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Flexible microporous coordination polymers

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Abstract

In a decade, many porous coordination polymers have been synthesized, providing a variety of properties ranging from storage, separation and exchange of guests in their cavities, magnetism, conductivity and catalysis by their frameworks. Recent advent of flexible porous coordination polymers, which exhibit elastic guest accommodation in contrast to rigid three-dimensional (3-D) frameworks of conventional porous materials, have acquired a position as a new class of porous materials. Such flexible porous properties induce highly selective guest accommodation and magnetic modulation, which could now be a unique class of practical materials. In this review, we introduce recent flexible porous coordination polymers (**3**–**17**) and their functional properties, categorizing with the four types of pores with framework deformation.

Keywords: Microporous; Adsorption; Flexibility

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1. First, second, and third generation microporous coordination polymers

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" [1]. It is unsurprising that a wide range of 1-D, 2-D, and 3-D infinite frameworks have already been generated with simple, linear linkers such as 4,4′-bpy (4,4′-bipyridine) [2]. The achievement to date familiarize us with three generation categories, what we call "first, second and third generation" porous coordination polymers (Fig. 1) [3].

Porous coordination polymers have attracted attention of chemists, due to scientific interest in the creation of nanometer-sized spaces and finding of novel phenomena as well as commercial interest in their application in separations, storage, and heterogeneous catalysis [4]. The research stimulated us to search for unique functions for guest adsorption, which, in a certain case, are beyond the scope of the zeolites and activated carbons [5]. This new feature is associated with their complete regularity, high porosity, and highly designable frameworks [6]. One can take advantages in the synthesis that the reactions occur at mild conditions and choice of a certain combination of discrete molecular units leads to a desired extended network [2,5,7]. Recent activity in crystal engineering has afforded several examples of coordination polymers which have rigid open frameworks (Fig. 1), so-called "second generation" porous coordination polymers, and therefore have the potential to be functionally related to zeolites [5]. The $[Cu(SiF_6)(4,4'\text{-bpy})_2]_n$ (**1**) [8] and $[Zn_4O(BDC)_3]_n$ (**2**, BDC = benzenedicarboxylic acid) [9] were reported as a prototype in the context of "second generation" porous coordination polymers [3]. Both the

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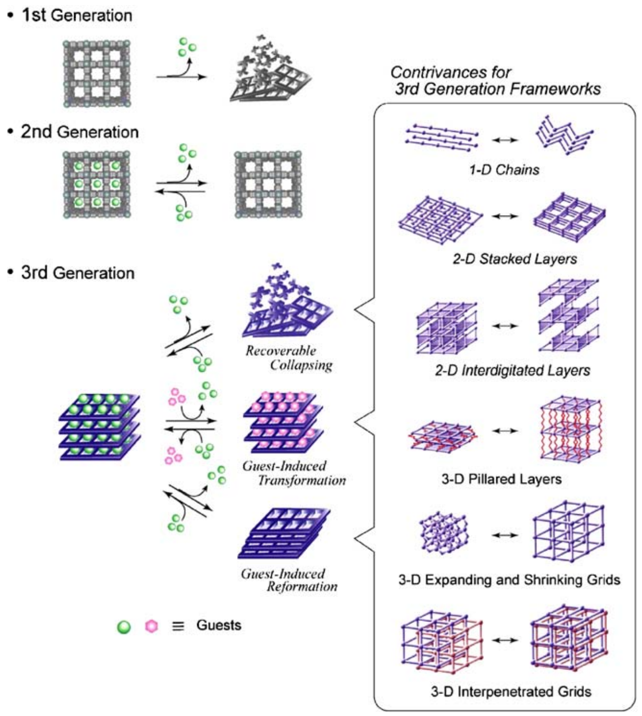

Fig. 1. Schematic view of first, second, third Generation microporous coordination polymers. Third Generation compounds (= flexible microporous coordination polymers) are divided into three kinds of the classification, "recoverable collapsing", "guest-induced transformation", and "guest-induced reformation", which are realized with flexible contrivances in coordination networks.

compounds containing the rigid and divergent character of the added linker allow the articulation into a 3-D framework, resulting in 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 carry out porous functionalities [5,8,10–16].

The next challenge in this field is to pay attention on a functional view of frameworks, which could be associated with dynamic aspect of frameworks [17]. Porous materials are often much more dynamic than generally believed, and especially organic hydrogen bonded networks, which has been extensively studied since 1970s [18–25], exhibit flexibility, linked with a sort of dynamic properties in the solid state. The state of the host component without guest molecules is referred to as the "apohost", which forms new crystalline phase. Dynamic pores could come from a sort of "soft" framework with bistability, whose two states go back from and forth to one of counter parts; a system could exist in one or two states for the same values of external field parameters [26–44]. The structural rearrangement of molecules proceeds from the "close" phase to the "open" phase responding to guest molecules like

$$\mathrm{H} + n\mathrm{G} \rightleftharpoons \mathrm{HG}_n\ (\mathbf{H} \supset n\mathbf{G}), \qquad (1)$$

where H is apohost, G is guest molecule, and n is stoichiometry of accommodated guest vs. apohost. (Hereafter, the number n is defined for the ratio of [the amount of adsorbed guest molecules]/[asymmetric unit of the crystal]). If porous coordination polymers gain such a flexibility, they also would develop an application to unique class of materials, which cannot be obtained in rigid porous material. Dynamic structural transformation based on flexible frameworks is one of the most interesting phenomena, presumably characteristic of coordination polymers, so-called "3rd generation" porous coordination polymers (Fig. 1) [3], which we subdivide into three types in Fig. 1 [17,26]; Type I framework of "recoverable collapsing" has a property that by removal of guest molecules a network collapses due to the close packing force, however it regenerates under the initial condition. Type II framework of "guest-induced transformation" has a property that structural shifts in the network are induced by the simultaneously exchanging of guest molecules. Type III framework of "guest-induced reformation" has a property that removal of guest molecules makes a structure change in network to another one, however it reverts to the original one under the initial condition.

