Supplementary Information

„Synthesis of the novel MOF hcp UiO-66 employing ionic liquids as linker precursor "

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1. Chemicals

All chemicals were used without further purification if not noted otherwise. Table S1 summarizes some information about the chemicals used in this communication.

Table S1: Chemicals used for the syntheses of all products in this communication.

	Supplier	Purity / %	CAS-Number
Zirconiumtetrachloride ($ZrCl_4$)	Aldrich Chemistry	≥99.5	10026-11-6
Terephthalic acid (H_2BDC)	Merck KGaA	≥98	100-21-0
Biphenyldicarboxylic acid (BPDCA)	MOLEKULA	98.6	787-70-2
Acetic acid (AA)	VWR Chemicals	99.9	64-18-6
Benzoic acid (BA)	VWR Chemicals	-	65-85-0
Formic acid (FA)	Fluka Analytical	≥98	64-18-6
N,N-Dimethylformamid for synthesis (DMF)	VWR Chemicals	≥99.8	68-12-2
N,N-Dimethylformamid technical (DMF)	VWR Chemicals	≥98	68-12-2
Acetonitrile	Carl Roth	>99.9	75-05-8
Dimethyl carbonate	Carl Roth	>99.8	616-56-1
Methanol	Carl-Roth	>99.9	67-56-1
Ethylimidazolium*	Solvent Innovation	98	1072-62-4
Terephthalic acid for IL synthesis	Alfa Aesar	>98	100-21-0
Tributylphophine	Sigma	97	998-40-3
Chloromethyl ethyl ether	Sigma	95	3188-13-4
Amberlite IRN-78	Alfa Aesar	-	3188-13-4

* Ethylimidazolium was distilled twice over KOH and stored under Argon before usage.

2. Synthesis and analysis

2.1. Synthesis of di-(tributyl- ethoxymethylphosphonium) terephthalate ([PBuMEE]$_2$[BDC])

Under an inert gas atmosphere, tributylphosphine (97 %, 25.00 g, 123.6 mmol) was dissolved in 100 mL of acetonitrile. Chloromethyl ethylether (95 %, 12.27 g, 129.7 mmol), dissolved in 50 mL of acetonitrile, was added slowly, using common Schlenk techniques. Upon addition, the reaction mixture was stirred for 72 h under reflux. The solvent was removed under reduced pressure and the obtained crude chloride IL was washed three times with 50 mL of diethyl ether. For further purification, the ionic liquid was dried *in vacuo* at 60 °C for three days and its purity was confirmed *via* ^{1}H, ^{13}C and ^{31}P-NMR spectroscopy (33.01 g, 111.2, mmol, 90 %). In a second step, an aqueous solution of [PBu$_3$MEE]Cl (0,5 M) was treated with an Amberlite IRN-78 anion exchange resign, to give a solution of [PBu$_3$MEE]OH (1 l, 0,069 M), which was subsequently neutralized with 0.5 eq. of terephthalic acid. H_2O was removed under reduced pressure and the remaining IL was further dried *in vacuo* at 60 °C for 72 h. The product was obtained as a highly viscuous, colorless liquid (26,35 g, 38,4 mmol, 69 %).

2.2. Synthesis of 1-ethyl-3-methylimidaziolium terephthalate ([EMIM]$_x$[BDC])

A 100 mL Ace pressure tube was charged with 1-ethylimidazole (9.613 g, 100 mmol), dimethylcarbonate (36.03 g, 400 mmol) and 25 mL of methanol. The tube was sealed and the reaction mixture was stirred at 120 °C for 24 h in an oil bath. The mixture was cooled to room temperature and slowly added to the respective amount of tetrephthalic acid in a 100 mL three necked flask. Strong foaming and gas evolution was observed. After stirring at room temperature over night, excess MeOH and dimethylcarbonate were removed under reduced pressure. The white [EMIM]$_x$bdc salts were collected, dried *in vacuo* and storred under argon. ($Y_{[EMIM]bdc}$ = 27.46 g, >99 %; $Y_{[EMIM]2bdc}$ =19.231 g, >99 %)

2.3. Details for the synthesis of **hcp** UiO-66

In a typical synthesis, 20 ml of water was submitted in a 100 ml screw-cap bottle and subsequently 0.28 g of $ZrCl_4$ was dissolved in the water. Afterwards a modulator (benzoic acid, acetic acid or formic acid) and a linker source were added. The total amount of modulator and linker source varied, however, the molar ration of metallic salt:linker:modulator:water was fixed to 1:0,6:87:926 in each synthesis. The sealed screw-cap bottle was placed in a preheated convection oven at 100 °C for 72 h. After the reaction time was expired, the sample was cooled down to room temperature. The resulting white powder was separated from the liquid by centrifugation at 9000 rpm for 5 min. The work-up procedure consisted of two washing steps with water followed by centrifugation. Finally the powder was dried at 100 °C in a convection oven for approximately 24 h. Table S1 summarizes the syntheses reported in this communication. Please note that the samples synthesized with H_2BDC, Na_2BDC and

[EMIM][HBDC] as linker source was additionally extracted in 300 ml DMF and soxhlet-extracted with ethanol for 24 h to remove the remaining DMF in the pores, after the powder diffraction measurements.

Table S2: Overview of the used materials in each synthesis.

	$ZrCl_4$ / g	Linker /g	Modulator / ml	Water / ml
$[PBuMEE^+]_2[BDC^{2-}]$	0.28	0.50	6	20
$[EMIM^+][HBDC^-]$	0.28	0.20	6	20
$[EMIM^+]_2[BDC^{2-}]$	0.28	0.28	6	20
H_2BDC	0.28	0.12	6	20
H_2BDC (BA)	0.28	0.12	12.18 g*	20
H_2BDC (FA)	0.28	0.12	3.96	20

*Benzoic acid was added as a solid material.

2.4. Synthesis of UiO-66

For the synthesis of UiO-66, 0.2 g of $ZrCl_4$ were dissolved with 50 ml of *N,N*-dimethylformamid (DMF) in a 100 ml screw-cap bottle. Subsequently 1.475 ml of acetic acid was added and the screw-cap bottle was sealed. The mixture was treated with ultrasound until a clear mixture was received. Finally 0.1425 g of terephthalic acid was added to the clear solution and the sealed screw-cap bottle was placed in a preheated convection oven at 120 °C for 24 h. After the reaction was terminated the mixture was cooled down to room temperature and the resulted white powder was separated from the liquid by filtration. It followed directly two washing steps first with technical DMF and subsequently with Ethanol. Next the UiO-66 was dried over night at room temperature and was extracted for 24 h with 150 ml of technical DMF to remove unreacted terephthalic acid. Again the powder was separated from the liquid by filtration and finally after a drying step it was soxhlet-extracted with ethanol for 24 h to remove the remaining DMF in the pores.

