

Two Azolium Rings Are Better Than One: A Strategy for Controlling Catenation and Morphology in Zn and Cu Metal–Organic Frameworks

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Supporting Information

ABSTRACT: Four new azolium-containing metal—organic frameworks (MOFs) have been synthesized, where the azoliums are potential organocatalyst precursors. Modifying the number of azoliums on a standard biphenyl dicarboxylate strut affects the morphology or the degree of interpenetration in two representative types of MOFs: NbO-type Cu-paddlewheel 2D sheets and cubic IRMOFs.



Metal-organic frameworks (MOFs) have emerged as a Mpromising class of functional materials due to their microporosity, high internal surface area, and the ability to tune their structural and physical parameters.¹ These properties have led to the investigation of their application as materials for gas storage,² gas separation,³ and catalysis.⁴ In contrast to the numerous reports regarding the application of MOFs toward the goals listed above, there are far fewer reports on strategies for purifying these materials⁵ or for controlling their catenation (i.e., network interweaving or interpenetration). Nevertheless, a few strategies for regulating MOF catenation have been investigated, including "liquid-phase epitaxy",⁶ solvent or additive templating,⁷ solvent and/or concentration manipulation,⁸ and rational ligand design.⁹

The most widely reported means of controlling catenation is by either solvent or additive-directed templating. For example, Zhou and co-workers have used oxalic acid^{7a} as a templating agent and 1,10-phenanthroline^{7e} as a sterically demanding group occupying coordination sites usually reserved for solvent. In a related report, Su and co-workers were able to demonstrate catenation control by guest inclusion in Cd(II)/Mn(II) 2D networks.^{7c} Lin and co-workers have exploited the steric parameters of their solvent—dimethylformamide (DMF) vs diethylformamide (DEF)—to achieve catenation control.^{7b,d} A different approach was taken by Zhang et al.^{8b} and by Eddaoudi et al.,^{8a} who employed low concentrations along with temperature parameters to modulate interpenetration. These strategies constitute important advances, but it remains to be seen if there is broad generality across different linkers, metals, and topologies.

We (Farha, Hupp, and co-workers) have recently disclosed an orthogonal approach to influence catenation by ligand design.^{9a} Catenation can be influenced by modulating the size of substituents projected into the void space of certain MOF materials. This strategy has been successful across different strut types and even when incorporating large tetracarboxylate ligands.^{10,9a} We have been investigating incorporating azolium salts—*N*-heterocyclic carbine (NHC) precursors—into metal–organic

frameworks,¹¹ a goal that has attracted considerable interest.¹² While NHCs are versatile ligands for transition metals¹³ as well as organocatalysts in their own right,¹⁴ the potential application of coordination polymers containing these heterocyclic motifs is significant. Regarding their function as ligands, MOFs bearing NHCs could be functionalized with a metal of choice postsynthetically, yielding reusable heterogeneous transition metal catalysts with permanent microporosity. With respect to organocatalysis, NHCs immobilized in a MOF would not physically be capable of dimerization (a known nonproductive pathway under homogeneous conditions).¹⁵ Heterogeneous materials for catalysis bearing azolium salts have been reported, but these materials lack defined/rigid structure and/or suffer from low porosity.¹⁶ On the basis of our experience with homogeneous NHC catalysis, we envisioned that robust systems and increased turnover numbers might be possible with suitable azolium-MOF materials. With these goals, we have defined three objectives: (1) synthesize azolium salts capable of being incorporated into MOFs, (2) incorporate these unique, charged ligands into MOFs, and (3) utilize these metal-azolium frameworks as precursors for catalysts. Herein we report four new metalazolium framework (MAF) materials using struts that vary the number, size, and electrostatic charge of the "side arm" type functional groups. This approach in turn has led to a new tactic to control catentation or morphology.

In the course of our studies toward synthesizing catalytically active MAF materials, we prepared two bpdc (biphenyl dicarboxylate) based linkers with appended methyl imidazolium salts (Scheme 1; see the Supporting Information for more details). We set out to synthesize new materials for catalysis using 3 and 4. When 3 was combined with $Cu(NO_3)_2 \cdot 3H_2O$ in a 1:1 DMF/EtOH mixture at 110 °C, deep blue crystals with a

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Scheme 1. Preparation of Two bpdc Based Linkers with Appended Methyl Imidazolium Salts^{*a*}



^{*a*} Conditions: (a) NBS, AIBN, CCl₄, 90 °C; (b) 1-methylimidazole, CH₃CN, 80 °C; (c) 10 equiv of LiOH, 1:1 THF/H₂O, 23 °C. 60% yield over 3 steps for 3 (42% overall for 4).



Figure 1. Single crystal X-ray structures: Left: a subunit of NU-501 and view down the *c*-axis of the unit cell, with each of the two independent networks shown in a distinct color. Right: a subunit of NU-502 and view down the *c*-axis of the unit cell, with each of the two independent networks shown in a distinct color.

framework formula of $Cu_2(3) \cdot 2(DMF_x/EtOH_{1-x})$ (NU-501; NU = Northwestern University) were obtained after sitting overnight. Single crystal X-ray diffraction revealed these crystals to contain two independent sets of 2D sheets, each containing $Cu_2(CO_2)_4$ paddlewheel SBUs bridged by 3 (Figure 1), yielding a subunit similar to the one reported by Jeong and co-workers. While interesting, the catenation resulted in small pore size, thereby minimizing their potential utility in catalytic applications. We postulated that by projecting more sterically demanding groups into the pore (using strut 4), we could reduce the extent of catenation. Thus, combining 4 with $Cu(NO_3)_2 \cdot 3H_2O$ under identical reaction conditions as used to make NU-501 yielded deep blue crystals with a framework formula of $Cu_2(4) \cdot 2$ $(DMF_x/EtOH_{1-x})$ and designated NU-502. Single crystal X-ray diffraction revealed NU-502 to still contain two independent sets of 2D sheets and the same repeating unit as NU-501. However, NU-502 possesses a different morphology than NU-501 and contains much larger channels (ca. 13 Å across).

