

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

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S Supporting Information

ABSTRACT: Reactions of $ZrCl_4$ and single or mixed linear dicarboxylic acids bearing methyl or azide groups lead to highly stable isorecticular 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 by anchoring various functional groups with controlled loadings onto the pore walls via the click reaction, endowing the MOFs with tailor-made interfaces. Significantly, the framework and crystallinity of the functionalized MOFs are well-retained, and the engineered pore surfaces have been demonstrated to be readily accessible, thus providing 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 20 years because of 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} The permanent porosity and chemical environment of the internal surfaces of MOFs are crucial for such applications. However, modification of the pore surfaces with desired functional groups in well-defined MOFs remains a significant challenge. Currently, the modification of MOF pore surfaces is mostly based on the use of predesigned ligands with specific functional groups.⁶ This approach is somewhat limited because of the cumbersome multistep process of ligand synthesis and the often unpredictable coordination between reactive functional groups (e.g., $-OH$, $-COOH$, 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, as it would endow MOFs with tailor-made internal surfaces to meet specific application requirements.

Postsynthetic modification (PSM) represents a powerful tool for anchoring functional groups onto MOFs. For instance, Cohen and co-workers 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 for enriching the chemical diversity of MOFs.^{8–10} Sada and co-workers employed a Zn-based MOF bearing azide groups for

PSM through click chemistry, although the MOF dissolved upon soaking in a solution with “reactive” molecules, such as reactants bearing an amine or carboxylic acid group, significantly limiting the utility of the approach.⁹ The Hupp and Nguyen groups and Farrusseng and co-workers also applied click reactions in PSM of MOFs, where very careful deprotection of an acetylene group or transformation of an amine to an azide group was a necessary step prior to the click reaction.^{10a–e} 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 been achieved to date. Herein we report the preparation of highly stable isorecticular Zr-based MOFs with accessible, reactive azide groups in large pores that 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 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 the pore walls of the MOFs with precise control over the loading, density, and functionality.

To design an azide-appended MOF material with large enough cavities whose openings can be fully accessed by various molecules with an alkyne group for the click reaction, we designed four elongated linear dicarboxylic acids with three benzene rings in each, 2',5'-dimethylterphenyl-4,4''-dicarboxylic acid (TPDC-2CH₃) and 2',3',5',6'-tetramethylterphenyl-4,4''-dicarboxylic acid (TPDC-4CH₃), and their corresponding azide derivatives (TPDC-2CH₂N₃ and TPDC-4CH₂N₃) as organic linkers [section 2 in the Supporting Information (SI)]. To ensure structural integrity during the click reaction, we aimed to construct Zr-based MOFs, which are well-known for their superior stability compared with common Zn/Cu-centered MOFs.¹¹ It is especially difficult to obtain single crystals of Zr-based MOFs because the inert coordination bonds between Zr⁴⁺ cations and carboxylate anions make ligand exchange reactions extremely slow, which is unfavorable for defect repair during crystal growth.¹¹ To overcome this difficulty, a modulated synthetic strategy was adopted, and benzoic acid was introduced into the synthetic system.^{11c} To our delight, octahedron-shaped crystals suitable for single-crystal X-ray diffraction (XRD) were obtained from a reaction mixture containing zirconium(IV) chloride, the elongated organic linkers, benzoic acid, and *N,N*-

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dimethylformamide (DMF), which was allowed to stay at 100 °C in an oven for 2 days or at 120 °C for 12–18 h (section 3 and Figure S40 in the SI).¹² The four MOFs, $Zr_3O_2(OH)_2(TPDC-R)_3$ [$R = 2CH_3$ (PCN-56), $4CH_3$ (PCN-57), $2CH_2N_3$ (PCN-58), $4CH_2N_3$ (PCN-59); PCN stands for “porous coordination network”] were confirmed to possess isorecticular structures similar to the UiO type structure on the basis of single-crystal XRD structural and powder XRD (PXRD) analyses (sections 4 and 5 in the SI).^{11a} In the absence of benzoic acid, these MOFs could also be obtained but only in fine powders, revealing the vital role of benzoic acid in the growth of crystals (Figure S45). The characteristic IR band of the azide group ($\sim 2100\text{ cm}^{-1}$) was absent for PCN-56 and -57 and stronger for PCN-59 than for PCN-58, consistent with the suggested structures. Moreover, digested PCN-58 and -59 crystals in dimethyl sulfoxide afforded almost the same ^1H NMR spectra as those of the corresponding organic linkers (Figure S25), further demonstrating the intactness of ligand in the MOFs.

