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Electronic Supplementary Information

for

Selective Mechanochemical Conversion of Post-Consumer Polyethylene Terephthalate Waste into hcp and fcu UiO-66 Metal-Organic Frameworks

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Materials

Terephthalic acid (abcr GmbH), sodium hydroxide (abcr GmbH), potassium hydroxide (abcr GmbH), zirconium(IV) propoxide - 70 wt % 1-propanol solution (abcr GmbH), and methanol (abcr GmbH) were obtained from commercial sources. All chemicals were used as purchased without any further purification. Water was deionized using a milli Q purification system (Merck Millipore, 18.2 MΩ). PET was obtained from commercial transparent plastic bottles and post-consumer textile polyester and subsequently washed, dried, shredded, and milled to powder.

Characterization

Ex-situ PXRD patterns were obtained by a D8 Advance Diffractometer (Bruker AXS, Karlsruhe, Germany) operating in Bragg-Brentano Geometry and utilizing Cu-Kα radiation (λ = 1.542 Å; step width: 0.02°). Samples were prepared in custom made PVC sample holders and measured over a range of 2θ = 5° to 50°.

The IR spectra were recorded with a Nicolet 670 FT-IR (ThermoFisherScientific GmbH) in attenuated total reflection (ATR), with which a ”Golden Gate” sample holder was used. After each measurement, the sample holder was cleaned with ethanol and acetone. The background spectrum was measured in air. 32 scans with a resolution of 4 cm–1 were recorded per measurement. The spectra were recorded in absorption mode in a spectral range of 4000–600 cm–1. The instrument was controlled with OMNIC software.

TGA/DSC measurements were conducted using a METTLER Toledo TGA/DSC 3+ instrument. A sample was subjected to a thermal analysis, being heated from 25 °C to 950 °C in an open 70 µL aluminium oxide crucible with a nitrogen flow of 80 mL/min. The heating rate was set at a rate of 10 °C per minute.

NMR experiments were performed on a 500 MHz NMR spectrometer system (VNMRS500, Varian Associates, Palo Alto, USA).

In-situ X-ray diffraction experiments were performed at the µSpot beamline (BESSY II, Helmholtz Centre Berlin for Materials and Energy). The used photon energy amounted to 17.44 keV using a double crystal monochromator (Si 111). The beam was positioned slightly inside of the milling jar, by scanning the wall of the jar and then moving approximately 50 µm inside. The sample detector distance was 229.70 mm. Scattered intensities were collected with a two-dimensional X-ray detector (Eiger 9M, HPC 3110 x 3269 pixel, pixel size 75 x 75 µm) and a time-resolution of 10 s. The obtained scattering images were processed employing an algorithm of the computer program DPDAK.[1] 2D time-resolved plots of in situ monitoring data were created in MATLAB and the background of each diffraction pattern was subtracted prior to plotting using the Sonneveld-Visser algorithm.[2] For comparison, the theoretical XRD patterns of the starting materials and final products were retrieved from the ICSD or CCDC and simulated using Mercury (Version 4.3.0, CCDC).

Raman spectra were recorded using a RamanRXN1 AnalyzerTM (Kaiser Optical Systems, France) with a system power of 400 mW, utilizing λ = 765 nm as an excitation wavelength. The contactless probe was adjusted to a spot size of 1 mm, in a distance of approximately 6 cm from the sample. Each spectrum consists of 5 accumulations of 5 s each. For in-situ measurements, the probe is adjusted onto the filled milling jar (reactants, milling ball and grinding liquid).

For gel permeation chromatography, 1 x PFG linear M 7µm 30 x 0.8 cm and 1 x PL-PFG linear 7 µm 25 x 0,46 cm columns were used. Column temperature was 35°C and eluent was 100% HFIP. Detection was achieved by refractive index, RI (35°C). We used flowrate of 0.5 mL/min and 100 μL of injection volume. Calibration was performed using 9 PMMA Standards (150 to 8,1x105 g/mol) (PSS, now Agilent). Semi-quantitative estimation of PET content was performed by comparing detector response intensities for the starting PET and the sample. To enable that, same concentration of the PET from the starting reference and that in the sample was used (assuming no depolymerization).

For gas adsorption measurements, samples were first activated by soaking in MeOH for 6 h and exchanging the supernatant with fresh MeOH. After exchanging the supernatant three times, samples were dried under vacuum oven at 60 °C. The samples were then degassed under dynamic vacuum on a SmartVacPrep at 120 °C for 12 h or until the outgassing rate of ≤ 0.02 mm Hg min^{-1} was reached. The nitrogen isotherms of the activated samples were then measured on ASAP 2020 instrument from Micromeritics at 77 K with liquid nitrogen bath. Specific surface areas were determined and calculated from the adsorption branch of the isotherm using the Brunauer, Emmett, and Teller (BET) method.[3]

<u>Mechanochemical synthesis of disodium terephthalate</u>

In a typical synthesis, a 1:2 stochiometric amount of PET (0.55 mmol, 106.6 mg), calculated by its monomer-equivalent, and NaOH (1.1 mmol, 44.4 mg) were placed in a 4 mL milling jar (stainless steel caps and PMMA central part) together with 100 μL of H_2O and one stainless steel milling ball (8mm, 1.83 g). The mechanochemical synthesis was carried out using a vertical ball mill (Pulverisette 23, FRITSCH GmbH, Germany) at 50 Hz for 2 hours. The obtained white wet paste was dried for 1h in an oven at 60°C and ground into a fine powder for analysis by PXRD.

