Post-Synthetic Modification of the Metal Organic Framework Compound UiO-66

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Experimental Methods.

Starting materials were purchased and used without further purification from commercial suppliers (Sigma- Aldrich and Alfa Aesar). Dried, distilled and deoxygenated solvents were used.

Postsynthetic modification of UiO-66-NH2. In a typical procedure, 28.6 mg dried UiO-66-NH2 (ca. 0.10 mmol equiv of NH2) were suspended in 1.00 mL CH2Cl2 in a 4 mL vial, and 23.5 µL acetic anhydride (0.25 mmol) was then added to the mixture. The vial was capped and left on the bench for a period of days to weeks. The reaction was stopped by removing the reaction solution and washing the solids 3-4 times with fresh CH2Cl2 before soaking in 10 mL CH2Cl2 for another 3 days (with daily exchange of fresh CH2Cl2). The solid was then dried under vacuum for 5 h at 60 °C and ≈33 mg of dried, modified UiO-66-NHOCH3 (2) was obtained. Compounds UiO-66-NHCOCH2CH3 (3), UiO-66-NHCO(CH3)=CH2 (4) and UiO-66-NHCO-OC(CH3)3 (5) were synthesized similar manner but replacing acetic anhydride by propionic anhydride, methacrylic anhydride and Boc anhydride respectively.

**FTIR.** IR experiments were performed in transmission mode on a FTIR Bruker VERTEX 80 spectrometer equipped with a DTGS detector (spectra range 4000-400 cm⁻¹). Post-synthetic modified MOFs under study were measured in the form of thin film deposited on a silicon wafer. The thin film has been prepared from an ethanol suspension of the sample. Solvent and possible unreacted reagents removal has been obtained by introducing the silicon wafer in a quartz cell that allows “in situ” spectra collection in controlled atmosphere and treated at 373 K under dynamic vacuum (residual pressure <10⁻² Pa) for 30 min.

Deuterium exchange. H exchange with D has been obtained by contacting in the IR cell, the thin film of the UiO-66-NHOCH3 (2) sample with D2O vapours. After a contact time of about 8 h the excess of D2O has been removed by treating the sample at 373 K under vacuum for 30 min.

Digestion and Analysis by ES-MS. Approximately 3 mg of dried UiO-66-NH2 or UiO-66-NHOCH3 was transferred to a screw-cap Teflon vial and dissolved in 1.0 mL 15 % HF for an hour. The vial was then immersed in boiling water to allow HF evaporation, and to obtain dried product. The dried product was diluted by MeOH for ES1-MS.
**PXRD Analysis.** Approximately 3 mg of UiO-66-NH$_2$ and modified samples which were soaked in ethanol dispersed and dried as a thin layer on a glass plate before the PXRD measurements. PXRD data were collected at ambient atmosphere and temperature on a Bruker D5000 instrument with monochromatic CuK$_\alpha_1$ radiation ($\lambda = 1.540$ Å) operated in Bragg-Bretano geometry.

**Gas Sorption Measurements.** Langmuir specific surface areas were determined from nitrogen adsorption/desorption isotherms that were performed on BELSORP MINI II system (BEL Japan). Before surface area analysis, the samples were activated in vacuum at 80 °C for 1h and then the temperature was raised to 150 °C and held for 2 h.

**Molecular mechanics structure optimization.** Simulation of the structures with different ligands and different degree of substitution has been performed with the Accelrys Materials Studio modeling package version 5.1. Structures were optimized with the Forcite module using the Universal force field with ultra fine settings and using Ewald summation for charges and van der Waal forces.

**Safety Note.** HF is corrosive and extremely hazardous liquid and vapor. Causes severe burns which may not be immediately painful or visible. May be fatal if swallowed or inhaled. Liquid and vapor can burn skin, eyes, and respiratory tract. Causes bone damage. See MSDS safety sheets for further details. A HF resistant dispenser was employed in these experiments, in order to minimize the volumes handled and the risk of spilling.
**FTIR**

![FTIR spectra](image)

**Fig. S1** FTIR spectra of the ν(N-H) region measured on UiO-66-NH$_2$ (1) and post-synthetic modified MOFs, UiO-66-NH: -COCH$_3$ (2), -COCH$_2$CH$_3$ (3), -COC(CH$_3$)$_2$-CH$_2$ (4) and –CO-OC(CH$_3$)$_3$ (5). after 3 days (Part a) and 2 weeks (Part b) reaction time.

Fig. S1 shows the N-H stretching region of different postsynthetically modified UiO-66-NH$_2$ after 3 days (Part a) and 2 weeks (Part b) of reaction. Post synthetic reactions produce an erosion of the -NH$_2$ peaks ($\nu_{\text{sym}}$(NH$_2$)= 3516 cm$^{-1}$ and $\nu_{\text{asym}}$(NH$_2$)= 3395 cm$^{-1}$) with a parallel formation of bands that can be ascribed to the formations of secondary amide groups ($\nu$(N-H) peak at 3340 cm$^{-1}$). This observation can be considered as clear evidence that –NH$_2$ groups are the reactive center that allows the postsynthetic functionalization of MOF structure. FTIR analysis was further used to determine the degree of conversion. Approximate conversion percentage was determined by normalizing FTIR spectra to the band at 760 cm$^{-1}$ assigned to the characteristic C-C vibrational mode in aromatic compounds. Among all the other possible bands suitable for spectra normalization the choice of this band has been done considering that it is relatively little affected by ring substituents$^1$ and there is no overlap from other vibrational modes. After spectra normalization, the conversion in percent was determined by comparing the relative intensity of the $\nu$(N-H) peak at 3340 cm$^{-1}$ of the postsynthetically modified sample and considering a complete reaction (100% conversion) for the –NHCOCH$_3$ (2) sample after 2 weeks reaction that show a complete disappearance of peaks due to the -NH$_2$ group (Fig. S1 Part b). In Fig. S2 FTIR spectra, recorded in the whole spectra range (4000-700 cm$^{-1}$), of postsynthetically modified samples outgassed at 373 K under dynamic vacuum are reported.
Fig. S2 FTIR spectra of UiO-66-NH₂ (1) and the postsynthetically modified MOF UiO-66-NH₂: -COCH₃ (2), -COCH₂CH₃ (3), -COC(CH₃)=CH₂ (4) and –CO-OC(CH₃)₃ (5) after 2 weeks of reaction: Part (a): O-H, N-H and C-H stretching region; Part (b): MOF framework region; Part (c): enlargement of the ν(C=O) region; Part (d): enlargement of the ν(C-H) region; Part (e): enlargement of the ν(C=N) region.

