Part One
Design of Multifunctional Porous MOFs

Metal-Organic Frameworks: Applications from Catalysis to Gas Storage, First Edition. Edited by David Farrusseng.

1

Design of Porous Coordination Polymers/Metal–Organic Frameworks: Past, Present and Future

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1.1

Introduction

At the end of the 1990s, a new porous compound with an inorganic–organic hybrid framework had an impact on the field of porous materials and represented a new family for porous chemistry. Porous coordination polymers (PCPs), also known as metal–organic frameworks (MOFs), have regular pores ranging from micro- to mesopores, resulting in a large pore surface area, and a highly designable framework, pore shape, pore size, and surface functionality. Their structures are based on organic ligands as linkers and metal centers as the connectors. The rich functionality and designability of the organic ligands and the directability and physical properties of the metal ions are fascinating for the design of various functions, not only conventional adsorptive functions such as storage, separation, and catalysis, but also other physical/chemical functions that can be integrated in the frameworks. Whereas the components of PCPs are connected by coordination bonds and other weak interactions or noncovalent bonds (H-bonds, π-electron stacking, or van der Waals interactions), the interactions lead to structural flexibility and dynamics in the crystalline state, which also promotes the unique character of PCPs in the field of porous materials. As synthetic techniques and knowledge have increased in the last decade, we are now ready to design advanced porous functions by making full use of the chemical components and structural topologies. In this chapter, we introduce the background of PCPs/MOFs with some of the main framework designs and describe the unconventional porous properties of multifunctional porous materials based on ligand–metal networks.

1.2

Background and Ongoing Chemistry of Porous Coordination Polymers

Coordination polymers (CPs) are a family of compounds with extended structures formed by metal ions and organic and/or inorganic ligands with coordination bonds.

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They can provide various frameworks constructed from one-, two-, and three-dimensional networks. The late transition metal elements (Cu, Ag, Zn, and Cd) tend to provide this type of framework and the chemistry of CPs has been elucidated with the development of single-crystal X-ray crystallography. The term "coordination polymer" was used in a paper in 1916 [1], but there was no means of demonstrating infinite frameworks without single-crystal X-ray crystallography. A three-dimensional coordination framework connected by a CN bridge was realized in 1936 [2], namely the well-known Prussian Blue compounds. Currently, coordination polymers having porous properties are termed PCPs or porous MOFs, and therefore we suggest "coordination framework" as an all-inclusive term because the chemistry of the background is defined as "chemistry of coordination space." To understand the background of this chemistry, there are three important concepts: (1) framework, (2) molecular metal–organic hybrid, and (3) porosity.

1) Concept of Framework

   It is well known that CPs provide us with one-, two-, and three-dimensional motifs. In particular, the structural concept of a framework was demonstrated by Hofmann and Küspert [3], whose compounds are known as the family of Hofmann compounds having a two-dimensional layer-based architecture. The first X-ray crystallographic structure was obtained in 1949 [4]. The complete three-dimensional framework, the so-called Prussian Blue complex, appeared in 1936 and a comprehensive study was performed by Iwamoto *et al.* in 1967 [2, 5].

2) Molecular Metal–Organic Hybrid

   Hofmann and Prussian Blue compounds have structures bridged by the inorganic ion CN^-, and therefore have a restricted variety of structures. On the other hand, frameworks having organic linkers afford not only designability but also functionality of frameworks. The X-ray crystal structure of the metal–organic coordination framework of $[Cu(adiponitrile)_2]\cdot NO_3$ appeared in 1959 [6]. Since then, many compounds in this category have been synthesized and characterized crystallographically. Yaghi *et al.* termed these compounds "metal–organic frameworks (MOFs)" in 1995 [7]. $[Cu(adiponitrile)_2]\cdot NO_3$ contains the NO_3^- anion in the voids. Such compounds are regarded as clathrate-type CPs, however, which are not categorized as "porous" compounds. By the late 1990s, many clathrate-type CPs/MOFs had been synthesized.

3) Porosity

   Porosity means "the quality or state of being a porous entity, which has many small holes that allow water, air, and so on, to pass through." The porosity is antithesis to Aristotle's proposition, "Nature abhors a vacuum." Indeed, closely packed solid structures formed by molecules and ions can easily form. Researchers have often misunderstood that the crystallographic structure of MOFs having guest species in their voids is a porous material. In 1997, "porosity" was demonstrated to give a compound that maintains a porous structure without guests in the pores; gas sorption experiments under ambient conditions were carried out for stable apohosts [8, 9]. Reversible gas storage properties were identified and the PCPs have attracted wide attention as new porous materials.

Since that point, the number of reports on PCPs has been increasing rapidly, and many researchers have been developing strategies for the design of porosity, some of which are intrinsically unique to PCP materials.

1.2.1
Frameworks with High Surface Area

One of the great advantages of PCPs/MOFs is their high surface area, attributable to the low density of the porous structure. An MOF composed of Zn_4O clusters connected by benzenedicarboxylate (bdc), $[Zn_4O(bdc)_3]$ (MOF-5), was synthesized in 1999 and possesses a cubic structure with an ordered three-dimensional (3D) porous system (Figure 1.1a) [10]. This compound has a BET surface area of $3800\,m^2\,g^{-1}$ [11]. Many porous compounds have been synthesized on the basis of this structural motif, and this approach has been intensively developed to design important porous frameworks. Some related frameworks, $[Zn_4O(btb)_2]$ (MOF-177) and $[Zn_4O(bbc)_2]$ (MOF-200) {btb = 1,3,5-benzenetribenzoate; bbc = 4,4′,4″-[benzene-1,3,5-triyltris(benzene-4,1-diyl)]tribenzoate)} also possess high porosity; the reported BET surface areas for these compounds are 4746 and $6260\,m^2\,g^{-1}$, respectively [12, 13]. The self-assembly process of structure growth often faces network interpenetration, which precludes a high surface area, but further

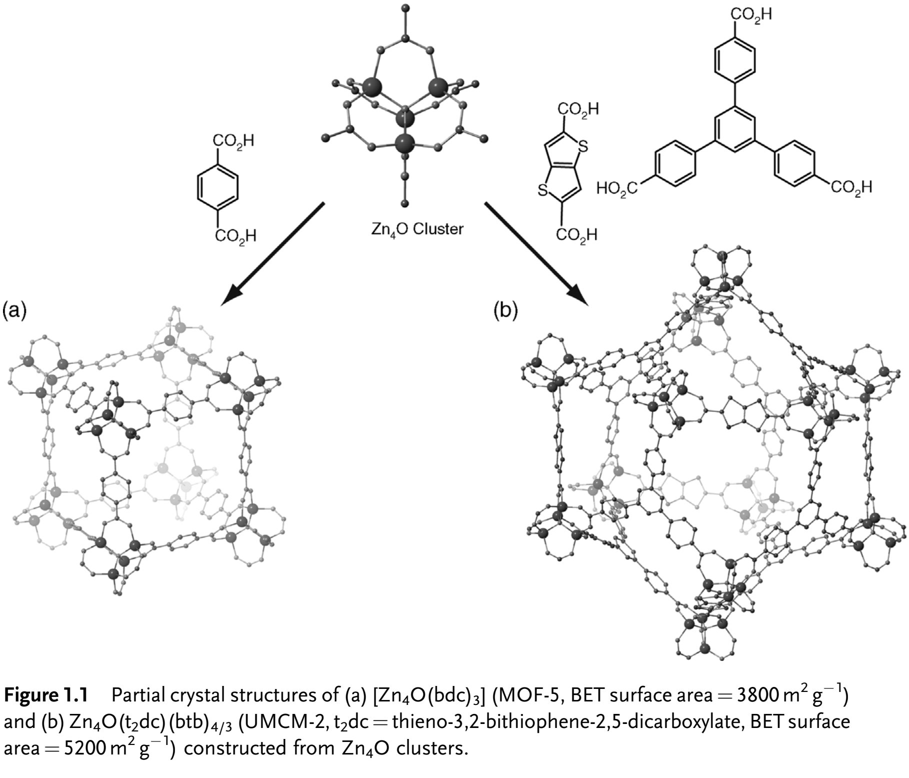

Figure 1.1 Partial crystal structures of (a) $[Zn_4O(bdc)_3]$ (MOF-5, BET surface area = $3800\,m^2\,g^{-1}$) and (b) $Zn_4O(t_2dc)(btb)_{4/3}$ (UMCM-2, t_2dc = thieno-3,2-bithiophene-2,5-dicarboxylate, BET surface area = $5200\,m^2\,g^{-1}$) constructed from Zn_4O clusters.

improvements in the design of pore network topologies could avoid interpenetration to achieve extremely high surface areas.

