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Postsynthetic Modification of an Alkyne-Tagged Zirconium Metal–Organic Framework via a "Click" Reaction

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Supporting Information

ABSTRACT: Herein, we report the synthesis and postsynthetic modification of a novel alkyne-tagged zirconium metal–organic framework, UiO-68-alkyne. The alkynyl groups in the pore surface were subjected to a "click" reaction, achieving quantitative conversion and maintaining the crystallinity of the framework.

Metal–organic frameworks (MOFs), a novel class of hybrid nanoporous solids with structural periodicity and diversity, have gained considerable attention over the past 2 decades because of their usefulness for gas storage/separation,[1] catalysis,[2] sensing,[3] and drug delivery.[4] With the development of MOF chemistry, the demand of the incorporation of diverse functional groups into MOFs has increased noticeably because it can enhance possible functions associated within the cavities. However, many chemical functionalities are incompatible with the conditions for MOF assembly. Postsynthetic modification (PSM),[5] as an alternative and simple method, has recently emerged as a powerful tool to chemically tailor the interior of MOFs and can thus provide MOFs with enhanced properties for specialized applications. For example, Cohen et al. reported the synthesis of reactive isocyanate- and isothiocyanate-tagged MOFs from MIL-53(Al)-NH_2, which could further react with other species to generate new functionalized MOFs with different gas sorption isotherms.[6] Therefore, using the PSM approach to modify and functionalize MOFs has become a vibrant area of MOF chemistry.

In order to testify the versatility of the PSM approach, dozens of organic reactions have been utilized to covalently modify the organic linkers of MOFs.[7] Among these reactions, Sharpless "click" chemistry is highly appealing[8] because the reaction can proceed efficiently with high yields and high specificity in the presence of various functional groups. For example, Zhou et al. reported the quantitative introduction of diverse functional groups into the MOFs using the 1,3-dipolar cycloaddition of azides and terminal alkynes, with well-retained frameworks and accessible functionalized pores.[9] Until now, several azide-tagged MOFs have been reported and can be further used as platforms to graft various functional groups to enrich the chemical diversity of MOFs.[9,10] However, compared to azide-tagged MOFs, alkyne-tagged MOFs are far-away explored.[11] Because it is relatively easy to modify the organic compounds with azide functional group, more alkyne-functionalized MOFs need to be developed.

There have been a very limited number of alkyne-tagged MOFs reported up to now,[11] partially because alkynyl groups can coordinate with metal ions[12] and then may interfere with the MOF formation. As an alternative approach, the alkynyl groups can also be protected before the formation of MOFs. However, the alkyne-protected MOFs should be deprotected prior to performing the click reaction,[11a] which usually has to face low efficient conversion. With these considerations in mind, we report herein a novel MOF (UiO-68-alkyne; Figure 1) with accessible and reactive alkynyl groups, by choosing the

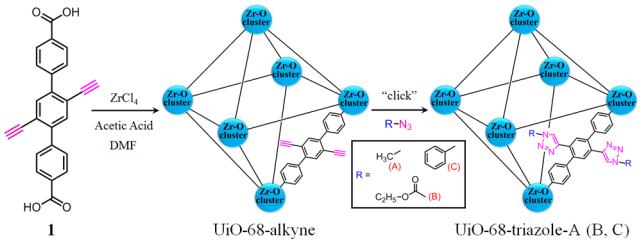

Figure 1. Scheme for the synthesis and PSM of UiO-68-alkyne. The topology is shown in a simplified form as an octahedral cage.

zirconium metal–organic framework (Zr-MOF)[13] as the substrate. This highly stable Zr-MOF can be used as an ideal platform for pore surface engineering via a quantitative click reaction with various azide compounds while maintaining the crystallinity and porosity.