3. Instruments used for analysis

The nitrogen adsorption isotherms were collected at 77 K on a Micromeritics ASAP 2000 instrument with micropore option used.

The SEM pictures were recorded with a Carl Zeiss ULTRA 55 field emission scanning electron microscope.

For the thermogravimetric analysis a SETSYS Evolution TGA© from SETARAM Instrumentation was used. The samples were heated with 2 K/min in a range from 30 °C to 700 °C and air was used as carrier gas.

The solid state ^{1}H and ^{13}C Magic Angle Spinning (MAS) NMR spectra were recorded on an Agilent DD2 500WB spectrometer at resonance frequencies of 500.13 and 125.758 MHz, respectively. All MAS NMR experiments were carried out with a commercial 1.6 mm triple resonance MAS probe. The chemical shift of ^{13}C are referenced to tetramethylsilane (TMS) at 0 ppm. Saturation combs were applied prior to all repetition delays. All ^{1}H MAS NMR spectra were recorded using single pulse excitation (1D) at a sample spinning frequency of 30 kHz. Typical 90° pulse length for the ^{1}H was 2.2 us and recycle delays of 3.0-5.0 s. ^{13}C{^{1}H} spectra based on ramped cross-polarization (CP) with magic angle spinning (CPMAS) were acquired at a sample spinning frequency of 20 kHz with a recycle delay of 5.0 S and a contact time of 5.0 ms.[1]

Powder X-ray diffraction patterns were collected on a PANalytical EMPYREAN diffractometer in Bragg-Brentano geometry equipped with a pixcel^{3D} line detector. The copper X-ray tube providing CuKα_1 (λ = 1.5406 Å) radiation was operated at 40 kV and 40 mA.

CHNS analysis were performed with an Euro EA 3000 device from Euro Vector.

For the IR measurements, a Jasco FT/IR-4100 device was used equipped with a PIKE GladiATR base.

4. Results

4.1. Powder X-ray diffraction and structure analysis of **hcp** UiO-66

As a starting point for the structure analysis of **hcp** UiO-66(Zr), we assumed the same space group $P6_3/mmc$ (*no*. 194) of the previously reported isoreticular **hcp** UiO-67(Hf).[2] The unit cell parameters (Table S3) were determined by a Pawley-fit (Figure S1) within the program X'Pert High Score Plus. Subsequently, the atom positions were determined. Therefore, characteristic coordinates predefined by their Wyckoff position within the isoreticular **hcp** UiO-67 structure (e.g. *4f* for H4, O4, O7; *12j* for H6, O8) were kept constant as well as the atomic distances within the SBU ($Zr_{12}O_8(OH)_{14}$). The terephthalate atom positions were calculated to fulfill the symmetry requirements.

Table S3: Crystal structure data of **hcp**-UiO-66.

Compound name	**hcp**-UiO-66
Formula	$Zr_6O_{29}C_{36}H_{25}$
Molar weight / g mol^{-1}	1468.91
Space group	$P6_3/mmc$
Crystal system	hexagonal
a / Å	14.7130(9)
c / Å	36.9794(9)
V / Å^3	6932.65

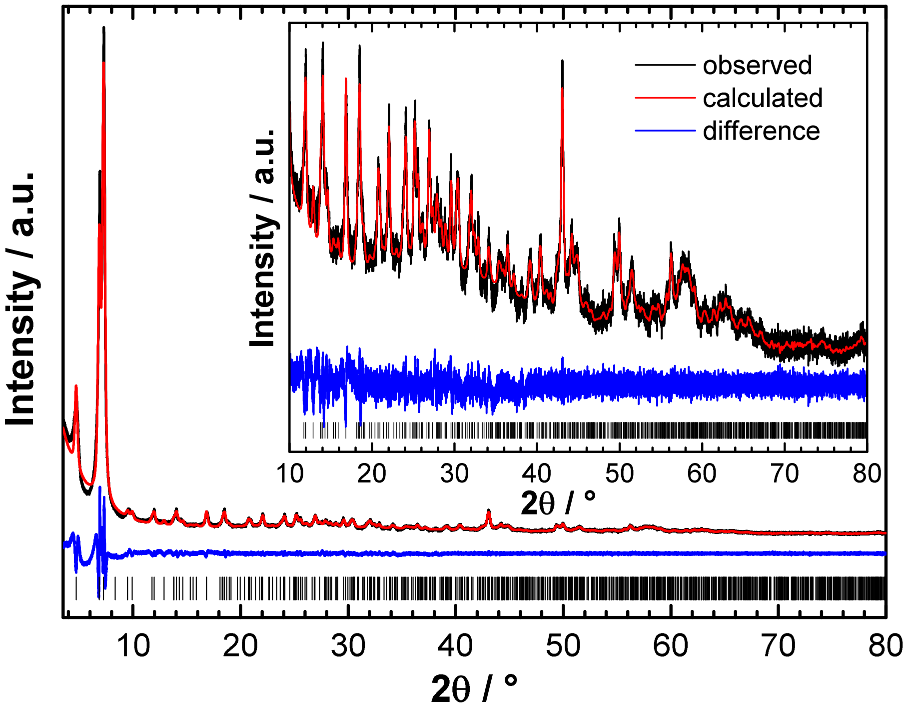

Figure S1: Pawley-fit for **hcp** UiO-66. Observed PXRD pattern (black), calculated pattern (red), difference plot (blue) and allowed Bragg positions (black vertical bars).