Porous frameworks constructed from two or more kinds of ligands are in some cases effective in the design of high surface area compounds. $Zn_4O(t_2dc)(btb)_{4/3}$ (UMCM-2) (t_2dc = thieno-3,2-bithiophene-2,5-dicarboxylate) (Figure 1.1b) is also made up of Zn_4O clusters and two distinct ligands contribute to the construction of the porous framework [14]. There is a narrow distribution of micropores at 1.4–1.6 and 1.6–1.8 nm and a mesopore at 2.4–3.0 nm and the calculated BET surface reaches 5200 $m^2\,g^{-1}$.

Another framework, $[Cr_3F(H_2O)O(bdc)_3]$ (MIL-101), is made from the linkage of terephthalate and chromium trimer units that consist of three Cr cations and the μ_3O oxygen anion [15]. The pore space is constructed from two cages with diameters of 2.9 and 3.4 nm which are connected with windows with diameters of 1.2 and 1.45 nm, respectively. The compound has a BET surface area of 4100 $m^2\,g^{-1}$ and, compared with the Zn_4O-type metal cluster, the framework is more stable against water and other chemical species and it has also been utilized as a porous matrix for post-synthesis or hybridization with other species such as metal particles [16].

A paddle-wheel-type dimetal cluster is a popular building unit to construct frameworks. Many transition metals can form this type of cluster and it affords square grid extended networks. $[Cu(H_2O)]_3(ntei)$ (PCN-66) is prepared by the combination of 4,4′,4″-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl)triisophthalate (ntei) and a Cu^{2+} paddle-wheel cluster and the BET surface area is 4000 $m^2\,g^{-1}$ [17]. Isostructures have been made using other hexatopic carboxylate ligands and it is anticipated that even higher surface areas can be designed.

So far, these compounds represent carbon-containing materials with one of the highest surface areas and the feature of complete crystallinity is a significant platform for a high capacity of gas uptake and it also acts as accumulation areas for other materials such as metal particles, functional molecules and polymers, and gases with high density.

1.2.2
Lewis Acidic Frameworks

The design of porous frameworks having guest interaction sites has also been intensively investigated. Especially unsaturated metal sites on the pore interior, which act as Lewis acid sites, have been synthesized because of interest in the storage of gases such as H_2 and CO_2 and for heterogeneous catalysis.

$[Cu_3(btc)_2]$ (HKUST-1), based on Cu_2 paddle-wheel units linked by benzenetricarboxylic acid (btc) is one of the early PCPs with unsaturated metal sites [18]. This compound possesses a 3D channel with a pore size of 1 nm and has high thermal stability and aqueous durability. The axial sites of Cu^{2+} are accessible to guests and gas capture and heterogeneous catalysis have been reported [19, 20]. This motif is available for other metal ions such as W, Fe, and Cr, and $[Cr_3(btc)_2]$ shows O_2 adsorption at 298 K with a Type I isotherm with which adsorption occurs at very low

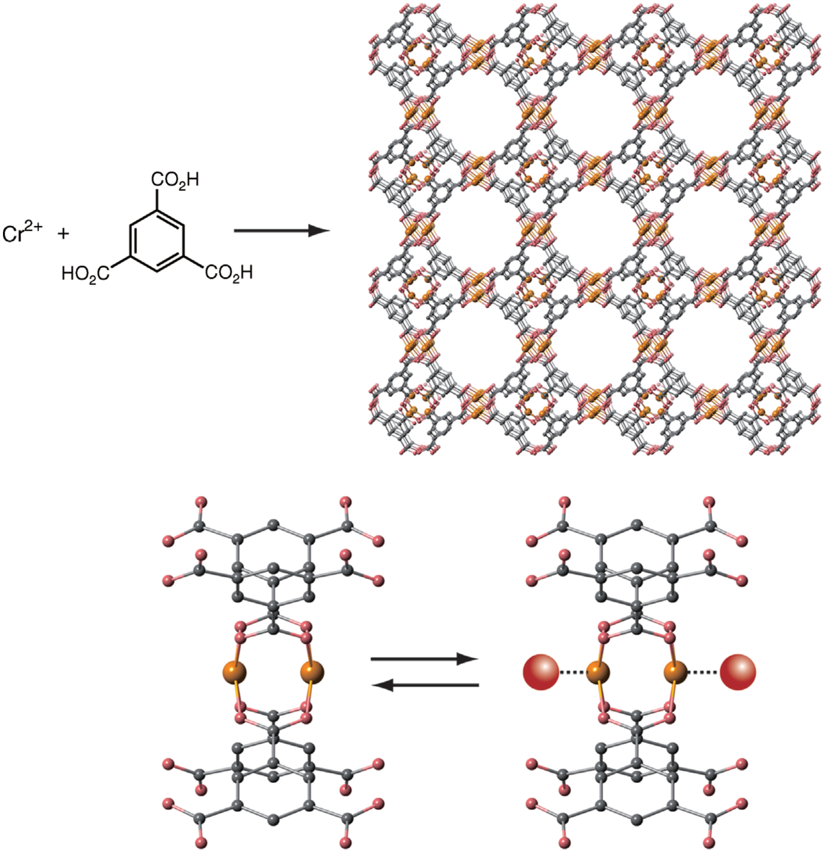

Figure 1.2 3D crystal structure of $[Cr_3(btc)_2]$ (btc = benzenetricarboxylate) and reversible O_2 sorption processes at paddle-wheel Cr dimer unit. Red spheres represent O_2 molecules.

pressures [21–23]. In the case, the redox active Cr centers bind O_2 molecules (Figure 1.2) to show reversible chemisorption behavior with negligible N_2 uptake under the same conditions.

In M_2(dhtp) (H_4dhtp = 2,5-dihydroxyterephthalic acid; M = Mg, Mn, Co, Ni, Zn), the framework has hexagonal one-dimensional (1D) channels and a high concentration of unsaturated metal sites [24, 25]. One of this series of frameworks, Mg_2(dhtp), shows a large CO_2 uptake at 298 K and 1 atm (35.2 wt% of CO_2) because of the light weight of the framework skeleton and the strong interaction of CO_2 and unsaturated metal sites [26]. This framework is relatively stable towards water and has a strong hydrophilic nature. This compound is applicable not only for the capture of CO_2 but also other gases such as NO, and it is also promising as a biocompatible material [27].

The large-pore compound $[Cr_3F(H_2O)O(bdc)_3]$ (MIL-101) mentioned above also has unsaturated Cr^{3+} centers in the mesoporous cages and works as a catalyst [28, 29]. The large pores therein are also advantageous for a high rate of substrate diffusion in heterogeneous catalytic reactions.