To obtain an alkyne-appended Zr-MOF with large cavities, we designed a novel building block, 2′,5′-diethynylterphenyl-4,4″-dicarboxylic acid (ligand **1**; Figure 1), which was synthesized according to Scheme S1 in the Supporting Information (SI). After treatment of a reaction mixture containing $ZrCl_4$, ligand **1**, acetic acid, and *N*,*N*-dimethylformide (DMF) in a preheated 100 °C oven for 48 h, UiO-68-alkyne was obtained as octahedron-shaped crystals in reasonable yield. The structure and composition of UiO-68-alkyne was conclusively established by several methods. Single-crystal X-ray diffraction studies performed at the Beijing Synchrotron Facility revealed a UiO-type structure for UiO-68-

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alkyne with an fcu topology, which crystallizes in the $Fm\bar{3}m$ space group and contains both tetrahedral and octahedral cages (Figure 2), with cage sizes of 7.2 and 17.6 Å, respectively. This

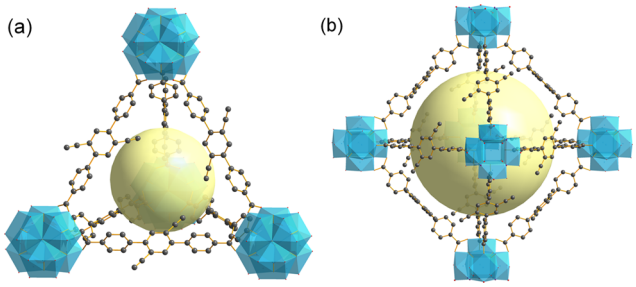

Figure 2. UiO-68-alkyne crystalline structure (Zr, polyhedra; C, pale; O, red): (a) tetrahedral cage; (b) octahedral cage. The cavities are highlighted with yellow spheres.

structure was also confirmed by a powder X-ray diffraction (PXRD) experiment because the PXRD pattern of UiO-68-alkyne (Figure 3) is identical with the pattern simulated from

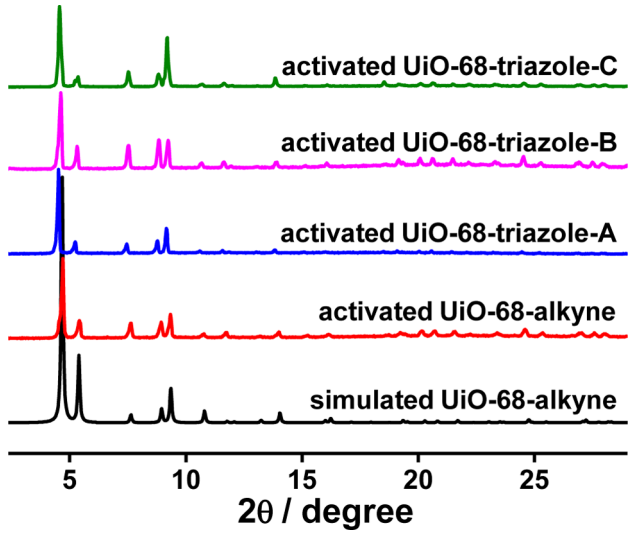

Figure 3. PXRD patterns simulated from the single-crystal structure (black line), activated UiO-68-alkyne (red line), activated UiO-68-triazole-A (blue line), activated UiO-68-triazole-B (pink line), and activated UiO-68-triazole-C (green line).

its single-crystal structure. In addition, the Fourier transform infrared spectrum of activated UiO-68-alkyne displayed (Figure S13 in the SI) a peak at 3286 cm^{-1}, which could be assigned to the C−H stretching band of the terminal alkynyl group. The ^1H NMR spectrum of digested UiO-68-alkyne is almost the same as that of ligand **1** (Figure S3 in the SI), indicating that the ligands remained intact in the MOF. Finally, gas sorption experiments with N_2 at 77 K indicated that UiO-68-alkyne was highly porous and displayed a type I gas sorption isotherm (Figure 4). The Brunauer−Emmett−Teller (BET) surface areas of UiO-68-alkyne was found to be 3155 $m^2\ g^{-1}$.

