

# Dynamic porous properties of coordination polymers inspired by hydrogen bonds

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Received 29th June 2004

First published as an Advance Article on the web 4th January 2005

DOI: 10.1039/b313997m

In a decade, many porous coordination polymers have been synthesized, providing a variety of properties ranging from storage, separation, exchange of guests in their cavities, magnetism, conductivity and catalysis by their frameworks. In this *tutorial review*, we focus on the hydrogen bonding type arrangements for dynamic porous coordination polymers exhibiting elastic guest accommodations, in contrast to rigid three-dimensional (3-D) frameworks. Such dynamic porous properties induce highly-selective guest accommodation and magnetic modulation, and could now be considered a new class of practical materials.

## 1. Functional coordination polymers with stable pores

In the last decade coordination compounds with infinite one-, two-, and three-dimensional (1-, 2-, and 3-D) network structures have been intensively studied. In particular, compounds with backbones constructed by metal ions as “nodes” and ligands as “linkers” form a family of polymers, which are called “coordination polymers”.<sup>1</sup> The key to the rational synthesis to realize a certain desired framework is the judicious choice of metal ion(s), ligand(s), and framework motifs. In addition, that the architecture of coordination polymers can be reasonably well predicted rests upon the simple premise that the coordination geometry of metal ions can be propagated with rigid bridging ligands.<sup>2</sup> It is therefore unsurprising that a wide range of 1-D, 2-D, and 3-D infinite frameworks has already been generated with simple, linear linkers such as 4,4'-bpy (4,4'-bipyridine). On the basis of this achievement as to what we call “first generation compounds”, in principle, a wide variety of chemical and/or physical properties, such as catalytic, magnetic, electrical, and optical properties, might be rationally put in such frameworks.

In particular, porous coordination polymers have attracted the attention of chemists, due to scientific interest in the creation of nanometre-sized spaces and the finding of novel phenomena as well as commercial interest in their application in separations, storage, and heterogeneous catalysis.<sup>3</sup> In 1998, porous coordination compounds were first classified in the three categories, 1st, 2nd and 3rd generation.<sup>4</sup> The 1st generation compounds have microporous frameworks, which are sustained only with guest molecules and show irreversible framework collapse on removal of guest molecules. The 2nd generation compounds have stable and robust porous frameworks, which show permanent porosity without any guest molecules in the pores. The 3rd generation compounds have flexible and dynamic frameworks, which respond to external stimuli, such as light, electric field, guest molecules, and change their channels or pores reversibly. Many inorganic porous materials constructed by covalent bonds are classified as 2nd generation compounds. On the other hand, porous coordination polymers could afford not only robust “2nd generation compounds” but also flexible and dynamic “3rd generation ones”. Fig. 1 shows the advent of chemical/physical properties in chronological order. These results stimulated us to search



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compounds, particularly the chemical and/or physical properties of porous coordination polymers, from which a “nano-channel laboratory” is being developed through the next decades.

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for unique functions for guest adsorption, which, in certain cases, are beyond the scope of the zeolites and activated carbons. This new feature is associated with their complete regularity, high porosity, and highly designable frameworks. One can take advantage of the fact that in the synthesis the reactions occur under mild conditions and the choice of a certain combination of discrete molecular units leads to the desired extended network.<sup>5-7</sup> Recent activity in crystal engineering has afforded several examples of coordination polymers which have rigid open frameworks, and therefore have the potential to be functionally related to zeolites. The  $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]_n$  (**1**) was reported as a prototype in the context of coordination polymers since it can be regarded as having been generated from square-grid coordination polymers that are cross-linked by  $\mu\text{-SiF}_6$  anions.<sup>8</sup> Also,  $[\text{Zn}_4\text{O}(\text{BDC})_3]_n$  (**2**, BDC = benzenedicarboxylic acid) was synthesized on the basis of the ideas from metal carboxylate-supported polynuclear core chemistry, where an organic dicarboxylate linker is used in a reaction that gives super-tetrahedron metal cores capped with monocarboxylates.<sup>7</sup> This porous coordination polymer was realized by utilizing the geometrical shapes of the metal cores relative to secondary building units (SBUs).<sup>7</sup> Both these compounds containing added linkers of rigid and divergent characters allow articulation into a 3-D framework, resulting in a structure with higher apparent surface area and pore volume. Over the past few years a considerable number of studies have been made on the synthesis of thermally stable and robust 3-D frameworks without guest molecules, in order to determine porous functionalities.<sup>2,7-14</sup> This is the second achievement in coordination polymers, and therefore we call them “second generation compounds”.<sup>4</sup>

## 2. Flexible porous materials based on discrete molecules and infinite frameworks

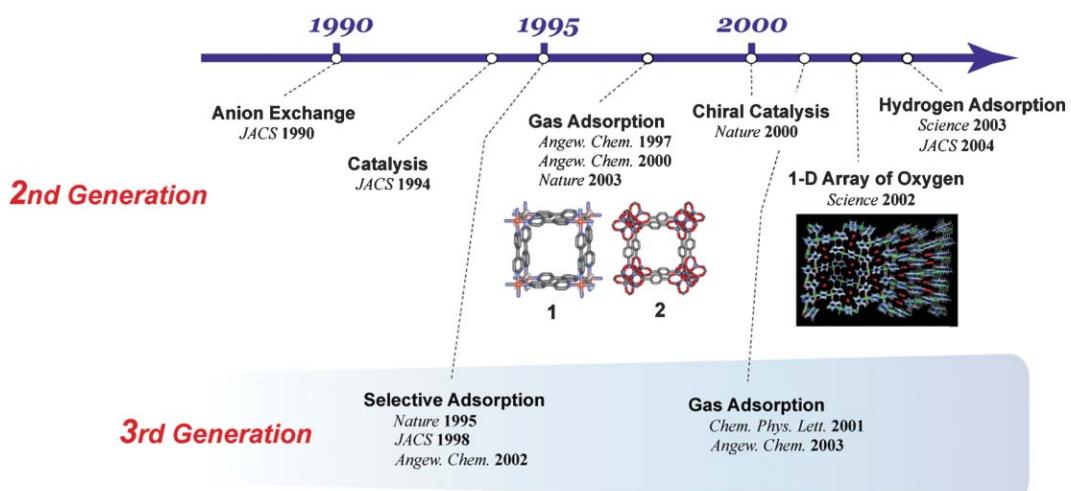
Porous materials are often much more dynamic than generally believed, and especially organic hydrogen bonded networks, which have been extensively studied since the 1970s,<sup>15</sup> exhibit

flexibility in the solid state. Discrete organic molecules crystallize accommodating guest molecules (= solvent) with elastic hydrogen bonds,<sup>16-18</sup> achieving optimal packing with guest molecules and revealing conformational flexibility unlike rigid systems. The state of the host component without guest molecules is referred to as the “apohost”, which forms a new crystalline phase. Dynamic pores could come from a sort of “soft” framework with bistability, whose two states exchange between the component parts; a system could exist in one or two states for the same values of external field parameters. The structural rearrangement of molecules proceeds from the “closed” phase to the “open” phase responding to guest molecules as in eqn. (1).<sup>19</sup>



