Pore Space Partition in Metal−Organic Frameworks

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CONSPECTUS: Metal−organic framework (MOF) materials have emerged as one of the favorite crystalline porous materials (CPM) because of their compositional and geometric tunability and many possible applications. In efforts to develop better MOFs for gas storage and separation, a number of strategies including creation of open metal sites and implantation of Lewis base sites have been used to tune host−guest interactions. In addition to these chemical factors, the geometric features such as pore size and shape, surface area, and pore volume also play important roles in sorption energetics and uptake capacity. For efficient capture of small gas molecules such as carbon dioxide under ambient conditions, large surface area or high pore volume are often not needed. Instead, maximizing host−guest interactions or the density of binding sites by encaging gas molecules in snug pockets of pore space can be a fruitful approach. To put this concept into practice, the pore space partition (PSP) concept has been proposed and has achieved a great experimental success. In this account, we will highlight many efforts to implement PSP in MOFs and impact of PSP on gas uptake performance.

In the synthetic design of PSP, it is helpful to distinguish between factors that contribute to the framework formation and factors that serve the purpose of PSP. Because of the need for complementary structural roles, the synthesis of MOFs with PSP often involves multicomponent systems including mixed ligands, mixed inorganic nodes, or both. It is possible to accomplish both framework formation and PSP with a single type of polyfunctional ligands that use some functional groups (called framework-forming group) for framework formation and the remaining functional groups (called pore-partition group) for PSP. Alternatively, framework formation and PSP can be shouldered by different chemical species. For example, in a mixed-ligand system, one ligand (called framework-forming agent) can play the role of the framework formation while the other type of ligand (called pore-partition agent) can assume the role of PSP.

PSP is sensitive to the types of inorganic secondary building units (SBUs). The coexistence of SBUs complementary in charge, connectivity, and so on can promote PSP. The use of heterometallic systems can promote the diversity of SBUs coexistent under a given condition. Heterometallic system with metal ions of different oxidation states also provides the charge tunability of SBUs and the overall framework, providing an additional level of control in self-assembly and ultimately in the materials' properties. Of particular interest is the PSP in MIL-88 type (*acs-type topology*) structure, which has led to a huge family of CPMs (called *pacs* CPMs, *pacs* = partitioned *acs*) exhibiting low isosteric heat of adsorption and yet superior CO_2 uptake capacity.
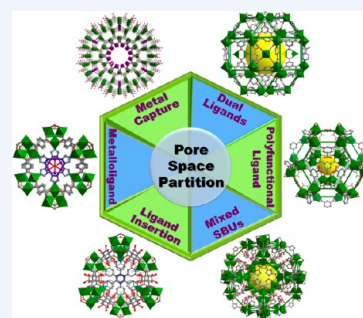
1. INTRODUCTION

Metal−organic frameworks (MOFs) are a class of crystalline porous materials (CPMs) and have attracted much attention owing to their potential applications such as gas storage and separation, catalysis, and drug delivery.[1] MOFs are constructed from metal ions or clusters and organic ligands to form extended systems.[2,3] Because a prominent application of CPMs is in catalysis for which the large pore size is often beneficial, there has been a strong interest in developing CPMs with large pore size and high surface area. However, a separate and opposite trend toward small pore size is taking shape, because studies have shown that large pore size, high surface area, or high pore volume

are not necessarily advantageous for applications involving small gas molecules, especially under ambient conditions.

Targeting efficient capture of small gas molecules such as H_2 and CO_2 at ambient conditions, we have developed multiple strategies including the use of lightweight elements (Li, B, and Mg), implantation of high-density open nitrogen-donor sites, and creation of charged frameworks.[4−9] We further observed that tuning of host−guest interactions and density of binding sites by encaging gas molecules in small pockets of pore space is a fruitful

approach. To put this concept into practice, we proposed a pore space partition (PSP) concept and reported a number of strategies. In this account, we will survey the development of PSP in MOFs.

PSP refers to the division of large cage or channel space into smaller segments with the aim to increase the density of binding sites and tune host−guest interactions. PSP can have many other effects. For example, it can significantly enhance the framework stability.

In some cases, nonpartitioned frameworks can also be synthesized, allowing comparison of properties before and after PSP. In other cases, corresponding nonpartitioned frameworks have not been synthesized or may be too unstable to be synthesized. This does not diminish the importance of PSP. On the contrary, it highlights one powerful aspect of PSP: the ability to stabilize and create new materials that would otherwise not exist. In addition to guide synthesis, PSP can serve as a structure analysis tool. This manner of use is important in the materials design because it could provide feedback to future synthesis cycles.

PSP can take different forms, including framework interpenetration. In this case, there is no difference between framework-forming agents and pore-partition agents, and they are in fact interchangeable. Interpenetration has been well reviewed and will not be discussed here.[10]

Porous materials are generally associated with extra-framework species. They are an integral part for charged frameworks, but may be removed in neutral frameworks. Properly designed PSP using the size and shape of guest species could allow for more efficient use of pore space to enhance storage properties for small gas molecules. For charged frameworks, inorganic or organic ions with hydrophilic surface tend to stay near the framework without the PSP effect, whereas organic ions with hydrophobic surface are more likely located at the pore center with possible PSP effect.[11]

PSP was initially proposed in an effort to rationalize the effect of extra-framework species on gas sorption properties of a family of anionic (3,4)-connected frameworks (denoted here as CPM-1) constructed from 1,3,5-benzenetricarboxylate (BTC) and $[In(COO)_4]$.[11] CPM-1 can be made with different organic cations as charge-balancing species (Figure 1). Small cations are disordered in the large cage, but larger cations are ordered. When the pore is occupied with choline cations, the CO_2 and H_2 uptakes reach 70.6 cm^3 g^{-1} (273 K) and 151.1 cm^3 g^{-1} (77 K) at 1
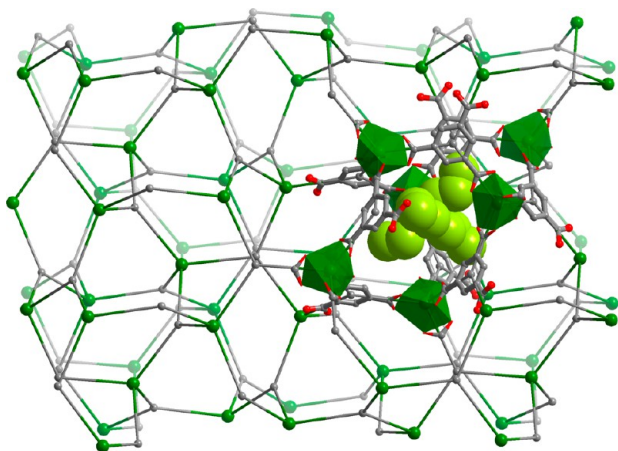

Figure 1. C$_3$N$_4$-type framework of CPM-1 showing guest species.

atm, respectively. It was suggested that organic cations may act as pore partition agent to tune the porosity of CPM-1 and modify its gas uptake performance. Several other studies demonstrated similar effects.[12−14]

2. PSP IN CAGE-TYPE MOFs

2.1. Polyfunctional Ligand Strategy

As mentioned above, CPM-1 could be synthesized with organic cations of different size, the smallest being choline. Our further studies in this indium-BTC system with DMF-water as solvent led to a transition from CPM-1 to CPM-5. It appears that there is a threshold for the size of organic cations at which a transition from CPM-1 to CPM-5 occurs. Specifically, $[NH_2(CH_3)_2]^+$ leads to CPM-5, while choline, $[N(CH_3)_3(CH_2CH_2OH)]^+$, was the smallest known cation capable of propping up CPM-1.

