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COMMUNICATION

Functional group effects on metal–organic framework topology†‡

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Functionalization of the ligand 1,3,5-tris(4-carboxyphenyl)benzene (H$_3$BTB) has been realized with methoxy (H$_3$BTB–[OMe]$_3$) and hydroxy (H$_3$BTB–[OH]$_3$) groups. Combining H$_3$BTB–[OMe]$_3$ and Zn(II) results in the formation of the first isostructural, functionalized analogue of MOF-177 (MOF-177–OMe), while the combination of H$_3$BTB–[OH]$_3$ and Zn(II) generates a rare, interpenetrated pcu-e framework.

Metal–organic frameworks (MOFs) continue to be one of the most highly investigated porous materials for a wide range of applications such as gas storage,[1,2] catalysis,[3] and chemical sensors.[4] Such applications may benefit from MOF materials due to the ability to alter their chemical composition, functionality, and molecular dimensions systematically without changing their underlying topology. The ability to control MOF topology was termed reticular synthesis by Yaghi and co-workers.[5] For example, Yaghi and co-workers pioneered the synthesis of cubic IRMOFs (IRMOFs = isoreticular MOFs) with different functional groups (*e.g.*, bromo, amino, naphthyl), and with increased dimensions (*e.g.*, biphenyl).[6] Notably, Yaghi and co-workers have also showed the ability to incorporate multiple functional groups into one single IRMOF crystal.[7] One crucial factor of reticular synthesis relies on the fact that the functional groups do not alter the topology of the desired MOF, which occurs most often when the functional groups can interact with metal ions in a way that would interfere with MOF synthesis. Reticular synthesis has been successfully applied to many MOF systems, including pillared paddlewheel MOFs,[8,9] UMCM (UMCM = University of Michigan Crystalline Materials),[10] UiO (UiO = University of Olso),[11] and others.[12]

In recent years, multitopic ligands have been of interest due to their potential to generate MOFs that have high surface areas for applications in gas storage.[13–15] Among these multitopic ligands, 1,3,5-tris(4-carboxyphenyl)benzene (H$_3$BTB) has been studied extensively by Matzger[16] and others to generate MOFs with high porosity.[17,18] For example, the combination of H$_3$BTB and Zn(II) generated the high surface area MOF-177 (BET surface area ~4500 m^2 g^{-1}).[19] Additionally, the copolymerization of

H$_3$BTB together with various dicarboxylate ligands and Zn(II) has produced a series of high surface area UMCM frameworks (UMCM-1, UMCM-2 with BET surface areas > 4000 m^2 g^{-1}).[20,21] Thus, the functionalization of H$_3$BTB is an attractive target for modifying the properties of these highly porous MOFs.

Only a few studies of modified H$_3$BTB ligands have been reported. In most cases, these studies extended the length of the H$_3$BTB ligand or functionalized the central benzene ring of H$_3$BTB.[22–24] Only one example of a functionalized H$_3$BTB ligand[25] with chiral oxazolidinone groups on the three benzoic acid aryl rings has been described, which formed a family of chiral MOFs with Zn(II). However, these chiral H$_3$BTB analogues did not produce a framework that was isostructural with MOF-177. The limited number of reports on functionalized H$_3$BTB ligands is likely due, in part, to the synthetic challenges of making derivatized analogues. Herein, we report the synthesis of functionalized H$_3$BTB ligands with methoxy (H$_3$BTB–[OMe]$_3$) and hydroxy (H$_3$BTB–[OH]$_3$) (Fig. 1) groups. These ligands were prepared *via* Pd-mediated cross-coupling reactions. The combination of H$_3$BTB–[OMe]$_3$ and Zn(II) allows for the formation of the first functionalized MOF-177 analogue, MOF-177–OMe. In contrast, the combination of H$_3$BTB–[OH]$_3$ and Zn(II) generates the first functionalized interpenetrated pcu-e (primitive cubic unit expansion) framework,[26,27] wherein the hydroxy groups remain free (not coordinated to the SBUs).