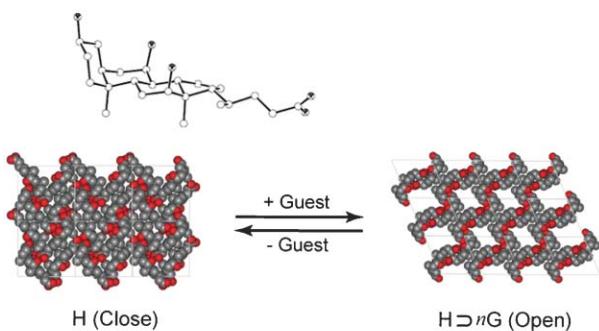
where H is apohost, G is guest molecule, and n is stoichiometry of accommodated guest vs. apohost (hereafter, the number n is defined as the ratio of [the amount of adsorbed guest molecules]/[asymmetric unit of the crystal]). In practice, the discrete complex,  $[\text{M}(\text{NCS})_2(4\text{-Me-py})_4]$ , which forms a “propeller” conformation with four coordinated pyridine rings, shows the structural transformation responding to guest vapors (Fig. 2b).<sup>20</sup> A wide variety of guest molecules may be entrapped by the crystalline host lattices of  $[\text{M}(\text{NCS})_2(4\text{-Me-py})_4]$ , ranging *e.g.* from noble gases to condensed aromatic hydrocarbons. If porous coordination polymers gain such flexibility, they also could be developed for application to a unique class of materials, which cannot be obtained in rigid porous materials.

Compared with discrete ensembles (molecule- and/or ion-based compounds), the flexibility of coordination polymers has been overlooked for a long time. This is because, in general, flexibility appears incompatible with robustness such that porous frameworks constructed from rigid components and linkage are maintained without guest molecules. Nevertheless, the importance of softness, *e.g.* elongation and shrinking with the accommodation of guest molecules, has been proposed and recognized in third generation

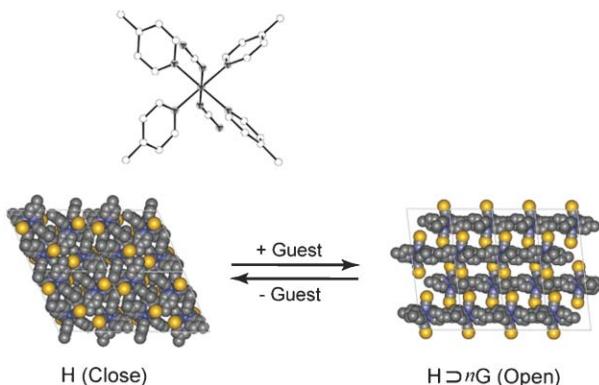


**Fig. 1** Historical view of functions of coordination polymers reported from 1990 to the present day. Structures of 3-D porous coordination polymers,  $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]_n$  (**1**, left),  $[\text{Zn}_4\text{O}(\text{BDC})_3]_n$  (**2**, right), and the 1-D oxygen array are listed.

(a) Organic Network; Cholic Acid



(b) Welner Complex;  $M(NCS)_2(4\text{-Mepy})_2$



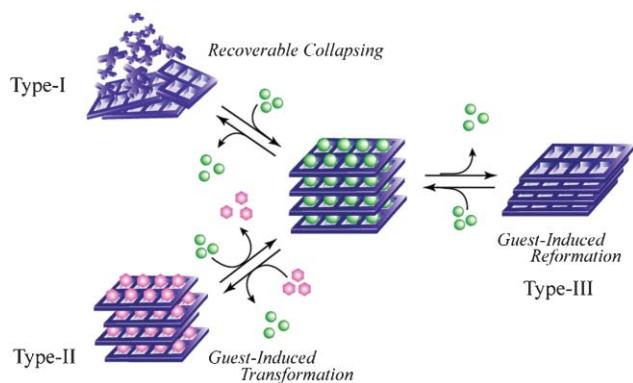
**Fig. 2** Schematic views of crystal-to-crystal structural transformation induced by guest adsorption/desorption; (a) cholic acid, and (b) Welner complex,  $M(NCS)_2(4\text{-Mepy})_2$ .

coordination polymers (Fig. 1 bottom).<sup>4,21–25</sup> The energy in coordination bonds, for example  $Cu(II)-N$ , is comparable to  $90\text{ kJ mol}^{-1}$ . Throughout the design, synthesis, and examination of robust porous coordination polymers, researchers have come to a better understanding that a certain coordination bond could not only sustain a porous framework but also transform the framework into a different one. In particular, coordination polymers have acquired softness for their porous frameworks in cooperation with weak bonds, such as hydrogen bonds and/or  $\pi-\pi$  stacking interactions. So-called dynamic structural transformation based on flexible porous frameworks is one of the most interesting phenomena in coordination polymers, which are categorized as the three types in Fig. 3.<sup>26</sup>

(1) A Type I framework of “recoverable collapsing” has the property that by removal of guest molecules a network collapses due to the close packing force, however it regenerates under the initial conditions.<sup>26–30</sup>

(2) A Type II framework of “guest-induced transformation” has the property that structural shifts in the network are induced by the simultaneous exchange of guest molecules.<sup>31,32</sup>

(3) A Type III framework of “guest-induced reformation” has the property that removal of guest molecules makes a structural change in the network to a different one; however it reverts to the original one under the initial conditions.<sup>23,25,26,33–41</sup>

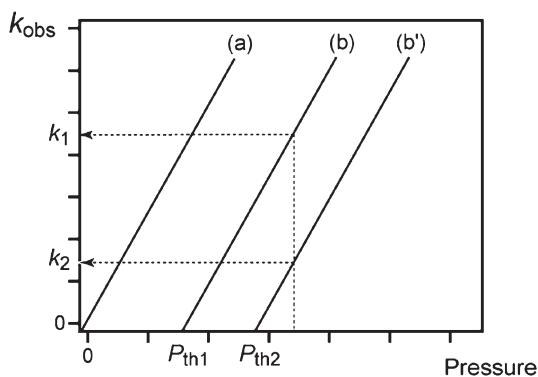


**Fig. 3** Classification of dynamic porous coordination polymers; “recoverable collapsing” (Type I), “guest-induced transformation” (Type II), and “guest-induced reformation” (Type III).

Type I is regarded as “crystal-to-amorphous transformation”, therefore, the approach used to create such a transformation could be applicable to brittle materials systems. Whereas Type II and III compounds show “crystal-to-crystal transformation”, “ $H \supset n \cdot G \leftrightarrow H \supset n \cdot G'$  (Type II; the crystallinity is different between  $H \supset n \cdot G$  and  $H \supset n \cdot G'$ )” and “ $H + n \cdot G \leftrightarrow H \supset n \cdot G$  (Type III; the crystallinity is different between  $H$  and  $H \supset n \cdot G$ )”, in a sense, this property results from the advantage of the molecular inorganic–organic hybrid system. Type II is found in heterogeneous anion exchange, where the guests are anions. Needless to say, porous coordination polymers having similar crystalline phases between the apohost and adsorbed forms are recognized as 2nd generation compounds.

