

# Guest-responsive porous magnetic frameworks using polycyanometallates†

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Received 14th April 2009, Accepted 22nd September 2009

First published as an Advance Article on the web 7th October 2009

DOI: 10.1039/b906442g

Three types of cyanide-bridged porous magnetic frameworks based on polycyanometallates exhibited reversible magnetic conversions associated with different guest-responsive structural transformation, which highlights the available strategy using a polycyanometallate for constructing the guest-responsive magnetic frameworks.

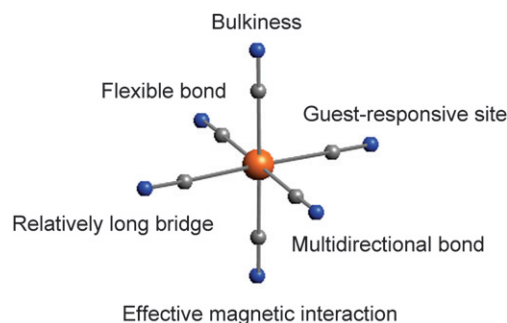
## Introduction

Molecular-based magnets (MMs) have been studied extensively since the end of the 1980s.<sup>1,2</sup> These studies started with the challenge to achieve long-range magnetic ordering with controlling magnetic interactions and arrangement of magnetic centres. Several functionalized MMs, *e.g.*, magnetic switches in response to light,<sup>3</sup> pressure,<sup>4</sup> solvent<sup>5</sup> *etc.*, have been developed through various trials. These efforts paved the way towards new magnetic materials, and developed into a new active research area.<sup>7</sup> The basic molecular design for MMs with infinite structures has aspects in common with that of coordination polymers (CPs) or metal–organic frameworks (MOFs) that have frameworks extended by coordination bonds.<sup>8</sup> Thus, MMs and CPs providing magnetic properties can be identified as coordination polymer magnets (CPMs). As is obvious, CPMs inherit the characteristics of CPs, such as high regularity, diversity, and flexibility in combining a wide range of components, *e.g.*, bridging ligands, metal ions, co-ligands, *etc.*, with elaborately designed frameworks. In particular, the flexible frameworks have the potential to respond to external physical and chemical stimuli. Herein, we focus on the design of CPMs to implement guest-responsive magnetic switching.

The porous framework is one noteworthy functionalized architecture derived from CPs. In the past decade, porous coordination polymers (PCPs) have emerged as a new class of porous materials, representing an evolved form of CPs.<sup>8</sup> Flexible PCPs' pores allow expansion or shrinkage of their framework in association with guest adsorption or desorption.<sup>9</sup> Therefore, PCPs are expected to be multifunctional platforms exhibiting porous properties with specific chemical and physical properties. From this perspective, porous coordination polymer magnets (PCPMs) incorporating magnetic properties into the framework

would be ideal multifunctional materials, particularly as chemoresponsive materials.<sup>6a,b</sup> Kahn *et al.* first introduced the concept of a “magnetic sponge” in molecular magnets that can reversibly release and reabsorb both non-coordinated and coordinated solvent molecules, accompanied by a drastic change of magnetic properties.<sup>5a,b</sup> Although this concept restricts the intended guest molecules to solvents in non-porous systems, it expresses the essence of guest-responsivity in PCPMs. Here we use “guest-responsive magnets” as an umbrella term instead of magnetic sponges.

To couple the magnetic and porous properties, we need a more sophisticated design strategy. Magnetic ordering requires short bridging structures to mediate strong magnetic interactions between magnetic centres, while porous frameworks generally consist of relatively long bridging ligands forming a large inner space. One rational design for PCPMs is based on using large paramagnetic compounds (linkers) to combine magnetic centres. From this viewpoint, a polycyanometallate anion,  $[M_A(CN)_n]^{m-}$  ( $n = 2-8$ ), is a suitable linker because it gives a relatively long  $M_B-NC-M_A-CN-M_B$  linkage (*ca.* 1 nm) for the inner pore and mediates effective magnetic interaction between  $M_A$  and  $M_B$  (Scheme 1). Prussian Blue,  $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$ , is representative of magnetic compounds using a polycyanometallate linker. A number of Prussian Blue analogues (PBAs) have been reported so far.<sup>10</sup> Several PBAs exhibit magnetic and porous properties, but the cyanide bridges do not perform structural flexibility except for structural defects because of their close-packed structures.<sup>6a,11</sup> A convertible structure responsive to chemical stimuli is a significant mechanism to develop guest-responsive magnets. The key to creating such a flexible but durable framework is to utilize weak molecular interactions in



**Scheme 1** Major characteristics of the polycyanometallate anion

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† CCDC reference numbers 645084, 746507 and 746508. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b906442g

addition to strong coordination bonds. From this perspective, we have extensively studied cyanide-bridged CPMs by the use of  $[M_A(CN)_n]^{m-}$  and secondary building units (SBUs) consisting of metal ions  $M_B^{n+}$  and auxiliary ligands (co-ligands).<sup>4e,f, 6h,i, 12,13</sup> The co-ligands play a significant role in avoiding the formation of a PB-type structure and deriving the desired frameworks based on rational molecular designs by limiting the available coordination sites on the SBU. In addition, the incorporation of co-ligands prevents formation of close-packed structures and results in non-bridging cyano groups in the framework. The non-bridging cyano groups act as guest-interactive sites by forming hydrogen bonds, which is of considerable importance for reversible structural conversion.

