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Pore Surface Engineering with Controlled Loadings of Functional Groups via Click Chemistry in Highly Stable Metal-Organic Frameworks

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Supporting Information Placeholder

ABSTRACT: Reactions of $ZrCl_4$ and single or mixed linear dicarboxylic acids bearing methyl or azide groups lead to highly stable isoreticular metal-organic frameworks (MOFs) with content-tunable, accessible, reactive azide groups inside the large pores. These Zr-based MOFs offer an ideal platform for pore surface engineering of anchoring various functional groups with controlled loadings onto pore walls via click reaction, endowing MOFs with tailor-made interfaces. Significantly, the framework and crystallinity of functionalized MOFs are well retained, and the engineered pore surfaces have been demonstrated to be readily accessible, thus bringing more opportunities for powerful and broad applications of MOFs.

As highly ordered porous materials, metal-organic frameworks (MOFs) have attracted great interest in the last twenty years due to their crystalline nature, pore tunability and structural diversity, as well as numerous potential applications such as gas storage/separation, catalysis, sensing and drug delivery.[1-5] Permanent porosity and chemical environment of the internal surface of MOFs are crucial for such applications. However, pore surface modification with desired functional groups in well-defined MOFs remains a significant challenge. Currently, the modification of MOF pore surfaces is mostly based on the pre-designed ligand with a specific functional group.[6] This approach is somewhat limited owing to the cumbersome multistep process of ligand synthesis and the often unpredictable coordination between reactive functional groups (such as, -OH, -COOH, N-donating groups, etc.) and metal centers during the MOF assembly process. Moreover, it is generally difficult to obtain MOFs with long and/or large groups appended on the pore walls by direct solvothermal reactions. Therefore, the development of a general strategy for systematic pore surface engineering of MOF pore walls is imperative, which would endow MOFs with a tailor-made internal surface to meet specific application requirements.

Postsynthetic modification (PSM) represents a powerful tool to anchor functional groups onto MOFs. For instance, Cohen and coworkers have employed MOFs bearing $-NH_2$ groups as platforms to graft various functional groups such as aldehydes, isocyanates, and anhydrides.[7] Recently, Sharpless click chemistry has also been demonstrated to be an alternative route to enrich the chemical diversity of MOFs.[8-10] Sada and coworkers have employed a Zn-based MOF bearing azide groups for PSM applying the click chemistry, although the MOF dissolves when soaking in a solution with "reactive" molecules, such as reactants bearing an amine or carboxylic acid group, which significantly limits the utility of the approach.[9] Hupp and Nguyen groups, Farrusseng and coworkers have also applied click reactions in PSM of MOFs, where very careful deprotection of acetylene group or transformation of amine to azide group is a necessary step prior to a click reaction.[10] Multiple steps in PSM often cause partial or complete framework collapse, especially when the MOF is not robust. In addition, grafting functional groups with controlled loadings in MOFs has not yet been achieved. Herein we report the preparation of highly stable isoreticular Zr-based MOFs with accessible, reactive azide groups in large pores, which enable the MOFs to undergo a quantitative click reaction with alkynes to form triazole-linked groups on the pore wall surfaces. Significantly, our synthetic route allows an accurate control of the loading of azide groups on the internal surface of the MOF for the first time. The highly stable Zr-based MOFs offer an ideal platform for pore surface engineering. A variety of functional groups can be anchored onto pore walls in MOFs with precise control over the loading, density, and functionalities.

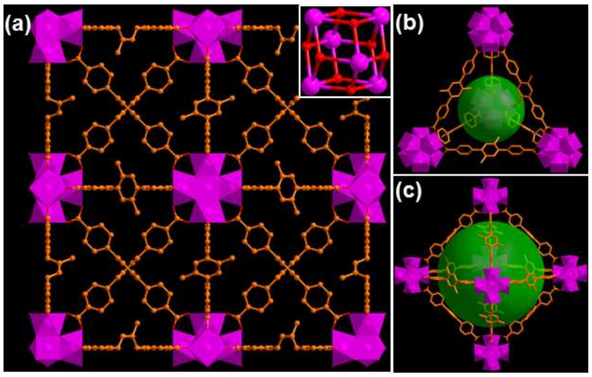

Figure 1. (a) View of the structure of PCN-56 as a representative, bearing two methyl groups in each TPDC-derived linker. Accordingly, four methyl, two methyl azide, and four methyl azide groups are involved in each organic linker, respectively for PCN-57, PCN-58 and PCN-59. Inset: the Zr_6 cluster. (b) Tetrahedral and (c) octahedral cages comprised Zr_6 clusters and organic linkers in PCN-56. The cavities are highlighted with green spheres.