All of the MOFs crystallized in the $Fm\bar{3}m$ space group, and the unique Zr atom, in a square-antiprismatic coordination environment, is coordinated by eight O atoms from four carboxylates and four $\mu_3\text{-O}$ or $\mu_3\text{-OH}$ groups. Sets of six Zr atoms are interconnected by O atoms to form $Zr_6O_4(OH)_4$ octahedral cores, the triangular faces of which are alternatively capped by $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ groups (Figure 1a, inset). All of the polyhedron

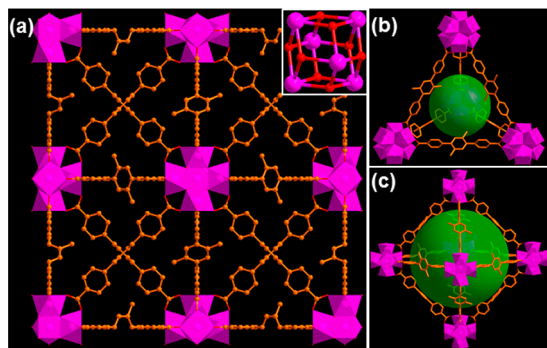


Figure 1. (a) View of the structure of PCN-56, in which each TPDC-derived linker bears two methyl groups. Accordingly, four methyl, two methyl azide, and four methyl azide groups are attached to each organic linker in PCN-57, PCN-58, and PCN-59, respectively. Inset: a Zr_6 cluster. (b) Tetrahedral and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

edges are bridged by carboxylates from the ligands to afford $Zr_6O_4(OH)_4(CO_2)_{12}$ clusters. The clusters are connected by 12 linear ligands, each of which links two clusters, giving rise to a three-dimensional (3D) network with two types of polyhedral cages (Figure 1a). One is tetrahedral, comprising four Zr_6 clusters and six ligands with a cavity diameter of ~ 1.1 nm (Figure 1b), and the other is octahedral, consisting of six Zr_6 clusters and 12 ligands with a cavity diameter of ~ 2.2 nm (Figure 1c).

With strong bonds between the Zr^{4+} cations and the O atoms, thanks largely to the high charge density (Z/r) and the consequential bond polarization, all of these MOFs exhibited exceptional robustness. Thermogravimetric analyses indicated that PCN-56 and -57 with methyl groups were stable up to 350–400 °C, while the frameworks of PCN-58 and -59 bearing azide groups remained intact to >200 °C, after which decomposition of the azide groups triggered the collapse of the whole framework.

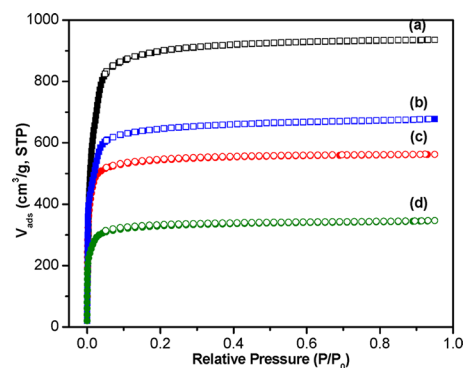


Figure 2. N_2 sorption properties for (a) PCN-56, (b) PCN-57, (c) PCN-58, and (d) PCN-59 at 77 K and 1 atm. Solid symbols, adsorption; open symbols, desorption. The BET surface areas of 3741, 2572, 2185, and 1279 m^2/g for PCN-56 to -59, respectively, are comparable to the calculated values (3317, 2416,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

Importantly, chemical stability examinations revealed that these MOFs can 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 (section 12 in the SI).