There are numerous reports including the technical term, “pore”, which could be classified into two types, “rigid pore” and “dynamic (or flexible) pore”. In many cases, the term is interchangeably referred to as “porous structure” and “open-framework”, without definitive proof of porosity. Because the term “porous” directly implies “having pores”, pores are a “minute opening through which fluids or gases can pass”. This is a wide definition, by which compounds having type I adsorption curve can be porous. In a narrow sense, compounds having permanent porosity are potentially porous. In either case, the demonstration of porosity through gas sorption isotherms is necessary to prove the existence of porosity.<sup>7</sup> Undoubtedly, many structures called “porous ...” were analyzed by only X-ray crystallography. Furthermore, in the organic zeolites, host molecules may be broadly classified into two main types:<sup>42</sup> (A) those that form lattice inclusion compounds by packing in such a manner as to leave cavities, channels, or layers in the crystal structure so as to accommodate various guest molecules, and (B) those that form molecular complexes by fitting convex guests into the concave cavity of the host. Needless to say, compounds of type (A) correspond to “porous” compounds. However, when guest-release and -accommodation occurs reversibly, even compounds B can be regarded as porous compounds in the wider sense.

In flexible compounds (type (B)), thermal analysis has been done to investigate their mechanism. Fig. 4 shows a schematic representation of  $k_{\text{obs}}$  vs. the guest pressure in the reaction



**Fig. 4** Schematic plot of observed rate constant *versus* guest vapor pressure of (a) rigid porous materials at  $T$  K, (b) flexible porous materials at  $T$  K, and (b') flexible porous materials at  $T + \alpha$  K. Sometimes, an interesting feature of the kinetics is observed that for a given pressure of guest vapor, the rate of the reaction decreases with increasing temperature. Such an anti-Arrhenius behavior has been observed for the accommodating of guest molecules.<sup>42</sup>

shown in eqn. (1), where  $k_{\text{obs}}$  is the observed reaction rate constant. The threshold pressure,  $P_{\text{th}}$ , where guest accommodation starts, was observed.<sup>17,42</sup> These threshold pressures increase with increasing temperatures, which is generally consistent with the inclusion compound having a greater propensity to decompose at higher temperatures. The graph of  $\ln P_{\text{th}}$  *vs.*  $1/T$  has a slope of  $\Delta H_{\text{ad}}/R$ , yielding the adsorption enthalpy change ( $\Delta H_{\text{ad}}$ ) using the Clausius–Clapeyron equation as in eqn. (2).

$$\frac{d(\ln P_{\text{th}})}{d(1/T)} = \Delta H_{\text{ad}}/R \quad (2)$$

Also, the graph of  $\ln k_{\text{obs}}$  *vs.*  $1/T$  has a slope of  $-E_{\text{ad}}/R$ , yielding the activation energy of adsorption ( $E_{\text{ad}}$ ) using the Arrhenius equation as shown in eqn. (3).

$$k_{\text{obs}} = A \exp(-E_{\text{ad}}/RT) \quad (3)$$

In the case of rigid porous compounds like type (A), it is clear that the graph of the  $k_{\text{obs}}$  *vs.* guest pressure passes through the zero point. Therefore, we can recognize porous compounds from the thermodynamic analysis; in a sense, line (a) indicates “rigid pores”, and line (b) indicates “dynamic pores”. Recently there has been a keen interest in dynamic porous coordination polymers that transform under a certain external stimulus to take on different functions, these sometimes being referred to as smart, responsive, or new generation materials.

### 3. Contrivance for dynamic porous coordination polymers

A guideline for rigid pores in coordination polymers is that stiff building units are linked with strong chemical bonds such as coordination and/or covalent bonds to form a 3-D framework. Dynamic pores however are subject to another constraint to give a flexible sort of framework, that is, building units (or motifs) with flexible moieties are linked with strong

bonds, or stiff building blocks (or motifs) are connected with weaker bonds. Another possible option is the combination of flexible building blocks (motifs) and weak linkages. The generation of a host framework that interacts with exchangeable guest species in a switchable fashion has implications for the generation of previously undeveloped advanced materials with applications in areas such as molecular sensing. For weak linkages, guest molecules readily give rise to changes in bond direction, distance, and to cleavage. It is worth noting that even weak interactions between guest and pore-wall molecules can induce a structural change because of a cooperative effect based on a large ensemble over an infinite framework. Coordination polymers form infinite networks, therefore extensive cooperativity would be expected between the molecules throughout the crystal, such that rearrangement can occur in a well-concerted fashion, in order to maintain its macroscopic integrity.

For the construction of dynamic porous coordination polymers, it is necessary to consider certain devices based on weaker interactions such as van der Waals forces,  $\pi$ – $\pi$  stacks, and hydrogen bonds *etc.* among the macroscopic integrities. One feasible idea is that a weak interaction device is put in between motifs (1-D, 2-D, and 3-D), forming a contrivance for dynamic coordination polymers, which are grouped as shown in Fig. 5;

**I. 1-D motifs (chains)** are packed in a crystal, of which voids are accommodated by small sized molecules.<sup>41</sup> Those consisting of silver(I) and 4,4'-bpy analogues have cationic frameworks and exhibit anion exchange with framework transformation.<sup>31,32</sup>

**II. 2-D motifs (single-type layers)** are superimposed on each other with one of two types of stacking, edge-to-edge or staggered,<sup>29</sup> where a weak interaction operates between the sheets. Modification of ligands, which constitute layers, could control the spatial dimensions of the grids, functionality of the channel interior, and the manner of stacking.<sup>24,26,29,30,35,39,40</sup> One typical example is a 2-D layer  $[\text{Ni}(\text{NO}_3)_2(\text{L}_1)]_n$  (3,  $\text{L}_1 = 4,4'$ -bis(4-pyridyl)biphenyl), which selectively includes *o*-xylene from xylene isomers, taking advantage of the sliding layers against neighboring layers.<sup>35</sup>

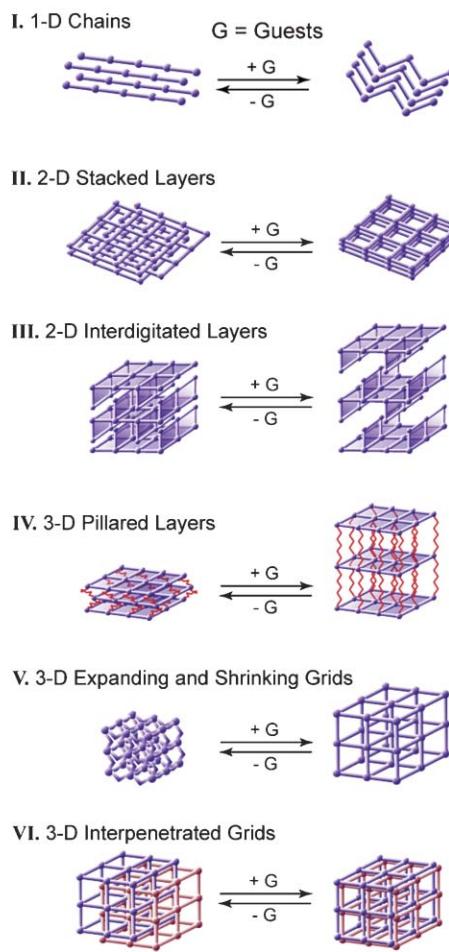
**III. 2-D motifs (interdigitated layers)** are superimposed on each other with ridges and hollows interlocked, to form 1-D channels. These channels are in “closed form” without guests, whereas certain guest molecules could pass through them as a result of the framework’s elongation.<sup>25</sup>

**IV. 3-D motifs (pillared layers)** have channels, whose interior properties are modulated by the judicious choice of layers and pillars. The reversible phenomena of interlayer elongation and shortening could be realized by non-rigid pillars; the channels are so flexible that the initial channels may re-form with guests even after their collapse without guests.<sup>23,36</sup>

**V. 3-D motifs (expanding and shrinking grids)** show sponge-like dynamic behaviors, reducing the interior spacing dramatically in response to guest removal, and elongating it with the inclusion of guest molecules.<sup>28,34,37,38</sup>

**VI. Two types of 3-D motifs (interpenetrated grids)** are mutually interpenetrated and therefore densely packed in the absence of guests, however guest molecules go into the pre-existing pores with the aid of framework sliding.<sup>25,27,33</sup>

## Contrivances for Dynamic Porous Coordination Polymers



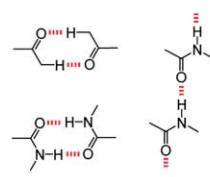
**Fig. 5** Contrivances for dynamic porous coordination polymers categorized with structural dimensionalities.