**MOF Framework region (part b)**

The intense peaks present can be assigned to the MOF’s skeletal mode (organic aromatic linker (H₂BDC) and ZrO₂ cornerstone). In particular, spectra of aromatic compounds display a few characteristic bands attributed to C-C vibrational modes, at 1600-1585 cm⁻¹, 1500-1430 cm⁻¹ and 700 cm⁻¹. In addition, the carboxylate anion has two strongly coupled C-O bonds with bond strengths intermediate between C=O and C-O. The carboxylate gives rise to two bands: asymmetrical stretching band near 1650-1550 cm⁻¹ and a weaker, symmetrical stretching band near 1400 cm⁻¹. Evidence for the presence of functional groups originating from post synthetic modification of the starting UiO-66-NH₂ can be observed in the whole spectral range with intensity depending mainly on the conversion percentage.

**Postsynthetic functionalized groups:**

ν(C-H) region (inset c) Further information about the functional groups can be obtained by analyzing the region where ν(C-H) groups are absorbing (see Fig. S2 part (c)). Even though a detailed assignation of the
C-H vibrations requires particular attention, it is possible to distinguish with good approximation peaks due to the presence of methyl, ethyl and vinyl groups. In this regard note the characteristic vinilydene peaks due to the $\nu_{\text{sym}} (=\text{CH})$ vibration at 2962 and 3010 cm$^{-1}$. For a more detailed bands assignment see Table S1 in the supporting information.

$\nu(\text{C}=\text{O})$ region (inset d) The stretching frequencies of the C=O bond of different amides is affected in position depending on the neighbouring substituents as seen in compound (2) to (5). The acetyl, propyl amido group in compound (2) and (3) show a C=O band at 1706 and 1701 cm$^{-1}$ respectively. The presence of C=C in compound (4) shift the $\nu(\text{C}=\text{O})$ at lower wavenumber (1685 cm$^{-1}$) due to the conjugation effect. In compound (5) this vibration is found at about 1725 cm$^{-1}$ due to electron attracting nature (inductive effect) of the adjacent oxygen atoms.

Note in this region the presence of the peaks at 1667 cm$^{-1}$ assigned to the C=O stretching vibration of residual DMF strongly adsorbed in the channels network.$^2$
Table S1 Main IR characteristic frequencies of the post synthetically modified MOFs UiO-66-NH: -COCH₃ (2), -COCH₂CH₃ (3), -COC(CH₃)=CH₂ (4) and –CO-OC(CH₃)₃ (5) after 2 weeks of reaction: sh: shoulder, n.d. = not defined (not visible)
Fig. S3 In the 110 direction of the structures are the trigonal windows that restrict the access to the tetrahedral and octahedral cages aligned. Above is structures with different ligands compared. The increased window blocking is clearly visible on going from the small NH\textsubscript{2} substituted ligand to the bulky CO-OC(CH\textsubscript{3})\textsubscript{3} ligand.

ESI-MS figures of the digested samples

Fig. S4 ESI-MS (positive mode) of the digested UiO-66-NH\textsubscript{2} modified with acetic anhydride UiO-66-NHCOCH\textsubscript{3} (2) (2 weeks). Sample was dried at 60 °C for 3 h. Approximately 3 mg of dried UiO-66-
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Fig. S5 ESI-MS (positive mode) of the digested UiO-66-NH$_2$ (1). Sample was dried at 60 °C for 3 h. Approximately 3 mg of dried UiO-66-NH$_2$ (1) was digested in 1.0 mL 15 % HF for an hour. Base peak at $m/z$ 180 represents H$_2$N-H$_2$BDC.

Fig. S6 ESI-MS (negative mode) of the digested UiO-66-NH$_2$ (1) Sample was dried at 60 °C for 3 h. Approximately 3 mg of dried UiO-66-NH$_2$ (1) was digested in 1.0 mL 15 % HF for an hour. Base peak at $m/z$ 184.9 represents [ZrF$_5$]$^-$.
High resolution ESI-MS

UiO-66-NH$_2$ (1) and the postsynthetically modified MOF UiO-66-NHCOCH$_3$ (2) have been further analyzed by high resolution ESI-MS in order to limit the possible elemental compositions and confirm unique composition.

Table S2 High resolution ESI-MS on of UiO-66-NH$_2$ (1) and the postsynthetically modified MOF UiO-66-NHCOCH$_3$ (2) after 2 weeks of reaction.

<table>
<thead>
<tr>
<th>Digested samples</th>
<th>Calculated value m/z</th>
<th>Observed value m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66-NH$_2$ (1)</td>
<td>180.0295</td>
<td>180.0296</td>
</tr>
<tr>
<td>UiO-66-NHCOCH$_3$ (2)</td>
<td>222.0399</td>
<td>222.0402</td>
</tr>
</tbody>
</table>

Reference