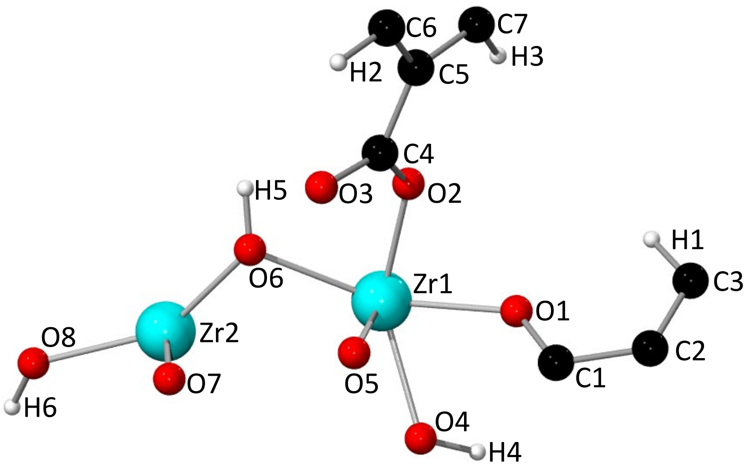

Figure S2: Illustration of the asymmetric unit of **hcp** UiO-66 including the atom symbols. The elements are depicted as follows: Zirconium in cyan, oxygen in red, carbon in black and hydrogen in white.

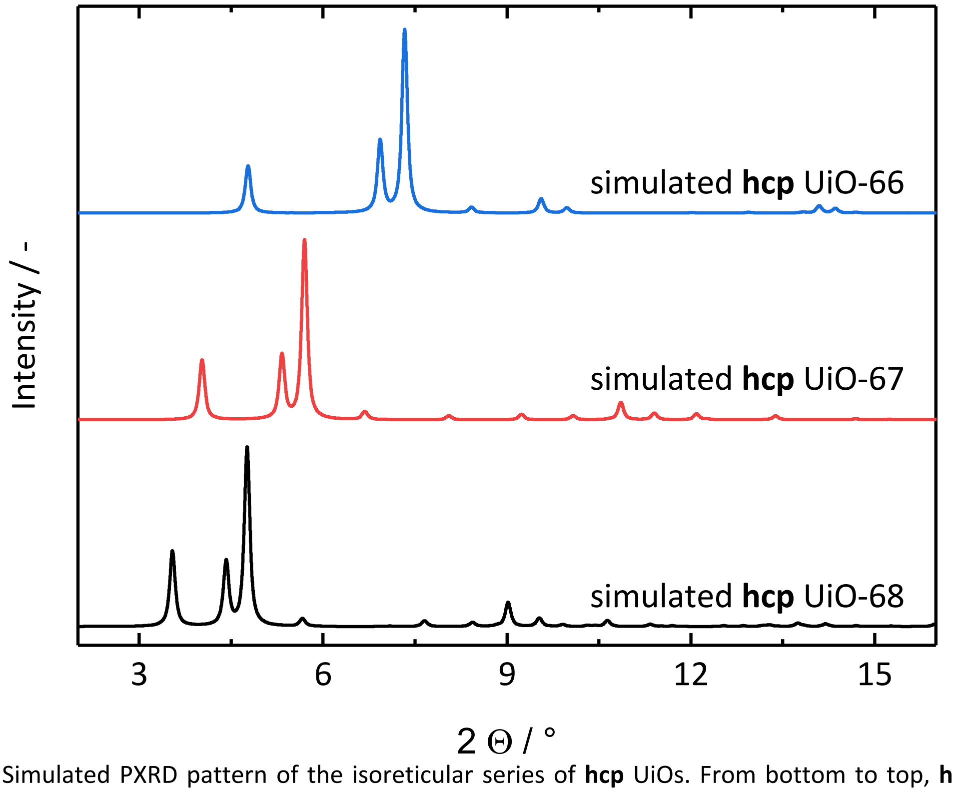

Figure S3: Simulated PXRD pattern of the isoreticular series of **hcp** UiOs. From bottom to top, **hcp** UiO-68 (based on the structure published by Ji *et al.*[3]), **hcp** UiO-67 (based on the structure published by Cliffe *et al.*[2]) and **hcp** UiO-66 (based on the crystallographic data, published in this communication).

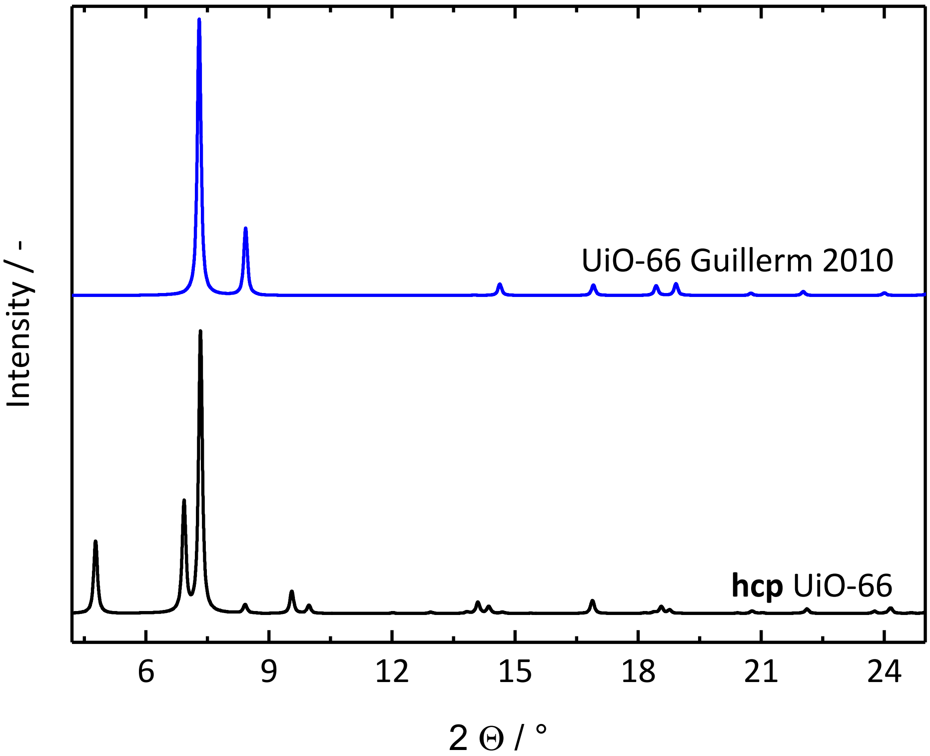

Figure S4: Simulated PXRD pattern of **hcp** UiO-66 (black line) and UiO-66 (blue line) from the crystal structure that was published by Guillerm *et al.*.[4]