<u>Mechanochemical synthesis of dipotassium terephthalate</u>

In a typical synthesis, a 1:2 stochiometric amount of PET (0.49 mmol, 94.7 mg), calculated by its monomer-equivalent, and KOH (0.99 mmol, 55.3 mg) were placed in a 4 mL milling jar together and 100 μL of H_2O and one stainless steel milling ball (8mm, 1.83 g). The mechanochemical synthesis was performed using a vertical ball mill (Pulverisette 23, FRITSCH GmbH, Germany) at 50 Hz for 2 hours. The obtained white wet paste was dried for 1h in an oven at 60°C and ground into a fine powder for analysis by PXRD.

Mechanochemical synthesis of disodium terephthalate (1 g scale) from waste PET

The gram-scale mechanochemical synthesis of disodium terephthalate was conducted using a 10 mL stainless steel milling jar with one 10 mm stainless steel milling ball. PET (704 mg) and NaOH (294 mg) were added to the milling jar together with the addition of 667 μL of H_2O. The synthesis was carried out using a vertical ball mill (Pulverisette 23, FRITSCH GmbH, Germany) at a frequency of 50 Hz for 4 h. The obtained wet paste, white or red (depending on the source), respectively, was dried for 1 h in an oven at 60°C and ground using a mortar and pestle into a fine powder for analysis by PXRD. To remove ethylene glycol, disodium terephthalate was washed with iPrOH and dried for 1 h at 60°C.

The disodium terephthalate obtained from the red polyester textile was de-colorized and purified. The material was suspended in 50 mL of H_2O. The unreacted solid residue was then filtered out. To remove the dye, activated carbon powder was added to the aqueous filtrate containing disodium terephthalate and heated for 10 minutes under reflux. The activated carbon was removed by filtration. Water was removed by rotary evaporation. The resulting powder was dried for 1 h in an oven at 60 °C and ground using a mortar and pestle into a fine powder for analysis by PXRD. We isolated 470 mg of disodium terephthalate starting from 704 mg of red textile sample (63% yield). To remove ethylene glycol, disodium terephthalate was washed with iPrOH and dried for 1 h at 60°C.

Mechanochemical synthesis of dipotassium terephthalate (1 g scale)

The gram-scale mechanochemical synthesis of dipotassium terephthalate was conducted using a 10 mL stainless steel milling jar with one 10 mm stainless steel milling ball. PET (631 mg) and KOH (369 mg) were added to the milling jar together with the addition of 667 μL of H_2O. The synthesis was carried out using a vertical ball mill (Pulverisette 23, FRITSCH GmbH, Germany) at a frequency of 50 Hz for 2 h. The obtained white waxy substance was dried for 1h in an oven at 60°C and ground into a fine powder for analysis by PXRD.

Synthesis of $(Zr_6O_4(OH)_4(CH_3COO)_{12})_2$ (zirconium acetate cluster)

Zirconium (IV) propoxide (70 wt % 1-propanol solution) (3 mL) was mixed with 10.5 mL of acetic acid in a sealed beaker. The mixture was left overnight at room temperature and the resulting colorless microcrystalline powder was collected by filter suction and washed with acetic acid. After drying at room temperature, a fine colorless powder with a yield of 2.65 g, 85% (based on zirconium (IV) propoxide) was obtained.

Mechanochemical synthesis of UiO-66 from Na_2TP

Zirconium acetate cluster (0.0385 mmol, 131 mg) and disodium terephthalate (0.304 mmol, 63.9 mg) were transferred into a 4 mL jar (stainless steel ends and PMMA central part). H_2O (98 μL) and TEA (42 μL, 1 equiv.) were added, or 140 µL of H_2O without TEA, respectively. The reagents were milled for 120 min at 50 Hz using one 8 mm stainless steel ball. The obtained product was washed with water and MeOH and analyzed by PXRD (isolated 120 mg).

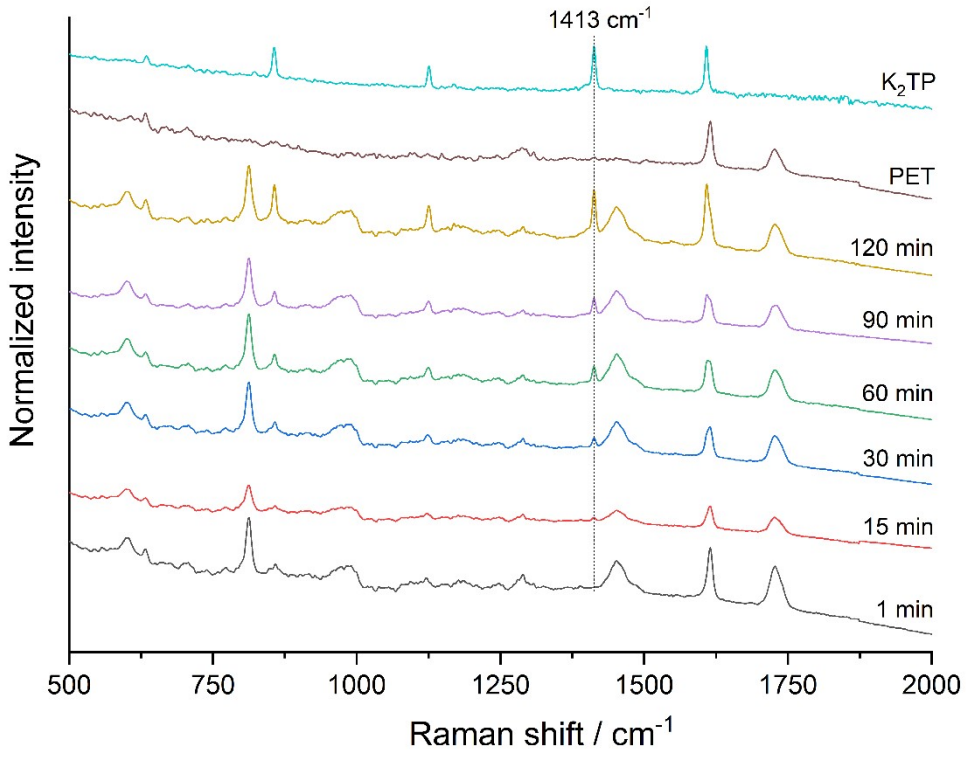

Figure S1. Time-resolved *in situ* Raman monitoring of milling PET (0.49 mmol, 94.7 mg), KOH (0.99 mmol, 55.3 mg), and 100 μL of H_2O. The reaction was performed in a 4 mL milling jar (stainless steel caps and PMMA central part) together with one stainless steel milling ball (8mm, 1.83 g).