In this paper, we highlight our strategy for constructing guest-responsive magnets based on the utility component, polycyanometallate, with three types of guest-responsive cyanide-bridged PCPMs, *i.e.*: (1) reversible magnetic and structural conversion of  $[Ni(dipn)]_2[Ni(dipn)(H_2O)][Fe(CN)_6]_2 \cdot 11H_2O$  (**1**: dipn = *N,N*-di(3-aminopropyl)amine)<sup>6h</sup> triggered by water desorption/adsorption; (2) reversible topochemical transformation of a ferrimagnet,  $[Mn(HL)(H_2O)][Cr(CN)_6] \cdot H_2O$  (**2**: L = *N,N*-dimethylethylenediamine);<sup>6i</sup> and (3) bidirectional magnetic chemoswitching of  $\{Fe(pz)[Pt(CN)_4]\}$  (**3**: pz = pyrazine).<sup>13</sup>

## Experimental

### Physical measurements

Variable-temperature X-ray powder diffraction was carried out on a Rigaku RINT-2000 Ultima diffractometer with Cu K $\alpha$  radiation. The magnetic susceptibilities of all samples were measured on a Quantum Design MPMS – XL5R SQUID susceptometer in the temperature range 2–300 K in an applied dc field of 500 Oe. The samples were placed in a glass tube and fixed

to the end of the sample transport rod. Dehydrated samples were prepared by vacuuming for 2 h in the SQUID sample chamber at 400 K. The guest molecules were injected into the glass tube through the sample transport rod with controlling its vapor pressure at 293 K. The molar magnetic susceptibility,  $\chi_M$ , was corrected for the diamagnetism of the constituent atoms.

X-Ray diffraction data of **1**, **2** and **2a** were collected on a Rigaku Mercury CCD system while **3(HS)** and **3(LS)** were collected on a Rigaku Varimax CCD system. In all cases, graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å) was used. A single crystal was mounted on a fiber loop with liquid paraffin and the temperature kept constant under flowing N<sub>2</sub>. The crystal parameters are listed in Table 1. All structures were solved by a standard direct method and expanded using Fourier techniques. Full-matrix least-squares refinements were carried out using Crystal Clear 1.4. (crystallographic software package of the Molecular Structure Corp. and Rigaku) for **1**, **3(HS)** and **3(LS)** and teXsan (crystal structure analysis package of the Molecular Structure Corp.) for **2** and **2a**, with anisotropic thermal parameters for all non-hydrogen atoms. All of the hydrogen atoms were placed in the calculated positions and refined using a riding model.

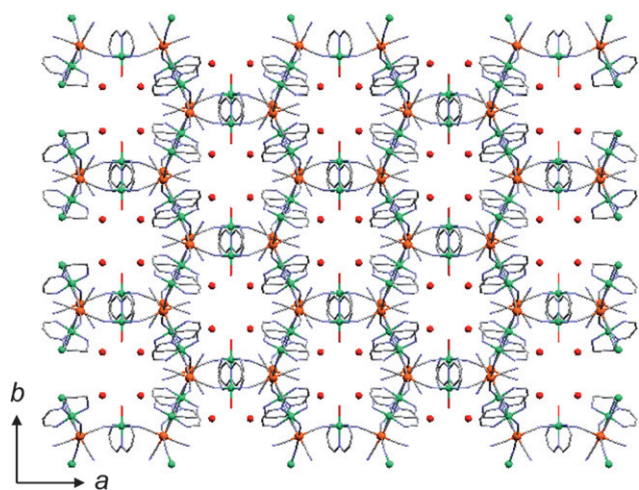
### $[Ni(dipn)]_2[Ni(dipn)(H_2O)][Fe(CN)_6]_2 \cdot 11H_2O$ (**1**)

Compound **1** was obtained as black crystals by the reaction of  $NiCl_2 \cdot 6H_2O$ , dipn and  $K_3[Fe(CN)_6]$  in a 3:3:2 mole ratio in DMF–water solution.<sup>6h</sup> The asymmetric unit of **1** consists of one  $[Fe(CN)_6]^{3-}$  anion, one  $[Ni(dipn)]^{2+}$  and one half  $[Ni_2(dipn)(H_2O)]^{2+}$  cations and 5.5 water molecules. In  $[Ni_2(dipn)(H_2O)]^{2+}$  unit, Ni<sub>2</sub> and central N atom the dipn lies on a twofold axis. In the lattice, this compound forms a 3-D porous framework consisting of 2-D layers extended by an alternating