The most fascinating feature of CPM-5 is the encapsulation of a small Archimedean cage (In$_{12}$ tetrahedral cage) inside a large Archimedean cage (In$_{24}$ sodalite cage).[15] As depicted in Figure 2,
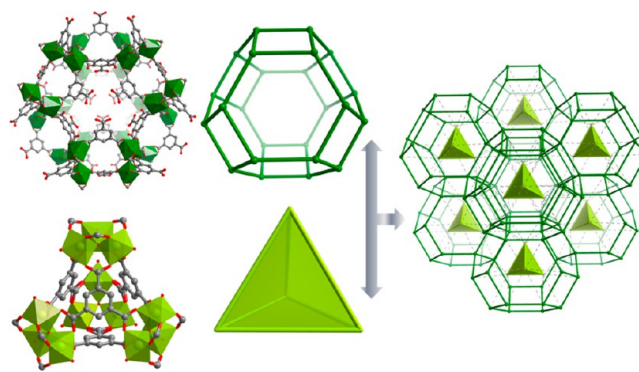

Figure 2. In$_{24}$ cage from $[In(COO)_4]$ monomer, In$_{12}$ cage from $[In_3O(COO)_6]$ trimer, and 3D In$_{12}$@In$_{24}$ cage-within-cage structure of CPM-5.

two adjacent In^{3+} sites on the In$_{24}$ cage are bridged by BTC using two carboxylate groups, forming a sodalite cage. The third carboxylate group interconnects the outer In$_{24}$ cage with the inner In$_{12}$ cage. The In$_{12}$ cage is built from four $[In_3O(COO)_6]$ trimers and four BTCs to form a truncated tetrahedron. The outer cage made from $[In(COO)_4]^-$ is negatively charged whereas the inner cage made from trimeric $[In_3O(COO)_6]^+$ is positively charged, leading to an electric field within the shell region between In$_{24}$ and In$_{12}$ cages.

It is clear that nonsymmetric bonding by symmetric BTC ligand is important for forming CPM-5. Such nonsymmetric bonding is helped by the coexistence of different SBUs (monomer and trimer). To bolster the probability for nonsymmetric bonding by diversifying SBUs, we explored heterometallic systems. As a result, the simultaneous formation of zeolite frameworks and covalent attachment of metal clusters are accomplished to give CPM-15-M (M = Mg, Mn, Co, Ni, Cd) (Figure 3).[16] CPM-15 can be regarded as defect CPM-5 with 50% of sodalite cages containing no BTC ligands inside. Such cages contain four pendant $[M_3(OH)]$ trimers tetrahedrally arranged inside.

2.2. Mixed Ligand Strategy

To form a cage-within-cage structure, it is helpful to develop a mechanism for establishing intercage communication. The initially formed cage must be able to communicate its features to dictate the growth of either inner or outer cage. The
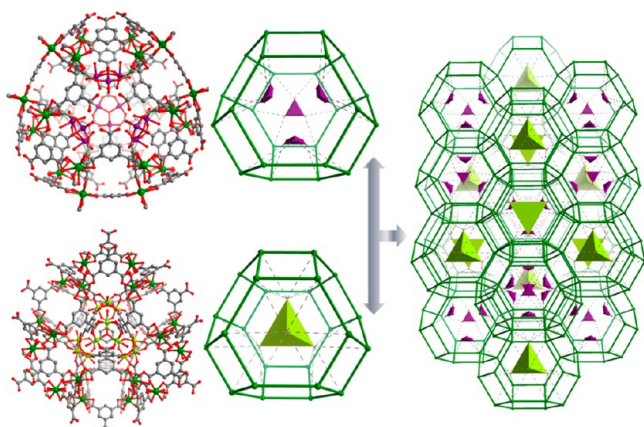
Figure 3. Sodalite cage containing four $[M_3(OH)]$ trimers and the sodalite cage with one supertetrahedron, and 3D packing of two kinds of sodalite cages in CPM-15.

combination of tritopic BTC and linear isonicotinic acid (IN) ligands led to CPM-24 (Figure 4).[17] CPM-24 has two kinds of
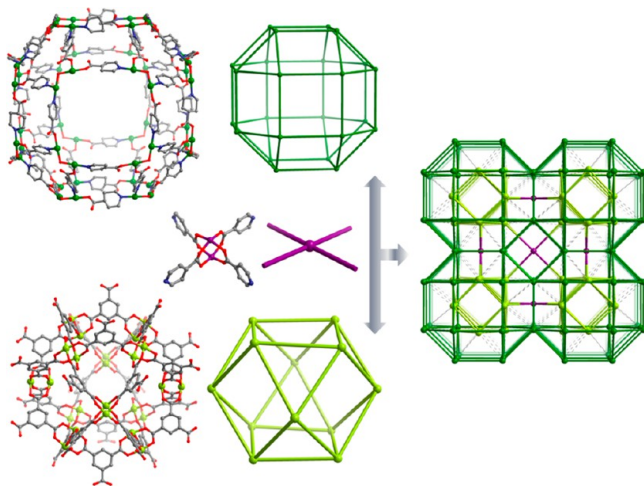

Figure 4. Co_{48} cage from IN, 4-connected paddlewheel units from IN, Co_{24} cage from BTC, and 3D cage-within-cage framework of CPM-24.

cobalt dimers (paddlewheel $[Co_2(CO_2)_4]$ and V-shaped $[Co_2(OH)]$), in contrast with monomeric $[In(CO_2)_4]$ and trimeric $[In_3O(CO_2)_6]$ in CPM-5. CPM-24 also differs from CPM-5 because it requires cooperation of two types of linkers (BTC and IN), whereas CPM-5 depends on cooperation of three functional groups on BTC.

Most important is the difference in intercage communication mechanism. In CPM-5, the third carboxylate group (the "hook" that joins together inner and outer cages) converges from the outer cage toward the inner cage. Quite oppositely, in CPM-24, 24 hooks radiate from the inner cage toward the 24 vertices of the outer cage. It is clear that mechanistically these 24 hooks define the positions of $[Co_2(OH)]$ dimers that form the vertices of the outer cage.

