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Towards multifunctional MOFs – from side reaction to post-synthetic protection/deprotection strategy

- SUPPORTING INFORMATION

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1. General information

All solvents and reagents were commercially available and used as received unless otherwise stated. Dichloromethane (CH_2Cl_2, 99.8%, POCH, Gliwice, Poland) was distilled from calcium hydride.

Sigma-Aldrich: 2-Aminoterephthalic acid ($H_2BDC-NH_2$, 99%), zirconium chloride ($ZrCl_4$, > 99.5%), ethyl formate ($HCOOC_2H_5$, reagent grade, 97%), azidotrimethylsilane ($(CH_3)_3Si-N_3$, TMS-N_3, 95%), *tert*-butyl nitrite ($(^tBu-ONO$, 90%), hydrofluoric acid (HF_{aq} 47-51%, TraceSELECT,), methanol (CH_3OH, CHROMASOLV for HPLC, >99.9%), chloroform ($CHCl_3$, puriss. p.a., > 99%), DMSO-d_6 (99.9 atom %D). Fluka AG: N,N-diethylformamide (pure, > 99%). UCB Belgium: formamide (HCO-NH_2, reagent grade,99.5%). POCH, Gliwice, Poland: acetic anhydride (ACS, pure p.a., 98%), sodium carbonate (Na_2CO_3, pure p.a., >99.5%), acetic acid (CH_3COOH, pure p.a.-basic, >99.5%), hydrochloric acid (HCl, pure p.a.-basic, 35-38%), N,N-dimethylformamide (DMF for HPLC, 99.8%). Euriso-top DMSO-d_6 + 0.03%TMS v/v (>99.8% D).

All thin layer chromatography (TLC) analyses were performed on TLC Silica gel 60 RP-18 F254S plates with aluminium sheets (Merck KGaA, Germany).

Nuclear magnetic resonance experiments

The NMR spectra were recorded using 400 MHz NMR Agilent spectrometer at ambient temperature in DMSO-d_6 or DMSO-d_6/HF_{aq} mixture. The chemical shifts are reported in parts per million (ppm) and the coupling constants *J* are given in hertz (Hz). Data are reported as follows: chemical shift, multiplicity (s-singlet, br.s –broad singlet, d – doublet, dd- doublet of doublets), coupling constant and integration. The residual signal of DMSO-d_6 solvent was used as an internal reference standard (δ_H = 2.500 ppm and δ_C = 39.50 ppm).

The composition of mixtures obtained after digestion of any analysed MOF material was determined according to the relative quantitation method.[1]

Mass spectrometry

Both low- (LR-MS) and high-resolution (HR-MS) mass spectrometry experiments were performed on a Micromass LCT TOF (Time-Of-Flight) mass spectrometer using electrospray ionization (ESI) technique and methanol as a spray solvent.

IR spectroscopy

Attenuated total reflection infrared (ATR-IR) spectra were recorded on a Bruker Vertex 80V spectrometer at room temperature in the range 400-4500cm^{-1}.

Measurement of N_2 sorption isotherms

All samples were heated at 150^{o}C for 24 h under high vacuum and stored in a desiccator. Samples were once again thermally activated and degassed immediately prior to the N_2 physisorption measurements for at least 12h at 150^{o}C. Exception was made for samples containing azide groups, which are unstable at high temperatures. These samples were thermally activated at 80^{o}C for 24 h under high vacuum and once again activated and degassed immediately prior to the N_2 physisorption measurements for at least 12h at 80^{o}C. Isotherms were determined at

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[1] a) F. Malz, H. Jancke, *J. Pharm. Biomed. Anal.*, 2005, **38**, 813-823; b) S. K. Bharti, R. Roy, *Trends Anal. Chem.*, 2012, **35**, 5-26.

liquid nitrogen temperature (77K) using a Micrometrics ASAP 2020 sorption analyser. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method using P/P_o values in the range 0.005-0.05. For all isotherm analyses we ensured that the two consistency criteria described by Rouquerol et al.[2] and Walton et al.[3] were satisfied.

Powder X-ray diffraction

All powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover X-ray diffractometer (CuKα radiation, parallel beam formed by Goebel mirror) equipped with a VANTEC 1 position sensitive detector. All measurements were performed in standard holders or on zero background monocrystalline silicon holder. If necessary, the diffractograms were baseline-corrected using the EVA2 (Bruker-AXS) software.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a TA Instruments Q600 simultaneous TG-DSC analyzer. Sample was heated in alumina crucibles from room temperature to 900 ^oC with a heating rate of 5 ^oC/min under a stream of Ar (100 ml/min). Sample of UiO-66-NH2/NHCHO(40/60) was activated at 150^{o}C under high vacuum for 12 h prior to the TGA measurement.

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[2] J. Rouquerol, P. Llewellyn, F. Rouquerol, *Stud. Surf. Sci. Catal.*, 2007, **160**, 49-56.

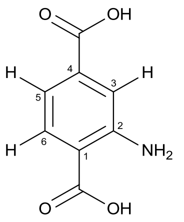
[3] K. S. Walton, R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552-8556.

2. The synthesis of UiO-66-NH$_2$ and identification of side products.

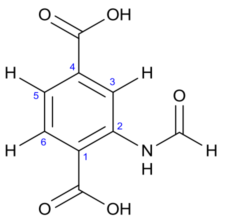
UiO-66-NH$_2$ was synthesized according to the procedures reported by: a) Garibay and Cohen,[4] b) Behrens and co-workers[5] and c) Hupp, Farha and co-workers.[6]

After the synthesis of UiO-66-NH$_2$ according to Garibay and Cohen, a small sample of the material (*ca*. 2 mg) was sonicated in DMSO-d$_6$ containing small amounts of hydrofluoric acid (5µl of HF$_{aq}$ in 700 µl of DMSO-d$_6$). Clear solution formed. Immediately after dissolution both ^{1}H NMR and gCOSY H,H spectra were recorded. Next, *ca*. 2 mg of 2-formamidoterephthalic acid was added to the same solution and ^{1}H NMR spectrum was recorded again.

For UiO-66-NH$_2$ synthesized according to Behrens and co-workers as well according to Hupp, Farha and co-workers only ^{1}H NMR spectra were recorded.



2-amino-benzenedicarboxylic acid (BDC-NH$_2$)



2-formamido-benzenedicarboxylic acid (BDC-NHCHO)

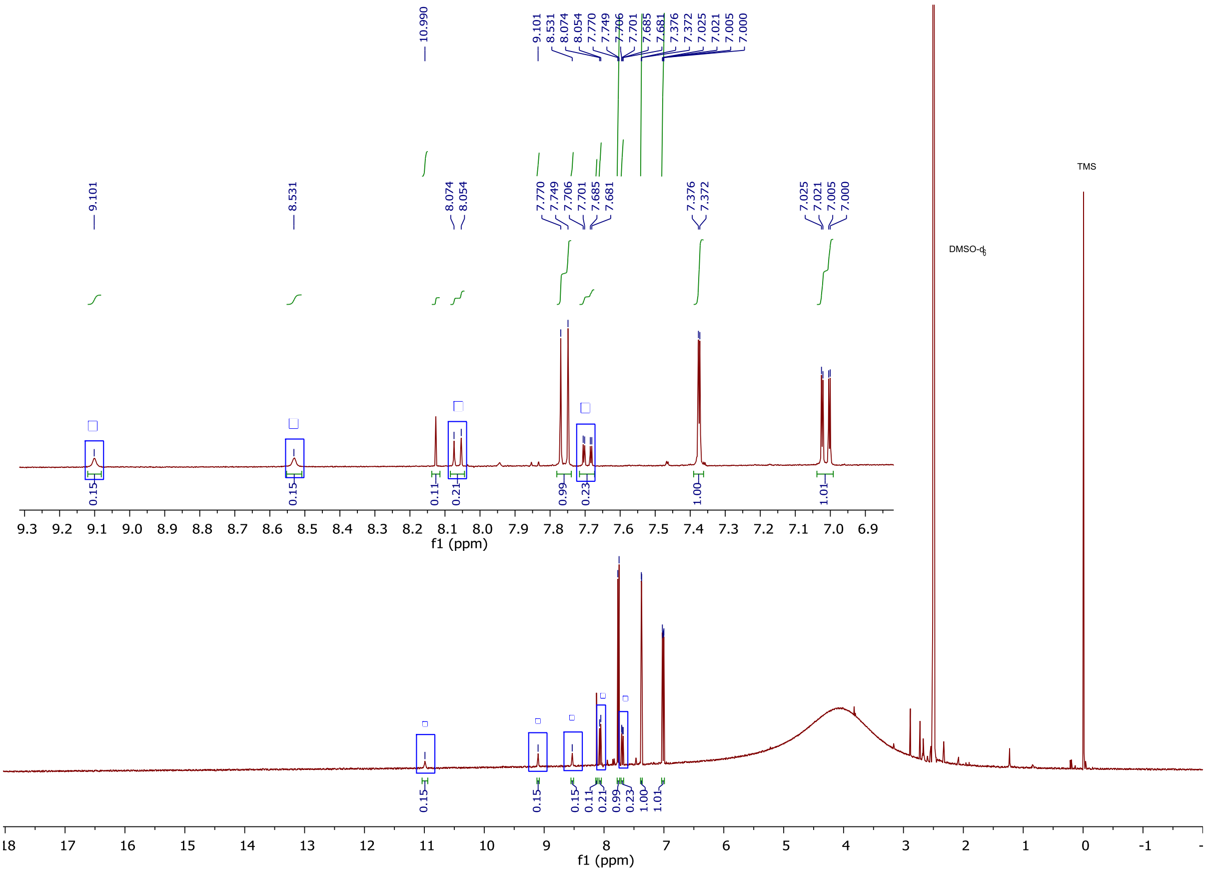


Figure S1. ^{1}H NMR spectrum of a solution obtained by digestion of UiO-66-NH$_2$ synthesized according to Garibay and Cohen in a DMSO-d$_6$/HF$_{aq}$ mixture.

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[4] S. J. Garibay, S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700-7702;

[5] A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17**, 6643-6651.

[6] M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449-9451.

$$\%NHCHO = [n_{H\text{-}6}/(n_{H\text{-}6} + n_{H\text{-}6})]*100\% = (0.21/1.20)*100\% = 17.5\%$$

$$\text{or } \%NHCHO = [n_{H\text{-}5}/(n_{H\text{-}5} + n_{H\text{-}5})]*100\% = (0.23/1.24)*100\% = 18.5\%$$

$$\text{average } \%NHCHO = (17.5+18.5)/2=18.0\%$$

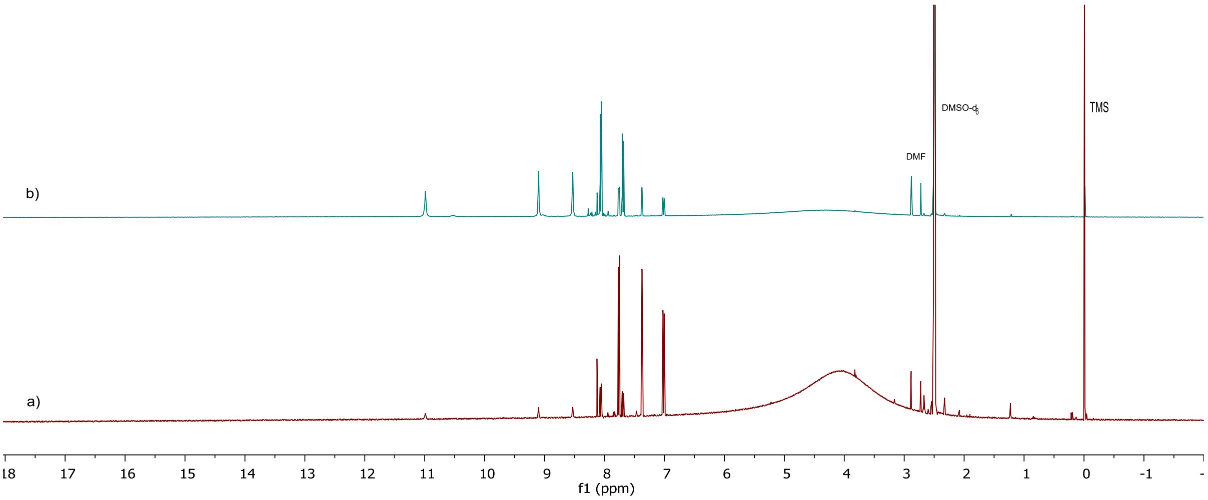


Figure S2. ^{1}H NMR spectrum of a solution obtained by the digestion of UiO-66-NH_2 synthesized according to Garibay and Cohen in DMSO-d_6/HF_{aq} mixture: a) before and b) after the addition of pure 2-formamidoterephthalic acid.

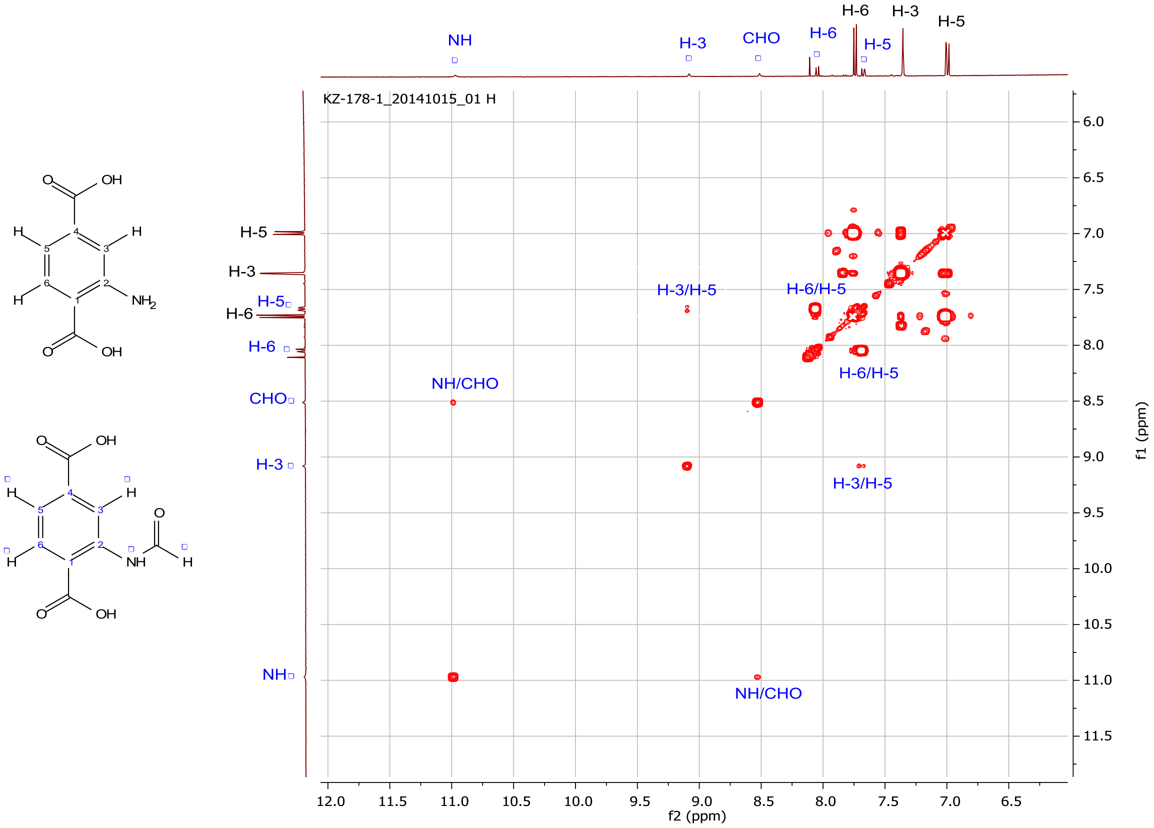


Figure S3. ^{1}H-^{1}H gCOSY spectrum of a solution obtained by the digestion of the UiO-66-NH_2 synthesized according to Garibay and Cohen in DMSO-d_6/HF_{aq} mixture.

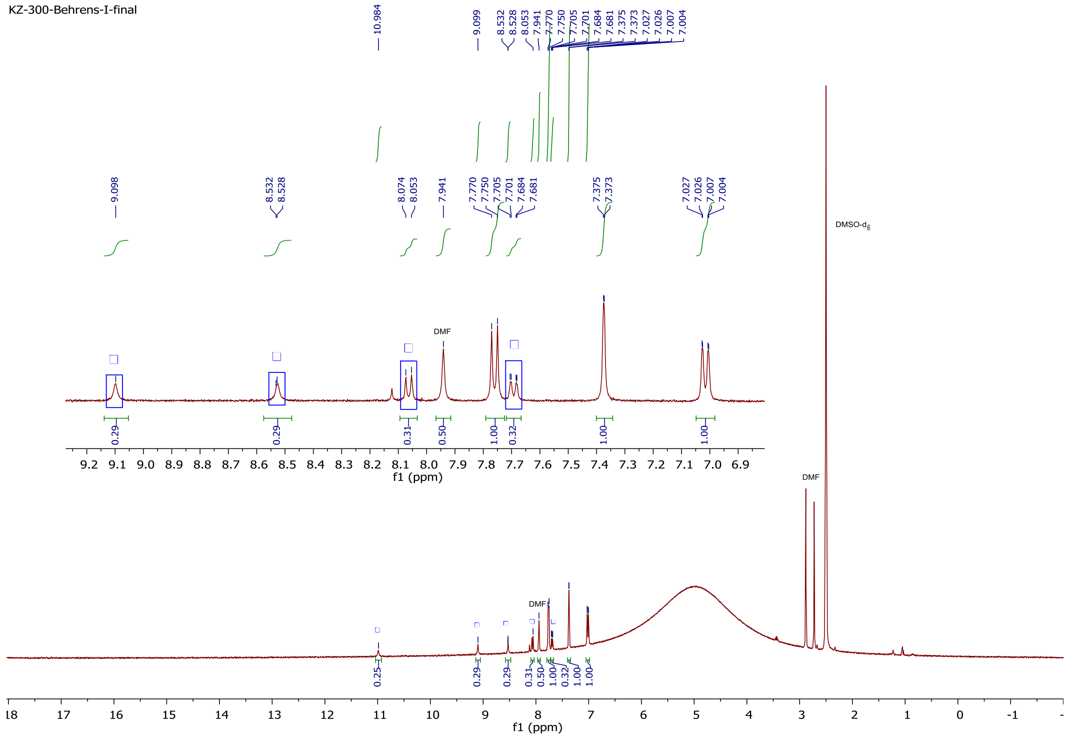


Figure S4. The ^{1}H NMR spectrum of a solution obtained by the digestion of UiO-66-NH_2 synthesized according to Behrens *et. al.* in a DMSO-d_6/HF_{aq} mixture.

$$\%NHCHO= [n_{H\text{-}6}/(n_{H\text{-}6} + n_{H\text{-}6})]*100\%= (0.31/1.32)*100\% = 23.5\% \text{ or } \%NHCHO= [n_{H\text{-}5}/(n_{H\text{-}5} + n_{H\text{-}5})]*100\% = (0.32/1.32)*100\% = 24.0\%;\ \text{average } \%NHCHO = (23.5+24.0)/2=23.8\%$$

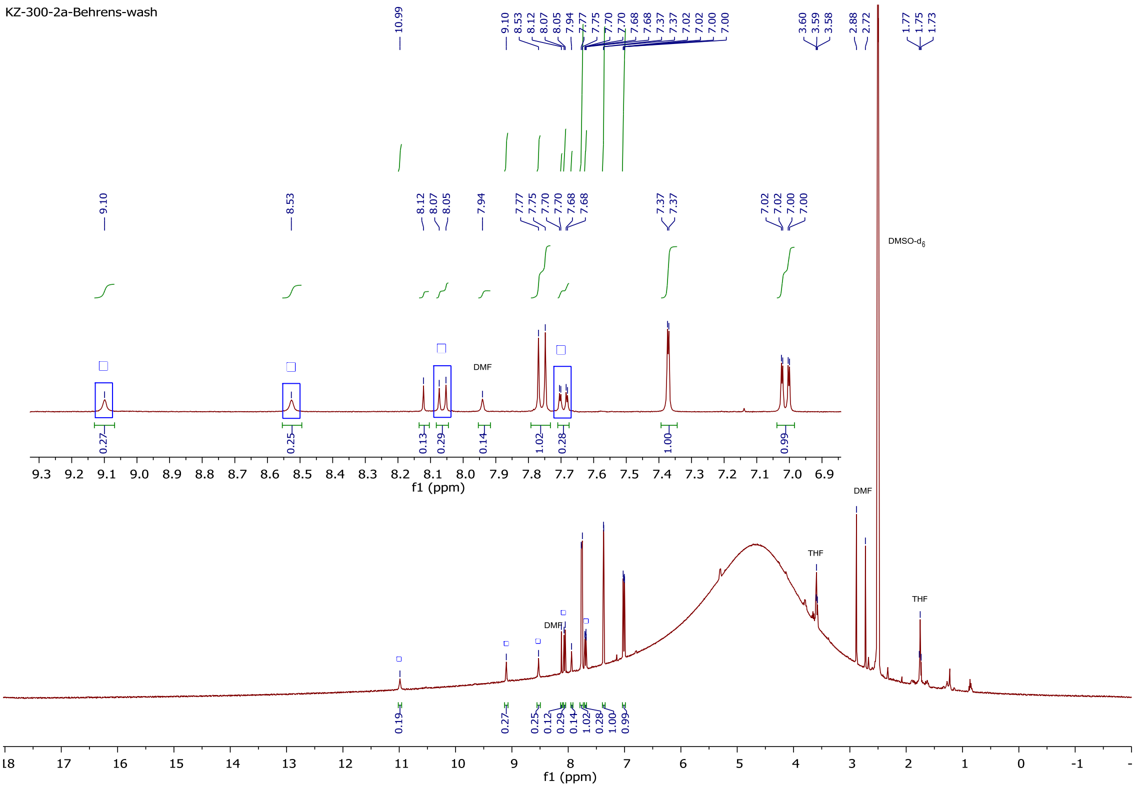


Figure S5. The ^{1}H NMR spectrum of a solution obtained by the digestion of UiO-66-NH_2 synthesized and washed in THF according to Behrens *et. al.* in a DMSO-d_6/HF_{aq} mixture.

