Advanced functional properties in nanoporous coordination framework materials

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Coordination framework materials display a rich array of host–guest properties and are notable amongst porous media for their extreme chemical versatility. This article highlights a number of areas where specific function has been incorporated into these framework host lattices.

Introduction

The field of coordination framework materials has undergone such dramatic advance over recent years that those unfamiliar with the area might be forgiven for believing it is a brand new area of chemistry. In fact, the structures and properties of coordination frameworks were considered topical way back in the very first volumes of this journal.[1] So where have we come since then?

The question raised above can be answered in any number of ways. On the one hand, the past 15 years have seen concerted efforts made in exploiting the strong directionality of coordination bonding to give a level of framework design – so-called "crystal engineering".[2] In the past decade, such design considerations have been extended to the generation of a fascinating array of host materials, leading to the extension of early appreciations of molecular clathrates to advanced understandings of structure–property relationships in nanoporous framework hosts.[3] Following the recent discovery of exceptional host–guest properties in these lattices (which include both extreme structural robustness and flexibility, very large pore volumes and surface areas, *etc.*), we stand at an enviable position where the immensely rich host–guest chemistry of coordination frameworks is now well recognised.

Most recently, some of the first efforts have been made to extend the design, synthesis and characterisation of coordination frameworks to include the incorporation of very specific function into these nanoporous hosts. In answering one aspect of the question raised above, this article aims to highlight a few examples where the versatility of molecular chemistry has been exploited in the pursuit of unique functional properties in nanoporous coordination frameworks.
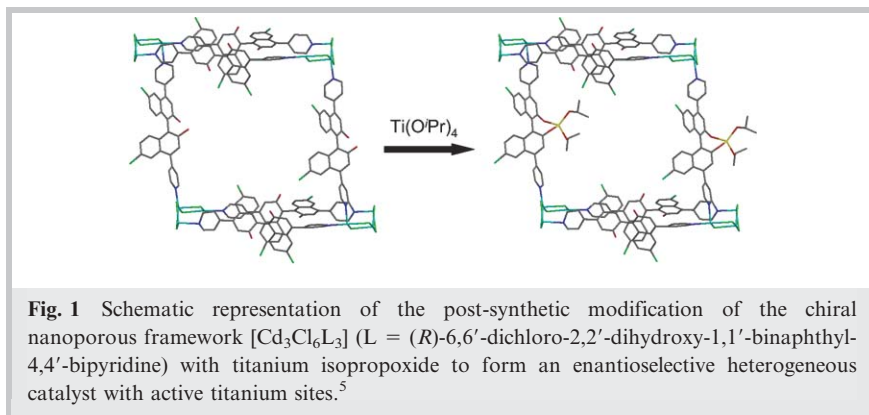
Chemical function

Among a number of chemical properties sought in nanoporous media, enantioselective host–guest function has proven to be one of the more challenging to achieve. Recently, the use of two separate approaches in the design of coordination frameworks has provided some of the first enantiomeric nanoporous phases capable of performing chiral separations and catalyses: 1) the use of homochiral directing agents to guide the handedness of intrinsically chiral networks;[4] and 2) the use of chiral ligands in the formation of open framework structures.[5–7] Of particular note in the second area is the recent report by Lin and co-workers of a chiral framework that displays enantioselective catalytic activity.[5] The synthesis of this material was achieved in two steps: first, the synthesis of a chiral nanoporous phase $[Cd_3Cl_6L_3]\cdot x(\text{guest})$ (L = (*R*)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine); and, second, the chemisorption of titanium isopropoxide sites onto the hydroxyl units of the chiral bridging ligands of the apohost (Fig. 1). The resulting functionalised solid was found to catalyse $ZnEt_2$ additions to aromatic aldehydes with efficiencies and enantioselectivities comparable to those for the

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Fig. 1 Schematic representation of the post-synthetic modification of the chiral nanoporous framework [Cd$_3$Cl$_6$L$_3$] (L = (*R*)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine) with titanium isopropoxide to form an enantioselective heterogeneous catalyst with active titanium sites.[5]

free Ti(O^{i}Pr)$_2$-functionalised ligand. Confirmation that the catalysis occurs within the nanopores was achieved through the demonstration of a distinct size selectivity for the heterogeneous reaction. This remarkable material lays the foundation for a new generation of molecular heterogeneous catalysts in which both the nanopore structure and catalytic sites are tuned for specific function.

