Comments on Inorganic Chemistry: A Journal of Critical Discussion of the Current Literature

Beyond Custom Design of Organic Ligands: An Integrative Strategy for Metal-Organic Frameworks Design

Wen-Yang Gao [a] & Shengqian Ma [a]

[a] Department of Chemistry , University of South Florida , Tampa , Florida , USA

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Beyond Custom Design of Organic Ligands: An Integrative Strategy for Metal-Organic Frameworks Design

Wen-Yang Gao and Shengqian Ma

Department of Chemistry, University of South Florida, Tampa, Florida, USA
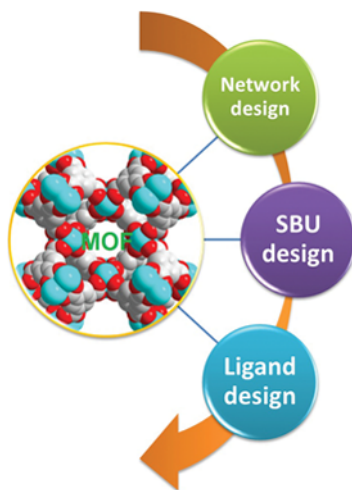
In this review, we systematically summarize our recent work on how metal-organic frameworks (MOFs) are constructed via custom design of organic ligands and beyond. Following a brief introduction of basic concepts and general background of MOFs, we explain how to fine-tune MOFs' structures via the design strategy of network,

Address correspondence to Shengqian Ma, Department of Chemistry, University of South Florida, Tampa, FL 33620, USA. E-mail: sqma@usf.edu

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gcic.

secondary building unit (SBU), and ligand. Amongst these, the custom design of organic ligands plays a fundamental yet important role in this field. In addition, the custom-designed ligands, which feature certain functional motifs, can further enrich the performances of targeted MOFs owing to the primary functionalities bestowed on the frameworks by the ligands. Therefore, the custom design of organic ligands and beyond can be a useful approach to task-specific functionalizing of the frameworks.

1. INTRODUCTION

Metal-organic frameworks (MOFs),[1] also known as porous coordination polymers, have emerged as a new type of porous material at a rapid pace over the past decades, capturing unparalleled attention from both academia and industrial communities due to their structural regularity and synthetic tunability. MOFs are built from metal ions or *in situ* generated metal clusters (also known as secondary building units (SBUs)) that are interconnected by multidentate organic ligands via coordination bonds to afford two- or three-dimensional (2D or 3D) periodic networks featuring controllable channels or cages.[2] A major driving force behind their exponential growth lies in their amenability to design: a desired structure can thus be targeted by judicious selection of the SBU and the organic ligand.[3] Furthermore, their modular nature means that their pore sizes, pore walls, surface area, and other structural features can be tailored by custom design of organic linkers. In contrast to other classes of porous materials, such as active carbon and zeolites, the designable and modular features of MOFs have given them great potential for a plethora of potential applications, such as gas storage,[4] gas separation,[5] catalysis,[6] sensors,[7] and others.[8]

In this review article, we focus on our recent progress on how MOF structures can be rationally designed and synthesized by virtue of custom design of organic ligands, rather than on the practical applications of MOFs. More specially, we explain how to fine-tune MOF structures via the design strategy of network, SBU, and ligand. Evidently, custom design of organic ligands plays a vital role in tailoring MOF structures. The "custom design" of organic ligands can be basically interpreted as the design of organic ligands under the guidance of a specific task or target. Illuminated by characteristic structural features of MOFs, we comprehensively demonstrate how the custom design of organic ligand exerts exquisite control over constructing the targeted MOFs from the perspectives of networks, metal-containing SBUs, and organic linkers.

2. NETWORK DESIGN

Metal-metalloporphyrin frameworks (MMPFs) are considered to be one of the most intriguing MOF subfields and stimulate intense research interest due to

the essential role of metalloporphyrin molecules for ubiquitous biochemical, enzymatic, and photochemical functions. Building coordination architectures based upon metalloporphyrin ligands thus becomes exceedingly desirable in pursuit of mimicking their diverse biological functionalities and imitating robust inorganic zeolites for versatile applications. More details can be found in a review article detailing the history, progress, and outlook of metal-metalloporphyrin frameworks.[9]

Generally, the porosity of 3D MOFs exists in the form of either perforative channel or polyhedral cage, both of which allow guest molecules to reside in the frameworks. Although a number of metalloporphyrin framework structures were reported in the past two decades,[9] polyhedral cage-type structures have rarely been incorporated into metalloporphyrin-based MOFs. An extensive effort to target the polyhedral cage-type metalloporphyrin frameworks via utilizing tetrakis(4-carboxyphenyl)porphyrin (tcpp) for assembly with highly symmetric metal-containing SBUs has generally afforded 2D layered structures or 3D pillared networks in which the active metal centers within porphyrin units are usually blocked.[9,10] It has been clearly shown that the construction of supermolecular metalloporphyrin-based nanoscopic polyhedral cages renders cage walls rich in π-electron density that can implement favorable interactions with target guest molecules and also facilitate synergistic interaction with substrates.[11] In contrast to the ordinary 2D layered or 3D pillared structures, the introduction of metalloporphyrin-based nanoscopic polyhedral cages into MOFs allows for the construction of π-electron-rich cage walls together with a high density of open mental sites confined in the nanospace. It can be expected to greatly benefit their behavior in versatile applications.

