Light-Activated MOFs

DOI: 10.1002/anie.201004736

Photochemical Activation of a Metal–Organic Framework to Reveal Functionality**

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In the field of metal–organic frameworks (MOFs), the concept of postsynthetic modification (PSM) has garnered increasing interest as a useful synthetic approach.[1] PSM has been found to be a powerful tool for introducing new functionality and hence new physical and chemical properties into these porous materials. In general, PSM has largely been described in the context of treating MOFs with reagents that can react with an available chemical "handle" on the MOF framework.[2–8] In contrast, the removal of chemical groups on and within a MOF to reveal new chemical functionality is far less well studied.[9,10] Here we describe how light can be used to remove protecting groups from the organic components of a MOF lattice in a single-crystal-to-single-crystal (SCSC) fashion. In this manner the MOF lattice is kept pristine, while unmasking new chemical functionality throughout the pores of the MOF. Our findings suggest that this kind of postsynthetic "deprotection" of MOFs may be an excellent strategy for producing porous materials containing complex functionality.

A small number of studies have described the deprotection of protecting groups within a MOF lattice using either chemical reagents or thermal treatment.[9,10] Recently, Telfer et al. performed a controlled postsynthetic deprotection by using a thermally labile protecting group (e.g., Boc = *tert*-butoxycarbonyl) to yield a free amino group within a MOF.[11] The MOF, which was prepared from Zn^{2+} and 2-(*tert*-butoxycarbonylamino)biphenyl-4,4′-dicarboxylic acid, was heated to $>150\,^{\circ}C$ to remove the Boc protecting group. ^1H NMR analysis of the digested sample and thermal gravimetric analysis (TGA) confirmed the successful deprotection. The MOF was found to remain intact by single-crystal X-ray diffraction, but attempts to confirm the deprotection by gas sorption were not achieved due to pore collapse upon solvent evacuation.

To the best of our knowledge, there are very few studies that have reported on the light-driven chemical modification or alteration of a MOF.[12–16] Light driven processes should be an efficient and relatively gentle method by which to initiate chemical reactions within a MOF lattice. Nitrobenzyl groups have been well established in the literature as photocleavable protecting groups for alcohols and amines.[17] A variety of nitrobenzylethers can be cleaved by irradiation with light ranging from ultraviolet to visible range. Herein, we demonstrate that photolabile protecting groups can be liberated within MOFs to yield materials with free hydroxy groups (Scheme 1). This is significant, as reports of MOFs with free, uncoordinated hydroxy groups are extremely rare.[18,19]

2-Hydroxy-1,4-benzenedicarboxylic acid (HO-BDC)[18] and 2,3-dihydroxy-1,4-benzenedicarboxylic acid (CAT-BDC, CAT = catechol)[20] were combined with *o*-nitrobenzyl bromide to generate protected dicarboxylate building blocks suitable for MOF construction (see Supporting Information). The resulting ligands, 2-((2-nitrobenzyl)oxy)terephthalic acid (NO_2BnO-BDC) and 2,3-bis((2-nitrobenzyl)oxy)terephthalic acid (($(NO_2BnO)_2$-BDC), were combined separately with 4,4′,4″-benzene-1,3,5-triyl-tribenzoate (BTB)[21] and Zn-$(NO_3)_2{\cdot}6H_2O$ to obtain UMCM-1-$OBnNO_2$ and UMCM-1-$(OBnNO_2)_2$ (UMCM = University of Michigan Crystalline Material, Scheme 1) as colorless needles (Supporting Information, Figures S1, S2). Both MOFs were found to be structural analogues of UMCM-1, a highly porous MOF that contains BDC and BTB.[22] The structure and composition of UMCM-1-$OBnNO_2$ and UMCM-1-$(OBnNO_2)_2$ were conclusively established by several methods. Digestion of the MOFs in dilute acid followed by ^1H NMR analysis showed that the materials contained both the BTB and the appropriate nitrobenzyl-protected BDC ligand (Figure 1). Powder X-ray diffraction (PXRD) of the MOFs gave a similar pattern as observed for UMCM-1 (Figures S3 and S4). Finally, gas sorption experiments with N_2 at 77 K indicated that UMCM-1-$OBnNO_2$ and UMCM-1-$(OBnNO_2)_2$ were highly porous and showed a characteristic step in the isotherm (Figure 2). The Brunauer–Emmett–Teller (BET) surface areas of UMCM-1-$OBnNO_2$ and UMCM-1-$(OBnNO_2)_2$ were found to be $3219 \pm 150\ m^2\,g^{-1}$ and $2661 \pm 172\ m^2\,g^{-1}$, respectively.

