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Photolabile protecting groups in metal–organic frameworks: preventing interpenetration and masking functional groups†‡

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Photolabile groups can be incorporated into metal–organic frameworks (MOFs) and then quantitatively cleaved following MOF formation. Here, a 2-nitrobenzyl ether prevents lattice interpenetration (catenation) in a cubic MOF derived from zinc(II). Subsequent photolysis unmasks a hydroxyl group, and produces an open MOF that cannot be synthesized directly.

The post-synthetic modification of crystalline metal–organic frameworks (MOFs) has emerged as a versatile and powerful method for tuning the functional attributes of these materials.[1] We are interested in the reverse of this process, *i.e.*, the controlled post-synthetic cleavage of specific framework components. In the first example of this concept, we recently demonstrated how a bulky *tert*-butoxycarbonyl (Boc) group appended to functionalized ligands could be decomposed into volatile fragments by simple heating.[2,3] The thermolysis reaction served to deprotect amino functional groups, which had hindered MOF formation when left exposed during the crystal growth step. Further, the steric bulk of the Boc group suppresses interpenetration, and its cleavage produces an open framework with significant void volumes.

This methodology builds on a significant body of work on thermolabile protecting groups.[4] We reasoned that the scope of our approach may be expanded by introducing *photolabile* protecting groups[5] into MOFs. This would serve to diversify the functional groups that can be surreptitiously incorporated into MOFs, allowing for a wider range of reaction conditions to be used for the synthesis of protected MOFs (specifically higher temperatures and low pH), and provide an alternative physical means by which deprotection of the frameworks can be induced. While this manuscript was in preparation, Cohen *et al.* published a superb demonstration of the viability of this concept. By incorporating 2-nitrobenzylether groups in UMCM-type MOFs (UMCM = University of Michigan Crystalline Material) they were able to mask hydroxyl groups during framework synthesis then reveal them in a post synthetic photolysis step.[6]

Several other pioneering studies have established that MOFs can be addressed and transformed by light. For example, carbonyl ligands of $Cr(CO)_3$ units appended to the phenyl struts of MOF-5 can be labilized by visible light,[7] and cycloaddition reactions of unsaturated ligands have been explored.[8] In very recent work, an azide group was converted into a nitrene within a coordination polymer using UV light[9] and long-lived radicals have been generated within a series of cadmium(II) frameworks upon irradiation.[10]

The design of a framework material for trialing our methodology was influenced by several considerations. First, it was recognized that some metal/ligand combinations may lead to undesirable photochemical reactions that may degrade the integrity of the framework. For example, carboxylate complexes of metals such as copper(II),[11] iron(III)[12] and cobalt(III)[13] are known to decarboxylate upon irradiation into their LMCT bands. Second, a relatively large protecting group is expected to prevent interpenetration and thus encourage the formation of a framework with a network of wide pores (after photolysis) suitable for applications in storage and catalysis. Third, the ideal protective group is one that can be released with a high quantum yield at a wavelength where the remainder of the structure is transparent.

With these considerations in mind, we designed ligand H_2**1** and envisaged that the synthesis and photolytic transformation of the MOF $[Zn_4O(\mathbf{1})_3]$ could be achieved as outlined in Scheme 1. The side-arm **1** features an hydroxyl group that is protected by a large 2-nitrobenzyl moiety. 2-Nitrobenzyl ethers are well established photolabile protecting groups that are cleaved with high efficiency upon irradiation around 350 nm to liberate the parent alcohol.[5,14] Since MOFs comprising zinc(II) and arylcarboxylate ligands transmit a large fraction of light of this wavelength, the light will be predominantly absorbed by the nitrobenzyl chromophore. 2-Nitrosobenzaldehyde is generated as a side product in this deprotection step.

The synthesis of H_2**1** was achieved in three steps starting from dimethyl 2-aminobiphenyl-4,4′-dicarboxylate. As expected on the basis of the pioneering work of Yaghi's group[15] and more recent reports from Burrows *et al.*,[16] and our own group,[2,3] the solvothermal reaction of H_2**1** with $Zn(NO_3)_2$ in *N*,*N*-diethylformamide (DEF) produced well-faceted colorless cubic crystals.