Other groups found more examples of cage-within-cage configurations including a molecular complex formed from bispyridinyl ligand and Pd^{2+}.[18] The combination of 2,4,6-tri(4-pyridyl)-1,3,5-triazine (TPT) and a tritopic carboxylate (TCMM, 2,4,6-tris[1-(3- carboxylphenoxy)ylmethyl]-mesitylene) led to another cage-within-cage MOF.[19]

2.3. Roles of Inorganic SBUs

A common feature between CPM-5 and CPM-24 is the coexistence of different SBUs, suggesting that having different SBUs helps PSP. The PSP mechanism in CPM-5 and CPM-24 depends on trifunctional BTC. Given the prevalence of dicarboxylates, PSP could be more impactful if it also works with dicarboxylates. In section 4, PSP in MIL-88 type is discussed. Here, CPM-7 based on 2,5-furandicarboxylate (FDA) is discussed, and it is another example that highlights the importance of the coexistence of different SBUs (Figure 5).[20] In
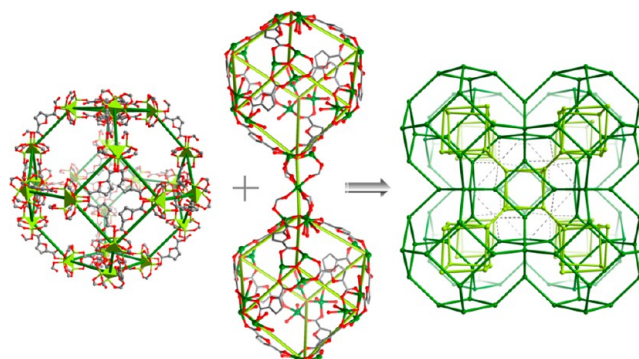

Figure 5. Sodalite cage from $[Zn_4O]$ tetramers, ACO type framework from $[Zn_3(OH)]$ trimers, and 3D $Zn_{24}@Zn_{104}$ framework of CPM-7.

fact, CPM-7 has three types of SBUs: $[Zn_4O]$ tetramer, $[Zn_3(OH)]$ trimer, and Zn^{2+} monomer, each of which plays a unique role. $[Zn_4O]$ tetramer and FDA form a sodalite cage which houses a cube formed from $[Zn_3(OH)]$ trimers and FDAs. The monomeric Zn^{2+} at the 6-ring face center of the sodalite cage allows cube-to-sodalite intercage connection, leading to a $Zn_{24}@Zn_{104}$ cage-within-cage architecture.

Other research groups found additional examples. For example, the coexistence of paddle-wheel $[Cu_2(COO)_4]$ and trimeric $[Cu_3(CN)(COO)_3]$ produces a cage-within-cage MOF.[21]

3. PSP IN CHANNEL-TYPE MOFs

3.1. Secondary Metal Insertion Strategy

We have shown that BTC can use two of its functional groups as framework-forming group and the remaining one as pore-partition group (Figure 6). We further found that depending on
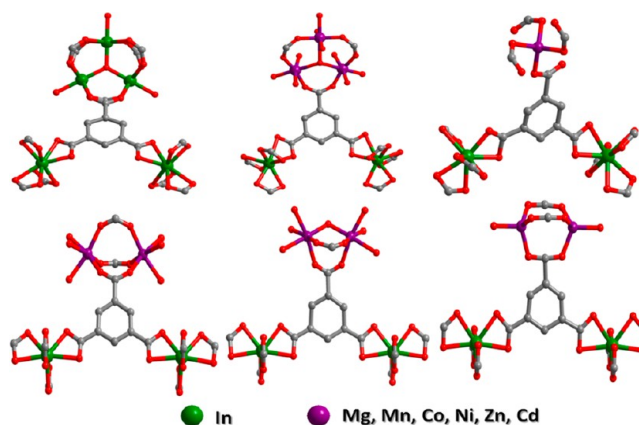

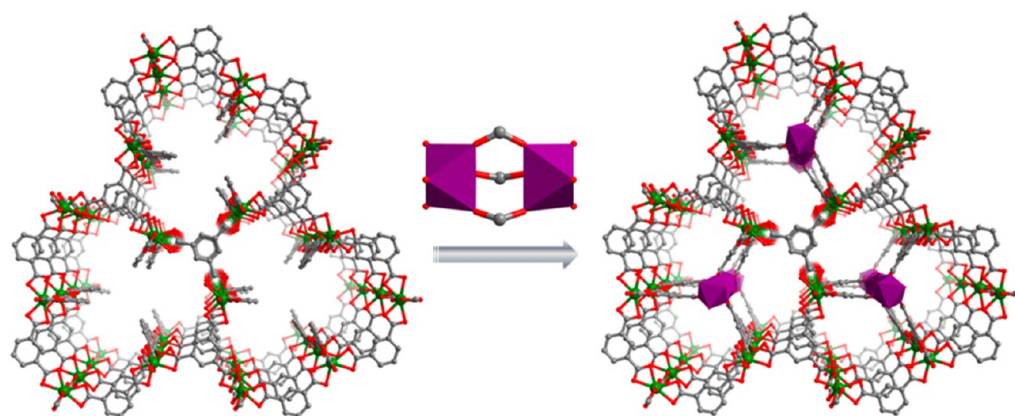**Figure 6.** Various nonsymmetric coordination modes of BTC.

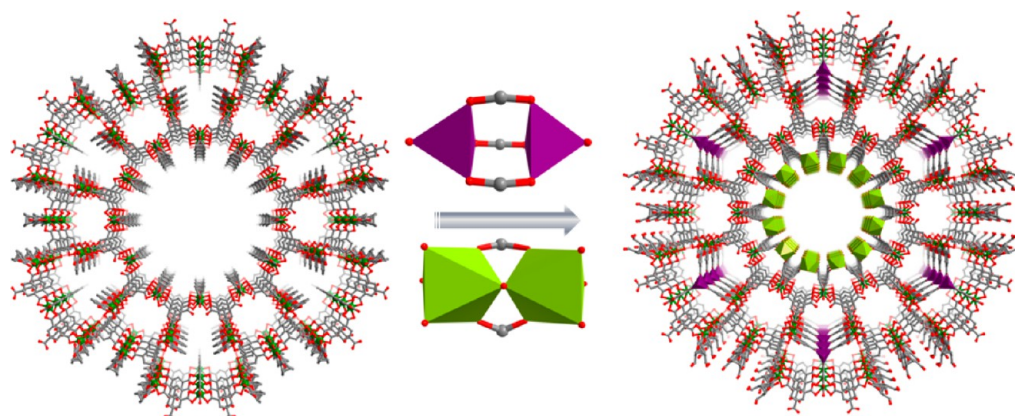**Figure 7.** Capture of cobalt dimers in CPM-4.