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 bond to form a 3-D framework [6]. On the other hand, dynamic pores are subject to another guideline for a sort of flexible framework, that is, building units (or motifs) with flexible moiety are linked with strong bond, or, stiff building blocks (or motifs) are connected with weaker bond [4]. Other possible option is the combination of flexible building block (motifs) and weak linkage. 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 the weak linkage, guest molecules readily give rise to change in bond direction, distance, and to cleavage. It is worth noting that even weak interaction 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 the 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. One of the feasible ideas is that an entity of weak interaction 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. 1; 1-D motifs (chains), 2-D motifs (single-type layers, and interdigitated layers), 3-D motifs (pillared layers, expanding and shrinking Grids, and a combination of 3-D motifs, i.e. interpenetrated grids) [17].

These dynamic contrivances influence on the pore deformation with two fundamental operations of shrink and expansion. Focused on the relationship between the pores (shape/size) and guest molecules, the pore behaviors may be divided into four types (Fig. 2):

(a) *Induced-fit type pores*: The shrinkage occurs on guest molecule inclusion and gives rise to a pore that is well suited to the size and shape of the guest molecule, and therefore, short range attractive interactions work effectively [36,45,46].
(b) *Breathing type pores*: The expansion makes a guest molecule fit tightly into the host when the size of the pore is smaller than the guest molecule [27,28,38,47–50].
(c) *Guest-exchange deformation type pores*: The pore shape is induced to change responding to guest shape in simultaneous guest exchange [30–32,51–54].
(d) *Healing type pores*: The collapsed pore in the absence of guest molecules are regenerated with the guest accommodation [40,43,44,55].

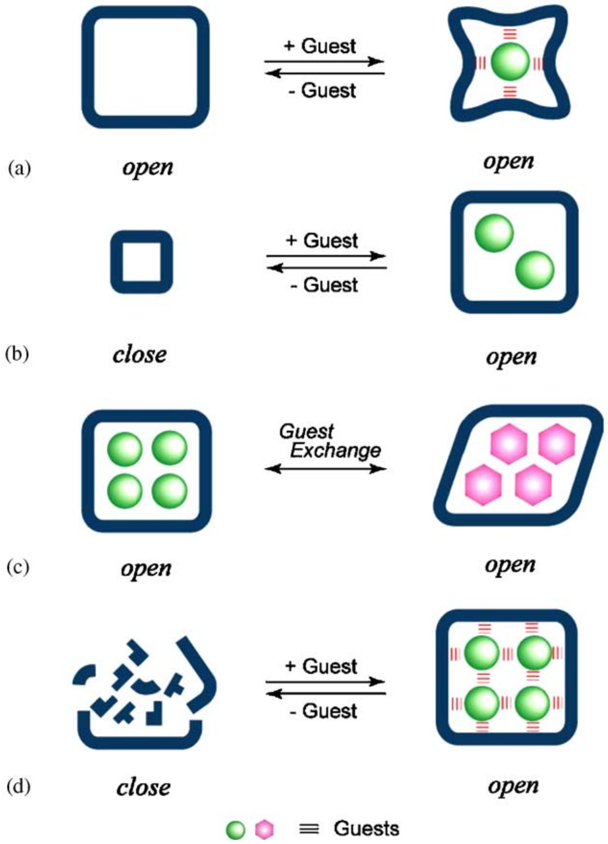

Fig. 2. Schematic microporous behaviors observed in adsorption/desorption of guest molecules; (a) induced-fit typed pores; (b) breathing pores; (c) guest-exchanging pores with deformation; and (d) healing pores.

The pores observed in type (a)/(c) exhibit the "*open*-to-*open*" deformation accompanying with guests inclusion. On the other hand, the pores in type (b)/(d) exhibit "*close*-to-*open*" deformation, and it is worth noting that type (a) and (b) is in opposite manner. Needless to say, type (c) and (d) are associated with "guest-induced transformation (type-II)" and "guest-induced reformation (type-I)", respectively (see Fig. 1). In the following context, we will introduce flexible microporous coordination polymers, compared to the pore model, type (a)–(d).

2. Induced-fit type pores (type (a))

The bioenzymes such as metalloproteins take advantages of their structural flexibility that appears to be essential for their superb molecular recognition [56]. For porous coordination polymers, flexibility of a host structure, so-called structural dynamism, is a key factor for accommodation and separation of a target molecule with highly selective recognition, which would afford a new class of practical materials. A microporous coordination polymer ($[Cu_2(pzdc)_2(bpy)]$ (**CPL-2**) (pzdc = pyrazine-2,3-dicarboxylate; bpy = 4,4′-bipyridine) as a host porous framework [57], shows a reversible structural change on sorption/desorption of benzene, which is a sort of "shape-responsive fitting" profiles on the guest adsorption with large crystalline shrinking.

The crystal structures of **CPL-2** and **CPL-2⊃benzene** have a neutral 2-D layer of $[Cu(pzdc)]_n$ forming in the *ac* plane, whose layers are connected by bpy as pillar ligands, resulting in a 3D pillared layer structure. Surprisingly, after exposed to benzene vapor (1 kPa), a contractive structure transformation occurred and the large reduction of the *b*-axis is observed by 6.8% although the benzene molecules occupy the channels.

In the structure of **CPL-2⊃benzene** (Fig. 3a and b), one benzene molecule as guests is located in the channel. The pillared layer framework undergoes such a deformation that the channel cavities suit benzene molecules very well, resulting in appreciable difference in the channel shape with and without benzene. The channel without benzene has nearly a rectangular shape of dimensions of 5.6 Å × 7.2 Å whereas that with benzene is no more rectangular shape but a "*Z*" letter-shape shown in Fig. 3c [45]. In the absence of benzene, the geometry around the copper ion is a square pyramidal, while that with benzene shows a square planar form. Eventually, the deformation produces a large contact area to the benzene plane.