4.2. Crystallographic data

```
data_hcp_UiO-66(Zr)

_pd_phase_name                          'hcp UiO-66(Zr)'
_xact_pref_orient_vector_h              0.00000000
_xact_pref_orient_vector_k              0.00000000
_xact_pref_orient_vector_l              1.00000000
_xact_pref_orient_param                 1.000000
_cell_length_a                          14.713091
_cell_length_b                          14.713091
_cell_length_c                          36.979496
_cell_angle_alpha                       90
_cell_angle_beta                        90
_cell_angle_gamma                       120
_symmetry_cell_setting                  'hexagonal'
_symmetry_space_group_name_H-M          'P 63/m m c'
_symmetry_Int_Tables_number             194
_symmetry_space_group_name_Hall         '-P 6c 2c'

_chemical_formula_sum                   'C36 H25 Zr6 O29'
_chemical_formula_weight                1468.911
```

```
loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'
  '-x, -y, -z'
  '-y, x-y, z'
  'y, -x+y, -z'
  '-x+y, -x, z'
  'x-y, x, -z'
  '-x, -y, z+1/2'
  'x, y, -z+1/2'
  'y, -x+y, z+1/2'
  '-y, x-y, -z+1/2'
  'x-y, x, z+1/2'
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  '-y, -x, z'
  'x-y, -y, -z'
  '-x+y, y, z'
  '-x, -x+y, -z'
  'x, x-y, z'
  '-y, -x, -z+1/2'
  'y, x, z+1/2'
  '-x+y, y, -z+1/2'
  'x-y, -y, z+1/2'
  'x, x-y, -z+1/2'
  '-x, -x+y, z+1/2'

loop_
  _atom_site_label
  _atom_site_type_symbol
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_symmetry_multiplicity
  _atom_site_Wyckoff_symbol
H1    H    1    0.674806    0.617739    0.471500    24    l
H2    H    1    0.558313    0.696379    0.297243    24    l
H3    H    1    0.770082    0.796505    0.389076    24    l
H4    H    1    0.666667    0.333333    0.430087    4     f
H5    H    1    0.793903    0.587807    0.305441    12    k
H6    H    1    0.887953    0.298845    0.250000    12    j
C1    C    1    0.565696    0.434304    0.435423    12    k
C2    C    1    0.531714    0.468286    0.468368    12    k
C3    C    1    0.598347    0.566710    0.484124    24    l
C4    C    1    0.665049    0.635187    0.341154    24    l
C5    C    1    0.664325    0.736134    0.342994    24    l
```

C6	C	1	0.605110	0.756291	0.317578	24	l
C7	C	1	0.724219	0.812806	0.369267	24	l
O1	O	1	0.656912	0.498315	0.422702	24	l
O2	O	1	0.721215	0.621805	0.364939	24	l
O3	O	1	0.612297	0.571233	0.315526	24	l
O4	O	1	0.666667	0.333333	0.403470	4	f
O5	O	1	0.601479	0.398521	0.353198	12	k
O6	O	1	0.757014	0.514027	0.312471	12	k
O7	O	1	0.666667	0.333333	0.287481	4	f
O8	O	1	0.864373	0.349783	0.250000	12	j
Zr1	Zr	1	0.745313	0.490625	0.375000	12	k
Zr2	Zr	1	0.829019	0.414509	0.297546	12	k

4.3. Further characterization of **hcp** UiO-66

Please note that for the following characterization steps the sample of **hcp** UiO-66 synthesized with H_2BDC was after the powder X-ray diffraction measurements in addition to the normal work-up procedure processed with a DMF extraction step to remove unreacted H_2BDC and an ethanol extraction step to remove the remaining DMF from the pores for 24 h each.

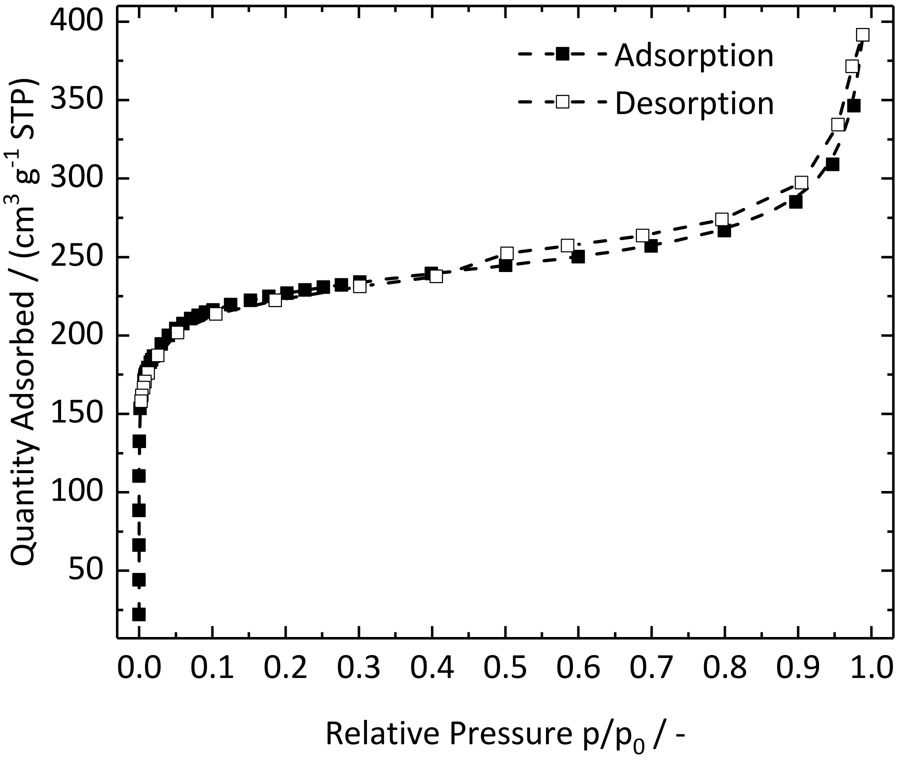

Figure S5: N_2 adsorption isotherms of **hcp** UiO-66 synthesized with [PBuMEE][BDC]. Filled symbols indicate the adsorption branch and empty symbols indicate the desorption branch.