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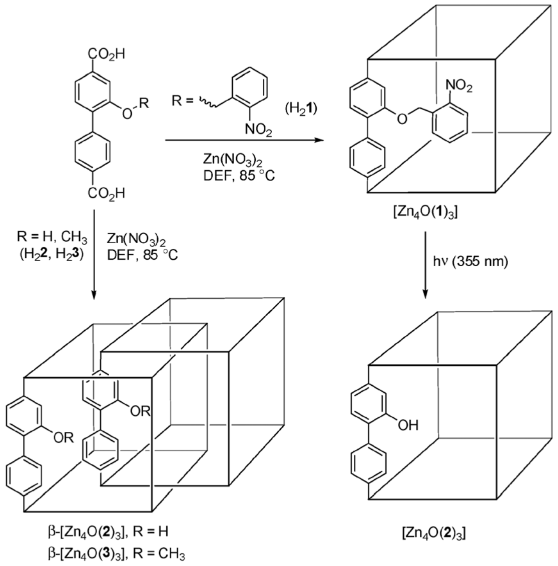

Scheme 1 Conversion of ligand H_2**1** to a noninterpenetrated cubic metal–organic framework, $[Zn_4O(\mathbf{1})_3]$, followed by the photolytic deprotection of the hydroxyl group to generate noninterpenetrated $[Zn_4O(\mathbf{2})_3]$. MOF synthesis using ligand H_2**2** or H_2**3** generates the interpenetrated frameworks β-$[Zn_4O(\mathbf{2})_3]$ and β-$[Zn_4O(\mathbf{3})_3]$.

X-Ray crystallography‡ revealed that these crystals comprised a cubic framework of Zn_4O nodes linked by bridging ligands of **1** (Fig. 1a and b). The overall stoichiometry of the framework is $[Zn_4O(\mathbf{1})_3]$, and it belongs to the space group $P\bar{4}3m$ with a unit cell length of 17.211(2) Å.

The cubic topology of $[Zn_4O(\mathbf{1})_3]$ is consistent with other MOFs derived from biphenyl-4,4′-dicarboxylic acid ligands. The framework exhibits an open, non-interpenetrated structure, as observed for a related ligand appended with a bulky *tert*-butylcarbamate group,[2] but in contrast to similar ligands that feature small functional groups, which typically yield interpenetrated structures.[15,16] It appears that the nitrobenzyl group of ligand **1** presents sufficient steric bulk to discourage the formation of interpenetrated frameworks.

The nitrobenzyl group could not be located in the Fourier difference map, due to the statistical disorder over four sites coupled with likely conformational disorder at each of these sites. However, ^1H NMR spectroscopy on digested crystals indicated that this group remained intact in the MOF and analysis of the residual electron density within the framework voids was consistent with its presence. The atoms of this unit were placed in calculated positions to complete the refinement. The phase purity of $[Zn_4O(\mathbf{1})_3]$ was established by powder XRD; the observed diffraction pattern (Fig. 2b) closely matched that predicted from the single-crystal structure (Fig. 2a).