Because of their microporosity and robustness, all of the MOFs displayed typical type-I gas sorption isotherms with a range of surface areas, with PCN-56 presenting a Brunauer–Emmett–Teller (BET) surface area as high as 3741 m^2/g (Figure 2). Although PCN-58 and -59 had decreased surface areas due to occupation of the pores by azide groups, the introduction of the azide groups improved the adsorption enthalpy of CO_2 (20, 22, 25, and 33 kJ/mol respectively for PCN-56 to -59) and effectively enhanced the CO_2 capture performance because of the polarity of the 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. On the basis of the current study and literature reports, it was evident that appending azide groups to the linker did not change the final MOF structure.^{6b,13} Hence, it was reasonable to assume that preadjusting the molar ratio of ligands with CH_3 and CH_2N_3 groups would allow control of the azide loading in the resultant MOFs. To test this hypothesis, MOFs with N_3 loadings of 25 and 75% were obtained by employing a 1:1 ratio of TPDC- $2CH_3$ and TPDC- $2CH_2N_3$ and a 1:1 ratio of TPDC- $2CH_2N_3$ and TPDC- $4CH_2N_3$, respectively (Figure 3). These MOFs showed PXRD patterns similar to those of PCN-56 to -59, indicating retention of the framework structure. They also had similar IR features, but the intensity and peak area of the azide absorption band at $\sim 2100\text{ cm}^{-1}$ increased almost linearly with increasing azide loading (Figure 4); together with elemental analysis data, these results further demonstrated the consistency between the theoretical and actual azide group contents in the MOFs (section 11 in the SI). This remarkable synthetic strategy can be further extended to the synthesis of other isorecticular MOFs with azide loadings anywhere between 0 and 100% under similar reaction conditions simply by adjusting the ligand ratio. Most importantly, when coupled with a postsynthetic click reaction, such a synthetic strategy for MOF functionalization via coassembly with mixed ligands provides a universal pathway toward MOFs with desired internal surface properties, which are vital for their applications.

Zr-based 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 °C in DMF. After the reaction

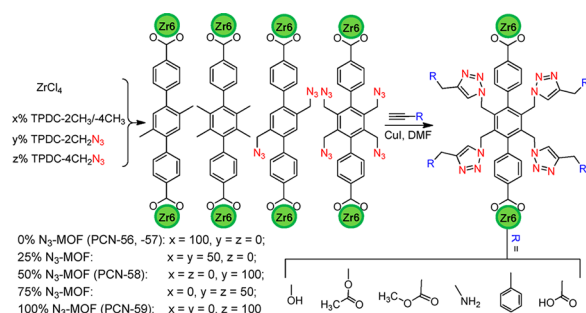


Figure 3. Schematic illustration of the general strategy for pore surface engineering of MOFs with precise control over the composition, density, and functionality by two steps in the current synthetic system: (1) introduction of azide groups into the MOF with a desired loading (any value from 0 to 100%)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

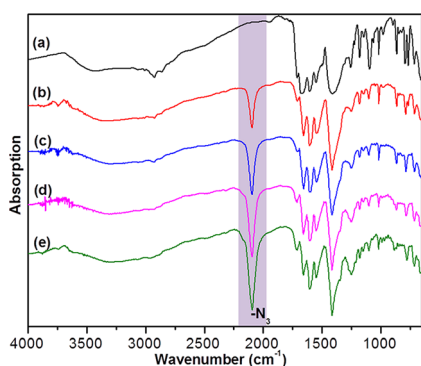


Figure 4. IR spectra of Zr-based MOFs with (a) 0% N_3 (PCN-56), (b) 25% N_3 , (c) 50% N_3 (PCN-58), (d) 75% N_3 , and (e) 100% N_3 (PCN-59). The intensity of the characteristic IR band of the azide group at $\sim 2100\text{ cm}^{-1}$ (highlighted in light purple) is proportional to the azide loading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

was terminated, the products were isolated in quantitative yields by centrifugation and washing with acetone. It was demonstrated that very few Cu species ($< 2\text{ wt } \%$) from the CuI catalyst remained in the product (section 14 in the SI), similar to the previous report.¹⁴ PXRD studies confirmed the retention of the framework integrity and the crystallinity of the resultant MOFs anchored with various loadings of hydroxyl groups (section 13 in the SI). As direct evidence of a complete click reaction, the characteristic IR band for the azide group disappeared completely (sections 8 and 10 in the SI).

