Communication

"Clickable" Metal#Organic Framework

Yuta Goto, Hiroki Sato, Seiji Shinkai, and Kazuki Sada

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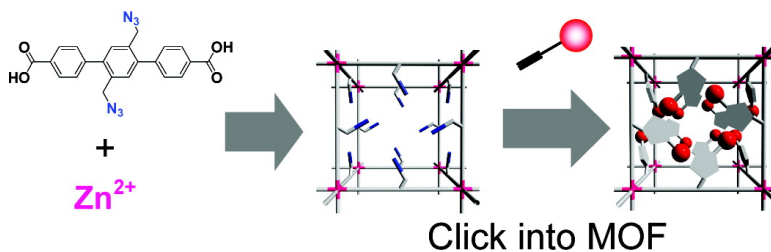
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"Clickable" Metal−Organic Framework

Yuta Goto, Hiroki Sato, Seiji Shinkai, and Kazuki Sada*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

Received December 26, 2007; Revised Manuscript Received August 28, 2008; E-mail: sadatcm@mail.cstm.kyushu-u.ac.jp

Metal−organic frameworks (MOFs) constructed from organic ligands as linkers and metal ions as nodes have become one of the most fascinating porous materials for gas storage,[1] catalysts,[2] and sensors,[3] owing to their isoreticular frameworks. In particular, the robust frameworks have enabled us to design the sizes and shapes of the nanosize pores by replacement of the organic linkers and metal ions. More recently, growing interests have been attracted for development of new functions of MOFs by photochemical processes between guest molecules and metal ions in the nodes for sensing and introduction of functional groups in the organic linkers for catalysis. Such functionalized MOFs have been generally prepared from the conventional solvothermal reactions between the functionalized organic linkers and the metal ions. The server conditions for the functional groups in the solvothermal synthesis and unpredictable deformation of the reticular frameworks by incorporation of the functional groups into the coordination networks proved difficult for introducing various functional groups into the well-defined MOFs. One of the most promising approaches for modification of MOFs is postmodification by chemical reactions without any deformation of the open frameworks. Indeed, this approach has recently been realized successfully by Cohen and co-workers.[4] They used MOFs with amino groups as a starting MOF that was treated with acetic anhydride to yield acetamide MOFs. However, this system also did not have wide applicability as the modification method for MOFs, and development of more applicable and sophisticated reactions is still being sought.

A copper(I)-catalyzed azide-alkyne cycloaddition reaction, a so-called "click reaction," has received a great deal of use in such diverse fields as bioconjugation *in vitro*[5] and *in vivo*,[6] dendrimer synthesis and polymer ligation, combinatorial organic synthesis, and surface science.[7] It proceeds efficiently even at micromolar concentrations of reactants with high yields and high specificity in the presence of various functional groups. Such key features prompted us to use it for the modification of well-defined MOFs. This paper describes the click reaction between azide groups in the reticular network of MOFs and external alkynes with various functional groups as guest molecules.

The organic linker (**N3**) with the azide functional group was prepared according to Figure S1 in the Supporting Information (SI) and treated with zinc nitrate hexahydrate in *N,N*-diethylformamide (DEF) at 353 K for 18 h to yield pale-yellow cubic crystals (Figure S1). The resulting cubic crystals were characterized by X-ray powder diffractions (XRPD) as shown in Figure 2. The XRPD pattern was the same as that of the predicted pattern of **IRMOF-16** prepared from a zinc ion and unmodified terphenylenedicarboxylic acid under the same conditions.[8] Moreover, preliminary X-ray single crystal analysis indicated that the cubic crystal had similar crystal lattice parameters[8] (Cubic I, $a = b = c = 21.725$, $\alpha = \beta = \gamma = 90°$, $V = 10\ 253.7$ Å³). In the IR spectrum, the cubic crystals have the stretching band of the azide group at 2100 cm⁻¹ with the C−O stretching band of zinc carboxylate at 1400 cm⁻¹,
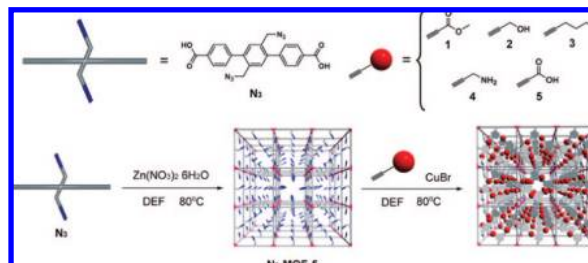