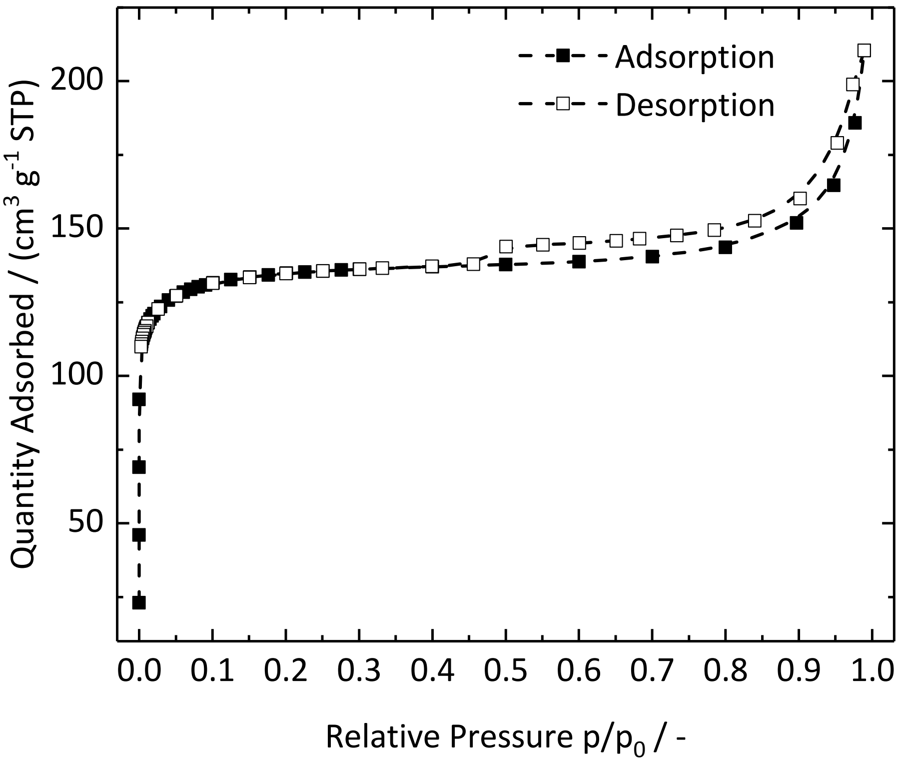

Figure S6: N_2 adsorption isotherms of **hcp** UiO-66 synthesized with [EMIM][HBDC]. Filled symbols indicate the adsorption branch and empty symbols indicate the desorption branch.

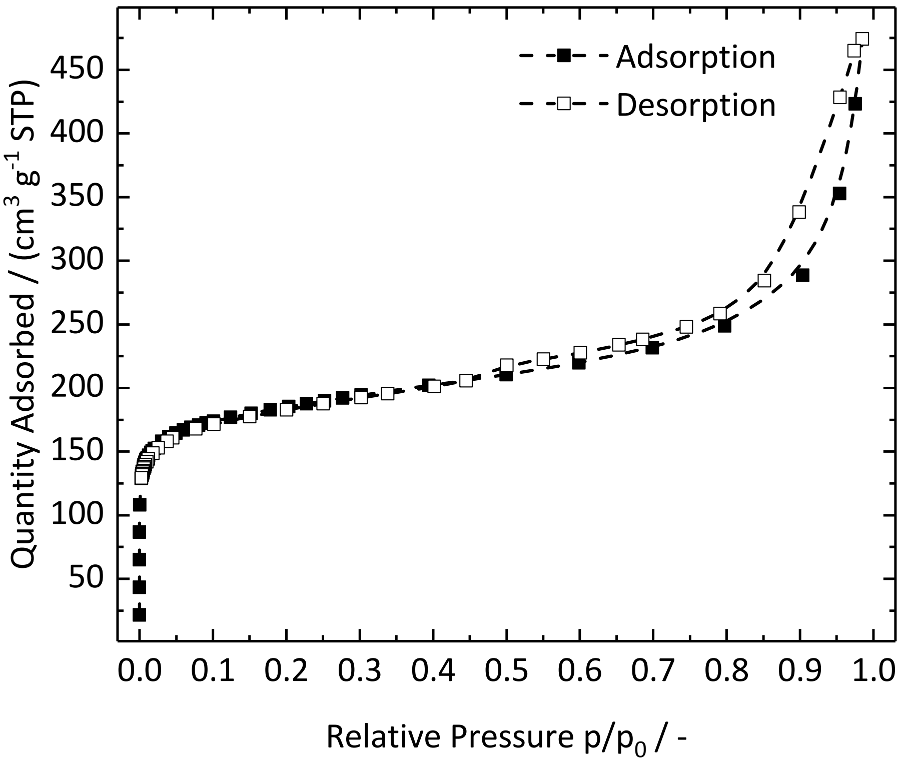

Figure S7: N_2 adsorption isotherms of **hcp** UiO-66 synthesized with $[EMIM]_2[BDC]$. Filled symbols indicate the adsorption branch and empty symbols indicate the desorption branch.

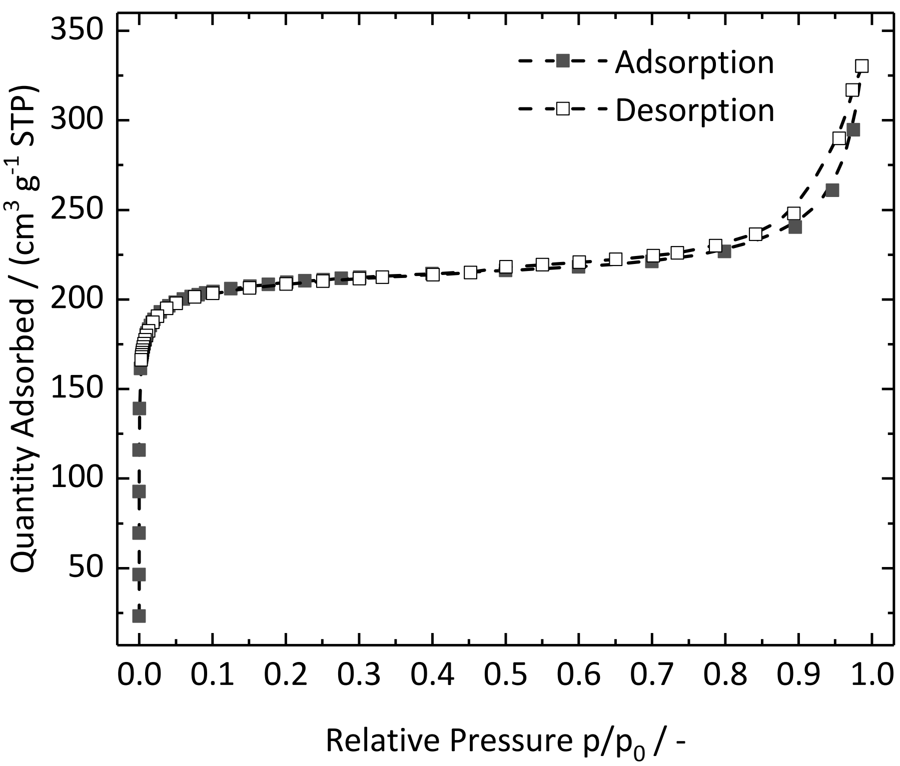

Figure S8: N_2 adsorption isotherms of **hcp** UiO-66 synthesized with H_2BDC. Filled symbols indicate the adsorption branch and empty symbols indicate the desorption branch.