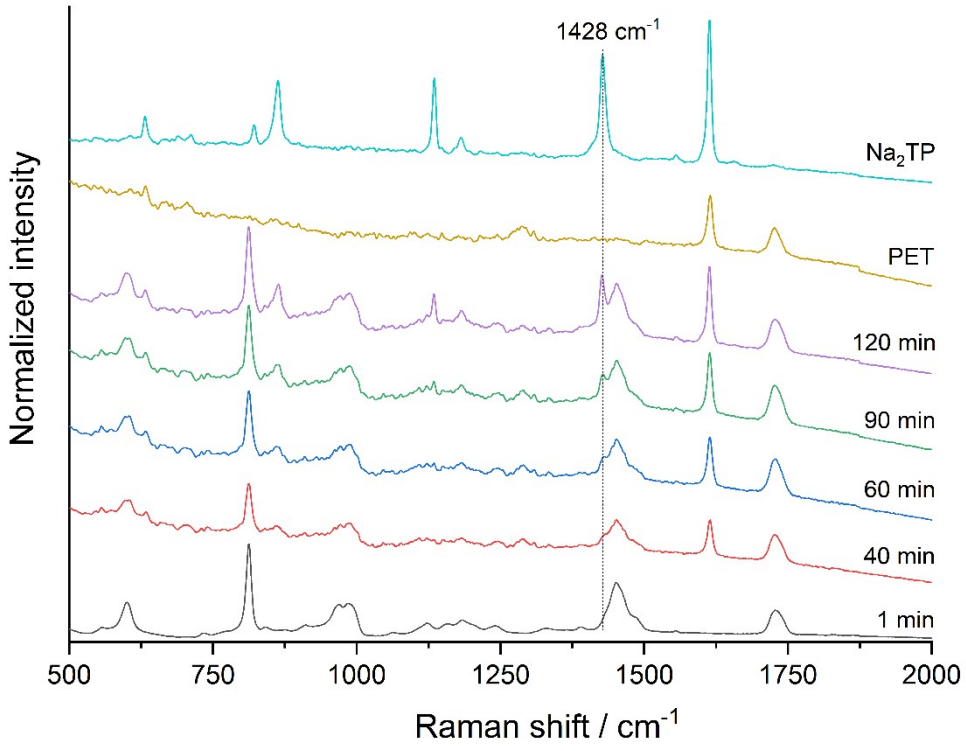

Figure S2. Time-resolved *in situ* Raman monitoring of milling PET (0.55 mmol, 106.6 mg), NaOH (1.1 mmol, 44.4 mg), and 100 μL of H_2O. The reaction was performed in a 4 mL milling jar (stainless steel caps and PMMA central part) together with one stainless steel milling ball (8mm, 1.83 g).

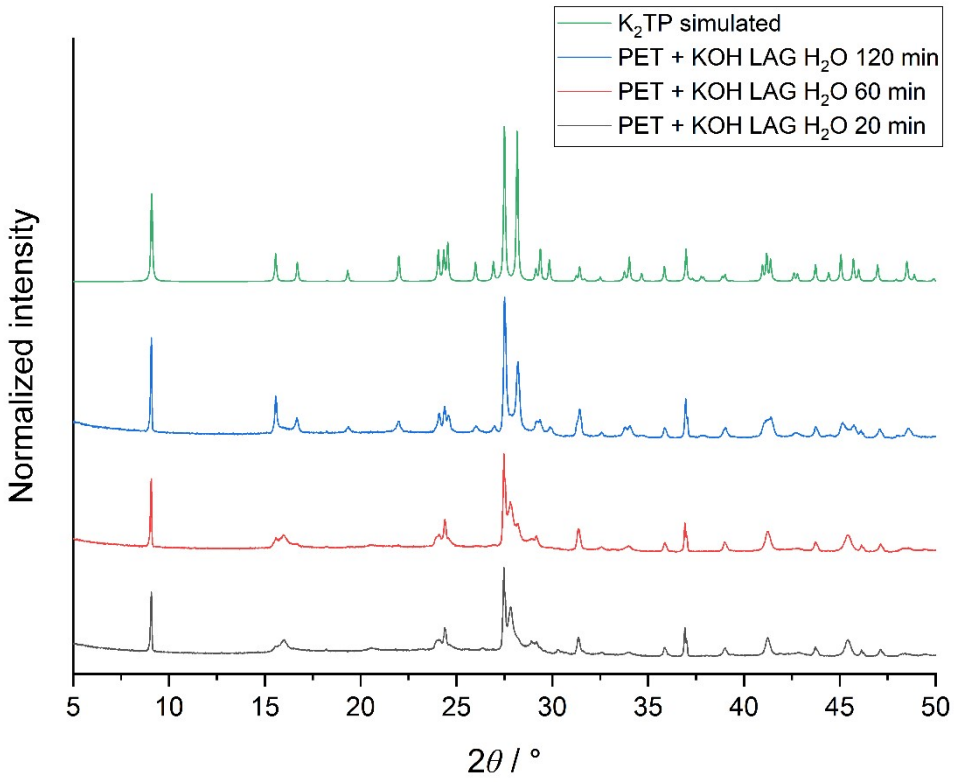

Figure S3. PXRD patterns for milling PET with KOH under different LAG conditions (λ = 1.542 Å).