Dynamic pores are subject to a guideline for a sort of flexible framework, that is, building units (or motifs) with flexible moiety are linked with strong bond, or stiff building blocks (or motifs) are connected with weaker

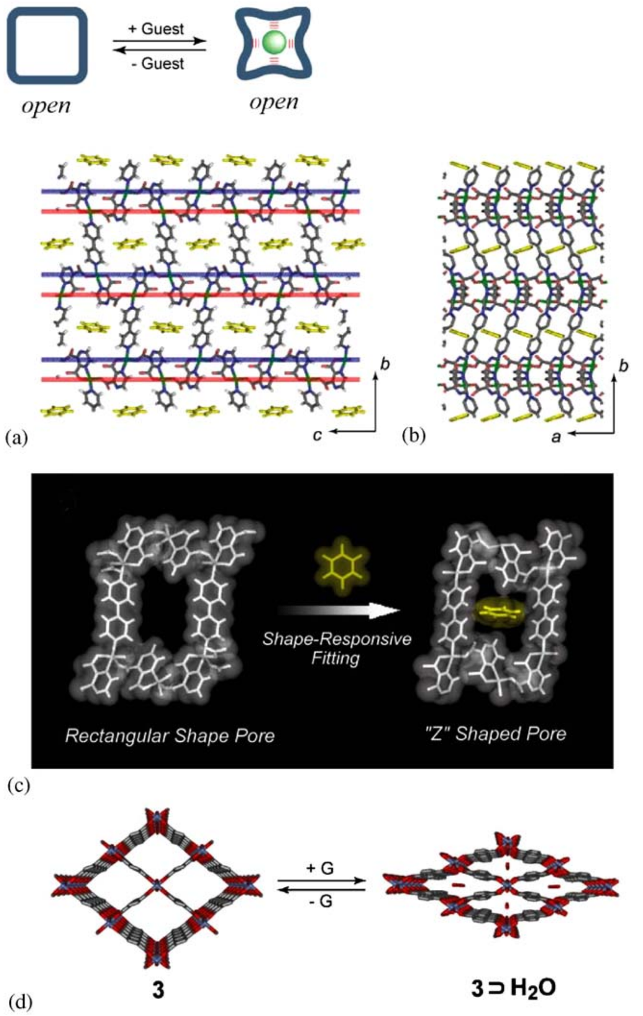

Fig. 3. Structures and schematic views of the induced-fit typed pores (type-(a)): (a) crystal view of $\{[Cu_2(pzdc)_2(bpy)]\cdot C_6H_6\}_n$ **(CPL-2⊃benzene)** along the *a*-axis. The benzene molecules are located in the each channel. Blue and red lines indicate the copper atom sheets projected down to the *a*-axis, which practically form a layers; (b) crystal view of **CPL-2⊃benzene** along the *c*-axis; (c) representation of the shape-responsive fitting structural transformation from **CPL-2 to CPL-2⊃benzene**; and (d) crystal structure of $\{[Cr(OH)(BDC)]\cdot H_2O\}_n$ (**3⊃H$_2$O**).

bond. These combinations would afford a subtly balancing porous framework, namely, a soft framework. In the case of **CPL-2**, the gadgets are bpy and pzdc rings as stiff motifs, the rotatable carboxyl group in pzdc and fluxional coordination geometry of the Cu ion, all of which provide a contrivance for a unique flexible channel structure: the dynamic structural transformation of **CPL-2** is derived from the change of the coordination mode based on the cleavage of the apical long Cu–O bond in the Cu geometry and the rotation of carboxyl group subsequently.

The host flexibility can improve efficiency of the adsorption by the aid of host structural transformation suited for the guest molecules. Most of porous materials have been synthesized with the aim of robust structure. However, flexible framework proves pore structure suited for a certain guest molecule, much more useful for molecular recognition or selective guest inclusion than the robust porous structure. This "shape-responsive fitting" property is one of the most important essences for a novel recognition system of crystal materials.

$\{[Cr(OH)(BDC)]\cdot H_2O\}_n$ (**3⊃H$_2$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. 3d) [36,46] The transition between the hydrated form **3⊃H$_2$O** and anhydrous solid **3** 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 **3⊃H$_2$O**, whereas dmf is incorporated into the pore instead of H_2O. This selectivity is attributed to the higher capability of dmf toward the formation of strong hydrogen bonds with the hydroxyl groups of the framework.

3. Breathing pores responding to guest (type (b))

When the size of a guest is larger than the pore, the guest molecule penetrates into the host to expand the pore window. Compounds of bis(acetylacetonato)*M*(II) ($M = $ Cu, Zn, Ni) derivatives afford characteristic inclusion phenomena [47,48]. $[Cu(L_1)_2]$ ($HL_1 = CF_3CO\,CH_2COC(OMe)Me_2$) forms two different crystal packing resulting in dense and nonporous $[Cu(L_1)_2]$ (**4**, α-form) and porous $[Cu(L_1)_2]\cdot 2/3C_6H_6$ (**4⊃2/3C$_6$H$_6$**, β-form). In the β-form, oxygen atoms of methoxy groups coordinates axial sites of Cu(II) to form six-membered cyclic structure (Fig. 4a). The porous β-form has a strong affinity for guest molecules as evident from the efficient α-form → β-form conversion on contact not only with liquid guests but also with organic vapors. The **4⊃no Guest** (empty β-form) undergoes slow crystal structure transformation to dense **4**, and quick transformation when it is exposed to propane. Labile coordination between Cu(II)–OMe is essential for this dynamic structure transformation. $\{[Zn(BDC)(H_2O)]\cdot dmf\}_n$ (**5⊃H$_2$O**) shows a 2-D layer of dimeric Zn units with terminally coordinated waters, which are further hydrogen bonded to guest molecules [38] and the anhydrous **5** forms a new crystalline structure. Reverse reaction, **5→5⊃H$_2$O**, results from adsorption of water molecules, which is ascribed to the hydrogen bond formation.

In $\{[Cu_2(dhbc)_2(4,4'\text{-}bpy)]\cdot H_2O\}_n$ (**CPL-p1⊃H$_2$O**, Hdhbc = 2,5-dihydroxybenzoic acid), 2-D bilayers are constructed by a mutual interdigitation as illustrated in Fig. 4b [28]. XRPD study shows that **CPL-p1⊃H$_2$O**