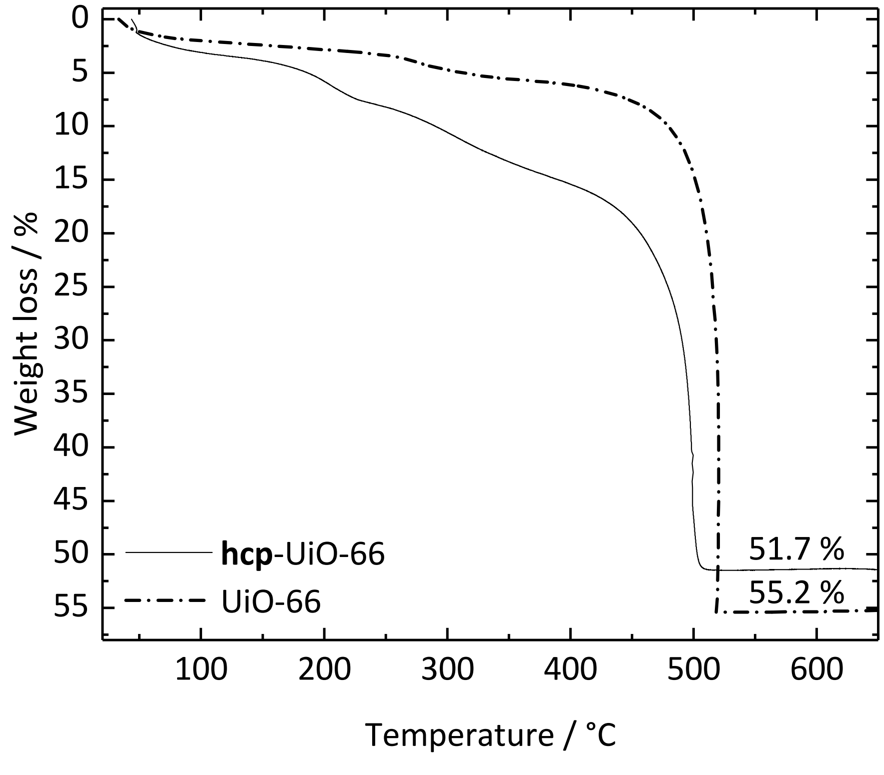

Figure S9: Thermogravimetric analysis of **hcp** UiO-66 (solid line) and UiO-66 (broken line).

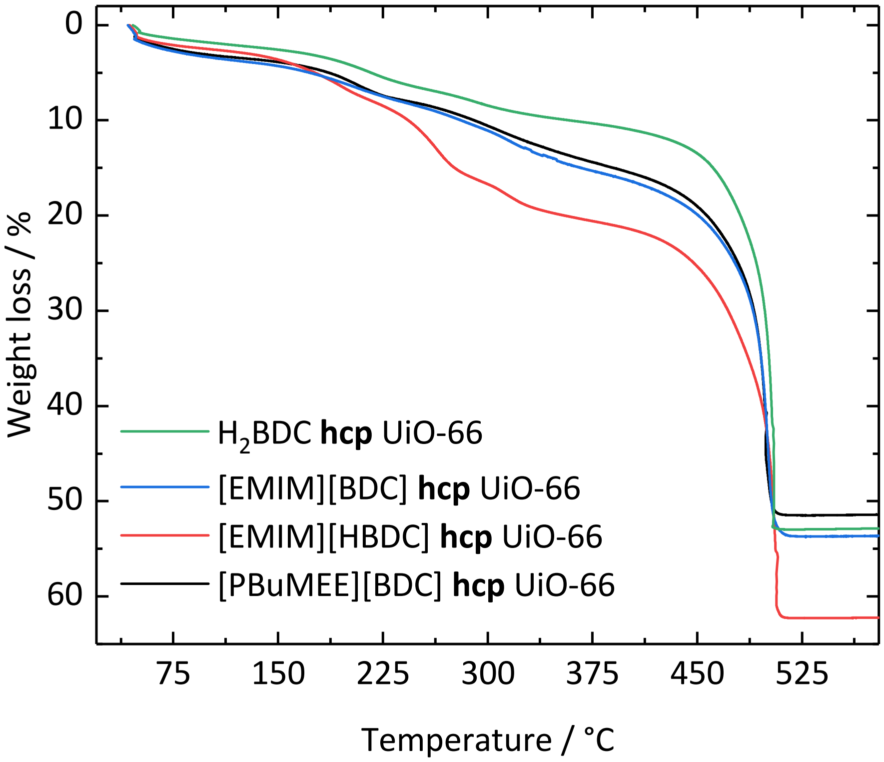

Figure S10: Thermogravimetric analysis of **hcp** UiO-66, synthesized with different linker sources.

Table S4: Summary of BET areas and number of missing linkers derived from N_2 sorption measurements and thermogravimetric analysis.

	BET surface area / (m^2g^{-1})	Missing Linker
$[PBuMEE^+]_2[BDC^{2-}]$	874	2.5
$[EMIM^+][HBDC^-]$	531	0
$[EMIM^+]_2[BDC^{2-}]$	696	3
H_2BDC	836	1.5

Table S5: Experimental and theoretical values of carbon (C), hydrogen (H) and zirconium (Zr) revealed by CHNS Elemental Analysis and inductively coupled plasma mass spectrometry.