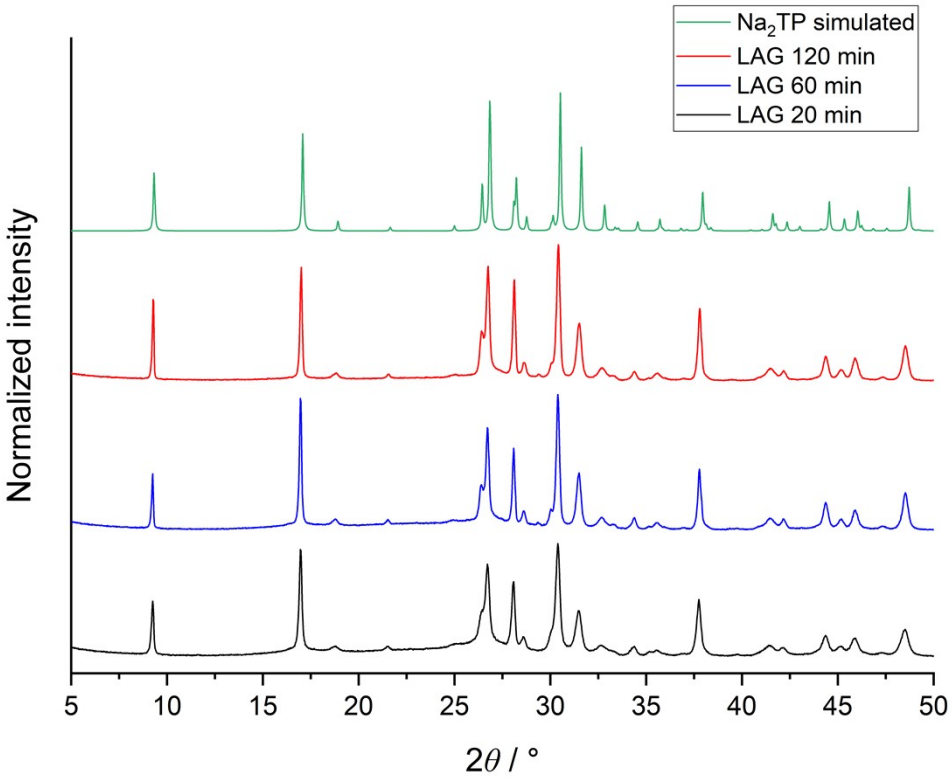

Figure S4. PXRD patterns for milling PET with NaOH under different LAG conditions (λ = 1.542 Å).

Figure S5. Photograph of the product of milling PET (704 mg), NaOH (294 mg), and 667 μL of H_2O at a frequency of 50 Hz for 2 h. 10 mL stainless steel milling jar with one 10 mm stainless steel milling ball was used.

Figure S6. Photograph of the product of milling PET (631 mg), KOH (369 mg), and 667 μL of H_2O at a frequency of 50 Hz for 2 h. 10 mL stainless steel milling jar with one 10 mm stainless steel milling ball was used.