Single-crystal X-ray diffraction of UMCM-1-$OBnNO_2$ and UMCM-1-$(OBnNO_2)_2$ unambiguously showed that both MOFs had the same topology as UMCM-1 (Tables S1–S4). A disordered oxygen atom was located and assigned on the BDC ligand of UMCM-1-$OBnNO_2$; however, the nitrobenzyl substituent could not be located in the electron density map due to positional disorder. In contrast, both protecting groups

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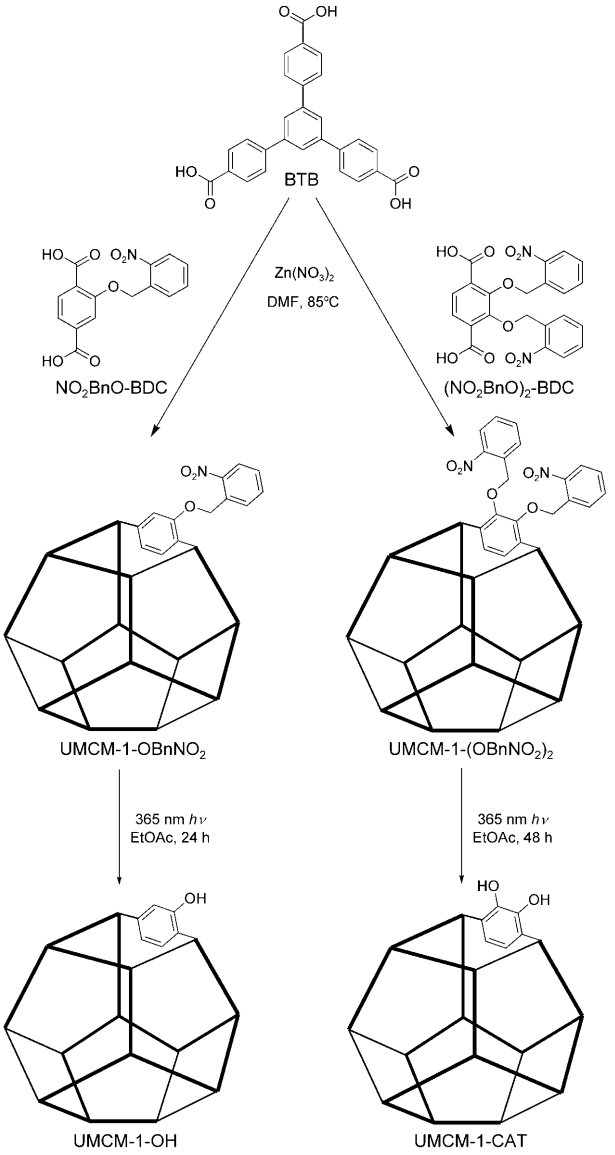
[**] C.A.A. and K.K.T. were equal contributors to this work. We thank Dr. M. Rouffet for synthesis of CAT-BDC, D. Martin for assistance with X-ray crystallography, and Dr. Y. Su for performing mass spectrometry experiments. We thank Prof. R. Snurr (Northwestern University) and Dr. Y.-S. Bae for BET calculations. This work was supported by UCSD, the NSF (new MOF synthesis CHE-0952370; instrumentation grants CHE-9709183, CHE-0116662 and CHE-0741968), and the DOE (gas sorption studies, PXRD, BES Grant No. DE- FG02-08ER46519).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004736.



Scheme 1. Synthesis and postsynthetic photochemical deprotection of UMCM-1-OBnNO$_2$ (left) and UMCM-1-(OBnNO$_2$)$_2$ (right).

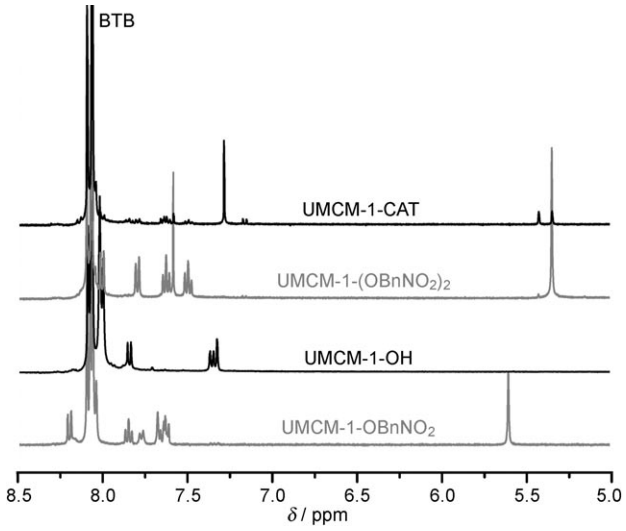


Figure 1. ^{1}H NMR spectra of digested UMCM-1-OBnNO$_2$, UMCM-1-OH, UMCM-1-(OBnNO$_2$)$_2$, and UMCM-1-CAT (DCl/[D$_6$]DMSO).