These compounds produce guest-accessible unsaturated metal centers after proper evacuation (or activation) of coordinating guest molecules and the metal ions simultaneously working as nodes of the frameworks. Further, an unsaturated metal center can also incorporated in the organic linker [30]. The compound $[Zn_2(bpdc)_2L]$ {bpdc = 4,4′-biphenyldicarboxylate; L = (*R*,*R*)-(2)-1,2-cyclohexanediamino-*N*,*N*′-bis[3-*tert*-butyl-5-(4-pyridyl)salicylidene]}, containing chiral salen units, has a grid-type porous framework in which the metal centers of the salen ligand are exposed to the surface of channels [31, 32]. This compound acts as an asymmetric heterogeneous catalyst for alkene epoxidation.

It has been difficult to design very strong Lewis acid sites in the PCP framework via a self-assembly process; however, the high designability of PCPs provides a guideline for multifunctional catalysts. For example, bifunctional-type catalysts such as with acid–base properties for domino reactions and ultra-hydrophobic Lewis acid catalysts are significant targets. On the other hand, incorporation of unsaturated metal centers in porous frameworks can be achieved by applying "post-synthesis" or "grafting" procedures. This is a powerful approach to incorporating functional groups in porous frameworks for catalysis and other functions, and the detailed strategy is described in Chapter 2.

1.2.3
Soft Porous Crystals

In contrast to the robust porous framework, there are studies in which the soft properties of PCPs is evident in terms of structural flexibility and dynamic properties. We can identify compounds showing guest accommodation with reversible nonporous to porous transformations, even if the compound cannot maintain the porous structure in the guest removal process. These compounds are categorized as "soft porous crystals," and are studied owing to their unique properties [33–35]. The adsorption isotherms of this type of compound sometimes cannot be classified according to the conventional IUPAC classification because of the dynamic guest accommodation behavior [36]. For instance, a "gate-type" sorption profile (Figure 1.3) shows no uptake at low concentrations of the guest molecules, and an abrupt increase in adsorption after a threshold concentration. This behavior is associated with a structural transformation from a nonporous to a porous phase and an example is O_2 capture by hemoglobin, which shows gate-opening type sensing and capture of O_2 when the concentration of O_2 reaches a certain level [37]. The softness of the compounds is very sensitive for gas species to be accommodated and often useful for gas separation.

A two-dimensional (2D) layer structure is a typical motif of soft porous crystals showing gate-type sorption behavior because it is readily transformable in response to the guest accommodation [38]. In particular, an interdigitated layer structure is important because we can control interactions between the sheets by modification of the groups to be interdigitated. Several compounds have been reported and each compound shows a characteristic transformation via guest incorporation [39].

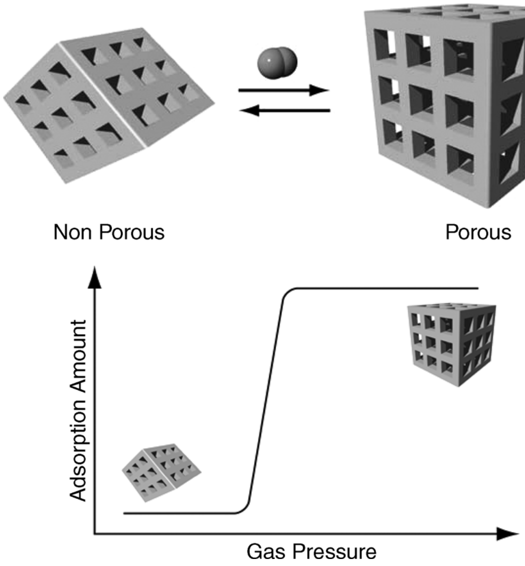

Figure 1.3 Schematic illustration of structure transformation of soft porous crystal. Below is a typical gas adsorption isotherm with gate-opening behavior.

The series of [Zn(dicarboxylate)(bpy)] (CID-1) compounds (CID = coordination polymers with an interdigitated structure; bpy = 4,4′-bipyridyl) provides us with a platform of interdigitated 2D layers [40, 41]. The 2D layer in this series is composed of a V-shaped dicarboxylate, bpy, and dinuclear metal units, and the various dicarboxylate ligands impact on the interaction with the next layers and influences the gate-type sorption behavior. Their flexibility in the layers assists the separation of CO_2 from CH_4–CO_2 gas mixtures and the separately adsorbed CO_2 gas can easily be retrieved with low energy consumption, because we use only structural flexibility to separate the CO_2 without strong interactions. The phenomenon is different from conventional CO_2 separation with strong binding energy.

Even for a 3D porous framework with coordination bonds, some PCPs demonstrates their intrinsic flexibility. [Al(bdc)(OH)] (MIL-53) is a framework containing diamond-shaped 1D channels [42]. One axis is connected by Al–OH–Al chains and the angle of the Al–O–Al bond changes with guest sorption. The softness is derived from the reorientation of the coordination bonds and even with small changes in bond angle/distance, the overall porous structure transforms dramatically. The guest-dependent flexibility in [Al(bdc)(OH)] is applied for the selective sorption of xylene isomers and drug delivery, for example [43, 44].

The flexibility of PCP frameworks is observed both in rearrangements of network topologies and local bond reorientation. Regarding network rearrangement, we have another motif; interpenetration often affords soft properties due to the rearrangement of adjacent networks. [$Zn_2(bdc)_2(bpy)$] (MOF-508), which has square grid 3D networks with twofold interpenetration, can have both a closed form and an open form with change in the relative position of the two networks [45, 46].

The transformation from closed to open form depends on the accessing guests and the behavior can separate linear and branched isomers of pentane and hexane like a gas chromatographic separation column.

This type of flexibility in the PCP frameworks is often dramatic and sensitive for identifying the guest molecules. Their binding ability for functional molecules is studied for application of drug delivery systems and gas separation on an industrial scale and conditions. Further, the dynamic behavior is also significant for the design of multifunctional materials in the next step; guest-recognizing flexible catalysts, guest-sensing dielectric materials, and guest-dependent actuating systems are the candidates selected for future design. Some of the ideas are outlined below.

1.3
Multifunctional Frameworks

The high designability and the variety of combinations of organic linkers and metal ions suggest the possibility of the creation of multifunctional porous frameworks, in which two or more physical/chemical properties are integrated in the crystal. For example, some PCPs have permanent porosity and guest-responsive magnetic activity in the framework and these are potentially unique for switching of magnetic properties by use of guest storage/release. In the last 5 years, many researches have focused on the design of multifunctional characteristics in PCP structures, and in this section we introduce some important ideas for such materials.

1.3.1
Porosity and Magnetism

PCP magnets incorporating magnetic properties in the framework are unique multifunctional materials, particularly as chemo-responsive materials, because of the mutual interplay of porous functions and magnetic switching. Many reports on porous magnets using a PCP framework have appeared; however, there are few examples that show a combination of porous and magnetic functions, because most porous magnets undergo a magnetic transformation at very low temperature (critical temperature, T_c), whereas the adsorptive functions occur at ambient temperature. On the other hand, spin crossover (SC), in which electron configurations can be switched between high- and low-spin states in response to external stimuli, producing changes in magnetism, color, dielectric properties, and structure, is often observed at ambient temperature and we could design a real interplay of SC phenomena and adsorption properties.