To design an azide-appended MOF material with large enough cavities whose openings can be fully accessed by various molecules with alkyne group for click reaction, we designed four elongated linear dicarboxylic acids with three benzene rings in each, 2',5'-dimethyl-terphenyl-4,4"-dicarboxylic acid (TPDC-$2CH_3$) and

2',3',5',6'-tetramethyl-terphenyl-4,4"-dicarboxylic acid (TPDC-$4CH_3$), as well as their corresponding azide derivatives (TPDC-$2CH_2N_3$ and TPDC-$4CH_2N_3$), as organic linkers (Supporting Information, Section 2). To ensure the structural integrity during click reaction, we aimed to construct Zr-based MOFs, which are well-known for their superior stability to the common Zn/Cu-centered MOFs.[11] It is especially difficult to obtain single crystals of Zr-based MOFs due to the inert coordination bonds between Zr^{4+} cations and carboxylate anions, making ligand exchange reactions extremely slow, which is unfavorable for defects repair during crystal growth.[11] To overcome this difficulty, modulated synthetic strategy was adopted and benzoic acid was introduced to the synthetic system.[11c] To our delight, octahedron-shaped crystals suitable for single crystal X-ray diffraction studies have been obtained from a reaction mixture containing zirconium(IV) chloride, the elongated organic linkers, benzoic acid, and DMF, which was allowed to stay at 100 ºC in an oven for 2 days (or 120 ºC for 12-18 h) (Supporting Information, Section 3 and Figure S40).[12] Four MOFs, $Zr_3O_2(OH)_2(TPDC\text{-}R)_3$ (R = $-2CH_3$, PCN-56; $-4CH_3$, PCN-57; $-2CH_2N_3$, PCN-58; $-4CH_2N_3$, PCN-59. PCN represents porous coordination networks), have been confirmed to possess isoreticular structures, which are similar to the UiO type structures, based on single crystal X-ray structural and powder X-ray diffraction (PXRD) analyses (Supporting Information, Sections 4 and 5).[11a] In the absence of benzoic acid, these MOFs can also be obtained but only in fine powders, revealing the vital role of benzoic acid for the growth of crystals (Figure S45). Characteristic infrared (IR) band of azide group (at ~2100 cm^{-1}) is absent for PCN-56 and -57 whereas it is stronger for PCN-59 than that for PCN-58, consistent with the suggested structures. Moreover, digested PCN-58 and -59 crystals in DMSO afford almost the same ^1H NMR spectra as those of the corresponding organic linkers, further demonstrating the intactness of ligand in the MOFs (Figure S25).

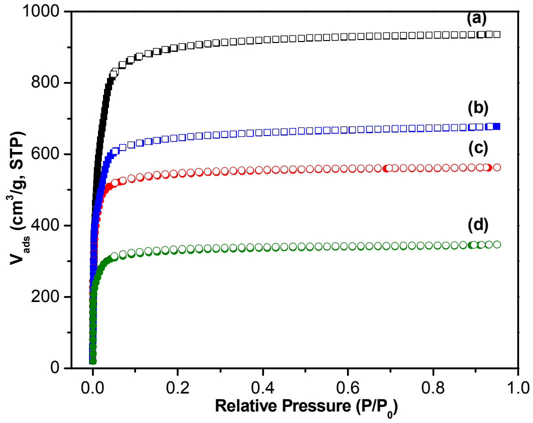

Figure 2. N_2 sorption properties for (a) PCN-56, (b) PCN-57, (c) PCN-58, and (d) PCN-59 at 77 K and 1 atm. Solid circles or squares: adsorption; open: desorption. The BET surface areas are 3741, 2572, 2185 and 1279 m^2/g, respectively for PCN-56 to -59, which are comparable to calculated values (3317, 2416, 2131 and 1168 m^2/g, respectively for PCN-56 to -59).