More generally, the considerable versatility of molecular frameworks has been exploited in the control of host–guest selectivity. Such control includes the achievement of hydrophilic and hydrophobic surfaces and, indeed, of both surface types in separate channels within the one material.[7] The generation of coordinatively unsaturated metal sites by the desorption of coordinated guest species has also received much recent attention; such sites promise very specific control over host–guest processes and have been recognised as having potential importance in hydrogen storage coordination framework materials.[8]

Among a range of other chemical functions that may be envisaged for molecular hosts is the ability of frameworks to convert reversibly between different structural forms and, therefore, host–guest chemistries. Just such a property has been reported by Ripmeester and co-workers in Cu(CF$_3$COCHCOC-(OCH$_3$)(CH$_3$)$_2$)$_2$·(guest), for which temperature pulsing causes a conversion from a porous phase containing exclusively the *trans*-isomer of the complex to a dense phase containing a mixture of *cis*- and *trans*-isomers; subsequent exposure of the dense phase to sorptive vapour reverts the material to its porous form.[9] A much more subtle host

flexibility, involving the activated opening of narrow pore windows, has been proposed by Thomas and co-workers to be the cause of hysteretic dihydrogen sorption/desorption in certain framework phases.[10] Such an effect allows hydrogen gas to be adsorbed at high pressures but stored at lower pressures, a property of great potential benefit in the area of hydrogen storage.

Electronic and magnetic function

Whilst intensive efforts have been made over recent decades to incorporate a range of electronic and magnetic properties into molecular materials, it has only been recently that these efforts have been extended to their incorporation into porous molecular lattices. A strong impetus for such efforts is the elucidation of structure–property relationships, since variation of sorbed guests provides a convenient method for systematically perturbing the host framework structure and, therefore, the property of interest. Moreover, unique desorption/sorption behaviours may be expected in instances where the host–guest interactions are coupled to changes in electronic/magnetic properties.
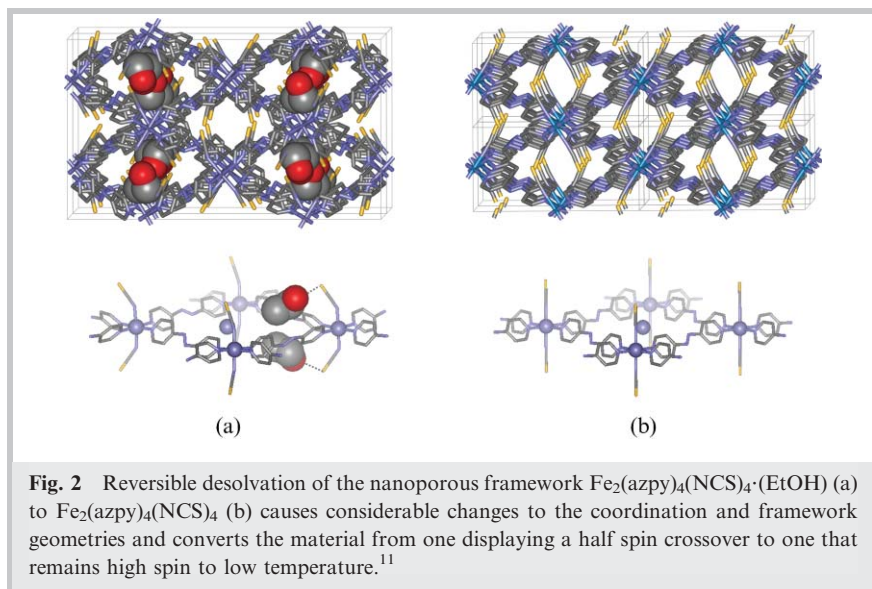
Electronic switching

Of particular interest among electronic/magnetic phenomena are electronic switching transitions, for which host–guest interactions are coupled through both steric and electronic effects. Among these transitions, spin crossover (SCO) is a well-known form of molecular switch in which the *d*-electron configuration of certain first-row transition metal ions (d^4–d^7) changes between high- and