The highly porous structure of UiO-68-alkyne should allow the alkynyl groups inside to be accessible. To assess the applicability of UiO-68-alkyne for PSM, we first treated the octahedral crystals with an excess amount of azidoethane (A) in the presence of CuI at 60 °C in DMF (Figure 1). After 24 h, the reaction was terminated and UiO-68-triazole-A was isolated

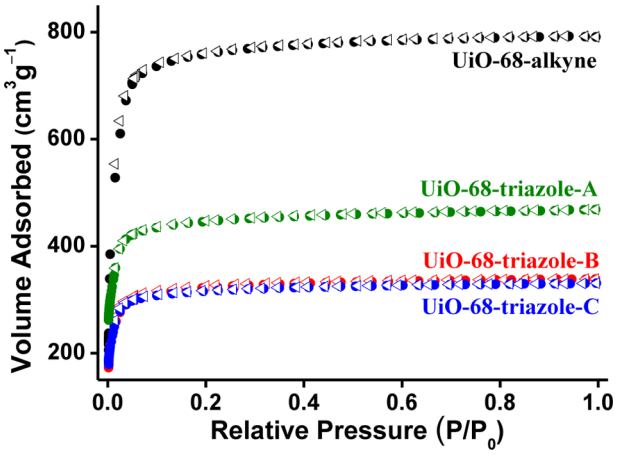

Figure 4. N_2 sorption properties at 77 K for UiO-68-alkyne (black line), UiO-68-triazole-A (green line), UiO-68-triazole-B (red line), and UiO-68-triazole-C (blue line).

in quantitative yields by centrifugation and washing with DMF and ethanol. To verify the extent of the click reaction, we investigated the ^1H NMR spectrum of digested UiO-68-triazole-A (Figure S7 in the SI). Obviously, no starting material remained, and the corresponding triazole derivative was formed. In addition, the high-resolution electrospray ionization mass spectrum (HR-ESI-MS) of digested UiO-68-triazole-A (Figure S8 in the SI) also confirmed formation of the corresponding triazole derivative. More importantly, the positions of the PXRD peaks of UiO-68-triazole-A are similar to those of UiO-68-alkyne, signifying retention of the framework. N_2 adsorption isotherms of UiO-68-triazole-A at 77 K also showed type I gas sorption isotherms, and the BET surface area was calculated to be 1851 $m^2\ g^{-1}$ (Figures 4 and S16 in the SI), suggesting that the porosity was maintained. The observed decreases in the surface area compared to those of UiO-68-alkyne were largely attributed to the formation of triazole groups on the pore surface.

On the basis of the above study, the PSM of UiO-68-alkyne via the click reaction may be general. We then investigated the reaction of UiO-68-alkyne with other azide compounds (Figure 1), ethyl azidoacetate (B) and azidomethylbenzene (C). Following the same procedure, UiO-68-triazole-B and UiO-68-triazole-C were also isolated as single crystals in quantitative yield. As direct evidence of a complete click reaction, the characteristic IR band for the alkynyl group disappeared (Figure S13 in the SI). The ^1H NMR spectra of digested samples of UiO-68-triazole-B (Figure S9 in the SI) and UiO-68-triazole-C (Figure S11 in the SI) demonstrated formation of the corresponding triazole derivative, which was further confirmed by HR-ESI-MS spectra (Figures S10 and S12 in the SI). Moreover, the crystallinity of UiO-68-alkyne was maintained after the click reaction, as is evidenced by PXRD experiments (Figure 3). From the N_2 adsorption isotherms, the BET surface areas of UiO-68-triazole-B and UiO-68-triazole-C decreased to 1299 and 1283 $m^2\ g^{-1}$ (Figures 4 and S17 and S18 in the SI) because of the incorporation of large substitutes.

In conclusion, we have reported an isoreticular Zr-MOF (UiO-68-alkyne) with alkynyl groups inside the pores and in situ click reactions with azide compounds. Our results demonstrated that the click reaction can procede quantitatively in UiO-68-alkyne while maintaining the framework. Moreover, the resultant triazole-based MOFs are still highly porous.

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Therefore, UiO-68-alkyne offers an ideal platform for facile pore surface engineering via the click reaction. On the basis of the above studies, the strategy of PSM of UiO-68-alkyne via the click reaction should be general. It will allow us to anchor other desired functional groups onto the pore walls, enabling more potential applications. Efforts toward grafting other functional groups are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Details of the synthesis, PSM, MOF characterization, and crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00535.

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Notes

The authors declare no competing financial interest.

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