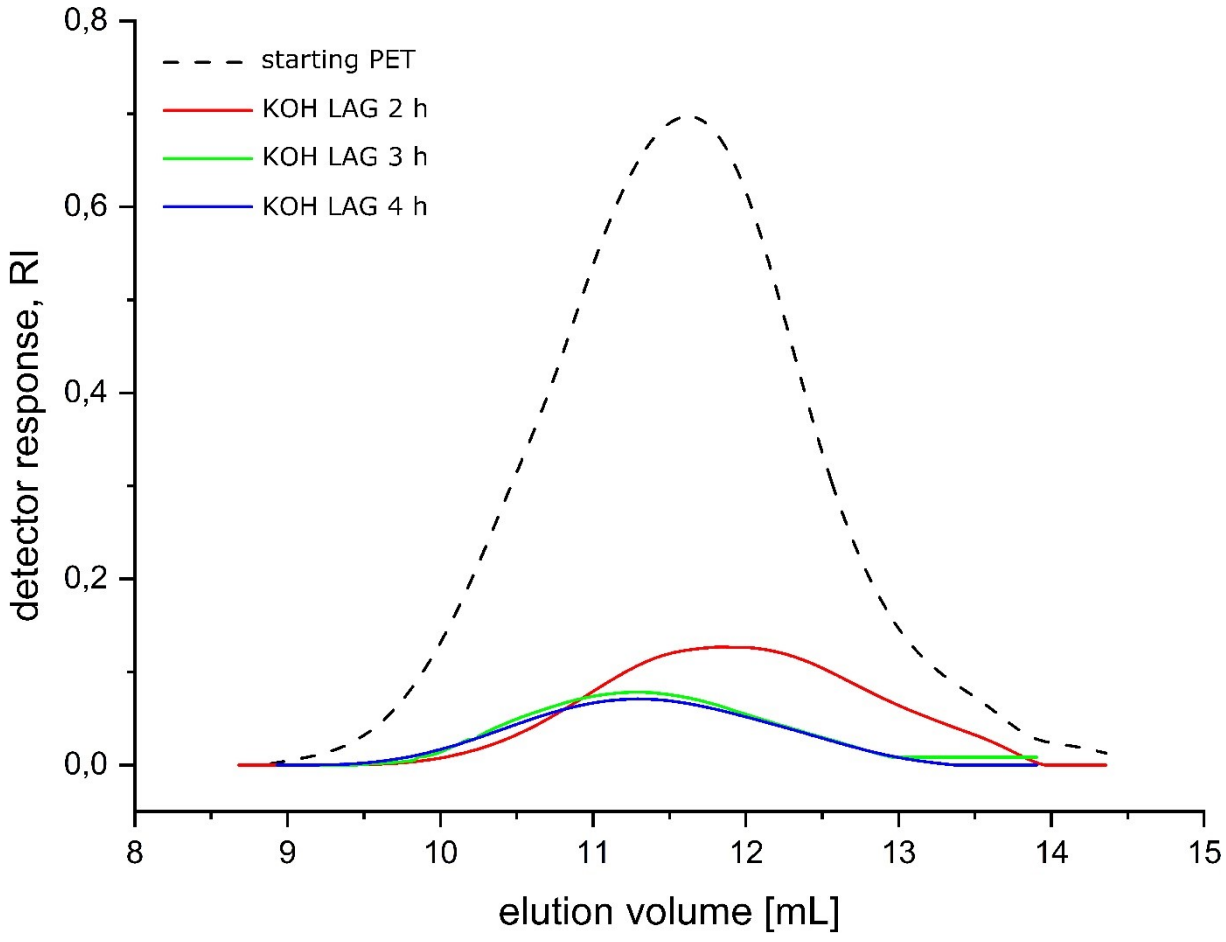

Figure S7. GPC chromatograms for milling PET with KOH under LAG conditions with H_2O.

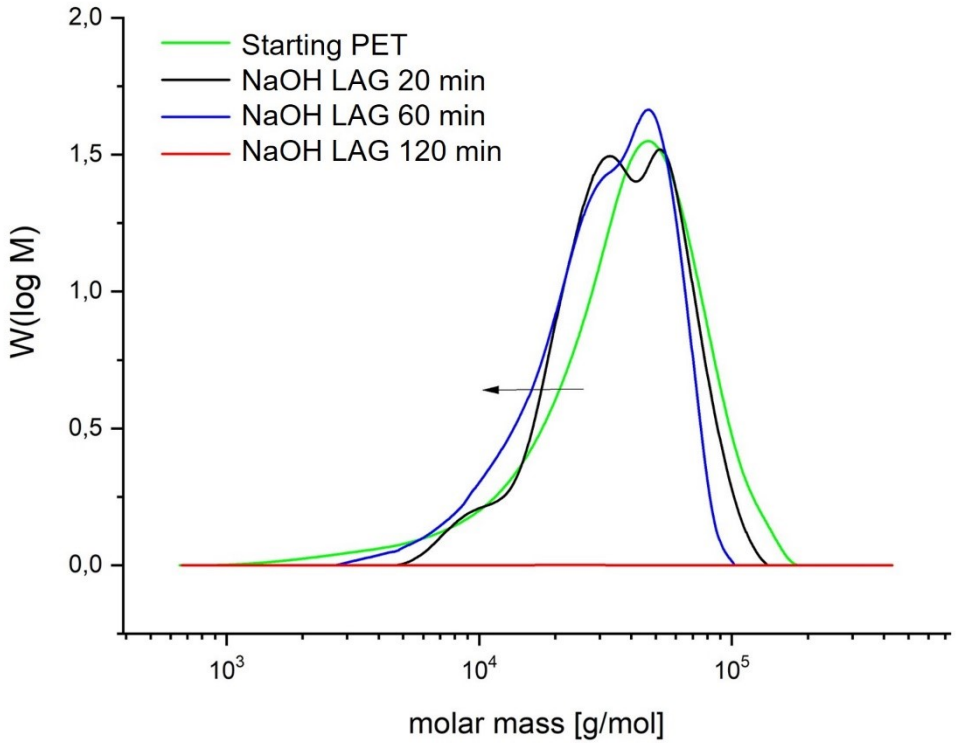

Figure S8. GPC chromatograms showing molar mass distribution for milling PET with NaOH under LAG conditions with H_2O.

Table S1. Number average (M_n), weight average (M_w), and dispersity ($Đ$) for milling PET with NaOH under LAG conditions with H_2O (Figure S8).

sample	M_n [kg/mol]	M_w [kg/mol]	$Đ$
Starting PET	21	38	1.8
NaOH LAG 20 min	24	39	1.5
NaOH LAG 60 min	21	36	1.7
NaOH LAG 120 min	-	-	-

