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Two Principles of Reticular Chemistry Uncovered in a Metal–Organic Framework of Heterotritopic Linkers and Infinite Secondary Building Units

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Supporting Information

ABSTRACT: Structural diversity of metal–organic frameworks (MOFs) has been largely limited to linkers with at most two different types of coordinating groups. MOFs constructed from linkers with three or more nonidentical coordinating groups have not been explored. Here, we report a robust and porous crystalline MOF, $Zn_3(PBSP)_2$ or MOF-910, constructed from a novel linker PBSP (phenylyne-1-benzoate, 3-benzosemiquinonate, 5-oxidopyridine) bearing three distinct types of coordinative functionality. The MOF adopts a complex and previously unreported topology termed **tto**. Our study suggests that simple, symmetric linkers are not a necessity for formation of crystalline extended structures and that new, more complex topologies are attainable with irregular, heterotopic linkers. This work illustrates two principles of reticular chemistry: first, selectivity for helical over straight rod secondary building units (SBUs) is achievable with polyheterotopic linkers, and second, the pitch of the resulting helical SBUs may be fine-tuned based on the metrics of the polyheterotopic linker.

To date, the majority of metal–organic frameworks (MOFs) have been built from highly symmetric linkers that consist of one or two types of coordinating groups.[1] It is believed that symmetry and uniformity of coordinating groups in the linker facilitate assembly into a crystalline extended structure of high symmetry.[2] One reason for this prevailing view is that if all the coordinating groups are identical, conditions in which bond formation to the metals is reversible can be achieved for all of these groups simultaneously so that they ultimately reticulate into a crystalline rather than amorphous phase.[3] Also, a highly symmetric linker has a greater probability of aligning to form a periodic structure since its ligating groups are the same and therefore easily interchangeable during crystal growth. Thus, it has been an article of faith in MOF chemistry that symmetric building units should be employed for the synthesis of highly symmetric extended structures. However, our work demonstrates that infinite secondary building units (SBUs) accommodate irregular polytopic linkers into a crystalline extended structure. By examining the novel MOF described here in the context of the MOF literature, we uncovered two principles of reticular chemistry involving selectivity of helical over straight rod SBUs and control of SBU helicity.

The tritopic linker PBSP (phenylyne-1-benzoate, 3-benzosemiquinonate, 5-oxidopyridine, Figure 1a) lacks symmetry elements (C_1 point group) and supports three different coordinative functionalities: benzoate, semiquinonate, and pyridonate. We linked it with Zn(II) into a highly symmetric 3D porous framework based on infinite SBUs (rods) formulated as $Zn_3(PBSP)_2$ and termed MOF-910. Single-crystal X-ray diffraction (XRD) revealed that this MOF crystallizes in the trigonal space group $R\overline{3}c$ and comprises helical 1D SBUs that form hexagonal channels 21 Å in diameter (Figure 1b). MOF-910 adopts a new topology, termed **tto**, and it is the first example of a MOF based on a heterotritopic linker. Construction of MOFs from less symmetric linkers with multiple different coordinating groups is a new method to target helical rod MOFs in which the helical pitch is predetermined by the linker. MOFs based on rod-like SBUs are desirable due to their resistance to interpenetration, potential for isoreticular expansion, and breathing functionality.[4] While the discovery of helical rather than straight rod MOFs relies on trial and error when symmetric, homotopic molecules serve as the linkers,[5] we find that MOFs based on helical SBUs are preferred for syntheses with less symmetric linkers due to the nonuniform distances between the coordinating groups. The power to impart helicity to SBUs is promising for the design of noncentrosymmetric MOFs for asymmetric catalysis and chiral resolution.[6]

The three distinct coordinative functionalities of the PBSP linker were chosen for their propensities to bind in a bidentate or bridging fashion and for their high number of possible coordination modes.[7] While benzoate moieties are ubiquitous in MOF chemistry, semiquinonate or catecholate moieties were incorporated into very few 3D MOFs.[8] A small number of MOFs are based on 2-hydroxypyrimidine,[9] but the less-symmetric derivative 2-pyridone had yet to be incorporated into an extended framework. We find that stark differences between the pK_a values of these three groups (4.2, 9.5, and 11)[10] do not preclude MOF formation by one-pot solvothermal conditions.