low-spin forms in response to external stimuli such as variations in temperature, pressure and irradiation. Physical consequences of this transition include pronounced changes in colour, magnetism and coordination bond distances. Guest-exchange in nanoporous SCO systems provides a new approach for investigating features such as the ligand field, electronic communication between SCO centres, and lattice dynamics (*e.g.*, activation barriers that may cause hysteretic transitions). Such materials also promise applications in sensing, with molecular recognition achieved through the selectivities of both the pore structure and the host–guest interaction near the SCO centre. Of further interest is the use of external stimuli to modify the environment of the guest in a switchable fashion, allowing possible control over processes such as guest-exchange.
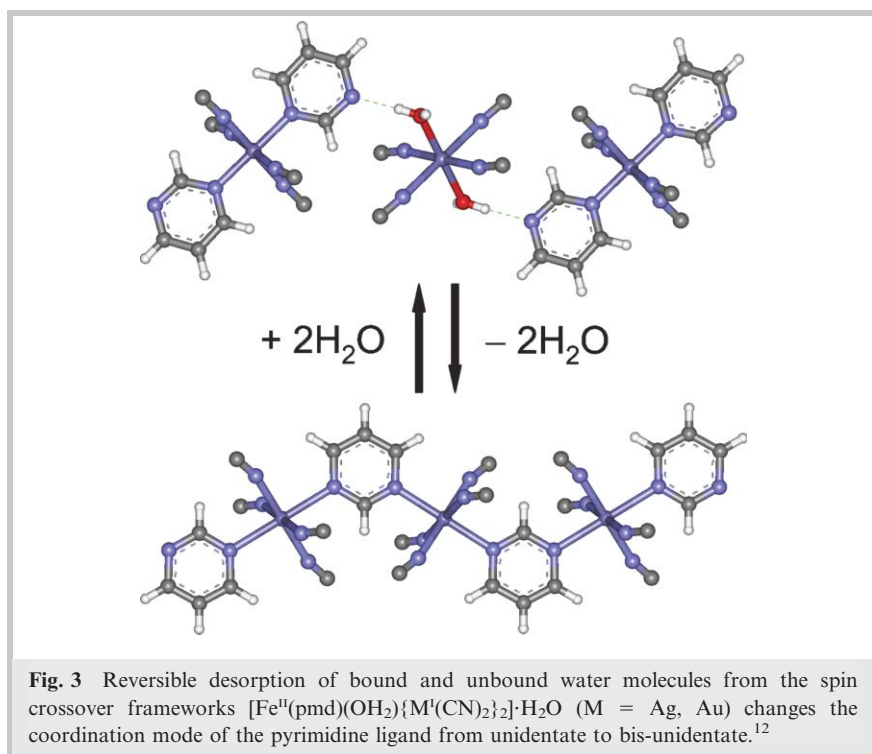
Spin crossover has recently been incorporated directly into porous molecular lattices through the bridging of iron(II) SCO centres to form open frameworks. The nanoporous phase Fe$^{II}_2$(azpy)$_4$-(NCS)$_4$·(EtOH) (azpy = *trans*-4,4′-azo-pyridine) displays a broad half SCO transition that depends on guest inclusion.[11] Desorption of the unbound ethanol guests from this interpenetrated phase leads to a reversible single crystal to single crystal structural transformation in which the 1D pore channels collapse partially (Fig. 2). In contrast to the ethanol loaded material, the desorbed phase remains high spin to low temperature, a feature that may reflect a weakening of the ligand field with distortion of the coordination geometries following guest removal. Notable structural changes in the vicinity of the iron(II) site include the rotation of pyridyl donors and the loss of hydrogen bonding interactions between the ethanol guest and the thiocyanate ligand bound at the iron(II) crossover site. Sorption of other alcohol guests 'switches back on' the SCO sites, with subtle differences in behaviour attributed to the steric influence of the guest on local iron(II) coordination geometry.

Real and co-workers have recently reported two further systems that display guest-dependent SCO.[12,13] The isostructural compounds [Fe^{II}(pmd)(OH$_2$)-{M^I(CN)$_2$}$_2$]·H$_2$O (pmd = pyrimidine; M = Ag, Au) contain two independent

Fig. 2 Reversible desolvation of the nanoporous framework $Fe_2(azpy)_4(NCS)_4 \cdot (EtOH)$ (a) to $Fe_2(azpy)_4(NCS)_4$ (b) causes considerable changes to the coordination and framework geometries and converts the material from one displaying a half spin crossover to one that remains high spin to low temperature.[11]