A representative PCP that shows coupling properties of SC behavior is {Fe(pyrazine)[$Pt(CN)_4$]} [47]. The 2D layers are extended by Pt–CN–Fe linkages and are linked by pyrazine to form a pillared layer-type compound. This compound displays a first-order spin transition at ambient temperature [T_c (up) = 285 K and T_c (down) = 309 K] with 25 K wide hysteresis. The guest-free form adsorbs various guest molecules and the spin state changes depending on the guests (Figure 1.4). The

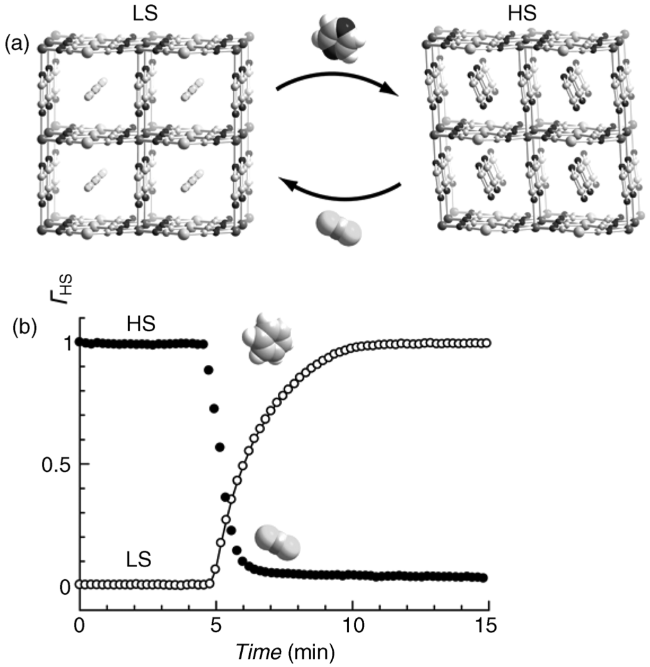

Figure 1.4 (a) Alteration of the porous structure of {Fe(pyrazine)[Pt(CN)$_4$]} by exchange of guest molecules of CS$_2$ and pyrazine. (b) The high-spin (HS) state can be converted to low-spin (LS) state by insertion of CS$_2$ at 298 K. LS to HS conversion can be achieved by accommodation of several guests. Γ_{HS} is the relative existence of the HS state in the system.

reversible conversion of low- and high-spin states is achievable by guest sorption under ambient conditions. The guest-dependent switching of the SC phenomenon is also observed in other compounds [48].

Recently, studies of ion conductivity using a PCP platform by tuning of the pore size and chemical environment have increased. Highly hydrophilic networks with an open structure can store large amounts of H_2O molecules resulting from the proton conductivity at high relative humidity [49–52]. $Co^{II}[Cr^{III}(CN)_6]_{2/3}\cdot 4.8H_2O$ is a Prussian Blue analog and contains water of crystallization molecules that contribute to the proton conductivity [53]. The temperature–conductivity curve has a flexion point at 313 K that corresponds to the magnetic phase transition temperature. This suggests that there is a coupling effect between magnetostriction and ionic conductivity in the structure and a multifunctional effect between the conductivity and magnetism is expected.

Although there have been many attempts to synthesize frameworks that have both porous and magnetic properties, only a limited number showing “real” interplay have been observed because of the temperature gap issue. One answer is a combination of SCs and we expect that the further design of frameworks, with not only micro-scale but especially also meso-scale integration of porous host and magnetic species (network or molecule), would open new methodologies. Partially related approaches are described below.

1.3.2
Porosity and Conductivity/Dielectricity

Incorporation of electric conductivity in the porous materials is widely regarded as a challenging task. A combination of porosity and electric conductivity is applicable for gas sensors, such as electrodes. Only limited numbers of conductive coordination polymers have been reported and the coexistence of permanent porosity is still rare [54]. The compounds $Cu[M(pdt)_2]$ (M = Cu, Ni; pdt = pyrazine-2,3-dithiolate) exhibit electric conductivity [55, 56]. The motif of bisdithiolate complexes is redox-active species, connected by $M(pyrazine)_4$ units to have porous framework with a BET surface area of $385\,m^2\,g^{-1}$ (when M = Ni). Even though the framework of $Cu[Ni(pdt)_2]$ shows low conductivity ($1 \times 10^{-8}\,S\,cm^{-1}$) at room temperature, it increases to $\sim 1 \times 10^{-4}\,S\,cm^{-1}$ on doping with iodine, which act as an oxidant. I_2 vapor is introduced into the framework, resulting in $[Ni(pdt)_2]^{2-/-}$ oxidation.

Multifunction porosity–dielectric properties have also been studied in recent years. For example, $[Mn_3(HCOO)_6](C_2H_5OH)$ having 1D channels occupied by ethanol as guest shows a ferrimagnetic transition at 8.5 K due to the magnetic transition of the Mn^{2+} spin [57]. The dielectric constant of this framework is heavily dependent on the axis of the crystal and the specific axis of the guest ethanol which aligns in parallel has a large constant ($\varepsilon_r = 45$). The temperatures of phase transition and maximum peak dielectric constant are nearly same. Phase transition is attributed to reorientation of the guest molecules and it contributes to the ferroelectricity in the framework. The guest-induced ferroelectricity is unique for porous materials and the interplay between the porosity, magnetism and ferroelectricity, in other words, porous materials with multiferroic behavior, is of great interest for multifunctional porous design [58–61].

1.3.3
Porous Flexibility and Catalysis

As shown above, some PCPs show intrinsic structural flexibility upon guest incorporation and release. This flexibility is one of the unique characteristics among the various porous materials and combination of structural flexibility and catalytic activity is an attractive challenge. As is known, some enzymes show intelligent guest-selective conversion inside the pocket of their structure and the design of such a flexible porous catalyst by use of PCPs is an important aim [62].

There are few examples of PCPs having such catalytic behavior. $\{[Cd(4\text{-btapa})_2(NO_3)_2]\cdot 6H_2O\cdot 2DMF\}$ 4-btapa = 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide] is a flexible PCP having Lewis base catalytic activity [63]. The framework consists of Cd^{2+} and a tridentate pyridyl ligand having amide groups as nodes. The guest-free phase is amorphous and the crystallinity can recover on guest accommodation, especially with small guest molecules such as methanol and ethanol, suggesting their reversible flexibility. The soft compound has amide group-derived Lewis basicity and it promotes Knoevenagel condensation for only small substrates. The compound can activate malononitrile but not ethyl cyanoacetate and cyanoacetic acid *tert*-butyl ester because of the size effect.

1.4
Preparation of Multifunctional Frameworks

Many efforts have been made to create new structures of PCPs with the aid of crystallographic analyses. The number of possible combinations of metal ions and organic ligands is huge and, in principle, the researcher can play the whole field of synthetic chemistry. On the other hand, rather than simple reaction screening of combinations of metal ions and organic ligands, other approaches to designing functional PCPs have been developed in recent years. Some of them are significant for the design of multifunctionality in the framework which is not feasible by simple mixing of metal ions and organic ligands. Especially it has been found that some functions of PCPs originate not only from microscopic structures, but also from more large-scale, so-called meso-domain regions. The functionality of PCPs has been evaluated mainly by the use of bulk solids such as powders and single crystals, and we could expect that the multifunctionality will depend on the method of fabrication. Some of the approaches are introduced below.

1.4.1
Mixed Ligands and Mixed Metals

In principle, PCP frameworks can be constructed from multiple organic ligands and metal ions. However, there are a limited number of reports on frameworks having more than two kinds of ligands or metal ions. Considering that the doping approach has been popular in the area of inorganic materials such as metal oxides and metals, the on-demand doping of metal ions or organic ligands in the PCP frameworks should become another important strategy for multifunctional systems.

Some of the reports about ligand mixing system are outlined here. $[Zn_4O(bdc)_x(abdc)_{3-x}]$ was synthesized, in which the terephthalate linkers are partially substituted by 2-aminobenzene-1,4-dicarboxylate (abdc) [64]. X-ray diffraction revealed the materials to have a random distribution of the two linker molecules according to Vegard's law, as shown schematically in Figure 1.5. The reason for the success of partial ligand doping in $[Zn_4O(bdc)_3]$ is the similar crystal cell parameters of $Zn_4O(bdc)_3$ and $Zn_4O(abdc)_3$, which allows the formation of a grid-type porous framework even with a random distribution of each ligand. The paper also reported the catalytic activity of the mixed-linker compound for formation of propylene carbonate from propylene oxide and CO_2.