**Table 1** Crystal parameters of compounds **1**, **2**, **2a**, **3(HS)** and **3(LS)**

| Compound                                                          | <b>1</b>                                                                                        | <b>2</b>                                                          | <b>2a</b>                                          | <b>3(HS)</b>                                                     | <b>3(LS)</b>                                                     |
|-------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|----------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|
| Formula                                                           | C <sub>30</sub> H <sub>63</sub> N <sub>31</sub> Fe <sub>2</sub> Ni <sub>3</sub> O <sub>11</sub> | C <sub>10</sub> H <sub>17</sub> CrMnN <sub>8</sub> O <sub>2</sub> | C <sub>10</sub> H <sub>13</sub> CrMnN <sub>8</sub> | C <sub>8</sub> H <sub>8</sub> N <sub>6</sub> FeO <sub>2</sub> Pt | C <sub>8</sub> H <sub>8</sub> N <sub>6</sub> FeO <sub>2</sub> Pt |
| Formula weight                                                    | 1209.86                                                                                         | 388.23                                                            | 352.20                                             | 471.11                                                           | 471.11                                                           |
| No. of water                                                      | 11                                                                                              | 2                                                                 | 0                                                  | 2                                                                | 2                                                                |
| Crystal system                                                    | Monoclinic                                                                                      | Monoclinic                                                        | Monoclinic                                         | Tetragonal                                                       | Tetragonal                                                       |
| Space group                                                       | C2/c                                                                                            | P2 <sub>1</sub> /n                                                | P2 <sub>1</sub> /c                                 | P4/mmm                                                           | P4/mmm                                                           |
| <i>T</i> /K                                                       | 243                                                                                             | 243                                                               | 323                                                | 293                                                              | 293                                                              |
| <i>a</i> /Å                                                       | 24.044(8)                                                                                       | 7.680(3)                                                          | 7.84(2)                                            | 7.457(4)                                                         | 7.184(6)                                                         |
| <i>b</i> /Å                                                       | 14.343(4)                                                                                       | 14.499(5)                                                         | 14.31(3)                                           | 7.457(4)                                                         | 7.184(6)                                                         |
| <i>c</i> /Å                                                       | 16.688(5)                                                                                       | 16.596(5)                                                         | 12.96(2)                                           | 7.259(4)                                                         | 6.783(5)                                                         |
| $\beta$ /°                                                        | 100.552(4)                                                                                      | 97.323(5)                                                         | 90.07(3)                                           | 90                                                               | 90                                                               |
| <i>V</i> /Å <sup>3</sup>                                          | 5658(3)                                                                                         | 1833.0(10)                                                        | 1455.6(4)                                          | 403.6(4)                                                         | 350.1(5)                                                         |
| <i>Z</i>                                                          | 4                                                                                               | 4                                                                 | 4                                                  | 1                                                                | 1                                                                |
| $\mu$ /mm <sup>−1</sup>                                           | 1.547                                                                                           | 1.298                                                             | 1.616                                              | 9.503                                                            | 10.957                                                           |
| No. of total data                                                 | 21405                                                                                           | 4294                                                              | 3173                                               | 3697                                                             | 2796                                                             |
| No. of unique data                                                | 6442                                                                                            | 4134                                                              | 3046                                               | 412                                                              | 278                                                              |
| No. of data ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                 | 4745                                                                                            | 2333                                                              | 1020                                               | 344                                                              | 266                                                              |
| <i>R</i> <sub>int</sub>                                           | 0.0628                                                                                          | 0.0647                                                            | 0.0984                                             | 0.0472                                                           | 0.0494                                                           |
| <i>R</i> (all data)                                               | 0.0833                                                                                          | 0.0947                                                            | 0.1567                                             | 0.0597                                                           | 0.0512                                                           |
| <i>R</i> <sub>w</sub> (all data)                                  | 0.2049                                                                                          | 0.0955                                                            | 0.1368                                             | 0.0844                                                           | 0.0737                                                           |
| <i>D</i> <sub>c</sub> /g cm <sup>−3</sup>                         | 1.420                                                                                           | 1.407                                                             | 1.607                                              | 1.938                                                            | 2.234                                                            |
| <i>D</i> <sub>c</sub> /g cm <sup>−3</sup> (without lattice water) | 1.188                                                                                           | 1.341                                                             | 1.607                                              | 1.790                                                            | 2.064                                                            |
| Solvent-accessible void/%                                         | 28.2                                                                                            | 5.2                                                               | 0.0                                                | 22.4                                                             | 18.1                                                             |
| Ref.                                                              | 6h                                                                                              | 6i <sup>a</sup>                                                   | 6i <sup>a</sup>                                    | 13                                                               | 13                                                               |

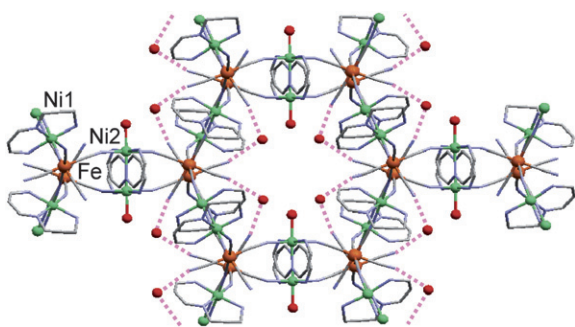
<sup>a</sup> The structures of **2** and **2a** were re-examined using newly-processed diffraction data.