In 2011, driven by the above-mentioned advantages, our group described the first example of a polyhedral cage-based metalloporphyrin framework, MMPF-1, constructed from a custom-designed porphyrin ligand, 5,15-bis(3,5-dicarboxyphenyl)porphine (bdcpp) and a judiciously selected dicopper paddlewheel SBU, as illustrated in Figure 1(a).[12] $[Cu_2(COO)_4]$ paddlewheel moieties have been broadly adopted for the construction of metal-organic polyhedra (MOP), as they are ubiquitous in coordination chemistry and their square geometry is versatile in this context.[13] Furthermore, vertex-linking of the square SBUs with isophthalate ligands typically generates a variety of different faceted MOPs. These faceted MOPs have only recently been employed as supermolecular building blocks (SBBs) to build up highly porous and symmetrical MOFs by bridging the isophthalates with various organic moieties through their 5-positions, illustrated by MOPs based upon isophthalate derivatives and square dicopper paddlewheel SBUs.[14] Inspired by these established systems, the polyhedral cages have been successfully incorporated into the porphyrin-based network by designing an isophthalate-derived porphyrin ligand, bdcpp, in which a pair of isophthalates is bridged by a porphine macrocycle.
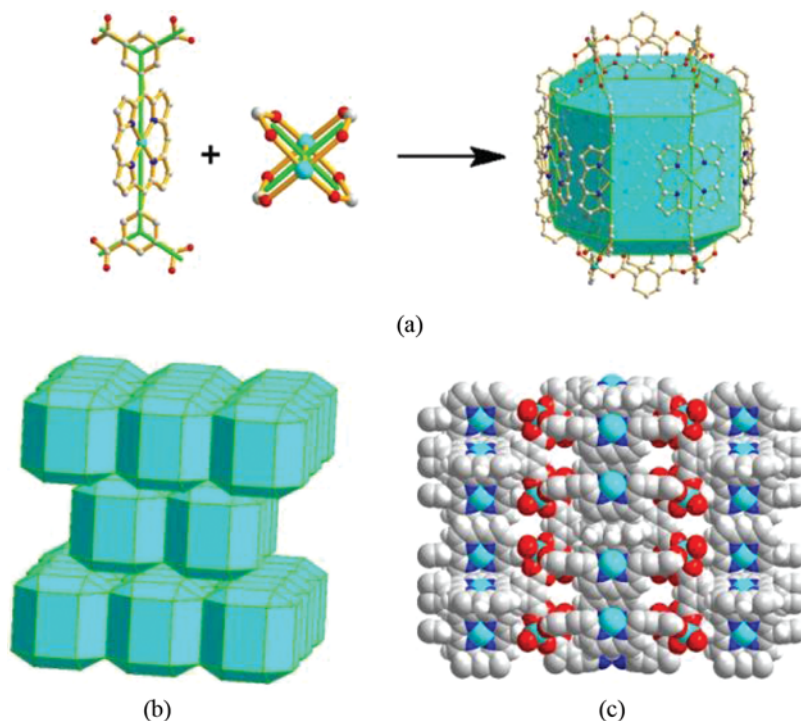
Figure 1: (a) Illustration of linking bdcpp ligand and dicopper paddlewheel to form the irregular rhombicuboctahedral cage; (b) ``ABAB'' packing of rhombicuboctahedron layers in MMPF-1; (c) space-filling model on the (100) plane indicating the open pore size of ~3.4 Å × 3.5 Å.[12] © American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reuse must be obtained from the rightsholder.

In the case of MMPF-1,[12] eight paddlewheel SBUs are interconnected by 16 bdcpp ligands to generate a nanoscopic cage. Four dicopper paddlewheel SBUs are bridged by four isophthalate moieties from four different bdcpp ligands to form the top of the cage; they are pillared to four dicopper paddlewheel SBUs at the bottom of the cage through eight different bdcpp ligands. The porphyrin macrocycle of the bdcpp ligand is metalated *in situ* by a Cu(II) ion that is free of coordinated solvent molecules, thus leaving both the distal and proximal positions open. In each cage, there are eight open copper sites associated with the porphyrin rings of the bdcpp ligands and eight open copper sites from dicopper paddlewheel SBUs that are activated by thermal liberation of aqua ligands. All 16 open copper sites point toward the center of the cage, resulting in an unprecedentedly high density of open metal sites in a nanoscopic cage ($\sim$7 open metal sites per nm^3). Connecting the centers of all isophthalate phenyl rings and the centers of the eight paddlewheels, the polyhedral cage can be depicted as a polyhedron that has 24 vertices, 26 faces, and 48 edges. Given its similar shape to the rhombicuboctahedron

by 24 isophthalates and 12 paddlewheel SBUs in MOP and some MOFs, this polyhedron can also be depicted as an irregular rhombicuboctahedron. The MOP serves as an SBB to extend in the *ab* plane and then pack along the *c* axis via "ABAB" stacking to sustain a 3D porous metalloporphyrin framework structure, demonstrating a very high density of open metal sites in the confined nanoscopic polyhedral cage, shown in Figure 1(b and 1c). The "ABAB" packing of the polyhedral cages in MMPF-1 constricts its pore size, which facilitates selective adsorption of H_2 and O_2 over N_2, and CO_2 over CH_4.

Soon after the first example of nanoscopic MOP-based porphyrin networks, we reported a design approach to building MMPFs from high-connectivity, high-symmetry SBBs, which are based upon uniform polyhedra.[15] They are constructed from regular polygons with congruent vertices, and they are highly symmetric in terms of reflective and rotational symmetry. Such an approach complements the parallel development of the chemistry of discrete nanoscale molecular polygons and polyhedra.[16] A library of molecular building blocks (MBBs), which serve as the polygonal components to build types of high-symmetry and high-connected SBBs, has been established.[17] Even though there are 80 uniform polyhedra, not all can serve as blueprints for the construction of infinite structures. Amongst them, *Platonic solids, Archimedean solids, and faceted polyhedra* represent the three subsets of uniform polyhedra, 27 in total, which are most practically appropriate for blueprints. Taking the ubiquity of square and triangular MBBs into consideration, the polyhedra of rhombicuboctahedron (shown in Figure 2) remain appropriate targets for self-assembly. The rhombicuboctahedron or its edge skeleton are targets for face-directed or edge-directed self-assembly, respectively, whereas the two faceted polyhedra are accessible by vertex-directed self-assembly of squares and triangles or squares only.