The neutral, closed-shell form of the heterotritopic linker, termed PBCP (phenylyne-1-benzoic acid, 3-catechol, 5-

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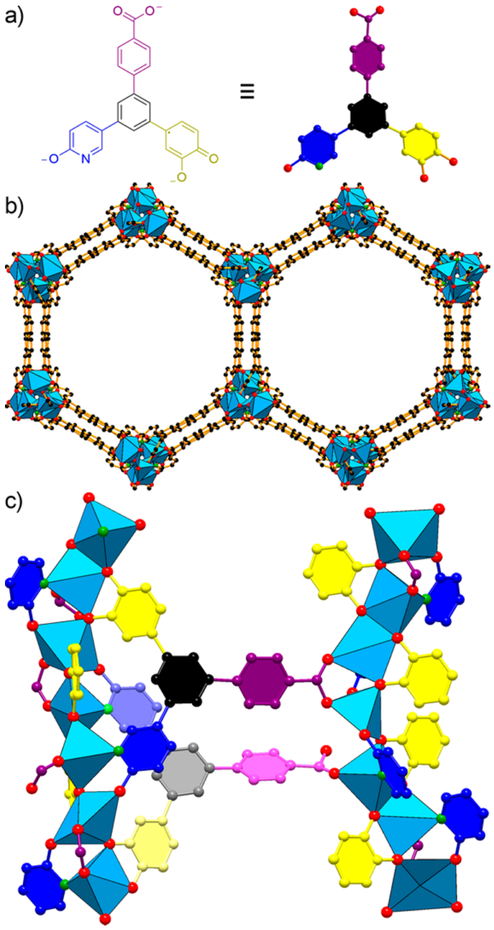

Figure 1. (a) PBSP heterotritopic linker. (b) Structure of MOF-910 viewed along the *c*-axis in the direction of hexagonal channels. Disorder in benzoate moieties is omitted for clarity. (c) Coordination of PBSP heterotritopic linker to Zn ions viewed perpendicular to channels. Zn, light blue; C, black; O, red; N, green; benzoate rings, purple; semiquinonate rings, yellow; pyridonate rings, dark blue. Hydrogen atoms are omitted for clarity.

pyridone), was attained in three synthetic steps requiring one column purification (Schemes S1−S3). Solvothermal synthesis with PBCP and $ZnCl_2$ under basic conditions yielded 100 μm hexagonal needles of MOF-910 (Scheme S4). Structural elucidation by single-crystal XRD revealed MOF-910 belongs to the space group $R\bar{3}c$ (No. 167) with lattice parameters $a = b = 47.239(2)$ Å and $c = 27.122(1)$ Å. The heterotritopic linker crystallizes in a space group belonging to the Laue class $\bar{3}m$ despite the lack of symmetry usually imparted by the linker in MOF syntheses.[11]

Although the three ligating groups are quite different in acidity and MOF synthesis commences with the linker in its neutral, protonated form, each of the three coordinating groups forms bonds to metal ions in the extended structure. The asymmetric unit includes one linker molecule and two distinct Zn atoms, one on a general position in the unit cell and the other on a two-fold rotational axis. This composition corresponds to the chemical formula $Zn_3(PBSP)_2$. The metal to linker molar ratio and the knowledge that +2 is the only common oxidation state of Zn imply the linker exists as a trianion in the MOF structure. This charged state is reasonable given that catechol-based linkers undergo aerobic oxidation to semiquinone radicals under similar MOF synthesis conditions.[12] MOF channels are lined with a double wall built from pairs of closely associated linkers (Figure 1b). Gaps between each pair of linkers create 4.1 Å windows in the double wall. The 1D SBUs exist in equal populations of left- and right-handed helical conformations such that the overall structure is centrosymmetric.