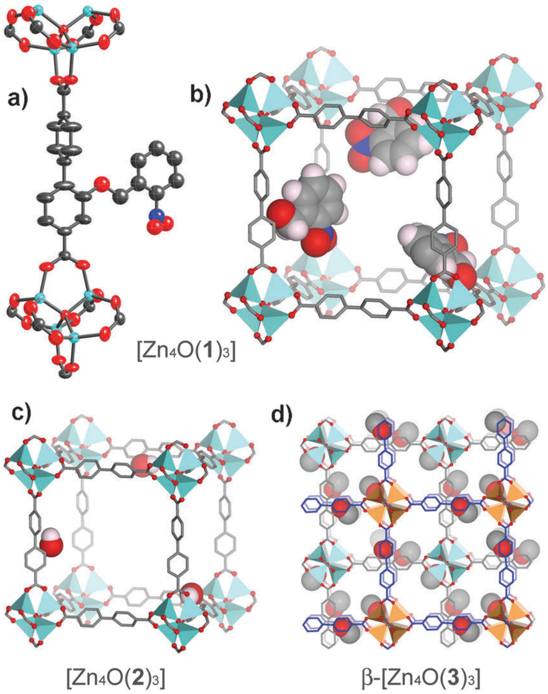

Fig. 1 (a and b) The structure of $[Zn_4O(\mathbf{1})_3]$ as determined by single crystal X-ray crystallography. For clarity only three nitrobenzyl groups are shown at representative positions in CPK format in (b); (c) the proposed structure of $[Zn_4O(\mathbf{2})_3]$, produced by the photolysis of $[Zn_4O(\mathbf{1})_3]$, as deduced from X-ray diffraction and ^1H NMR spectroscopy; (d) the structure of interpenetrated β-$[Zn_4O(\mathbf{3})_3]$, which serves as a model for β-$[Zn_4O(\mathbf{2})_3]$, as determined by X-ray crystallography. The methoxy groups are shown in CPK format and the carbon and zinc atoms of the two lattices are coloured differently for clarity.

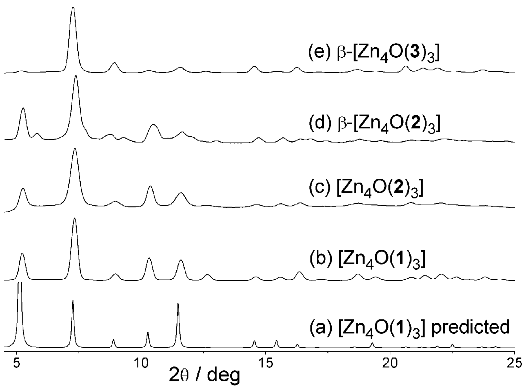

Fig. 2 Powder X-ray diffractograms (Cu Kα radiation) of (a) the pattern predicted from the single-crystal structure of $[Zn_4O(\mathbf{1})_3]$, (b) $[Zn_4O(\mathbf{1})_3]$, (c) $[Zn_4O(\mathbf{2})_3]$ produced by photolysis of $[Zn_4O(\mathbf{1})_3]$, (d) β-$[Zn_4O(\mathbf{2})_3]$, and (e) β-$[Zn_4O(\mathbf{3})_3]$.

To effect the single-crystal-to-single-crystal photolytic conversion of $[Zn_4O(\mathbf{1})_3]$ to $[Zn_4O(\mathbf{2})_3]$, crystals of $[Zn_4O(\mathbf{1})_3]$ suspended in DMF or THF were irradiated with 355 nm laser light with stirring. Reaction progress was monitored by digesting the MOF in DMSO-d_6/DCl and recording the ^1H NMR spectrum (Fig. S1‡). We were delighted to observe that, after around two hours, a remarkably clean conversion to $[Zn_4O(\mathbf{2})_3]$ had taken place in a single-crystal-to-single-crystal fashion. The expected photolysis by-product, 2-nitrosobenzaldehyde, is not directly observed due to decomposition *via* secondary photolysis reactions.[17] The powder XRD diffractogram of the photolyzed material (Fig. 2c) is very similar to that of $[Zn_4O(\mathbf{1})_3]$, indicating that the skeletal structure of the framework is unchanged by photolysis and that long-range order is maintained. By combining the NMR and PXRD results, a structural model of $[Zn_4O(\mathbf{2})_3]$ can be developed, as depicted in Fig. 1c. In these experiments, the mechanical agitation of a suspension of crystals of $[Zn_4O(\mathbf{1})_3]$ promotes the photolysis reaction by grinding the material into microcrystallites. When similar photochemical reactions were performed on large single crystals of [$Zn_4O(\mathbf{1})_3$], it was impossible to drive the photochemical reaction to beyond 50% completion (as indicated by ^1H NMR spectroscopy on digested samples). Although the external form of the crystals was maintained, they became noticeably opaque upon irradiation. Retardation of the photolysis reaction in this case may be attributed to the difficulty of photons penetrating to the core of the crystals as a consequence of (i) scattering from defects and (ii) absorption from competing chromophores (given the density of chromophores in the crystal, even weakly absorbing transitions may prevent the transmission of a significant fraction of the photons). This is a clear drawback of photochemical deprotection as compared to thermolytic deprotection. Single-crystal XRD experiments on the partially photolyzed crystals produced sharp diffraction spots to a resolution beyond 0.90 Å, however a full structural determination was not pursued (see ESI‡ for details).