%NHCHO= [$n_{H\text{-}6}$/($n_{H\text{-}6}$ + $n_{H\text{-}6}$)]*100%= (0.29/1.29)*100% = 22.5% or %NHCHO= [$n_{H\text{-}5}$/($n_{H\text{-}5}$ + $n_{H\text{-}5}$)]*100% = (0.28/1.28)*100% = 21.9%; average %NHCHO = (22.5+21.9)/2=22.2%

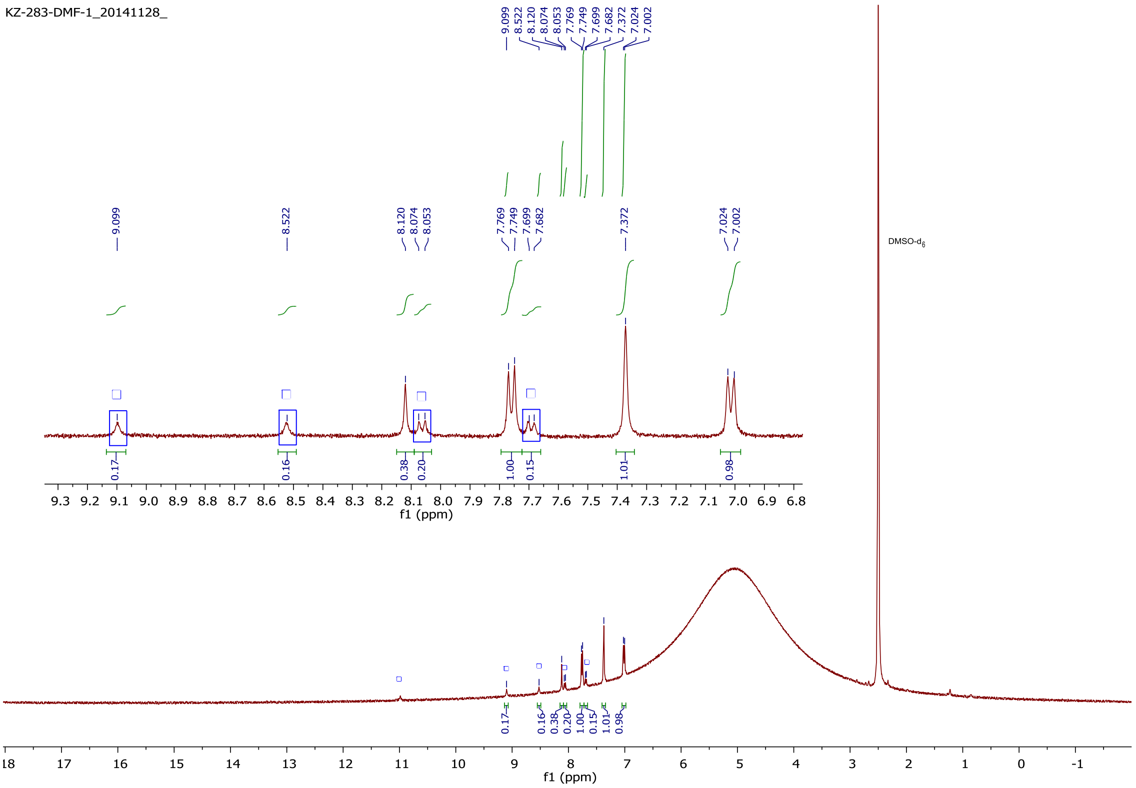


Figure S6. The ^{1}H NMR spectrum of a solution obtained by the digestion of UiO-66-NH_2 synthesized according to Hupp, Farha *et. al.* in DMSO-d_6/HF_{aq} mixture.

%NHCHO= [$n_{H\text{-}6}$/($n_{H\text{-}6}$ + $n_{H\text{-}6}$)]*100% = (0.2/1.2)*100% = 16.7% or %NHCHO= [$n_{H\text{-}5}$/($n_{H\text{-}5}$ + $n_{H\text{-}5}$)]*100% = (0.15/1.13)*100% = 13.3%; average %NHCHO = (16.7 + 13.3)/2 = 15%

3. Sample digestion conditions, resolution of mixtures and analysis by the ESI-MS

a) Digestion of the UiO-66-NH_2 under acidic conditions:

Ca. 2 mg of UiO-66-NH_2 was digested in a DMSO-d_6/HF_{aq} mixture (700:10), and the clear solution was applied to a RP-C18 TLC plate. The TLC plate was dried at 120°C and developed in water/methanol (1:1, v:v). The spots on the TLC plate were detected under ultraviolet wavelengths of 254 and 366 nm. Only one yellow spot at R_f value of 0.5 was observed and assigned to 2-aminoterephthalic acid.

b) Digestion of the UiO-66-NH_2 under basic conditions:

Ca. 6 mg of UiO-66-NH_2 was digested in a solution of sodium hydroxide (obtained by dissolving 7 mg NaOH in 200 µl of distilled water) and sonicated for one minute. The resulting suspension was left until supernatant clarifies (*ca*. 10 minutes). The supernatant was analysed by RP TLC. Aside from yellow spot of 2-aminoterephthalic acid (R_f=0.5) there was also clearly visible spot at an R_f value of 0.7 which can be assigned to the major by-product.

To isolate the unidentified by-product in a pure form three plates were developed with a solvent mixture of water/methanol (1:1, v:v) and dried. The thin layer of fluorescing spots at an R_f value of 0.7 were scraped off, put into an Eppendorf tube and extracted with 200 µl of methanol for 2 minutes with vigorous shaking. The extraction was repeated using a further aliquot of 200 µl of methanol. The combined extracts were filtered and evaporated to dryness on a rotary evaporator. The solid residue was then analysed by ESI-MS.

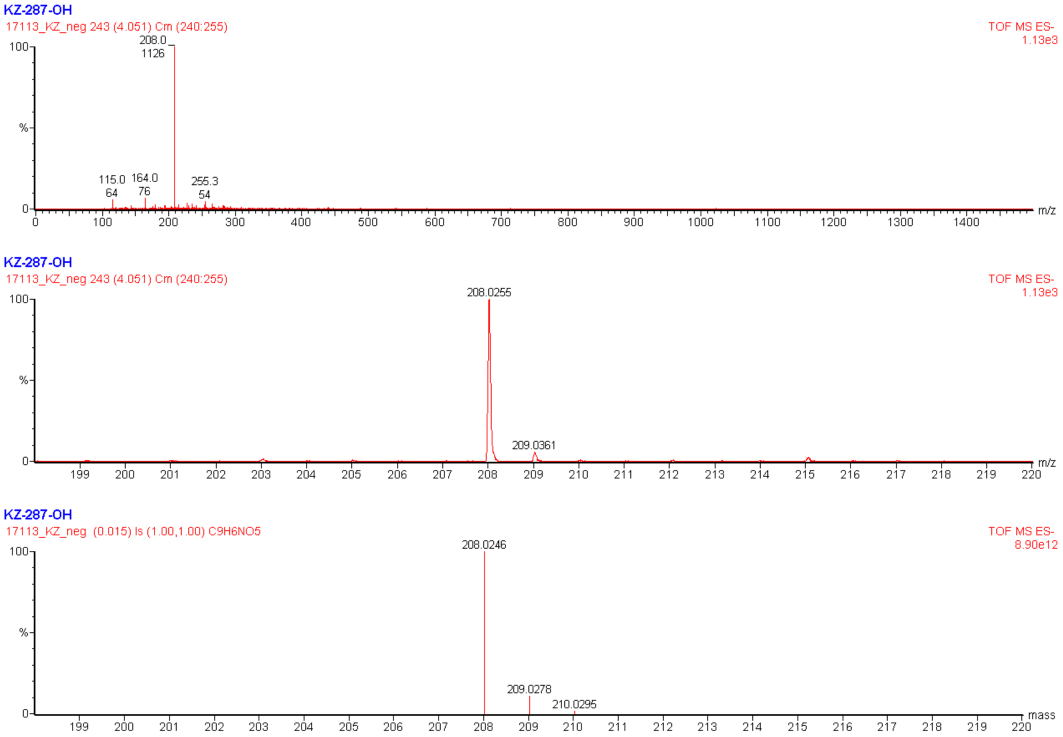
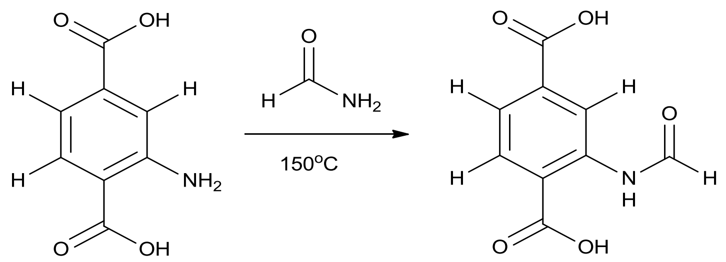


Figure S7. Negative mode HR-ESI MS spectrum of the side-product isolated by RP TLC from the as-synthesized UiO-66-NH_2 upon digestion in diluted NaOH.

4. Synthesis and spectral characterization of a 2-formamidoterephthalic acid [2-(formylamino)terephthalic acid]

2-Formamidoterephthalic acid was prepared according to the literature procedure[7] with slight modification.



A suspension of 2-aminoterephthalic acid (4.500 g, 21.515 mmol) in formamide (70 ml) was heated in oil bath at 150°C for 1 h. The resulting clear yellow solution was slowly cooled down to room temperature. Copious white precipitate formed, which was filtered off on a Schott funnel and washed twice with distilled water (10 ml). The white solid was dried in air at 120°C overnight. The crude product was recrystallized by dissolving in 150 ml of 1.7% Na_2CO_3 solution, filtering and acidifying the filtrate with acetic acid (10-15 ml). The precipitated white solid was filtered off, washed twice with water (2×10 ml) and dried in air at 120°C overnight.

The product can be additionally recrystallized from DMF:H_2O (v:v, 5:2) if high purity is desired.

^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H 13.59 (2 H, br.s, COOH), 11.00 (1 H, s, NH), 9.09 (1 H, s, H-3), 8.52 (1 H, s, CHO), 8.04 (1 H, d, *J* = 8.2 Hz, H-6), 7.67 (1 H, dd, *J* = 8.2, 1.6 Hz, H-5).
^{13}C NMR (101 MHz, DMSO-d$_6$) δ_C 168.4 (COOH), 166.4 (COOH), 161.19 (CHO), 139.56 and 135.27 (C-1 and C-4), 131.40 (C-6), 123.50 (C-5), 121.39 (C-3), 120.36 (C-2).

FIIR-ATR (cm^{-1}): 3137, 2808, 1693, 1626, 1588, 1530, 1423, 1400, 1299, 1211, 750, 668.

HR MS (ESI-): Mass calcd for $C_9H_6NO_5$ [M-H]$^-$ 208.0246 Da, found: 208.0254 [M-H]$^-$.

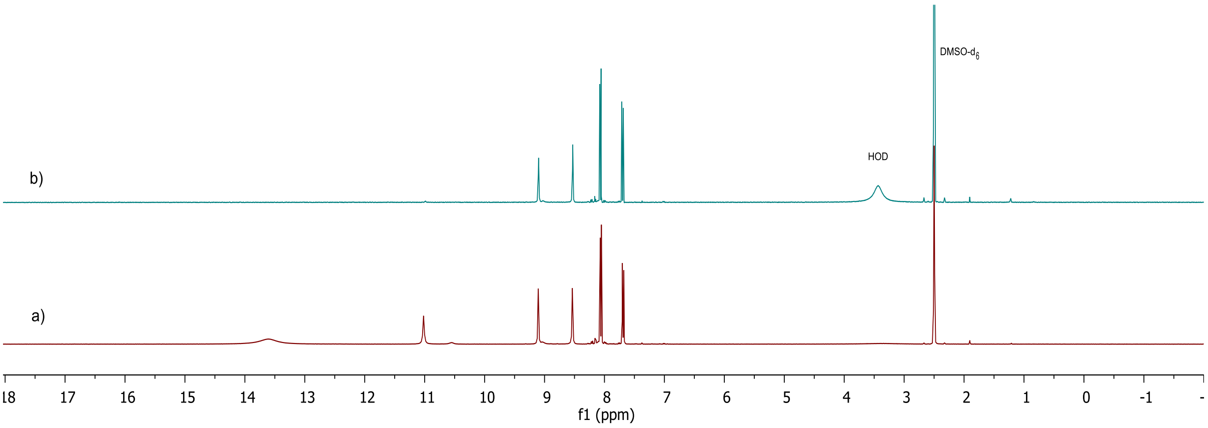


Figure S8. ^{1}H NMR spectrum of 2-formamidoterephthalic acid in DMSO-d$_6$: a) before and b) after the addition of D_2O (12 µl). Both signals at δ_H 11.0 and 13.6 ppm disappear after D_2O addition.

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[7] E. B. Skibo, J. H. Gilchrist, *J. Org. Chem*., 1988, **53**, 4209-4218;

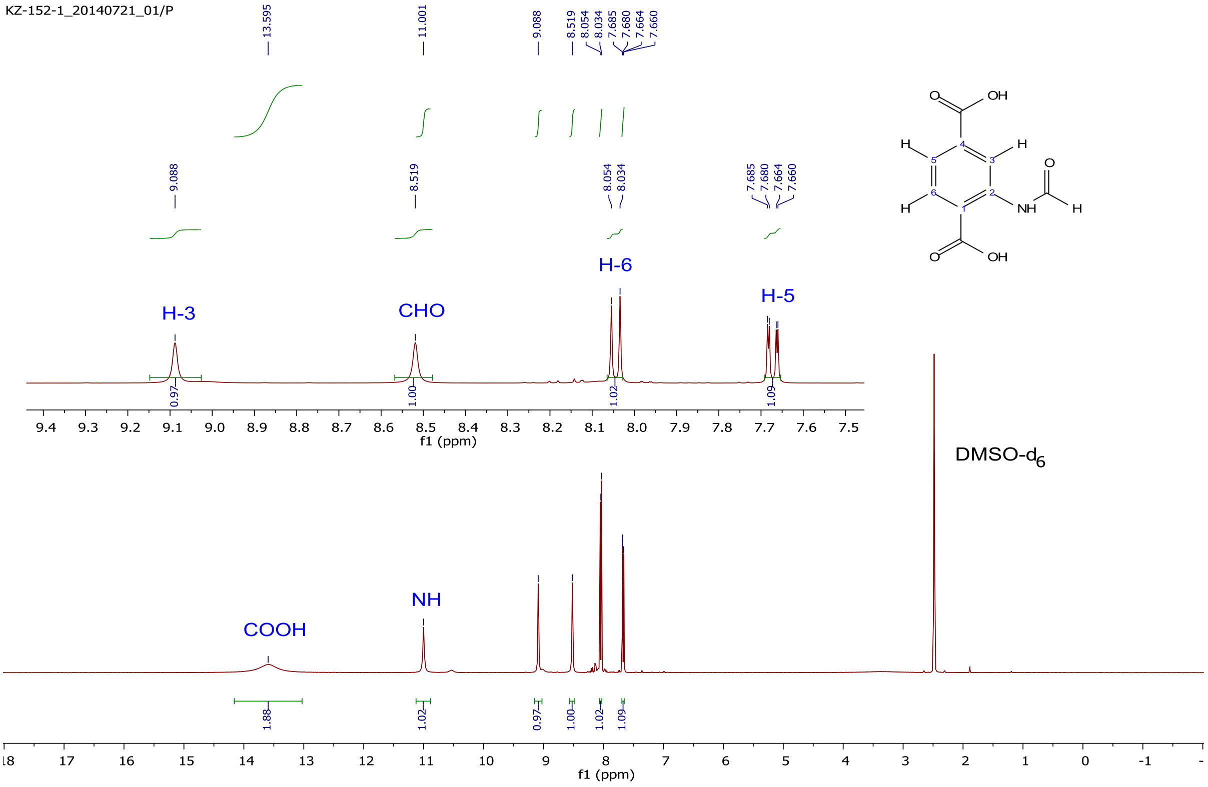


Figure S9. ^{1}H NMR spectrum of 2-formamidoterephthalic acid in DMSO-d$_6$.

The –CHO signal appears in the ^{1}H NMR spectra at δ 8.52 ppm and not at 11.0 ppm as previously reported. Gradient selected two dimensional NMR experiments (^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC) facilitated correct assignment of –CHO and other signals in the ^{1}H and ^{13}C NMR spectra (*vide infra*).

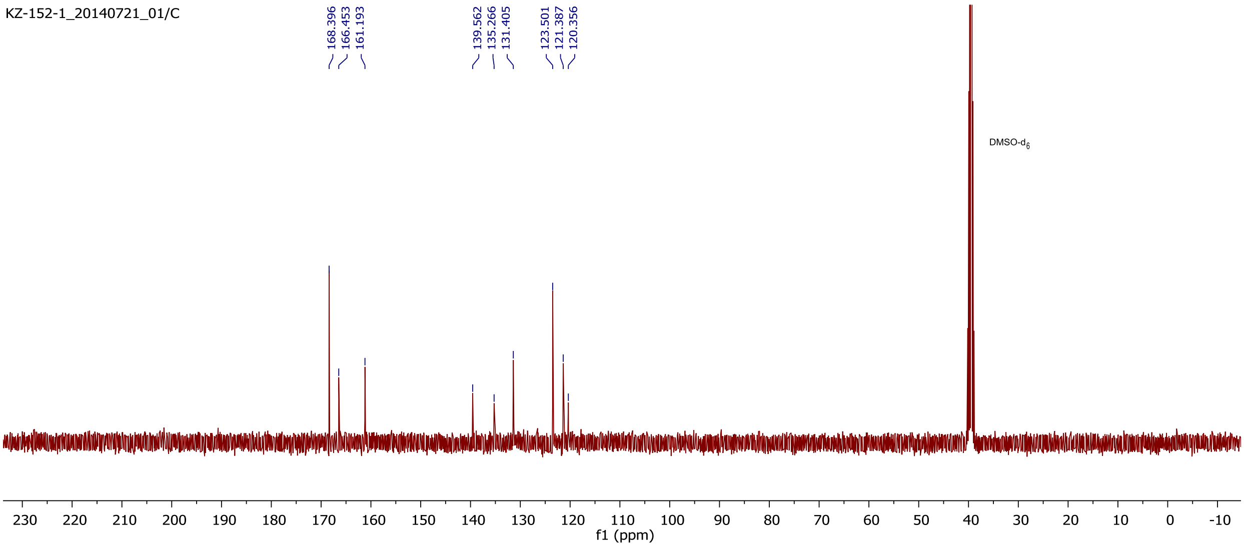


Figure S10. ^{13}C NMR spectrum of the 2-formamidoterephthalic acid in DMSO-d$_6$.

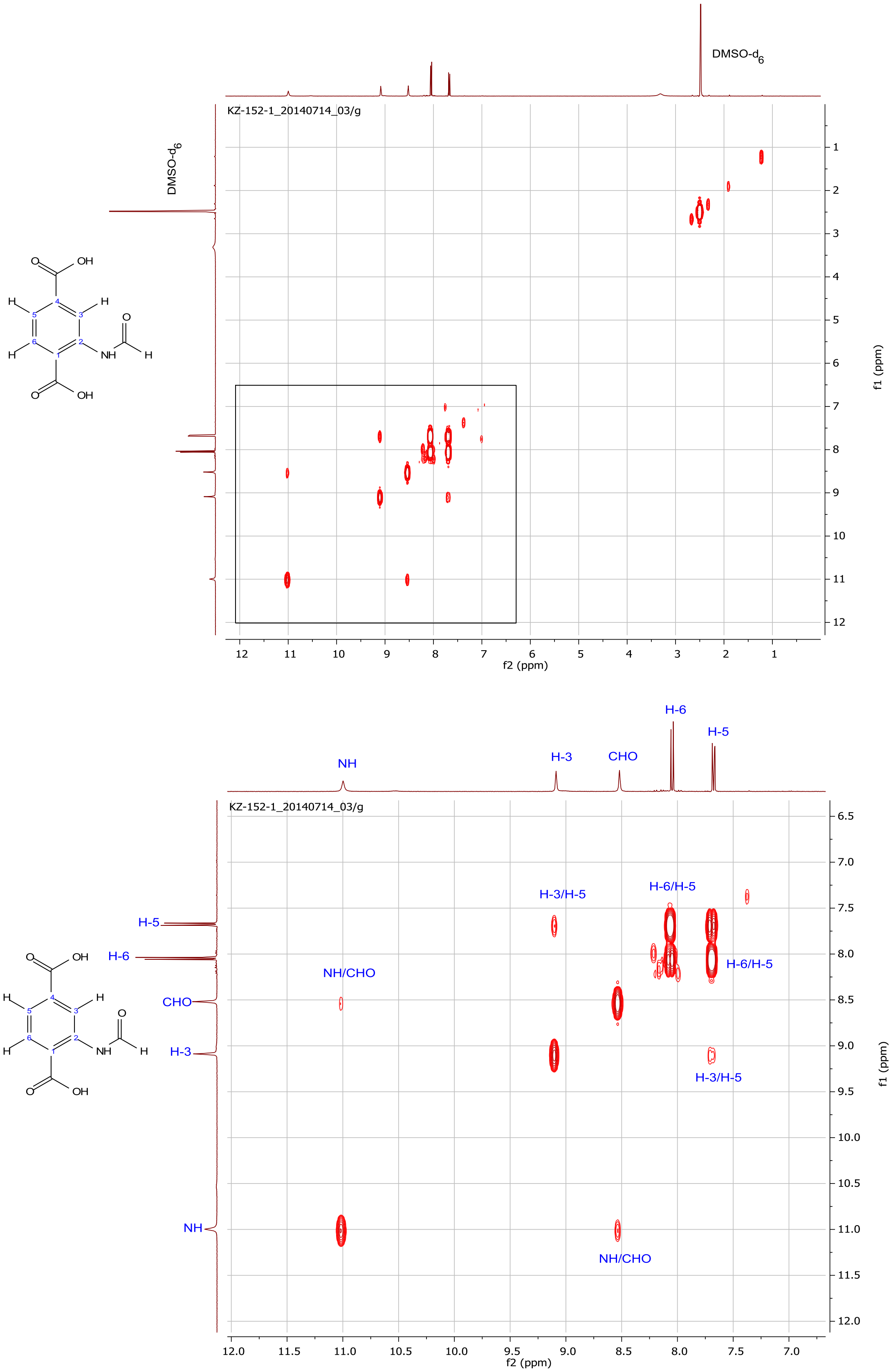


Figure S11. The ^{1}H-^{1}H gCOSY spectrum of 2-formamidoterephthalic acid in DMSO-d$_6$.

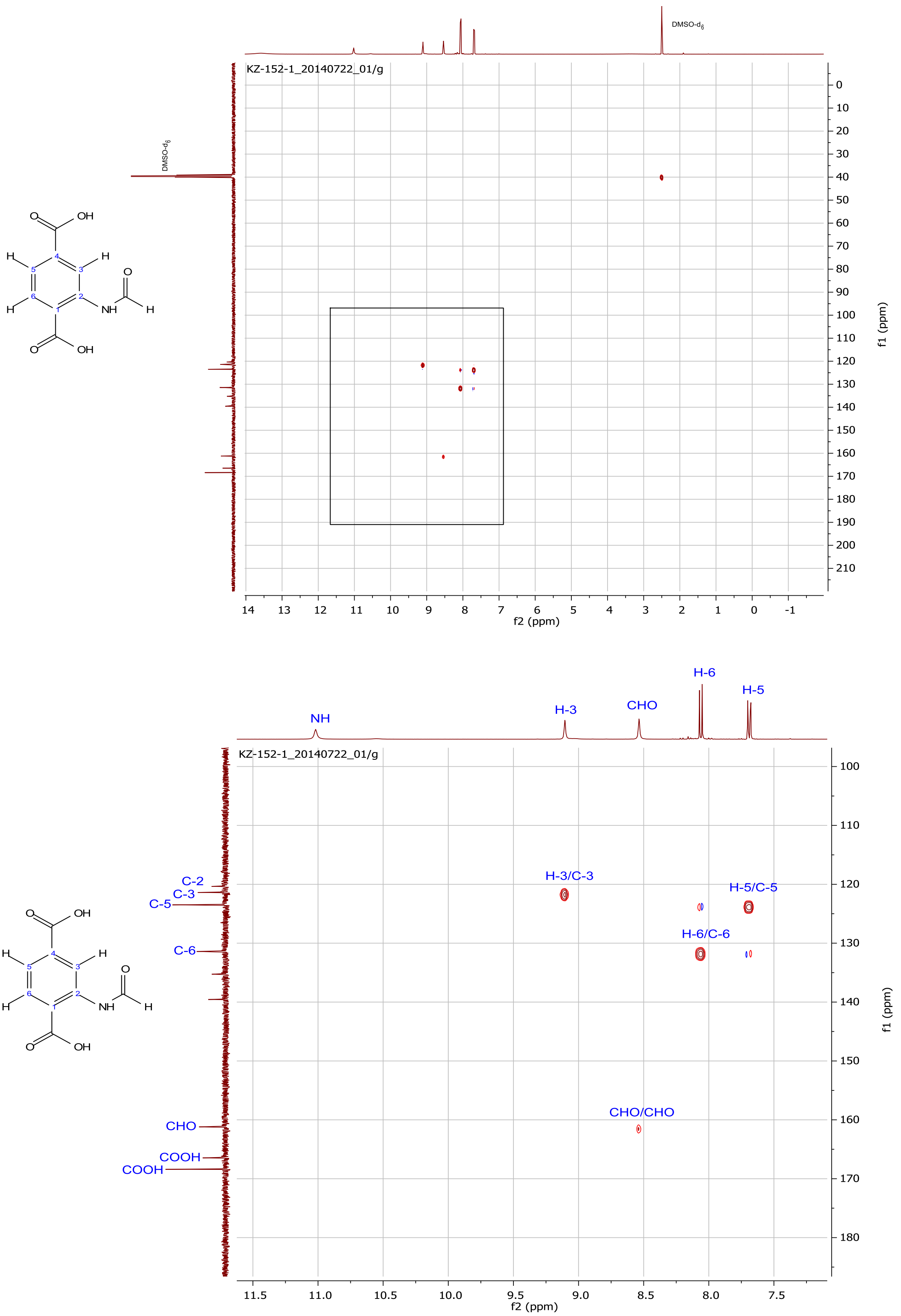


Figure S12. The gHSQC spectrum of 2-formamidoterephthalic acid in DMSO-d_6.