To achieve the target of utilizing uniform polyhedra as high-symmetry and high-connected SBBs to devise MOFs, a porphyrin ligand, tetrakis(3,5-dicarboxyphenyl)porphine (tdcpp), is custom-designed to serve as square MBBs that bridge triangular $[Zn_2(CO_2)_3]^+$ or $[Cd(CO_2)_3]^-$ moieties to form 3D frameworks, termed MMPF-4 (Zn) or MMPF-5 (Cd).[15] The small cubicuboctahedron SBBs, which are thereby generated via vertex-directed self-assembly, are the first SBBs that are uniform polyhedra based on porphyrin MBBs. The resulting SBB is a small cubicuboctahedron composed of the faces of six Zn-tdcpp moieties that are linked by eight $Zn_2(CO_2)_3$ moieties, as illustrated in Figure 2(a). The opposite face of each Zn-tdcpp moiety in MMPF-4 serves as the face of an adjacent SBB. Each of the resulting SBBs of MMPF-4 can be regarded as one lattice point of the cube, thereby making it a six-connected **pcu** net. The cage formed between the SBBs can be described as an octahemioctahedron, which is enclosed by eight triangular $Zn_2(CO_2)_3$ paddlewheel MBBs from eight different SBBs. The eight $Zn_2(CO_2)_3$ paddlewheel MBBs are bridged through 12 isophthalate moieties from 12 tdcpp ligands. Similarly, MMPF-5 is
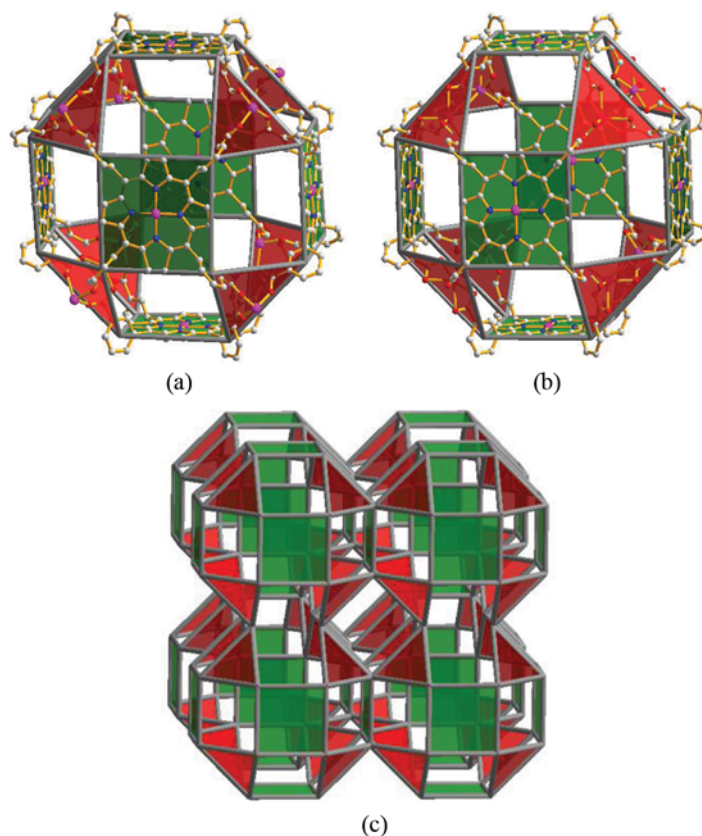
Figure 2: (a) The small cubicuboctahedron in MMPF-4 is formed by six square Zn-tdcpp MBBs and eight triangular $Zn_2(CO_2)_3$ MBBs; (b) the small cubicuboctahedron in MMPF-5 formed by six square Cd-tdcpp MBBs and eight triangular $Cd(CO_2)_3$ MBBs; (c) the extended 3D framework presented by packing cubicuboctahedral cages.[15] © Royal Society of Chemistry. Reproduced by permission of Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

also based upon a small cubicuboctahedron SBB composed of six Cd-tdcpp moieties that are linked by eight $Cd(CO_2)_3$ moieties, shown in Figure 2(b). SBBs are fused with six adjacent SBBs through six Cd-tdcpp moieties to support an augmented **pcu** network in Figure 2(c). The high symmetry of the small cubicuboctahedron SBBs distinguishes MMPF-4 and MMPF-5 from MMPF-1, in which cages are formed by pillaring two sets of four copper paddlewheel moieties through eight closely connected porphyrin ligands. The cages in MMPF-1 therefore possess much lower symmetry compared to those in MMPF-4 and MMPF-5. These high-symmetry porphyrin-based cubicuboctahedral cages are very rare in metalloporphyrin-containing frameworks.

According to the previous discussion, the networks featuring polyhedral cages have been precisely designed and synthesized by virtue of assembling selected metal-containing SBUs with custom-designed isophthalate-derived

porphyrin ligands. The demonstrated strategy engenders a promising opportunity to further explore MMPF platforms for various applications.

3. SECONDARY BUILDING UNIT (SBU) DESIGN

In addition to the network design, the strategy of SBU design represents another approach to investigating how to rationally design MOF structures via employing a variety of intriguing SBUs. The traditional or classical coordination modes of some transition metals are beyond the scope of this review, since they have been thoroughly discussed in other reviews.[18] Herein, we mainly examine our distinctive way to build up SBUs as nodes for MOF construction. Among various types of MOFs, highly connected structures have been intensively pursued given their robust framework and remarkable surface area. Existing approaches to constructing highly connected MOF structures heavily rely on the utilization of multitopic organic ligands (e.g., the **rht**-topology MOFs are mainly based on hexacarboxylate ligands[19] and the **scu**-topology MOFs are built from octacarboxylate ligands[20]), which requires multistep complex organic synthesis. Therefore, an alternative strategy of employing highly connected SBUs with linear linkers to afford highly connected structures is proposed to overcome this obstacle.