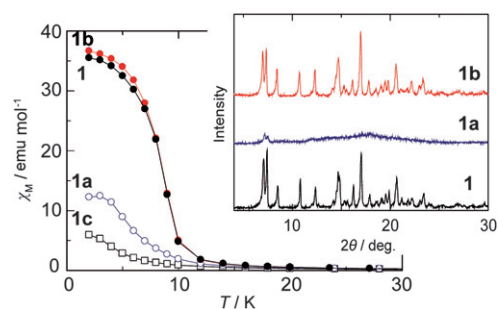
**Fig. 1** Projection of **1** onto the *ab* plane. Disordered lattice water molecules are omitted. Atoms: Fe (orange), Ni (green), O (red), N (light blue), C (gray).

array of  $[\text{Ni}1(\text{dipn})]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ , and  $[\text{Ni}2(\text{dipn})(\text{H}_2\text{O})]^{2+}$  units linking the 2-D layers (Fig. 1). The porous framework has a honeycomb-type channel structure with a solvent-accessible void of 29.0%. The tridentate co-ligand, dipn, coordinates to  $\text{Ni}^{2+}$  in meridional positions and gives three coordinable sites on the SBU,  $[\text{Ni}(\text{dipn})]^{2+}$ . Four cyano groups of  $[\text{Fe}(\text{CN})_6]^{3-}$  coordinate to the adjacent  $\text{Ni}^{2+}$  ions, and the other two in *cis* positions are non-bridging and face the pore. Most of the lattice water molecules are disordered and reside in the pore. In the asymmetric unit, only one lattice water molecule is immobilized by forming bidirectional hydrogen bonds with two non-bridging cyano groups (Fig. 2).

The as-synthesized compound **1** exhibited ferromagnetic ordering at 8.5 K based on the strict orthogonality of magnetic orbitals of  $\text{Ni}^{2+}$  and low-spin  $\text{Fe}^{3+}$ . After vacuum treatment at room temperature, a dehydrated form,  $[\text{Ni}(\text{dipn})]_2[\text{Ni}(\text{dipn})(\text{H}_2\text{O})][\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$  (**1a**), was obtained and this form showed amorphous-like XRPD patterns and paramagnetic behaviour (Fig. 3). The dehydrated form **1a** adsorbed water at room temperature with a maximum uptake of 9.93 mol/mol. The rehydrated form (**1b**) showed the same XRPD pattern and magnetic behaviour of the initial form **1** (Fig. 3). The reversible crystal-to-amorphous-like phase transformation could be



**Fig. 2** Bidirectional hydrogen bonds (pink dotted lines) between lattice water molecules and non-bridging cyano groups.



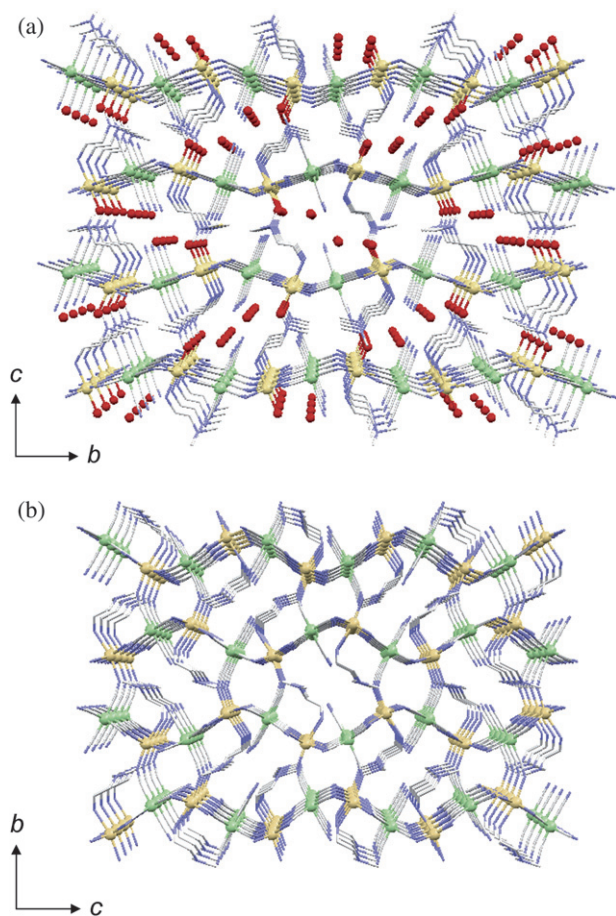
**Fig. 3** Temperature dependences of  $\chi_M$  for the initial form **1** (●), the dehydrated form **1a** (○), the rehydrated form **1b** (●) and the anhydrous form **1c** (□) in an applied dc field of 500 Oe. The insert shows the corresponding XRPD patterns.

performed repeatedly by water desorption/adsorption processes. In contrast, the anhydrous form,  $[\text{Ni}(\text{dipn})]_3[\text{Fe}(\text{CN})_6]_2$  (**1c**), was an amorphous paramagnet and did not recover the initial crystallinity and ferromagnetic phase upon exposure to gaseous water or immersion in water.