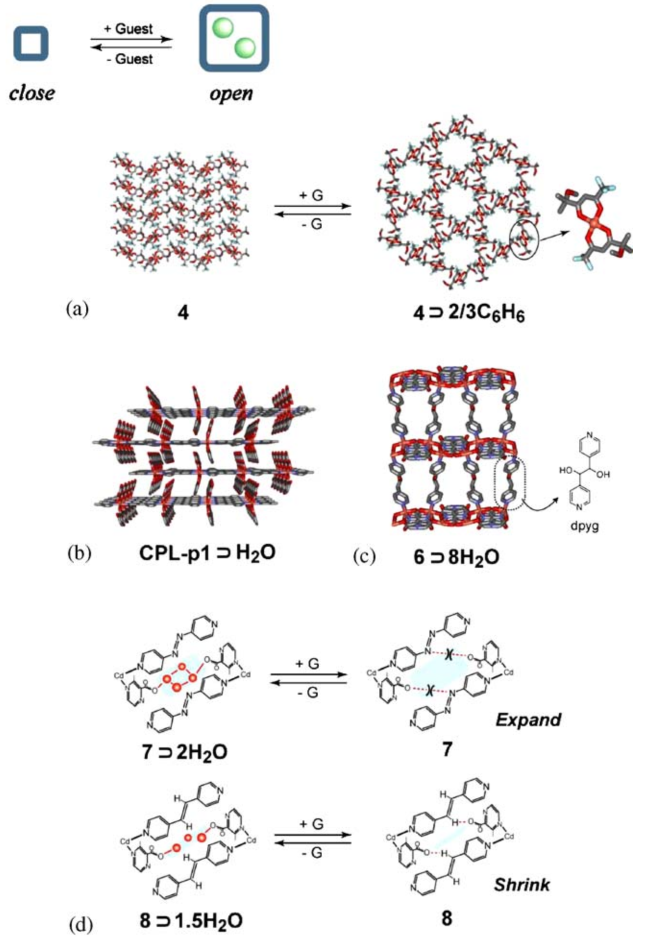

Fig. 4. Structures and schematic views of the breathed pores (type-(b)): (a) $[Cu(L_1)_2]$ (4, α-form) and porous $[Cu(Li)_2] \cdot 2/3C_6H_6$ (**$4 \supset 2/3C_6H_6$**, β-form); (b) $\{[Cu_2(dhbc)_2(4,4'\text{-bpy})] \cdot H_2O\}_n$ (**CPL-pl ⊃ H_2O**, Hdhbc = 2,5-dihydroxybenzoic acid); (c) $\{[Cu_2(pzdc)_2(dpyg)] \cdot 8H_2O\}_n$ (**$6 \supset 8H_2O$**, pzdc = pyrazine-2,3-dicarboxylate, dpyg = 1,2-di(4-pydidyl)glycol); and (d) $\{[Cd(pzdc)(azpy)] \cdot 2H_2O\}_n$ (**$7 \supset 2H_2O$**, azpy = py–N = N–py) and $\{[Cd(pzdc)(bpee)] \cdot 1.5H_2O\}$ (**$8 \supset 1.5H_2O$**, bpee = py–CH = CH–py). In all structures, the guest molecules are omitted for clarity.

exhibits drastic crystal structure transformation triggered by included water desorption and guest adsorption. This structural transformation of **CPL-p1 ⊃ H_2O**, especially change of the length of *c*-axis, is accompanied by shrinking of the layer distance, which is attributable to a glide motion of the two π-stack ring moieties, dhbc, resulting in a decrease in the channel cross section. Interestingly, structure re-expansion was observed (confirmed by XRPD) when it is exposed to N_2 vapor. This contraction and expansion behavior could be repeated many times.

$\{[Cu_2(pzdc)_2(dpyg)] \cdot 8H_2O\}_n$ (**$6 \supset 8H_2O$**, pzdc = pyrazine-2,3-dicarboxylate, dpyg = 1,2-di(4-pydidyl)glycol) exhibits 3-D porous framework with a cross section of $4 \times 6\,Å^2$; 2-D layer constructed with the pzdc ligands are linked to form a 3-D pillared-layer structure (Fig. 4c) [27]. The anhydrous compound, **6**, shows structural change with the entire crystallinity maintained, which is mainly attributed to a variation of the inter-layer distance. 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.

$\{[Cd(pzdc)(azpy)] \cdot 2H_2O\}_n$ (**$7 \supset 2H_2O$**, azpy = py–N = N–py) and $\{[Cd(pzdc)(bpee)] \cdot 1.5H_2O\}_n$ (**$8 \supset 1.5H_2O$**, bpee = py–CH = CH–py) form 3-D porous frameworks consisting of $[Cd(pzdc)]_n$ as 2-D corrugated layer pillared with azpy/bpee [49]. The framework possesses 1-D micro-channels with window dimensions of $3.5\,Å \times 6.1\,Å$ (**$7 \supset 2H_2O$**) and $3.5 \times 4.5\,Å$ (**$8 \supset 1.5H_2O$**) fulfilled with four and three water molecules in each pore, respectively. The different phenomenon in the process of adsorption/desorption of water molecules, expanding and shrinking, were realized in **$7 \supset 2H_2O$** and **$8 \supset 1.5H_2O$**, respectively (Fig. 4d). In **$7 \supset 2H_2O$**, this is associated with the lone pair–lone pair electronic repulsion from the oxygen atom of C = O and nitrogen atom of the azo group. On the other hands, the interlayer distance of **$8 \supset 1.5H_2O$** becomes decrease upon the removal of water molecules. Considering that the carbonyl oxygen atoms in **$8 \supset 1.5H_2O$** closely contact with ethylene hydrogen atoms, dehydrated **$8 \supset 1.5H_2O$** is closely packed with the stronger (C–H···O) interaction. Thus, **$7 \supset 2H_2O$** and **$8 \supset 1.5H_2O$** correspond to type (b) and (a), respectively. The expanded channel in **7** adsorbs five kinds of vapor, H_2O (surface area; $10.5\,Å^2$), MeOH ($18.0\,Å^2$), EtOH ($23.1\,Å^2$), THF ($28.7\,Å^2$), Me_2CO ($26.8\,Å^2$), whereas, shrunk **8** only adsorb H_2O and MeOH. It is noteworthy that **8** exhibits a selective adsorption; H_2O and MeOH are adsorbed, whereas EtOH, THF and Me_2CO are not. Taking into account for the result that the larger sized molecules are not adsorbed, this selectivity is ascribed to the relative size of channel windows in **8** against the dimension of adsorbates. This kind of coordination polymer will find application at fine gas separation and actuator.