Following activation by supercritical CO_2,[18] N_2 gas sorption experiments gave an average BET surface area of 131 m^2 g^{-1} (Fig. S4‡), which is lower than predicted on the basis of X-ray crystallography,[19] indicating a degree of pore collapse upon desolvation, but on par with previous studies.[3]

It is noteworthy that the direct solvothermal reaction of $H_2\mathbf{2}$ with $Zn(NO_3)_2$ in DEF produces a crystalline material, β-[$Zn_4O(\mathbf{2})_3$]. Single-crystal XRD of β-[$Zn_4O(\mathbf{2})_3$] showed a clear set of diffraction spots out to a resolution of around 1.30 Å (Fig. S3‡). Although satisfactorily indexing to a reasonable unit cell (see ESI‡ for a full discussion) was impossible, the data are consistent with the presence of a pair of non-commensurate interpenetrating lattices *i.e.*, β-[$Zn_4O(\mathbf{2})_3$] is an interpenetrated analogue of the phase produced by the photolysis of [$Zn_4O(\mathbf{1})_3$].

To gather complementary evidence that β-[$Zn_4O(\mathbf{2})_3$] is an interpenetrated phase, we determined the structure of β-[$Zn_4O(\mathbf{3})_3$], which is derived from 2-methoxybiphenyl-4,4′-dicarboxylic acid, $H_2\mathbf{3}$ (Scheme 1).[20] This structure, which belongs to the tetragonal space group $P\bar{4}2_1m$, comprises a commensurate doubly-interpenetrated pair of cubic lattices built up from struts of **3** and Zn_4O nodes (Fig. 1d). It is noteworthy that, to date, all known non-interpenetrated zinc(II) MOFs based on biphenyl-4,4′-dicarboxylic acid ligands belong to cubic space groups,[2,15,21] while interpenetrated variants belong to non-cubic space groups.[15,16,21]

Thermal gravimetric analyses (TGA) were conducted on the MOFs (Fig. S2‡). For [$Zn_4O(\mathbf{1})_3$], fragmentation of the nitrobenzyl groups in the region 300–350 °C[6] is followed by framework decomposition beyond ~400 °C. The onset of decomposition occurs at a similar temperature for [$Zn_4O(\mathbf{2})_3$], while β-[$Zn_4O(\mathbf{2})_3$] and [$Zn_4O(\mathbf{3})_3$] exhibit slightly greater thermal stability. This is probably a consequence of the mutual bracing of one lattice by the other in these interpenetrated materials.

In summary, these results demonstrate that photolabile groups can be introduced to MOF ligands to (i) prevent framework interpenetration, and (ii) mask hydroxy functional groups during MOF synthesis. Point (ii) complements the results obtained by Cohen *et al.*,[6] while point (i) adds a new dimension to the photolabile protecting group strategy: in the absence of the photolabile group, it is shown that interpenetrated frameworks, which are inherently less open and porous, are produced. This methodology for the surreptitious incorporation of functional groups that line the pores of open MOFs is potentially quite general in terms of the framework topology, the ligand backbone, and the functional group itself. It may find applications in the synthesis of MOFs that cannot be prepared directly, for example because the ligands bear functional groups that cannot withstand the solvothermal reaction conditions or that hinder MOF growth by coordinating to the metal ion. This opens up new perspectives on tailoring the chemical space within MOFs to optimize interactions with incoming guest molecules, particularly for applications in gas sorption and catalysis. We are actively exploring these research avenues employing both photolabile and thermolabile protecting groups.

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