Since 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 bearing various substituents, such as propargyl acetate, methyl propiolate, propargylamine, phenylacetylene, and propiolic acid. Under reaction conditions similar to those for propargyl alcohol, various functional groups were successfully anchored onto the MOF pore walls via triazole linkages formed by the click reaction; the positions and loadings of the functional groups were identical to those of the azide-appended MOF precursors. The identities of the functionalized MOFs were validated by PXRD and IR characterizations. To verify further the proposed products of the

Table 1. Experimental BET Surface Areas^a (in m^2/g) for MOFs with Different N_3 Loadings That Were Functionalized with Diverse Groups via Click Reactions

	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

^aFrom data for $0.005 < P/P_0 < 0.15$. ^bi.e., PCN-58. ^ci.e., PCN-59.

click reaction, we investigated the ^1H NMR spectra of the digested solutions for all of the PCN-58-derived products; the results showed that the corresponding triazole derivatives were formed and almost no starting material remained (section 8 in the SI). On the basis of the above studies, the coupled strategy of postsynthetic click reaction and MOF functionalization through coassembly with mixed ligands may be general. It will allow us to anchor almost any desired functional group onto the pore walls in MOFs with precisely controlled loadings, enabling more potential applications.

Upon the introduction of diverse functional groups that may have different affinities for 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 streams. Compared with the MOF precursors, all of the functionalized MOFs obtained by click reaction exhibited moderate BET surface areas ($400\text{--}1000\text{ m}^2/\text{g}$ for PCN-58-derived products and $200\text{--}450\text{ m}^2/\text{g}$ for PCN-59 derived products; Table 1), indicative of space filling by the functional groups introduced. Their N_2 uptake at 273 K was almost undetectable, although they could adsorb a significant amount of CO_2 at 273 or 296 K and 1 atm (sections 8 and 10 in the SI). As shown in Figure 5, it is evident that the introduction of azide groups increased the selectivity for CO_2 over N_2 (see above). Different loadings of azide groups in the MOF enabled us to anchor the corresponding amounts of hydroxyl groups onto the

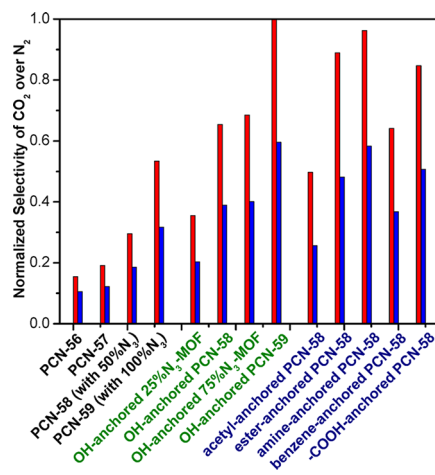


Figure 5. Normalized adsorption selectivity for CO_2 over N_2 [obtained as the CO_2 sorption amount (1 atm and 273 K for red bars; 1 atm and 296 K for blue bars) divided by the N_2 sorption amount at 1 atm and 77 K] for three sets of samples: Zr-based MOFs with various azide loadings, black labels; hydroxyl group-functionalized Zr-MOFs with various azide loadings, green labels; PCN-58 functionalized with diverse groups, blue labels.

pore walls. Overall, the selectivity for CO₂ over N₂ was also proportional to the loading of hydroxyl groups. In addition, various functional groups embedded into PCN-58 resulted in different selectivities for CO₂ over N₂, with amine being the functional group that showed the highest selectivity as a result of not only the polarity interaction but also the “acid–base” reaction between the alkylamine and CO₂, in agreement with previous reports.¹⁵ In summary, preliminary results have revealed that pore surface engineering of MOFs with diverse groups and controlled loading can significantly affect their gas sorption selectivity.

In conclusion, reactions of ZrCl₄ and single or mixed linear ligands bearing methyl or azide groups led to highly stable isoreticular Zr-MOFs with tunable loadings of azide groups inside the pores. The system offers for the first time an ideal platform for facile pore surface engineering through the introduction of various functional groups with controlled loadings via the click reaction. Remarkably, the resultant click products have been demonstrated to possess well-retained frameworks and accessible functionalized pores. This work provides a general approach for introducing diverse functional groups, especially large and/or reactive groups, into MOF pores to create MOFs that otherwise could not be directly synthesized by conventional solvothermal reactions. The tailoring of pore surfaces in MOFs with control over both the type and density of functional groups will extend their functionalities further toward broader applications.

■ ASSOCIATED CONTENT

Supporting Information

Sample preparation, 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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