$\{[Ni_2(C_{26}H_{52}N_{10})]_3[BTC]_4 \cdot 6C_5H_5N \cdot 36H_2O\}_n$ (**$9 \supset 6C_5H_5N \cdot 36H_2O$**) assembled from bismacrocyclic nickel(II) complex $[Ni_2(C_{26}H_{52}N_{10})(Cl)_4] \cdot H_2O$ and sodium 1,3,5-benzenetricarboxylate (Na_3BTC) forms pillared bilayer open framework having 3-D channels [50]. The channel window size on the side of the bilayer is 14.52(1) Å, and the voids of the channels occupy 61% of the total volume, which are filled with water and pyridine guest molecules. **$9 \supset 6C_5H_5N \cdot 36H_2O$** shows a sponge-like dynamic behavior responding to the amount of guest molecules, without breaking the single-crystal nature. Furthermore, crystal **$9 \supset 6C_5H_5N \cdot 36H_2O$** reacts with I_2 via single-crystal-to-single-crystal transformation to produce $\mathbf{9 \supset (I_3)_4 \cdot \mathit{n}I_2 \cdot 17H_2O}$ that consists of positively charged framework incorporating nickel(III) and nickel(II) ions and the channels including I_3^- and I_2.

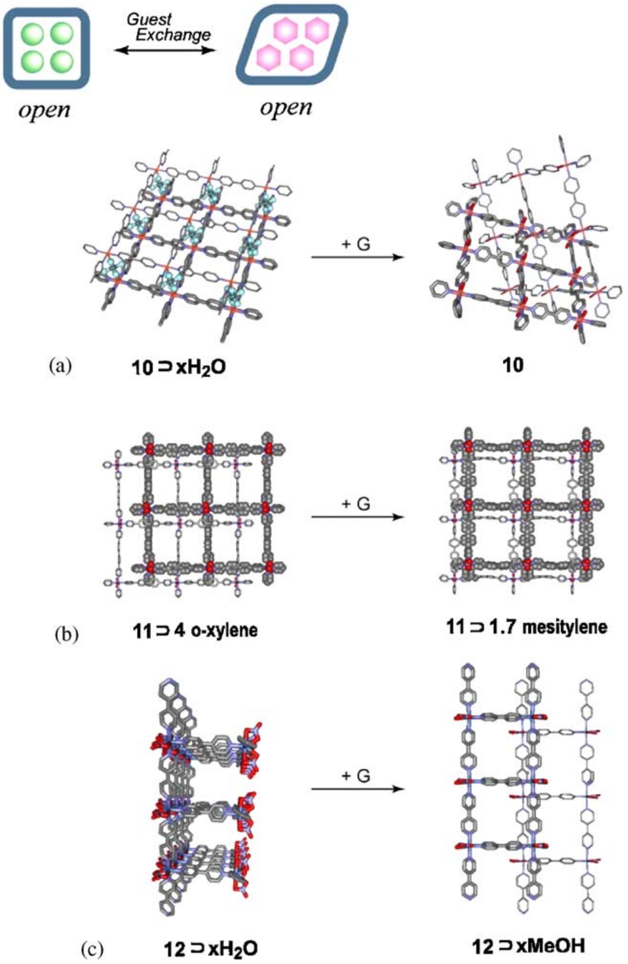

Fig. 5. Structures of the guest-exchanging deformation of pores (type-(c)): (a) $\{[Cu(AF_6)(4,4'\text{-bpy})_2] \cdot xH_2O\}_n$ ($\mathbf{10 \supset \mathit{x}H_2O}$, A = Si, Ge, and Ti) and $\{[Cu(4,4'\text{-bpy})_2(H_2O)_2] \cdot AF_6\}_n$ (**10**); (b) $\{[Ni(L_2)_2(NO_3)_2] \cdot 4(o\text{-xylene})\}_n$ (**11 ⊃ 4 *o*-xylene,** L_2 = 4,4′-bis(4-pyridyl)biphenyl) and $\{[Ni(L_2)_2(NO_3)_2] \cdot 1.7(\text{mesitylene})\}_n$ (**11 ⊃ 1.7 mesitylene**); and (c) $\{[Ni_2(bipy)_3(NO_3)_4]_n \cdot xH_2O\}_n$ ($\mathbf{12 \supset \mathit{x}H_2O}$, polymorph B) and $\{[Ni_2(bipy)_3(NO_3)_4]_n \cdot xMeOH\}_n$ (**12 ⊃ *x*MeOH**, polymorph A). In all structures, the guest molecules are omitted for clarity.

4. Labile guest exchange in microporous frameworks

Coordination polymers of Ag(I) cations are attracting a great deal of attention because of simply a linear coordination around Ag(I) atoms ready to form 1-D chains [7]. It is worth noting that silver cations accompany a positive charge into the chain, and therefore, the counter anions such as PF_6^- and BF_4^- are nested around the chains. The anions could be exchanged accompanying with structural transformation [51,52], when the crystal is soaked in solution containing another anion. Microporous coordination polymers also show structural transformation in such simultaneous neutral guest exchanges.

3-D frameworks of $\{[Cu(AF_6)(4,4'\text{-bpy})_2] \cdot xH_2O\}_n$ ($\mathbf{10 \supset \mathit{x}H_2O}$, A = Si, Ge, and Ti) form layers linked with coordinating AF_6^- ions to give a 3-D structure without interpenetration [8,53] $\mathbf{10 \supset \mathit{x}H_2O}$ was transformed into 2-D interpenetrating networks of $\{[Cu(4,4'\text{-bpy})_2(H_2O)_2] \cdot AF_6\}_n$ [10] on being immersed in a H_2O solution (Fig. 5a). To prove the occurrence of this dynamic structural transformation in the solid state, 3-D frameworks of $\mathbf{10 \supset \mathit{x}H_2O}$ were exposed in a H_2O vapor for a few days. Similar transformation into 2-D interpenetrating framework was observed, clearly indicative of the solid-state conversion. This transformation causes not only the formation and cleavage of weak Cu–O (H_2O) and Cu–F (AF_6) bonds, respectively, but also regular Cu–N (4,4′-bpy) bond formation and cleavage. Practically, recognized is an important role of elongated axial sites of Cu(II) compounds.