Figure 1. Azide modified linker (**N3**), schematic drawing of MOF (**N3-MOF-5**) of **N3** by Zn(II), and alkynes(**1−5**) as substrates for the click reaction.
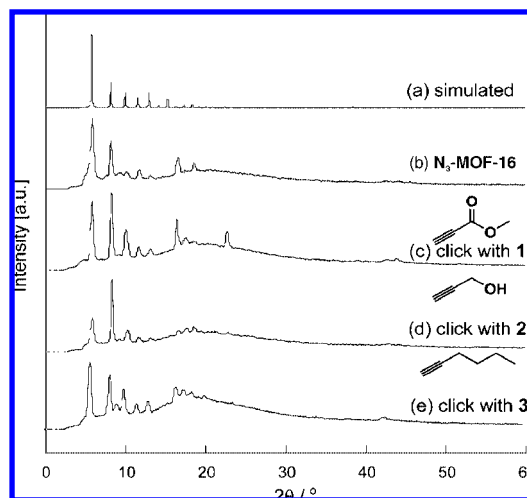

Figure 2. XRPD patterns of (a) simulated form **IRMOF-16**, (b) as synthesized **N3-MOF-16**, and MOFs after click reaction for 24 h with (c) **1**, (d) **2**, and (e) **3**.

as shown in Figure 3. The similarity of the XRPD pattern to the parent **IRMOF-16** and existence of the azide band in the IR spectrum suggested formation of azide-modified MOF (**N3-MOF-16**) with the same network as **IRMOF-16**. The crystal data of **IRMOF-16** indicated that **N3-MOF-16** also had large host cavities with steric dimensions of *ca.* 8 Å × 8 Å.[8]

We further tried the *in situ* click reaction between the azide groups in the MOF network and the external alkynes. The cubic crystals of **N3-MOF-16** were treated with an excess amount of the small alkynes with various functional groups in the presence of CuBr at 353 K in DEF. The click reaction was monitored by IR spectra after isolation of the MOFs by removal of unreacted alkynes and solvents by repeated washing and drying *in vacuo*, as shown in Figure 3. For example, in the case of **1** as the substrate for the click reaction, the azide stretching band at 2100 cm⁻¹ decreased within 30 min and completely disappeared after 3 h. The carbonyl stretching band at 1739 cm⁻¹ increased with an increase in reaction
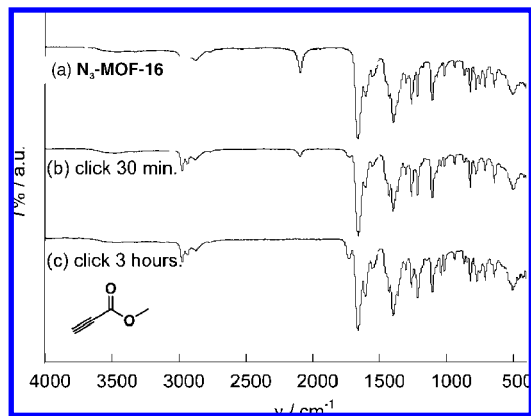
Figure 3. Click reaction of **1** into **N3-MOF-16**, monitored by IR: (a) as synthesized **N3-MOF-16**, (b) 30 min, and (c) 3 h.