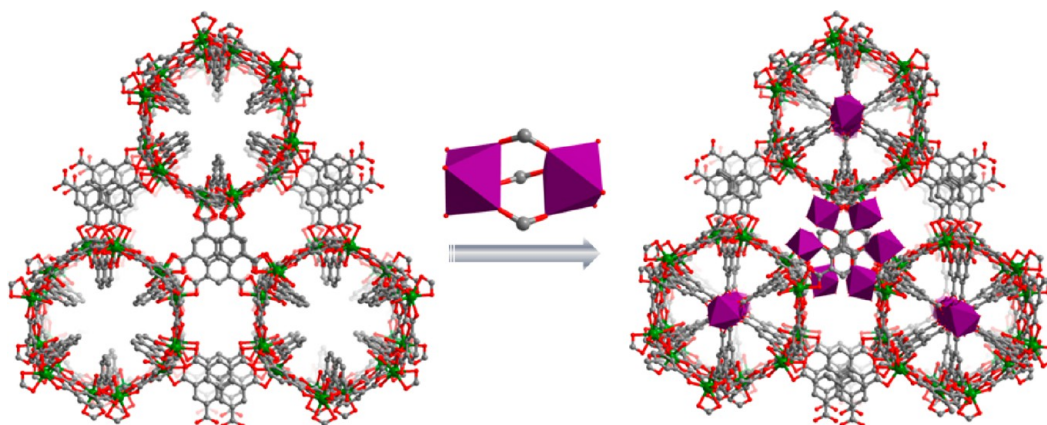**Figure 8.** Immobilization of two different dimers in CPM-16.

Figure 9. Capture of dimers within CPM-17.

MOF topology and channel size, two, three, or even four pore-partition groups can be positioned and oriented in such a way that they cooperatively capture a metal ion or cluster.

CPM-4 has a 3D framework with 1D hexagonal channels. It features graphite-like 3-connected In-BTC layers pillared by BTCs. Each interlayer BTC uses two − COO groups for pillaring, leaving the third − COO group free to capture a paddlewheel dimer, $[Co_2(CO_2)_3(DMF)_6]^+$, at channel centers (Figure 7).[22] For larger channels, the −COO group is not long enough to reach the channel center, causing captured clusters to be near the channel wall as shown in CPM-16.

Three types of SBUs are in CPM-16: tetrahedral $[In(COO)_4]$, V-shaped $[Co_2(OH) (COO)_2(H_2O)_6]$, and paddlewheel $[Co_2(COO)_3(H_2O)_2]$ (Figure 8).[23] There are also three kinds of BTC ligands: one symmetrically bonded to three In^{3+} nodes, one unsymmetrically bonded to two In^{3+} nodes and one $[Co_2(OH)]$ dimer, and one unsymmetrically bonded to two In^{3+} nodes and one Co_2 dimer. CPM-16 resembles $AlPO_4$-5 formed from stacking of 3-connected 4.6.12 Archimedean layer, except that in CPM-16 metal and ligand positions are exchanged within the 4.6.12 layer. The BTC ligands within the 4.6.12 layer are symmetrically bonded to three In^{3+} sites. Adjacent layers are pillared by connecting In^{3+} nodes in 4.6.12 layers with BTC
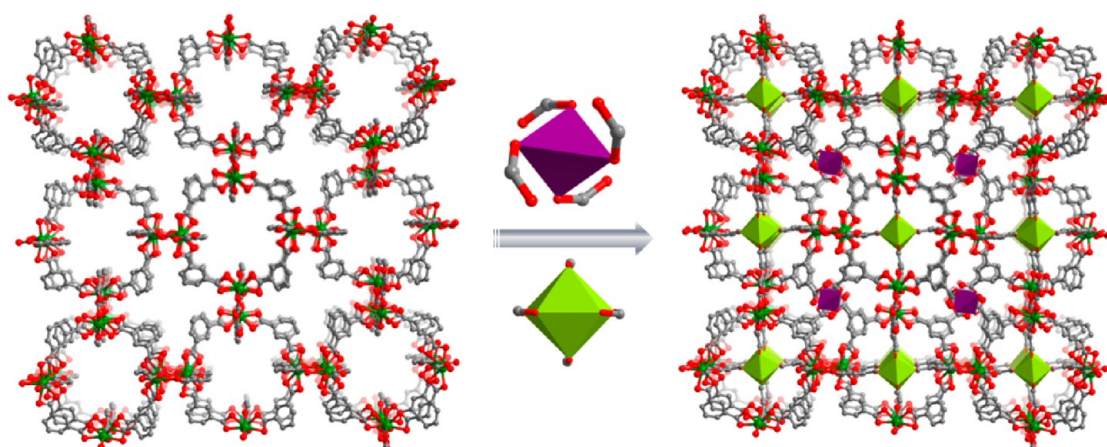
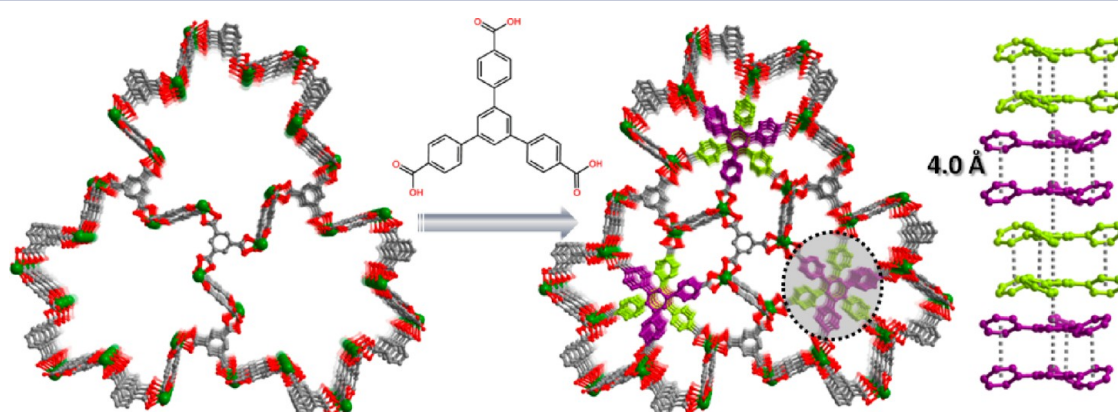**Figure 10.** Capture of In^{3+} and Co^{2+} in CPM-26.

Figure 11. Combination of BTC and BTB, and the channel structure in CPM-12.

ligands that only use two − COO groups to pillar the 4.6.12 layers, with the third group left as pore-partition group.

Unlike CPM-5 and CPM-16 with a mix of symmetrical and nonsymmetrically bonded BTC, CPM-17 has only nonsymmetrically bonded BTC (Figure 9),[23] which uses two −COO groups to form a framework with the *lcs* net containing only $[In_6(BTC)_6]$ 6-rings and 3D intersecting channels. The third COO^- points toward the channel center to coordinate with a Co dimer there.