It has been proved that the 1,2,3-triazolate donor group featuring three nitrogen atoms as coordination sites favors the formation of highly connected multinuclear metal clusters, particularly when combined with a carboxylate donor group.[21] This renders triazolate-carboxylate bifunctional ligands that are promising candidates for the construction of highly connected robust MOFs[22] with the *in situ* generated multinuclear metal clusters as highly connected nodes. In consequence, a bifunctional linear ditopic ligand, 4-(1,2,3-triazol-4-yl)-benzoate (tab, Figure 3a), is employed to assemble with Zn(II) under solvothermal conditions, resulting in a rare (6,9)-connected robust MOF, MTAF-4.[23] The *in situ* formed tetranuclear (Figure 3b) and heptanuclear (Figure 3c) zinc cluster moieties serve as six- and nine-connected nodes, respectively. The SBU of $Zn_4(\mu_4\text{-}O)(CO_2)_6$ is ubiquitous in Zn-based MOFs and serves as a six-connected node. In comparison, the SBU of $Zn_7(\mu_4\text{-}O)_2(CO_2)_3(C_2N_3)_6$ has not been presented in either discrete metal complexes or existing MOFs, and represents a new heptanuclear zinc cluster moiety bridged by carboxylate and 1,2,3-triazolate groups. Every $Zn_7(\mu_4\text{-}O)_2(CO_2)_3(C_2N_3)_6$ SBU serves as the nine-connected node to link six $Zn_4(\mu_4\text{-}O)(CO_2)_6$ SBUs and three other $Zn_7(\mu_4\text{-}O)_2(CO_2)_3(C_2N_3)_6$ SBUs through nine linear tab linkers, and each $Zn_4(\mu_4\text{-}O)(CO_2)_6$ SBU serves as the six-connected node to bridge six $Zn_7(\mu_4\text{-}O)_2(CO_2)_3(C_2N_3)_6$ SBUs via six tab linkers. This affords an unprecedented (6,9)-connected binodal robust network, as illustrated in Figure 4.
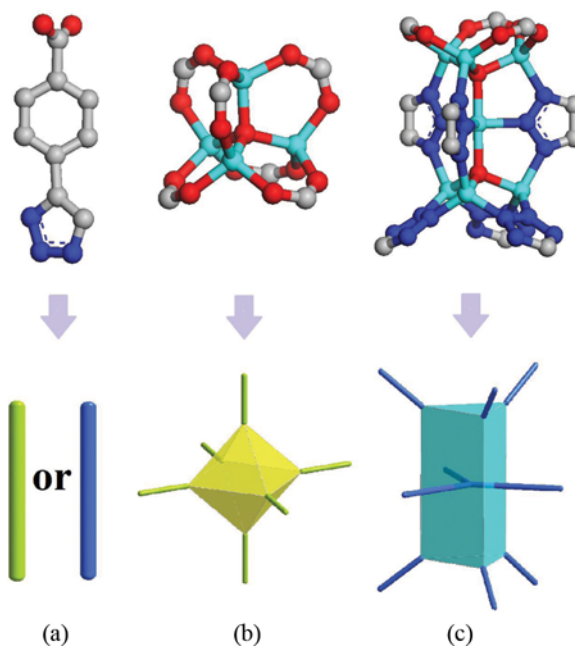
Figure 3: Schematic representations of (a) 4-(1,2,3-triazol-4-yl)-benzoate (tab) ligands as linear linkers; (b) tetranuclear zinc clusters as six-connected nodes; (c) heptanuclear zinc clusters as nine-connected nodes (color scheme: C, gray; O, red; N, blue; Zn, turquoise).[23] © Royal Society of Chemistry. Reproduced by permission of Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.
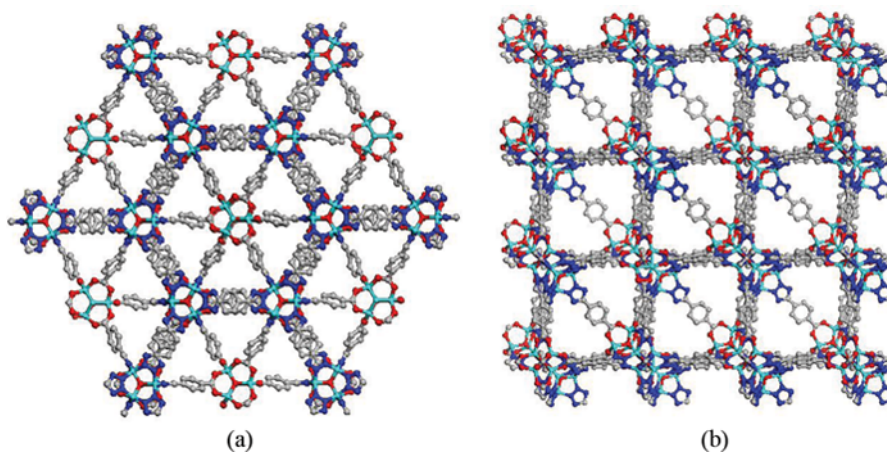
Figure 4: (a) Packing picture of MTAF-4 from c direction; (b) packing picture of MTAF-4 viewed along special axis (1,-1,1).[23] © Royal Society of Chemistry. Reproduced by permission of Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

Another case illuminating the coordination versatility of multinuclear SBUs from a triazolate-carboxylate bifunctional ligand occurs with MTAF-1, a porous double-walled robust framework.[24] Different reaction conditions from the synthesis of MTAF-4 afford another highly porous structure, which adopts the $Zn_5(\mu_3\text{-}O)_2(CO_2)_5(C_2N_3)_5$ cluster as the multinuclear SBU. Each pentanuclear zinc cluster SBU is connected by 10 organic ligands embraced with five carboxylate groups and five 1,2,3-triazolate groups to afford a rare double-walled 3D robust framework (Figure 5). MTAF-1 represents the first example of a double-walled MOF based upon a unitary organic linker, and this kind of double-walled arrangement has prevented the formation of interpenetration and can enhance the robustness of the framework.

(a)   (b)

(c)
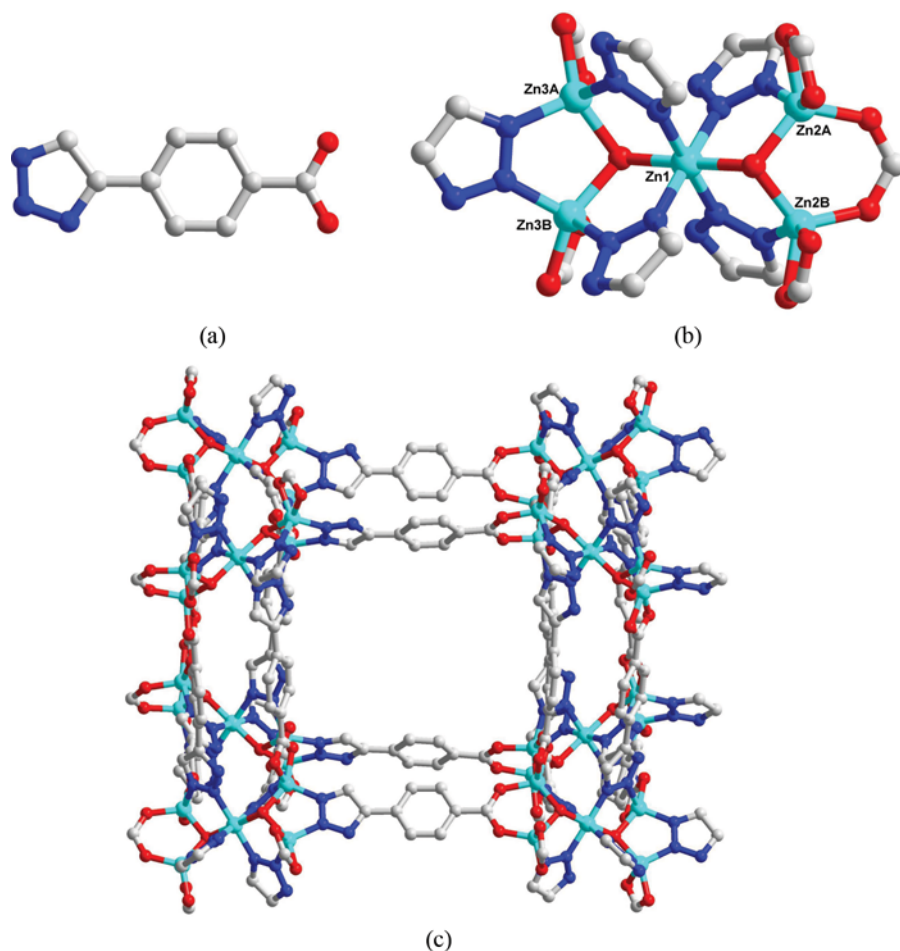
Figure 5: (a) 4-(1,2,3-triazol-4-yl)benzoate (tab); (b) pentanuclear zinc cluster SBU; (c) structure of MTAF-1.[24] © American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reuse must be obtained from the rightsholder.

