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Postsynthetic Addition of Ligand Struts in Metal−Organic Frameworks: Effect of Syn/Anti Addition on Framework Structures with Distinct Topologies

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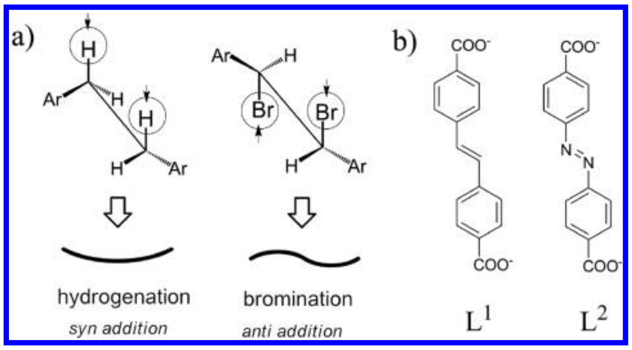
Supporting Information

ABSTRACT: For the parent metal−organic framework (MOF) of UiO-type **1**, postsynthetic bromination (anti addition) was readily carried out on the stilbene-ligand struts by directly adding excess bromine, whereas successful hydrogenation (syn addition) can only be achieved by slowing the reaction rate; otherwise, the crystalline structure of **1** will be irreversibly damaged. Meanwhile, Kagomé-like MOF **2** can be smoothly modified by both postsynthetic bromination and hydrogenation. This study of the structural conversion not only represents the first example that adopts postsynthetic hydrogenation for modifying MOFs but also reveals various factors such as the reaction manner of syn/anti, framework topology, and reaction rate that can influence postsynthetic modification on the ligand struts of MOFs.

Postsynthetic modification (PSM) has been widely used as an effective method for functionalization of metal−organic frameworks (MOFs).[1] Compared with the majority of PSM occurring on pendant moieties,[2] there have been fewer examples that PSM was carried out on ligand struts.[3,4] However, it is particularly attractive to study this PSM of the ligand struts, which can not only influence the framework structure to a great extent but also endow MOFs brand-new properties. For instance, Forgan and co-workers modified and fully characterized a series of UiO-type MOFs with unsaturated alkene and alkyne struts by halogenation.[3b−d] Nanoindentation measurement showed that bromination of these MOFs leaded to a reduced elastic modulus.[3b] Very recently, our work presented that the modified MOF after postsynthetic bromination of the ligand strut exhibited interesting dynamic behaviors, such as reversible structural deformation, vapor sorption hysteresis, and unexpected adsorption of bulky guest molecules, which was quite different from the rigid parent MOF.[4] Despite some progress, it is still very difficult to develop new PSM reaction types and framework systems. An intrinsic challenge is that the great configuration change of the ligand struts in the PSM process would readily damage the framework structure because of the relatively weak coordination bonds. Thus, it is highly required to understand various parameters, particularly structural factors at the molecular level, that could affect the PSM result.

Because of its importance and relative simplicity, the process of addition reaction is clearly understood. In general, it adopts two different manners, i.e., syn and anti addition, in which two substituents can be added to the same or opposite side of an unsaturated bond. The typical examples of syn and anti addition are hydrogenation[5] and bromination[6] of olefins, respectively, which can lead to intermediates with distinct geometry and stereochemistry. As shown by Scheme 1a, angular and staggered configurations of the intermediates can accordingly originate from the syn and anti addition of olefin ligands. If syn/anti addition reactions are both employed to modify the ligand struts in MOFs with different topologies, the structural relationship between the linker configuration and network topology may be revealed. Particularly for syn addition, it is very attractive to investigate the effect of a dramatic configuration change of the linkers on the framework stability. Therefore, this reaction system of syn/anti addition on the olefin-containing MOFs may provide an excellent platform to obtain theoretical and practical knowledge for successfully modifying MOFs.

Scheme 1. (a) Schematic Representation of the Geometrical Configurations of Intermediates in Syn and Anti Addition Reactions and (b) Structures of L^1 and L^2



In this work, 4,4′-stilbenedicarboxylate (L^1, Scheme 1b) with an unsaturated alkene unit was chosen as the ligand for preparing two highly stable MOFs of $[Zr_6O_4(OH)_4(L^1)_6]_n$ (**1**) and $[Al(OH)(L^1)]_n$ (**2**) with distinct topologies. For the parent Zr-MOF **1**, postsynthetic bromination (anti addition) was readily

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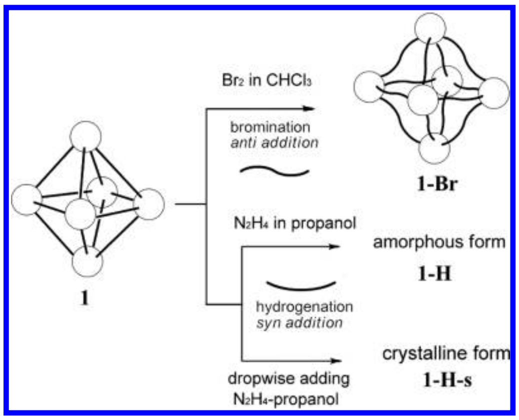
carried out on stilbene-ligand struts by directly adding excess bromine, whereas successful hydrogenation (syn addition) can only be achieved by slowing the reaction rate; otherwise, the crystalline structure of **1** will be irreversibly damaged. Different from **1**, syn and anti additions of Kagomé-like **2** were both carried out smoothly, and the final crystalline structures were retained after PSM. Analogues of the MOFs **3** and **4** prepared from the azo ligand L^2 displayed similar results after postsynthetic hydrogenation.