CPM-26 mimics a rare mineral zeolite called Mg-BCTT (Figure 10).[23] Its asymmetric unit has two In^{3+} sites (an in-framework In1 and an extra-framework In2), one Co^{2+}, and two BTC ligands. The In1 ions are cross-linked by two carboxylate groups to form a zeolitic BCT topology with the $[In_{12}(BTC)_{12}]$ laumontite cage. CPM-26 features the simultaneous capture of two different metal species (In^{3+} and Co^{2+}/Zn^{2+}). It takes four carboxylate groups in a bidentate chelating mode to capture the "extra-framework" In^{3+} ion at the center of the lau-cage. In comparison, each Co^{2+} is trapped at the center of 8-ring channels by four COO^- groups in a monodentate mode.

The above examples show the flexibility of BTC to adopt either C_3-symmetric or non-C_3-symmetric modes, which endows BTC with the ability to form diverse topologies. CPM-17 shows the feasibility to form PSP with 100% nonsymmetric mode, which hints at the usefulness of polyfunctional ligands with lower symmetry. Indeed, we have two examples that illustrate this design strategy. In this case, 3,5-pyridinedicarboxylate uses two carboxylate groups for bonding to trimers to form MIL-88 type

while the pyridyl site bonds to Ag^+ or Cu^+ to form a partitioned pacs MOF.[24]

3.2. Secondary Ligand Insertion Strategy

In contrast with the introduction of the secondary metal, the secondary ligand can also be used. CPM-12 is an example constructed from size-complementary L^{3-}/L^{3-} ligands (1,3,5-tri(4-carboxyphenyl)benzene, BTB and BTC) (Figure 11).[25] Two types of structural motifs, $[In_2(OH) (BTC)]$ chain and $[[In_2(OH)]_3(BTC)_2]$ column, interconnect through sharing $[In_2(OH)]$ to form a giant channel, which houses BTB ligands as pore-partition agent arranged in parallel and in pairs (benzene to benzene center distance of 4.0 Å).

4. THE pacs PLATFORM FOR HIGH-PERFORMANCE CPMs

The above PSP examples demonstrate that PSP can be realized in different structure types through various mechanisms. A typical feature in these examples is that framework-forming agents and pore-partition agents are not separated. For example, in CPM-5, the same BTC ligands that form the sodalite cage also participate in PSP. Here, we turn our focus to a modular PSP system in which framework-forming agents and pore-partition agents are separated. One advantage of this modular approach is the independent tuning of framework-forming agents and pore-partition agents. It is also possible to synthesize both partitioned and nonpartitioned materials, allowing comparison of properties before and after PSP.
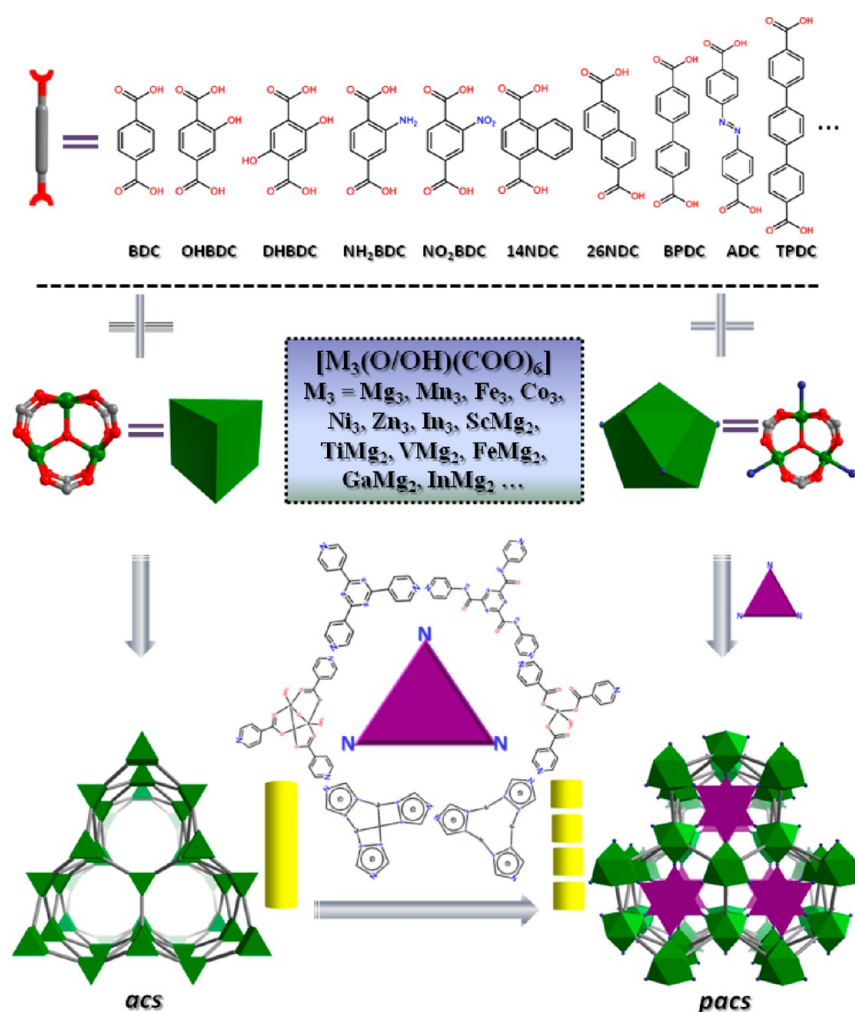
Figure 12. Schematic drawing of the *pacs*-MOF platform, as compared to the *acs* platform.

We recently developed such a modular strategy: symmetry-matching regulated insertion of pore-partition agents. It is based on symmetry and size matching between pore-partition agents and open-metal sites and allows the insertion of a pore-partition ligand into a primary framework.

The MIL-88 (the *acs type*) type was selected to implement this strategy. In *acs*-MOFs, metals in trimers are coordinated by terminal ligands at three axial positions. These pendant groups can be removed to produce open metal sites. At various heights along the *c* axis, three such M−L bonds from three different trimers are coplanar with C_3 symmetry and point to the center of hexagonal channels. This feature allows the insertion of C_3-symmetric ligands to occupy all three open metal sites.

Initially, the tritopic TPT ligand was used. MIL-88 frameworks are flexible, which relaxes the size-matching requirement and makes it easier to fit a ligand in the channel. We first reported a series of Ni-MOFs, one of which (denoted CPM-33a) was made from $Ni(NO_3)_2$, BDC, and TPT in DMF or DMA.[26] In contrast to MIL-88 in which trimers are 6-connected, trimers in CPM-33a are 9-connected with three axial positions occupied by pyridyl groups from TPT and such topology is denoted as *pacs*. The *pacs* framework is rigidified, leading to a more stable structure. The original continuous hexagonal channel is partitioned by TPT ligands into infinite number of finite segments (Figure 12).