In these arrangements, weak interactions perform as the linkages between motifs (1-D, 2-D, and 3-D frameworks). Of the weak interactions, hydrogen bonds are not only relevant for the formation of infinite frameworks but also useful for control of the strength and directionality,<sup>43</sup> importantly affording the framework flexibility. Recent progress on crystal engineering utilizing “supramolecular synthons” helps us to accomplish infinite frameworks with hydrogen bonds (Fig. 6).<sup>44</sup> In the case of metal complexes, building motifs can be formed independently and then connected to themselves or other (complementary) building motifs. The role of hydrogen bonding in coordination compounds is ligand-based hydrogen-bond functionalities as “supramolecular glue”, a useful addition to the field of crystal engineering,<sup>45,46</sup> providing several flexible ones have been reported.

## 4. Dynamic porous coordination polymers originating from hydrogen bonds

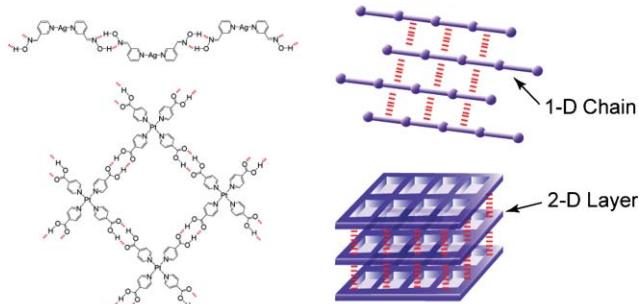
Throughout the consideration of the framework dimensionalities, several devices arising from hydrogen bonds have been

## “Supramolecular Synthon”



— = Hydrogen Bond

## “Supramolecular Glue”



**Fig. 6** Schematic view of “supramolecular synthons” and “supramolecular glue”. Like assemblies of  $[\text{Ag(I)}(\text{nicotinamide})]$  and  $[\text{Pt(II)}(\text{isonicotinate})_2(\text{isonicotinic acid})_2]$ , the infinite 1-D chains and 2-D layers are expected to join together with the hydrogen bonds.<sup>45</sup>

developed in coordination polymers. They are briefly described as follows.

### 1-D chains

Coordination polymers of  $\text{Ag(I)}$  cations are attracting a great deal of attention primarily perhaps because they are readily available, and simply a linear coordination around  $\text{Ag(I)}$  atoms to form 1-D chains. It is worth noting that silver cations are accompanied by a positive charge into the chain, and therefore, the counter anions such as  $\text{PF}_6^-$  and  $\text{BF}_4^-$  are nested around the chains. The first well-characterized anion exchange framework by soaking crystals in a solution containing another anion was reported,<sup>2</sup> and thereafter, numerous compounds appeared.<sup>31,32,47</sup> A recent paper<sup>48</sup> has shown that anion exchange processes previously thought to be solid-state processes are in fact solvent-mediated; thus care should be taken in reporting apparent anion exchange processes where the sample is immersed in solution. The anions could be exchanged accompanying a structural transformation,<sup>31,32</sup> but the anion exchange properties associated with hydrogen bonds are rare.  $\{[\text{Ag}(\text{L}_3)] \cdot \text{ClO}_4\}_n$  (**4**  $\supset \text{ClO}_4^-$ ;  $\text{L}_3 = N,N'$ -bis(3-pyridinecarboxamide)-1,6-hexane), whose 1-D chain motif zips up itself into 2-D undulating layers *via* inter-chain amide hydrogen bonds, utilizes hydrogen bonds in an anion exchange process.<sup>32</sup> The counter anions,  $\text{ClO}_4^-$ , are sandwiched between adjacent layers and associated with the silver atoms, and **4**  $\supset \text{NO}_3^-$  and **4**  $\supset \text{CF}_3\text{SO}_3^-$  also aggregate into 2-D corrugated layers *via* complementary amide hydrogen bonds. The anion exchange among the three coordination polymers is

highly selective: only the conversion from  $\mathbf{4} \supset \text{NO}_3^-$  ( $\mathbf{4} \supset \text{CF}_3\text{SO}_3^-$ ) to  $\mathbf{4} \supset \text{ClO}_4^-$  is possible, of which the selectivity is governed by the hydration energy of anions and energy for the structural reorganization. Reports on this type of hydrogen bond-inspired conversion are sparse notwithstanding the many structural conversions induced by the anion exchange.

## 2-D layers

2-D porous coordination polymers such as square grids, rectangular grids, and honeycomb layers have the potential to put a flexible device within a layer or in between layers.  $\{[\text{Zn}(\text{BDC})(\text{H}_2\text{O})]\cdot\text{DMF}\}_n$  ( $\mathbf{5} \supset \text{H}_2\text{O}$ ) shows a 2-D layer of dimeric Zn units with terminally coordinated waters, which are further hydrogen bonded to guest molecules (Fig. 7a),<sup>39</sup> and the anhydrous  $\mathbf{5}$  forms a new crystalline structure. The reverse reaction,  $\mathbf{5} \rightarrow \mathbf{5} \supset \text{H}_2\text{O}$ , results from adsorption of water molecules, which is ascribed to the hydrogen bond formation. The dynamic porous 2-D layers exhibit a unique adsorption profile and magnetic properties.  $\{[\text{Cu}(4,4'\text{-bpy})(\text{BF}_4)_2(\text{H}_2\text{O})_2]\cdot 4,4'\text{-bpy}\}_n$  ( $\mathbf{6}$ ) forms non-interpenetrated 2-D layer having cavities of a cross-sectional area of  $7.7 \times 11.6 \text{ \AA}^2$ .<sup>24</sup> The ligand, 4,4'-bpy, has two unique roles; one links two Cu

atoms by direct coordination while the other bridges Cu atoms by hydrogen bond *via* coordinated water molecules (Fig. 7b). Micropores for accommodation of guest molecules cannot be observed because the neighboring layers obstruct the pores. However, the adsorption of  $\text{N}_2$ , Ar, and  $\text{CO}_2$  suddenly begins at a definite relative pressure regardless of almost nil adsorption below this threshold pressure. This phenomenon is attributed to the hydrogen bond regulated microporous nature; hydrogen bonds in pores block adsorption below the threshold pressure.