Scheme 2. Postsynthetic Addition of the UiO-Type MOF 1 by Anti Bromination and Syn Hydrogenation



Cuboctahedron-shaped single crystals of **1** with high quality were synthesized according to the literature,[4] which shows a UiO isoreticular structure with fcu topology by arranging the octahedral cages in three dimensions.[7] By immersion of sample **1** in a chloroform solution of Br_2, the quantitative bromination of the alkene units and the integrality of the framework were proven by ^{1}H NMR, powder X-ray diffraction (XRD), and even single-crystal XRD.[3b,4] As illustrated by Scheme 2, although L^1 after bromine addition adopts a staggered configuration, the two coordination carboxylates of the brominated ligand are still oriented at 180° with a linear mode, without breaking the long-range order in three dimensions of **1**. Thus, the framework structure after bromination can still be maintained, without altering the framework topology and space group.[3b,4,8] Different from bromination, hydrogenation reaction generates an angular intermediate, which means a temporary bending of the ligand struts. In order to react under mild conditions, we selected a solution reaction system of hydrazine as the hydrogen source, guanidine as the catalyst, and propanol as the solvent at 80 °C, according to the literature.[5] In sharp contrast to the bromination process, hydrogenation of **1** was unsuccessful by the direct addition of excess hydrazine solution and the framework was largely destroyed, almost losing its long-range order (denoted by **1-H**, Figure 1a). The results are presumably caused by two possible reasons, that is, breaking of the Zr−O coordination bond under the hydrogenation conditions or configurational twisting of the ligand struts during syn addition. As a comparison experiment, an isoreticular Zr-MOF of UiO-67 was prepared from biphenyl-4,4′-dicarboxylic acid[9] and then immersed in the above-mentioned reaction solutions. Powder XRD demonstrated that UiO-67 still remained its original structure, indicating that the hydrogenation conditions did not damage the Zr−O coordination bond in this situation (Figure S4). Therefore, it is reasonable to assume that the unsuccessful hydrogenation of **1** is ascribed to the changed configuration of the ligand struts in MOFs. When the syn addition was rapidly carried out, a considerable number of angular diarylethane intermediates, which did not satisfy the symmetry of the fcu topology, were generated and resulted in a fast destruction of the framework. Interestingly, when the hydrogenation reaction was slowed by the dropwise addition of a hydrazine solution to the reaction system, the MOF **1** could be quantitatively modified to afford **1-H-s**, which retained excellent crystallinity (Figure 1). This may be because slowing the rate of linker hydrogenation allows the MOF **1** to accommodate a small number of angular linker "defects" and retain its structural integrity. Subsequently, the angular intermediates, temporarily generated during the syn addition, might be able to convert to a more stable staggered configuration that satisfies the symmetry of the UiO-type structure. As the reaction proceeds, L^1 can be completely hydrogenated and the whole framework structure remains intact.

To evaluate the effect of the framework topology in the PSM process, the Al-based **2** with distinct topology was synthesized by the reaction of L^1 and aluminum chloride in solvothermal synthesis as reported (also known as CYCU-3).[10] The MOF **2** is based on one-dimensional Al−O inorganic chains as building blocks, which are further linked together by ligand L^1 to generate two types of one-dimensional open channels: hexagonal mesopores (3.0 nm diameter) and triangular micropores (1.5 nm diameter) (Scheme 3). This structure can be viewed as an analogue of MIL-68 with Kagomé topology.[11] The literature showed that **2** displays a high thermal and chemical stability[10] and is a suitable parent MOF for modification by postsynthetic addition.

In contrast to the hydrogenation of **1**, the experimental results demonstrated that postsynthetic hydrogenation of **2** can be smoothly carried out to quantitatively form **2-H**, with no need of slowing the hydrogenation rate, and the overall crystalline structure was well maintained (Figure 2). Although the

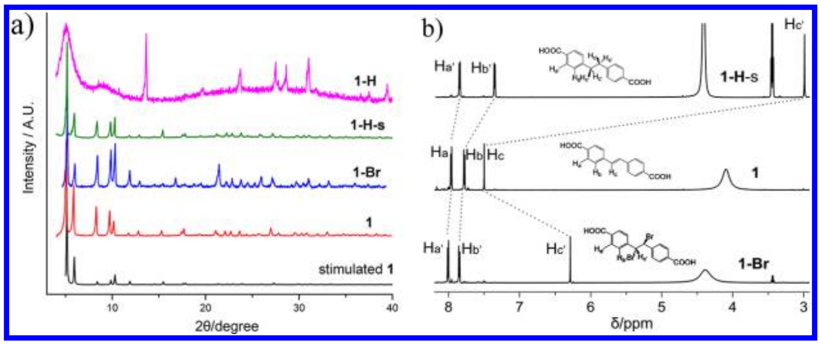


Figure 1. (a) Powder XRD patterns of **1**, **1-Br**, **1-H-s**, and **1-H**. (b) ^{1}H NMR spectra of digested **1**, **1-Br**, and **1-H-s**.