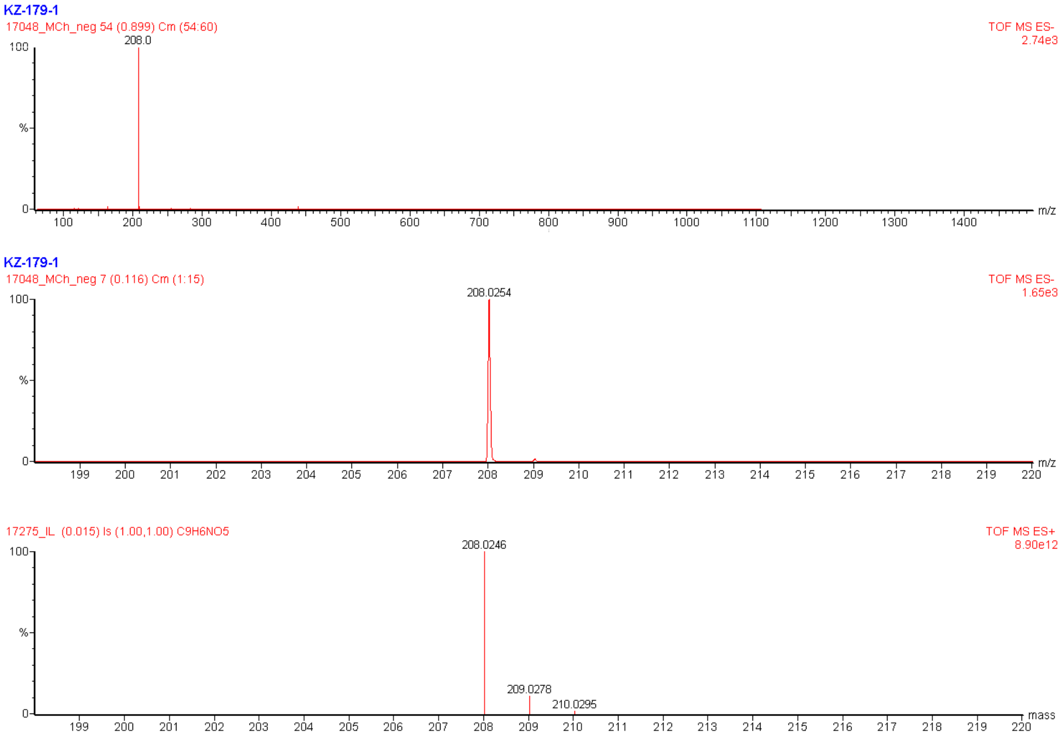


Figure S13. HR-ESI MS spectrum of 2-formamidoterephthalic acid recorded in negative mode (-).

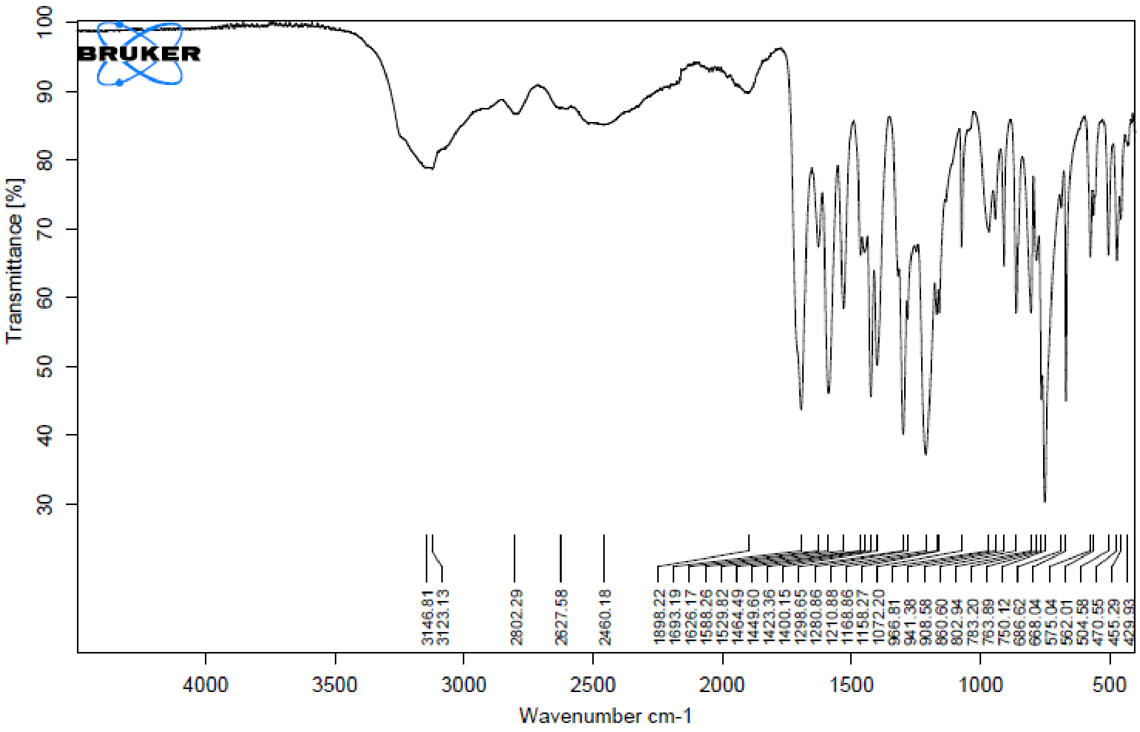


Figure S14. FTIR-ATR spectrum of 2-formamidoterephthalic acid.

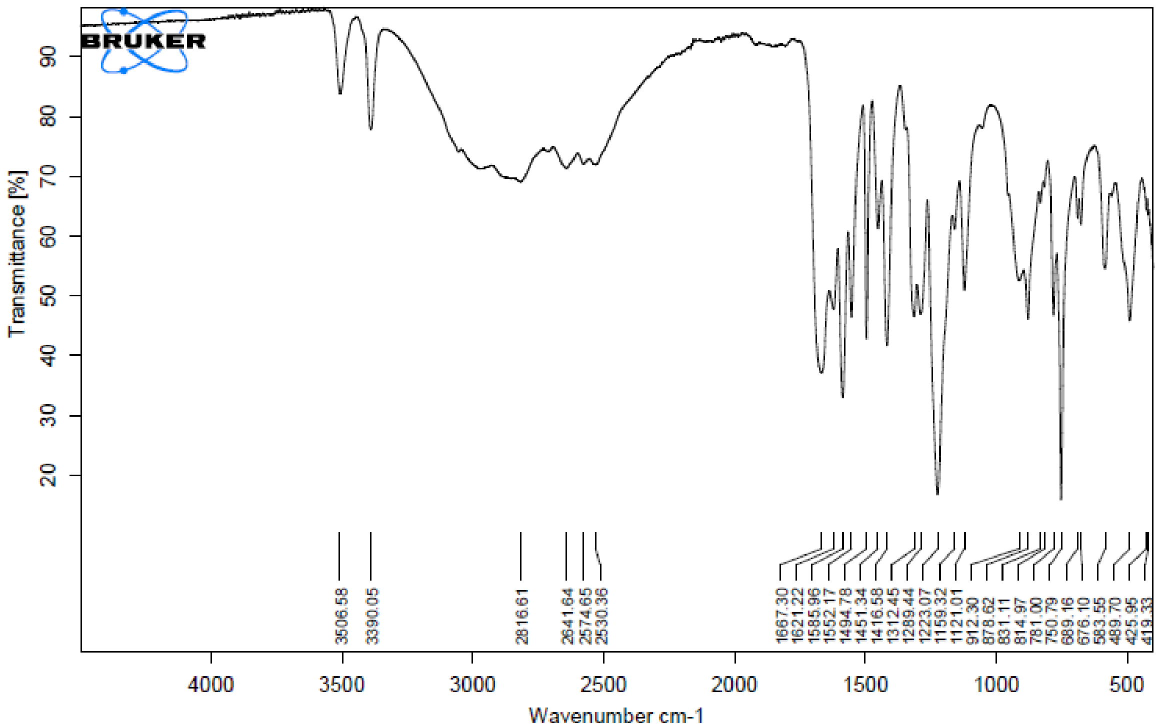


Figure S15. FTIR-ATR spectrum of 2-aminoterephthalic acid.

Sharp bands at 3507 and 3390 cm^{-1} are due to the symmetric and asymmetric N-H vibrations respectively.

5. Formylation of $H_2BDC\text{-}NH_2$ and UiO-66-NH_2 in the presence of various acids

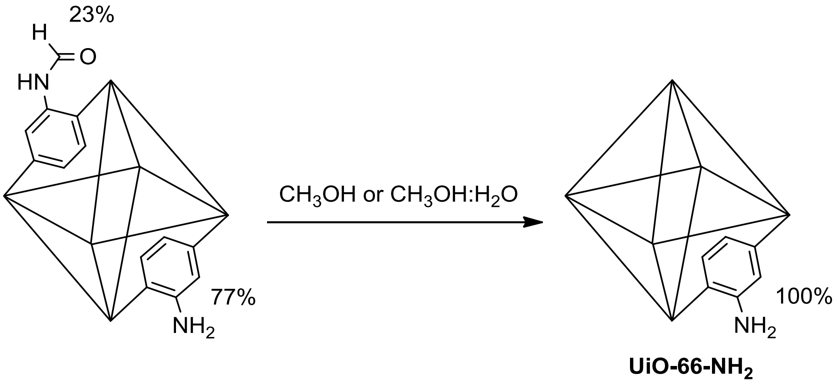
Five tightly sealed glass vials containing 2-aminoterephthalic acid ($H_2BDC\text{-}NH_2$, 20 mg, 0.11 mmol) and appropriate acidic catalyst (see table below) dissolved in DMF (2 ml) were placed in a preheated oven at 120°C for 24 hours. After cooling down each vial to room temperature, the solvent was evaporated to dryness on a rotary evaporator and the resulting material was dried under reduced pressure (10^{-3} mbar). Dry residues were re-dissolved in DMSO-d_6 and the resulting solutions were analysed by ^1H NMR.

Four tightly sealed glass vials containing 10 mg of pure UiO-66-NH_2 material (after complete removal of formyl groups) and an appropriate amount of respective acid (see table below) dissolved in DMF (2 ml) were placed in a preheated oven at 120°C for 24 hours. After cooling down each vial to room temperature the solvent was decanted, the resulting material was washed with fresh portion of DMF (2 ml) and decanted once again. Finally, the resulting material was dried under reduced pressure (10^{-3} mbar) and digested in a HF_{aq}/DMSO-d_6 mixture. The resulting solutions were analysed by ^1H NMR.

Table S1. Formylation of $H_2BDC\text{-}NH_2$ and UiO-66-NH_2 material in the presence of various acids.

No.	Ligand's/MOF's	Solvent	Additives	%NHCHO (from ^1H NMR)
1	$H_2BDC\text{-}NH_2$ (20 mg, 0.11 mmol)	DMF (2 ml)	- (blank experiment)	6%
2	$H_2BDC\text{-}NH_2$ (20 mg, 0.11 mmol)	DMF (2 ml)	50 µl HCOOH (1.33 mmol)	27%
3	$H_2BDC\text{-}NH_2$ (20 mg, 0.11 mmol)	DMF (2 ml)	5 µl HCOOH (0.133 mmol)	8%
4	$H_2BDC\text{-}NH_2$ (20 mg, 0.11 mmol)	DMF (2 ml)	14 µl 36% HCl (0.44 mmol)	3%
5	$H_2BDC\text{-}NH_2$ (20 mg, 0.11 mmol)	DMF (2 ml)	147 µl 36% HCl (4.60 mmol)	12%
6	UiO-66-NH_2 (10 mg)	DMF (2 ml)	- (blank experiment)	2%
7	UiO-66-NH_2 (32 mg, 0.018 mmol, containing 0.11 mmol of H2BDC-NH_2)	DMF (2 ml)	50 µl (1.33 mmol) HCOOH	32%
8		DMF (2 ml)	14 µl 36% HCl (0.44 mmol)	5%
9		DMF (2 ml)	147 µl 36% HCl (4.60 mmol)	26%

6. Deprotection of formylated NH_2 groups in UiO-66-NH_2.



UiO-66-NH_2 used for initial deprotection experiments was synthesized according to the procedure by Behrens *et. al.*[8] and contained *ca*. 23% of NHCHO groups.

6a.

The as-synthesized UiO-66-NH_2 material (20 mg) was refluxed in methanol (10 ml) or methanol-water mixture (10 ml, 4:1 v:v) in a round bottom flask fitted with reflux-condenser connected to a check-valve bubbler. A sample of the same material (20mg) was also suspended in DMF-water mixture (10 ml, 4:1 v:v) in a tightly sealed 20 ml glass vial and put into a preheated oven at 100°C. During the reaction samples from the reaction vessels were collected after 3 h, 7 h and 24 h. Samples were filtered, washed with methanol (2 ml) and dried. After drying under reduced pressure all samples were digested in a DMSO-d_6/HF_{aq} mixture and the resulting solutions were analysed by ^1H NMR to establish the actual degree of amino group conversion.

PXRD spectra were recorded for all the samples after 24 hours.

Table S2. Initial deprotection attempts of the as-synthesised UiO-66-NH_2 material containing *ca*. 23% of NHCHO groups.

No.	Deprotection conditions		% NHCHO (from ^1H NMR)			
	solvent	temperature	Before	After 3 h	After 7 h	After 24 h
1	CH_3OH	reflux	*ca*. 23%	18%	15%	0%
2	$CH_3OH : H_2O$	reflux	*ca*. 23%	15%	10%	0%
3	DMF : H_2O	100°C	*ca*. 23%	15%	14%	11%

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[8] A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17**, 6643-6651.

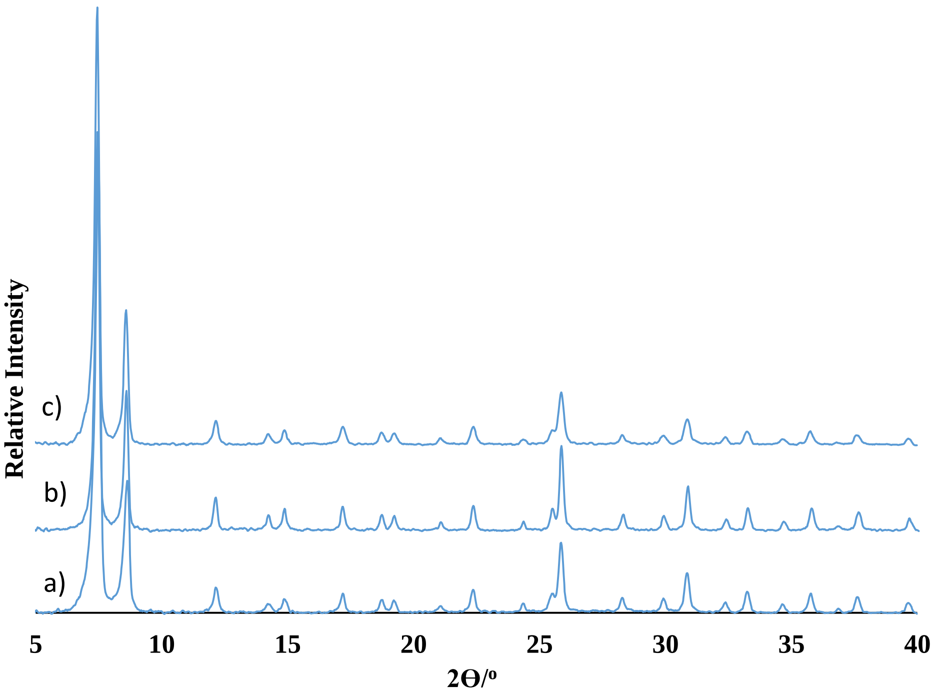

Figure S16. Powder X-ray diffraction patterns (PXRD) for UiO-66-NH_2/NHCHO(77/23) material after: a) refluxing in methanol for 24 h, b) refluxing in a methanol-water mixture for 24 h, and c) heating in a DMF-water mixture at 100°C for 24 h.

6b.

The as-synthesized UiO-66-NH_2 (*ca*. 500 mg) was immersed in methanol (50 ml) and left at RT overnight. After 24 h the solid was filtered off and dried by heating for 2 h at 120°C in a preheated oven. The resulting microcrystalline powder was purified by Soxhlet extraction with hot methanol for 24 h. During extraction samples were taken after 12h and 24h. After extraction microcrystalline powder was dried for 2 h at 120°C in a preheated oven.

Activation of UiO-66-NH_2 (100%):

The material purified as described above was activated under dynamic vacuum (10^{-3} mbar) at 150°C for 24 h. During the activation the white material turned pale yellow.

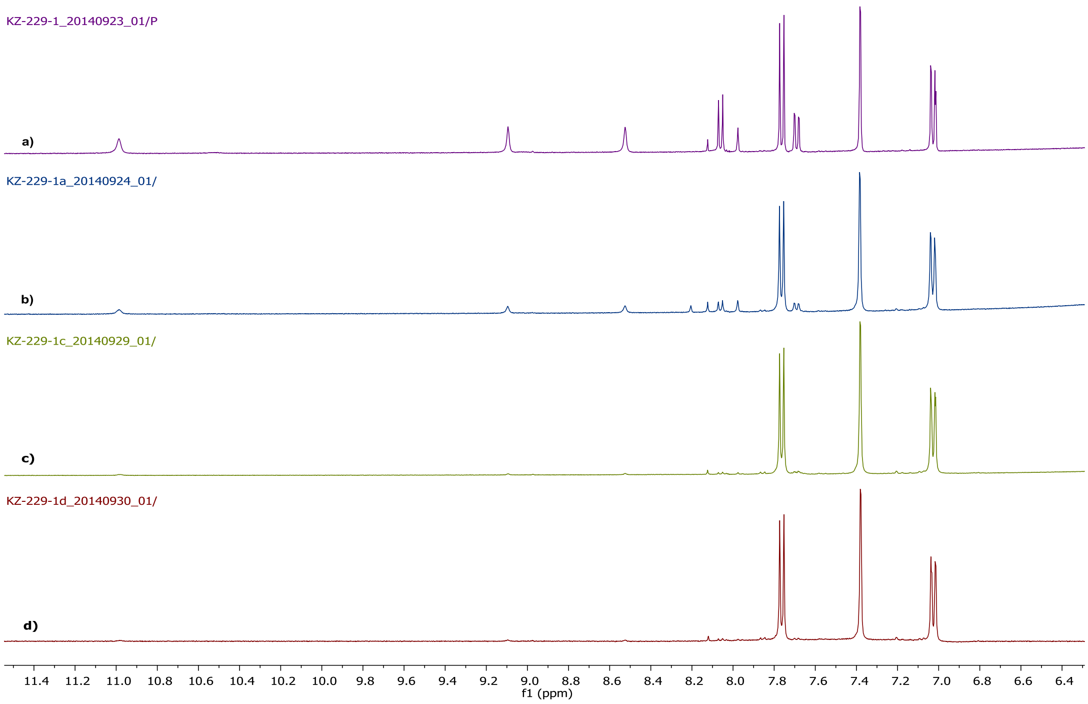

Figure S17. ^{1}H NMR spectra of digested samples of UiO-66-NH$_2$ materials: a) after washing with cold CH$_3$OH for 24 h, b) after washing with hot CH$_3$OH in a Soxhlet extractor for 12 h, c) after washing with hot CH$_3$OH in a Soxhlet extractor for 24 h, d) after activation at 150°C under vacuum for 24 h.

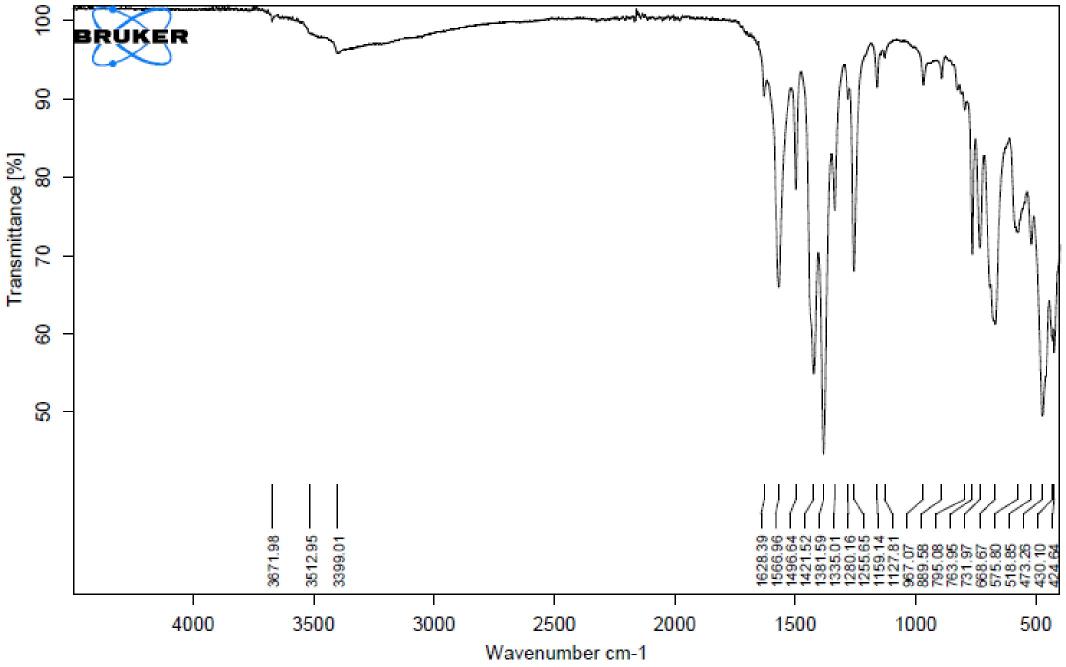

Figure S18. FTIR-ATR spectrum of pure UiO-66-NH$_2$.

The most prominent bands in the IR spectrum of pure UiO-66-NH$_2$ are the characteristic vibrational bands of carbonyl groups. Characteristic asymmetric stretching frequencies of the C=O from carboxylate groups complexed[9], are clearly observed at 1566 and 1497 cm^{-1}, while symmetric stretching frequencies are present at

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[9] T. Loiseau,C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Ferey, *Chem. Eur. J.*, 2004, **10**, 1373-1382.

1421 and 1382 cm^{-1}. Much less intense peaks at 3399 and 3513 cm^{-1} are related to amino groups. The C-N vibrations are also visible at 1335 and 1256 cm^{-1}.