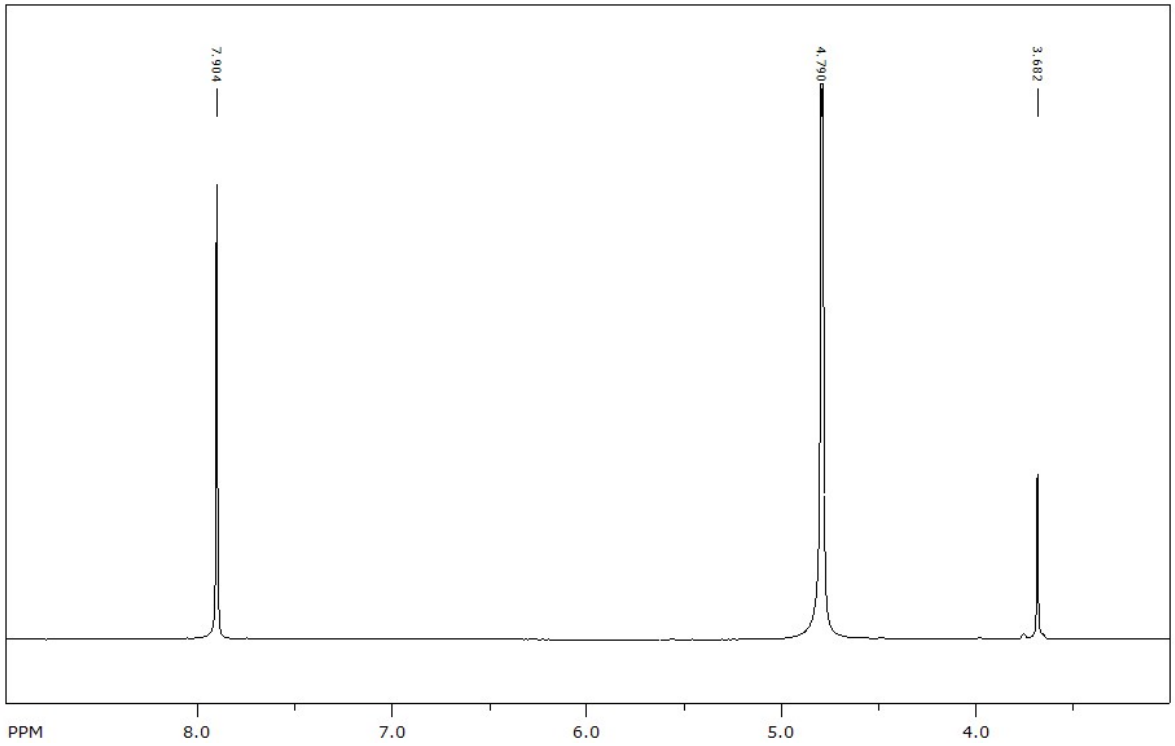

Figure S9. ^{1}H spectra of unwashed Na_2TP in D_2O (EG peak at 3.68 ppm).

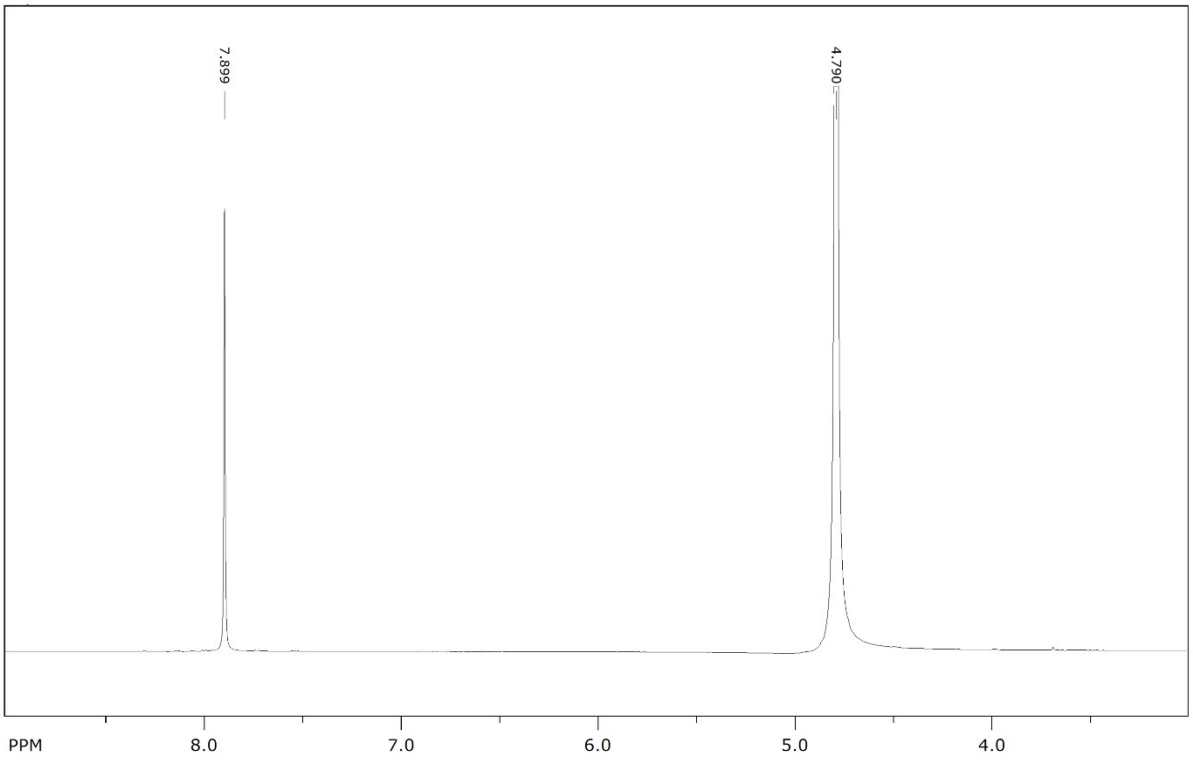

Figure S10. ^{1}H spectra of washed Na_2TP in D_2O (no EG peaks).