In the earlier report of Kaskel and co-workers,[25] the functionalization of H$_3$BTB was obtained *via* the trimerization of an acetophenone derivative. In our study, the functionalization of H$_3$BTB is achieved by the Pd cross-coupling reaction between 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and methyl 4-iodo-2-methoxybenzoate (Scheme S1, ESI‡), the product of which can be used to obtain both H$_3$BTB–[OMe]$_3$ and H$_3$BTB–[OH]$_3$. In an attempt to make isostructural functional MOF-177, H$_3$BTB–[OMe]$_3$ was combined with Zn(II) in *N,N*-dimethylformamide (DMF) under solvothermal conditions, which produced the desired MOF-177–OMe as clear colorless
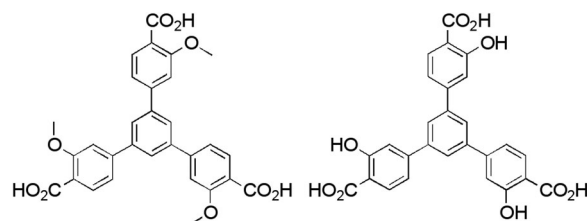
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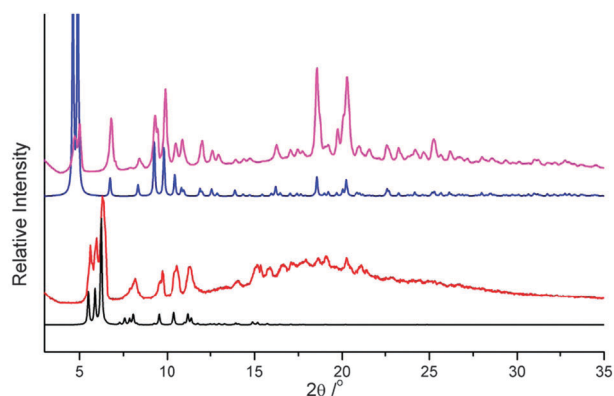

Fig. 1 Molecular structures of H$_3$BTB–[OMe]$_3$ (left) and H$_3$BTB–[OH]$_3$ (right).

Fig. 2 PXRD patterns of MOF-177 (simulated, black), MOF-177–OMe (red), Zn(II)–MOF–BTB[OH]$_3$ (simulated, blue), and Zn(II)–MOF–BTB[OH]$_3$ (magenta).

hexagonal crystals (Fig. S1, ESI‡). H$_3$BTB–[OH]$_3$ combined with Zn(II) under the same reaction conditions did not yield any crystals. Interestingly, the combination of H$_3$BTB–[OH]$_3$ and Zn(II) in DMF and H$_2$O (2 : 0.1 DMF : H$_2$O ratio) under solvothermal condition yields clear colorless crystals suitable for single-crystal X-ray diffraction analysis (XRD). This new phase, designated Zn(II)–MOF–BTB[OH]$_3$ was not isostructural to MOF-177.

The powder X-ray diffraction (PXRD) analysis of MOF-177–OMe verifies the isostructural relationship when compared to the parent MOF-177 material (Fig. 2). Although large single crystals of MOF-177–OMe were produced (Fig. S1, ESI‡), the crystals only diffracted to low resolution (~1.7 Å), limiting the data analysis to determination of the cell parameters. Nevertheless, the unit cell parameters of MOF-177–OMe are very similar to MOF-177,[19] and the space group assignment is identical (Table S1, ESI‡). Therefore, the topology of MOF-177–OMe, being the same as MOF-177, is a (6,3)-coordinated net with the 6-fold vertex centered on the Zn$_4$O SBUs and the 3-fold vertex centered on the BTB–[OMe]$_3$ ligands. A high Brunauer–Emmett–Teller (BET) surface area of ~3900 m^2 g^{-1} was determined for MOF-177–OMe, which also supports the formation of the isostructural material.

PXRD analysis of Zn(II)–MOF–BTB[OH]$_3$ reveals the framework possesses an entirely different structure when compared to MOF-177 (Fig. 2). Single-crystal XRD shows the structure of Zn(II)–MOF–BTB[OH]$_3$ has a zinc oxide SBU with an overall molecular formula of [Zn$_2$(OH)](BTB–[OH]$_3$)$_2$(DMF) (Fig. 3). The SBUs of this framework consist of four Zn(II) ions linked together by hydroxy bridges with the formula Zn$_4$(OH)$_2$. While the two terminal Zn(II) ions of the SBUs are 6-coordinate, bound by the BTB–[OH]$_3$ ligands, hydroxy bridges, and DMF molecules, the other two Zn(II) ions are 5-coordinate with donation from the hydroxy bridges and BTB–[OH]$_3$ ligands. The SBUs of the Zn(II)–MOF–BTB[OH]$_3$ are coordinated by eight different BTB–[OH]$_3$ ligands, where six of them act as bridging, bidentate ligands, and the other two act as monodentate donors (Fig. 3). The non-coordinated oxygen atoms of the two monodentate carboxylate donors from BTB–[OH]$_3$ interact with the hydroxy bridges via hydrogen bonding forming a six-membered ring (Fig. 3, O–H–O ~ 1.8 Å). Charge balance indicates that the SBU is overall a dianion, thus, counter cations must be present
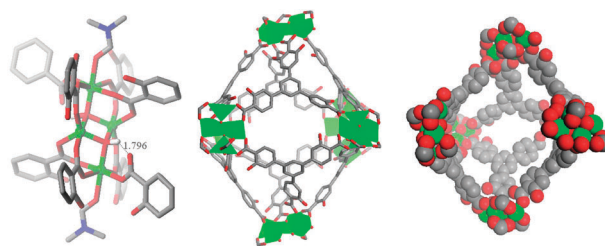

Fig. 3 Structure of the SBU of Zn(II)–MOF–BTB[OH]$_3$ (left), view of the octahedral cage (middle, SBUs are displayed in polyhedron style), and space-filling model of the octahedral cage with the removal of two BTB–[OH]$_3$ ligands, showing the void space of the cage (right). Hydrogen atoms and some disordered hydroxyl groups are omitted for clarity. Color scheme: Carbon (grey), nitrogen (blue), oxygen (red), and zinc (green).

in the framework, but were not located in the XRD analysis. The underlying topology of the framework is an (8,3)-coordinated net with the 8-fold vertex centered on the SBU and the 3-fold vertex centered on the BTB–[OH]$_3$ ligands.