Overall, the bifunctional linear ditopic ligand provides an opportunity to afford multinuclear SBUs, which can further be adopted to construct robust, highly porous frameworks. It must be mentioned here that, beyond MTAFs, many other robust, high-connected frameworks are also based on high-connected SBUs, such as UiO-66 and others.[22b,22c] Thus, it is clear that the highly connected robust network can also be built from high-connected metal-containing SBUs other than multitopic organic ligands. In addition, we can anticipate that the designability and amenability of metal-containing SBUs would endow MOF synthesis with more proficient rational design.

4. ORGANIC LIGAND DESIGN

From the perspectives of network and SBU design, it has been demonstrated that the custom design of organic ligand exerts a decisive control on the construction of target MOF structures. In this section, more attention is focused on how to custom-design the functional organic ligands to incorporate desired functionality within the frameworks. In particular, the modular nature of MOFs means that prototypal existing MOFs can serve as blueprints or platforms for a plethora of derivatives with controlled pore size, surface area, and specific functionalities.

High-symmetry MOFs based upon high-connectivity polyhedral cage MBBs that are, in effect, supermolecular building blocks (SBBs) can provide exquisite control over structure because of their high connectivity, and also afford the features of confined nanospace and extra-large surface area. Meanwhile, metalloporphyrins have been broadly investigated as catalytically active species for a variety of chemical reactions.[25] The aforementioned facts allow us to employ metalloporphyrin ligands to construct polyhedral cage-based structures. In a nutshell, it is feasible to generate metalloporphyrin-walled polyhedral MOFs by custom-designing metalloporphyrin moieties so that they can serve as edges or faces of the polyhedra for catalytic activities. A custom-designed porphyrin ligand (Scheme 1b)[26] is thus conceived to target a previously reported **fcu** topology net, fcu-MOF-1. The blueprint of **fcu** topology net is built from 12-connected cubohemioctahedral SBBs of formula $[Co_2(\mu_2\text{-}H_2O)(H_2O)_4]_6(bdc)_{12}$ and benzoimidephenanthroline tetracarboxylate (bipa-tc) linkers (Scheme 1a).[27] As exemplified, MMPF-3 with **fcu** topology was successfully engineered via incorporation of a custom-designed metalloporphyrin ligand, featuring three types of unique polyhedral cages shown in Figure 6. Furthermore, the active metalloporphyrin units residing on the vertices of polyhedral cages bring about the opportunity for catalytic studies of MMPF-3.

Similarly, a functional, custom-designed ligand integrated with 1,2,3-triazolate moiety is incorporated into a pillared framework to remarkably

(a)	(b)
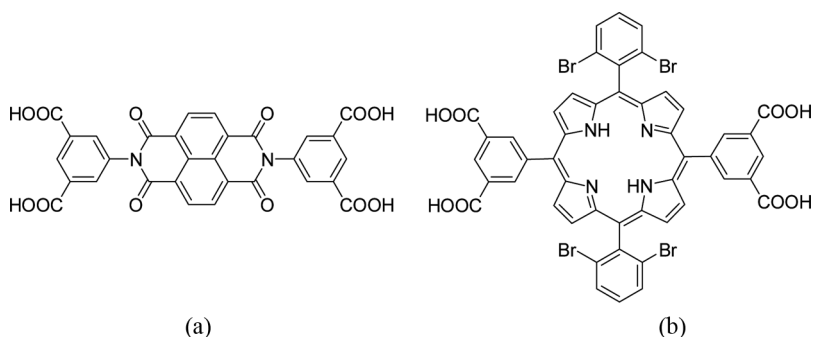
Scheme 1: The ligands that serve as linkers in fcu-MOF-1 and MMPF-3:
(a) benzoimidephenanthrolinetetracarboxylic acid (H$_4$bipa-tc); (b) 5,15-bis(3,5-dicarboxyphenyl)-10,20-bis(2,6-dibromophenyl)porphyrin (H$_4$dcdbp).[26] © WILEY-VCH. Reproduced by permission of WILEY-VCH. Permission to reuse must be obtained from the rightsholder.

enhance CO_2 uptake.[28] Pillared MOFs have recently been widely exploited as a type of platform for gas storage/separation; they consist of 2D layers that have ligating sites for linkage with ditopic pillars, usually of dipyridine derivatives into 3D architectures.[29] The structures and properties of pillared MOFs are readily tailored by functionalizing either the linkers within the 2D layers or the ditopic pillared ligands. One of the prototypal pillared MOF structures is MOF-508 (Figure 7a), in which the 2D layers based upon 1,4-benzenedicarboxylate (bdc) and the dizinc paddle-wheel cluster are pillared by 4,4′-bypyridine (bpy) to afford a 3D two-fold interpenetrating **α-Po pcu** network (Scheme 2).[29c] While the 1,2,3-triazolate group demonstrates exceptional advantages to generate high-connected multinucear metal clusters, as mentioned in section 2, it can also be grafted into the ligand with exposed nitrogen atoms as relative, moderate, Lewis-base centers to interact with guest molecules. Therefore, a new dipyridine derivative ligand, 4,4′-(2H-1,2,3-triazole-2,4-diyl)dipyridine (tadp), is designed to decorate pillared MOF-508 with 1,2,3-triazolate moieties. As expected, the self-assembly of tadp with bdc and dizinc paddle-wheel cluster generated *in situ* gave rise to MTAF-3 (Scheme 2, Figure 7b), which is isostructural with MOF-508 but exhibits much higher CO_2 uptake capacity than the parent MOF-508.