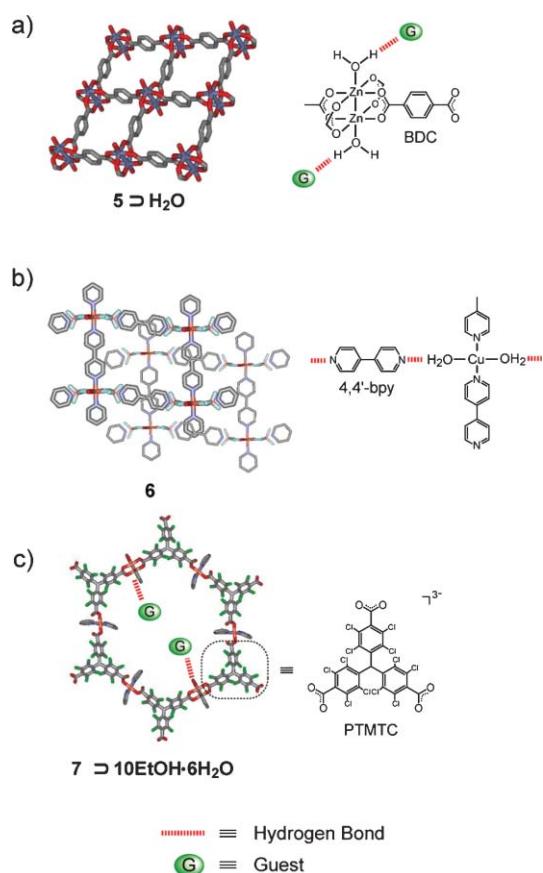
By utilizing a radical bridging ligand, PTMTC (polychlorinated triphenylmethyl with three carboxyl groups),  $\{[\text{Cu}_3(\text{PTMTC})_2(\text{py})_6(\text{EtOH})_2(\text{H}_2\text{O})]\cdot 10\text{EtOH}\cdot 6\text{H}_2\text{O}\}_n$  ( $\mathbf{7} \supset 10\text{EtOH}\cdot 6\text{H}_2\text{O}$ ) exhibits a sponge-like magnetic behavior.<sup>30</sup>  $\mathbf{7} \supset 10\text{EtOH}\cdot 6\text{H}_2\text{O}$  forms a 2-D layer with a honeycomb structure (Fig. 7c), and the different layers arrange themselves between them, by means of weak  $\pi\text{-}\pi$  and van der Waals interactions, forming an open-framework structure. Ten and six molecules of ethanol and water, respectively, per formula unit are hydrogen-bonded with the coordinated water molecules. On exposed to air, the single crystal lost solvent molecules very rapidly at room temperature, becoming an amorphous material, which recovers its structural integrity when re-immersed in liquid ethanol, indicating solvent-induced ‘shrinking–breathing’ process, which strongly influences the magnetic properties.  $[\text{Cd}(1,5\text{-nds})(\text{H}_2\text{O})_2]_n$  ( $\mathbf{8}$ , 1,5-nds = 1,5-naphthalenedisulfonate), which forms a 2-D layer connected by the hydrogen bonds between the coordinated water molecules and the free O-atoms of the sulfonate groups, also can selectively intercalate ammonia and amines *via* a solid–vapor reaction at room temperature.<sup>40</sup>

Needless to say, 2-D dynamic coordination polymers  $\mathbf{5}$ – $\mathbf{8}$  involve an arrangement of “2-D Stacked Layers” (Fig. 5), where coordinated water molecules play a key role in the dynamic hydrogen bond;  $\mathbf{5}$ ,  $\mathbf{7}$ , and  $\mathbf{8}$  involve a type of hydrogen bond with guests while those in  $\mathbf{6}$  are with coordinated water in the framework.

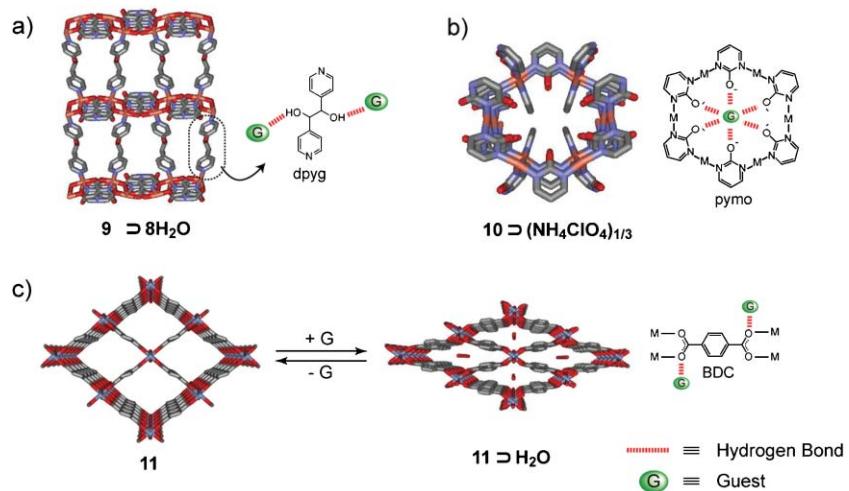
## 3-D pillared layers and grids

$\{[\text{Cu}_2(\text{pzdc})_2(\text{dpyg})]\cdot 8\text{H}_2\text{O}\}_n$  ( $\mathbf{9} \supset 8\text{H}_2\text{O}$ , pzdc = pyrazine-2,3-dicarboxylate, dpyg = 1,2-di(4-pyridyl)glycol) exhibits a 3-D porous framework with a cross-section of  $4 \times 6 \text{ \AA}^2$ ; 2-D layers constructed with the pzdc ligands are linked to form a 3-D pillared-layer structure (Fig. 8a).<sup>23</sup> The anhydrous compound,  $\mathbf{9}$ , shows structural changes with the entire crystallinity maintained, which is mainly attributed to a variation of the inter-layer distances. Although the size of the channel cross-section is smaller than that of methanol and water, the original structure is regenerated on the inclusion of the guests with hydrogen-bond capability. Interestingly, methane is not adsorbed. The hydrogen-bonding with dpyg and the guest molecule is so effective that the gate opens up to introduce the guests.

$\{[\text{Cu}(\text{pymo})_2]\cdot(\text{NH}_4\text{ClO}_4)_{1/3}\}_n$  ( $\mathbf{10} \supset (\text{NH}_4\text{ClO}_4)_{1/3}$ , pymo = 2-hydroxypyrimidine) reveals that the combination of square planar Cu(II) ions with  $120^\circ$  bond angles provided by Hpymo generates a 3-D porous framework with ammonium and perchlorate ions included in the pores (Fig. 8b).<sup>28</sup> This



**Fig. 7** Structures and schematic views of 2-D layer type coordination polymers; (a)  $\{[\text{Zn}(\text{BDC})(\text{H}_2\text{O})]\cdot\text{DMF}\}_n$  ( $\mathbf{5} \supset \text{H}_2\text{O}$ ), (b)  $\{[\text{Cu}(4,4'\text{-bpy})(\text{BF}_4)_2(\text{H}_2\text{O})_2]\cdot 4,4'\text{-bpy}\}_n$  ( $\mathbf{6}$ ), and (c)  $\{[\text{Cu}_3(\text{PTMTC})_2(\text{py})_6(\text{EtOH})_2(\text{H}_2\text{O})]\cdot 10\text{EtOH}\cdot 6\text{H}_2\text{O}\}_n$  ( $\mathbf{7} \supset 10\text{EtOH}\cdot 6\text{H}_2\text{O}$ ). In (b), two layers stack, and the thin and thick lines show the upper and lower layer, respectively. In all structures, guest molecules are omitted for the clarity.