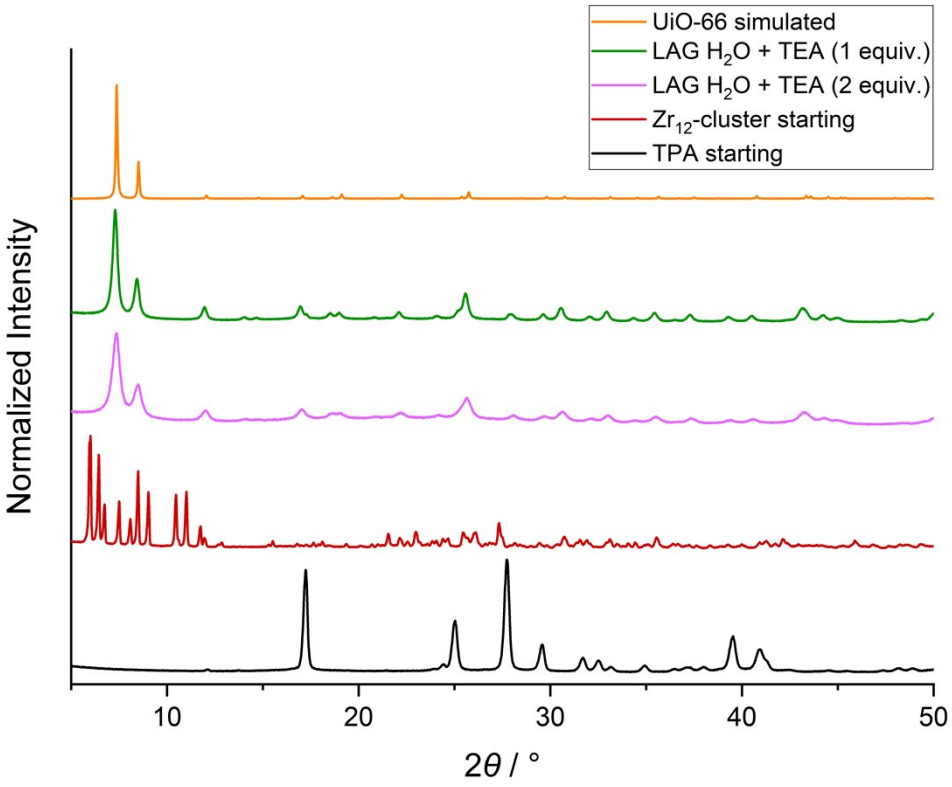

Figure S11. PXRD patterns for mechanochemical synthesis of UiO-66 starting from TPA (λ = 1.542 Å).

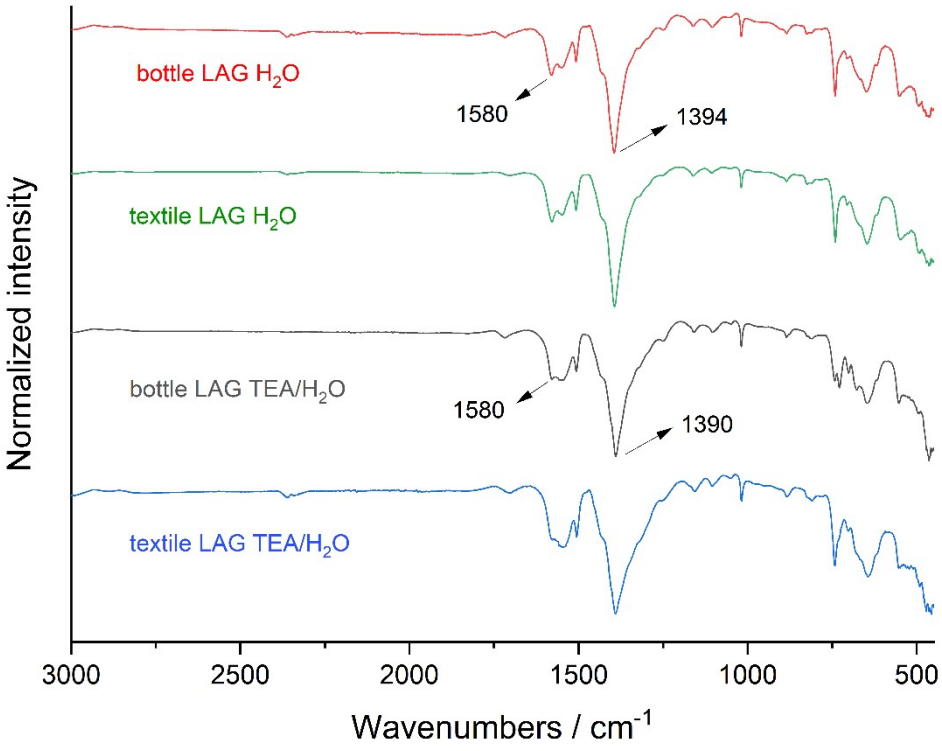

Figure S12. FTIR spectra of hcp UiO-66 samples (red and green) and fcu UiO-66 samples (grey and blue).

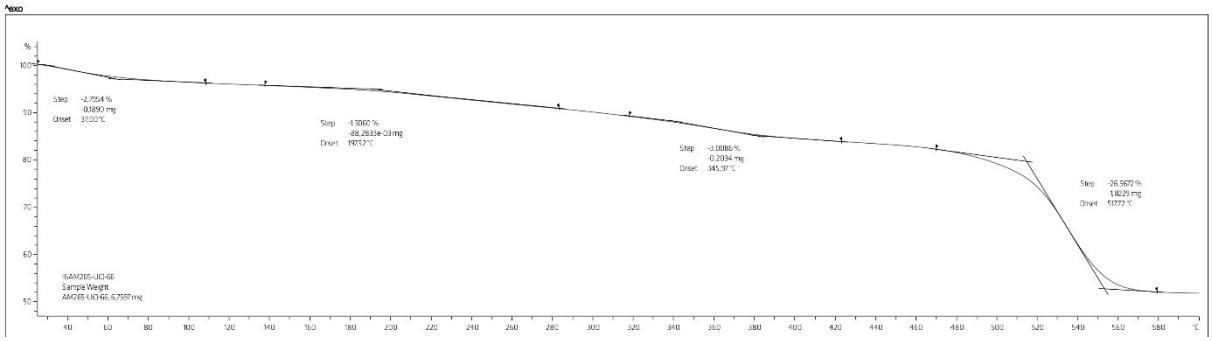

Figure S13. TGA curve for fcu UiO-66 (bottle LAG TEA/H_2O) obtained by milling washed and dried Na_2TP (0.304 mmol, 63.9 mg), obtained after milling PET bottle with NaOH, with zirconium acetate cluster (0.0385 mmol, 131 mg), 42 μL of triethylamine (one equiv.), and 98 μL of H_2O.