iron(II) centres with differing coordination.[12] Each of the phases undergoes sharp half SCO transitions with appreciable hysteresis. Following the removal of both coordinated and uncoordinated water with reversible dehydration, a remarkable topochemical conversion occurs in which the pyrimidine molecules, previously bound only through one nitrogen atom, now bridge the two independent iron(II) centres (Fig. 3). This conversion results in a change in the framework topology from the interpenetration of three separate 3D networks to a single 3D network, and to large accompanying changes to the SCO properties: for the Ag phase the SCO transition moves to lower temperature and has a larger hysteresis, whereas for the Au phase the transition is eliminated completely. In contrast, dehydration of the SCO Hofmann clathrate phase $[Fe^{II}(pz)\{Pt^{II}(CN)_4\}] \cdot n(H_2O)$ (pz = pyrazine; $n \approx 2$–3), which consists of $FePt(CN)_4$ layers bridged by pyrazine, leads to an increase in both the temperature and width of the SCO hysteresis loop.[13] Whilst not reported, it seems likely that framework connectivity is retained in the apohost and that the dehydration is reversible. This material is particularly noteworthy in that irradiation in the bistable temperature region leads to photoinduced structural relaxations between the metastable high-spin/low-spin states.

An interesting related challenge is the incorporation of valence tautomeric centres to yield nanoporous materials that display irradiation induced metal–ligand electron transfer, a transition with substantially longer photoexcited lifetimes at ambient temperature than spin crossover. Interesting photomechanical effects have been observed in non-porous valence tautomeric compounds, including the macroscopic bending of crystals following photoexcitation between valence states.[14] Such a property would have fascinating consequences on host–guest chemistry if achieved within a porous lattice.

Magnetic ordering

A considerable challenge in the formation of nanoporous magnets lies in the dual requirement of combining short magnetic exchange pathways and interconnected pore volume; structural features that are largely inimical. Despite this challenge, some notable successes have appeared recently in the coordination framework arena. The discovery of solvatomagnetic effects in such materials is of particular interest, both for the systematic elucidation of magnetostructural relationships and for possible applications in areas such as molecular sensing. Further, magnetic interactions between paramagnetic guests (*e.g.*, O_2) and magnetic host lattices are yet to be investigated.

Of the small number of nanoporous molecular magnets reported to date, the Prussian Blue family provides many interesting phases with small pore dimensions. Solvatomagnetic effects have recently been reported in this family by Ohkoshi, Hashimoto and co-workers, who showed that the peach-coloured, ferromagnetically coupled defect phase $Co^{II}_{1.5}[Cr^{III}(CN)_6] \cdot 7.5(H_2O)$ converts to a blue, antiferromagnetically coupled phase of formula

Fig. 3 Reversible desorption of bound and unbound water molecules from the spin crossover frameworks $[Fe^{II}(pmd)(OH_2)\{M^I(CN)_2\}_2] \cdot H_2O$ (M = Ag, Au) changes the coordination mode of the pyrimidine ligand from unidentate to bis-unidentate.[12]
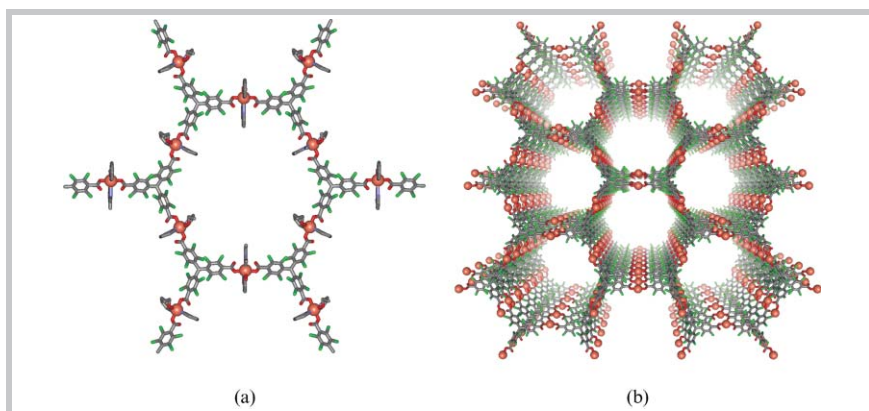
Fig. 4 The 2D hexagonal layers (a) of the nanoporous magnet $Cu_3(PTMTC)_2(py)_6(CH_3CH_2OH)_2(H_2O)$ contain two spin sites, one on the Cu(II) ion and one centred on the trigonal carbon atom of the radical ligand, PTMTC. The layers stack to form extended 1D channels (b; bound and unbound species removed for clarity).[19]