$\{[Ni(L_2)_2(NO_3)_2] \cdot 4(o\text{-xylene})\}_n$ (**11 ⊃ 4 *o*-xylene**, L_2 = 4,4′-bis(4-pyridyl)biphenyl) contains 2-D layers that are formed by square grids of dimension $20 \times 20\,Å^2$ (Fig. 5b) [31,58]. These layers have a short interlayer separation of 4.1 Å and can slide on each other as the binding forces between the layers are only weak aromatic and C–H···O interactions that are reformed after the sliding is completed. Surprisingly, the single-crystal X-ray analysis of the crystals with mesitylene as the new guest (**11 ⊃ 1.7 mesitylene**) reveals that considerable sliding of the layers on each other occurs such that the dimension of the channels is bigger than that of **11 ⊃ 4 *o*-xylene**. In **11 ⊃ 4 *o*-xylene** the layers pack on each other such that they overlap in one direction and are offset in the other direction, determining the cross section of a channel with the dimension of about $10 \times 20\,Å^2$. Unlike **11 ⊃ 4 *o*-xylene**, the offset packing was not observed in **11 ⊃ 1.7 mesitylene** as the layers slide on each other to give the cross section of the channel with the dimensions of approximately $15 \times 20\,Å^2$. The role of mesitylene seems to be important in this transformation as a similar transformation or guest exchange was not observed when the crystals of **11 ⊃ 4 *o*-xylene** were immersed for even longer in the other guest solvents such as benzene, *m*-xylene, or 1,2- or 1,3-dimethoxybenzene.

The frameworks $\{[Ni_2(bipy)_3(NO_3)_4]_n \cdot xH_2O\}_n$ ($\mathbf{12 \supset \mathit{x}H_2O}$, polymorph B) form by T-shaped coordination of bipy to Ni^{2+} with nitrate counter ions, which complete pseudo-square pyramidal coordination at the metal [12,30,59,60]. The assembly of these basic units can be described as a tongue-and groove structure (polymorph B) creating channel cavities of about 3×6 and 3×3 Å fulfilled with water molecules. On the other hand, another **12 ⊃ *x*MeOH** (polymorph A) forms with MeOH guests adopts the “ladder” structure. Exposure of polymorph B to MeOH vapor results in a transition to the ladder structure **$12 \supset x$MeOH** in which crystal habit is preserved (Fig. 5c) [30]. Given the close relationship between the two structure types, possible mechanisms for interconversion involving minimal bond cleavage can be proposed.

The crystal-to-crystal guest exchange of large organic molecules via guest removal and re-inclusion within a porous 3-D coordination network, $[(ZnI_2)_3(L_3)_2]_n$ **(13)**, where L_3 is 2,4,6-tris(4-pyridyl)triazine, was studied [32,54]. The 3-D net of **13** possesses large pores filled by nitrobenzene columns, to be $\{[(ZnI_2)_3(L_3)_2] \cdot 5.5(\text{nitrobenzene})\}_n$ (**$13 \supset 5.5$ nitrobenzene**). Immersion of single crystals of **$13 \supset 5.5$ nitrobenzene** in a saturated cyclohexane solution of anthracene gives rise to a guest exchange to afford $\{[(ZnI_2)_3(L_3)_2] \cdot 1.4(\text{anthracene}) \cdot 2.2(\text{cyclohexane})\}_n$ (**$13 \supset 1.4$ anthracene**) without loss of crystallinity, accompanying with the crystal color turned deep yellow. Crystallographic analysis showed efficient stacking of the guest and ligand. Moreover, characteristic color change is attributed to the donor–acceptor interaction between the electron-rich guests and the electron-deficient ligand, which is supported by UV-vis spectroscopy measurements and DFT calculation.

5. Healing frameworks by guest adsorption

In several compounds, "*amorphous*-to-*crystal*" transformation takes place on guest adsorption and/or desportion, regarded as "recoverable collapse". In practice, the approach to create such a transformation could be applicable to brittle materials systems [61].

$\{[Ni(cyclam)(H_2O)_2]_3[btc]_2 \cdot 24H_2O\}_n$ (**$14 \supset 24H_2O$**, btc = 1,3,5-benzenetricarboxylate) has hydrogen bond links between Ni(II) macrocyclic complexes and btc via coordinated waters, affording 2-D layers with the channel of 10.3 Å cross section, which accommodates water molecules (Fig. 6a) [40]. Removal of water molecules from **$14 \supset 24H_2O$** produces an amorphous form, and when this solid is suspended in water the original crystal form is regenerated.

$\{[Cu(pymo)_2] \cdot (NH_4ClO_4)_{1/3}\}_n$ (**$15 \supset (NH_4ClO_4)_{1/3}$**, pymo = 2-hydroxypyrimidine) reveals that the combination of square planar Cu(II) ion with 120° bond angles provided by Hpymo generates a 3-D porous framework with ammonium and perchlorate ions included in the pores (Fig. 6b) [43]. This compound loses ammonia upon heating, giving the corresponding activated acidic material **$15 \supset (HClO_4)_{1/3}$** which upon exposure to gaseous ammonia regenerates **$15 \supset (NH_4ClO_4)_{1/3}$**. This behavior agrees with the observed guest-induced structure phase change taking place in the framework after guest inclusion.

$\{[Cu_3(ptmtc)_2(py)_6(EtOH)_2(H_2O)] \cdot 10EtOH \cdot 6H_2O\}_n$ (**$16 \supset 10EtOH \cdot 6H_2O$**, ptmtc = polychlorinated triphenyl methyl with three carboxyl group) exhibiting a sponge-like magnetic behavior [44]. **$16 \supset 10EtOH \cdot 6H_2O$** forms a 2-D layer with a honeycomb structure, and the different layers arrange themselves between them, by means of weak π–π 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, forming an amorphous material, which recovers its structural integrity when re-immersed in liquid ethanol, indicating solvent-induced 'shrinking-breathing' process, that strongly influence the magnetic properties.

As observed in **14–16**, hydrogen bonds in the networks would play an important role in realizing "*amorphous*-to-*crystal*" transformation. Therefore, rational introduction of hydrogen bond into framework is necessary for realizing such transformation. The bridging ligands py–Amide–py would satisfy the requirement, since metal ions prefer the pyridyl group (py) by far to the amide group [17,26,55]. The py groups at both ends are used for the formation of a framework backbone while the middle amide group can serve as hydrogen bonding sites; H acceptor (–NH–) and receptor (–CO–) in a space surrounded by a framework. A layer-type motif is relevant to create a dynamic porous structure, which exhibits reversible transformation from a form to another, caused by an external stimulus. The dynamic event could occur between the layers [26,31].