The potential of the mixed-ligand approach in the framework of $Zn_4O(L)_3$ ($L =$ terephthalic acid derivatives) was extended by use of a high-throughput technique [65]. In the scaffold of the structure, various terephthalic acid derivatives can be

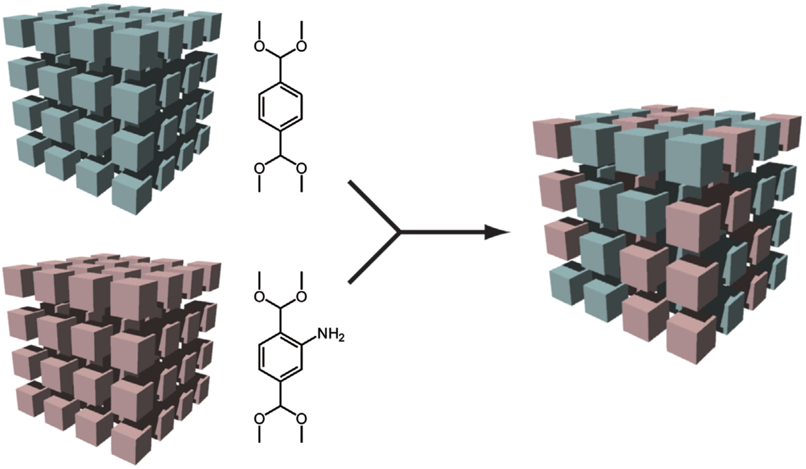

Figure 1.5 Schematic illustration of mixed-ligand structure of $[Zn_4O(bdc)_x(abdc)_{3-x}]$, where bdc = benzenedicarboxylate and abdc = 2-aminobenzenedicarboxylate. Cell parameters are similar with two original structures and each ligand locates randomly in the framework.

incorporated to create a porous structure, and one of them has eight terephthalic acid derivatives in the crystal structure. The distribution of functional groups in the ligands is disordered and the adsorption property of some of the members of this series exhibits up to 400% better selectivity for CO_2 over CO compared with the best same-link counterparts. This also suggests that the matching of the interval of ligands and comparable strengths of coordination bonds are the key to integrating the different ligands in the structure, although each of them has different substituent groups. The reaction conditions should be optimized to synthesize mixed-ligand PCPs and powerful screening with the aid of robots is becoming important.

Not only robust and cubic-type frameworks, but also low-dimensional PCPs with a flexible nature are being developed for mixed-ligand systems [66]. Soft porous coordination polymers with a 2D interdigitated motif $[Zn(5\text{-}NO_2\text{-}ip)(bpy)]$ (CID-5) and [Zn(5-MeO-ip)(bpy)] (CID-6) (ip = isophthalate) are two representatives of soft-type PCP frameworks. CID-5 has high flexibility in the framework and represents a "porous" to "nonporous"-type structure transition, whereas CID-6 has a relatively rigid framework and the crystal structures do not change in desolvated/solvated phases. As synthesized, these compounds have similar cell parameters and they can be mixed with arbitrary ratios of ligand. The series of $[Zn(5\text{-}NO_2\text{-}ip)_{1-x}(5\text{-}MeO\text{-}ip)_x(bpy)]$ compounds have their own cell parameters, which means that each compound has a single phase structure. As shown in Figure 1.6, it can be called a ligand-base solid solution and the flexibility of the structures is controllable by tuning each ligand ratio as confirmed by gas adsorption. Optimization of the flexibility in $[Zn(5\text{-}NO_2\text{-}ip)_{1-x}(5\text{-}MeO\text{-}ip)_x(bpy)]$ results in better performance in CO_2 separation from CH_4 compared with their original frameworks (CID-5 and CID-6). The control of structural flexibility in the PCP has been a major challenge

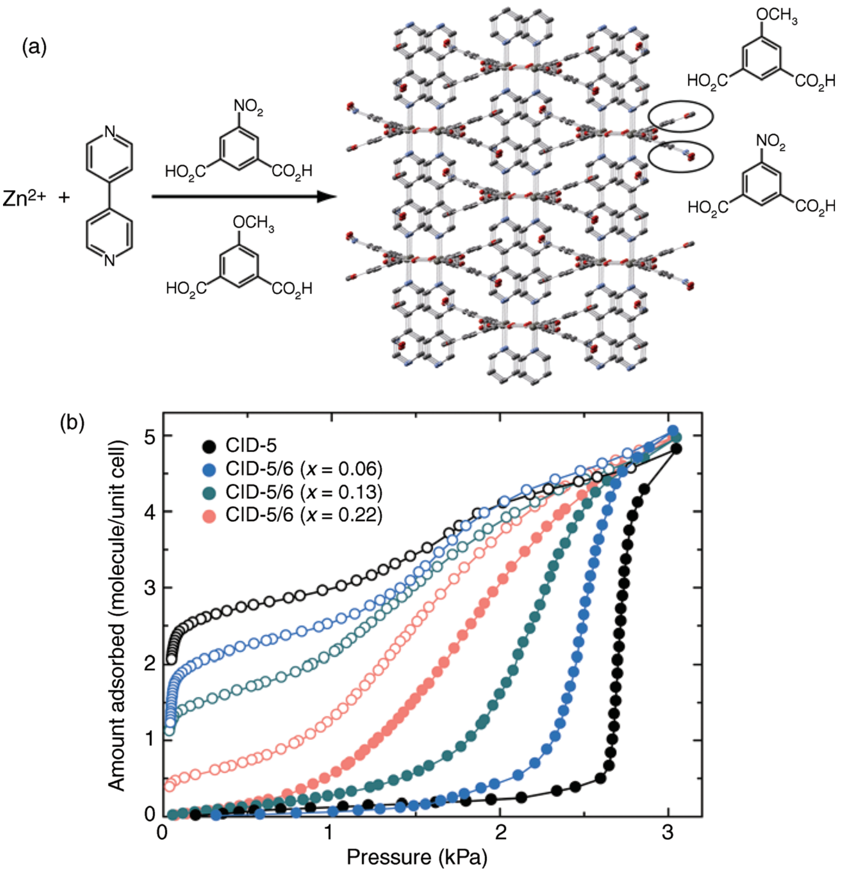

Figure 1.6 (a) Crystal structure of ligand-base solid solution of flexible 2D PCP; $[Zn(5\text{-}NO_2\text{-}ip)_{1-x}(5\text{-}MeO\text{-}ip)_x(bpy)]$ (ip = isophthalate), where x is the ratio of 5-MeO-ip ligand in the framework. (b) Adsorption (closed circles) and desorption (open circles) isotherms of water at 298 K for $[Zn(5\text{-}NO_2\text{-}ip)_{1-x}(5\text{-}MeO\text{-}ip)_x(bpy)]$ with change in x.

because a small difference in flexibility often contributes to the gas separation. The ligand doping approach for soft-type PCPs is a significant approach to regulate the flexibility.

Not only ligand mixing in the single structure, but also mixing of metal species have been reported. Co^{2+} doping to replace Zn^{2+} ions in the framework of $[Zn_4O(bdc)_3]$ has been reported [67]. Co is coordinated to six oxygen atoms in the metallic cluster, two of which belong to diethylformamide molecules. The CoZn-MOF-5 materials prepared have higher adsorption capacities for H_2, CO_2, and CH_4 at high pressure than their Co-free homologs. Other well-known PCPs such as $[Cu_3(btc)_2]$ (HKUST-1) and $[Al(bdc)(OH)]$ (MIL-53) have also been prepared for doping of metal sites and their magnetic behavior and thermal stability have been studied [68, 69].