The *pacs* type is a highly tunable platform. In addition to BDC, nine additional dicarboxylates with different functional groups or

length (DHBDC, OHBDC, NH_2BDC, NO_2BDC, 14NDC, 26NDC, ADC, BPDC, TPDC) have been used as the framework-forming ligand. Furthermore, pore-partition ligands can be extended. N,N',N''-tri(4-pyridinyl)-1,3,5-benzene-tricarboxamide (TPBTC), an extended version of TPT, has been utilized in *pacs* MOFs such as CPM-37, -87, -88, and -89.[28] For inorganic nodes, in addition to Ni_3, other homometallic (Mg_3, Mn_3, Fe_3, Co_3, Zn_3 and In_3) and heterometallic (Mg₂Sc, Mg₂Ti, Mg₂V, Mg₂Fe, Mg₂Ga and Mg₂In) compositions have also been achieved, resulting in a large family of isostructures denoted as CPM-141 to CPM-293 (Figure 12).[27]

Isonicotinate clusters, $[Zn(IN)_3(H_2O)]$ and $[Co_2(OH)(IN)_3(H_2O)_2]$, can also serve as pore-partition ligands as shown in CPM-31 and CPM-32,[22] respectively (Figure 13). Three IN ligands use three carboxylate groups to connect zinc monomers or cobalt dimers, while three pyridine N atoms coordinate with open indium sites from the *acs* net. These pore-partition ligands offer not only PSP, but also a route for adjusting framework charge. For example, incorporation of anionic $[Zn(IN)_3(H_2O)]^-$ in cationic CPM-30 gives the neutral framework of CPM-31.

PSP can also be achieved by symmetry-guided in situ formation of metal triazolate clusters.[24] As shown in Figure 13, three types of metal triazolate motifs, $[Ag_3(trz)_3]$, $[Cu_3O-(trz)_3X_6]$ (X = H_2O or Cl), $[M_2(trz)_3X_6]$ (M = Ag, Cu, Zn, Mn, Co, Ni, Fe, In, etc., X = H_2O or Cl), have been demonstrated. It is
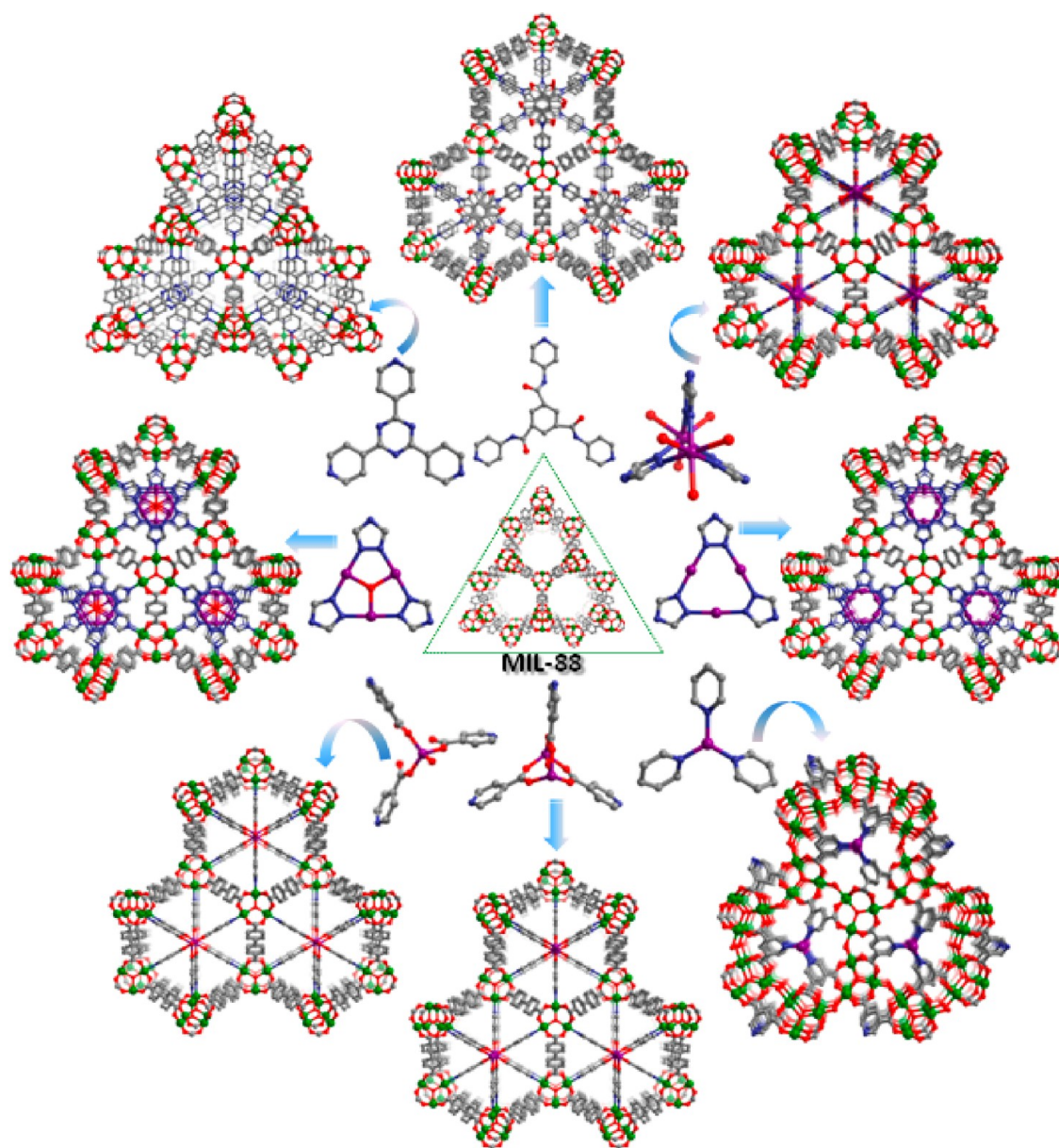
Figure 13. 3D frameworks of eight types of *pacs*-MOFs with different pore-partition agents.

of interest to comment on the loss and regeneration of open-metal sites on the pacs platform. The acs type has one open metal site per metal ion on the framework. On the pacs platform, these framework open metal sites are consumed by pore-partition ligands. However, when isonicotinate and triazolate clusters are used, new open-metal sites are generated on such clusters. This represents a transfer of open metal sites from the framework to the channel center. In addition to the location change, the chemical nature of open metal sites is also altered.

In materials design, there has been a relentless pursuit of novel structure types. For PSP, equally important is the identification of known structure types suitable for PSP. A powerful platform goes beyond just accommodating large chemical and structural variations for which the *pacs* platform is superbly capable of. Equally impressive is its power to induce the formation of chemical entities that would otherwise not form. We have found that pore-partition agents can play an active role in templating the formation of the primary MOF framework, which is why chemical species (e.g., Mg_2Ti) not seen elsewhere in MOFs are

also found on the *pacs* platform. The *pacs* is arguably the most versatile platform among CPMs.