$Co^{II}_{1.5}[Cr^{III}(CN)_6]\cdot2.5(H_2O)\cdot2.0(EtOH)$ on exposure to ethanol, an effect attributed to a change from six- to (average) four-coordination at the Co^{II} centre.[15] Among a number of approaches for achieving larger pores, the use of the formate anion to link metal centres has had some notable recent success,[16] as has the bridging of low-dimensional metal hydroxide systems by organic linkers.[17,18] A novel further strategy for the synthesis of molecular magnets is the use of radical bridging ligands. This approach has been used successfully by Veciana and co-workers to form the highly flexible nanoporous magnet $Cu_3(PTMTC)_2(py)_6(CH_3CH_2-OH)_2(H_2O)$, a 2D layered structure that contains Cu(II) centres bridged by polychlorinated tris(4-carboxyphenyl)methyl radicals (PTMTC) (Fig. 4).[19] This material shrinks and expands by up to 30 vol% with ethanol desorption/sorption and displays subtle solvatomagnetic effects associated with framework collapse and the removal of coordinated guests. Unexpectedly, a highly pronounced solvatomagnetic effect has recently been observed in a robust nanoporous framework in which no change in metal coordination occurs with guest desorption. Reversible dehydration/rehydration of $[Co^{II}_3(OH)_2(C_4O_4)_2]\cdot3H_2O$ leads to a reversible interconversion from antiferromagnetic to ferromagnetic ordering at low temperature.[17] The host lattice, which consists of 1D $[Co^{II}_3(\mu_3-OH)_2]^{4+}$ ribbons linked by squarate anions to form a porous 3D network (Fig. 5), undergoes only minimal changes

(< 2% in bond distances and angles) with dehydration, suggesting that significant magnetic exchange coupling may occur through the hydrogen-bonded cavity water molecules in the hydrated phase.

Conductivity

Among a range of other electronic properties of interest for incorporation into nanoporous frameworks is

electrical conductivity, leading to possible applications in molecular sensing and selective electrode materials. Highly conducting non-porous coordination frameworks include the Cu–DCNQI system (DCNQI = a range of *N,N*-dicyanoquinonediimines),[20] in which electronic delocalisation and metallic conductivity occur due to a close matching of donor–acceptor electronic energy levels and strong intraframework orbital overlap. A notable recent achievement in this general area is the development by Kitagawa and co-workers of the porous framework $Cu(H_2dithiooxamide)$ (Fig. 6), in which combined electron and proton conductivity is attributed to the proton-coupled redox activity of the copper dimer centres.[21]

Thermal and mechanical function

The relatively open, structurally robust nature of coordination frameworks makes investigation of their thermal and mechanical properties of some interest. Unprecedented negative thermal expansion (NTE; *i.e.*, contraction upon heating) has recently been discovered in a broad family of metal-cyanide
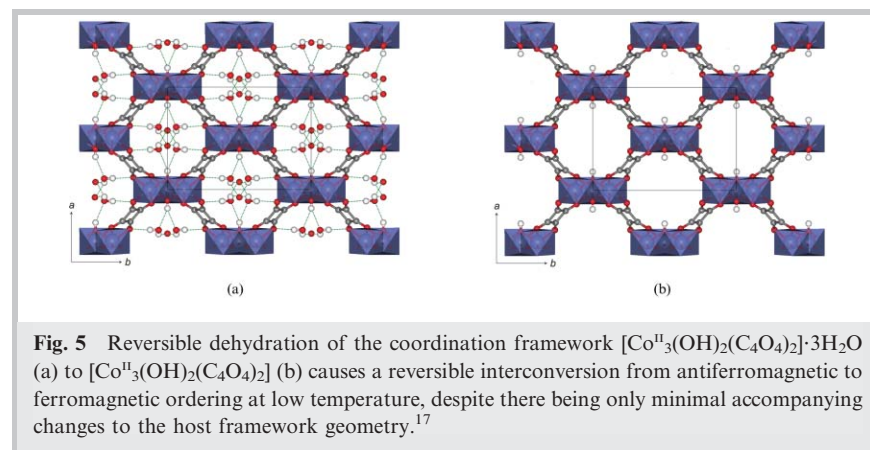