In $\{[Co(NCS)_2(4\text{-peia})_2] \cdot 4Me_2CO\}_n$ (**$17 \supset 4Me_2CO$**, 4-peia = *N*-(2-Pyridin-4-yl-ethyl)-isonicotinamide), the cobalt ions are linked by 4-peia to form a 2-D layer composed of a square grid motif with the dimension of 15.8 Å × 15.8 Å [55]. The hydrogen-bonding links of the $NH \cdots O{=}C$ ($N \cdots O = 2.780(7)$ Å) groups between the adjacent layers create complementary-amide binding network (Fig. 6c). A channel with the dimension of 4.4 Å × 4.4 Å is observed, where acetone molecules are accommodated with no significant interaction. The framework of **17** cannot withstand a high level of stress on an extensive loss of the guest, resulting in amorphous form. Throughout the characterization of **17** by XRPD, IR and EPR, indicates that the 2-D motif of **17** does not collapse, and the amorphous form is attributed to the random layer slip against the neighboring layers accompanying with the deformation of grid framework. Interestingly, upon exposing to acetone vapor, the original crystal structure (**$17 \supset 4Me_2CO$**) comes back completely, where hydrogen bonds among the layers perform effectively.

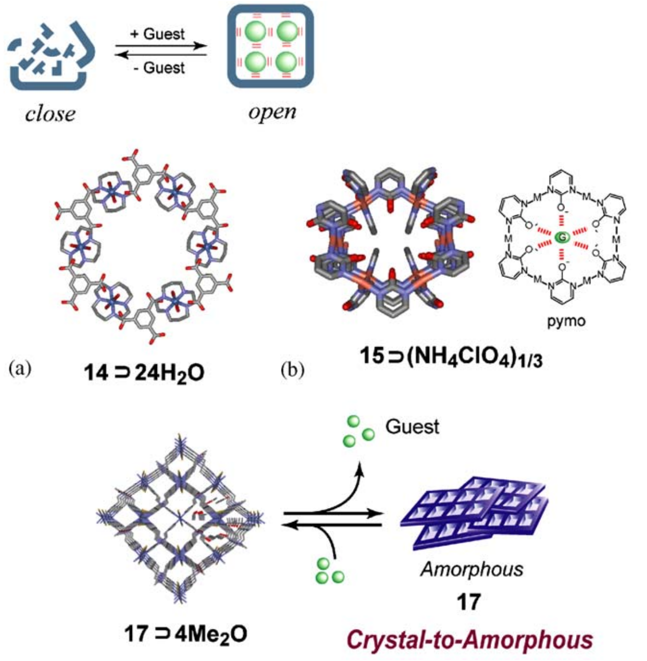

Fig. 6. Structures and schematic views of the healed pores (type-(d)): (a) $\{[Ni(cyclam)(H_2O)_2]_3[btc]_2\cdot24H_2O\}_n$ (**$14\supset24H_2O$**, btc = 1,3,5-benzenetricarboxylate); (b) $\{[Cu(pymo)_2]\cdot(NH_4ClO_4)_{1/3}\}_n$ (**$15\supset(NH_4ClO_4)_{1/3}$**, pymo = 2-hydroxypyrimidine); and (c) $\{[Co(NCS)_2(4\text{-peia})_2]\cdot4Me_2CO\}_n$ (**$17\supset4Me_2CO$**, 4-peia = *N*-(2-Pyridin-4-yl-ethyl)-isonicotinamide).

6. Adsorption/desorption energetics of third generation compounds

As seen in **3–17**, flexible microporous coordination polymers provide characteristic properties, which is not observed in rigid frameworks (second generation). Although a number of third generation compounds have been reported to date, the extensive investigation of their flexible mechanism is sparse. Regarding soft materials, which exhibit a difference between the initial and final frameworks, the unique functionalities such as the donor–acceptor interactions found in **$13\supset1.4$ anthracene** and the redox property in **$9\supset6C_5H_5N\cdot36H_2O$** are received a renaissance, rather than pursuing the mechanism.

Adsorption measurement is the standard method for analyzing the porous coordination polymers, however, the interpretation of their isotherms is complicated (especially in third generation compounds) due to the soft nature of coordination polymers. Fig. 7a shows the methanol adsorption/desorption isotherm at 298 K on **6** [27]. The isotherm shows a sudden rise at point A (relative pressure, $P/P_0 = 0.23$) and attains a saturated level at point B ($P/P_0 = 0.5$). On the other hand, the desorption isotherm does not trace the adsorption one any more, instead, showing an abrupt drop at point C ($P/P_0 = 0.1$). This sharp adsorption jump/desorption drop with the hysteresis indicates the occurrence of a framework transformation in the crystal state, which should permit guest inclusion. A similar adsorption isotherm with a hysteresis profile is observed in the case of Me_2CO vapor on **17** (Fig. 7b) [55]. **CPL-p1** also shows characteristic hysteretic adsorption isotherm of CO_2 vapor and various super critical gases, CH_4, O_2 and N_2 as shown in Fig. 7c [28]. In **CPL-p1**, it should be noted that only dynamic frameworks by van der Waals-type could induce a drastic structure transformation triggered by adsorption and desorption of supercritical gases.

In the adsorption/desorption process on the solid, the phase rule for the equilibrium between three phases (two solid phases for apohost and adduct and one gaseous phase for guest) consisting of two components (host and guest) leaves one degree of freedom, i.e., $f = c - p + 2 = 2 - 3 + 2 = 1$ (f: variance, c: component, p: phase) [21]. When the temperature as the sole variance is fixed, the corresponding equilibrium pressure is automatically fixed. The hysteresis curves observed in **6**, **17**, and **CPL-p1** are therefore in conflict with the phase rule. That is difficult and complicated, however interesting aspect of third generation compounds.

