 (91.37)	2.158 (148.78)	2.171 (154.60)	3HS-1LS
<b>1</b> (100 K)	2.175 (163.13)	1.963 (91.58)	1.974 (94.76)	2.016 (106.71)	1.5HS-2.5LS
<b>1</b> (20 K) LIESST	2.153 (157.90)	1.964 (96.00)	2.140 (149.90)	2.137 (151.50)	3HS-1LS
<b>2</b> (250 K)	1.957 (82.18)	1.961 (85.90)	2.015 (105.79)	2.010 (111.78)	2HS-2LS
<b>2</b> (100 K)	1.952 (81.67)	1.959 (85.40)	1.967 (85.34)	1.961 (87.27)	4LS
<b>2</b> (20 K) LIESST	1.962 (89.90)	1.998 (97.30)	2.027 (108.40)	2.059 (119.40)	2HS-2LS



**Figure 3.** Cyclic voltammogram of **1** (top) and complex-supported ITO electrode (bottom).

The electrochemical properties of **1** were investigated. Four pseudo-reversible redox waves, attributed to stepwise Fe(II)/Fe(III) processes from 0.61 V to 1.10 V were observed, correlating well and falling in the same potential range as those of the previously reported  $[\text{Fe}^{\text{II}}_4(\text{L}')_4](\text{BF}_4)_4$  grid. These four redox processes can be assigned as  $[\text{Fe}^{\text{III}}_4] / [\text{Fe}^{\text{III}}_3\text{Fe}^{\text{II}}]$ ,  $[\text{Fe}^{\text{III}}_3\text{Fe}^{\text{II}}] / [\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_2]$ ,  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_2] / [\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_3]$ , and  $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_3] / [\text{Fe}^{\text{II}}_4]$ . To probe the translation of the solution phase electrochemical properties to the solid state, an ITO electrode was

soaked in a solution of compound **1** to generate a supported hybrid electrode. Broad redox peaks were observed in the range of 0.71 – 1.09 V, which suggests that the surface of the ITO electrode had been effectively functionalized with the tetranuclear iron grid complexes. Loading analysis based on the number of moles of adsorbed species and the coverage factor indicate that the  $[\text{Fe}_4]$  molecules formed a monolayer (Supporting information).

In summary, carboxylic acid functionalized iron grid complexes were synthesized. One-step SCO behaviors for both complexes were observed and their electronic states were confirmed by X-ray structural analyses, magnetic measurements and Mössbauer spectra. Fabrication of a grid complex-supporting ITO electrode was performed and the solution phase redox processes of the molecular species were effectively translated to the solid. Analysis of the hybrid electrode suggested that the carboxyl acid functionalized tetranuclear complex was adsorbed as a monolayer. The present study illustrates how the physical properties of SCO-active molecular materials can be influenced by manipulation of the supporting ligands and how the switchable clusters may be adopted as components in future devices. Future work will focus on the external stimuli responsive molecular devices.

## ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic data in CIF format, network structures of **1** and **2**, magnetic data of dried sample of **2**, and Mössbauer spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 1850741-1850746 contain the supplementary crystallographic data for **1** at 100 K, 300 K, 20K (after light-irradiation), **2** at 100 K, 250 K and 20K (after light-irradiation) can also be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## AUTHOR INFORMATION

### Corresponding Author

\* E-mail: oshio@chem.tsukuba.ac.jp

\* E-mail: shiga@chem.tsukuba.ac.jp

### Author Contributions

The manuscript was written through contributions by all authors.

### ORCID

Takuya Shiga: 0000-0002-6834-6011

Graham N. Newton: 0000-0003-2246-4466

Hiroki Oshio: 0000-0002-4682-4705

### Notes

The authors declare no competing financial interests.

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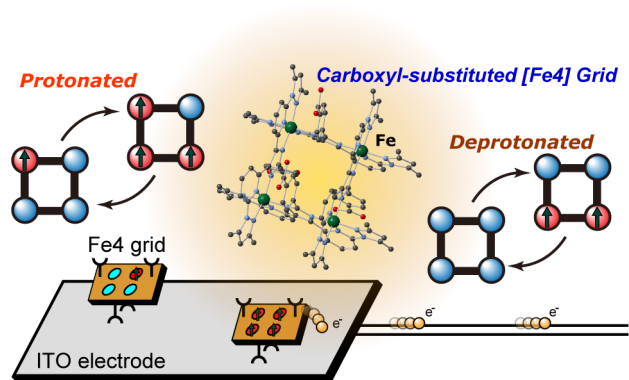
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Two carboxylic acid-substituted tetranuclear [2 × 2] iron(II) grids were synthesized and found to exhibit contrasting thermal photo-induced spin transition phenomena. The carboxylic acid moieties facilitated the preparation of cluster-modified ITO electrodes solution phase redox processes of the molecular species were effectively translated to the solid.