# Postsynthetic Modification for the Functionalization of Metal-Organic Frameworks

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Much of the initial enthusiasm over the class of metal-organic frameworks (MOFs) came from their high surface areas and hence an extremely high capacity to capture gases of interest in energy-related technologies.[1] The development of MOFs for applications related to gas uptake is becoming increasingly reliant on the development of MOFs that possess complex chemical functionality. However, the preparation of highly functionalized MOFs has been largely limited by the solvothermal synthetic approaches used to prepare most MOFs. Fortunately, postsynthetic methods that modify MOFs with chemical reagents with preservation of the lattice structure make it possible to integrate functional groups into MOFs (Scheme 1).[2]


(a)

(b)

(c)
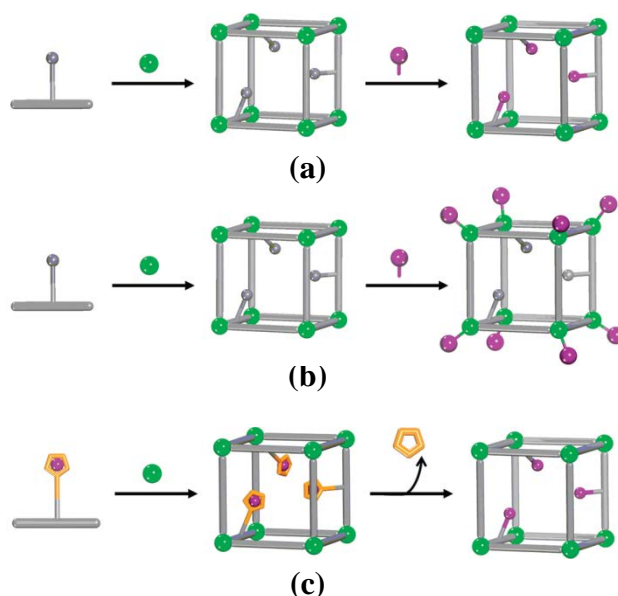
Scheme 1. Three postsynthetic methods (a) covalent PSM, (b) dative PSM and (c) postsynthetic deprotection

Based on this concept, a number of reports describing the utility of postsynthetic approach as a means to chemically alter MOFs began to appear since 2007. The term "postsynthetic modification" (PSM) was first proposed by the Cohen group in 2007 to describe the reaction of IRMOF-3 with acetic anhydride,[3] and subsequent reports were mainly focused on either amine-[4,5] or aldehyde-tagged[6,7] MOFs (Scheme 2). In 2008 the Cohen group demonstrated the versatility of NH_2-BDC (BDC = 1,4-benzenedicarboxylic acid) as a building block: it is able to smoothly undergo PSM in three different prototypical MOF topologies: IRMOF-1, DMOF-1 (D = 1,4-diazabicyclo[2.2.2]octane (DABCO)), and UMCM-1 (UMCM = University of Michigan Crystalline Material).[8] MOFs without chemical tags are a particularly challenging target for covalent PSM. However, Fischer and coworkers described a rare covalent functionalization of secondary building units (SBUs) in a MOF;[9] Abrahams et al. showed covalent PSM reaction could be performed by utilizing photochemical [2 + 2] cycloadditions.[10]
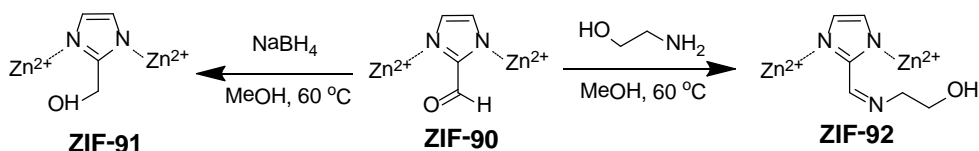
Scheme 2. Covalent PSM on aldehyde-tagged MOFs

Dative PSM at the SBUs of MOFs has become a mainstream approach for tuning the pore functionality of MOFs. In 2011 Hupp and coworkers reported systematic studies on dative PSM at the SBUs by using a Zn(II) paddlewheel-derived MOF.[11] An alternative method that made use of unsaturated metal sites was reported by the Navarro group, in which [Cu$_3$(BTC)$_2$] (BTC = 1,3,5-benzenetricarboxylate) was modified with ethylenediamine after being desolvated under vacuum to produce vacant coordination sites (Scheme 3).[12] In 2013, Cohen and coworkers synthesized a MOF containing pyridyl donors, which was converted to an active heterogeneous catalyst by postsynthetic treatment with [Ir(COD)(OCH$_3$)]$_2$ (COD = 1,5-cyclooctadiene).[13]
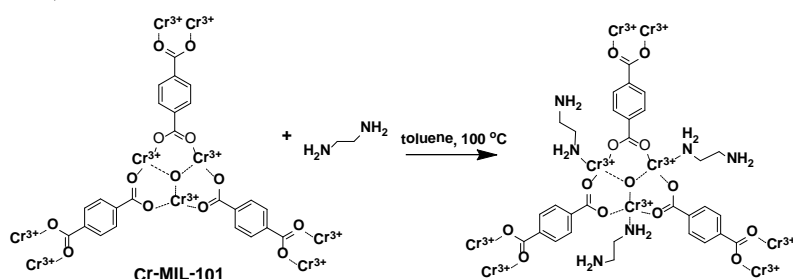
Scheme 3. Dative PSM with alkylamines

To date, postsynthetic deprotection is just beginning to gain attention as a postsynthetic functionalization method. The concept behind this method is that a protected functional group is introduced onto an organic linker before the protecting group is removed in a postsynthetic fashion (Scheme 4). Kitagawa and coworkers clearly demonstrated the utility of thermally induced deprotection in 2010 with a bulky tert-butylcarbamate (Boc) protecting group.[14] In addition to thermal methods, photochemistry has also been employed to initiate this type of reaction. In the same year, by employing a classic photochemical protecting group, 2-nitrobenzyl ether, Cohen and coworkers were able to reveal stable functional groups within a MOF that would otherwise be incompatible with the solvothermal synthetic method. [15]
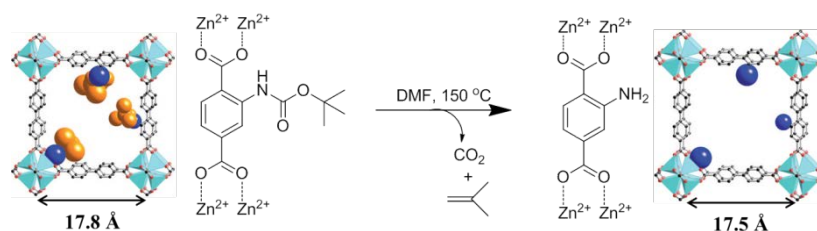
Scheme 4. Typical postsynthetic deprotection

This talk will focus on the postsynthetic methodologies for the functionalization of MOFs that have been developed during the past decade. The generality of PSM, in both scope of chemical reactions and range of suitable MOFs, clearly indicates that the approach is broadly applicable. Brief analysis of new properties relative to gas sorption and catalysis

upon modification will be involved in the talk. Finally, some prospects about the combination of multiple PSMs will also be discussed.

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