The presence of three distinct bidentate coordinating groups in the linker makes it unlikely that all metal ions in the structure would exist in a single type of coordination environment. Indeed, the Zn ions of this MOF adopt two configurations distinct in the metal−link bonds involved. In two-thirds of the cases, each Zn ion has three benzosemiquinonate oxygens, one carboxylate oxygen, and one pyridonate nitrogen in its inner coordination sphere. The other third of the Zn ions are each bound by two benzosemiquinonate oxygens, two pyridonate oxygens, and one carboxylate oxygen. The linker is low enough in symmetry that the three coordinating groups are non-interchangeable in the MOF structure. Within each closely stacked pair of linkers that lines the channels, the pyridonate and benzosemiquinonate moieties of one linker align with the pyridonate and semiquinonate moieties of the partner linker, while benzoate moieties of the two linkers align together (Figure 1c). This preferential association could bring cooperative side chains on linkers together in space in a controllable manner to direct segregation of functionalities in multivariate MOF systems.[13]

Preferential alignment of coordinating groups also instills disparate rigidity. While the pyridonate and benzosemiquinonate moieties are inflexible since they form two points of attachment to the same SBU, the benzoate moiety of each linker is disordered because it is the single point of attachment to the opposing SBU. Specifically, each benzoate moiety adopts one of two equally likely conformations. In one conformation, the benzoate ring is coplanar with the central aromatic ring to which it is bonded, and the carboxylate binds to two Zn ions in a bridging fashion. In the other conformation, the benzoate ring is tilted with respect to the central aromatic ring, and a single carboxylate oxygen is coordinated to a Zn ion (Figure 1c).

Additional analytical techniques performed on MOF-910 corroborate the structure solved by single-crystal XRD. Powder XRD substantiates the bulk phase purity (Figure S7). Elemental analysis of MOF-910 after activation to remove guests from the pores supports the chemical formula as $Zn_{1.5}(PBSP)\cdot 2H_2O$ (calcd C, 56.36%; H, 2.96%; N, 2.74%; found C, 54.48%; H, 2.77%; N, 3.09%). The symmetric resonance reflecting a *g* factor of 2.050 in the solid-state electron paramagnetic resonance spectrum is consistent with the characterization of the linker as a monoradical semiquinonate species (Figure S9). Fourier transform infrared spectroscopy verifies each of the MOF's six ligating atoms is deprotonated (Figure S10). The ^{1}H NMR spectrum of MOF-910 postdigestion exclusively exhibits resonances attributable to the linker (Figure S5). The absence of any resonances due to counterions, such as triethylammonium or dimethylammonium, confirms the chemical composition as a neutral framework with a fully deprotonated trianionic linker. Thermogravimetric analysis measured in air establishes high thermal stability of MOF-910. The residual wt % of ZnO reflects the chemical formula (Figure S11). Framework decomposition does not begin until 320 °C. Greater basicity of benzosemiquinonate and pyridonate compared to that of carboxylates of typical linkers likely contributes to the high thermal stability of MOF-910.[14] Maintenance of crystallinity after suspension in pH 4 and pH 8 aqueous solutions and a number of organic solvents (Figure S8) demonstrates the good chemical stability of MOF-910.

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The N_2 adsorption isotherm at 77 K confirms permanent porosity of MOF-910 and that its pores are free of counterions. The type IV profile and step at a relative pressure of $P/P_0 = 0.075$ verifies the presence of a mesopore (Figure S12).[15] A Brunauer–Emmett–Teller surface area of 2120 $m^2 g^{-1}$ was derived from the sorption isotherm and matches the expected value of 2100 $m^2 g^{-1}$ determined from the single-crystal structure. The calculated pore size distribution indicates a single pore width that matches the van der Waals pore diameter of 21 Å determined by single-crystal XRD (Figure S13).