The alluring features bestowed by macrocycles have rendered a variety of applications for the ligands, such as activation of small molecules, ion recognition and capture in supramolecular chemistry, and others.[30] To integrate the ascendency of macrocycles in host-guest chemistry into MOF networks, an azamacrocyclic tetracarboxylate ligand, 1,4,7,10-tetrazacyclododecane-N,N′,N″,N‴-tetra-p-methylbenzoic acid (tactmb), is rationally designed, merging the coordination diversity of a carboxylate group and the merits of a flexible macrocycle.[31,32] On the other hand, the macrocyclic ligand, tactmb,
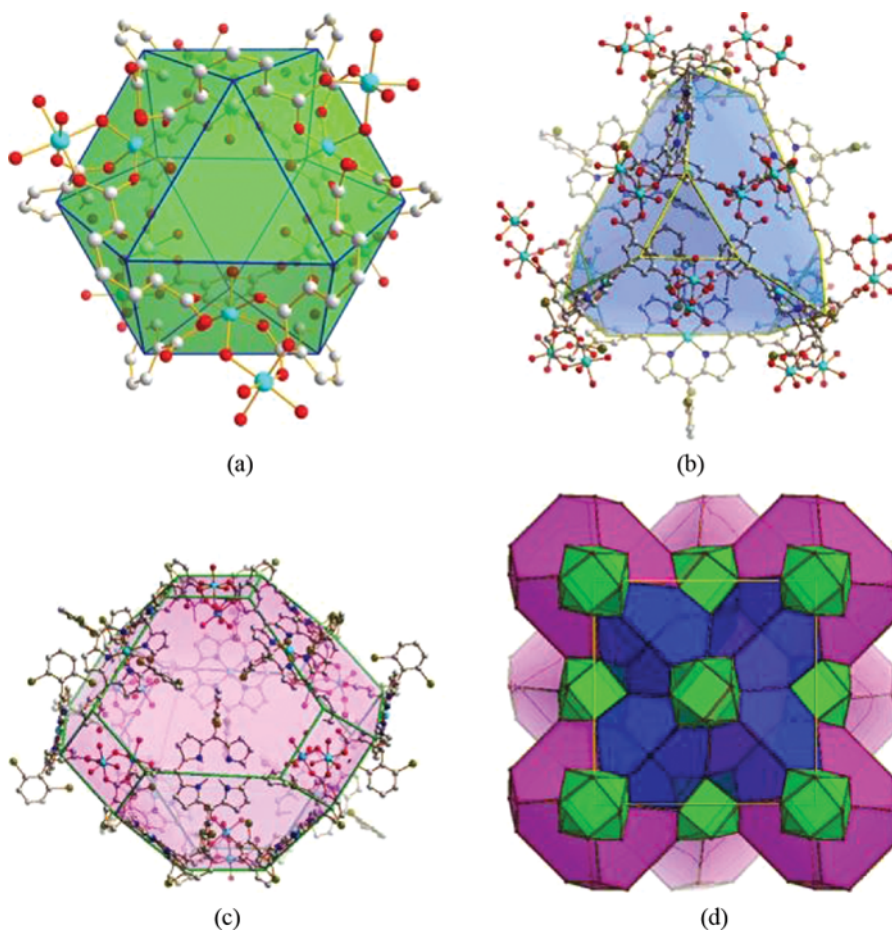
Figure 6: The three types of polyhedral cages present in MMPF-3: (a) cubohemioctahedron; (b) truncated tetrahedron; (c) truncated octahedron; (d) 3D structure of MMPF-3 illustrating how its polyhedral cages are connected.[26] © WILEY-VCH. Reproduced by permission of WILEY-VCH. Permission to reuse must be obtained from the rightsholder.

is employed to target the prototypal **nbo** topology framework, comprised of close packing of cuboctahedral cages.[33] The prototypal **nbo** MOF platform is exemplified by MOF-505,[33a] which is based upon 3,3′,5,5′-biphenyltetracarboxylate ligand (bptc; Scheme 3a) and copper paddlewheel secondary building units (SBUs). MOF-505 consists of a cuboctahedral cage with 12 copper paddlewheels residing on the vertexes (Figure 8a). As the 12 copper centers on the vertexes are not well-oriented toward the center of the cuboctahedral cage, their full accessibility for the substrates entering the cage could be restricted, thus leading to possible limited performances as Lewis acid catalysts. One way to introduce additional active copper sites that can be aligned toward the cage center, thus promoting the interactions between active sites and substrates, is
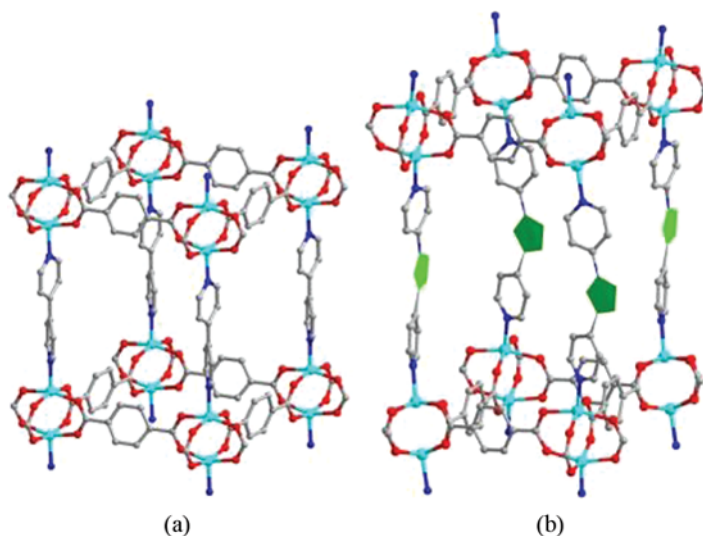
Figure 7: (a) Building unit of MOF-508; (b) building unit of MTAF-3.[28] © Royal Society of Chemistry. Reproduced by permission of Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

through decorating the six square faces of the cuboctahedral cage with copper centers.

This has been achieved by a crystal engineering approach in the **nbo** topology MOF, MMCF-2 (MMCF denotes metal–macrocyclic framework), as

Scheme 2: Illustration of approaches to constructing MOF-508 and MTAF-3.[28] © Royal Society of Chemistry. Reproduced by permission of Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