Figure 4. IR spectra of (a) as synthesized **N3-MOF-16** and after click reaction with (b) **2** and (c) **3**.

time. Without alkynes, no decrease of the azide band and no increase of the carbonyl band were observed under the same conditions. These results suggested progress of the click reaction in the **N3-MOF-16** network. On the other hand, the C−O band at 1400 cm^{-1} was not changed during the reaction conditions, which indicated that the MOF framework constructed by zinc ions and carboxylate anions was preserved during the click reaction. This was confirmed by the similar XRPD patterns after the click reaction, as shown in Figure 2c. Moreover, after the click reaction, the clicked **N3-MOF-16** crystal was still kept in a cubic shape, but the crystal edges became slightly round under microscope observation (Figure S2 in the SI). Slight dissolution occurred during the incubation, but most of the crystal remained unchanged. Therefore, we believe that the click reaction proceeded without dissolution and reconstruction of MOF in DEF.

To verify the click reaction, we investigated the ^{1}H NMR spectrum of the reaction product from **N3-MOF-16** and **1** after decomposition of MOF by DCl−D$_2$O−DMSO-d_6. The solution ^{1}H NMR spectrum of the reaction product illustrated that the corresponding triazole derivative was formed in the reaction of **N3-MOF-16** as the major product and that no starting material was detected. Thus, we believe that **N3-MOF-16** underwent the click reaction with the external guest alkyne of **1**.

We further investigated click reactions with other small alkynes (**2**−**5**). In the cases of **2** and **3**, the click reaction proceeded in the presence of CuBr in DEF. All of the azide stretching bands of **N3-MOF-16** in the presence of **2** and **3** decreased in the presence of the alkynes, as shown in Figure 4. The reactions were much slower than that of **1**, but the azide stretching bands disappeared after incubation for 24 h and the XRPD patterns were identical to those of the starting **N3-MOF-16**. On the other hand, after soaking **N3-MOF-16** in a solution of **4** and **5**, all of the crystals were dissolved into the reaction mixtures and no crystals remained after 24 h. Under these conditions, the MOF was unstable, and the amine and carboxylic acid moieties decomposed the metal−organic frameworks of the zinc ion and **N3**. These results indicated that **N3-MOF-16** can react with some small alkynes, if the functional groups in the alkynes did not decompose the metal−organic frameworks.

In this report, we demonstrated formation of an MOF bearing the azide group in the organic linkers and *in situ* click reactions with some small alkynes. The XRPD patterns indicated that the click reaction proceeded without any decomposition of the original MOF network. Wide applicability of the click reactions in the presence of various functional groups would provide us postmodi-
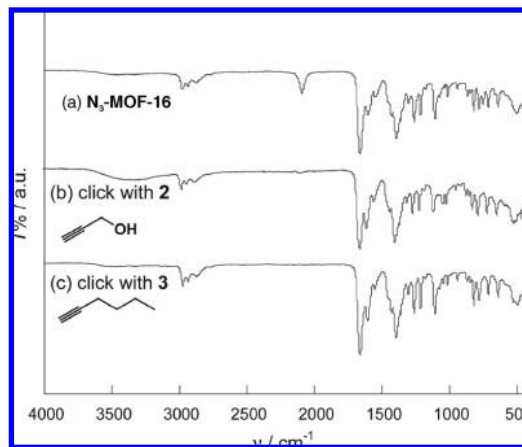
fied MOFs bearing various functional groups. Moreover, the click reactions should be applied selectively for the outside surfaces of MOFs by utility of bulky alkynes, which implies wrapping of MOFs by other polymeric materials and the gating functional groups. Thus, we believe that our clickable MOFs have a wide scope for materials sciences. Such modifications of MOFs' inside as well as outside surfaces are under current investigation.

Supporting Information Available: Synthetic procedure of **N3** and ^{1}H NMR spectrum of the reaction product from **N3-MOF-16** and **1**. This material is available free of charge via Internet at http://pubs.acs.org.

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