Small peak at 3672 cm^{-1} is due to the bridging OH groups from inorganic Zr clusters[10].

No signals that could be related to carbonyl groups of both unreacted (free) 2-amino-terephthalic acid (stretching frequency at 1667 cm^{-1}) or solvent molecules (DMF, DEF) can be observed in the IR spectrum, what confirms that the thermally activated UiO-66-NH$_2$ is pure and its pores were completely evacuated.

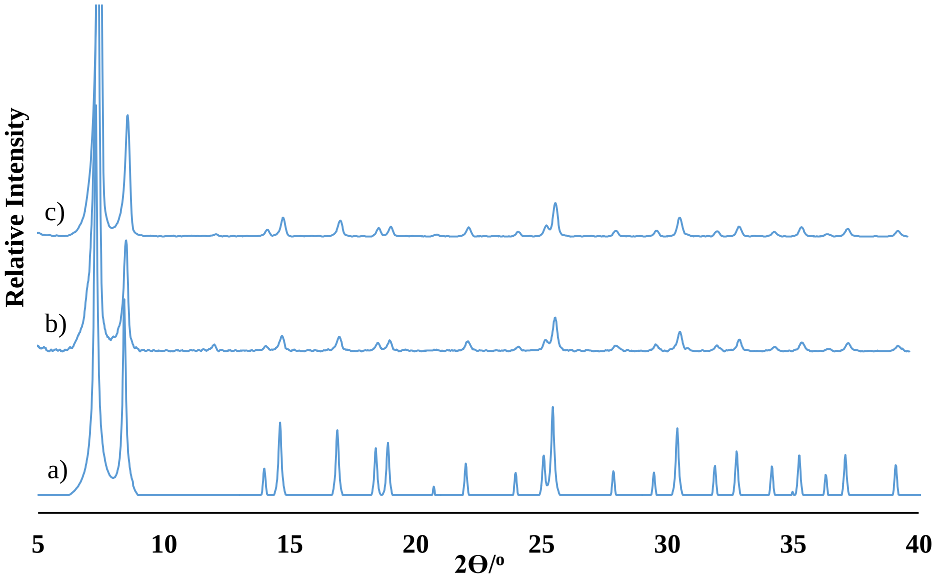
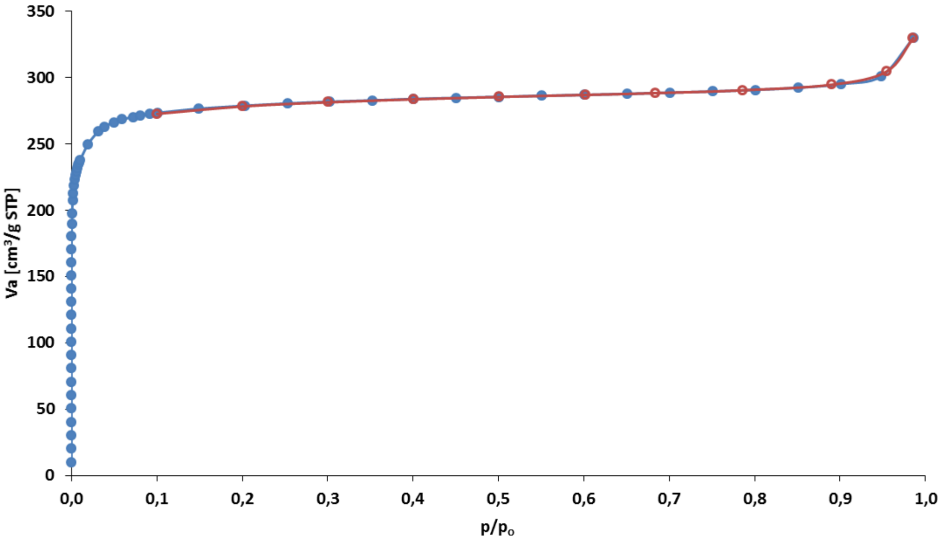


Figure S19. Powder X-ray diffraction patterns (PXRD) for: a) the pristine UiO-66 (simulated), b) pure UiO-66-NH$_2$ after Soxhlet extraction and drying, c) pure UiO-66-NH$_2$ after activation (heating to 150°C under vacuum 10^{-2} mbar).



S_{BET}=1122m^2/g

Figure S20. N$_2$ adsorption isotherms (77K) of the pure UiO-66-NH$_2$(100%) material, activated at 150°C for 48h (adsorption points denoted by blue and desorption by red circles).

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[10] Ch. Larabi, E. A. Quadrelli, *Eur. J. Inorg. Chem.*, 2012, **18**, 3014-3022.

7. Attempts of post-synthetic formylation of UiO-66-NH_2 by formamide

A sample of pure UiO-66-NH_2 (60 mg) material was suspended in formamide (6 ml) in a 20 ml glass vial, tightly sealed and put into a preheated oven at 80°C for 24 hours. After 24 h the sample was collected by filtration. The sample was digested and analysed by ^{1}H NMR to determine the content of free amine group in the resulting material. Only minor amount (<5%) of the expected formylation product was observed.

A sample of pure UiO-66-NH_2 (60 mg) material was suspended in formamide (6 ml) in a 20 ml glass vial, tightly sealed and put into a preheated oven at 120°C for 24 hours. After cooling down to RT, the solid material was collected by filtration, washed twice with methanol (2x5ml) and air dried.

PXRD spectra were recorded for both samples.

After prolonged treatment of UiO-66-NH_2 material with formamide at 120°C the intensities of its PXRD reflections were decreased and broadened, what suggests decomposition of the framework and formation of amorphous phase.

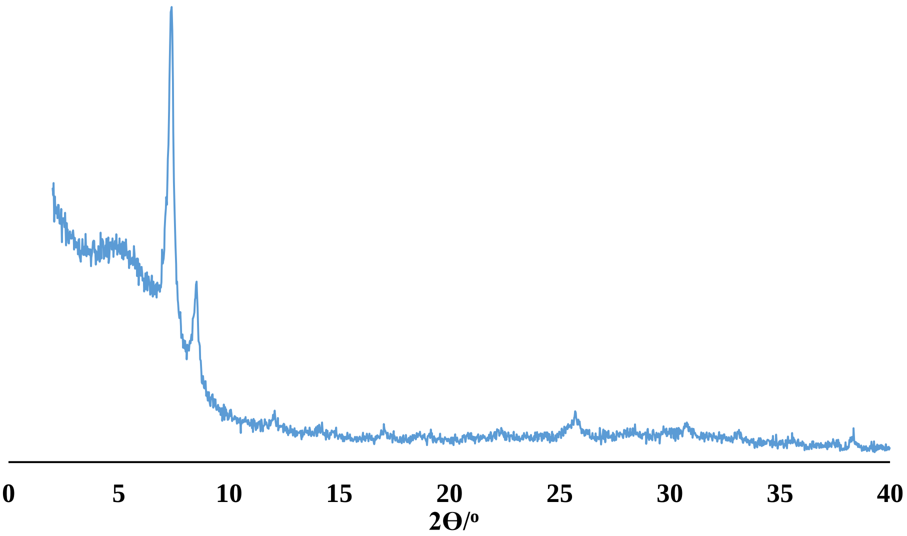
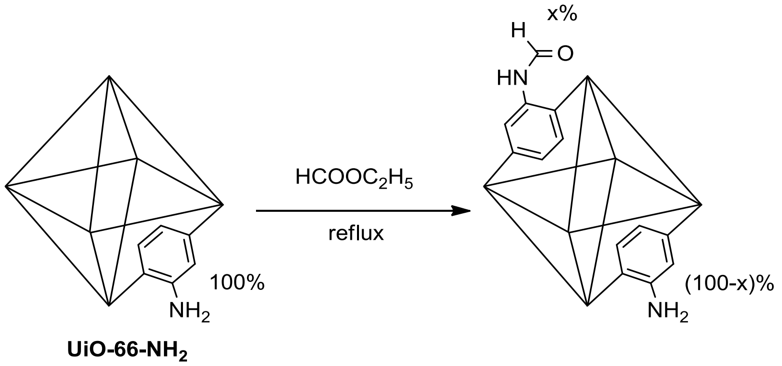


Figure S21. Powder X-ray diffraction patterns (PXRD) for pure UiO-66-NH_2 material after formamide treatment at 120°C for 24 h.

8. Post-synthetic formylation of UiO-66-NH$_2$ by ethyl formate



Pure UiO-66-NH$_2$ (500 mg, completely deformylated) was refluxed in ethyl formate (50 ml) in a round bottom flask fitted with reflux condenser. During the reaction samples from the reaction vessel were collected after 1 h, 4 h, 6 h, 7 h and 7 days filtered and dried. After drying under reduced pressure all the samples were digested in a DMSO-d$_6$/HF$_{aq}$ (700:10) mixture and the resulting solutions were analysed by ^{1}H NMR to establish the actual degree of amino group conversion.

Table S3. Formylation of pure UiO-66-NH$_2$ material with ethyl formate under reflux

Reaction time	1 h	4 h	6 h	7 h	7 days
%NHCHO	15%	30%	40%	45%	75%

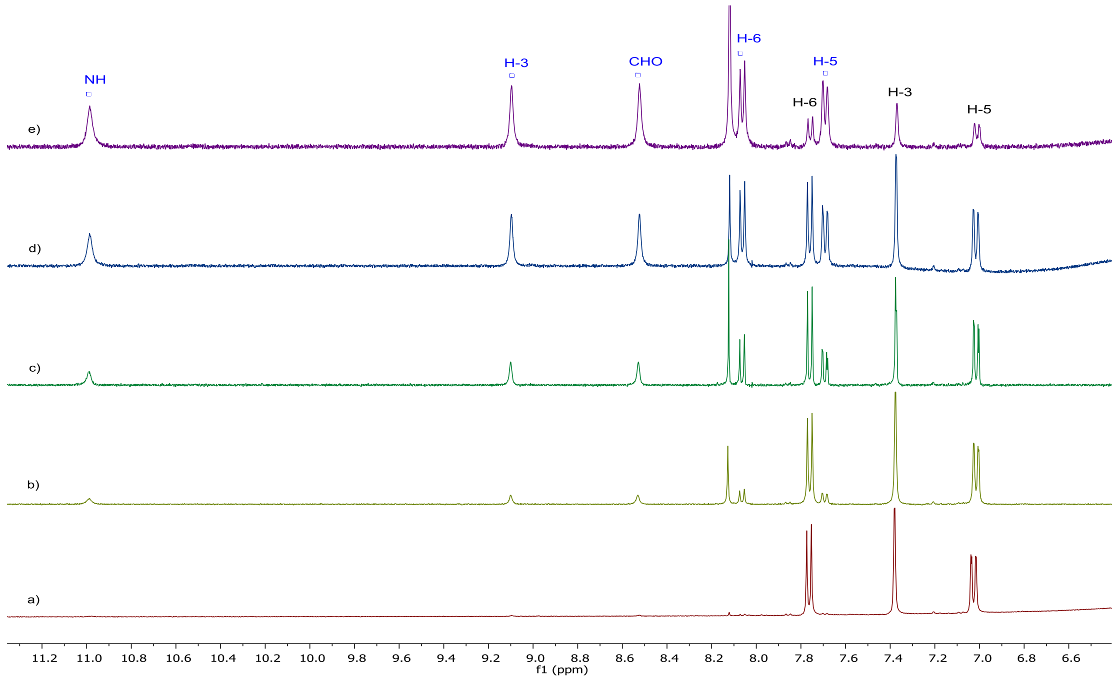


Figure S22. Downfield region of ^{1}H NMR spectra of digested UiO-66-NH$_2$/NHCHO materials obtained after refluxing in ethyl formate for: a) 0 h, b) 1 h, c) 4 h, d) 7 h and e) 7 days.

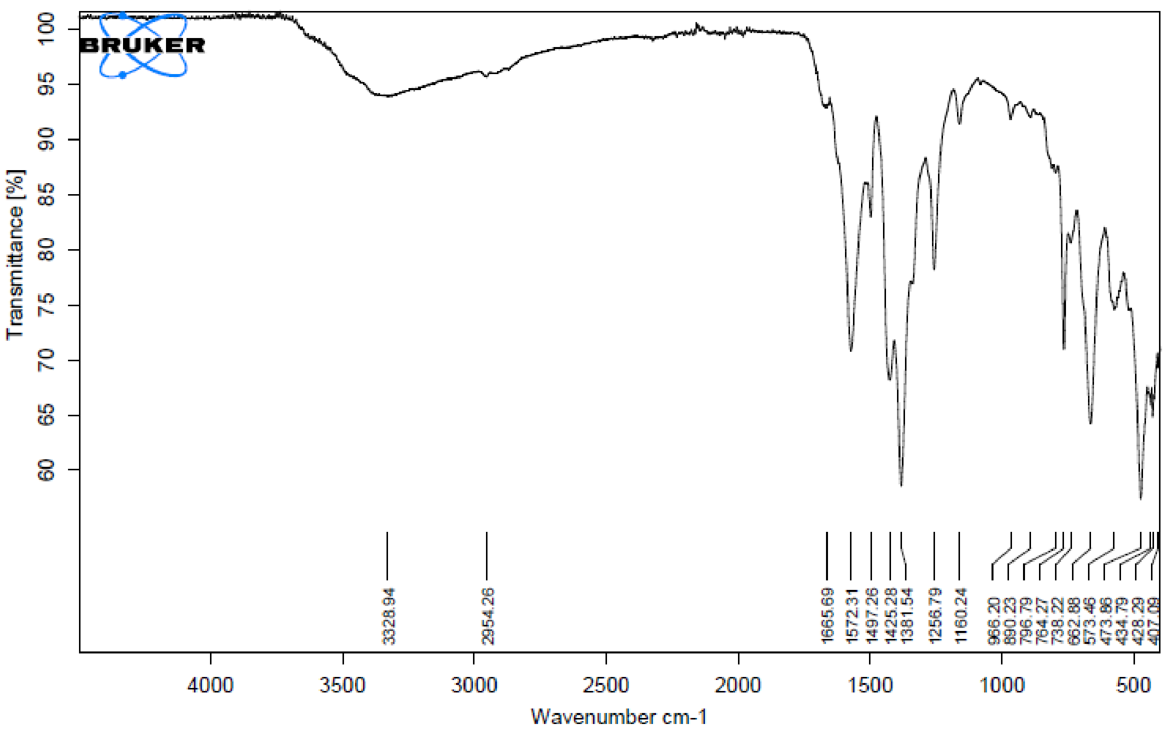


Figure S23. FTIR-ATR spectra of UiO-66-NH$_2$/NHCHO(70/30)

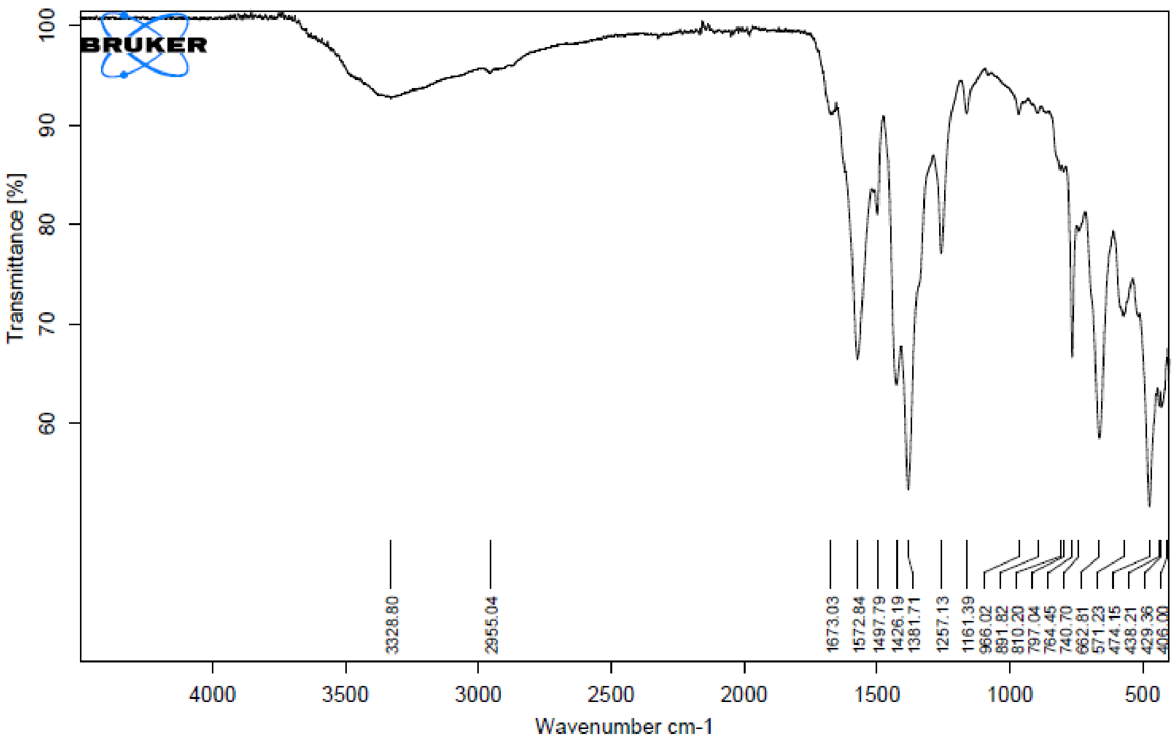


Figure S24. FTIR-ATR spectra of UiO-66-NH$_2$/NHCHO(55/45)

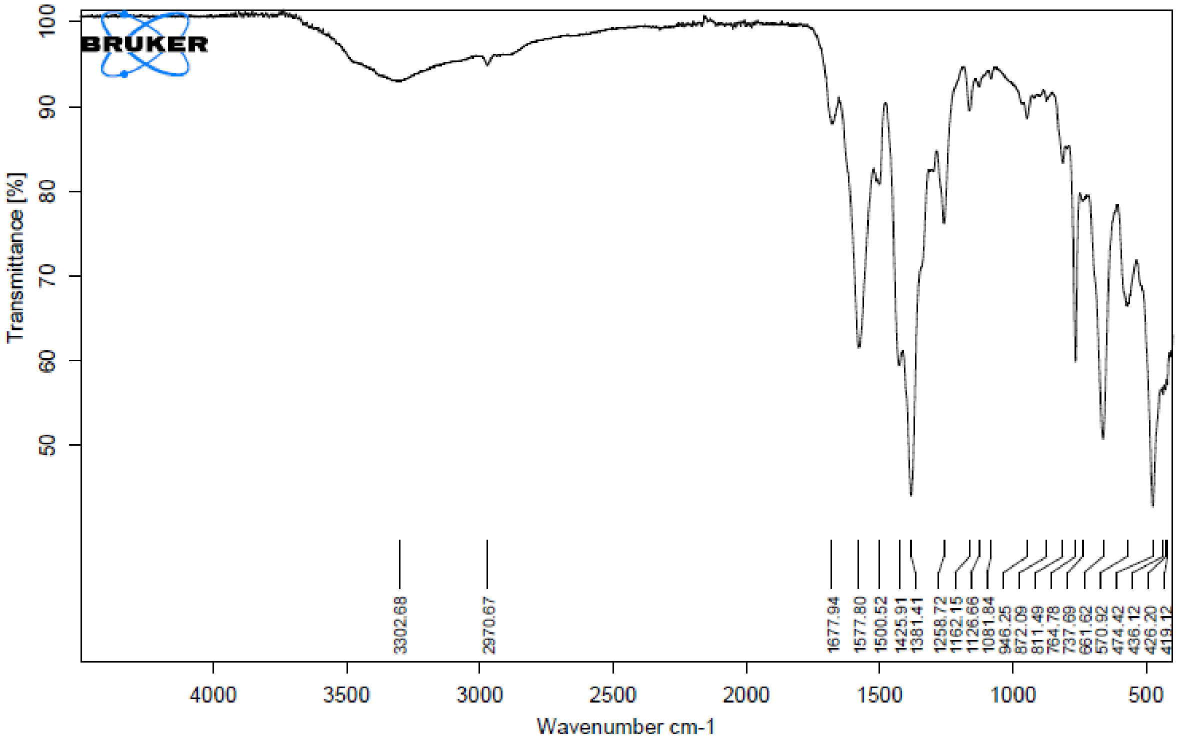


Figure S25. FTIR-ATR spectra of UiO-66-NH_2/NHCHO(25/75)

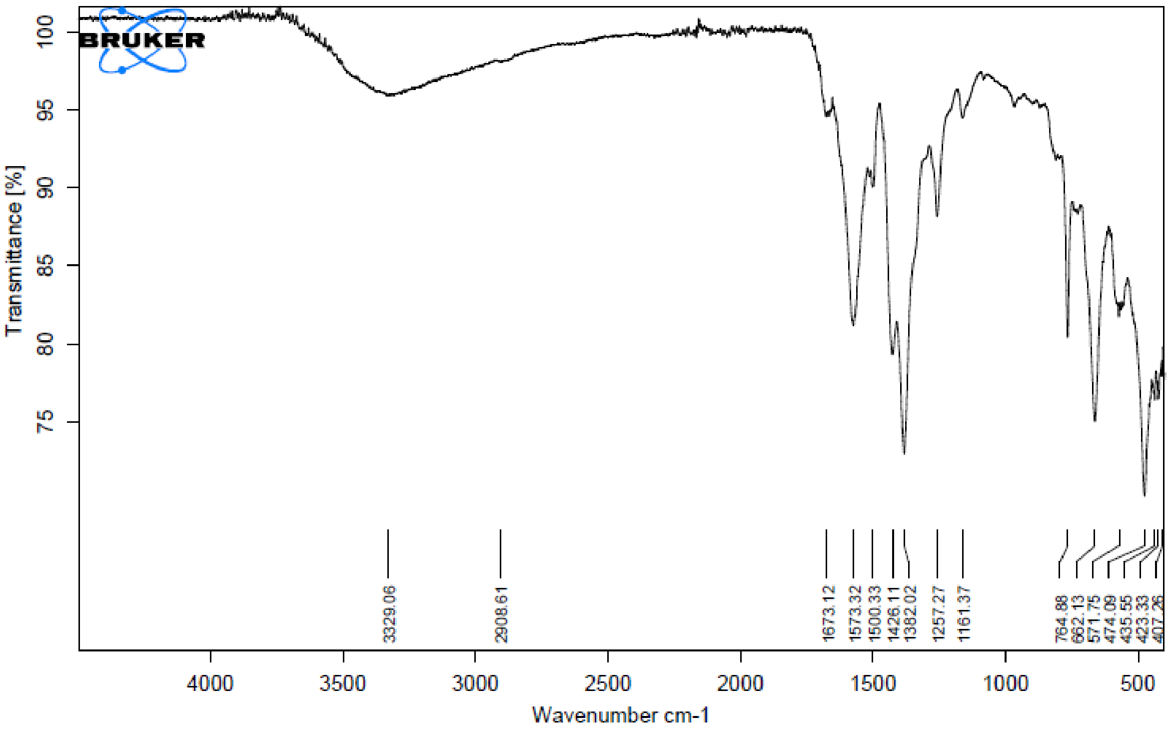


Figure S26. FTIR-ATR spectra of UiO-66-NH_2/NHCHO(13/87)

The FTIR spectra of UiO-66-NH_2/NHCHO materials reveal that there is little change in the vibrational modes upon partial functionalization of the NH_2 groups. However, additional small peaks due to the C=O stretching vibrations of the amide bonds are clearly visible at ca. 1666 cm^{-1}. For highly formylated samples peaks due to the C=O stretching vibrations of the amide bonds are slightly shifted to ca. 1673 cm^{-1}. The NH_2 vibrations are overshadowed by a large band cantered at ca. 3328 cm^{-1}, which is probably due to the presence of small amount of water inside the pores.