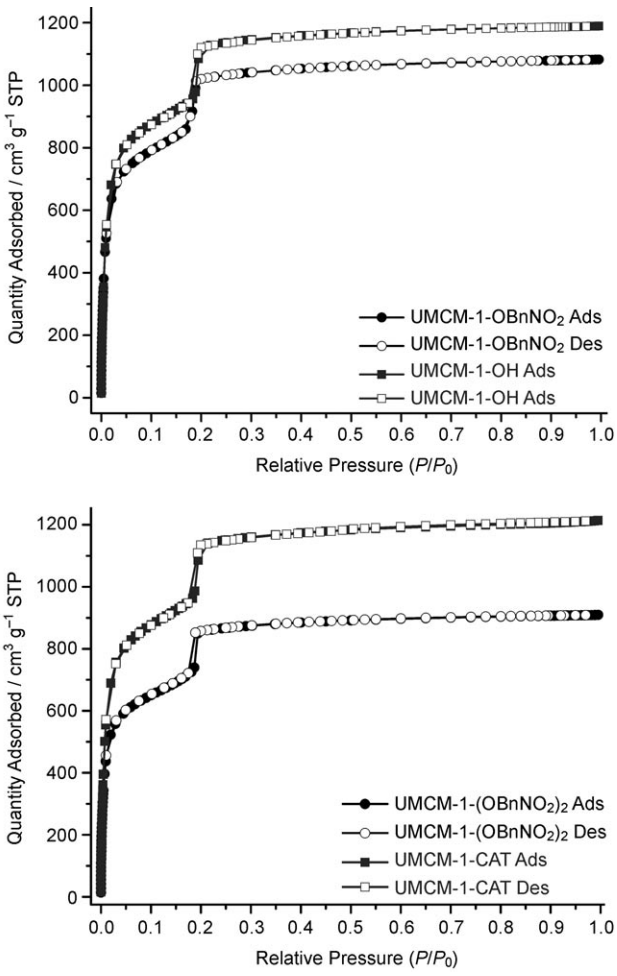


Figure 2. N$_2$ sorption and desorption isotherms for UMCM-1-OBnNO$_2$/UMCM-1-OH (top) and UMCM-1-(OBnNO$_2$)$_2$/UMCM-1-CAT (bottom) at 77 K.

were located and assigned for the structure of UMCM-1-(OBnNO$_2$)$_2$ (Figure 3, Figures S7, S8). Electron density for the NO$_2$ groups was located, but could not be effectively refined due to severe disorder.

UMCM-1-OBnNO$_2$ and UMCM-1-(OBnNO$_2$)$_2$ were irradiated with 365 nm light for 24–48 h; both MOFs underwent a distinct color change from colorless to orange, which was indicative of the photochemical reaction (Figures S1, S2), and release of 2-nitrosobenzaldehyde (which was confirmed by electronic spectroscopy and ESI-MS, data not shown).[17,23,24] Examination by ^{1}H NMR spectroscopy upon digestion of the MOFs in dilute acid showed that the protecting groups were cleaved (Figure 1). UMCM-1-OBnNO$_2$ readily underwent quantitative deprotection to UMCM-1-OH within 24 h. UMCM-1-(OBnNO$_2$)$_2$ was found to achieve ca. 75% deprotection to UMCM-1-CAT under the best conditions identified to date. As additional evidence for the deprotection process,

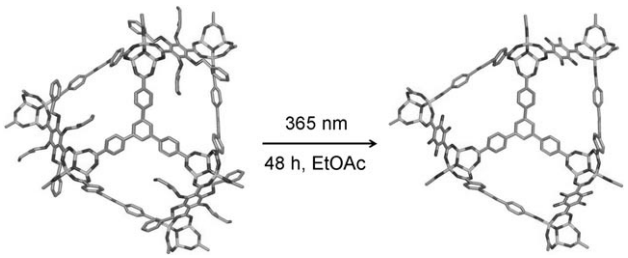


Figure 3. X-ray crystal structure of UMCM-1-$(OBnNO_2)_2$ (left) and after photochemical deprotection to produce UMCM-1-CAT (right).