Recently, Zhang et al. showed that $[2 + 2 + 2]$ cyclo-trimerization[29] of organonitrile, alkyne, and alkene monomers bearing a pyridyl group can be realized in Fe–MIL-88 channels. The guest-loading study in Na–Zn–FDA MOF shows that PSP can lock the pores to prevent the guest leaching.[30] A structure similar to CPM-32 with cobalt trimers was recently reported.[31]

5. PSP-ENHANCED GAS UPTAKE PERFORMANCE

PSP has contributed to enhanced CO_2 and H_2 uptake performance. CPM-5 exhibits a high CO_2 uptake capacity of 81.3 $cm^3 g^{-1}$ at 273 K and 1 atm. For H_2 gas, 139.2 $cm^3 g^{-1}$ (1.24 wt %) at 77 K and 1 atm is achieved. Further improvement is achieved by varying the size of organic cations. CPM-6 with the smallest possible organic cations ($CH_3NH_3^+$) shows much enhanced CO_2 (106.7 $cm^3 g^{-1}$ at 273 K and 1 atm) and H_2 uptake capacities (210.6 $cm^3 g^{-1}$ (1.88 wt %) at 77 K and 1 atm).
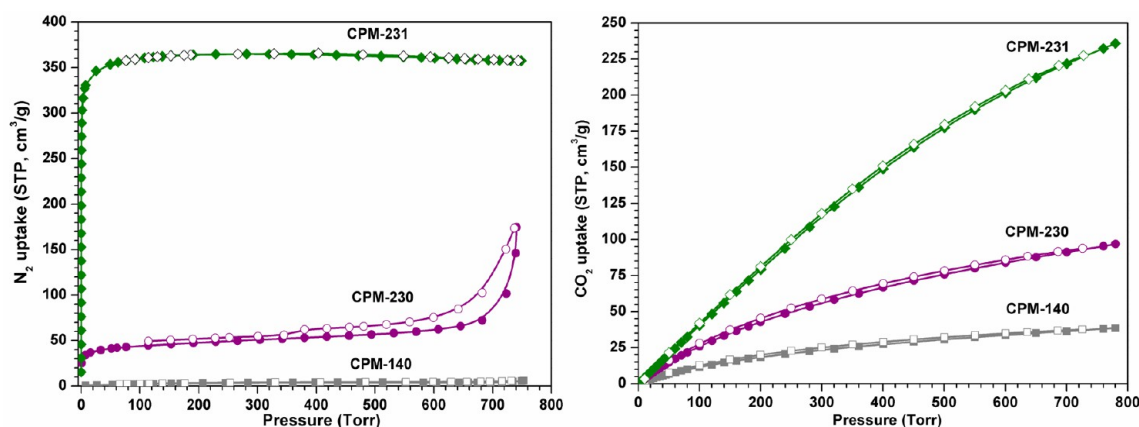
Figure 14. N_2 sorption isotherms at 77 K (left) and CO_2 sorption at 273 K (right) for CPM-140, CPM-230, and CPM-231.
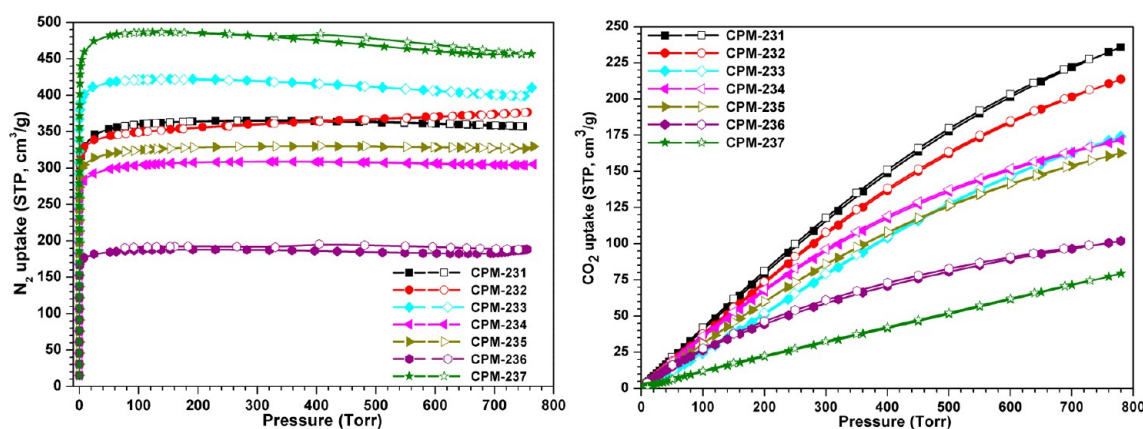

Figure 15. N_2 sorption isotherms at 77 K (left) and CO_2 sorption at 273 K (right) for CPM-231 to CPM-237.
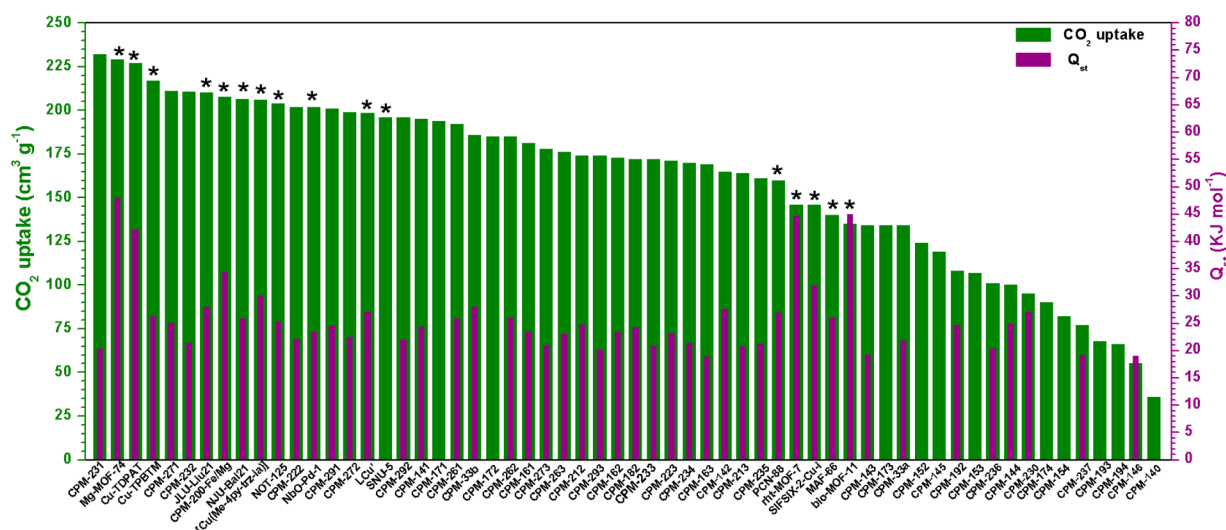
Figure 16. Summary of CO_2 uptake (273 K and 1 atm) and Q_{st} for selected *pacs*-MOFs and top MOFs reported in the literature (marked with *): Mg-MOF-47,[32] Cu-TDPAT,[33] Cu-TPBTM,[34] JLU-Liu21,[35] CPM-200-Fe/Mg,[36] NJU-Bai21,[37] [Cu(Me-4py-trz-ia)],[38] NOTT-125,[39] NbO-Pd-1,[40] LCu′,[41] SNU-5,[42] PCN-88[43] rht-MOF-7,[44] SIFSIX-2−Cu-I,[45] MAF-66,[46] and bio-MOF-11.[47]