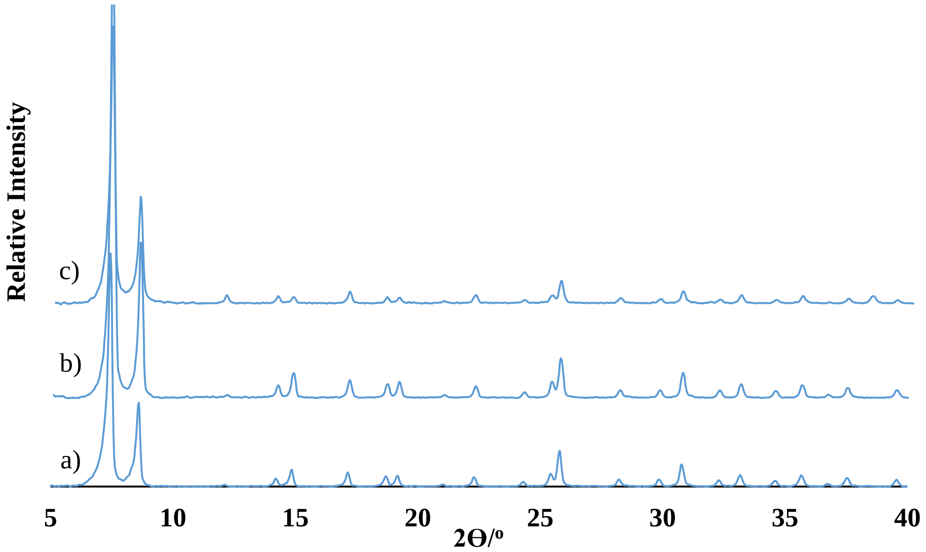
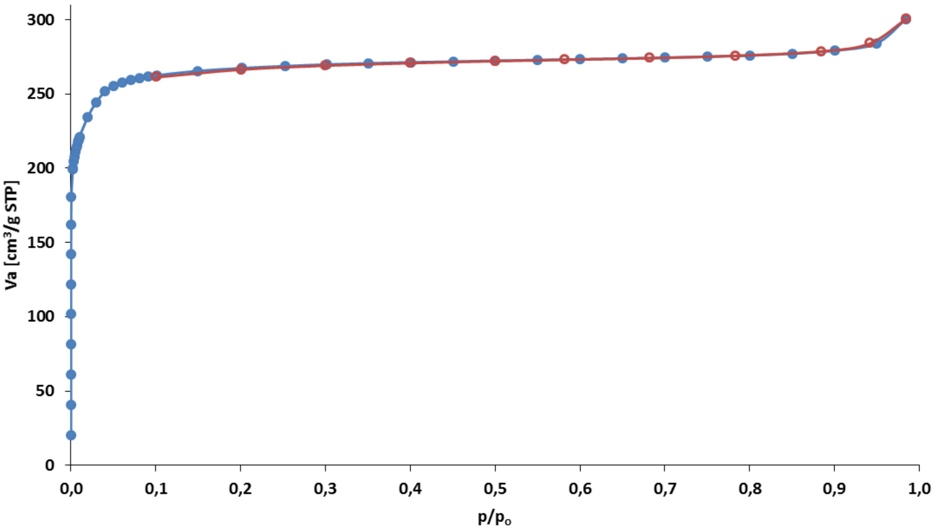


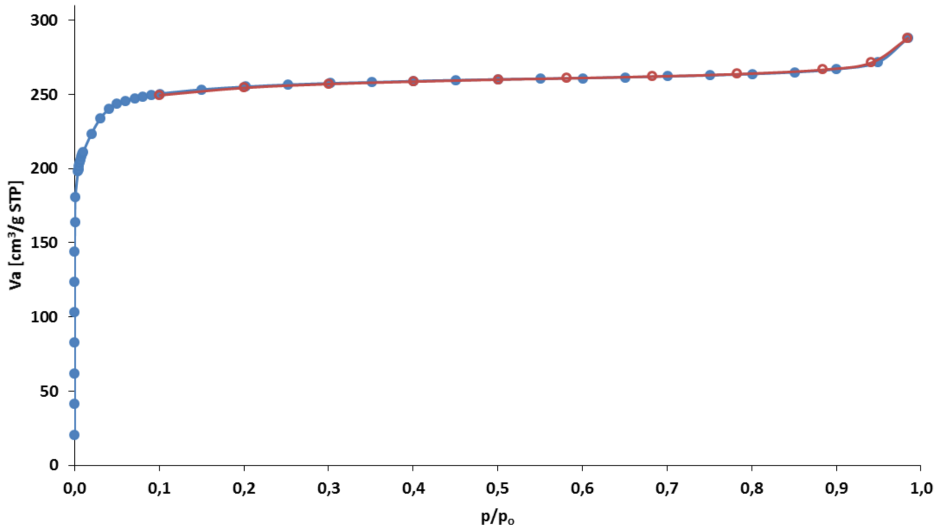
Figure S27. Powder X-ray diffraction patterns (PXRD) for UiO-66-NH_2/NHCHO obtained from pure UiO-66-NH_2 by refluxing in ethyl formate for: a) 4 h, b) 7 h and c) 7 days.

To investigate the effect of the post-synthetic formylation of the UiO-66-NH_2 on porosity, the Brunauer-Emmett-Teller (BET) specific surface areas of four modified samples with general formula UiO-66-$(NH_2)_x$/$(NHCHO)_{100-x}$ (where x= 30%-75%) were measured via N_2 adsorption at 77 K. The surface areas are gradually reduced from the initial value of 1150 m^2/g for pure UiO-66-NH_2 to 1077, 1029 and 880 m^2/g for materials containing 30, 45 and 75% NHCHO groups respectively. Only small reduction in specific surface areas of materials containing up to 45% NHCHO groups in comparison with pure UiO-66-NH_2 was observed.



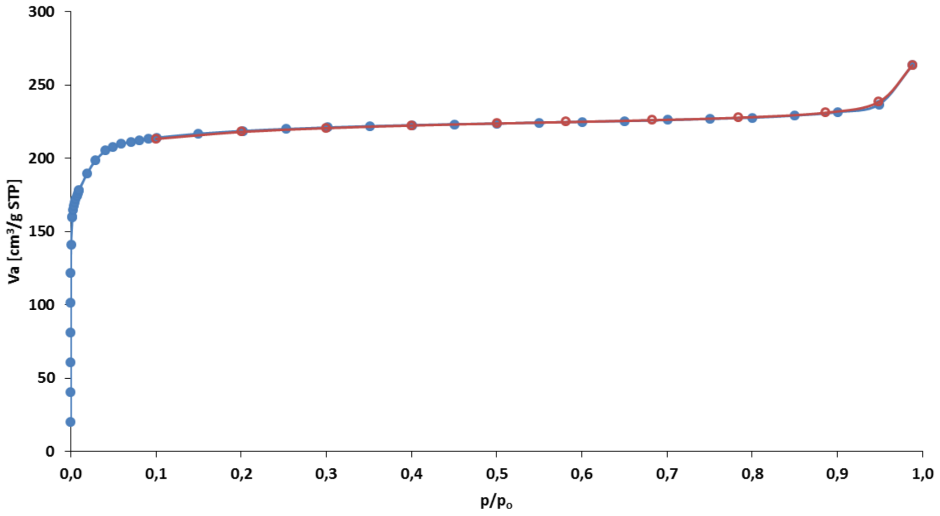
S_{BET}=1077 m^2/g UiO-66-NH_2/NHCHO(70/30)

Figure S28. N_2 adsorption isotherms (77K) of the UiO-66-NH_2/NHCHO(70/30) material, activated at 150°C for 48h (adsorption points denoted by blue and desorption by red circles).



S_{BET}=1029 m^2/g UiO-66-NH$_2$/NHCHO(55/45)

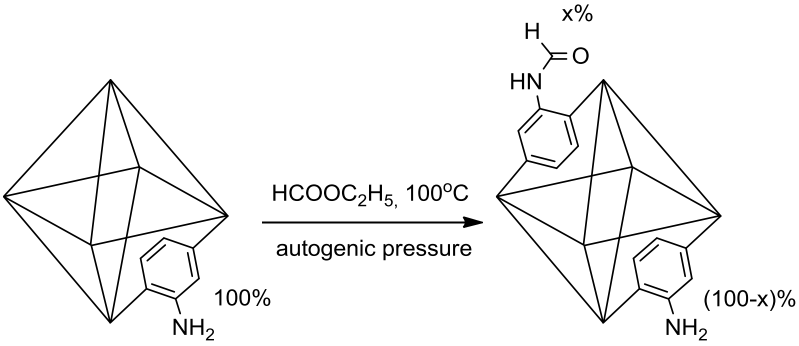
Figure S29. N_2 adsorption isotherms (77K) of the UiO-66-NH$_2$/NHCHO(55/45) material, activated at 150°C for 48h (adsorption points denoted by blue and desorption by red circles).



S_{BET}=880 m^2/g UiO-66-NH$_2$/NHCHO(25/75)

Figure S30. N_2 adsorption isotherms (77K) of the UiO-66-NH$_2$/NHCHO(25/75) material, activated at 150°C for 48h (adsorption points denoted by blue and desorption by red circles).

9. Post-synthetic formylation of UiO-66-NH$_2$ by ethyl formate at 100^{0}C under autogenous pressure



UiO-66-NH$_2$

Five tightly sealed Ace-Glass high-pressure tubes containing pure UiO-66-NH$_2$ (10 mg) and ethyl formate (5 ml) were placed in a preheated oven at 100^{o}C. Tubes were removed from the oven after 1 h, 3 h, 5 h, 7 h and 24 h respectively. After cooling down to RT the solvent was decanted and the solid residue dried under reduced pressure (10^{-3} mbar). All the samples were digested in a DMSO-d_6/HF$_{aq}$ (700:5) mixture and the resulting solutions were analysed by ^{1}H NMR.

Table S4. Formylation of pure UiO-66-NH$_2$ with ethyl formate at 100^{o}C under autogenous pressure

Reaction time	1 h	3 h	5 h	7 h	24 h
%NHCHO	32%	45%	54%	62%	75%

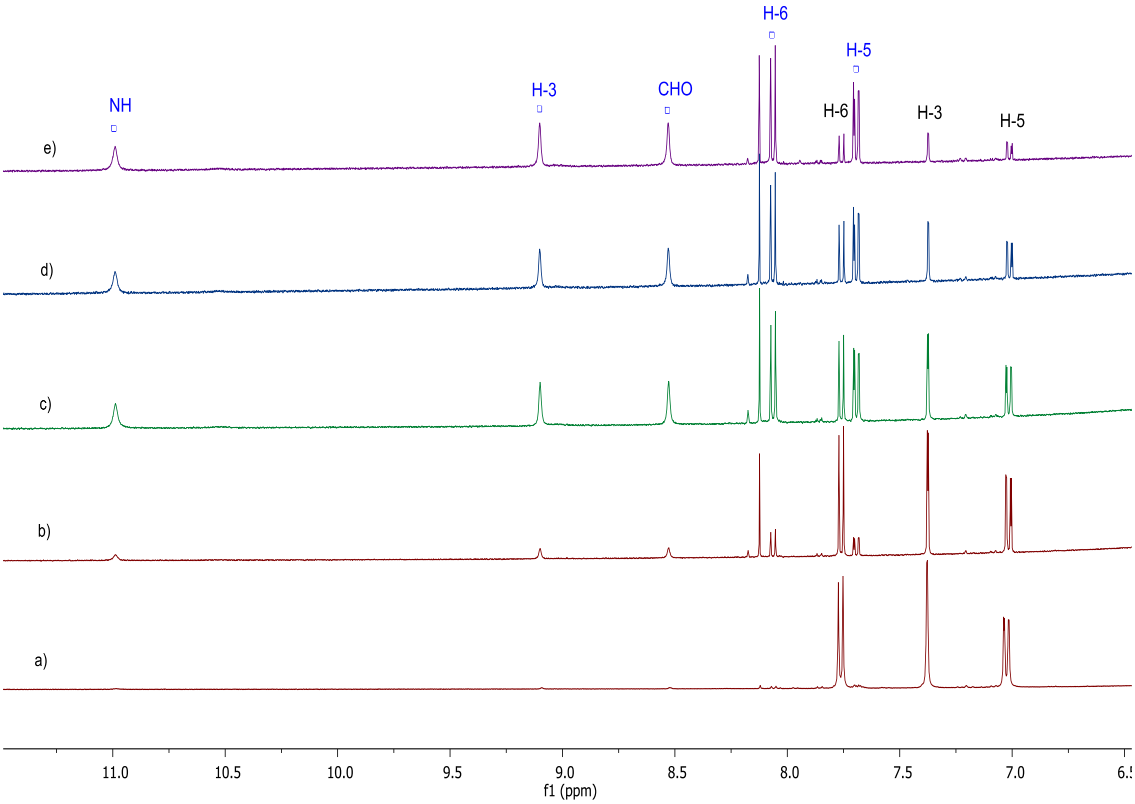
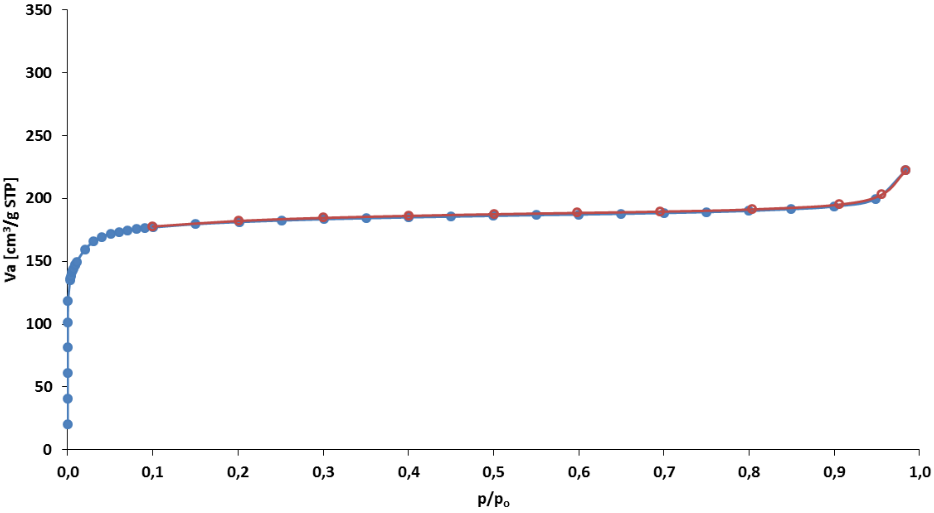


Figure S31. Downfield region of ^{1}H NMR spectra of digested UiO-66-NH$_2$/NHCHO materials obtained after heating UiO-66-NH$_2$ in ethyl formate at 100^{0}C for: a) 0 h, b) 1 h, c) 5 h, d) 7 h and e) 24 h.

Table S5. Formylation of pure UiO-66-NH_2 material with ethyl formate at high temperature under autogenous pressure.

No.	Reaction conditions		% NHCHO	% NH_2	% by-product
1	100°C, 24 h	Ace-Glass high-pressure tubes	80%	20%	-
2	120°C, 24 h		80%	18%	2%
3	120°C, 92 h		87%	9%	4%
4	150°C, 24 h	autoclave	82%	10%	8%



S_{BET}=726 m^2/g UiO-66-NH_2/NHCHO(13/87)

Figure S32. N_2 adsorption isotherms (77K) of the UiO-66-NH_2/NHCHO(13/87) material, activated at 150°C for 48h (adsorption points denoted by blue and desorption by red circles).

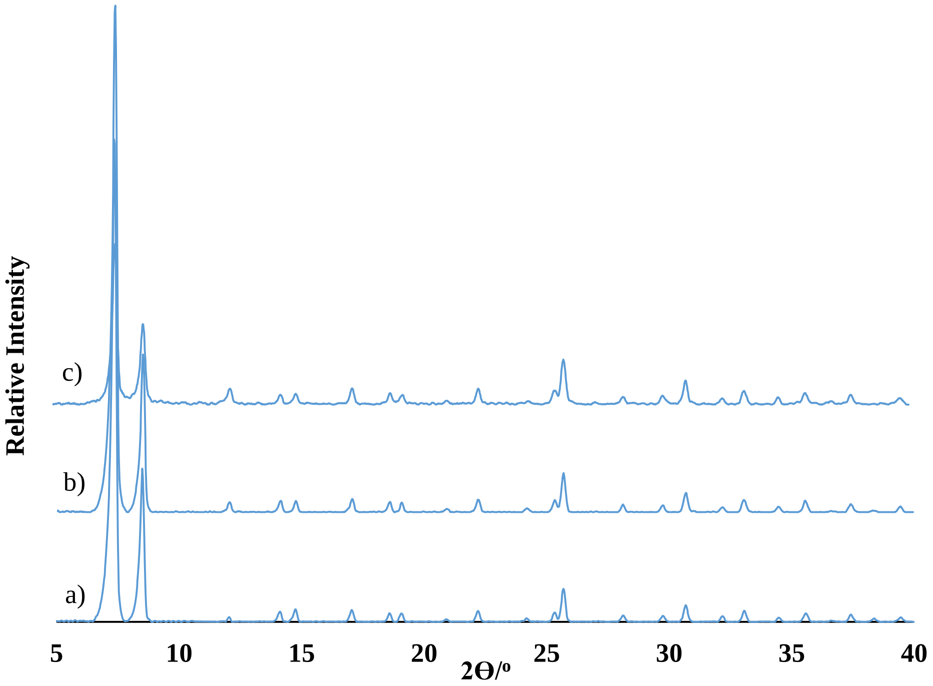


Figure S33. Powder X-ray diffraction patterns (PXRD) for UiO-66-NH_2/NHCHO obtained from pure UiO-66-NH_2 after heating in ethyl formate: a) at 120°C for 24 h, b) at 120°C for 92 h, and c) at 150°C for 24 h.

10. Thermal and chemical stability of UiO-66-NH_2/NHCHO materials

a) Thermal stability:

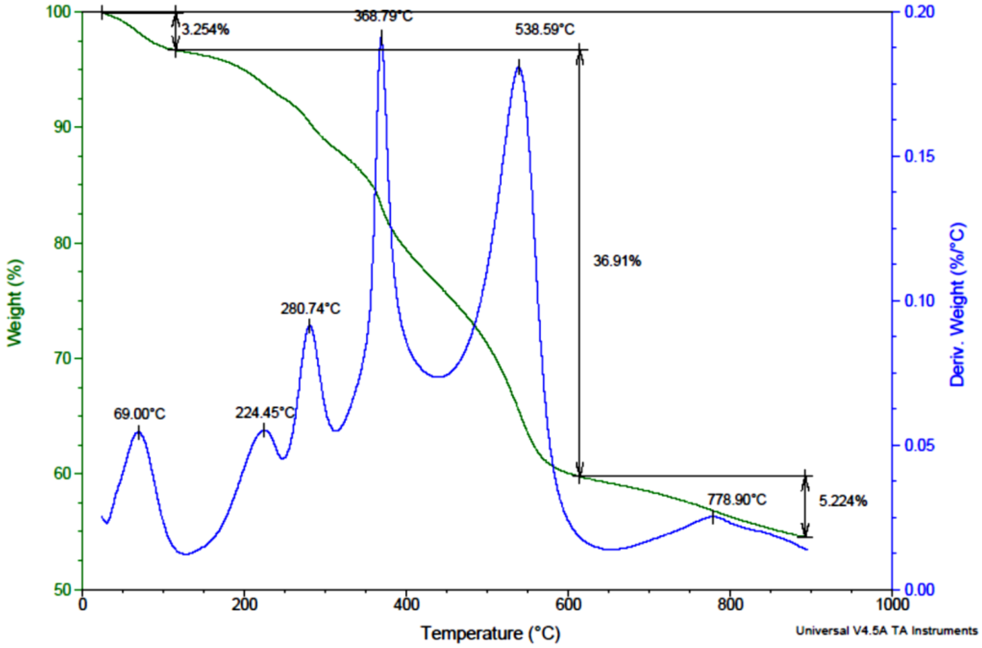


Figure S34. Thermogravimetric analysis (TGA) in a flow of Ar of activated UiO-66-NH_2/NHCHO(40/60) sample.

The TGA profile of UiO-66-NH_2/NHCHO(40/60) is quite complex. The first weight loss of 3.25 % occurs between room temperature and 125 °C and is probably due to the vaporization of physisorbed water. The second weight loss, which occurs between c.a. 150 °C and 300 °C, consists of two interfering processes, which we assume to be the thermal decomposition of the –NHCHO moiety and the dehydroxylation of the inorganic $Zr_6O_4(OH)_4$ clusters. The dehydroxylation of the inorganic clusters has been previously observed in the TGA curves of the parent UiO-66 framework between 250-300 °C.[11] UiO-66-NH_2/NHCHO(40/60) shows also two weight loss processes between c.a. 300 °C and 600 °C, which might be due to decomposition of ligands with loss of interconnection binding similar to the parent UiO-66-NH_2 material.[12]

b) Chemical stability

Chemical resistance of UiO-66-NHCHO/NH2(60/40) towards aqueous hydrochloric acid (1M HCl), bases (1M NaOH, Et_3N) and various polar solvents (water, acetonitrile, acetone) was also investigated. Ca. 20 mg samples of the as-synthesized material was treated with 2 ml of 1 M HCl or 1 M NaOH solution for 2 h at rt, or with 2 ml of Et_3N, water, acetonitrile or acetone for 12 h also at room temperature. After this time the solvents were decanted and solid residues were dried at room temperature under high vacuum for 1 h. Dry materials thus obtained were analyzed by PXRD and ^1H NMR (after digestion).

Treatment of UiO-66-NHCHO/NH2(60/40) with 1 M NaOH (pH = 14) led to the total decomposition of the framework within 5 minutes at room temperature, as is the case also with the parent material UiO-66-NH_2. All other samples maintain their high crystallinity as revealed by their unaltered PXRD patterns. However, the content of NHCHO groups dropped from 60% to ca. 15% after 2h in 1 M HCl, as revealed by ^1H NMR analysis of digested samples. The compositions of samples treated with water, Et_3N, acetone and acetonitrile did not change over 12 h.