All MOFs crystallize in the *Fm-3m* space group and the unique Zr atom, in a square-antiprismatic coordination environment, is coordinated by eight oxygen atoms from four carboxylates and four μ_3-O and μ_3-OH groups. Six Zr atoms are interconnected by O atoms to form a $Zr_6O_4(OH)_4$ octahdedral core, the triangular faces of which are alternatively capped by μ_3-O and μ_3-OH groups (Figure 1a, inset). All of the polyhedron edges are bridged by carboxylates from the ligands to afford a $Zr_6O_4(OH)_4(CO_2)_{12}$ cluster. Each cluster is connected by twelve linear ligands and each linear ligand links two clusters giving rise to a three-dimensional (3D) network with two types of polyhedral cages (Figure 1a). One is tetrahedral comprising three Zr_6 clusters and six ligands with a cavity diameter of ~1.1 nm (Figure 1b), the other is octahedral with a cavity diameter of ~2.2 nm surrounded by six Zr_6 clusters and twelve ligands (Figure 1c).

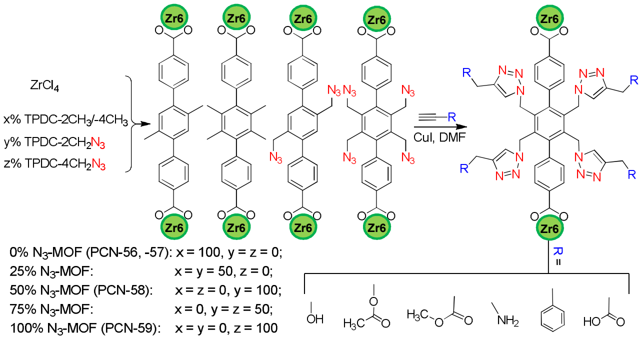

Figure 3. Schematic illustration for the general strategy of pore surface engineering of MOFs with precise control over the composition, density and functionalities by two steps in current synthetic system: 1) introducing azide group with a desired loading into the MOF (any value from 0 to 100%) by simply changing the molar ratio of methyl- and azide-appended ligands only; 2) various functional groups are grafted onto the pore walls of MOFs via click reaction between azide and alkyne groups in quantitative yield. The green spheres represent Zr_6 clusters.

With strong bonds between the Zr^{4+} cation and the O atoms thanks largely to the high charge density (*Z*/*r*) and the consequential bond polarization, all these MOFs exhibit exceptional robustness. Thermal gravimetric analyses indicate that PCN-58 and -59 with methyl groups are stable up to 350-400 ºC, while frameworks of PCN-58 and -59 bearing azide group remain intact over 200 ºC, after which the decomposition of the azide groups triggers the collapse of the whole framework. Importantly, chemical stability examinations reveal that these MOFs not only survive water treatment but also remain intact in dilute acid (pH = 2 solution with HCl) and base (pH = 11 solution with NaOH) for some time (Supporting Information, Section 12).

Given the microporosity and robustness, all of the MOFs display typical type-I gas sorption isotherms with a range of surface areas, in which PCN-56 presents BET surface area as high as 3741 m^2/g (Figure 2). Although PCN-58 and -59 have decreased surface areas due to the occupied pores by azide groups, the introduction of azide group improves the adsorption enthalpy of CO_2 (20, 22, 25 and 33 kJ/mol respectively for PCN-56 to -59) and effectively enhances CO_2 capture performance because of the polarity of azide groups.

The loading of azide groups on the pore walls can be accurately tuned by varying the ratio of ligands with and without azide groups during the MOF synthesis. Based on the current study and literature reports, it is evident that appending azide groups to the linker does not change the final MOF structure.[6b,13] Hence, it is reasonable to assume that pre-adjusting the molar ratio of TPDC-CH_3 : TPDC-CH_2N_3 will allow the control of azide loading in the resultant MOFs. To test this hypothesis, MOFs with 25% and 75% $-N_3$ loadings have been obtained by employing 1:1 of TPDC-$2CH_3$ and TPDC-$2CH_2N_3$, and 1:1 of TPDC-$2CH_2N_3$ and TPDC-$4CH_2N_3$ ligands, respectively (Figure 3). These MOFs show PXRD patterns similar to those of PCN-56 to -59, indicating the retention of the framework structure. They also have similar IR features but the intensity and peak area of the azide absorption band at ~2100 cm^{-1} almost linearly increase as the azide loading become higher (Figure 4), together with elemental analysis results, further demonstrating the consistency between theoretical and actual contents of azide groups in MOFs (Supporting Information, Section 11). This remarkable synthetic strategy can be further extended to the synthesis of other isoreticular MOFs with any azide loadings between 0 and 100% under similar reaction conditions by simply adjusting the ligand ratio. Most importantly, if coupled with postsynthetic click reaction such a synthetic strategy of MOF functionalization via co-assembly with mixed ligands provides a universal pathway toward MOFs with desired internal surface properties, which are vital for their applications.