UMCM-1-CAT was found to fluoresce blue ($\lambda_{ex} = 365$ nm), which is characteristic of CAT-BDC ligand, while UMCM-1-$(OBnNO_2)_2$ showed no fluorescence emission. TGA analysis also revealed differences between the protected and deprotected UMCM MOFs (Figures S9, S10). It is important to note that neither UMCM-1-OH nor UMCM-1-CAT could be prepared by direct solvothermal synthesis from HO-BDC and CAT-BDC (see Supporting Information), thus demonstrating the usefulness of the postsynthetic approach.

Unambiguous evidence for removal of the nitrobenzyl groups in a SCSC fashion was provided by single-crystal X-ray diffraction. The X-ray structure of UMCM-1-OH showed that the framework remained intact after irradiation (Figures S11, S12) and electron density for the hydroxy group on the BDC ligand was resolved. In contrast, deprotection of UMCM-1-$(OBnNO_2)_2$ to UMCM-1-CAT was readily evident by the X-ray structure with the disappearance of the nitrobenzyl protecting groups from the electron density map and appearance of the expected catechol group (Figure 3).

Postsynthetic deprotection of the MOFs was clearly manifest in the gas sorption behavior. N_2 isotherms (77 K) of UMCM-1-OH and UMCM-1-CAT showed significant increases in BET surface area (Figure 2). The BET surface areas were determined to be $3705 \pm 177\ m^2 g^{-1}$ and $3541 \pm 38\ m^2 g^{-1}$ for UMCM-1-OH and UMCM-1-CAT, respectively. The difference between the protected and deprotected MOFs is ca. $500\ m^2 g^{-1}$ and ca. $900\ m^2 g^{-1}$, which is reasonable for the removal of either one (UMCM-1-OH) or two (UMCM-1-CAT) protecting groups from each structure. Although it is not intuitively obvious whether the surface area should increase or decrease upon removal of the protecting groups, calculated surface areas for UMCM-1-$(OBnNO_2)_2$ and UMCM-1-CAT confirm that the there should be an increase upon removal of the protecting groups (see Supporting Information). Furthermore, the changes in BET surface area are consistent with our observations in related systems, where upon introducing substituents by postsynthetic modification we see a decrease in BET surface area.[4] The complete gas sorption isotherms show a substantial increase in capacity at saturation pressures, also consistent with removal of the nitrobenzyl protecting groups. Finally, in both systems, the average pore size distribution changes from ca. 7.5 to 7.9 Å upon removal of the protecting groups (Horvath–Kawazoe model, data not shown). Overall, the gas sorption experiments show that the lattice is intact, the material is highly porous, and that the deprotection reaction results in the expected increase in surface area.

To show that the newly revealed functional groups are accessible, both UMCM-1-$(OBnNO_2)_2$ and UMCM-1-CAT were treated with $[Fe(acac)_3]$ in EtOAc. After 24 h, UMCM-1-$(OBnNO_2)_2$ was a light orange color while UMCM-1-CAT was a deep red-purple color (Figure S21). These color changes were confirmed by diffuse reflectance solid-state electronic spectroscopy of UMCM-1-$(OBnNO_2)_2$, UMCM-1-$(OBnNO_2)_2$ treated with $[Fe(acac)_3]$, UMCM-1-CAT, and UMCM-1-FeCAT, which showed clear differences in absorbance between non-metalated and metalated samples (Figure S22). As expected, UMCM-1-$(OBnNO_2)_2$ did not show any significant absorbance above 400 nm. Both UMCM-1-CAT and UMCM-1-$(OBnNO_2)_2$ treated with $[Fe(acac)_3]$ showed a transition at 500 nm. UMCM-1-CAT also had an additional shoulder around 400 nm, which was indicative of the catechol substituent. UMCM-1-FeCAT exhibited a smaller shoulder at 400 nm, but displayed a strong absorbance between 500 and 600 nm consistent with known Fe^{3+}–catechol complexes.[23,24]

In summary, hydroxy and catechol moieties were successfully incorporated into a MOF by using postsynthetic photochemical deprotection. UMCM-1-OH and UMCM-1-CAT maintained their structural and thermal stabilities under the photochemical conditions. Moreover, UMCM-1-OH and UMCM-1-CAT exhibited significant increases in porosity, which is consistent with the liberation of the bulky nitrobenzyl substituents. Preliminary metalation tests with UMCM-1-CAT confirmed the presence of the catechol unit, as evidenced by binding of Fe^{3+} to the MOF. UMCM-1-OH and UMCM-1-CAT demonstrate the promise of postsynthetic deprotection to obtain MOFs with unprecedented functionality, which may lead to new applications of these materials.

Received: July 30, 2010
Revised: September 13, 2010
Published online: November 9, 2010

Keywords: catechols · metal–organic frameworks · photochemistry · postsynthetic modifications · zinc

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