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[11] a) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, J. Am. Chem. Soc., 2008, 130, 13850-13851; b) Ch. Larabi, E. A. Quadrelli, Eur. J. Inorg. Chem., 2012, 3014-3022;

[12] H. R. Abid, J. Shang, H.-M. Ang, S. Wang, Int. J. Smart Nano Mat., 2013, 4, 72-82;

Table S6. Results of chemical stability assays performed on UiO-66-NHCHO/NH2(60/40) sample

No	Solvent	Immersion time	% NHCHO group	PXRD
1	Acetone	12 h	60 %	Crystalline
2	Acetonitrile	12 h	60 %	Crystalline
3	Triethylamine	12 h	60 %	Crystalline
4	Water	12 h	60 %	Crystalline
5	1M HCl (pH = 1)	2 h	15 %	Crystalline
6	1 M NaOH (pH = 14)	5 min	NA	Sample decomposition

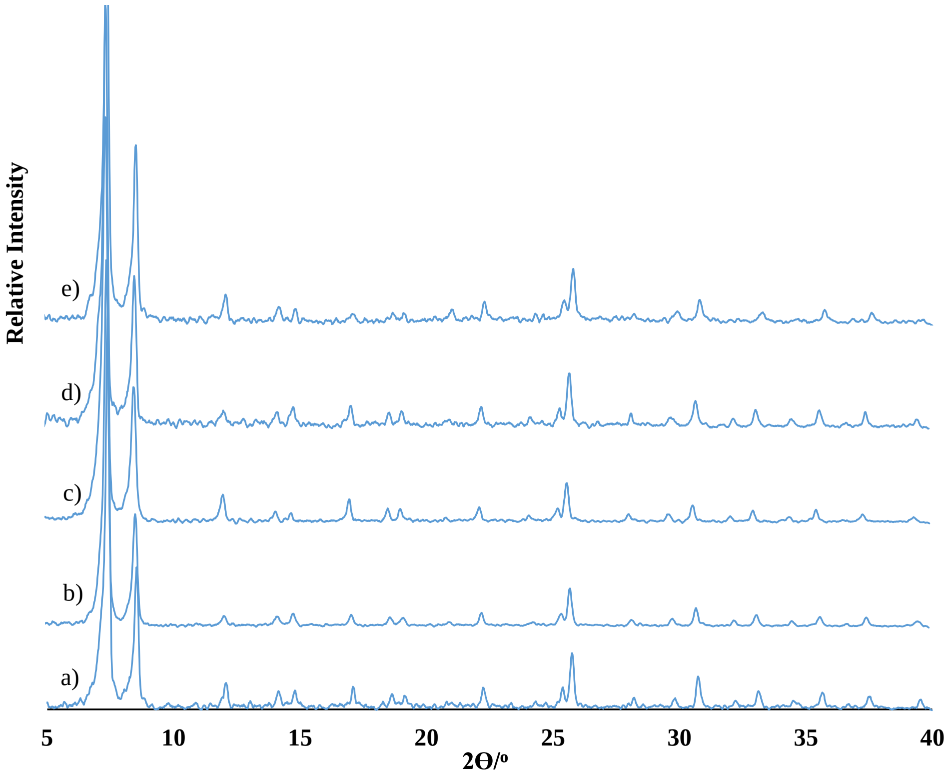
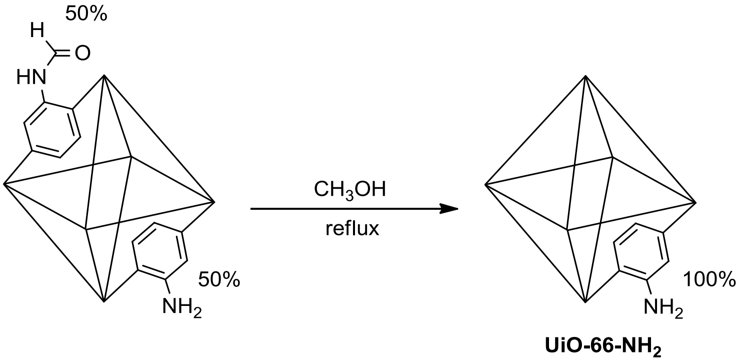


Figure S35. Powder X-ray diffraction patterns (PXRD) for UiO-66-NH_2/NHCHO(40/60) sample immersed in: a) acetone, b) acetonitrile, c) triethylamine, d) water and e) 1 M HCl solution.

11. Removal of the NHCHO group (deprotection of the –NH_2 group) from UiO-66-NH_2/NHCHO(50/50)

a) Deprotection of NHCHO groups by refluxing in methanol



A 50 mg sample of mixed UiO-66-NH_2/NHCHO(~50/50) material was refluxed in methanol (20 ml) in a round bottom flask fitted with reflux condenser connected to a check-valve bubbler. During the reaction samples were collected after 1, 7, 24, 48 and 72 h. Each sample was filtered and washed with methanol (2 ml). After drying under reduced pressure the samples were digested in DMSO-d_6/HF_{aq} (700:10) mixture and the resulting solutions were analysed by ^1H NMR to establish the actual degree of amine group conversion.

Table S7. Deprotection of UiO-66-NH_2/NHCHO(~50%) material by refluxing in methanol

Reaction time	0 h	1 h	3 h	7 h	24 h	48 h	72 h
%NHCHO	50%	40%	37%	33%	20%	12%	8%

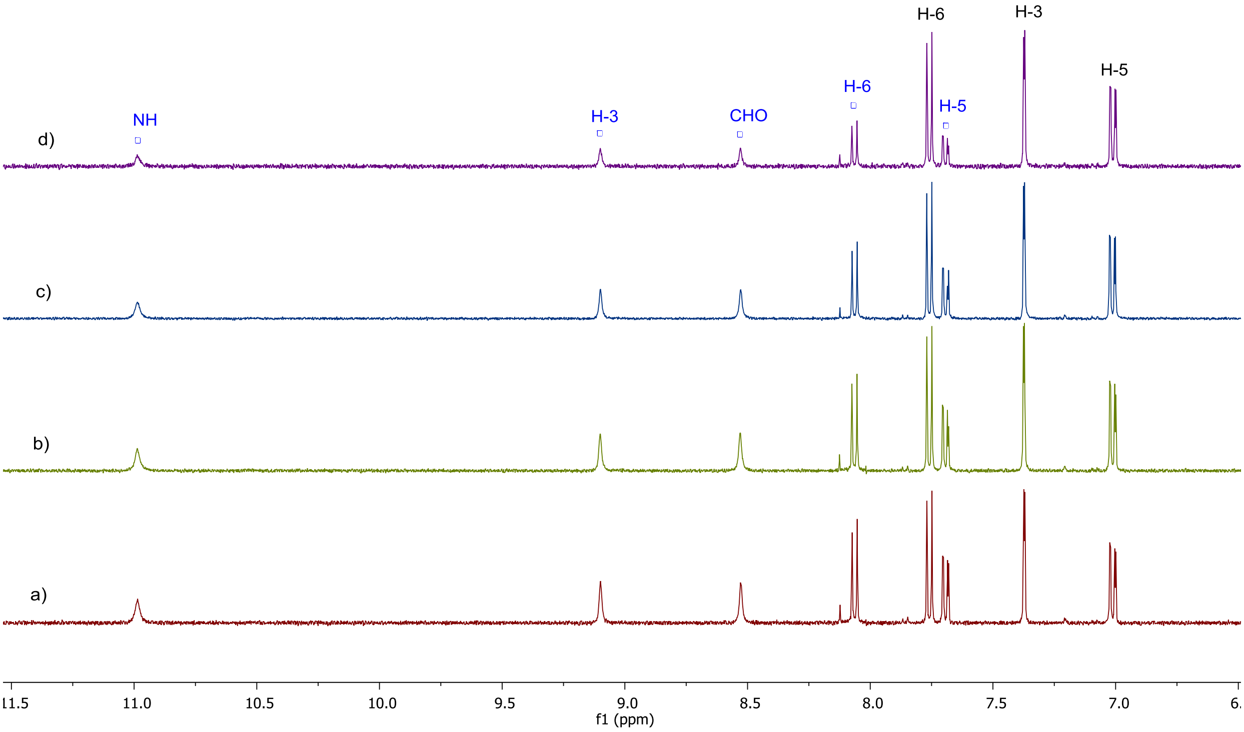
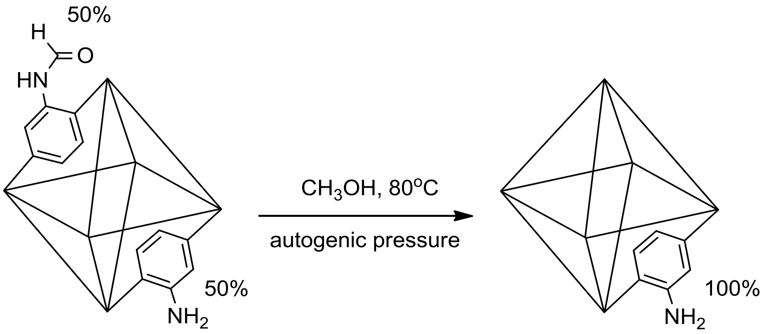


Figure S36. Downfield region of ^1H NMR spectra of digested UiO-66-NH_2/NHCHO(50/50) material obtained after refluxing it in methanol for: a) 1 h, b) 3 h, c) 7 h and d) 24 h.

b) Deprotection of NHCHO groups by heating in methanol under autogenous pressure



UiO-66-NH$_2$

A sample of mixed UiO-66-NH$_2$/NHCHO(~50/50) (65 mg) material was suspended in methanol (10 ml) in an Ace-Glass high-pressure tube. The reaction vessel was tightly sealed and placed in a preheated oven at 80°c for 24 hours. A sample from the reaction mixture was taken after 4 h, 24 h and 48 h. After cooling the high-pressure tube to RT the solvent was decanted, fresh portion of methanol (10ml) was added and the procedure was repeated. Finally, microcrystalline material was filtered off and dried in air in a preheated oven at 120°C for 24h. After further drying under reduced pressure all the samples were digested in a DMSO-d$_6$/HF$_{aq}$ (700:10) mixture and the resulting solutions were analysed by ^{1}H NMR.

Table S8. Deprotection of UiO-66-NH$_2$/NHCHO(~50/50) material in methanol at 80^{0}C under autogenous pressure

Reaction time	0 h	4 h	24 h	48 h
%NHCHO	50%	29%	7%	0%

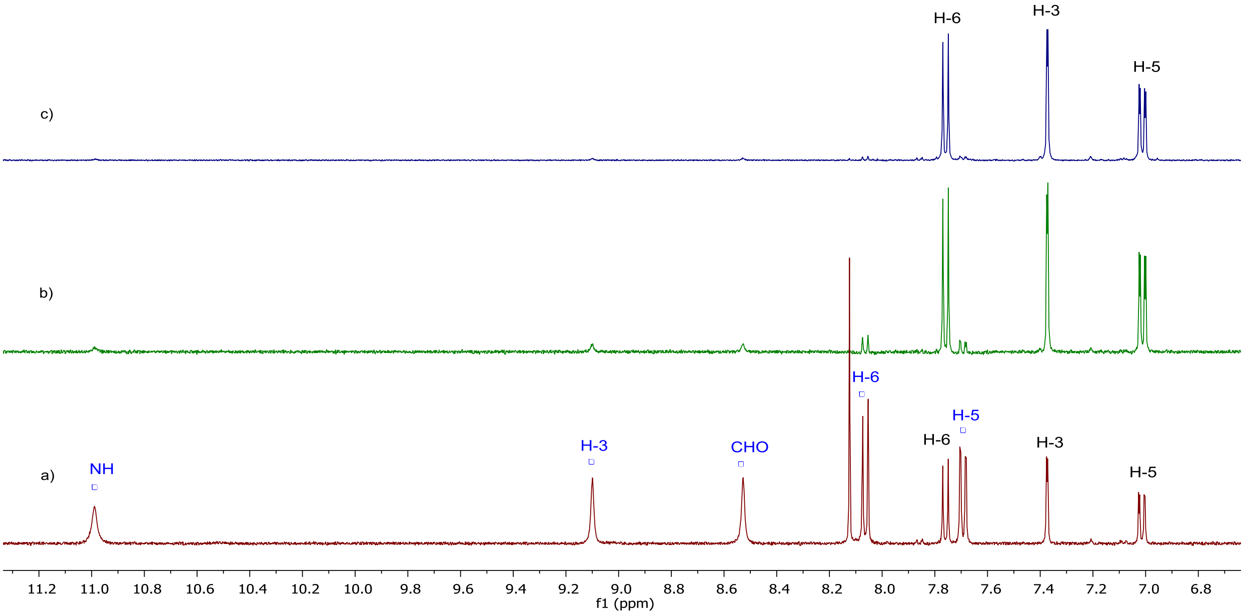


Figure S37. Downfield region of ^{1}H NMR spectra of digested UiO-66-NH$_2$/NHCHO(50/50) samples obtained after heating in methanol at 80 ^{0}C under autogenous pressure for: a) 4 h, b) 24 h and c) 48 h.

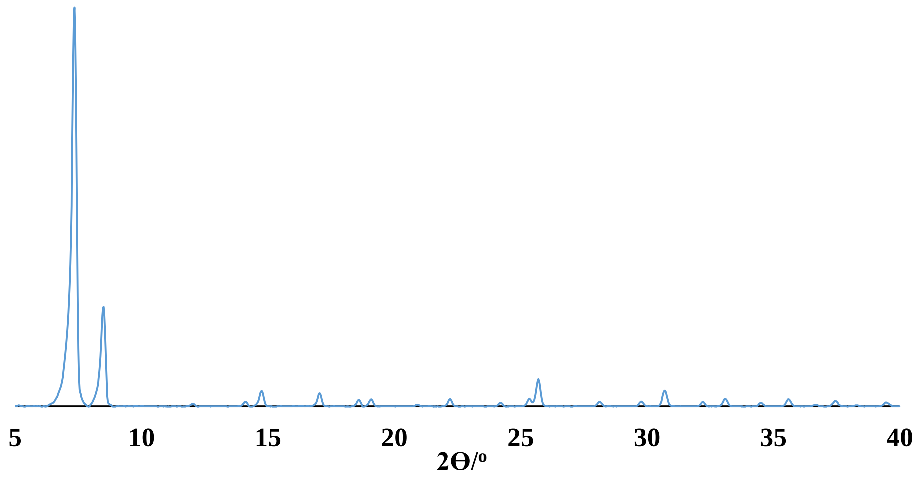
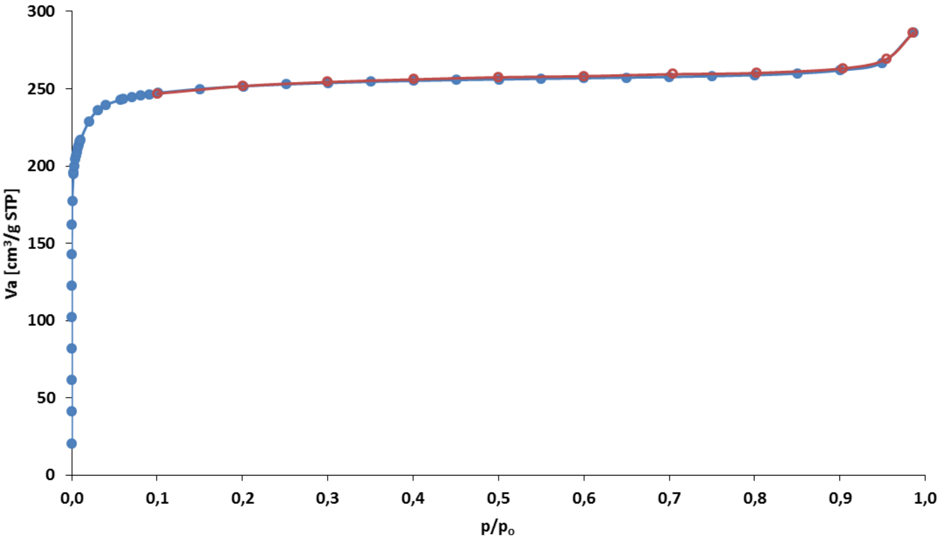


Figure S38. Powder X-ray diffraction patterns (PXRD) for pure UiO-66-NH_2 obtained after heating in methanol at 80°C under autogenous pressure.



S_{BET}=1020 m^2/g

Figure S39. N_2 adsorption isotherms (77K) of the pure UiO-66-NH_2(100%) material obtained from UiO-66-NH_2/NHCHO(~50/50) by deprotection under autogenous pressure, and activated at 150°C for 48 h (adsorption points denoted by blue and desorption by red circles).

c) Mixed deprotection strategy:

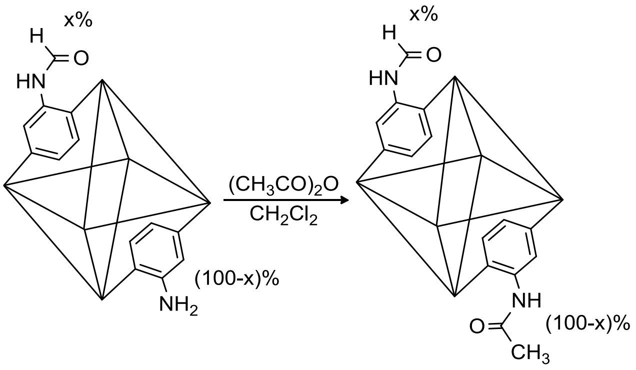
A sample of 100 mg of the mixed UiO-66-NH_2/NHCHO(~50/50) material was suspended in an appropriate solvent or a mixture of solvents and placed in a scintillation vial or high-pressure tube (Ace glass). The reaction vessels were tightly sealed and placed in a preheated oven for 24 hours. After cooling the reaction mixtures to room temperature the solid materials were filtered off, washed twice with methanol (2 x 5 ml) and air dried. After further drying under reduced pressure all the samples were digested in a DMSO-d_6/HF_{aq} (700:10) mixture and the resulting solutions were analysed by ^1H NMR experiments.

Table S9. Deprotection of UiO-66-NH_2/NHCHO(~50/50) material under various conditions

No.	material	Deprotection conditions		%NHCHO (from ^1H NMR)
		solvents	temperature	
1	100 mg	CH_3OH (5 ml)	80°C high-pressure tube	9%
2	100 mg	CH_3OH : H_2O (5 ml, v:v 4:1)	80°C high-pressure tube	22%
3	100 mg	DMF : H_2O (5 ml, v:v 4:1)	120°C sealed vial	22%

To remove the remaining *ca*. 9-22% of NHCHO groups, the material may be additionally extracted with hot methanol in a Soxhlet apparatus for 24 hours (see experiments for deprotecting NHCHO groups in as-synthesized materials).

12. Synthesis of the UiO-66-NHCOCH3/NHCHO hybrid material



200 mg of microcrystalline UiO-66-NH$_2$/NHCHO (50/50) material was activated by heating at 120°C overnight under high vacuum (10^{-2} mbar) prior to the post-synthetic modification.

Freshly activated UiO-66-NH$_2$/NHCHO (50/50) material was transferred to a vial containing a solution of acetic anhydride (102 µl, 1.08 mmol) in dry dichloromethane (2ml). The vial was tightly sealed and placed in an oil bath preheated to 55°C. The suspension was gently stirred on a magnetic stirrer and heated at 55°C for 72 hours. After this time the solvent was decanted and the microcrystalline material was soaked in dry CH$_2$Cl$_2$ (5 ml) for three days, with fresh portion of CH$_2$Cl$_2$ exchanged every 24 h. Prolonged soaking was necessary to completely remove the unreacted acetic anhydride and reduce the content of acetic acid inside microcrystalline structure of the modified material.

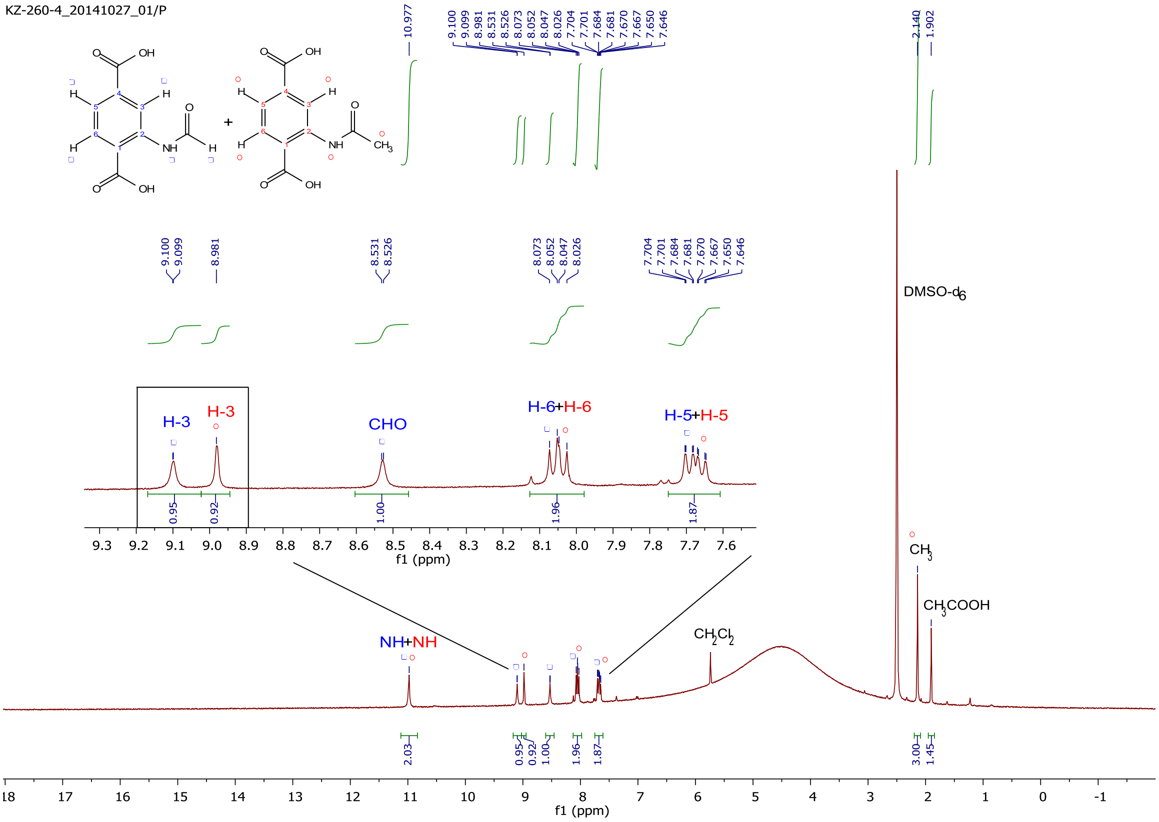


Figure S40. ^{1}H NMR spectrum of a solution obtained by digestion of a UiO-66-NHCHO/NHCOCH$_3$ material in a DMSO-d$_6$/HF$_{aq}$ mixture. Protons numbering scheme shown on the chemical structures.

%NHCHO=[$n_{H\text{-}3}$/($n_{H\text{-}3}$+$n_{H\text{-}3}$)]*100% = [0.95/(0.95 + 0.92)]*100% = 50.8%

NHCHO=(1.03 + 0.95 + 1 + 0.96 + 0.87)/5 = 0.96; CH_3CO=(1+1+1+1+3)/7=1; %NHCHO=0.96/1.96=49%. %CH_3CONH=1/1.96=51%.

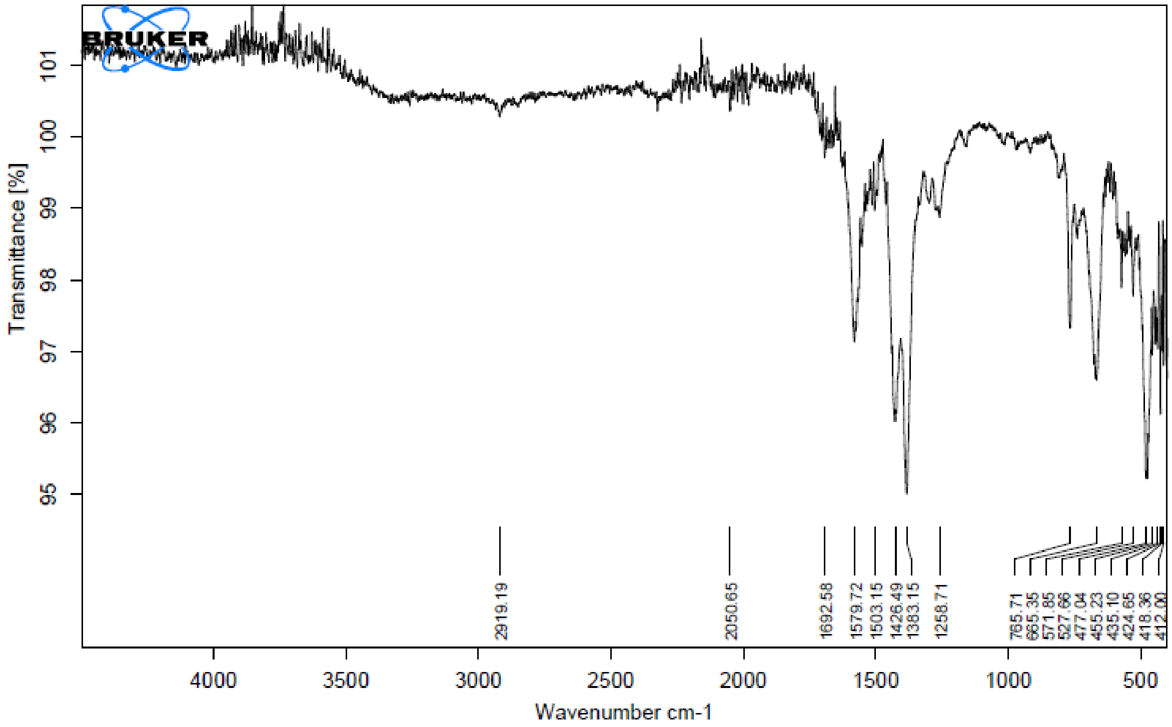


Figure S41. FTIR-ATR spectrum of UiO-66-NHCHO/$NHCOCH_3$(50/50).