The most dramatic impact of PSP on gas sorption properties occurs on the *pacs* platform. When combined with heterometallic cooperative crystallization (HCC), PSP becomes even more versatile and powerful. In particular, we have realized a step-by-step transition from pure anionic magnesium CPM-140 (Mg$_3$-MIL-88) to neutral heterometallic CPM-230 (Mg$_2$V-MIL-88) and further to neutral pore-partitioned CPM-231 (Mg$_2$V-DHBDC), which led to a dramatic increase in N_2 and CO_2 uptake capacity (Figure 14) even with the loss of all open-metal sites and reduced binding affinity. Compared to the negligible or small N_2 uptakes of CPM-140 and CPM-230, CPM-231 exhibits a saturated sorption amount of 366.5 cm^3 g^{-1} (16.4 mmol g^{-1}).

Significantly, the combination of HCC and PSP strategies boosts CO_2 uptake by 650% from 35.6 cm^3 g^{-1} in CPM-140 to 95.3 cm^3 g^{-1} in CPM-230, and to 232.3 cm^3 g^{-1} (10.37 mmol g^{-1}, 45.6 wt %) in CPM-231 at 273 K and 1 bar.[26] This value compares favorably with that of MOF-74-Mg (<230 cm^3 g^{-1} under the same condition) which had been the highest value since its discovery.

Gas uptake properties of *pacs* MOFs can be tuned by the types of framework-forming ligands.[26] With the same Mg$_2$V node, the Langmuir and BET surface areas of CPM-231 to CPM-237, tuned by the type of functional groups and the length of dicarboxylate linkers, vary from 823 to 2117 m^2 g^{-1} and from 588 to 1475 m^2 g^{-1} (Figure 15). Especially, the DHBDC^{2-} ligand, or more precisely, the −OH group, contributes to the CO_2 uptake capacity. Also, the short length and narrow width of the BDC core contributes significantly to the CO_2 uptake, because CPM-236 (with 1,4-NDC) and CPM-237 (with 2,6-NDC) show much lower CO_2 adsorption capacity.

Compared to MOFs with open metal sites, the effect of metal types on gas sorption on the *pacs* platform is subtle because the *pacs* materials made from TPT-type pore-partition ligands have no open metal sites. As shown in Figure 16, for a given dicarboxylate linker, Mg$_2$M (M = Sc^{3+}, Ti^{4+}, V^{3+}, Fe^{3+}, Ga^{3+}, and In^{3+}) heterometallic CPMs exhibit high CO_2 uptake at 273 K and 1 bar. Among six series of homometallic CPMs (Mg$_3$, Mn$_3$, Fe$_3$, Co$_3$, Ni$_3$, and Zn$_3$), Mn$_3$ and Zn$_3$ materials have lower CO_2 uptakes for the same dicarboxylate. Still, compared to most other MOF materials, nearly all *pacs* MOFs have good gas sorption properties. Impressively, such very high uptake capacities by *pacs* MOFs are accomplished with low isosteric heat of adsorption (Q_{st}, 19.0−28.0 kJ mol^{-1}, Figure 16). Specially, with comparable CO_2 uptake capacity at 273 K and 1 atm, the Q_{st} of CPM-231 (20.4 kJ mol^{-1})[26] is less than half of that of MOF-74.[32] The low-Q_{st} and high-capacity features of *pacs* MOFs could enable new or more cost-effective applications in gas storage and separation.

6. CONCLUDING REMARKS AND FUTURE OUTLOOK

In this Account, we have described the development of PSP methods in MOFs and dramatic impact of PSP on gas sorption properties. PSP is more than just a way to partition the pore space; it is a new direction in materials design. Despite its rapid progress, PSP is still at an early developmental stage. A computational understanding of its effect on gas sorption properties is also helpful in promoting its further development.[48] Among many opportunities and challenges, we highlight some below.

First, the role of extraframework species as pore-partition agents requires clarification. Related to this is the role of pendent species which can protrude into channels for PSP. However, the current interest is on the removal of such pendent species for purposes of generating open metal sites or greater pore space. We predict that in some cases, the PSP benefits and related enhanced stability from pendent ligands may outweigh the benefits from open metal sites or extra pore space.

Second, the selection or the design of polyfunctional ligands requires further exploration. The PSP mode exhibited by BTC is desirable, because it is capable of creating a new generation of zeolite-like materials whose frameworks are decorated with crystallographically ordered metal centers that can serve as functional sites for many applications such as catalysis or adsorption. Zeolite-type frameworks decorated with long-range ordered metal sites are basically nonexistent.

Third, the development of new mechanisms that divide roles of functional groups of polyfunctional ligands or assign complementary roles of framework-forming agents and pore-partition agents to various ligands and metalloligands is desirable. For cage-within-cage frameworks, the possibility of having even larger Archimedean cages (or other types of large cages) in MOFs is intriguing. Also intriguing is the intrinsic compatibility of PSP with heterometallic systems, both of which promote the formation and coexistence of inorganic clusters of various types, including those previously unknown. Clearly, PSP has a unique ability to enrich inorganic aspects of MOF chemistry, especially heterometallic chemistry in MOFs.

Fourthly, the symmetry-matching regulated pore-partition ligand insertion strategy has generated an enormously tunable *pacs* platform, which awaits further exploration with different types of metal ions, framework-forming agents, and pore-partition agents. The design and selection of these components are only limited by chemists' ingenuity. So far, we have limited ourselves to a narrow range of compositions and pore sizes, because of our focus on gas sorption, especially CO_2 uptake. For other applications such as catalysis, large pore sizes are often more desirable, but we have explored little in this regard.

Finally, much of the studies on the impact of PSP center on gas sorption. Given the power of PSP in not only partitioning pore space, but also in enabling new compositions, new topologies, greater stability, and so on, the impact of PSP should extend to many other areas. It is therefore desirable to explore other properties of partitioned MOFs. We anticipate that PSP will extend beyond just a synthetic method or a structure analysis concept to become a versatile method for engineering many properties of CPMs.

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