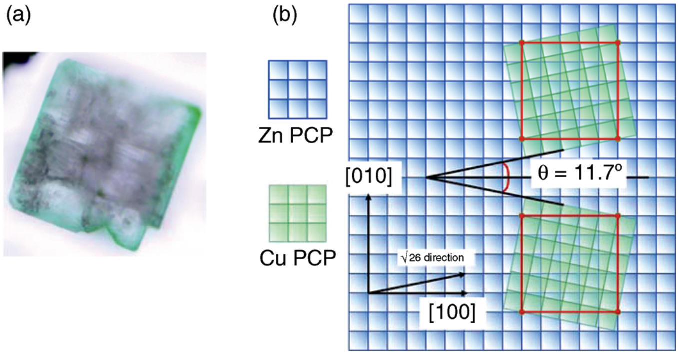

Figure 1.7 (a) Optical microscopic image of the sliced core–shell crystal of $[Zn_2(ndc)_2(dabco)]$ (core) and $[Cu_2(ndc)_2(dabco)]$ (shell) (ndc = 1,4-naphthalenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane). (b) Schematic model of the structural relationship between the core lattice and the shell lattice on the (001) surface. The red lines indicate the commensurate lattice between the core lattice and the shell lattice.

1.4.2
Core–Shell

Incorporation of multiple functions into PCP frameworks has been studied mainly on an atomic scale. The coexistence of different functional groups in the single porous framework described above is an example. In addition to the micrometer-scale integration of different functional moieties, meso-scale combinations of multiple distinct functional PCP frameworks are also of interest for the preparation of multifunctional frameworks.

The core–shell system of PCPs is a candidate for this purpose. Ideally, the epitaxial growth-type core–shell PCP would have multiple functions contributed by the core PCP and shell PCP. Like the core–shell crystal of different metals, some PCPs with an epitaxial core–shell structure have been fabricated. A series of tetragonal frameworks $[M_2(dicarboxylate)_2(N\text{-}ligand)]$, in which dicarboxylate layers link to dimetal clusters to form 2D square lattices, which are connected by dinitrogen pillar ligands to the lattice, have been employed for core–shell fabrication [70]. Step-by-step solvothermal reaction of $[Zn_2(ndc)_2(dabco)]$ and $[Cu_2(ndc)_2(dabco)]$ (ndc = 1,4-naphthalenedicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane) affords clear core (Zn)–shell (Cu) crystals (Figure 1.7). The 3D configuration was determined by confocal laser scanning microscopy, which showed that the crystals have an anisotoropic configuration; for instance, only four surfaces of the core crystal are covered by the shell crystal. $[Zn_4O(dicarboxylate)_3]$-type frameworks are also a good platform to prepare the core–shell-type framework [71, 72]. Two cubic frameworks constructed from the ligands bdc (MOF-5) and 2-NH_2-bdc (IRMOF-3) can be crystallized with a core–shell system by a stepwise solvothermal reaction. Although some reports do not discuss cell parameter matching between the core crystal and shell crystal, a multilayered crystal which is interesting for integration of multiple functions in crystals with hetero-junctions has been demonstrated.

Guests such as gases and organic substrates access from the outer surface of PCP crystals and the structural characteristics of the core–shell would control the stepwise adsorptive functions. For instance, integration of a shell crystal having a selective guest sorption ability and a core crystal having catalytic activity make selective conversion of guest molecules possible. Regarding the diffusion of the guest for conversion, the core–shell would have a better diffusion performance for the substrate than a pure selective PCP catalyst and the core–shell system is important for multifunctional PCPs in the sense of time-dependent functions.

1.4.3
PCPs and Nanoparticles

Mutual hybridization of PCP compounds and other solid materials is of interest for complementary multifunctions. The advantages of PCP frameworks again are a high surface area with ordering and there have been several studies on preparation of hybrids of PCPs and nanoparticles which are dispersed inside the porous framework. Introducing metal precursors into the porous framework is mainly executed by chemical vapor deposition (CVD) or immersion methods and additional reduction or hydrogenation of the precursors generates the metal nanoparticles in the PCP framework [73, 74]. The size of the particles depends on the combination of PCPs and method of fabrication of particles, and some studies have reported highly dispersed nanoparticles with retention of the porous structure.

$[Cu_2(BTC)_{4/3}]_6[HnXM_{12}O_{40}]\cdot(C_4H_{12}N)_2$ (X = Si, Ge, P, As; M = W, Mo) is a framework in which the various Keggin polyoxometalates are uniformly incorporated in the nanochannels of HKUST-1 (Figure 1.8) [75]. The size of the polyoxometalate is well

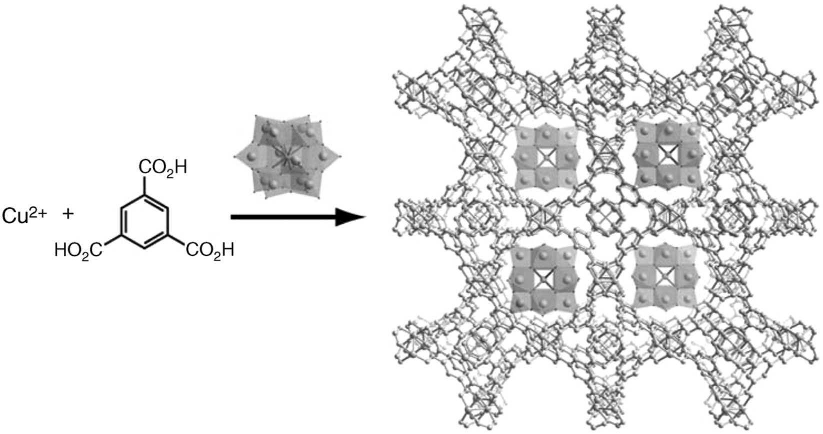

Figure 1.8 Reaction scheme and crystal structure of $[Cu_3(btc)_2]$ (HKUST-1) (btc = benzenetricarboxylate) with Keggin polyoxometalates. Polyoxometalates locate in the pocket of cavities alternately.

fitted to the diameter of the pores and they are distributed with sufficient porosity remaining inside. It has acid catalytic activity for the hydrolysis of esters in excess water and the uniform pores of the hybrid allow only small substrates for the catalytic reaction. This is a notable example of the integration of two different solids, one being the PCP framework.

A further example is the hybridization of a PCP and ammonia borane (AB) (borazane; NH_3BH_3) for the preparation of hydrogen storage materials under moderate conditions [76]. Some of technical challenges with pure AB are a high dehydrogenation temperature and formation of volatile byproducts. [Y(btc)] (JUC-32-Y) was employed to accommodate the AB particles and a simple infusion method gives a uniform hybrid of PCP and AB. The material can release hydrogen even at a low temperature of 85 °C and the AB inside could release 8.0 wt% hydrogen within 10 min. The unsaturated metal Y^{3+} sites of JUC-32-Y interact with AB to prevent the formation of ammonia. The hybridization gives a real synergetic effect of both PCP and AB and the approach would be very suitable for the preparation of other functional particles.

1.5
Perspectives

Since the discovery of the permanent porosity of PCPs/MOFs, confirmed by gas adsorption experiments in the late 1990s, the design of crystal structures has developed extensively. Owing to the huge efforts at synthesis, some conventional functions as adsorbents such as for gas storage and separation have reached a high level even in comparison with other well-known porous materials. However, achieving higher performance and accompanying higher stability and easier handling technique are still needed.