The flexible Fe–CN–Ni linkage, bidirectional hydrogen bonds between lattice water molecules and non-bridging cyano nitrogen atoms play crucial roles in the reversible structural and magnetic conversion. Other porous cyanide-bridged magnetic frameworks, *e.g.*,  $\text{Cu}_3[\text{W}(\text{CN})_8](\text{pym})_2 \cdot 8\text{H}_2\text{O}$  (pym = pyrimidine),<sup>6f</sup>  $\{[\text{Mn}(\text{HL})(\text{H}_2\text{O})]_2\text{Mn}[\text{Mo}(\text{CN})_7]_2\} \cdot 2\text{H}_2\text{O}$  (L = *N,N*-dimethylalaninol)<sup>6f</sup> and  $\{[\text{Ni}(\text{cyclam})]_3[\text{W}(\text{CN})_8]_2\} \cdot 16\text{H}_2\text{O}$  (cyclam = 1,4,8,11-tetraazacyclotetradecane)<sup>6m</sup> have been reported, and showed both porous and magnetic properties. These results demonstrate the viability of our strategy of using a polycyanometallate and co-ligands for the construction of porous magnetic frameworks.

### $[\text{Mn}(\text{HL})(\text{H}_2\text{O})][\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$ (**2**)

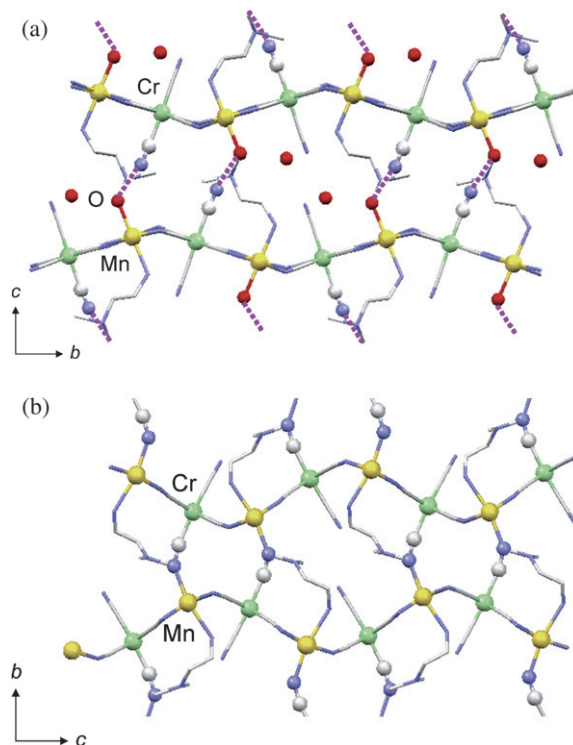
Compound **2** was prepared as pale-green crystals by reaction of  $\text{K}_3[\text{Cr}(\text{CN})_6]$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and co-ligand L (NNdmn) in a deoxygenated aqueous solution at room temperature.<sup>6f</sup> The asymmetric unit of **2** consists of  $[\text{Mn}(\text{HL})(\text{H}_2\text{O})]^{3+}$  cation,  $[\text{Cr}(\text{CN})_6]^{3-}$  anion and a lattice water molecule. In the lattice the compound forms a 2-D layer structure extended by Cr–CN–Mn linkages (Fig. 4a). Four cyano nitrogen atoms in the equatorial positions of  $[\text{Cr}(\text{CN})_6]^{3-}$  coordinate to adjacent  $\text{Mn}^{2+}$  ions, and the other two in axial positions, are non-bridging. One protonated co-ligand and one water molecule are located at the axial positions of the  $\text{Mn}^{2+}$  ion as monodentate ligands. The coordinated water molecules form  $\text{Mn}-\text{OH}_2 \cdots \text{NC}-\text{Cr}$  hydrogen bonds with non-bridging cyano groups in the next layer (Fig. 5a). The hydrogen bonds adjust the topology between layers. A dehydrated form,  $[\text{Mn}(\text{HL})][\text{Cr}(\text{CN})_6]$  (**2a**), was obtained as a single crystal by careful heating of **2** at 343 K. After dehydration, the 2-D layers were changed to a 3-D pillared-layer framework, in which the coordinated water molecules were eliminated and extra Cr–CN–Mn bridges were generated between neighbouring sheets by a topochemical reaction (Figs. 4b and 5b). The dehydrated form has a very narrow 1-D channel based on a highly distorted  $\text{Mn}_2\text{Cr}_2$  quadrangular gate ( $0.8 \times 1.6 \text{ \AA}^2$  based on the van der Waals radii).



**Fig. 4** Projections of the initial form **2** onto the *bc* plane (a) and the dehydrated form **2a** onto the *ab* plane (b). Atoms: Cr (green), Mn (yellow), O (red), N (light blue), C (gray).

