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Isoreticular synthesis and modification of frameworks with the UiO-66 topology†

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Abstract

Amino, bromo, nitro, and naphthalene functionalized UiO-66 metal–organic frameworks have been synthesized through reticular chemistry. UiO-66–NH_2 is shown to be suitable for postsynthetic modification with a variety of anhydrides to generate new, functionalized frameworks.

Metal–organic frameworks (MOFs), which are comprised of metal ions or metal clusters connected by organic ligands,[1–3] have been increasingly studied in the past decade for a variety of applications. Through the careful choice of organic ligands and metal precursors, a vast number of topologies can be rationally designed and synthesized.[1,4,5] Indeed, Yaghi and co-workers have previously demonstrated the isoreticular synthesis of topologically identical frameworks with a series of related organic ligands.[6] Due to their high porosity, these hybrid materials have been extensively studied for gas storage,[7–12] separation,[13,14] catalysis,[15] and drug delivery[16,17] applications. However, a major limitation of MOFs, especially those based on zinc-carboxylate secondary building units (SBUs), is their low chemical stability to atmospheric moisture and protic media.[18]

Several recent studies have shown that specialized functionalities can be introduced into porous MOFs through a postsynthetic modification (PSM) approach.[19] However, access to novel functionalities through PSM and their subsequent exploitation in new MOF applications are still limited by the inherent chemical stability of the parent framework. Because of this limitation, utilization of PSM in more chemically robust systems has been increasingly investigated.[20] Lillerud *et al.* synthesized the first example of a zirconium(IV) dicarboxylate porous material (UiO-66). Owing to the highly oxophilic nature of zirconium(IV), the Zr_6-cluster SBU formed in these MOFs makes these materials very resistant towards various solvents and elevated pressures.[21] Recently, $Cr(CO)_3$ was successfully grafted to the arene moieties of UiO-66 through thermal decomposition in a postsynthetic fashion.[22] Subsequent photolysis of the $Cr(CO)_3$ modified material with UV light in an N_2 atmosphere led to photoinduced substitution of one of the CO ligands with an N_2 molecule. However, prolonged exposure to UV light (>30 min) led to decomposition of the arene–$Cr(CO)_3$ species. In an effort to expand the number of chemically robust materials available for covalent PSM, we sought to incorporate a variety of organic functionalities into the UiO-66 framework through a combination of reticular chemistry (Scheme 1) and PSM (Scheme 2). The synthesis of –NH_2, –Br, –NO_2, and naphthalene-substituted UiO-66

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†Electronic supplementary information (ESI) available: Synthetic details, characterization of all compounds, and details of cleavage assays. Scheme S1, Fig. S1–S10. See DOI: 10.1039/c0cc02990d

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analogues is presented. With respect to PSM, we described the synthesis and modification of an amine functionalized UiO-66 analogue. Overall, the UiO-66 framework is found to be a robust motif that is highly amenable to isoreticular functionalization and modification.

The syntheses of $–NH_2$, –Br, $–NO_2$, and naphthalene functionalized UiO-66 analogues were performed using a slightly modified procedure of Lillerud *et al.*[21] To obtain these materials, equal molar amounts of $ZrCl_4$ and terephthalic acid precursors (0.35 mmol) were combined in DMF (~0.09 M) and heated.[‡] Under these conditions all of the functionalized terephthalic acid precursors led to materials possessing powder X-ray diffraction (PXRD) patterns that were remarkably consistent with that reported for the UiO-66 topology (Fig. 1).[21,23] The thermal stability of the UiO-66 analogues varied by functionality. While the bromide and naphthalene analogues UiO-66–Br and UiO-66-1,4–Naph show thermal stability comparable to the parent UiO-66 material, the amino and nitro functionalized analogues UiO-66–NH_2 and UiO-66–NO_2 showed significant weight losses (25% to 30%) at ~400 °C, presumably due to ligand decomposition (Fig. 2).