	C / wt.-%	H / wt.-%	Zr / wt.-%
Experimental	27.0	2.3	30.0
Theoretical	29.4	1.7	37.2

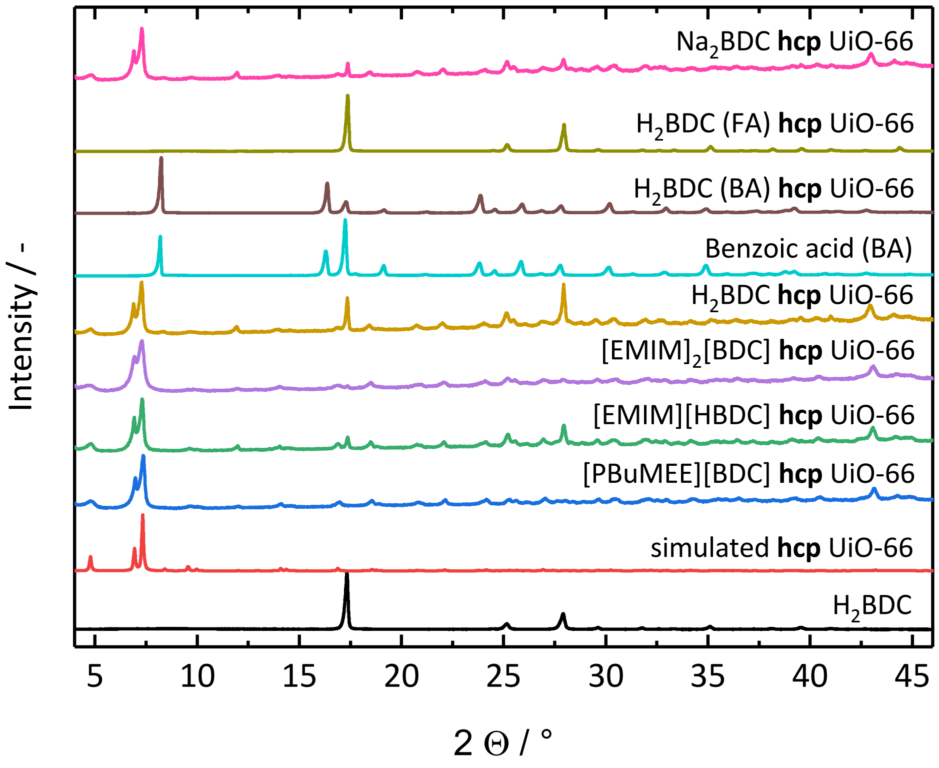

Figure S11: Normalized powder X-ray diffraction pattern of different syntheses approaches with varying linker sources and modulators. Furthermore PXRDs of pure terephthalic acid (black) and benzoic acid (turquoise) were added. A simulated diffractogram of **hcp** UiO-66 (red) is shown for comparison.

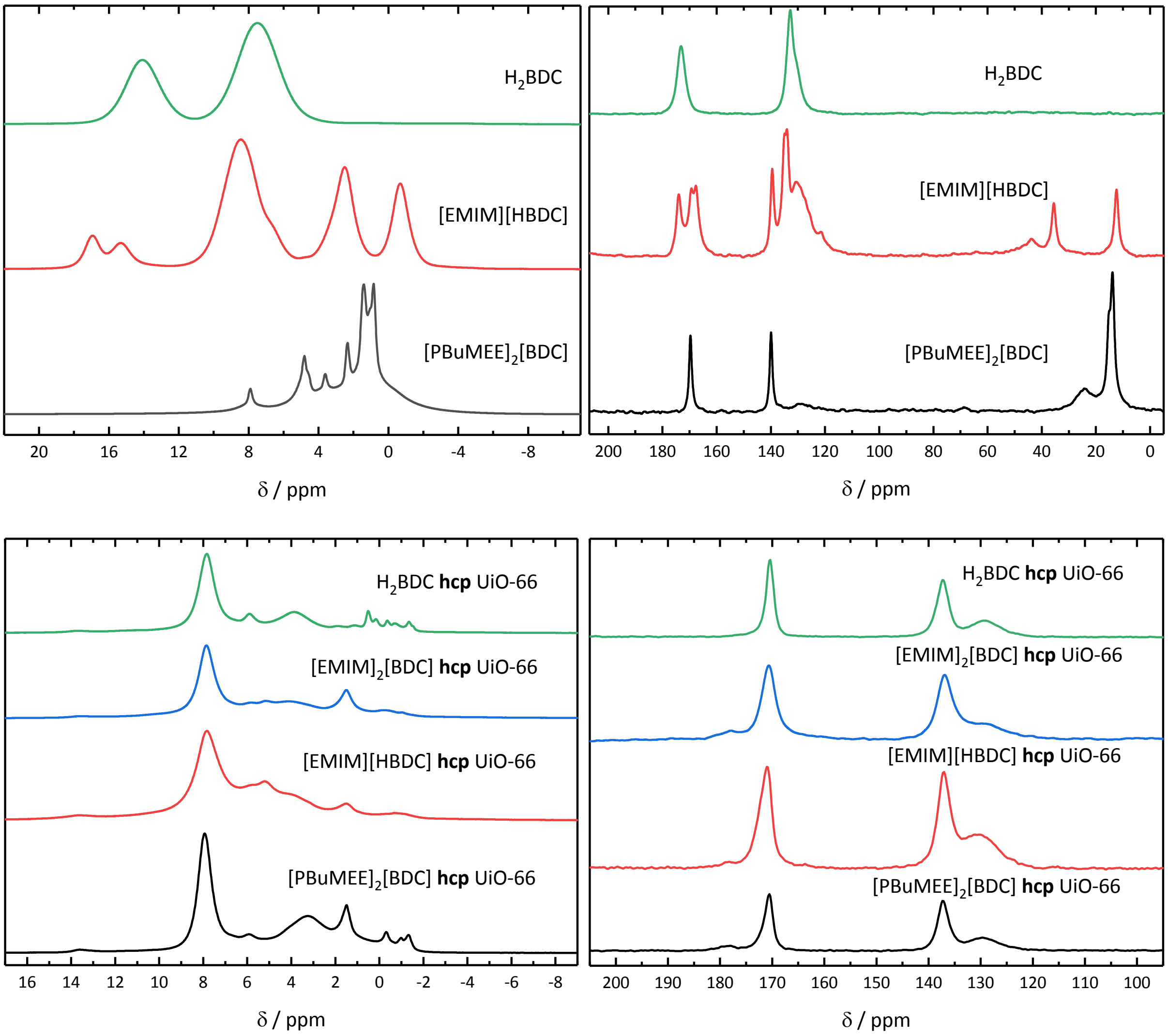

Figure S12: ^{1}H NMR spectra (left) and ^{13}C NMR spectra (right) of the linker precursors (top) used in the synthesis of **hcp** UiO-66 (bottom). [EMIM]$_2$[BDC] couldn't be measured in the solid state NMR due to its hydrophilic properties.

