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Generic Postfunctionalization Route from Amino-Derived Metal−Organic Frameworks

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The secondary building unit (SBU) approach for engineering of metal−organic frameworks (MOFs) with tunable pore sizes is very attractive for designing practical properties such as separation by molecular sieving and shape-selective catalysis.[1] The conceptual approach used to increase the pore sizes of MOFs through the use of longer ligands has also been extended to the design of multifunctional MOFs bearing a functional group on the organic moiety. This is the case for IRMOF-3,[2] MOF-101(-Br),[3] and MIL-53(Al)-NH_2,[4] to name a few. However, this extension is not straightforward in practice.[5] Indeed, the chemistry of MOF network formation is very sensitive to the chemical reactivity and solubility of the functionalized linkers.[6] This is particularly the case for functions such as −OH, −COOH, and N-donating groups, which can interfere with the coordination chemistry associated with the assembly of the nodes.

When self-assembly fails in the synthesis of an MOF with functionalized linkers, the postfunctionalization of a parent MOF appears to be a very valuable alternative.[7] In fact, postsynthesis opens the door to advanced porous solid engineering by multiple synthesis steps[8] and, as a consequence, to the design of new types of adsorbents and catalysts. Postfunctionalization consists of modifying the organic part of the MOF by a chemical reaction that takes place within the porous framework. In this case, the parent MOF must possess accessible reactive functions. Similar issues have been resolved for MCM-like materials, for which various functionalization methods have been developed.[9] In a similar fashion to alkylamino-functionalized MCMs,[10] amino-derived MOFs such as IRMOF-3 and DMOF-NH_2[11] are excellent platforms for the grafting of various synthons such as aldehydes, isocyanates, and acid anhydrides. That said, the suitability, diversity and availability of such synthons can appear limited when one considers the ever-increasing demands for different functionalities and the ambitious projects imagined by chemists.

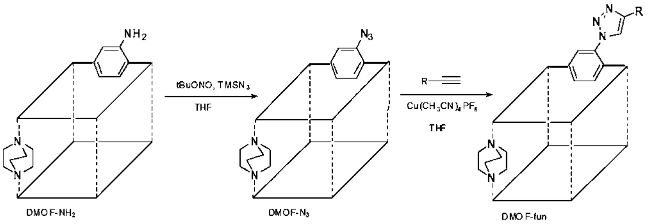
Valuable alternatives lie in the development of all kinds of generic postfunctionalization methods that are soft, do not liberate byproducts that may react or remain blocked in the pores, and enable grafting of a wide variety of chemical functions with high efficiency and selectivity. The Sharpless "click" reaction using Cu^I-catalyzed Huisgen cycloaddition of azides to alkynes fulfills all of these criteria.[12,13] The corresponding azide linkers are, however, highly unstable and not commercially available; this significantly limits the synthesis of MOFs bearing azide groups by self-assembly methods.

The objective of this work was to develop a one-pot, two-step functionalization method starting from already available amino-derived MOF compounds.[14] The first step involves an original method to convert a MOF in its amino form to the corresponding azide compound. Next, the desired functionalized material is obtained by "clicking" a synthon onto the azide without isolation of the intermediate.

The starting materials DMOF-NH_2 [Zn(bdc-NH_2)(DABCO)] (section S1 in the Supporting Information) and MIL-68(In)-NH_2 [In(OH)(bdc-NH_2)][15] (section S5) were selected as representative compounds. The former is a zero-dimensional-type MOF with a layered structure made of Zn carboxylate sheets supported by 1,4-diazabicyclo(2.2.2)octane (DABCO) pillars. It is representative of a large class of porous coordination polymers (PCPs).[16] On the other hand, MIL-68(In)-NH_2 belongs to another important class of MOFs characterized by a one-dimensional rod-shaped structure. This class has been reviewed by Yaghi et al.[17]

It should be noted that the usual route for preparing azide compounds from the corresponding amines via their diazonium salts cannot be applied here because DMOF-NH_2 dissolves under acidic conditions. Instead, we investigated another pathway that uses mild conditions and involves stable, nonexplosive compounds.[18]

Scheme 1. One-Pot, Two-Step Functionalization of DMOF-NH_2



In a typical synthesis (Scheme 1), the freshly dried DMOF-NH_2 was treated with tBuONO and $TMSN_3$ in THF overnight at room temperature to produce the corresponding azide intermediate compound DMOF-N_3.[19] In the same vessel, the functionalized DMOF (DMOF-fun) was obtained by addition of excess phenylacetylene in the presence of $Cu^I(CH_3CN)_4PF_6$ followed by continuous stirring for 24 h (section S3). For characterization purposes, the synthesis was stopped after formation of the azide intermediate DMOF-N_3.

MIL-68(In)-NH_2 was modified by applying a similar procedure.[20] For sake of brevity, details are given in section S6 in the Supporting Information.