Powder X-ray diffraction (PXRD) likewise showed these materials to be distinct from one another (see Supporting Information). Apart from the crystallographic evidence, the



Figure 2. (A) Catenated repeating units of NU-503 and (B) PXRD of NU-503 (simulated in red, experimental in blue).

different morphology is apparent in TGA (thermogravimetric analysis) traces for NU-501 and NU-502. As anticipated, NU-502 exhibits greater mass loss (solvent DMF and EtOH molecules) than NU-501 between 25 and 275 $^{\circ}$ C (see Supporting Information). NU-501 loses approximately 25% of its weight before decomposition, whereas NU-502 loses roughly 60%. While we had succeeded in synthesizing a material (NU-502) with wide enough channels for the envisioned catalysis applications, we determined that amine and alkoxide bases (used for NHC generation) degraded the material—rendering it ineffective for catalysis.

We then sought to synthesize an analogue of a known highly porous MOF in hopes of accessing materials with pore sizes large enough for our envisioned catalysis and potentially increased stability. Toward this end, we hypothesized that when combined with $Zn(NO_3)_2 \cdot 6H_2O$ strut 3 would yield cubic networks with Zn₄O nodes, similar to the noncatenated material IRMOF-10,^{8a} since 3 is similar to bpdc but possesses more steric bulk. When we combined 3 with $Zn(NO_3)_2 \cdot 6H_2O$ in DMF and heated at 90 °C for 2 days, colorless block crystals with a framework formula of $Zn_4O(3)_3$ (NU-503) were observed. Single-crystal X-ray analysis revealed the crystals to comprise a catenated pair of networks, i.e. analogous to IRMOF-9 instead of IRMOF-10 (Figure 2). While we had succeeded in replicating a known MOF using our bpdc strut derivative, catenation precludes pore-based catalysis, since molecular substrates would not be able to reach internal catalytic sites. In hopes of producing an IRMOF-10 derivative, we combined 4 with $Zn(NO_3)_2 \cdot 6H_2O$ in DMF and heated at 90 °C for 2 days. Once again, colorless block crystals (NU-504) were obtained. However, these crystals did not furnish a satisfactory single crystal diffraction pattern.

Consequently, we turned to other techniques to characterize NU-504, seeking to determine if this material was in fact an IRMOF-10 analogue. PXRD revealed NU-504 to be distinct from NU-503 (Figure 3), and the powder pattern for NU-504 closely resembled a predicted powder pattern generated from a computational model that removed one of the interpenetrating



Figure 3. (A) TGA traces of NU-503 (red) and NU-504 (blue); (B) PXRD of NU-504 (simulated in red, experimental in purple); and (C) density separation experiment.

networks in NU-503. This comparison supports the assessment that NU-504 is an IRMOF-10 analogue. In addition to the PXRD data, a density separation experiment provided further support for NU-504 possessing an uncatenated framework, since it possessed a lower density respective to NU-503.⁵ Figure 3 shows that NU-503 (the catenated material) sinks to the bottom whereas NU-504 floats with the appropriate solvent composition (0.8:1 v:v DMSO/CH₂BrCl), even though the strut is heavier. We next turned our attention to TGA measurements. As anticipated, NU-504 experiences greater solvent loss than NU-503 (45% of its weight as opposed to 25% for NU-503). The combined experiments of TGA, comparison of simulated and predicted PXRD, and density separation support the conclusion that NU-504 is indeed the noncatenated, double azolium framework analogous to IRMOF-10 (Figure 3).

The primary factor contributing to the observed inhibition of catenation or change in morphology is the additional azolium "side arm" of strut 4 (vs 3) which projects into the pore of NU-504 (vs NU-503). This structural element (steric substituent directing into the pore) has been implicated in the generation of other IRMOF-10-type derivatives in a related system.¹⁸ Although a few examples of influencing catenation by adding steric elements have recently appeared in the MOF literature, it remains possible that each case (including our own) is systemspecific. Furthermore, while this strategy results in higher porosity due to the removal of an interpenetrated network, the additional steric elements in the existing framework may result in pores that are partially or fully blocked. Another influence on catenation is presumably the unusual electrostatic environment created by increasing the number of imidazolium groups arrayed within the pore of this new material (NU-504). This unusual property of azolium-based MOFs is currently under investigation and contributes to unusually high hydrogen absorption energies (unpublished studies). To date, all bases (various alkoxides and amines) to which NU-504 has been exposed, with the aim of creating catalytically active NHCs, have been found to promote framework degradation. Consequently, studies are ongoing to explore new modes of azolium to NHC activation in these and related MAF materials.

In conclusion, we have demonstrated the ability to manipulate the morphology of distinct Cu-paddlewheel and cubic systems using new azolium-based ligands **3** and **4**: 2D copper paddlewheel sheets and isoreticular networks similar to IRMOF-9 and -10. Catenation control was observed by a combination of single crystal X-ray diffraction, PXRD, density separation, and TGA experiments. The incorporation of different numbers of azolium cores (one vs two) into porous materials can impact the level of catenation or morphology; these studies provide the impetus to explore other classes of struts with these unusual and versatile heterocycles. Further investigation, as well as the application of MAFs as catalysts, is ongoing and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectral data for new compounds, CIF files, additional PXRD and TGA data, and NMR comparisons of struts and MOFs. This material is available free of charge via the Internet at http://pubs. acs.org.

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