**Fig. 8** Structures and schematic views of 3-D coordination polymers; (a)  $\{[\text{Cu}_2(\text{pzdc})_2(\text{dpyg})]\cdot 8\text{H}_2\text{O}\}_n$  (**9**  $\supset 8\text{H}_2\text{O}$ ) without guest molecules, (b)  $\{[\text{Cu}(\text{pymo})_2]\cdot (\text{NH}_4\text{ClO}_4)_{1/3}\}_n$  (**10**  $\supset (\text{NH}_4\text{ClO}_4)_{1/3}$ ) without guest molecules, and (c)  $\{[\text{Cr}(\text{OH})(\text{BDC})]\cdot \text{H}_2\text{O}\}_n$  (**11**  $\supset \text{H}_2\text{O}$ ).

compound loses ammonia upon heating, giving the corresponding activated acidic material **10**  $\supset (\text{HClO}_4)_{1/3}$  which upon exposure to gaseous ammonia regenerates **10**  $\supset (\text{NH}_4\text{ClO}_4)_{1/3}$ . This behavior agrees with the observed guest-induced structural transformation taking place in the framework after guest inclusion.  $\{[\text{Cr}(\text{OH})(\text{BDC})]\cdot \text{H}_2\text{O}\}_n$  (**11**  $\supset \text{H}_2\text{O}$ ) exhibits a 3-D structure built up from Cr(III) octahedra and BDC ions, creating a 3-D framework with a 1-D pore channel system (Fig. 8c).<sup>37</sup> The transition between the hydrated form **11**  $\supset \text{H}_2\text{O}$  and anhydrous solid **11** is fully reversible and followed by a very high breathing effect, the pores being clipped in the presence of water molecules and reopened when the channels are empty. No acetone or ethanol could be incorporated in **11**  $\supset \text{H}_2\text{O}$ , whereas DMF is incorporated into the pores instead of  $\text{H}_2\text{O}$ . This selectivity is attributed to the higher capability of DMF toward the formation of strong hydrogen bonds with the hydroxyl groups of the framework.  $\{[\text{Cu}_2(\text{in})_2]\cdot 2\text{H}_2\text{O}\}_n$  (**12**  $\supset 2\text{H}_2\text{O}$ , in = isonicotinate) has square pyramidal copper atoms, which are linked by five two-connected tridentate units in such a way that a novel five-connected 3-D network is formed with spiral open-framework channels.<sup>38</sup> A number of hydrogen bonds between the guest water molecules and the carboxylate groups in the framework have been formed. By soaking the crystals of **12** in mixed EtOH–pentane or EtOH–1-propanol, the adsorption processes are very selective with only EtOH molecules included in the framework with a slight expansion. Coordination polymers **10–12** are classified in the “3-D Expanding and Shrinking Grids” group.

## 5. Rational device-integration into coordination polymers: metallo-amino acid

For coordination polymers, it is important to assign the roles of coordination and hydrogen bonding as the origin of the framework properties. Our proposal for the assignment is that coordination bonds are for a basic framework, so-called motif formation, while hydrogen bonds lead to a flexible device for a dynamic structure. However, when multifunctional ligands

containing both coordination donor and hydrogen bonding groups are utilized, the bonding sites tend to be out of control in the formation of coordination polymers. There must be several ways to overcome this difficulty, and a typical example is mentioned below.

A ligand system of py-Amide-py is synthesized since metal ions prefer the pyridyl group (py) by far to the amide group.<sup>26,29</sup> The py groups at both ends are used for the formation of a framework backbone while the middle amide group can contribute hydrogen bonding sites; H acceptor ( $-\text{NH}-$ ) and receptor ( $-\text{CO}-$ ) in a space surrounded by a framework. Interestingly, two types of hydrogen bonds operate in the coordination polymers; one is for guest molecules while the other is for motif-linking in a solid.

Fig. 9 shows backbones containing a metal ion as a connector and the py-Amide-py ligand as a linker, which is a common structural aspect for a coordination polymer. When one views the backbone from a different angle such that the amino and carbonyl groups of the amide moiety are connectors instead of linkers, a repeating unit,  $\text{NH}-\text{py}-\text{M}-\text{py}-\text{CO}$ , is considered as a building block for this backbone. This is a sort of “amino acid fragment” in polypeptides, therefore, this unit may be called a “metallo-amino acid fragment”, which is symbolized as  $\text{X}(\text{g},\text{n},\text{I};\text{q},\text{s})$ . Numerous metallo-amino acid fragments constructed by modified ligands and judicious choice of metal ions would be obtained, and here, a systematic representation,  $\text{D}[\text{X}^{\text{r}}(\text{n}^{\text{i}};\text{c}^{\text{j}})]$  based upon symbol for describing and analyzing 3-D structures is introduced (Table 1). Coordination network motifs are identified by one of three designators, C (chain), L (layer), or G (grid). The motif depends implicitly on the oxidation state and coordination number of the metal ion, which are, therefore, omitted in the designation. A benefit of using graph sets is that it brings the focus not only on to the metal properties but also on to the structural aspects. For instance, protein structures are described as  $\text{C}[\text{A}, \text{B}, \text{C}, \dots]$  where A, B, C... correspond to the amino acid residues. Hereafter, we will show a series of  $\text{D}[\text{X}^{\text{r}}(\text{n}^{\text{i}};\text{c}^{\text{j}})]$ , which affords a new system of amido-containing coordination polymers leading to dynamic porous properties.

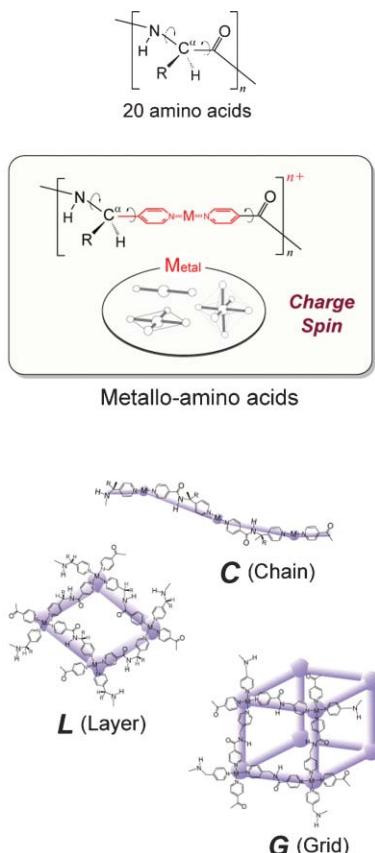


Fig. 9 Schematic view of “Metallo-amino acids”.