The covalent postsynthetic modification of UiO-66–NH_2 was explored using a series of alkyl anhydrides to produce amide modified frameworks designated UiO-66–AM (Scheme 2). In a typical reaction UiO-66–NH_2 (~60 mg, 0.2 mmol-NH_2) was suspended in 2 mL of $CHCl_3$, treated with one equivalent of anhydride, and heated at 55 °C for 24 h, followed by extensive rinsing with methanol to extract by-products from the porous solids.[‡] As described in our earlier studies, modification was confirmed by nuclear magnetic resonance (NMR) spectroscopy.[20,24]

Samples of PSM treated UiO-66–NH_2 materials were digested with HF and [D_6]DMSO for examination by ^{1}H NMR spectroscopy. Digestion of unmodified UiO-66–NH_2 predominantly displayed resonances associated with 2-amino-1,4-benzene dicarboxylic acid, but some minor impurities were also observed in the aromatic region. These impurities appear to be associated with the amino-functionalized benzene-dicarboxylate (BDC) ligand, as they were not observed upon digestion of UiO-66, UiO-66–Br, UiO-66–NO_2, or UiO-66–Naph (Fig. S1, ESI[†]). Nonetheless, the ^{1}H NMR spectra of modified samples showed a distinct downfield shift of the aromatic proton resonances associated with the BDC ligand (Fig. 3). The percent conversion of the amine groups in the framework to amides was determined by comparing the relative integrated areas of the aromatic resonances (corresponding to the C-3 position of the BDC ring) between the modified and unmodified BDC ligands. The results are summarized in Table 1. As previously described for other MOF systems, conversion to the amide products decreased with increasing size (chain length) of the anhydride with yields of 88%, 49%, and 25% for acetic (–AM1), valeric (–AM4), and octanoic anhydride (–AM7), respectively. Additionally, reaction with the maleic anhydride produced UiO-66–AMMal with 25% conversion. The latter modification introduces a free carboxylate group into the framework, which could not be readily obtained by direct solvothermal synthesis and has been shown to generate acidic materials with catalytic properties.[25,26]

[‡] *Synthesis of isoreticular UiO-66 frameworks.* In a typical reaction, the functionalized terephthalic acids (0.35 mmol) along with $ZrCl_4$ (0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 °C for 24 h. The microcrystalline powders were then isolated by centrifugation and heated at 100 °C for 1–2 h. Residual DMF and terephthalic acid precursors were removed from microcrystalline UiO-66 (~60 mg) by methanol rinsing (3 × 15 mL), soaking for 3 d in methanol, and subsequent heating at 150 °C for 5 h.

PSM on UiO-66-NH_2 framework. Activated UiO-66–NH_2 (~60 mg, 0.2 mmol-NH_2) was treated with a 2 mL solution of $CHCl_3$ containing the anhydride (0.2 mmol) and heated at 55 °C for 24 h. After the reaction was complete the sample was rinsed and intermittently centrifuged with $CHCl_3$ (3 × 15 mL) and soaked for 3 d. The $CHCl_3$ rinsed sample was subsequently rinsed with methanol (3 × 15 mL) soaked for 3 d and dried at 150 °C for up to 2 h.

[†] Electronic supplementary information (ESI) available: Synthetic details, characterization of all compounds, and details of cleavage assays. Scheme S1, Fig. S1–S10. See DOI: 10.1039/c0cc02990d

Additional evidence for modification was obtained *via* infrared spectroscopy (IR) on UiO-66–AM1, UiO-66–AM4, UiO-66–AM7, and UiO-66–AMMal, which displayed a weak, but reproducible stretch around 1700 cm^{-1} associated with the carbonyl moieties of the amide functionality (Fig. S2 and S3, ESI[†]). The presence of the amide substituents was also confirmed by electrospray ionization mass spectrometry (ESI-MS) of digested modified samples (Fig. S4–S7, ESI[†]). Consistent with the UiO-66–NH_2 precursor framework, the amide-functionalized frameworks UiO-66–AM1, UiO-66–AM4, UiO-66–AM7, and UiO-66–AMMal show somewhat decreased thermal stabilities (Fig. 2) relative to UiO-66.