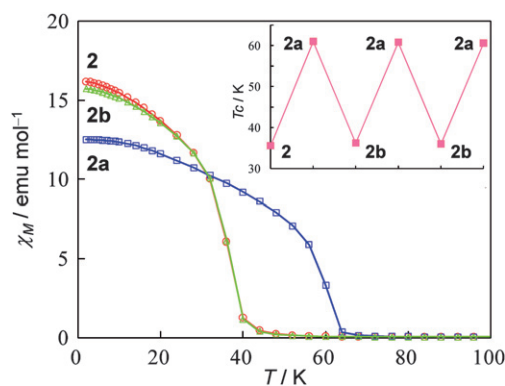
The initial form exhibited ferrimagnetic ordering with a  $T_c$  of 35.2 K, and the  $T_c$  was shifted to 60.2 K by dehydration due to increase of the magnetic interaction pathways (Fig. 6). Upon exposure to air or water vapour at 303 K, **2a** immediately reproduced the same XRPD pattern and magnetic behavior as **2**. The dehydrated form **2a** smoothly adsorbed water (2.3 mol/mol) with a large hysteresis because of the restoration of the initial 2-D layer structure, including replacement of the extra cyanide bridges to water molecules. In addition, **2a** showed size-selective solvent adsorption, linking chemi- and physisorption processes. The rehydrated form **2b** recovered the initial structure and magnetic behaviour of **2**. Compound **2** demonstrated a reversible single-crystal-to-single-crystal (SCSC) transformation with shift of  $T_c$  through the dehydration/rehydration processes and topochemical reaction.

Analogues using other co-ligands, 1,2-propanediamine (pn)<sup>12g,14a</sup> and ethylenediamine (en),<sup>14b,c</sup> also show similar 2-D/3-D conversion with shifting  $T_c$ . In addition, conversions between the 0-D paramagnet and 2-D ferromagnet of  $[\text{K}(\text{18-crown-6})(\text{MeOH})_2][\text{Mn}(\text{L})(\text{H}_2\text{O})(\text{MeOH})_2][\text{Fe}(\text{CN})_6] \cdot \text{MeOH}$  ( $\text{L} = N,N'$ -ethylene-di(5-chlorosalicylideneamine))<sup>5d</sup> and between the 1-D metamagnet and 2-D ferromagnet of  $[\text{Ni}(\text{dmen})_2][\text{Ni}(\text{dmen})_2(\text{H}_2\text{O})][\text{Fe}(\text{CN})_6](\text{bpds})_{0.5} \cdot 3\text{H}_2\text{O}$  ( $\text{dmen} = 1,1$ -dimethylethylenediamine,  $\text{bpds}^{2-} = 4,4'$ -biphenyldisulfonate)<sup>5e</sup> have been



**Fig. 5** Reversible topotactic structural transformation between **2** (a) and **2a** (b). Hydrogen bonds (pink dotted lines).

reported, based on the same strategy using hexacyanometallates. These compounds provide a flexible magnetic framework incorporating removable solvent co-ligands, and deliver structural and magnetic transformations in response to solvation/desolvation processes. The initial structures are stabilized thermodynamically using solvent co-ligands to avoid forming closed-packed structures. Each independent framework is interlinked to adjacent framework(s) through hydrogen bonds formed between solvent co-ligands and non-bridging cyano groups. The metastable desolvated form is obtained by a topochemical solid-state reaction directed by the hydrogen bonds, and cannot retain its structure under the solvent vapour. Steric



**Fig. 6** Temperature dependences of  $\chi_M$  for the initial form **2** (○), the dehydrated form **2a** (□) and the rehydrated form **2b** (△) in an applied dc field of 500 Oe. The insert shows the reversible  $T_c$  switching by dehydration/hydration treatments (red/blue arrows, respectively).

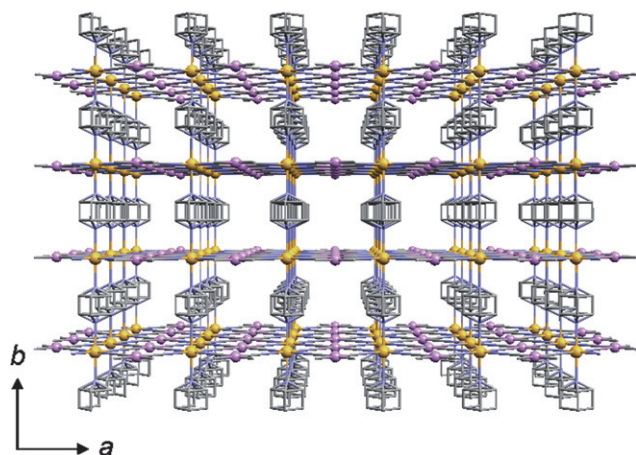
repulsion in the desolvated form would be a key driving force to recover the initial structure. From this perspective, the primary building units,  $[M_A(CN)_n]^{m-}$ , are advantageous for constructing guest-responsive (solvato-responsive) magnetic systems, because they: (1) contain extendable and flexible cyanide bridges; (2) are good magnetic mediators; (3) are able to hydrogen bond with protonic solvent molecules; and (4) are moderately bulky generating steric repulsion with co-ligands in adjacent SBUs.