We describe how MOF-910 uncovers two principles of reticular chemistry. Topologically, MOF-910 is an embedding of a new net with the RCSR symbol **tto** (triangles, **t**etrahedra, **o**ctahedra).[16] The structure has six points of extension: three located within the central aromatic ring of the linker and three located at the branching points of each bidentate coordinating group. Connecting the three points of extension within the central ring of each linker reduces this part of each linker to a triangle (Figure 2a). Connecting the points of extension within each coordinating group to those of neighboring linkers reduces the SBUs to helices in which octahedra share faces with the neighboring tetrahedra and tetrahedra share edges with other tetrahedra (Figure 2b). MOF-910 is the first structure with a topology based on an SBU of this kind. Although the high number of nodes makes this net complex, it has high symmetry ($R\bar{3}c$, Figure 2c).

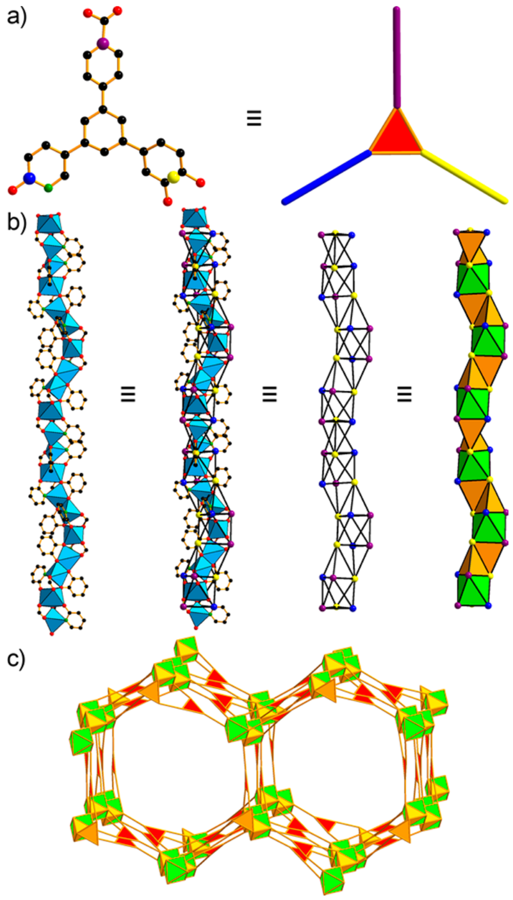

Figure 2. Deconstruction of MOF-910 for topological analysis. (a) PBSP heterotritopic linker is reduced to a triangle; (b) points of extension are connected to reduce SBU to a helical rod composed of octahedra alternating with pairs of tetrahedra; (c) **tto** topology.

Despite two decades of research, the field of MOFs remains lacking in the ability to predict and target structures based on building units.[17] In contrast to the organic constituents of MOFs, which are based on linkers that serve as preformed building units that remain largely unchanged during MOF synthesis, a major challenge is control of the metal-based components of MOFs. Recent efforts to target MOFs based on a specific discrete SBU rely on the presynthetic growth of metal clusters prior to linkage into an extended structure.[18] However, such a strategy is not possible with infinite SBUs. Selectivity for a MOF built from a particular type of infinite SBU is an unsolved problem.