The effects of functionalization on the porosity of the UiO-66 systems were investigated by measuring the Brunauer–Emmett–Teller (BET) surface areas with N_2 adsorption at 77 K. The results are summarized in Table 2. As shown by the surface measurements, the amino moieties in UiO-66–NH_2 do not show much effect on the porosity of the UiO-66 system; however, increasingly larger functional groups lead to diminished porosities (*e.g.* –Br, –NO_2, –Naph). Similarly, longer aliphatic chains introduced through PSM progressively reduced the inherent porosity of UiO-66–AM compounds.

In summary, we have synthesized and characterized –NH_2, –Br, –NO_2, and naphthalene functionalized UiO-66 analogues in an isoreticular manner. In comparison to UiO-66, the thermal stability of the amino and nitro functionalized UiO-66–NH_2 and UiO-66–NO_2 is somewhat decreased. The postsynthetic modification of UiO-66–NH_2 was accomplished with aliphatic and cyclic anhydrides and verified through a combination of ^{1}H NMR, IR, and ESI-MS analysis. The chemical stability of the UiO-66 framework and facile incorporation of functionalized or extended species, through reticular synthesis or postsynthetic modification, show that this class of porous solid can serve as a tunable, microporous scaffold for novel applications in separations, catalysis, and biotechnology.

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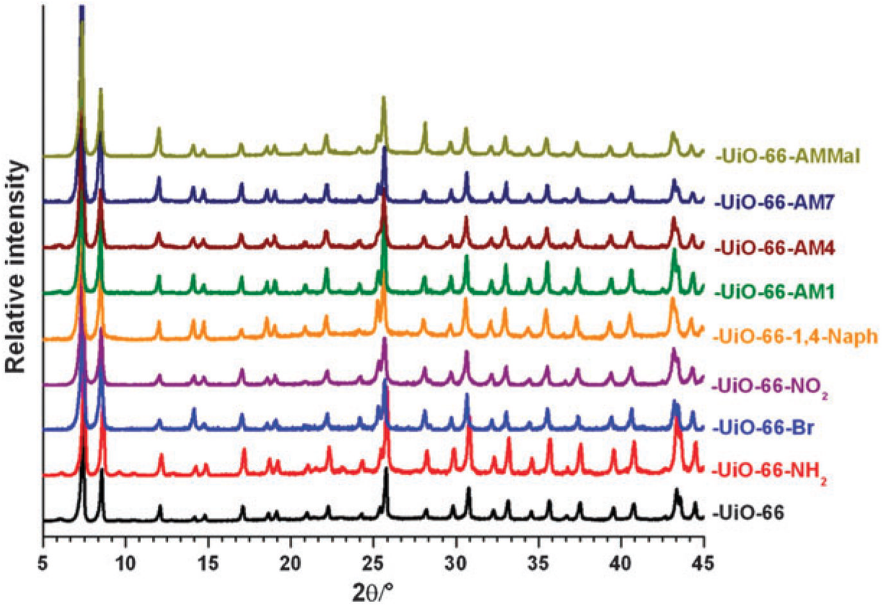


Fig. 1.

PXRD patterns of UiO-66 derivative materials.