### $\{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ (3)

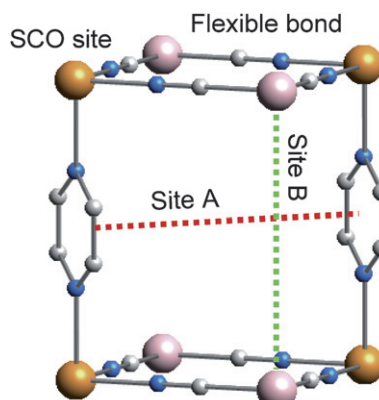
Spin crossover (SCO) is a well-known phenomenon in which electron configurations can be switched between high-spin (HS) and low-spin (LS) states in response to external stimuli (temperature, pressure and light irradiation), producing changes in magnetism, colour, dielectric property and structure.<sup>3f,13,15</sup> A number of SCO compounds have been elaborated, with control of their spin states in molecules and molecular assemblies, and some have successfully exhibited bistable states around room temperature.<sup>16</sup>

As mentioned above, guest-responsive magnetic conversion in PCPMs and CPMs has been reported but there is a large gap in working temperature between guest adsorption/desorption and the magnetic ordering temperature  $T_c$ . The SCO phenomenon would be one solution to overcome this temperature problem instead of ordered magnetism. PCPs incorporating SCO centres (SCO-PCP) may propagate the SCO cooperatively to the whole framework. Such SCO-PCPs may undergo first-order hysteretic spin transition (ST) producing a bistable state at high temperature, in which guest-responsive ST is expected.

Two representative SCO-PCPs,  $[\text{Fe}^{\text{II}}\text{L}_2(\text{NCS})_2] \cdot n\text{S}$  ( $\text{L} = 1,2$ -bis(4-pyridyl)ethylene,<sup>17a,b</sup> *trans*-4,4'-azopyridine,<sup>17c</sup> DL-1,2-bis(4-pyridyl)-1,2-ethanediol;<sup>17d</sup>  $\text{S} =$  alcohol molecule), and  $\{\text{Fe}(\text{pym})(\text{H}_2\text{O})[\text{M}^{\text{I}}(\text{CN})_2]_2\} \cdot \text{H}_2\text{O}$ ,<sup>17e</sup> have been reported by Real *et al.* and Kepert *et al.* These examples clearly display guest-responsive SCO; however, the SCO and guest adsorption-desorption are still not simultaneous. One of the ideal SCO-PCP,  $\{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]\}$  (3), using  $[\text{Pt}(\text{CN})_4]^{2-}$  and pyrazine (pz) co-ligand has been reported by Real *et al.*<sup>13,16b,18</sup> Compound 3 forms a 3-D Hofmann-type framework, in which pz forms rigid



**Fig. 7** Projection of 3 onto the *ac* plane. Lattice water molecules are omitted. Atoms: Fe (orange), Pt (pink), N (light blue), C (gray).

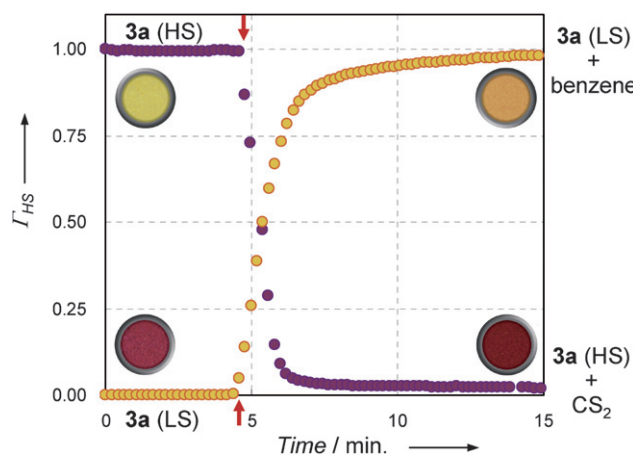


**Fig. 8** The functional cavity structure of 3.

bridges between Fe ions as pillars linking the 2-D layers extended by  $\text{Pt}-\text{CN}-\text{Fe}$  linkages and forms channels with square  $\text{Fe}_2\text{Pt}_2$  windows (Fig. 7). Note that this framework provides two guest-interactive sites: one between the pz bridges (site A) and another between the Pt centres (site B) (Fig. 8). These features should be important *a priori* for the chemical response of the framework.

This compound displays a first-order ST with *ca.* 25 K-wide hysteresis, with  $T_c^\downarrow$  of 285 K and  $T_c^\uparrow$  of 309 K. The solvent-accessible voids of the LS and HS states were estimated to be 18.1 and 22.4%, respectively. The guest-free form **3a** adsorbs various guest molecules in the gas phase or solution, and forms their clathrates. The spin state changes, depending on the guest molecules. *In situ* magnetic measurements following guest vapour injection elucidates the simultaneous guest adsorption and bidirectional spin transition (Fig. 9). Most guest molecules transform **3a** from the low-spin (LS) state to the high-spin (HS) state, whereas  $\text{CS}_2$  stabilizes the LS state exceptionally. The stabilized spin states are retained after removing guest molecules, and both spin states are interchangeable by exchanging the guest molecules with controlling vapour pressure.

