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Isoreticular Metalation of Metal−Organic Frameworks

Christian J. Doonan, William Morris, Hiroyasu Furukawa, and Omar M. Yaghi*

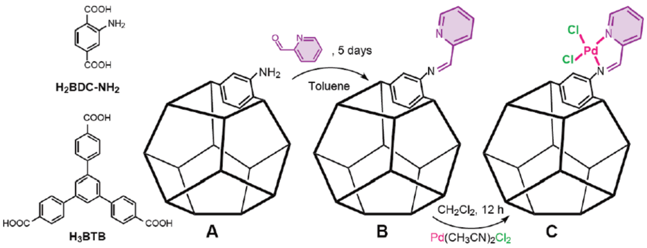
Center for Reticular Chemistry, Department of Chemistry and Biochemistry, University of California—Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095

Received April 23, 2009; E-mail: yaghi@chem.ucla.edu

Precise control of functionality in metal complexes is commonly achieved in molecular coordination chemistry. Developing the analogous chemistry within extended crystalline structures remains a challenge because of their tendency to lose order and connectivity when subjected to chemical reactions. Metal−organic frameworks (MOFs) are ideal candidates for performing coordination chemistry in extended structures because of their highly ordered nature and the flexibility with which the organic links can be modified. This is exemplified by the successful application of the isoreticular principle, where the functionality and metrics of an extended porous structure can be altered without changing its underlying topology.[1] Recently, this principle was also used in the covalent functionalization of various MOFs by carrying out organic reactions directly on MOF crystals.[2] Here we show that a given MOF material, chosen from the vast number reported in the literature, can be subjected to a sequence of chemical reactions to make a covalently bound chelating ligand, which can subsequently be used for the complexation of Pd(II). Specifically, crystals of $(Zn_4O)_3(BDC\text{-}NH_2)_3(BTB)_4$ (**A**) (Scheme 1)[3] were reacted with 2-pyridinecarboxaldehyde to form the covalently bound iminopyridine chelate derivative $(Zn_4O)_3(BDC\text{-}C_6H_5N_2)_3(BTB)_4$ (**B**), which was reacted with $PdCl_2(CH_3CN)_2$ to give the metal-complexed MOF $(Zn_4O)_3(BDC\text{-}C_6H_5N_2PdCl_2)_3(BTB)_4$ (**C**). Remarkably, these reactions and their respective products were achieved without loss of structural order or framework connectivity. This isoreticular metalation is a significant first step in harnessing the intrinsic advantages of molecular coordination chemistry for functionalization of extended solids.

MOFs with links containing transition-metal ions have been produced by a one-pot synthesis. This approach suffers from a lack of flexibility in variation of the metal and the inability to fine-tune the steric and electronic properties of the metal coordination sphere.[4] Two reports on covalent metalation describe materials that have not been demonstrated to be permanently porous.[5] Our strategy delineated in Scheme 1 overcomes these limitations. To illustrate this method, we chose MOF **A**, which has an extended structure with hexagonal channels surmounted by large cages with internal diameters of 30.7 and 23.2 Å, respectively. In this MOF, the amino functionalities point to the cage centers while the hexagonal channels remain free, allowing uninhibited diffusion of reactants. In contrast, the low conversions observed for covalent transformations performed on IRMOF-3, which has substantially smaller pore apertures (8 Å), may be the result of restricted access to functional groups within the crystal.[5b]

Scheme 1. Isoreticular Covalent Functionalization Followed by Metalation



Iminopyridine moieties have proved to be a versatile ligand system for binding a variety of transition metals in known coordination environments. Hence, we sought to incorporate such a moiety into **A** through condensation of the amine-functionalized framework and 2-pyridinecarboxaldehyde (Scheme 1). The isoreticular functionalized MOF **B** was synthesized by adding 1.5 equiv of 2-pyridinecarboxaldehyde to **A** in anhydrous toluene and allowing the reaction to proceed for 5 days, during which the needle-shaped crystals changed color from clear to yellow to give a product having a composition that coincided well with the expected formula, thus indicating quantitative conversion.[6] Powder X-ray diffraction (PXRD) studies (Figure 1) showed that **B** maintained crystallinity and possessed the same underlying topology as **A** subsequent to the covalent transformation. The presence of the iminopyridine unit was confirmed by mass spectrometry of digested samples of **B**, which showed a parent ion peak at m/z 269 ($[M - H]^-$) attributable to the ligand fragment.[7]

Isoreticular metalation was achieved by adding 1.5 equiv of $PdCl_2(CH_3CN)_2$ to **B** in anhydrous CH_2Cl_2, whereupon the yellow crystalline material became dark-purple within several minutes. After 12 h, the material was washed three times with 10 mL portions of CH_2Cl_2; the crystals were then immersed in dry CH_2Cl_2, and the solvent was refreshed every 24 h for 3 days to yield **C**.[7] Again, the PXRD pattern of **C** (Figure 1) confirmed that it retained crystallinity and possessed a framework topology identical to those of **A** and **B**. Removal of guest species from the pores was achieved by evacuating the crystals at 80 °C for 12 h. Elemental analysis performed on the guest-free framework of **C** gave a molecular formula $C_{50}H_{28}N_2O_{13}Zn_4PdCl_2$, whose Pd/Zn ratio of 1:4 is consistent with quantitative metalation of the iminopyridine sites.[8]

The porosities of **B** and **C** were assessed by performing an 87 K Ar isotherm (Figure 2).[7] Notably, both materials maintained porosity