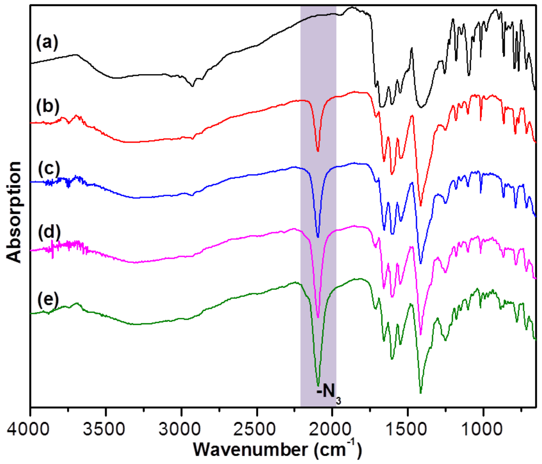

Figure 4. IR spectra of Zr-MOFs with (a) 0% N_3 (PCN-56), (b) 25% N_3, (c) 50% N_3 (PCN-58), (d) 75% N_3, and (e) 100% N_3 (PCN-59). The characteristic IR band (highlighted with light purple background) for azide group is at ~2100 cm^{-1}. The intensity of this band is proportional to the azide loading of each MOF.

The Zr-MOFs with various azide loadings (25%, 50%, 75% and 100%) were allowed to react with propargyl alcohol in the presence of CuI as a catalyst at 60 ºC in DMF. After the reaction was terminated, the products were isolated by centrifugation and washed with acetone to afford products in quantitative yields. It was demonstrated that very few Cu species (< 2 wt%) from the CuI catalyst remained in the product (Supporting Information, Section 14), similar to the previous report.[14] PXRD studies confirmed the retention of the framework integrity and the crystallinity of the resultant Zr-MOFs, which are now anchored by various loadings of hydroxyl groups (Supporting Information, Section 13). As the direct evidence of a complete click reaction, the characteristic IR band for the azide group disappeared completely (Supporting Information, Sections 8 and 10).

Given that various functional groups inside the pores will endow MOFs with distinct and novel properties, it is highly desirable to introduce a variety of functional groups into MOFs by postsynthetic click reaction. Bearing this in mind, we further investigated click reactions of PCN-58 and -59 with other alkynes involving various groups, such as propargyl acetate, methyl propiolate, propargylamine, phenylacetylene, and propiolic acid. Under reaction conditions similar to those for propargyl alcohol, various functional groups have been successfully anchored onto the MOF pore walls via a triazole linkage by click reaction. Herein, the positions and loadings of the functional groups are identical to those of the azide-appended MOF precursors. The identity of the functionalized MOFs is validated by PXRD and IR characterizations. To further verify the proposed products via click reaction, we investigated the ^{1}H NMR spectra of the digested solutions for all PCN-58-derived products; the results illustrated that the corresponding triazole derivatives were formed and almost no starting material was observed (Supporting Information, Section 8). Based on the above studies, the coupled strategy of postsynthetic click reaction and MOF functionalization through co-assembly with mixed ligands may be general. It will allow us to anchor almost any desired functional groups with precisely controlled loadings onto pore walls in MOFs, thus to realize more potential applications.