Analysis of MOF-910 provides insights to address these challenges. The metrics and coordination modes of the three ligating groups of the PBSP linker are markedly dissimilar, yet the linker reticulates into a symmetric, porous, and crystalline extended structure by way of infinite SBUs. The structure consists of a single type of infinite SBU that satisfies the disparate requirements of the three links (Figure 2b,c). Due to the lack of trigonal symmetry in the PBSP linker, the distance between the semiquinonate and pyridonate coordinating groups is shorter than that from either moiety to the carboxylate. For this reason, the semiquinonate and pyridonate bond to Zn ions of the same 1D SBU. This two-point attachment of the linker to a single SBU directs the formation of helical rather than straight rods. Coordination behavior of this heterotritopic linker contrasts with that of BTB (benzene-1,3,5-triyltribenzoate), a higher symmetry tritopic linker with a three-fold rotational axis. BTB forms straight rods rather than helices since no two coordinating groups bind to the same SBU (Figure 3a).[19] The PBSP heterotritopic linker reported here is more similar to BPT (biphenyl-3,4′,5-tricarboxylate), a desymmetrized derivative of BTB that forms straight rods when each of the three carboxylates coordinates to a different SBU[20] and helical rods when the two proximal carboxylates bind to the same SBU (Figure 3b).[21] Only two other MOFs, Fe(BDC) (BDC = 1,4-benzenedicarboxylate) and MOF-73, feature SBUs similar to those of MOF-910

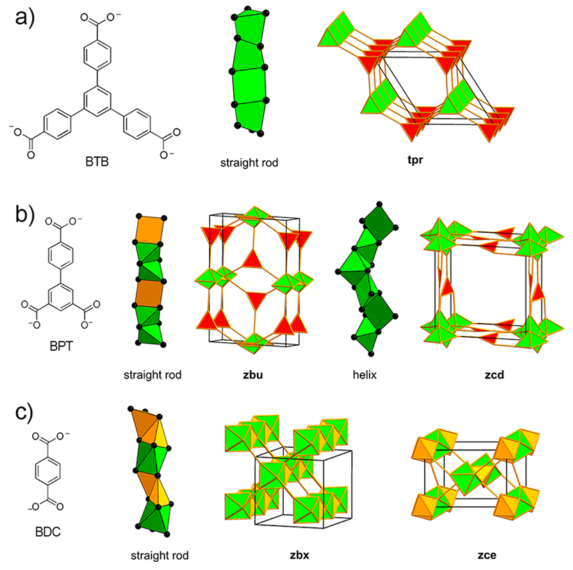

Figure 3. Effect of linker symmetry on SBU helicity. (a) Tritopic BTB produces straight rods (MIL-103). (b) Desymmetrized derivative of BTB produces straight rods [$Cd_3(BPT)_2(DMF)_2$] or helices [$Yb(BPT)(H_2O)$]. (c) Ditopic BDC produces straight rods [Fe(BDC) and MOF-73].

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comprising pairs of tetrahedra alternating with octahedra (Figure 3c). These SBUs are straight rather than helical rods because the linkers are ditopic rather than nontrigonal tritopic, as with the PBSP heterotritopic linker.[22,23] We identify a tenet of reticular chemistry from this work in the context of the MOF literature: *choice of a polytopic linker in which the distances between the coordinating groups are nonuniform facilitates formation of helical over straight rod SBUs.*

Another design element is the pitch of a helical SBU. Intramolecular distance between the coordinating atoms of the semiquinonate and pyridonate define the pitch of the MOF-910 SBUs as 27.122(1) Å or one unit cell along the *c*-axis. Helices are three-fold symmetric because the six linkers that provide the 12 coordinating groups present in one complete turn propagate in three directions. Four-fold helices would be possible with a greater semiquinonate to pyridonate distance. A shorter distance between the semiquinonate and pyridonate could yield a single-walled structure with three- or four-fold symmetry. This realization elucidates a second guiding principle of reticular chemistry: *the distance between the two proximal coordinating groups of a polyheterotopic defines the pitch of a helical SBU.* The two principles of reticular chemistry exposed by MOF-910 and described here are supported by a comprehensive analysis of known rod MOFs.[24]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07267.

Synthesis, NMR, SEM, XRD, EPR, IR, TGA, N_2 adsorption, and optical microscopy data (PDF)

Single-crystal data for MOF-910 (CIF)

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Notes

The authors declare no competing financial interest.

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