Examination of Zn(II)–MOF–BTB[OH]$_3$ shows that the structure is comprised of large pseudo-octahedral cages with the BTB–[OH]$_3$ ligands acting as the faces and the SBUs acting as the vertices of the cages (Fig. 3). These cages are connected together via the vertices to form a cubic framework that is classified as a pcu-e net (Fig. 4).[26] Interestingly, Zn(II)–MOF–BTB[OH]$_3$ is comprised of two frameworks, which are interpenetrated and interact with each other via π–π stacking between the BTB–[OH]$_3$ ligands (Fig. 5). Only two MOFs have been reported to have the similar interpenetrated, pcu-e net topology found with Zn(II)–MOF–BTB[OH]$_3$. Two early reports by Robson show that combining Zn(II) or Cu(I) together with the monodentate, tritopic 2,4,6-tri(4-pyridyl)-1,3,5-triazine) ligands produces interpenetrated, pcu-e nets.[28,29] The topology of Zn(II)–MOF–BTB[OH]$_3$ provides an example of the first, rare functionalized interpenetrated pcu-e framework, as the hydroxy groups on the ligand are not coordinated to the SBUs, but remain free in the pores of the MOF (Fig. 4). The pseudo-octahedral cages are large enough to accommodate guest molecules (Fig. S3, ESI‡, ~2700 Å^3); however, guests within the cage were disordered in the XRD analysis and could
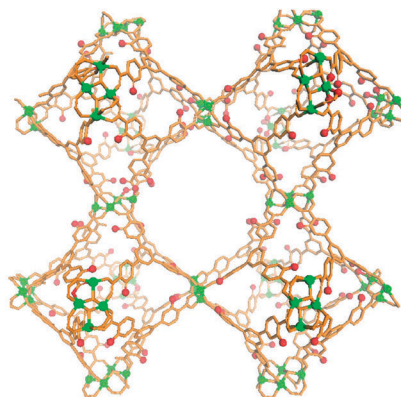

Fig. 4 Structure of one pcu-e net of Zn(II)–MOF–BTB[OH]$_3$, consisting of pseudo-octahedral cages. The framework is highlighted in orange, free hydroxy groups are displayed as red balls, and Zn atoms are displayed as green balls.
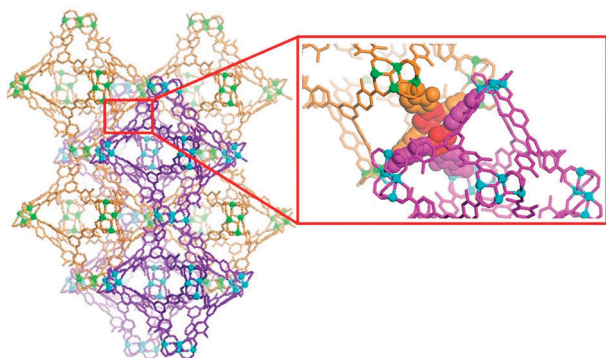
Fig. 5 Structure of the two interpenetrated nets of Zn(II)–MOF–BTB[OH]₃, highlighting the π–π stacking. The first net is highlighted in orange with Zn atoms displayed as green balls, and the second net is highlighted in purple with Zn atoms displayed as cyan balls.

not be definitively identified. Initial BET surface area measurements of Zn(II)–MOF–BTB[OH]₃ showed the material to be non-porous to dinitrogen; however, additional efforts to activate this material are underway (*e.g.* supercritical CO_2).

In conclusion, we present a route to functionalized tritopic H_3BTB ligands with either methoxy or hydroxy functional groups. While the combination of H_3BTB–[OMe]₃ and Zn(II) generates the first functionalized MOF-177, the combination of H_3BTB–[OH]₃ and Zn(II) allows the formation of the first functionalized interpenetrated pcu-e framework. These two H_3BTB ligands are the initial, necessary steps to obtaining functionalized, isostructural analogues of high surface area MOFs, such as MOF-177, UMCM-1, and others. These ligands may also provide a chemical handle for PSM approaches to further modifying these MOFs. Finally, the similar binding motif between H_3BTB–[OH]₃ and 2,5-dihydroxyterephthalic acid (DHTA) may also serve to generate MOFs with open metal site rich topologies such as MOF-74.[30] These studies will be reported in due course.

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