The guest molecules studied can be grouped into three major classes (Table 2), where class I shows no effect on the spin state;



**Fig. 9** Time dependence of the fraction of the HS state under a benzene (yellow) and  $\text{CS}_2$  (purple) atmosphere at 293 K. Red arrows indicate the starting points of guest injection (valve opening). The color circles are photos of samples.

**Table 2** Summary of the guest induced spin state of **3a** at 293 K

| Class | Guest molecule   | Number of guests per Fe (at rt) | Effect        |
|-------|------------------|---------------------------------|---------------|
| I     | CO <sub>2</sub>  | 1.1                             | No            |
|       | N <sub>2</sub>   | 0.1                             |               |
|       | O <sub>2</sub>   | 0.1                             |               |
| II    | H <sub>2</sub> O | 2~5                             | HS stabilized |
|       | D <sub>2</sub> O | 2~5                             |               |
|       | MeOH             | ~2                              |               |
|       | EtOH             | ~2                              |               |
|       | 2-PrOH           | ~2                              |               |
|       | Acetone          | ~2                              |               |
|       | Benzene          | 1                               |               |
|       | Pyrazine         | 1                               |               |
|       | Toluene          | 1                               |               |
|       | Thiophene        | 1                               |               |
|       | Pyrrole          | 1                               |               |
|       | Pyridine         | 1                               |               |
|       | Furan            | 1                               |               |
|       | THF              | 1                               |               |
| III   | CS <sub>2</sub>  | 1                               | LS stabilized |

class II stabilizes the HS state; and class III stabilizes the LS state. The structures of pz and CS<sub>2</sub> clathrates reveal that: (i) the pz guest molecules are located exclusively at site A; and (ii) the CS<sub>2</sub> molecules are located at sites A and B. These systematic structural and magnetic results point to three key factors for stabilizing the spin states: (1) the size and shape of the guest (G); (2) the G···pz interaction at site A; and (3) the G···Pt interaction at site B. Theoretical calculation of the binding energies between CS<sub>2</sub> and each site suggests that the CS<sub>2</sub> molecule interacts suitably with both sites, like a key molecule for the framework.<sup>13</sup> Compound **3** successfully delivers a desired magnetic switch in response to guest molecules at room temperature. The porous SCO framework is constructed by three functional components; (a) SCO Fe(II) ions as framework joints; (b) flat tetracyanometallate, [M(CN)<sub>4</sub>]<sup>2-</sup> (M<sup>II</sup> = Pt, Pd, Ni), providing guest-interactive sites (site B) and forming flexible M–CN–Fe linkages; and (c) pyrazine co-ligands as rigid pillars and guest-interactive sites (site A) (Fig. 8). The well-designed simple framework provides appropriate interactive pores and allows the spin transition coupled to guest adsorption/desorption processes while retaining its cooperativity.

## Conclusions

As shown above, the triad of polycyanometallate, SBU and co-ligand demonstrates the availability for designing and creating guest-responsive magnetic frameworks. In the case of PCPMs **1** and **2**, hexacyanometallates work as good linkers and magnetic mediators, but *T<sub>c</sub>* remains in the low temperature region. Guest adsorption and magnetic ordering are not simultaneous events in these compounds. It is necessary to shift the coexistence phase of magnetic and porous properties to a cooperative phase. A more elaborate porous magnetic framework that transcribes a backbone of PBAs with high *T<sub>c</sub>*, e.g., M<sup>III</sup><sub>3</sub>[Cr(CN)<sub>6</sub>]<sub>2</sub>·*n*H<sub>2</sub>O (*T<sub>c</sub>* = 240 K for M = Cr, 315 K for M = V),<sup>10</sup> would overcome the temperature problem. Recently, Sutter *et al.* reported a PCPM, {[Mn(HL)(H<sub>2</sub>O)]<sub>2</sub>Mn[Mo(CN)<sub>7</sub>]<sub>2</sub>}·2H<sub>2</sub>O (L = *N,N*-dimethylalaninol)<sup>6f</sup>,

which provides ring-shaped channels with potential void of 9.2% and exhibits ferrimagnetic ordering at 106 K in a dehydrated form. Such PCPMs with high *T<sub>c</sub>* would exhibit a unique synergy between the magnetic properties and guest molecules, e.g., paramagnetic, chiral or polar guests. On the other hand, the SCO–PCP {Fe(pz)[Pt(CN)<sub>4</sub>]} (**3**) notably delivered magnetic chemo-switching at room temperature that will open a route to evolving environmentally responsive materials. Controlling the interactions between the SCO framework and guest molecules will allow precise and universal magnetic switching. As the next step, more advanced functions, e.g., external control of selective guest adsorption, separation, or uptake and release of guest molecules, may be delivered using SCO–PCPs with shape-, volume- and chirality-changeable pores depending on the spin state.

## Acknowledgements

This work was supported by a ERATO JST Project “Kitagawa Integrated Pore Project”, CREST JST program, Grant-In-Aid for Science Research (B) (No. 20350026) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and the Mitsubishi fund.

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