## 6. Dynamic porous coordination polymers based on 2-D motifs of metallo-amino acids

A layer-type motif is relevant to create a dynamic porous structure, which exhibits reversible transformation from one form to another, in response to an external stimulus. The dynamic event could occur either within the layer or in between the layers.<sup>26,35</sup> In order to regulate this type of events, a device should be put into the framework. One of the relevant and systematic candidates is an aforementioned metallo-amino acid. A series of dynamic frameworks were synthesized with layer motifs from Co(II) and py-Amide-py type ligands;  $L[Co^{II}(m^0, p^0)]$  and  $L[Co^{II}(m^0, m^0)]$  from *N*-3-pyridylisonicotinamide (3-pia) and *N*-3-pyridylnicotinamide (3-pna), respectively, and *N*-(2-pyridin-4-ylethyl)isonicotinamide (4-peia) affords  $L[Co^{II}(p^2, p^0)]$ . As shown in Fig. 10, seven kinds of

frameworks based on layer motifs have been well-characterized,  $\{[Co(NCS)_2(3-pia)_2] \cdot 2EtOH \cdot 11H_2O\}_n$  (#1  $\supset 2EtOH \cdot 11H_2O$ ),  $\{[Co(NCS)_2(3-pia)_2] \cdot 4Me_2CO\}_n$  (#2  $\supset 4Me_2CO$ ),  $\{[Co(NCS)_2(3-pia)_2] \cdot 4THF\}_n$  (#3  $\supset 4THF$ ),  $\{[Co(NCS)_2(3-pna)_2\}_n$  (#4),  $\{[Co(NO_3)_2(3-pna)_2\}_n$  (#5),  $\{[Co(Br)_2(3-pna)_2\}_n$  (#6), and  $\{[Co(NCS)_2(4-peia)_2] \cdot 4Me_2CO\}_n$  (#7  $\supset 4Me_2CO$ ).<sup>26,29</sup> All the complexes form similar 2-D layers including Co(II), however the mutual relationship between the layers is different, which gives a clue to a dynamic arrangement. Since the two modes of hydrogen bonding (Amide–Amide or Amide–Guest) are well recognized (Fig. 11), #1–#3 indicates a layer pile in an edge-to-edge manner with the binding of guest molecules while #4–#7 adopt a staggered structure, precluding interpenetration.

In #1  $\supset 2EtOH \cdot 11H_2O$ , the cobalt ions are linked by 3-pia ligands to form a 2-dimensional sheet, denoted by the family  $L[Co^{II}(m^0, p^0)]$ , where two ethanol and eleven water molecules are incorporated; the ethanol molecules are trapped by hydrogen bonding with the amide moiety. The adjacent sheets are stacked offset with respect to each other, in an ABAB fashion. The framework of #1 cannot withstand the high level of stress on the extensive loss of guests, resulting in an amorphous structure (Fig. 12a).

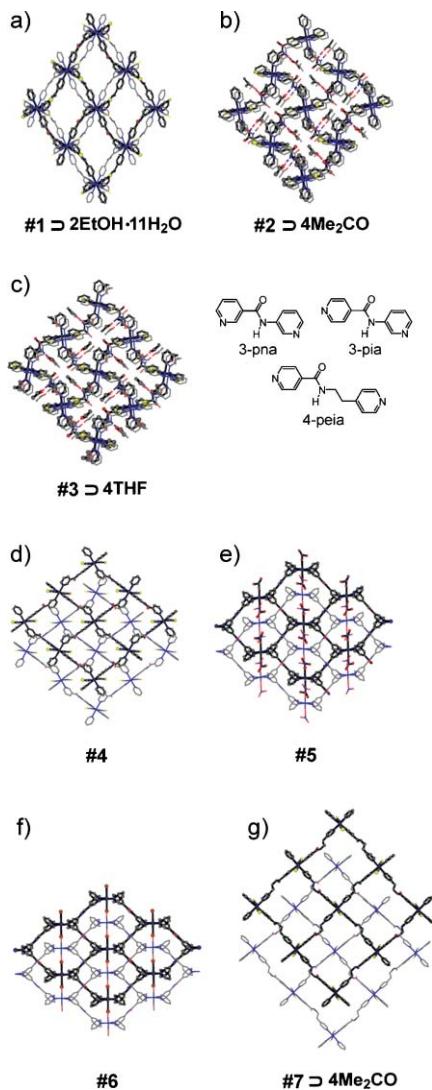
In #3  $\supset 4THF$ , THF molecules are entrapped in the cavity by the hydrogen bonds. As a result of the hydrogen bonding, the bond vector of the amide carbonyl group is coplanar to the sheet plane. A new crystalline sheet can be obtained by subjecting #3  $\supset 4THF$  to reduced pressure, and the original crystal structure comes back completely upon exposing to THF vapor. Interestingly, such a structural transformation induced by adsorption/desorption of THF vapor occurs reversibly (Fig. 12b). This mechanism is attributed to the arrangement of the adjacent layers so suited in regularity that the hydrogen-bond pillar framework forms efficiently; namely, “amide–guest” to “amide–amide” hydrogen bond transformation. This new layer-type crystal paves the way to the selective inclusion system reflecting the size/shape and hydrogen bonding capability; THF is adsorbed and cyclopentane is not adsorbed.

Now, a question arises as to why #1 shows “crystal to amorphous” behaviour and #3 (#2) undergoes “crystal to crystal” on the removal of guest molecules. In #1  $\supset 2EtOH \cdot 11H_2O$  the “double-edged axe-shaped” motifs in the adjacent sheets are not located just over the neighbour, whereas in #3  $\supset 4THF$  (#2  $\supset 4Me_2CO$ ), the motifs stack so perfectly as to overlap in an edge-to-edge fashion. Due to this regularity, the sheets in #3 (#2) can stack efficiently with a

Table 1 Representation of framework patterns,  $D[X^r(n^i;c^j)]$

Symbol	Explanation	Examples
D	Designator of patterns	$C, L, G^a$
X	Designator of metallo-amino acid fragment indicating metal element symbol used	$Co, Fe, \dots^b$
r	Oxidation state of a metal ion in Roman numbers	I, II, III...
n	Substituted position of NH-containing group	<i>o</i> ( <i>ortho</i> ), <i>m</i> ( <i>meta</i> ), <i>p</i> ( <i>para</i> )
i	Number of atoms in between NH- and py group	0, 1, 2...
c	Substitution position of CO-containing group	<i>o</i> ( <i>ortho</i> ), <i>m</i> ( <i>meta</i> ), <i>p</i> ( <i>para</i> )
j	Number of atoms in between CO- and py group	0, 1, 2...

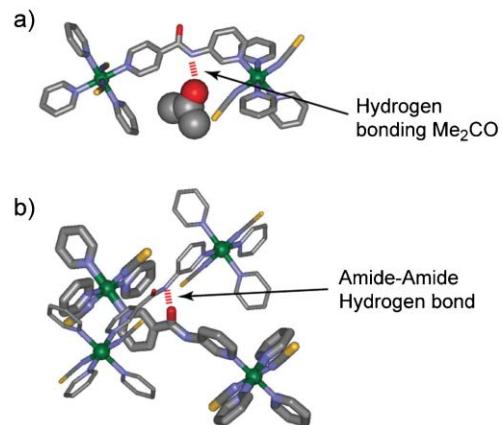
<sup>a</sup> C; chain, L; layer, G; grid. <sup>b</sup> When more than two kinds of the fragments are involved, the symbols  $X^r(n^i;c^j)$ ... are lined up, followed by a semi-colon, in parentheses.