Clear proof of azide formation and the subsequent (3 + 2) cycloaddition was obtained by IR spectroscopy. The absorption band of DMOF-N_3 at 2123 cm^{-1} is characteristic of the N_3 asymmetric stretching vibration (section S3). In addition, unambiguous characterization and quantification were provided by liquid

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10.1021/ja909613e

^{1}H NMR analysis. Samples of DMOF-N$_3$ were digested and dissolved in dilute DCl/D$_2$O/DMSO-d_6 solution (Figure 1) and then analyzed by ^{1}H NMR spectroscopy, which confirmed the formation of the azide compound by the appearance of new aromatic signals (7.74−7.85 ppm, m, 3H, ArH). This coincided with the complete disappearance of the aromatic signals of the amine (7 ppm, d, 1H, $J = 8.3$ Hz; 7.4 ppm, s, 1H; 7.74 ppm, d, 1H, $J = 8.3$ Hz), thus indicating full conversion to the azide form. On the other hand, the aliphatic moiety was not affected by the reaction (section S3).

DMOF-fun obtained after the one-pot synthesis was characterized using identical techniques. Here again, the conversion to the final compound was complete after 24 h. IR analysis revealed the complete disappearance of the azide stretching band at 2123 cm^{-1} (section S3). The liquid ^{1}H NMR spectrum of DMOF-fun illustrates that the corresponding triazole derivative was formed as the unique product; aromatic shifts of the grafted compound were assigned by ^{1}H−^{1}H correlation spectroscopy (COSY) experiments ($\delta = 7.38$, 7.49, 7.93, 8.04, 8.19, 9.15 ppm), and no azido or amino compound was detected (Figure 1). In addition, positive-mode mass spectrometry performed after digestion clearly showed a base peak at m/z 310 corresponding to the functionalized linker [2-(4-phenyl-1,2,3-triazol-1-yl)terephthalic acid]. The powder X-ray diffraction patterns indicated that the two-step reaction proceeded without loss of long-range order (section S3). We stress that the crystallinity of the parent DMOF-NH$_2$ is strongly affected by post-treatments such as solvent removal and/or solvent exchange (section S2).

Nitrogen physisorption experiments performed on the parent DMOF-NH$_2$ and DMOF-fun at 77 K revealed a decreases in the porous surface area (1320 to 244 m^2/g) and the microporous volume (0.54 to 0.08 cm^3/g) due to pore blocking (section S3).

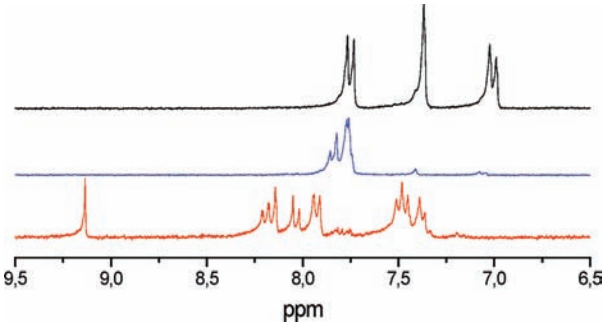

Figure 1. Liquid ^{1}H NMR spectra of digested materials: (top) DMOF-NH$_2$; (middle) DMOF-N$_3$; (bottom) DMOF-fun.

These investigations were also undertaken for the postfunctionalization of MIL-68(In)-NH$_2$, and the same results were obtained in terms of grafting rate (>90%), decrease in surface area (1260 to 120 m^2/g) and microporous volume (0.48 to 0.03 cm^3/g), and preservation of crystallinity (section S6).

Cycloaddition in azide-functionalized MOFs has recently been demonstrated for IRMOF-type compounds.[12] In this work, we have shown that direct functionalization from amino-derived MOFs is possible, provided that the pore cavity is large enough to accommodate a C$_5$ ring (section S3). The main advantage of this one-pot method is the ease of preparing amino-functionalized MOFs. To the best of our knowledge, five different structures based on 2-aminoterephthalic acid have been reported to date: IRMOF-3,[2] MIL-101-NH$_2$,[4] CAU-1,[21] DMOF-NH$_2$, and MIL-53(Al)-NH$_2$. The large library of amino acids also opens promising perspectives for new potential amino-functionalized MOFs as synthetic platforms. A second advantage is the softness of the method. Indeed, both reaction steps proceed at room temperature and do not liberate byproducts such as water, acids, or bases that could damage the structure by hydrolysis.[22] Finally, in contrast to the anhydride condensation method, which has a limited grafting yield (30−50%),[23] we have shown that this approach allows complete functionalization even for a bulky group. This is in line with molecular modeling results showing weak steric demand (section S3). Notably, the crystallite sizes of the two MOFs are ~1 μm (section S1), whereas Wang et al.[11] used DMOF-NH$_2$ crystallites with diameters of 100 μm. We believe that the accessibility of reactants to the centers of the crystals arises from the very small size of the MOF crystallites.

However, this small size comes at the expense of a decrease in microporous volume. Thanks to the efficiency of the azide formation, the grafting rate can be controlled by adding phenylacetylene in default with respect to −NH$_2$ functions. For a grafting rate of 50% on MIL-68(In)-NH$_2$, the surface area decreased only by 55% ($S_{\mathrm{BET}} = 571$ m^2/g), which is in line with other methods.[8]

In this study, controlled functionalization was performed with phenylacetylene as a proof of concept. A systematic study dealing with the grafting of moieties exhibiting different functions on diverse amino-MOF platforms will be reported soon. We believe that this method will allow the design of tailor-made catalysts with more complex functional groups.

Acknowledgment. We thank A. Camarata for the technical work, along with IRCELYON and IFP scientific services.

Supporting Information Available: Synthetic procedures, characterization data, and molecular modeling results. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA909613E