(a)   (b)
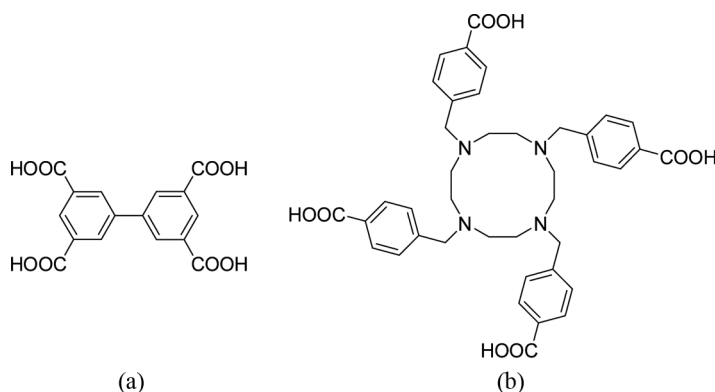
Scheme 3: The ligands that serve as linkers in MOF-505 and MMCF-2: (a) 3,3′,5,5′-biphenyltetracarboxylic acid (H$_4$bptc); (b) 1,4,7,10-tetrazazcyclododecane-N,N′,N″,N‴-tetra-p-methylbenzoic acid (H$_4$tactmb).[32] © WILEY-VCH. Reproduced by permission of WILEY-VCH. Permission to reuse must be obtained from the rightsholder.
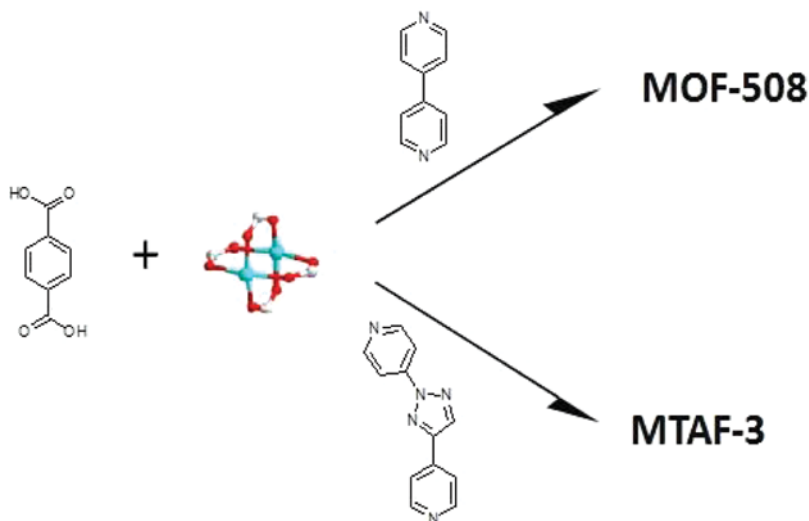
reported herein, in which each of the six square faces of the cuboctahedral cage is occupied by the Cu(II) metalated azamacrocycle (Figure 8b).[32] As expected, the cuboctahedral cage of MMCF-2 can function as a highly efficient Lewis acid-based nanoreactor for the cycloaddition of CO_2 and epoxide under ambient conditions, with twice the efficiency of the parent MOF-505.

On the basis of this, MOFs have exhibited high modularity and fine-tunability toward their structures and properties by virtue of the custom design of organic ligands. It is worth noting that the inherent features of the ligands endow various particular functionalities to the MOF structures. This actually paves the way to incorporating the primary functionalities from the custom-designed ligands to the frameworks.

(a)   (b)
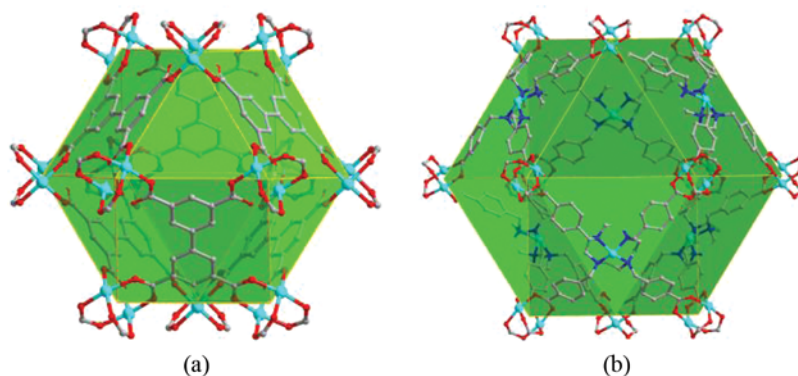
Figure 8: The cuboctahedral cage of (a) MOF-505 and (b) MMCF-2.[32] © WILEY-VCH. Reproduced by permission of WILEY-VCH. Permission to reuse must be obtained from the rightsholder.

5. CONCLUDING REMARKS

In summary, as shown in the aforementioned cases, the custom design of organic ligands and beyond has been examined as an effective and efficient approach to constructing MOF structures. As this review demonstrates, the frameworks and the metal-containing SBUs can be rationally targeted and achieved via custom designing of organic ligands. In addition, the highly connected multinuclear SBUs are potential candidates of highly connected nodes complementary to the multitopic ligand, when aiming at highly connected robust frameworks. Furthermore, the custom-designed organic ligand, owing to their inherent functional features, can enrich and enhance the performances of MOFs' blueprints. In a nutshell, the custom design of organic ligands and beyond, which lays the primary foundation for controlling the SBUs, plays an integrative role in for the design and synthesis of MOF networks.

FUNDING

REFERENCES

1. (a) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, 38, 1213–1214; (b) MacGillivray, L. R. *Metal-Organic Frameworks: Design and Application*; John Wiley & Sons: Hoboken, NJ, 2010; (c) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, 112, 673–674; (d) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, 341, 1230444.

2. (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, 423, 705–714; (b) Qiu, S.; Zhu, G. *Coord. Chem. Rev.* **2009**, 253, 2891–2911; (c) Lu, W.; Wei, Z.; Gu, Z.-Y.; Liu, T.-F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle III, T.; Bosch, M.; Zhou, H.-C. *Chem. Soc. Rev.* **2014**, 43, 5561–5593.

3. (a) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, 112, 675–702; (b) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, 295, 469–472; (c) Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towne, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M. *Science* **2010**, 327, 846–850.

4. (a) Ma, S.; Zhou, H.-C. *Chem. Commun.* **2010**, 46, 44–53; (b) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim D.-W. *Chem. Rev.* **2012**, 112, 782–835; (c) Wu, H.; Gong, Q.; Olson, D. H.; Li, J. *Chem. Rev.* **2012**, 112, 836–868; (d) He, Y.; Zhou, W.; Qian G.; Chen B. *Chem. Soc. Rev.* **2014**, 43, 5657–5678.

5. (a) Xiang, S.-C.; Zhang, Z.; Zhao, C.-G.; Hong, K.; Zhao, X.; Ding, D.-R.; Xie, M.-H.; Wu, C.-D.; Das, M. C.; Gill, R.; Mark Thomas, K.; Chen, B. *Nature Commun.* **2011**, 2, 204; (b) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, 112, 724–781; (c) Li, J.-R.;

Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, 112, 869–932; (d) Barea, E.; Montoro, C.; Navarro, J. A. R. *Chem. Soc. Rev.* **2014**, 43, 5419–5430.

6. (a) Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, 110, 4606–4655; (b) Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, 112, 1196–1231; (c) Dhakshinamoorthy, A.; Garcia, H. *Chem. Soc. Rev.* **2014**, 43, 5750–5765; (d) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. *Chem. Soc. Rev.* **2014**, 43, 6011–6061.