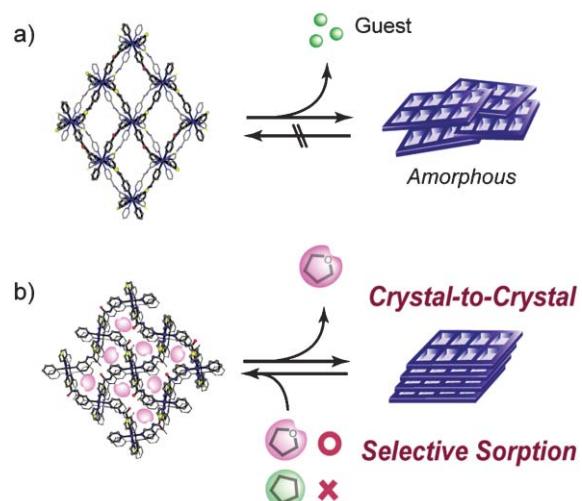
**Fig. 10** Two layer stacking of (a)  $\{[Co(NCS)_2(3\text{-pia})_2]\cdot 2EtOH\cdot 11H_2O\}_n$  (#1  $\supset 2EtOH\cdot 11H_2O$ ), (b)  $\{[Co(NCS)_2(3\text{-pia})_2]\cdot 4Me_2CO\}_n$  (#2  $\supset 4Me_2CO$ ), (c)  $\{[Co(NCS)_2(3\text{-pia})_2]\cdot 4THF\}_n$  (#3  $\supset 4THF$ ), (d)  $\{[Co(NCS)_2(3\text{-pna})_2]\}_n$  (#4), (e)  $\{[Co(NO_3)_2(3\text{-pna})_2]\}_n$  (#5), (f)  $\{[Co(Br)_2(3\text{-pna})_2]\}_n$  (#6), and (g)  $\{[Co(NCS)_2(4\text{-peia})_2]\cdot 4Me_2CO\}_n$  (#7  $\supset 4Me_2CO$ ). The thin and thick lines show the upper and lower layers, respectively.

locking mechanism by forming a hydrogen-bond pillar framework, and thus, withstands significant stress on the removal of guest molecules.

In #7  $\supset 4Me_2CO$ , the hydrogen-bonding links of the NH—O=C (N—O = 2.780(7) Å) groups between the adjacent layers create a complementary amide-binding network.<sup>29</sup> A channel with dimensions of 4.4 Å  $\times$  4.4 Å is observed, where acetone molecules are accommodated with no significant interaction. The framework of #7 cannot withstand the high level of stress on extensive loss of the guest, resulting in an amorphous form. On the other hand, the original crystal structure comes back completely upon exposure to acetone vapour (Fig. 13a). Since #7 shows structural regeneration when exposed to acetone vapor, an acetone adsorption experiment was carried out on #7. Fig. 13b shows the adsorption isotherms for acetone over

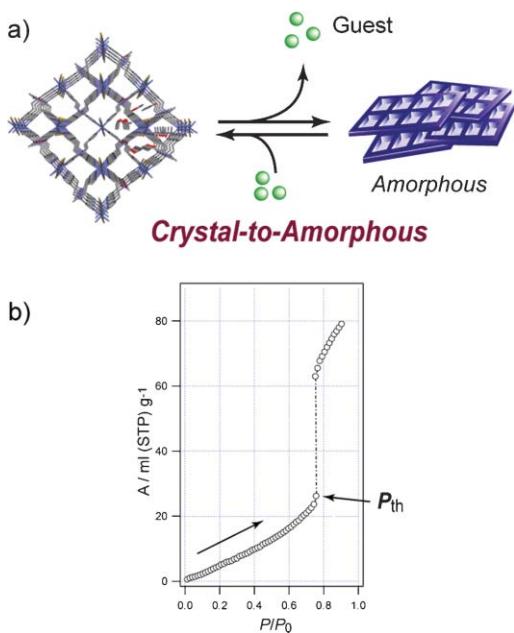


**Fig. 11** Two kinds of hydrogen bonding mode; (a) amide—guest hydrogen bond, and (b) amide—amide hydrogen bond.



**Fig. 12** Schematic view of crystal transformation found in (a) #1  $\supset 2EtOH\cdot 11H_2O$  and (b) #3  $\supset 4THF$ .

the relative pressure range from 0 to 0.9 at 298 K. The adsorption isotherm shows a slight increase and an abrupt rise at  $P/P_0 = 0.76$ . This characteristic adsorption profile clearly indicates the conversion of amorphous #7 (dried) to a crystalline form (#7  $\supset 4Me_2CO$ ). In this “amorphous-to-crystal” structural rearrangement in the Me<sub>2</sub>CO adsorption process, a threshold pressure ( $P_{th}$ ) is required to start the accommodating reaction, and this increases with increasing temperatures; 17.3 (288), 21.2 (293), 23.2 (298), 28.8 (303 K), 34.8 (308 K) and 40.9 kPa (313 K). Using the Clausius–Clapeyron equation as given in eqn. (2),  $\Delta H_{ad} = -25\text{ kJ mol}^{-1}$  for the inclusion of acetone was obtained, which is close to the vaporization enthalpy of acetone ( $\Delta H_{vap} = 30.99\text{ kJ mol}^{-1}$ ), implying that weak dispersive forces induce structural rearrangement in a well-concerted fashion. Furthermore, the remarkable difference between the discrete system and the infinite system was ascertained by thermodynamic analysis, which is now under preparation for publication.



**Fig. 13** (a) Schematic view of “crystal-to-amorphous” transformation found in “#7  $\supset$  4Me<sub>2</sub>CO  $\leftrightarrow$  #7” process. (b) Isotherm for acetone vapor adsorption (open circles) at 298 K of #7 over the pressure range from 0.507 to 27.756 kPa.  $P_0$  is the saturated vapor pressure, 30.593 kPa, of acetone at 298 K.

## 7. Summary and outlook

The numerous reported structures of “porous coordination polymers” can be classified into two types, “rigid pores” and “dynamic pores”, which are distinguished by thermodynamic analysis. To date much effort has been made to develop the “rigid pores”, which appear to be available for storage applications. On the contrary, dynamic pores have been overlooked for a long time possibly because of the difficulty of characterization, and, therefore, research in this area has just begun. In this review, we describe the dynamic porous coordination polymers based on hydrogen bonds, which are categorized into those as six kinds of flexible devices, which would afford a guide to the rational synthesis. The characteristic strength and directionality of hydrogen bonds are effective in regulating the mutual relationship among the motifs and, as a new branch, a hydrogen bond system for 2-D stacked layers has been realized by inventing “metallo-amino acids, D[X<sup>r</sup>(n<sup>i</sup>;c<sup>j</sup>)”.

This review also implies that coordination polymers are often much more dynamic than generally believed and that weak dispersion forces induce structural rearrangement in a well-concerted fashion, reminiscent of the “domino effect” for arranged tiles. Due to the large number of components, even a weak interaction could cause catastrophic change over the whole entity, and therefore, a flexible porous host could recognize even van der Waals molecules by the amplifying effect. This is an important advantage of dynamic frameworks. Herein, guest molecules for pores can be a chemical stimulus, which induces a change in the environment of metal centers and/or ligand moieties. Reports of these phenomena have recently been increasing. Functionalities such as nonlinear

optical properties, conductivity, magnetism, spin-crossover, chromism, and fluorescent properties are another aspect of coordination frameworks, which have been hitherto independently studied. Promising in this regard are the co-operative properties of future coordination polymers, whose motifs are linked by hydrogen bonds, with dynamic structures coupled with guest occlusion and/or other physical properties.

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