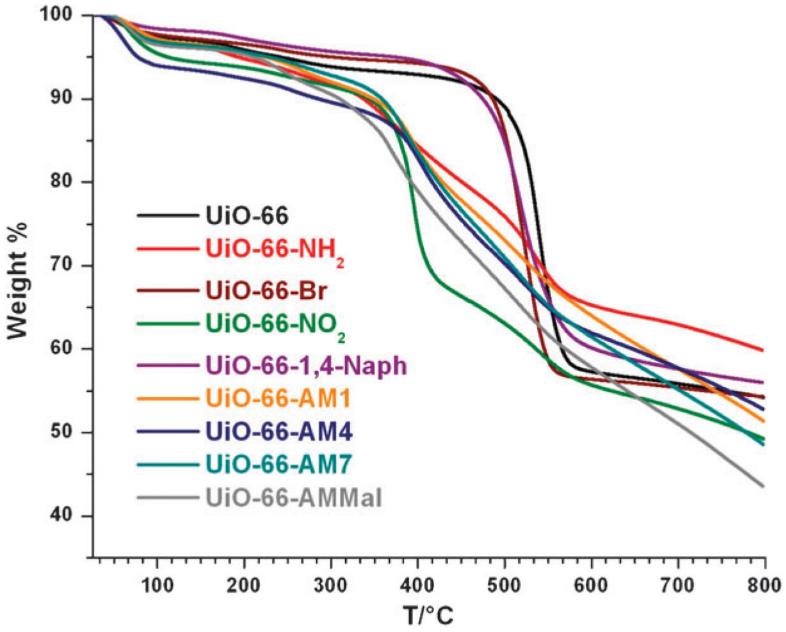


Fig. 2.

Thermogravimetric analysis of UiO-66 (black), UiO-66–NH_2 (red), UiO-66–Br (brown), UiO-66–NO_2 (green), UiO-66-1,4–Naph (purple), UiO-66–AM1 (orange), UiO-66–AM4 (navy blue), UiO-66–AM7 (cyan), and UiO-66–AMMal (gray).