7. (a) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. *Chem. Rev.* **2012**, 112, 1105–1125; (b) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. *Chem Rev.* **2012**, 112, 1126–1162; (c) Hu, Z.; Deibert B. J.; Li, J. *Chem. Soc. Rev.* **2014**, 43, 5815–5840.

8. (a) Bétard, A.; Fischer, R. A. *Chem. Rev.* **2012**, 112, 1055–1083; (b) Stavila, V.; Talin, A. A.; Allendorf, M. D. *Chem. Soc. Rev.* **2014**, 43, 5994–6010; (c) Ramaswamy, P.; Wong, N. E.; Shimizu, G. K. H. *Chem. Soc. Rev.* **2014**, 43, 5913–5932.

9. Gao, W.-Y.; Chrzanowski, M.; Ma, S. *Chem. Soc. Rev.* **2014**, 43, 5841–5866.

10. (a) Goldberg, I. *Chem. Commun.* **2005**, 1243–1254; (b) Goldberg, I. *Cryst. Eng. Comm.* **2008**, 10, 637–645; (c) DeVries, L. D.; Choe, W. *J. Chem. Crystallogr.* **2009**, 39, 229–240.

11. (a) Nakamura, Y.; Aratani, N.; Osuka, A. *Chem. Soc. Rev.* **2007**, 36, 831–845; (b) Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guilard, R.; Stern, C. *Chem. Rev.* **2009**, 109, 1659–1713; (c) Drain, C. M.; Varotto, A.; Radivojevic, I. *Chem. Rev.* **2009**, 109, 1630–1658.

12. Wang, X.-S.; Meng, L.; Cheng, Q.; Kim, C.; Wojtas, L.; Chrzanowski, M.; Chen, Y.-S.; Zhang, X. P.; Ma, S. *J. Am. Chem. Soc.* **2011**, 133, 16322–16325.

13. (a) Tranchemontagne, D. J.; Ni, Z.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem. Int. Ed.* **2008**, 47, 5136–5147; (b) Li, J.-R.; Zhou, H.-C. *Nature Chem.* **2010**, 2, 893–898.

14. (a) Perry, J. J.; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, 38, 1400–1417; (b) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, 130, 1833–1835.

15. Wang, X.-S.; Chrzanowski, M.; Gao, W.-Y.; Wojtas, L.; Chen, Y.-S.; Zaworotko, M. J.; Ma, S. *Chem. Sci.* **2012**, 3, 2823–2827.

16. (a) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, 389, 469–472; (b) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509–518; (c) Inokuma, Y.; Arai, T.; Fujita, M. *Nature Chem.* **2010**, 2, 780–783; (d) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, 111, 6810–6918; (e) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, 113, 734–777.

17. Tranchemontagne, D. J.; Mendoza-Cortes, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, 38, 1257–1283.

18. (a) Schoedel, A.; Zaworotko, M. J. *Chem. Sci.* **2014**, 5, 1269–1282; (b) Li, M.; Li, D.; O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2014**, 114, 1343–1370.

19. (a) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H.-C. *Angew. Chem. Int. Ed.* **2010**, 49, 5357–5361; (b) Farha, O. K.; Yazaydın, A. O.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nature Chem.* **2010**, 2, 944–948.

20. (a) Ma, L.; Mihalcik, D. J.; Lin, W. *J. Am. Chem. Soc.* **2009**, 131, 4610–4612; (b) Lu, W.; Yuan, D.; Makal, T. A.; Li, J.-R.; Zhou, H.-C. *Angew. Chem. Int. Ed.* **2012**, 51, 1580–1584.

21. (a) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, 131, 8784–8786; (b) Zhang, J.-P.; Zhang, Y.-B.; Lin, J.-B.; Chen, X.-M. *Chem. Rev.* **2012**, 112, 1001–1033.

22. (a) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, 309, 2040–2042; (b) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A. *J. Am. Chem. Soc.* **2008**, 130, 13850–13851; (c) Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, 136, 4369–4381.

23. Gao, W.-Y.; Cai, R.; Meng, L.; Wojtas, L.; Zhou, W.; Yildirim, T.; Shi, X.; Ma, S. *Chem. Commun.* **2013**, 49, 10516–10518.

24. Gao, W.-Y.; Yan, W.; Cai, R.; Meng, L.; Salas, A.; Wang, X.-S.; Wojtas, L.; Shi, X.; Ma, S. *Inorg. Chem.* **2012**, 51, 4423–4425.

25. (a) Meunier, B. *Chem. Rev.* **1992**, 92, 1411–1456; (b) Che, C.-M.; Lo, V. K.-Y.; Zhou, C.-Y.; Huang, J.-S. *Chem. Soc. Rev.* **2011**, 40, 1950–1975.

26. Meng, L.; Cheng, Q.; Kim, C.; Gao, W.-Y.; Wojtas, L.; Cheng, Y.-S.; Zaworotko, M. J.; Zhang, X. P.; Ma, S. *Angew Chem. Int. Ed.* **2012**, 51, 10082–10085.

27. Cairns, A. J.; Perman, J. A.; Wojtas, L.; Kravtsov, V. C.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2008**, 130, 1560–1561.

28. Gao, W.-Y.; Yan, W.; Cai, R.; Williams, K.; Salas, A.; Wojtas, L.; Shi, X.; Ma, S. *Chem. Commun.* **2012**, 48, 8898–8900.

29. (a) Kondo, M.; Okubo, T.; Asami, A.; Noro, S.; Yoshitomi, T.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Seki, K. *Angew. Chem. Int. Ed.* **1999**, 38, 140–143; (b) Dybtsev, D. N.; Chun, H.; Kim, K. *Angew. Chem. Int. Ed.* **2004**, 43, 5033–5036; (c) Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. *Angew. Chem. Int. Ed.* **2006**, 45, 1390–1393.

30. Lindoy, L. F.; Park, K.-M.; Lee, S. S. *Chem. Soc. Rev.* **2013**, 42, 1713–1727.

31. Gao, W.-Y.; Niu, Y.; Chen, Y.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S. *Cryst. Eng. Comm* **2012**, 14, 6115–6117.

32. Gao, W.-Y.; Chen, Y.; Niu, Y.; Williams, K.; Cash, L.; Perez, P. J.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S. *Angew. Chem. Int. Ed.* **2014**, 53, 2615–2619.

33. (a) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem. Int. Ed.* **2005**, 44, 4745–4749; (b) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schroder, M. *Angew. Chem. Int. Ed.* **2006**, 45, 7358–7364; (c) Lee, Y.-G.; Moon, H. R.; Cheon, Y. E.; Suh, M. P. *Angew. Chem. Int. Ed.* **2008**, 47, 7741–7745; (d) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, 130, 1012–1016.