4.4. Stability tests of **hcp** UiO-66

Please note that for the stability tests of hcp UiO-66 samples were used that were synthesized with a scaled-up synthesis approach. The scale-up was simply performed by simply increasing the amounts of educts from synthesis 1 in table S2 25 times. The resulting powder shows a lower crystallinity compared to the original synthesis, but it can be identified as **hcp** UiO-66. For the stability tests, fractions of 0.3 g powder were stored in aqueous solutions with varying pH values for three days.

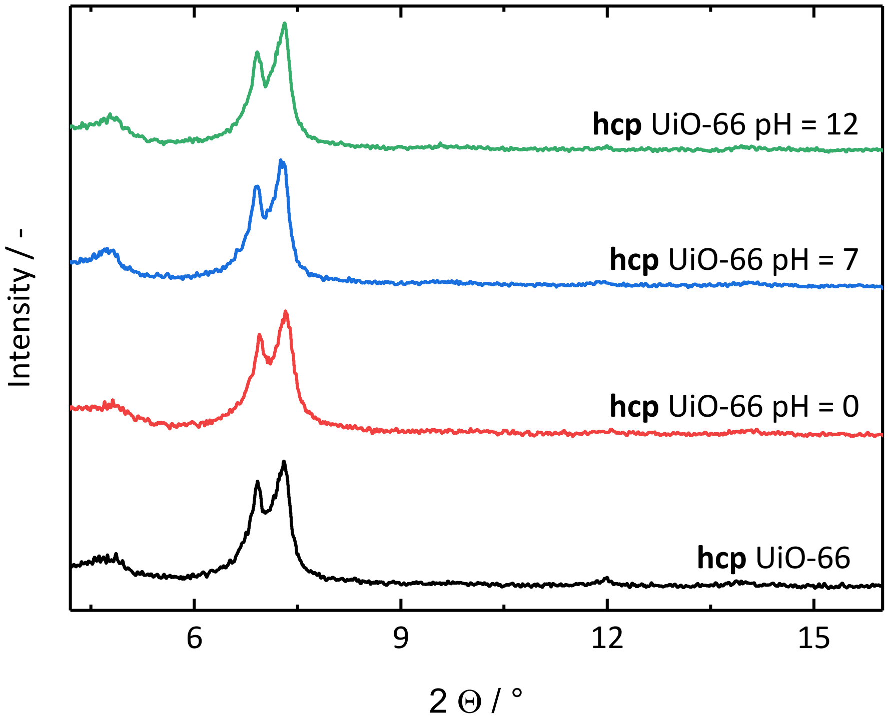

Figure S13: PXRD patterns, after storing **hcp** UiO-66 for three days in aqueous solutions with various pH values. These samples show a lower crystallinity, but can be identified as **hcp** UiO-66

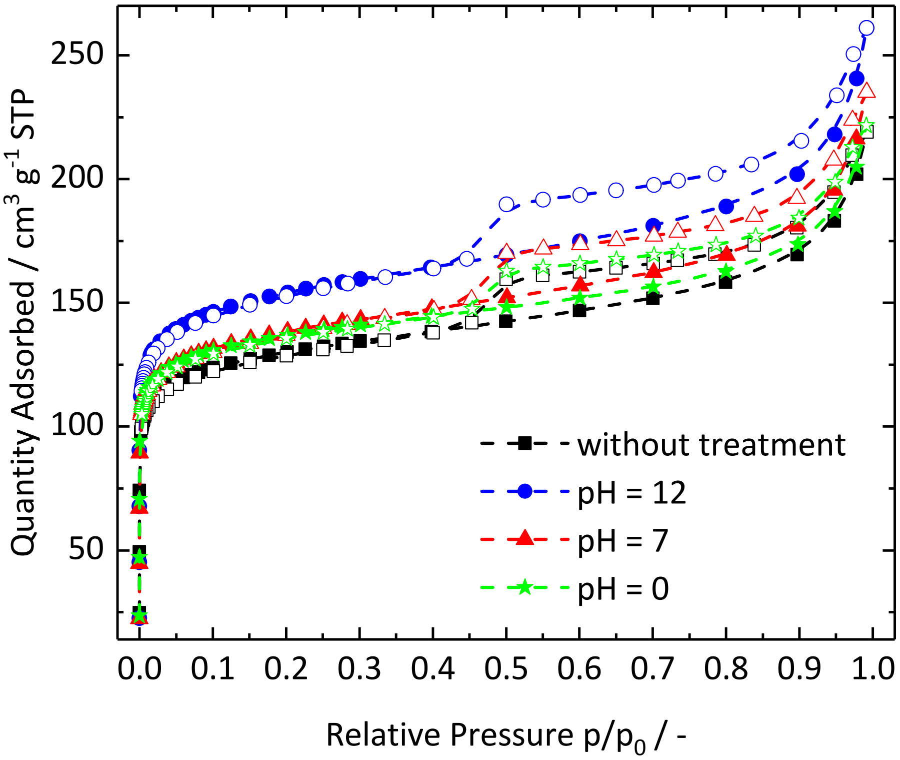

Figure S14: N_2 isotherms of hcp UiO-66, after three days of storing in aqueous media with varying pH values. Filled symbols show the adsorption branches, open symbols show the desorption branches.

Table S6: BET areas, calculated from the N_2 isotherms in Figure S14.

	untreated sample	pH = 0	pH = 7	pH = 12
BET areas / m^2g^{-1}	496	526	527	586

5. References

1. G. Metz, X. Wu and S. O. Smith, *Journal of Magnetic Resonance, Series A*, 1994, **110**, 219-227.
2. M. J. Cliffe, E. Castillo-Martínez, Y. Wu, J. Lee, A. C. Forse, F. C. Firth, P. Z. Moghadam, D. Fairen-Jimenez, M. W. Gaultois, J. A. Hill, O. V. Magdysyuo, B. Slater, A. L. Goodwin and C. P. Grey, *Journal of the American Chemical Society*, 2017, **139**, 5397-5404.
3. P. Ji, K. Manna, Z. Lin, X. Feng, A. Urban, Y. Song and W. Lin, *Journal of the American Chemical Society*, 2017, **139**, 7004-7011.
4. V. Guillerm, S. Gross, C. Serre, T. Devic, M. Bauer and G. Férey, *Chemical Communications*, 2010, **46**, 767-769.