The characteristic C-H vibrations of the CH_3 group gave weak band at 2919 cm^{-1}. Additional small peak due to the C=O stretching vibrations of the amide bonds is visible at ca. 1692 cm^{-1}.

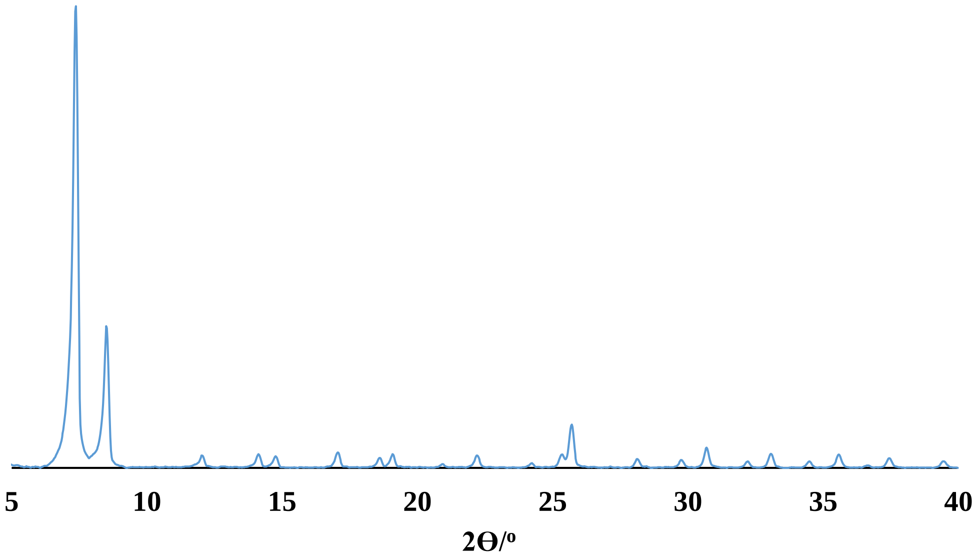
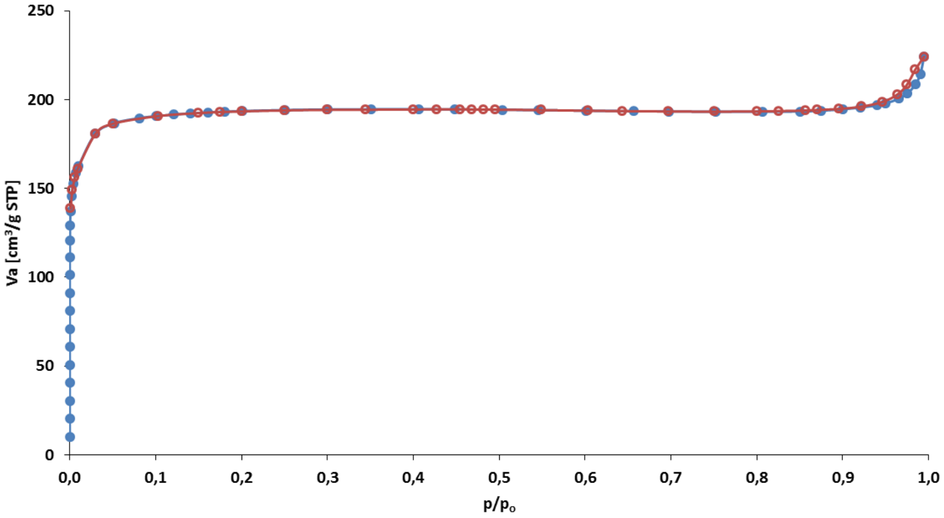


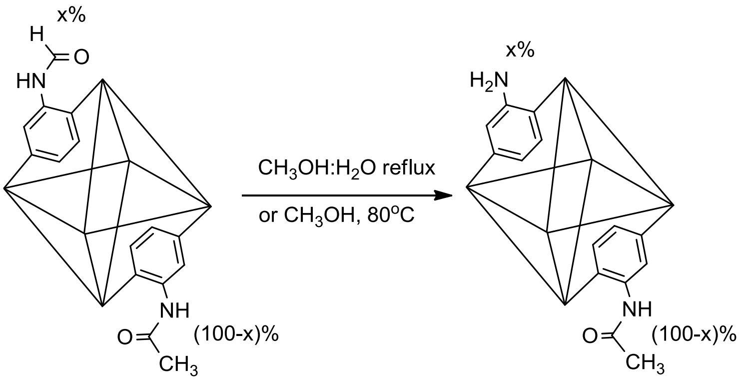
Figure S42. Powder X-ray diffraction patterns (PXRD) of UiO-66-NHCHO/$NHCOCH_3$(50/50).



S_{BET}=787 m^2/g

Figure S43. N_2 adsorption isotherms (77K) of the UiO-66-NHCHO/NHCOCH_3(50/50), activated at 150°C for 48h (adsorption points denoted by blue and desorption by red circles).

13. Removal of the NHCHO group (deprotection of the –NH_2 group) in the UiO-66-$NHCOCH_3$/NHCHO material



a) Deprotection of NHCHO groups using CH_3OH at 80°C under autogenous pressure

A sample of *ca*. 40 mg UiO-66-NHCHO/$NHCOCH_3$(50/50) material was suspended in methanol (10 ml) in an Ace-Glass high-pressure tube. The reaction vessel was tightly sealed and placed in a preheated oven at 80°C for 24 hours. After cooling the Ace-Glass high-pressure tube to room temperature the material was filtered and dried in air. Small sample of the dried material was taken for ^1H NMR analysis, which confirmed partial deprotection. The above procedure was repeated n-times (n=1, 2, 3) with fresh portions of methanol.

Table S10. Deprotection of UiO-66-NHCHO/$NHCOCH_3$(50/50) with CH_3OH at 80°C under autogenous pressure

Reaction time / Material composition	NH_2	NHCHO	CH_3CO
Starting material	0%	50%	50%
24 h	40%	16%	44%
48 h	47%	11%	42%
72 h	60%	3%	37%

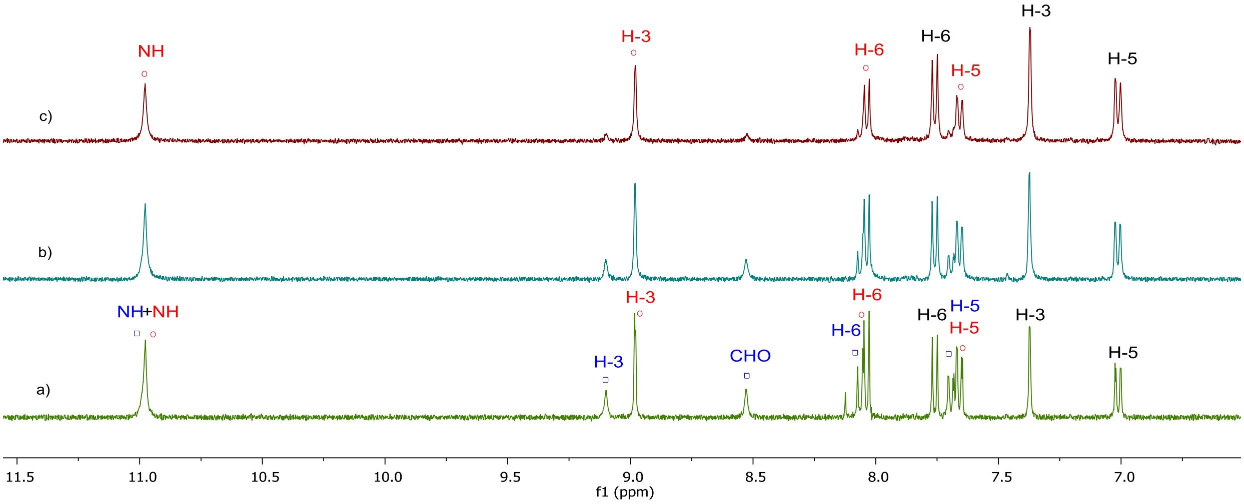
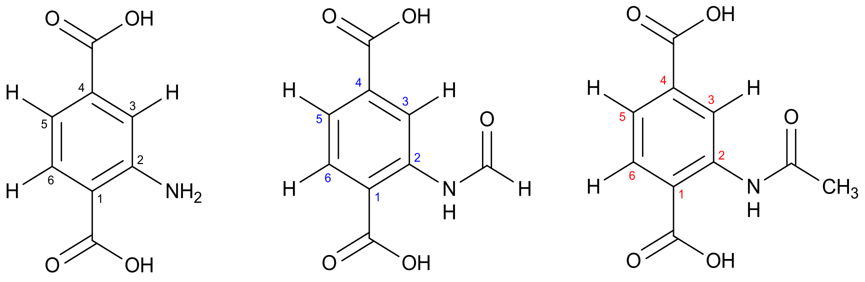


Figure S44. Downfield region of ^1H NMR spectra of digested UiO-66-NHCHO/$NHCOCH_3$ materials obtained after heating in methanol at 80°C for: a) 24 h, b) 48 h and c) 72 h.

Due to partial overlap of signals in the ^{1}H NMR spectra the material composition was determined by integration of signals from protons H-3 of ligands containing -NH$_2$, -NHCHO and NHCOCH$_3$ groups respectively.



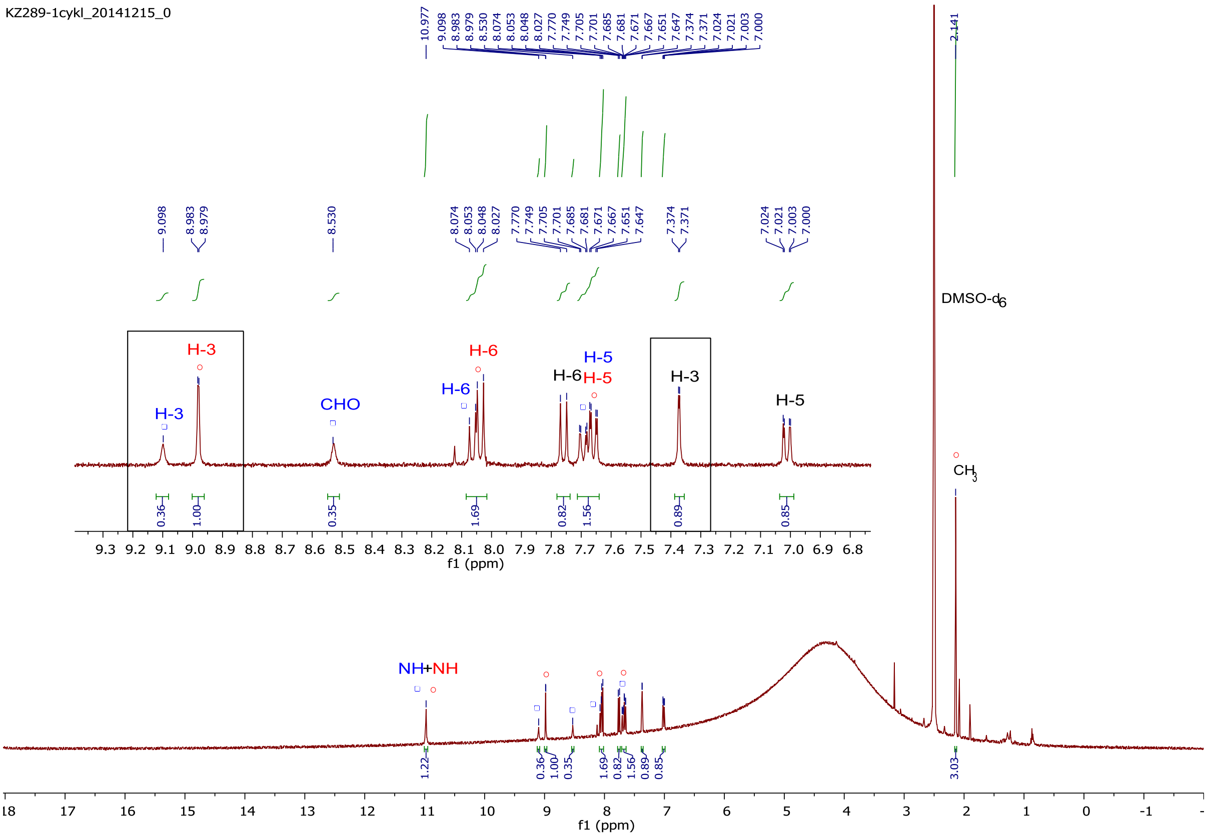


Figure S45. ^{1}H NMR spectrum of a solution obtained by digestion of UiO-66-NH$_2$/NHCHO/NHCOCH$_3$ material in DMSO-d$_6$/HF$_{aq}$ mixture. Protons numbering scheme shown on the chemical structures above.

Signal integrations: n_{H-3}=0.36, n_{H-3}=0.89, n_{H-3}=1.00

%NHCHO= $[n_{H-3}/(n_{H-3} + n_{H-3} + n_{H-3})]*100\% = [0.36/(0.36 + 1.00 + 0.89)]*100\% = (0.36/2.25)*100\% = 16\%$

%CH$_3$CONH= $[n_{H-3b}/(n_{H-3} + n_{H-3} + n_{H-3})]*100\% = [1.00/(0.36 + 1.00 + 0.89)]*100\% = (1.00/2.25)*100\% = 44.4\%$

%NH$_2$= $[n_{H-3}/(n_{H-3} + n_{H-3} + n_{H-3})]*100\% = [0.89/(0.36 + 1.00 + 0.89)]*100\% = (0.89/2.25)*100\% = 39.5\%$

b) Deprotection of NHCHO groups using CH_3OH/H_2O mixture

A sample of mixed UiO-66-NHCHO/$NHCOCH_3$(50/50) material (100 mg) was suspended in methanol (10 ml) containing 50 µl of distilled water and kept at 55°C in a tightly capped vial for 12h. Only minor change in the composition of the starting material was detected by ^1H NMR analysis of digested sample (see Fig. S36a).

A sample of mixed UiO-66-NHCHO/$NHCOCH_3$(50/50) material (100 mg) was suspended in a mixture of methanol and water (v:v 4:1, 10 ml) and refluxed for 72 h. During the reaction samples were collected after 24, 48 and 72 h, The samples were digested and analysed by ^1H NMR to monitor changes in the composition of the material.

Table S11. Deprotection of UiO-66-NHCHO/$NHCOCH_3$(50/50) material under reflux in the CH_3OH/H_2O (4:1 v/v) mixture.

Reaction time / Material composition	NH_2	NHCHO	CH_3CO
Starting material	0%	50%	50%
24 h reflux	35%	20%	45%
48 h reflux	45%	13%	43%
72 h reflux	53%	5%	41%

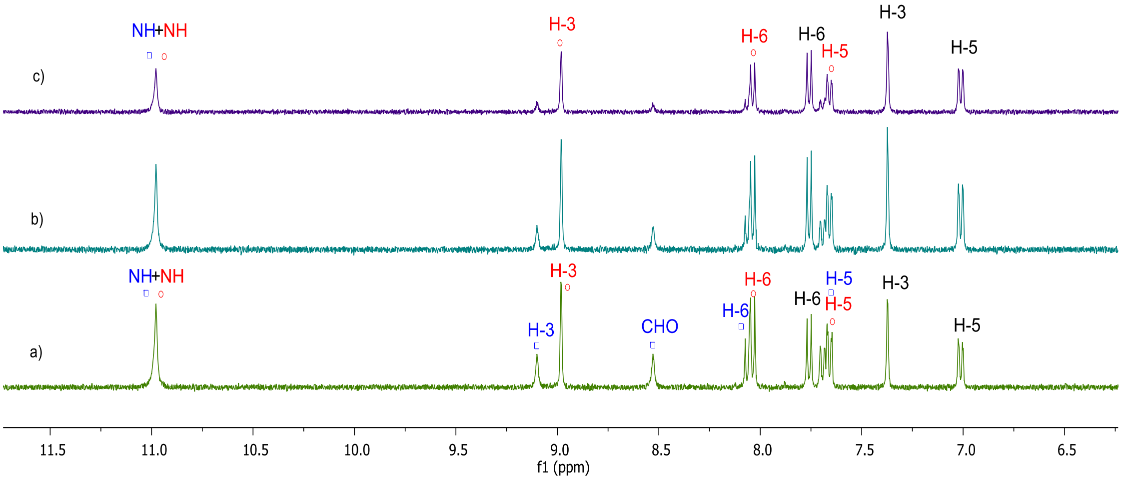


Figure S46. Downfield region of ^1H NMR spectra of digested materials obtained by refluxing UiO-66-NHCHO/$NHCOCH_3$(50/50) in a methanol-water (4:1 v/v) mixture for: a) 24 h, b) 48 h and c) 72 h.

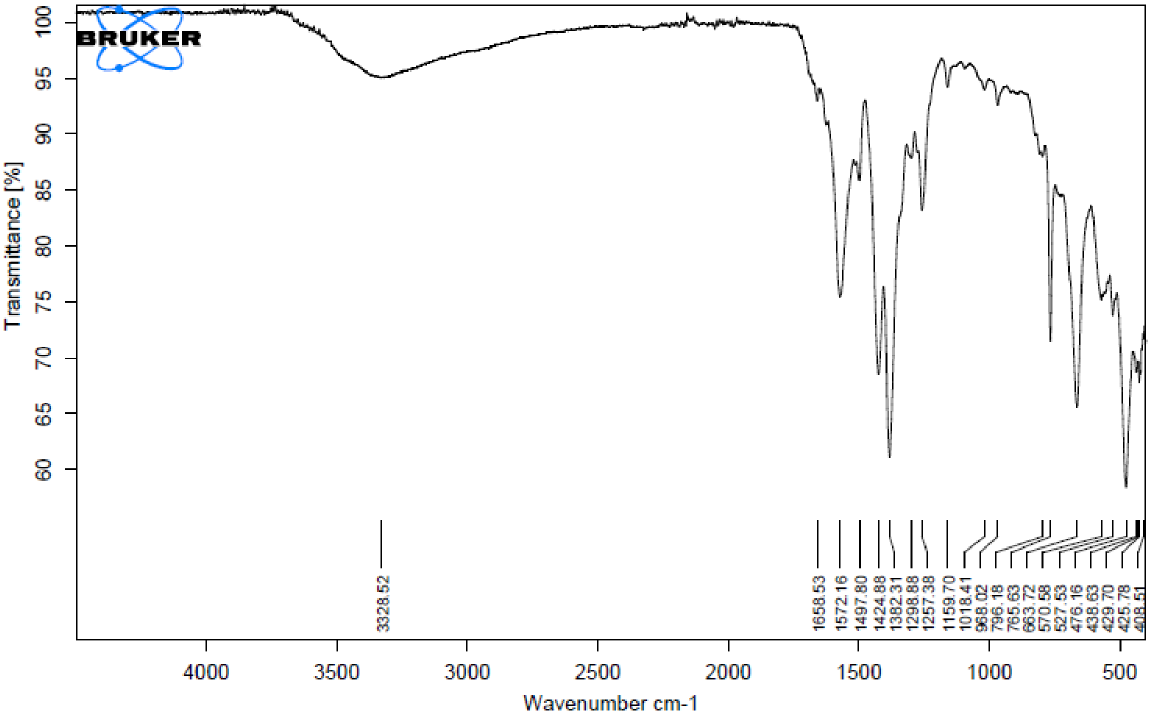


Figure S47. FTIR-ATR spectrum of UiO-66-NH_2/NHCHO/$NHCOCH_3$(53/5/41).

The amine groups NH_2 vibrations were overshadowed by one large band centered at 3328 cm^{-1}, which is probably due to the presence of small amount of water molecules inside the pores.

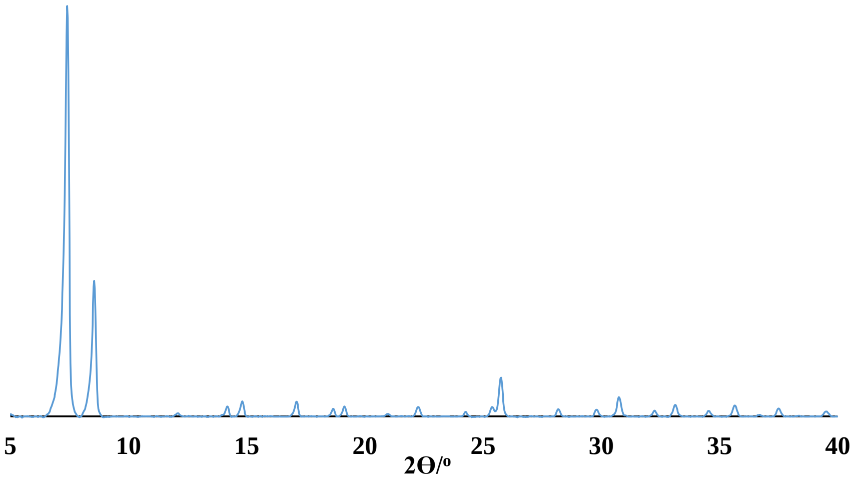
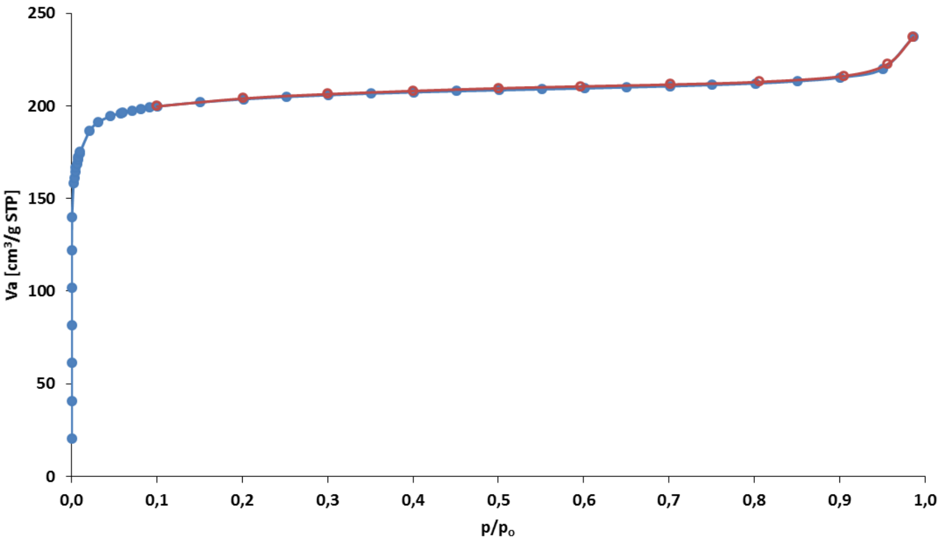


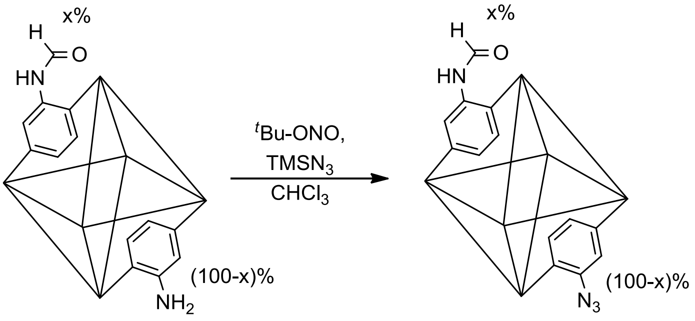
Figure S48. Powder X-ray diffraction patterns (PXRD) for UiO-66-NH_2/NHCHO/$NHCOCH_3$(53/5/41).