If we take full advantage of the designability of PCPs, we could go further in the design of frameworks as novel functional porous solids. One aspect is multifunctionality in porous structures. The multifunction here ideally is not the independent coexistence of different functions in one framework, but cooperative behavior of multiple chemical/physical properties. For instance, porosity and magnetism or catalysis and flexibility should be closely related each other and the system of interplay in the structure is a significant target. The last decade has mainly focused on the design of frameworks at the atomic scale, in other words, the design of components such as metal clusters and functional organic ligands to create versatile porous frameworks. Together with this approach, the control of integration of the functions of PCPs or with other materials at the meso-scale is also becoming important, and related advanced characterization techniques such as electron microscopy, tomography, and the quartz crystal microbalance [77, 78], and simultaneous *in situ* adsorption measurements to evaluate the porous characteristics, are also significant [79].

We believe that the established multifunctional PCPs would not necessarily be used in large-scale processes in conventional industry. They can be regarded as functional host solids which can open up future application fields such as biosensors, actuators, gas/ion transporters, and continuing efforts to achieve real hybridization of multiple functions and control of material morphology are strongly required.

References

1 Shibata, Y. (1916) *J. Coll. Sci. Imp. Univ. Tokyo*, **37**, 1–31.

2 Keggin, J.F. and Miles, F.D. (1936) *Nature*, **137**, 577–578.

3 Hofmann, K.A. and Küspert, F.A. (1897) *Z. Anorg. Allg. Chem.*, **15**, 204.

4 Powell, H.M. and Rayner, J.H. (1949) *Nature*, **163**, 566–567.

5 Iwamoto, T., Miyoshi, T., Miyamoto, T., Sasaki, Y., and Fujiwara, S. (1967) *Bull. Chem. Soc. Jpn.*, **40**, 1174–1178.

6 Kinoshita, Y., Matsubara, I., Higuchi, T., and Saito, Y. (1959) *Bull. Chem. Soc. Jpn.*, **32**, 1221–1226.

7 Yaghi, O.M., Li, G.M., and Li, H.L. (1995) *Nature*, **378**, 703–706.

8 Kondo, M., Yoshitomi, T., Seki, K., Matsuzaka, H., and Kitagawa, S. (1997) *Angew. Chem. Int. Ed.*, **36**, 1725–1727.

9 Li, H., Eddaoudi, M., Groy, T.L., and Yaghi, O.M. (1998) *J. Am. Chem. Soc.*, **120**, 8571–8572.

10 Li, H., Eddaoudi, M., O'Keeffe, M., and Yaghi, O.M. (1999) *Nature*, **402**, 276–279.

11 Kaye, S.S., Dailly, A., Yaghi, O.M., and Long, J.R. (2007) *J. Am. Chem. Soc.*, **129**, 14176–14177.

12 Chae, H.K., Siberio-Perez, D.Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A.J., O'Keeffe, M., and Yaghi, O.M. (2004) *Nature*, **427**, 523–527.

13 Furukawa, H., Ko, N., Go, Y.B., Aratani, N., Choi, S.B., Choi, E., Yazaydin, A.O., Snurr, R.Q., O'Keeffe, M., Kim, J., and Yaghi, O.M. (2010) *Science*, **329**, 424–428.

14 Koh, K., Wong-Foy, A.G., and Matzger, A.J. (2009) *J. Am. Chem. Soc.*, **131**, 4184–4185.

15 Férey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surble, S., and Margiolaki, I. (2005) *Science*, **309**, 2040–2042.

16 Hong, D.Y., Hwang, Y.K., Serre, C., Férey, G., and Chang, J.S. (2009) *Adv. Funct. Mater.*, **19**, 1537–1552.

17 Zhao, D., Yuan, D.Q., Sun, D.F., and Zhou, H.C. (2009) *J. Am. Chem. Soc.*, **131**, 9186–9187.

18 Chui, S.S.Y., Lo, S.M.F., Charmant, J.P.H., Orpen, A.G., and Williams, I.D. (1999) *Science*, **283**, 1148–1150.

19 Schlichte, K., Kratzke, T., and Kaskel, S. (2004) *Micropor. Mesopor. Mater.*, **73**, 81–88.

20 Alaerts, L., Seguin, E., Poelman, H., Thibault-Starzyk, F., Jacobs, P.A., and De Vos, D.E. (2006) *Chem. Eur. J.*, **12**, 7353–7363.

21 Kramer, M., Ulrich, S.B., and Kaskel, S. (2006) *J. Mater. Chem.*, **16**, 2245–2248.

22 Xie, L.H., Liu, S.X., Gao, C.Y., Cao, R.G., Cao, J.F., Sun, C.Y., and Su, Z.M. (2007) *Inorg. Chem.*, **46**, 7782–7788.

23 Murray, L.J., Dinca, M., Yano, J., Chavan, S., Bordiga, S., Brown, C.M., and Long, J.R. (2010) *J. Am. Chem. Soc.*, **132**, 7856–7857.

24 Dietzel, P.D.C., Morita, Y., Blom, R., and Fjellvag, H. (2005) *Angew. Chem. Int. Ed.*, **44**, 6354–6358.

25 Rowsell, J.L.C. and Yaghi, O.M. (2006) *J. Am. Chem. Soc.*, **128**, 1304–1315.

26 Caskey, S.R., Wong-Foy, A.G., and Matzger, A.J. (2008) *J. Am. Chem. Soc.*, **130**, 10870–10871.

27 McKinlay, A.C., Xiao, B., Wragg, D.S., Wheatley, P.S., Megson, I.L., and Morris, R.E. (2008) *J. Am. Chem. Soc.*, **130**, 10440–10444.

28 Henschel, A., Gedrich, K., Kraehnert, R., and Kaskel, S. (2008) *Chem. Commun.*, 4192–4194.

29 Kim, J., Bhattacharjee, S., Jeong, K.E., Jeong, S.Y., and Ahn, W.S. (2009) *Chem. Commun.*, 3904–3906.

30 Kitaura, R., Onoyama, G., Sakamoto, H., Matsuda, R., Noro, S., and Kitagawa, S. (2004) *Angew. Chem. Int. Ed.*, **43**, 2684–2687.

31 Cho, S.H., Ma, B.Q., Nguyen, S.T., Hupp, J.T., and Albrecht-Schmitt, T.E. (2006) *Chem. Commun.*, 2563–2565.

32 Lee, J., Farha, O.K., Roberts, J., Scheidt, K.A., Nguyen, S.T., and Hupp, J.T. (2009) *Chem. Soc. Rev.*, **38**, 1450–1459.

33 Fletcher, A.J., Thomas, K.M., and Rosseinsky, M.J. (2005) *J. Solid State Chem.*, **178**, 2491–2510.

34 Kitagawa, S. and Uemura, K. (2005) *Chem. Soc. Rev.*, **34**, 109–119.

35 Horike, S., Shimomura, S., and Kitagawa, S. (2009) *Nat. Chem.*, **1**, 695–704.

36 Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., and Siemieniewska, T. (1985) *Pure Appl. Chem.*, **57**, 603–619.

37 Li, G.Q. and Govind, R. (1994) *Ind. Eng. Chem. Res.*, **33**, 755–783.

38 Li, D. and Kaneko, K. (2001) *Chem. Phys. Lett.*, **335**, 50–56.

39 Kitaura, R., Seki, K., Akiyama, G., and Kitagawa, S. (2003) *Angew. Chem. Int. Ed.*, **42**, 428–431.

40 Horike, S., Tanaka, D., Nakagawa, K., and Kitagawa, S. (2007) *Chem. Commun.*, 3395–3397.

41 Nakagawa, K., Tanaka, D., Horike, S., Shimomura, S., Higuchi, M., and Kitagawa, S. (2010) *Chem. Commun.*, **46**, 4258–4260.

42 Loiseau, T., Serre, C., Huguenard, C., Fink, G., Taulelle, F., Henry, M., Bataille, T., and Férey, G. (2004) *Chem. Eur. J.*, **10**, 1373–1382.