Fig. 5 Reversible dehydration of the coordination framework $[Co^{II}_3(OH)_2(C_4O_4)_2]\cdot3H_2O$ (a) to $[Co^{II}_3(OH)_2(C_4O_4)_2]$ (b) causes a reversible interconversion from antiferromagnetic to ferromagnetic ordering at low temperature, despite there being only minimal accompanying changes to the host framework geometry.[17]
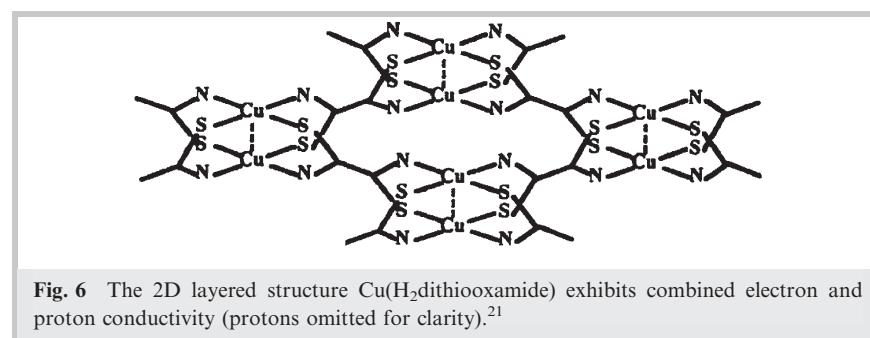

Fig. 6 The 2D layered structure $Cu(H_2dithiooxamide)$ exhibits combined electron and proton conductivity (protons omitted for clarity).[21]
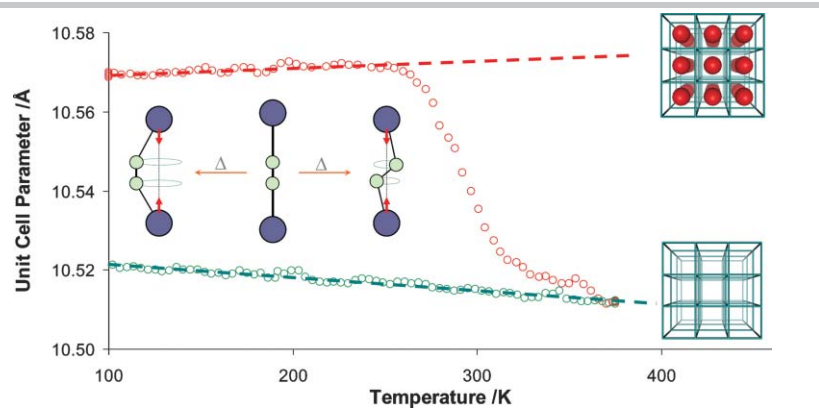
Fig. 7 Reversible dehydration of the Prussian Blue phase $Zn^{II}Pt^{IV}(CN)_6 \cdot 2(H_2O)$ to form $Zn^{II}Pt^{IV}(CN)_6$ results in a change from positive thermal expansion (PTE; red dashed line) to negative thermal expansion (NTE; green dashed line) behaviour. The inset shows the two local transverse vibrational modes of the Pt–C≡N–Zn bridge within this structure.[23]

framework systems,[22–24] with the largest isotropic negative coefficient of thermal expansion ($\alpha = d\ell/\ell dT$) yet reported of -20.4×10^{-6} K^{-1} for $Cd(CN)_2$.[23] The negative expansion behaviour of these materials has been attributed to transverse vibrations within the framework lattices, which have the effect of drawing the cyanide-bridged metal sites closer together with increased thermal population (see inset to Fig. 7). Variation of the metal sites in these materials, which modifies the transverse vibrational energies, causes systematic changes to the expansion properties. The thermal expansion of the nanoporous Prussian Blue phases changes with both the variation of the metal sites and with the degree of guest loading: *e.g.*, the hydrated phase $Zn^{II}Pt^{IV}(CN)_6 \cdot 2(H_2O)$ exhibits positive thermal expansion (PTE; $\alpha = +1.82 \times 10^{-6}$ K^{-1}) whereas the desorbed phase $Zn^{II}Pt^{IV}(CN)_6$ exhibits NTE ($\alpha = -3.38 \times 10^{-6}$ K^{-1}) (see Fig. 7).[22] In addition to having interesting thermal properties, the open, flexible structures of coordination frameworks promise exotic mechanical properties such as auxetic behaviour (*i.e.*, negative Poisson's ratios), which has been predicted to arise in a number of unusual framework topologies.[25]

Conclusion

Whilst a broad range of exciting materials properties have been highlighted above, these at best scratch the surface when considering the future scope for functionality in nanoporous coordination frameworks. If the Prussian Blue phases can still hold numerous surprises despite their discovery more than 300 years ago, then it is clear that a wealth of novel materials properties await. Armed with the considerable versatility of molecular coordination chemistry, and with an ever improving eye for ligand and framework design, we can look forward to the incorporation of numerous other exotic properties into nanoporous coordination frameworks in the years to come.

Acknowledgements

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