S_{BET}=824 m^2/g

Figure S49. N_2 adsorption isotherms (77K) of the UiO-66-NH_2/NHCHO/$NHCOCH_3$(53/5/41) activated at 150°C for 48 h (adsorption points denoted by blue and desorption by red circles).

14. Synthesis of UiO-66-N_3/NHCHO hybrid material



Microcrystalline UiO-66-NH_2/NHCHO(40/60) material (200 mg) was activated by heating at 120°C overnight under high vacuum (10^{-2}mbar) prior to the post-synthetic modification.

Freshly activated UiO-66-NH_2/NHCHO(40/60) material (200 mg) was transferred to a dry vial containing 2 ml of dry chloroform. Vial was cooled in an ice bath and tert-butyl nitrite (347.5 µl, 2.95 mmole, 10 eqv.) was added in one portion. Then trimethylsilyl azide (340 µl, 2.55 mmole, 8.8 eqv.) was added dropwise over 5 minutes. The vial was connected to a check-valve bubbler and left at room temperature for 24 hours. Finally, the solvent was decanted from the microcrystalline material and the residue soaked in dry $CHCl_3$ for three days, with fresh portion of 5ml $CHCl_3$ exchanged every 24h. Finally, the material was filtered off on a Schott funnel and dried at 70°C for 1h in air.

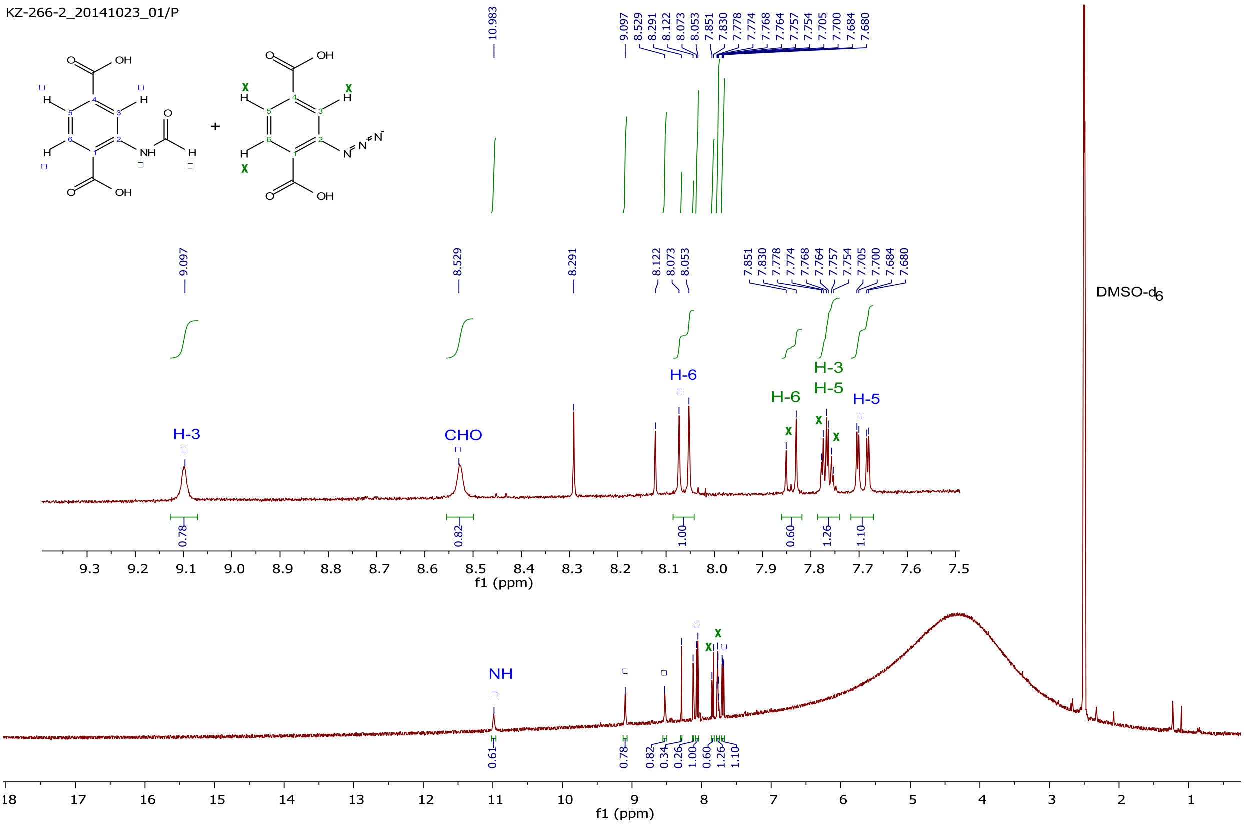


Figure S50. ^1H NMR spectrum of a solution obtained by digestion of a UiO-66-N_3/NHCHO material in a DMSO-d_6/HF_{aq} mixture. Protons numbering scheme shown on the chemical structures above.

$\%N_3 = [n_{H\text{-}6}/(n_{H\text{-}6} + n_{H\text{-}6})]*100\% = (0.6/1.6)*100\% = 37.5\%$

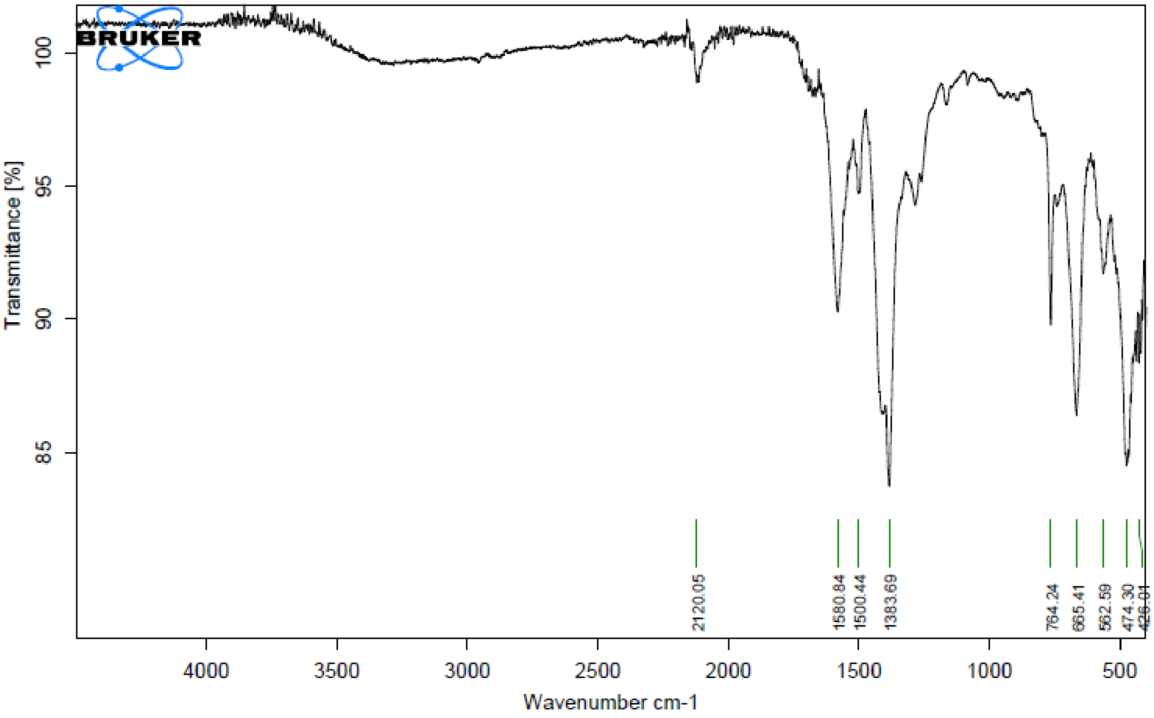


Figure S51. FTIR-ATR spectrum of UiO-66-N_3/NHCHO(40/60).

The characteristic band at 2120 cm^{-1} confirms the presence of azide groups. Additional peak due to the C=O stretching vibrations of the amide bond is clearly visible at 1666 cm^{-1}.

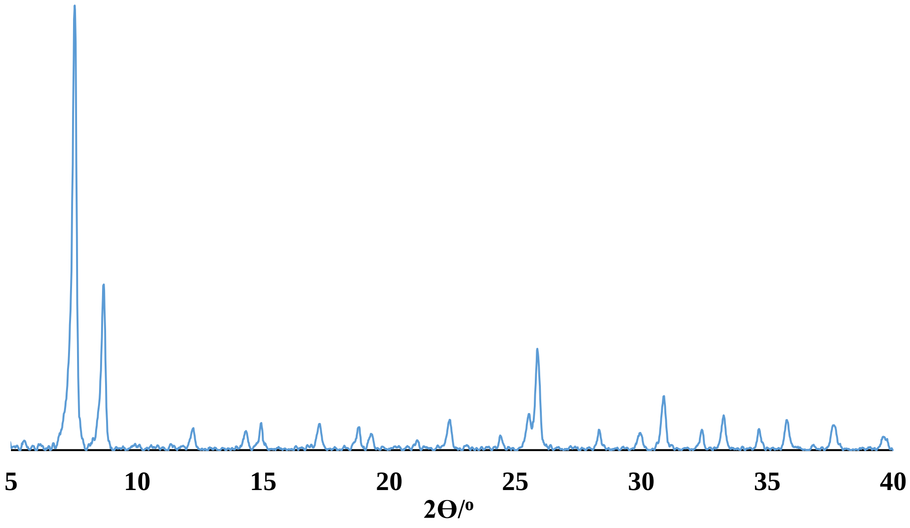
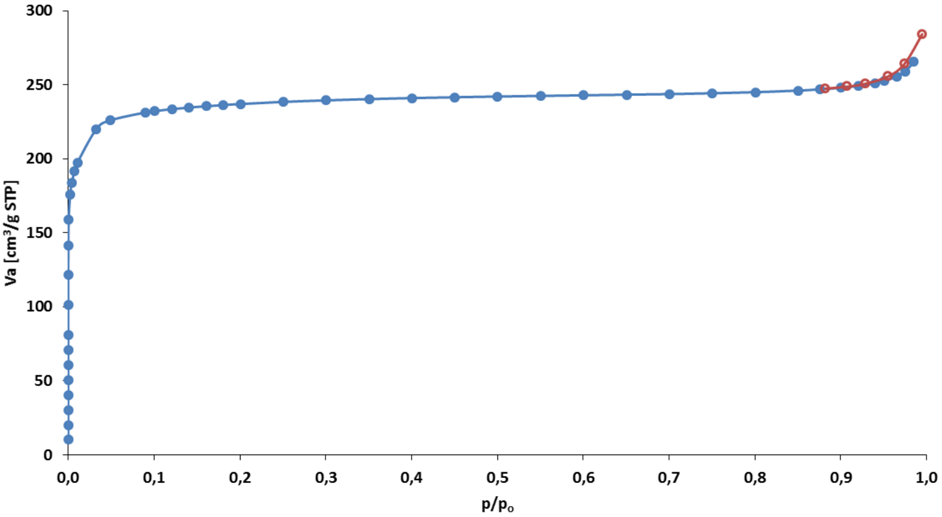


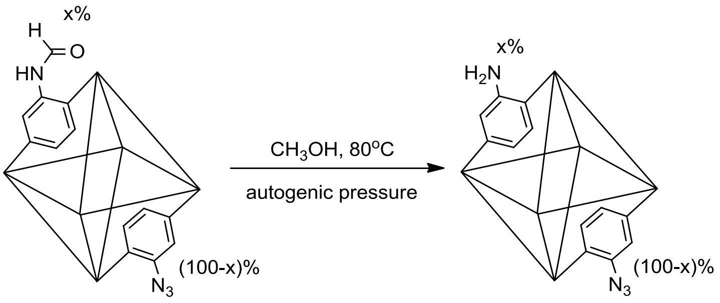
Figure S52. Powder X-ray diffraction patterns (PXRD) for UiO-66-N_3/NHCHO(40/60).



S_{BET}=953 m^2/g

Figure S53. N_2 adsorption isotherms (77K) of the UiO-66-N_3/NHCHO(40/60) activated at 80^{o}C for 48h (adsorption points denoted by blue and desorption by red circles).

15. Removal of the NHCHO group (deprotection of the –NH_2 group) in an UiO-66-$NHCOCH_3$/NHCHO material



A sample of UiO-66-N_3/NHCHO(40/60) hybrid material (*ca*. 30 mg) was suspended in methanol (10 ml) in an Ace-Glass high-pressure tube. The tube was tightly sealed and placed in a preheated oven at 80°C for 24 hours. After cooling the reaction vessel to room temperature the material was filtered off and dried in air. Small sample for the ^{1}H NMR analysis was taken and digested in the DMSO-d_6/HF_{aq} (700:10). ^{1}H NMR spectrum of the digested sample confirmed full deprotection.

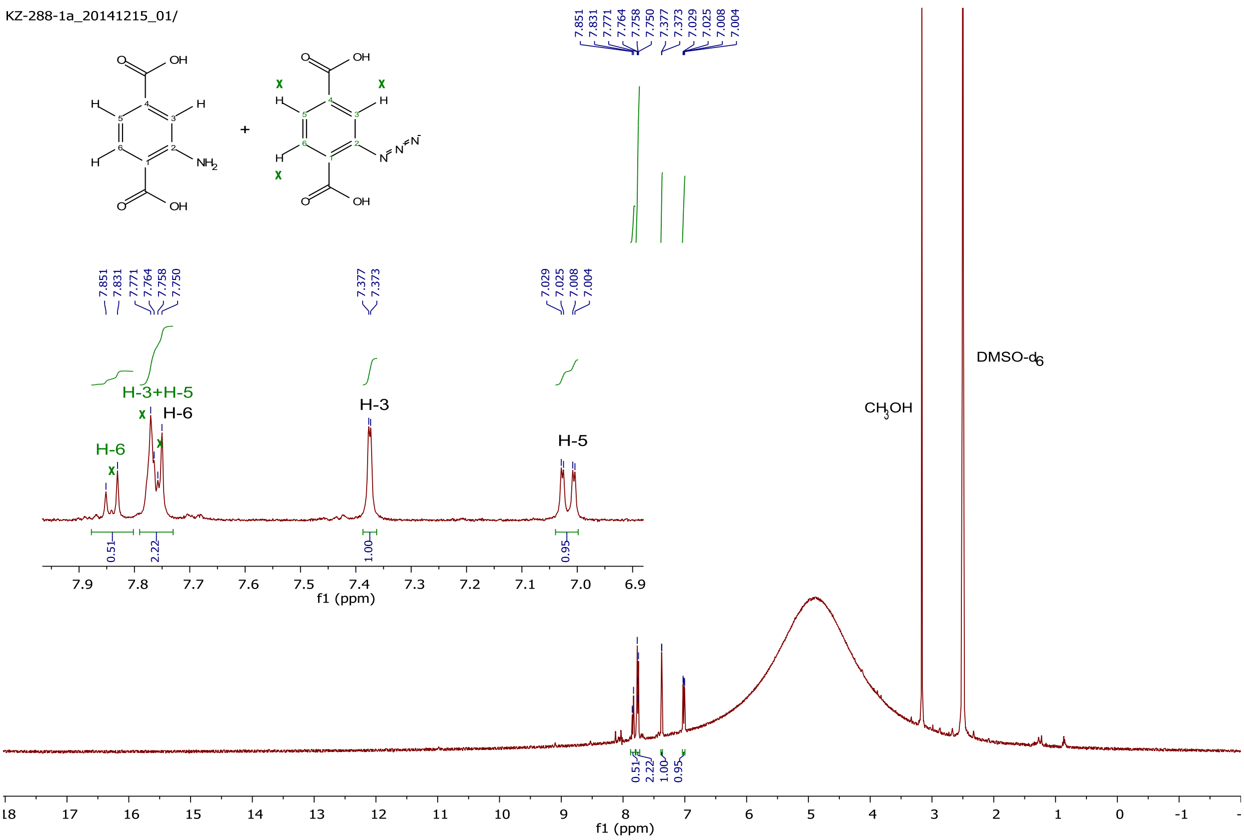


Figure S54. ^{1}H NMR spectrum of a solution obtained by digestion of a UiO-66-N_3/NH_2(40/60) material in a DMSO-d_6/HF_{aq} mixture. Protons numbering scheme shown on the chemical structures above.

Signals are partially overlapped, so the content of azide groups (%N_3) could only be estimated.

n_{N3}=(0.51 + 1.22)/3 = 1.73/3 = 0.58, n_{NH2}=(1.00 + 1.00 + 0.95)/3 = 2.95/3 = 0.98;

%N_3= [n_{N3}/(n_{NH2}+n_{N3})]*100% = (0.58/1.56)*100% = 37%

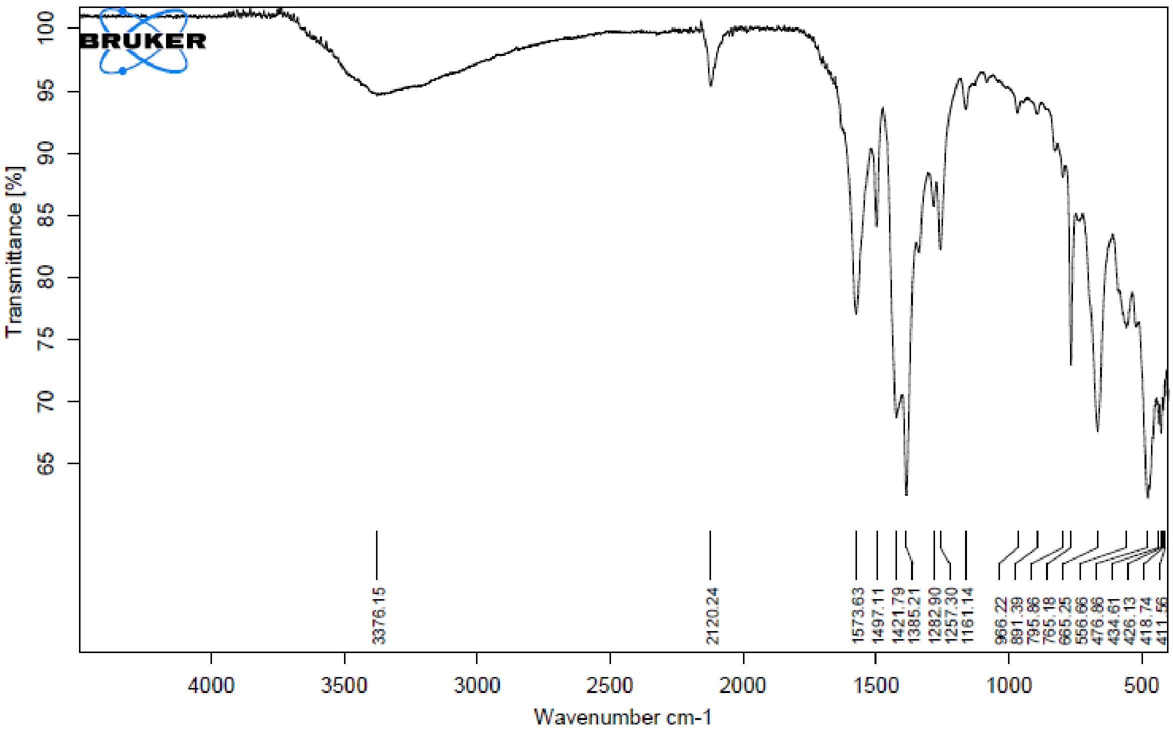


Figure S55. FTIR-ATR spectrum of UiO-66-N_3/NH_2(40/60).

The characteristic azide group vibrations can be seen at 2120 cm^{-1}. The amine group vibrations are overshadowed by one large band centered at 3376 cm^{-1}, which might be due to the presence of small amount of water molecules inside the pores. No peaks at 1666 cm^{-1} can be observed, what confirms complete deprotection of the NHCHO groups.

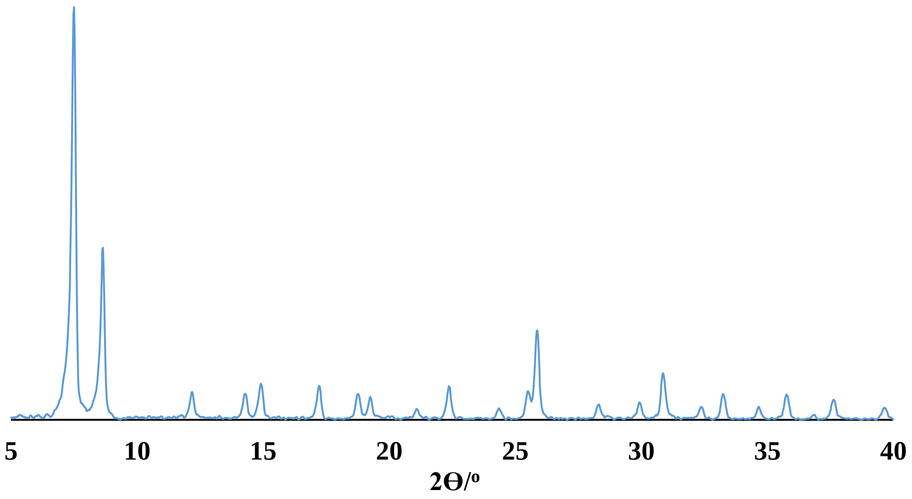
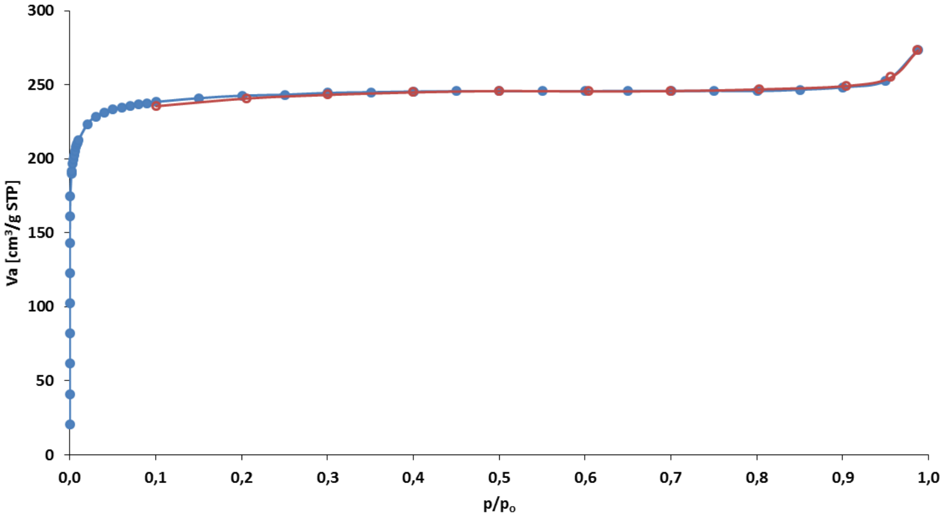


Figure S56. Powder X-ray diffraction patterns (PXRD) for UiO-66-N_3/NH_2(40/60).



S_{BET}=984 m^2/g

Figure S57. N_2 adsorption isotherms (77K) of UiO-66-N_3/NH_2(40/60), activated at 80°C for 48h (adsorption points denoted by blue and desorption by red circles).