43 Horcajada, P., Serre, C., Maurin, G., Ramsahye, N.A., Balas, F., Vallet-Regi, M., Sebban, M., Taulelle, F., and Férey, G. (2008) *J. Am. Chem. Soc.*, **130**, 6774–6780.

44 Finsy, V., Kirschhock, C.E.A., Vedts, G., Maes, M., Alaerts, L., De Vos, D.E., Baron, G.V., and Denayer, J.F.M. (2009) *Chem. Eur. J.*, **15**, 7724–7731.

45 Chen, B.L., Liang, C.D., Yang, J., Contreras, D.S., Clancy, Y.L., Lobkovsky, E.B., Yaghi, O.M., and Dai, S. (2006) *Angew. Chem. Int. Ed.*, **45**, 1390–1393.

46 Barcia, P.S., Zapata, F., Silva, J.A.C., Rodrigues, A.E., and Chen, B.L. (2007) *J. Phys. Chem. B*, **111**, 6101–6103.

47 Ohba, M., Yoneda, K., Agusti, G., Munoz, M.C., Gaspar, A.B., Real, J.A., Yamasaki, M., Ando, H., Nakao, Y., Sakaki, S., and Kitagawa, S. (2009) *Angew. Chem. Int. Ed.*, **48**, 4767–4771.

48 Southon, P.D., Liu, L., Fellows, E.A., Price, D.J., Halder, G.J., Chapman, K.W., Moubaraki, B., Murray, K.S., Letard, J.F., and Kepert, C.J. (2009) *J. Am. Chem. Soc.*, **131**, 10998–11009.

49 Nagao, Y., Fujishima, M., Ikeda, R., Kanda, S., and Kitagawa, H. (2003) *Synth. Met.*, **133**, 431–432.

50 Yamada, T., Sadakiyo, M., and Kitagawa, H. (2009) *J. Am. Chem. Soc.*, **131**, 3144–3145.

51 Bureekaew, S., Horike, S., Higuchi, M., Mizuno, M., Kawamura, T., Tanaka, D., Yanai, N., and Kitagawa, S. (2009) *Nat. Mater.*, **8**, 831–836.

52 Hurd, J.A., Vaidhyanathan, R., Thangadurai, V., Ratcliffe, C.I., Moudrakovski, I.L., and Shimizu, G.K.H. (2009) *Nat. Chem.*, **1**, 705–710.

53 Ohkoshi, S., Nakagawa, K., Tomono, K., Imoto, K., Tsunobuchi, Y., and Tokoro, H. (2010) *J. Am. Chem. Soc.*, **132**, 6620–6621.

54 Fuma, Y., Ebihara, M., Kutsumizu, S., and Kawamura, T. (2004) *J. Am. Chem. Soc.*, **126**, 12238–12239.

55 Takaishi, S., Hosoda, M., Kajiwara, T., Miyasaka, H., Yamashita, M., Nakanishi, Y., Kitagawa, Y., Yamaguchi, K., Kobayashi, A., and Kitagawa, H. (2009) *Inorg. Chem.*, **48**, 9048–9050.

56 Kobayashi, Y., Jacobs, B., Allendorf, M.D., and Long, J.R. (2010) *Chem. Mater.*, **22**, 4120–4122.

57 Cui, H.B., Wang, Z.M., Takahashi, K., Okano, Y., Kobayashi, H., and Kobayashi, A. (2006) *J. Am. Chem. Soc.*, **128**, 15074–15075.

58 Cui, H., Zhou, B., Long, L.S., Okano, Y., Kobayashi, H., and Kobayashi, A. (2008) *Angew. Chem. Int. Ed.*, **47**, 3376–3380.

59 Jain, P., Dalal, N.S., Toby, B.H., Kroto, H.W., and Cheetham, A.K. (2008) *J. Am. Chem. Soc.*, **130**, 10450–10451.

60 Jain, P., Ramachandran, V., Clark, R.J., Zhou, H.D., Toby, B.H., Dalal, N.S., Kroto, H.W., and Cheetham, A.K. (2009) *J. Am. Chem. Soc.*, **131**, 13625–13626.

61 Ye, H.Y., Fu, D.W., Zhang, Y., Zhang, W., Xiong, R.G., and Huang, S.D. (2009) *J. Am. Chem. Soc.*, **131**, 42–43.

62 Farrusseng, D., Aguado, S., and Pinel, C. (2009) *Angew. Chem. Int. Ed.*, **48**, 7502–7513.

63 Hasegawa, S., Horike, S., Matsuda, R., Furukawa, S., Mochizuki, K., Kinoshita, Y., and Kitagawa, S. (2007) *J. Am. Chem. Soc.*, **129**, 2607–2614.

64 Kleist, W., Jutz, F., Maciejewski, M., and Baiker, A. (2009) *Eur. J. Inorg. Chem.*, (24), 3552–3561.

65 Deng, H.X., Doonan, C.J., Furukawa, H., Ferreira, R.B., Towne, J., Knobler, C.B., Wang, B., and Yaghi, O.M. (2010) *Science*, **327**, 846–850.

66 Fukushima, T., Horike, S., Inubushi, Y., Nakagawa, K., Kubota, Y., Takata, M., and Kitagawa, S. (2010) *Angew. Chem. Int. Ed.*, **49**, 4820–4824.

67 Botas, J.A., Calleja, G., Sanchez-Sanchez, M., and Orcajo, M.G. (2010) *Langmuir*, **26**, 5300–5303.

68 Jee, B., Eisinger, K., Gul-E-Noor, F., Bertmer, M., Hartmann, M., Himsl, D., and Poppl, A. (2010) *J. Phys. Chem. C*, **114**, 16630–16639.

69 Marx, S., Kleist, W., Huang, J., Maciejewski, M., and Baiker, A. (2010) *Dalton Trans.*, 3795–3798.

70 Furukawa, S., Hirai, K., Nakagawa, K., Takashima, Y., Matsuda, R., Tsuruoka, T., Kondo, M., Haruki, R., Tanaka, D., Sakamoto, H., Shimomura, S., Sakata, O., and Kitagawa, S. (2009) *Angew. Chem. Int. Ed.*, **48**, 1766–1770.

71 Koh, K., Wong-Foy, A.G., and Matzger, A.J. (2009) *Chem. Commun.*, 6162–6164.

72 Yoo, Y. and Jeong, H.K. (2010) *Cryst. Growth Des.*, **10**, 1283–1288.

73 Hermes, S., Schroter, M.K., Schmid, R., Khodeir, L., Muhler, M., Tissler, A., Fischer, R.W., and Fischer, R.A. (2005) *Angew. Chem. Int. Ed.*, **44**, 6237–6241.

74 Sabo, M., Henschel, A., Froede, H., Klemm, E., and Kaskel, S. (2007) *J. Mater. Chem.*, **17**, 3827–3832.

75 Sun, C.Y., Liu, S.X., Liang, D.D., Shao, K.Z., Ren, Y.H., and Su, Z.M. (2009) *J. Am. Chem. Soc.*, **131**, 1883–1888.

76 Li, Z.Y., Zhu, G.S., Lu, G.Q., Qiu, S.L., and Yao, X.D. (2010) *J. Am. Chem. Soc.*, **132**, 1490–1491.

77 Turner, S., Lebedev, O.I., Schroder, F., Esken, D., Fischer, R.A., and Van Tendeloo, G. (2008) *Chem. Mater.*, **20**, 5622–5627.

78 Biemmi, E., Darga, A., Stock, N., and Bein, T. (2008) *Micropor. Mesopor. Mater.*, **114**, 380–386.

79 Seo, J., Matsuda, R., Sakamoto, H., Bonneau, C., and Kitagawa, S. (2009) *J. Am. Chem. Soc.*, **131**, 12792–12800.