The **6**, **17**, and **CPL-p1** exhibit adsorption jump. Namely, the point of jump is gate-opening pressure (the threshold pressure, P_{th}), where guest accommodation starts [21,25]. The acetone adsorption isotherm of **17** shows a slight increase and an abrupt rise at $P/P_0 = 0.76$ [55]. which characteristic adsorption profile clearly indicates a conversion of amorphous **17** (dried) to a crystalline form (**$17\supset4Me_2CO$**). In this "*amorphous*-to-*crystal*" structural rearrangement in Me_2CO adsorption process, the threshold pressure (P_{th}) is required to start the accommodating reaction, which 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). Regarding P_{th} as the equilibrium pressure, the graph of $\ln P_{th}$ vs. $1/T$ has a slope of $\Delta H_{ad}/R$, yielding adsorption enthalpy change (ΔH_{ad}) using the Clausius–Clapeyron equation, $d\ln P_{th}/d(1/T)) = \Delta H_{ad}/R$. Using the Clausius–Clapeyron equation, $\Delta H_{ad} = -25\,kJ/mol$ for the inclusion of acetone was obtained [55], implying that weak dispersive forces induces structural rearrangement in a well-concerted fashion.

An estimation of ΔH_{clath} can lead to a better understanding of the nature of soft pores and the mechanism of structural conversion. The differential scanning calorimeter (DSC) measurements are the standard method for obtaining ΔH_{ad}, however, it occasionally has some difficulty to obtain ΔH_{ad} directly, because such kinds of flexible microporous coordination polymers are unstable at room temperature and decomposed with the loss of guest molecules, usually with a concomitant rearrangement of the host compound to form the closed form. The estimation based on the

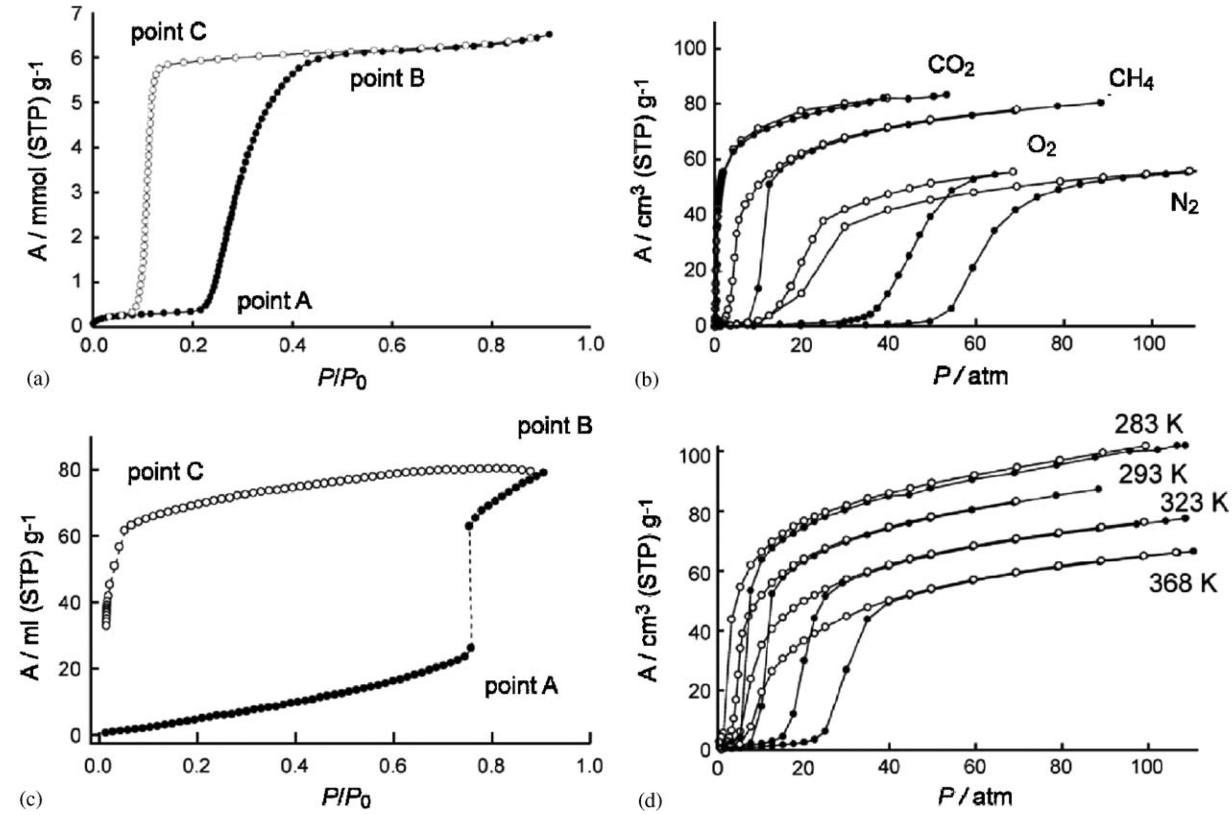

Fig. 7. (a) Methanol adsorption (●) and desorption (○) isotherms at 298 K on $[Cu_2(pzdc)_2(dpyg)]_n$ (**6**); (b) acetone adsorption (●) and desorption (○) isotherms at 298 K on $[Co(NCS)_2(4\text{-peia})_2]_n$ (**17**); (c) adsorption (●) and desorption (○) isotherms of N_2, CH_4, CO_2, and O_2 at 298 K on $[Cu_2(dhbc)_2(4,4'\text{-bpy})]$ (**CPL-pl**); and (d) temperature dependence of adsorption (●) and desorption (○) isotherms of CH_4 at 283, 293, 323, and 368 K on **CPL-pl**.

temperature dependence of P_{th} is useful approach to this problem.

7. Summary and perspectives

To date much effort has been made to develop the "rigid pores", which appear to be available for storage application. On the contrary, dynamic pores have been overlooked for a long time possibly because of difficulty of characterization, and, therefore, the research has begun just now. In this review, we showed some flexible microporous coordination polymers, classifying four kinds of adsorption behaviors; (a) induced-fit typed pores, (b) breathing type pores, (c) guest-exchange deformation type pores, and (d) healing type pores. They are useful for creation of chemical stimulus–responsive properties. This review also imply that coordination polymer is often much more dynamic than generally believed and that even a weak dispersion force induces structural rearrangement in a well-concerted fashion.

The reports of these phenomena are recently coming out. Functionalities such as nonlinear optical property, conductivity, magnetism, spin-crossover, chromism, and fluorescent property are another aspect of coordination frameworks, which have been hitherto independently studied. Promising in this regard are co-operative properties of future coordination polymers, whose motifs are linked by hydrogen bond, with dynamic structures coupled with guest occlusion and/or other physical properties.

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