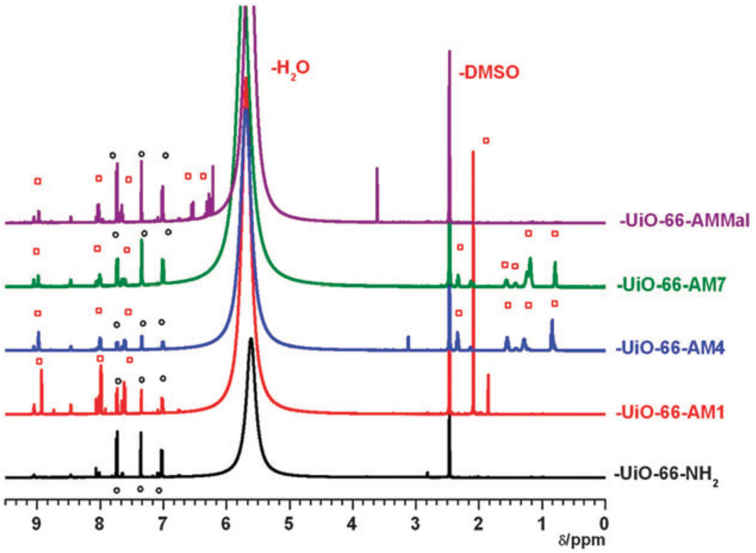
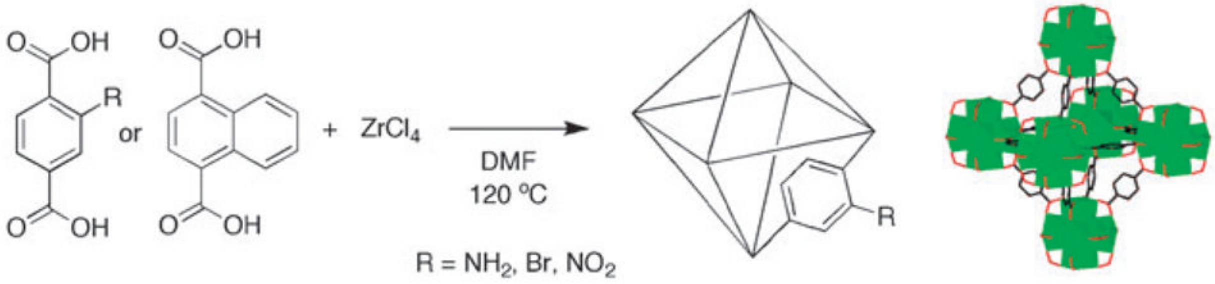
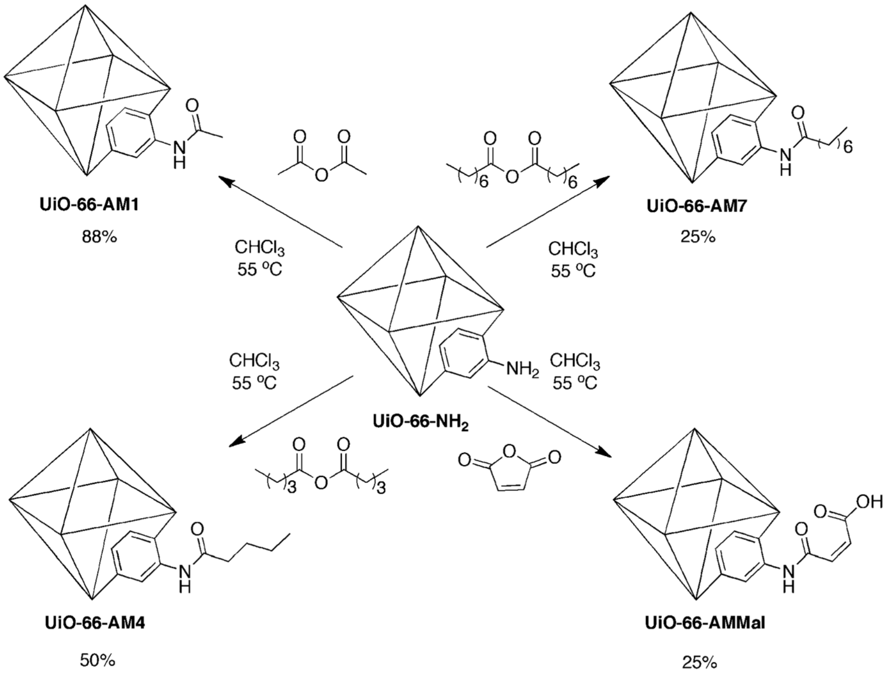


Fig. 3.

^{1}HNMR spectra of digested UiO-66 modified samples. Black circles indicate unmodified NH_2–BDC and red squares are from modified BDC ligands.



Scheme 1.
Synthesis of isoreticular UiO-66 functionalized analogues UiO-66–NH_2, UiO-66–Br, UiO-66–NO_2 (R = NH_2, Br, or NO_2), and UiO-66-1,4–Naph. The UiO-66 framework with its Zr_6O_6 cuboctahedron SBU (green) is schematically represented as an octahedron.



Scheme 2.

Postsynthetic modification of UiO-66–NH_2 with various anhydrides.

Table 1

Conversion of UiO-66–NH_2 to UiO-66–AM derivatives using different anhydrides

UiO-66–	Anhydride	% Conversion	STD[a]
AM1	Acetic	88	±6
AM4	Valeric	49	±7
AM7	Octanoic	25	±6
AMMal	Maleic	25	±5

[a] Percent conversion values are averaged from at least three independent experiments.

Table 2

BET surface areas of UiO-66 functionalized systems ($m^2\ g^{-1}$)

	BET surface area[a]	Langmuir surface area[a]
UiO-66	1110	1311
UiO-66–NH_2	1112	1313
UiO-66–Br	851	1004
UiO-66–NO_2	756	893
UiO-66-1,4–Naph	615	732
UiO-66–AM1	818	965
UiO-66–AM4	717	847
UiO-66–AM7	646	762
UiO-66–AMMal	814	962

[a] The results are the average from two independent experiments.