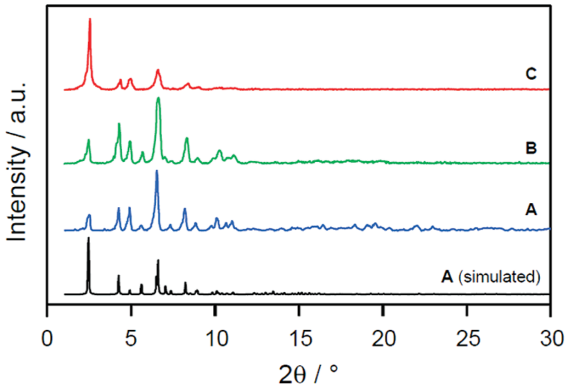


Figure 1. PXRD patterns for **A** (blue), **B** (green), and **C** (red) along with a simulated pattern for **A** (black).

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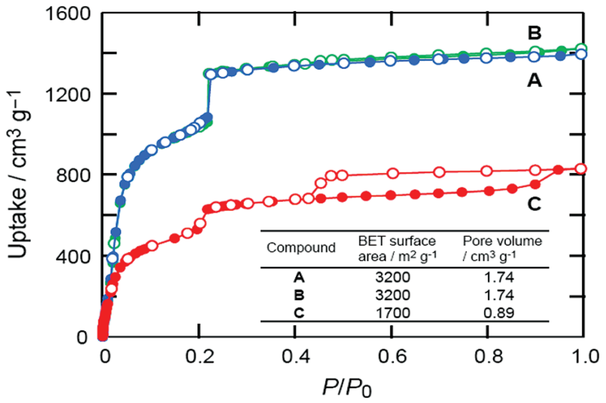
after two subsequent chemical transformations. Additionally, analogous profiles were observed for **A**−**C**; however, the small hysteresis present in the isotherm of **C** implies the presence of defects, presumably resulting from the sequence of chemical reactions carried out on the crystals.[9]



Compound	BET surface area / m^2 g^{-1}	Pore volume / cm^3 g^{-1}
A	3200	1.74
B	3200	1.74
C	1700	0.89

Figure 2. Ar gas adsorption isotherms for **A** (blue), **B** (green), and **C** (red) at 87 K, with adsorption and desorption points represented by solid and open circles, respectively.

To confirm that the Pd is complexed to the iminopyridine unit and to precisely determine the Pd coordination environment within the framework, we performed Pd K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy on samples of **C**. Figure 3 shows the EXAFS Fourier transform of **C** together with the results of the curve-fitting analysis. The data analysis indicated the presence of two Pd−Cl and two 2 Pd−N ligands at 2.276(2) and 1.993(2) Å, respectively. A survey of the Cambridge Structural Database showed that both of these distances are consistent with crystallographic data for analogous Pd compounds. Additionally, two Pd−C interactions at 2.793(4) Å, belonging to the ligand backbone, were required for the best data fit. The EXAFS data analysis provides a quantitative structural description of the Pd coordination environment within the MOF and clearly demonstrates that Pd is bound to the framework via the iminopyridine moiety. Furthermore, analysis of the X-ray absorption near-edge structure (XANES) spectrum indicated that the major chemical form of Pd within the framework of **C** was consistent with an iminopyridine-bound moiety and not the starting material, $PdCl_2(CH_3CN)_2$.[7]

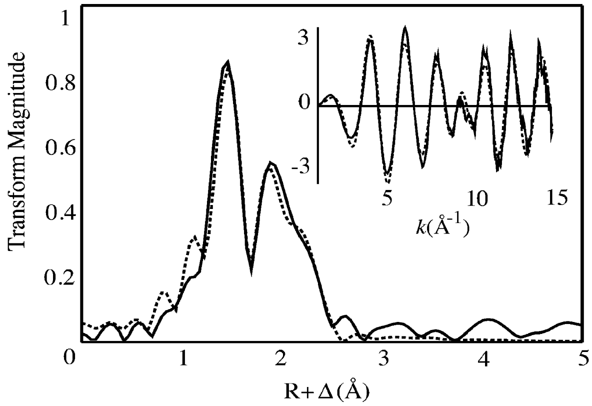


Figure 3. Pd K-edge EXAFS Fourier transforms and (inset) EXAFS spectra for **C**. Solid lines show the experimental data and dotted lines show the best fits using the parameters given in Table S1 in the Supporting Information.[7]

The successful isoreticular covalent transformation followed by metalation opens a route for incorporating metal ions into a wide range of frameworks. This work is an important first step toward exploiting such metalated frameworks in gas-storage and separation applications. Fundamentally, it expands the reaction space that can be carried out within MOFs.

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Supporting Information Available: Full synthetic and analytical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Elemental analysis: Calcd for $C_{50}H_{28}N_2O_{13}Zn_4 \cdot 3H_2O$: C, 50.88; H, 2.90; N, 2.37%. Found; C, 50.44; H, 2.64; N, 2.01%. The presence of water was confirmed by thermal gravimetric analysis, which showed a loss of 4% by weight (the expected value).

(7) See the Supporting Information for full experimental details.

(8) Elemental analysis: Calcd for $C_{50}H_{28}N_2O_{13}Zn_4PdCl_2$: C, 46.07; H, 2.16; N, 2.15; Pd, 8.16; Zn, 20.06. Found: C, 44.28; H, 2.16; N, 2.94; Pd, 8.84; Zn, 22.09.

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