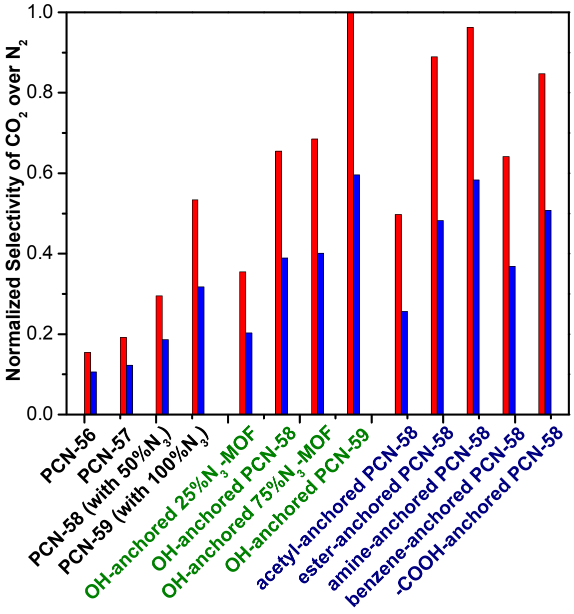

Figure 5. Normalized CO_2 adsorption selectivity over N_2 (obtained from CO_2 sorption amount (1 atm and 273 K for red bars; 1 atom and 296 K for blue bars) divided by N_2 sorption amount at 1 atm and 77 K) for three sets of samples (Zr-MOFs with various loadings of azide group, black marks; hydroxyl group anchored onto Zr-MOFs with various loadings of azide group, green marks; and diverse functional group anchored onto PCN-58, blue marks).

Upon the introduction of diverse functional groups that may have different affinities to specific gas molecules, the selective sorption capability of the resultant MOFs can be tuned. As a proof-of-concept study, we focused on the selective sorption of CO_2 over N_2, which is critical for carbon capture from air or flue gas stream. Compared to the MOF precursors, all functionalized MOFs exhibit moderate BET surface area (400-1000 m^2/g for PCN-58-derived products and 200-450 m^2/g for PCN-59 derived products) after click reaction (Table 1), indicative of space filling by the functional groups introduced. Their N_2 uptake at 273 K is almost undetectable, while they can adsorb significant amount of CO_2 at 273 or 296 K and 1 atm (Supporting Information, Sections 8 and 10). As shown in Figure 5, it is evident that the introduction of azide groups increases the selectivity of CO_2 over N_2 (*vide supra*). Different loadings of azide groups in the MOF enable us to anchor the corresponding amounts of hydroxyl group onto the pore walls. Overall, the selectivity of CO_2 over N_2 is also proportional to the loadings of the hydroxyl groups. In addition, various functional groups embedded into PCN-58 result in different selectivity of CO_2 over N_2, in which amine is the functional group that shows the highest selectivity due to the presence of not only polarity interaction but also "acid-base" reaction between alkylamine and CO_2 molecules, which is in agreement with previous reports.[15] In summary, preliminary results have revealed that pore surface engineering of MOFs with diverse groups and controlled loading significantly affect their gas sorption selectivity.

Table 1. Experimental BET Surface Area^a (m^2/g) for MOFs Bearing Different Contents of N_3 Group that Functionalized with Diverse Groups and Different Loadings via Click Reactions.

Group	OH	OCOMe	COOMe	NH_2	phenyl	COOH
25% N_3	1409	-	-	-	-	-
50% N_3[b]	845	907	405	595	721	560
75% N_3	848	-	-	-	-	-
100% N_3[c]	427	342	200	404	220	293

[a] Decided by $0.005 < P/P_0 < 0.15$. [b] i. e. PCN-58. [c] i. e. PCN-59.

In conclusion, reactions of $ZrCl_4$ and single or mixed linear ligands bearing methyl or azide groups lead to highly stable isoreticular Zr-MOFs with tunable loadings of azide group inside the pores. For the first time, the system offers an ideal platform for facile pore surface engineering by introducing various functional groups with controlled loadings via click reaction. Remarkably, the resultant click products have been demonstrated to possess well-retained framework and accessible functionalized pores. This work has enabled a general approach for introducing diverse functional groups, especially large and/or reactive groups, into MOF pores that otherwise could not be directly synthesized by conventional solvothermal reactions. The tailored pore surface with the control of both type and density of functional groups in MOFs will extend their functionalities further toward broader applications.

ASSOCIATED CONTENT

Supporting Information

Full details for sample preparation and characterization results, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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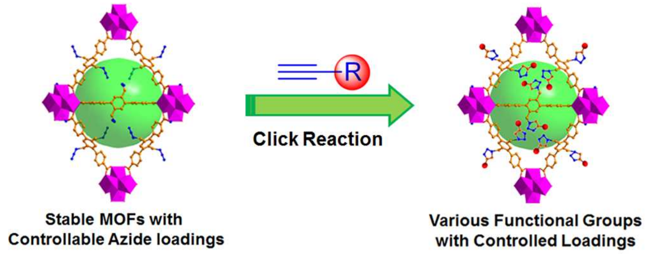
R
Click Reaction
Stable MOFs with
Controllable Azide loadings
Various Functional Groups
with Controlled Loadings