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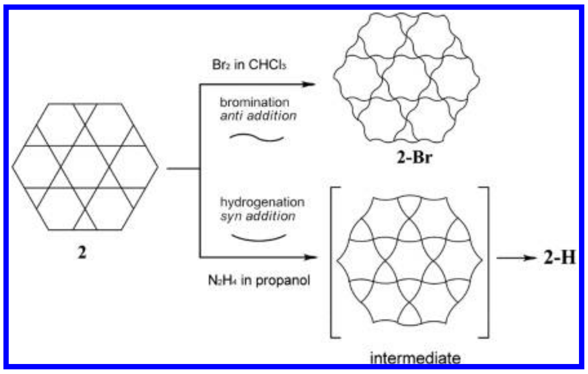
Scheme 3. Postsynthetic Addition of the MOF 2 by Anti Bromination and Syn Hydrogenation



Brunauer–Emmett–Teller surface area of **2-H** has a decrease compared to that of **2** (1320 vs 2327 m^2 g^{-1}; Figures S24 and S25), it possesses a similar pore-size distribution, indicating no detectable structural variation of **2** after hydrogenation (Figure S28). Successful postsynthetic hydrogenation of **2** is probably ascribed to the structural compatibility of the angular intermediates during syn addition and the framework symmetry of **2** (Scheme 3). In addition, the large hexagonal channel of **2** may allow reactants to easily diffuse into the internal surface of **2** without obvious steric hindrance,which is also beneficial for the smooth conversion.

Postsynthetic bromination of **2** was also allowed to occur. The bromination conversion reached 88% within the initial 2 h, but 100% for 1 day, which showed an uneven addition rate (Table S1 and Figures S18–S21). This may be due to the limited diameter of the triangular channel, and the initially added substituents are likely to hinder the diffusion of bromine species, which decreases the subsequent bromination efficiency. Although the original structure can be maintained after complete bromination, the powder XRD pattern of **2-Br** is not as smooth as that of the pristine **2**, possibly ascribed to the large volume of bromine that slightly distorts the structure of the triangular channel (Figure 2a).

To confirm the above factors that influence the PSM process, an azo ligand of 4,4′-azobenzenedicarboxylic acid (L^2) was used to prepare the UiO-type **3** (analogue of **1**) and the Kagomé-like **4** (analogue of **2**) instead of L^1. After their postsynthetic hydrogenation, the ordered structure of **3** was completely transformed only by the dropwise addition of a hydrazine solution, while **4** was successfully modified with no need for slowing the reaction rate (Figures S2 and S3). Because hydrogen addition to azo compounds also adopts syn addition,[12] these results completely coincide with the previous conclusion.

In conclusion, two highly stable MOFs of Zr-based **1** and Al-based **2** with distinct topologies were prepared from 4,4′-stilbenedicarboxylate with an unsaturated alkene unit. By postsynthetic hydrogenation (syn addition) and bromination (anti addition) of the ligand struts in the MOFs, **1** and **2** as parent MOFs were successfully modified under different reaction conditions. This study of structural conversion not only represents the first example that adopts postsynthetic hydrogenation for modifying MOFs, to our knowledge, but also reveals various factors such as the reaction manner of syn/anti, framework topology, and reaction kinetics that affect PSM on the ligand struts. These findings provide new insight into the design and rational preparation of MOFs with novel structures and properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02899.

> Detailed experimental procedures, ^1H NMR spectra, TGA, powder XRD patterns, N_2 adsorption isotherms, pore-size distribution, and UV–vis spectra (PDF)

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Notes

The authors declare no competing financial interest.

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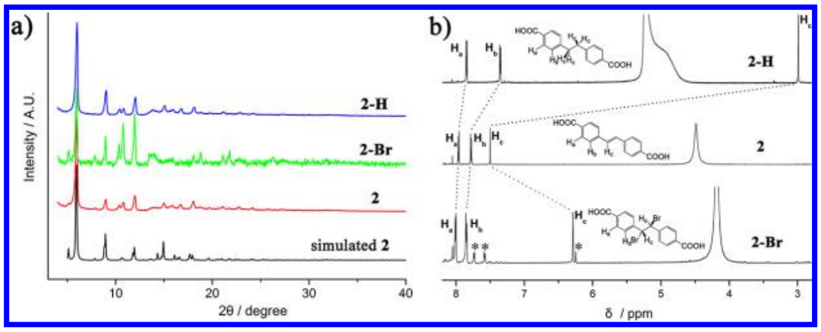

Figure 2. (a) Powder XRD of **2**, **2-Br**, and **2-H**. (b) ^1H NMR spectra of digested **2**, **2-Br**, and **2-H**. The signals of the racemic diastereomer of the brominated stilbene linker are marked with asterisks.[3a]

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