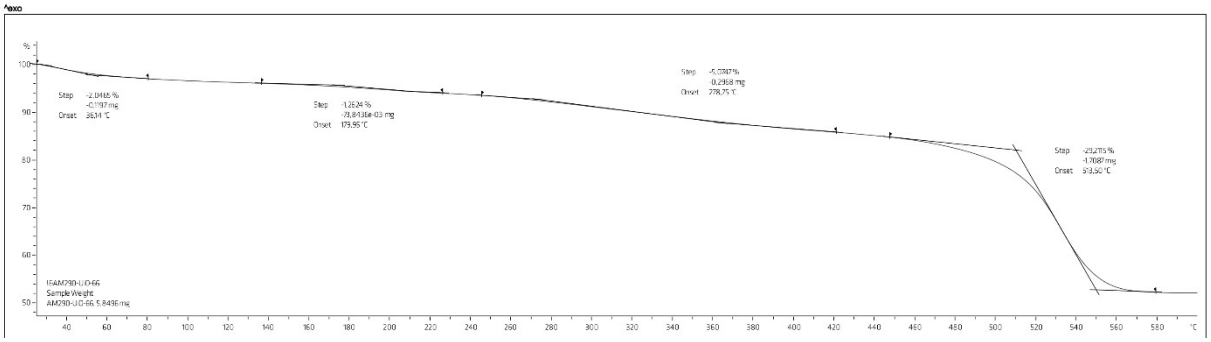

Figure S14. TGA curve for hcp UiO-66 (bottle LAG H_2O) obtained by milling washed and dried Na_2TP (0.304 mmol, 63.9 mg), obtained after milling PET bottle with NaOH, with zirconium acetate cluster (0.0385 mmol, 131 mg), and 140 μL of H_2O.

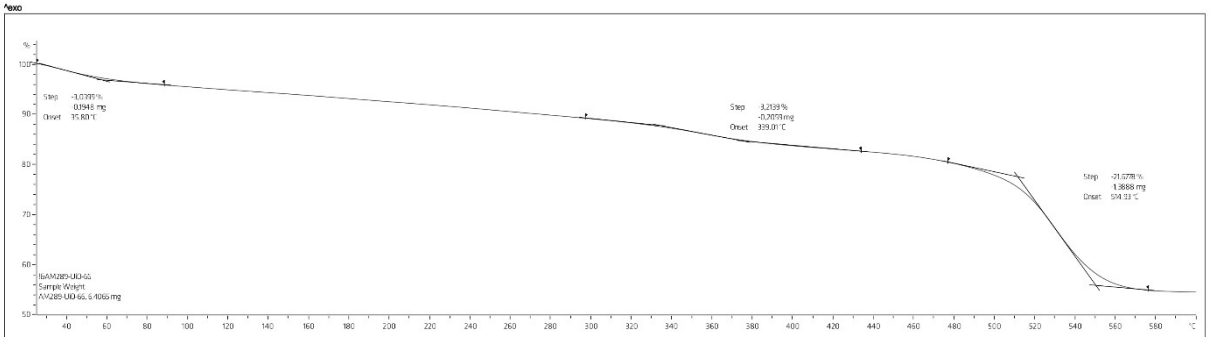

Figure S15. TGA curve for fcu UiO-66 (textile LAG TEA/H_2O) obtained by milling washed and dried Na_2TP (0.304 mmol, 63.9 mg), obtained after milling PET red textile with NaOH, with zirconium acetate cluster (0.0385 mmol, 131 mg), 42 μL of triethylamine (one equiv.), and 98 μL of H_2O.

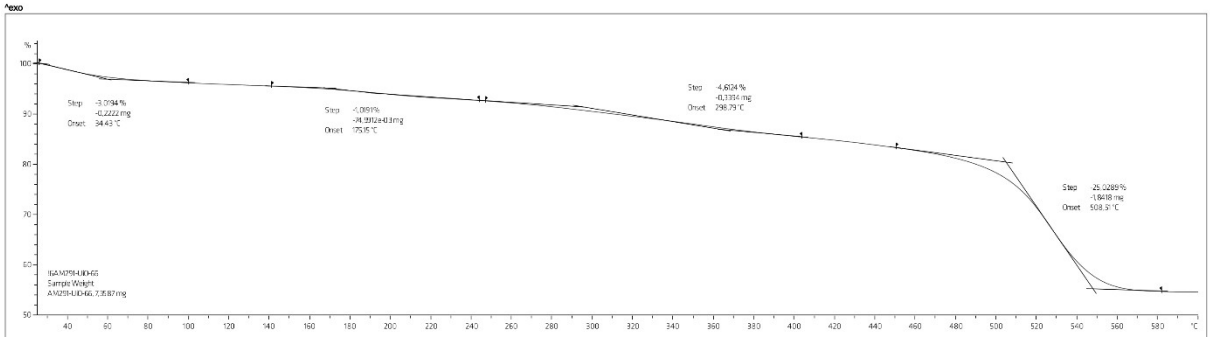

Figure S16. TGA curve for hcp UiO-66 (textile LAG H_2O) obtained by milling washed and dried Na_2TP (0.304 mmol, 63.9 mg), obtained after milling PET red textile with NaOH, with zirconium acetate cluster (0.0385 mmol, 131 mg), and 140 μL of H_2O.

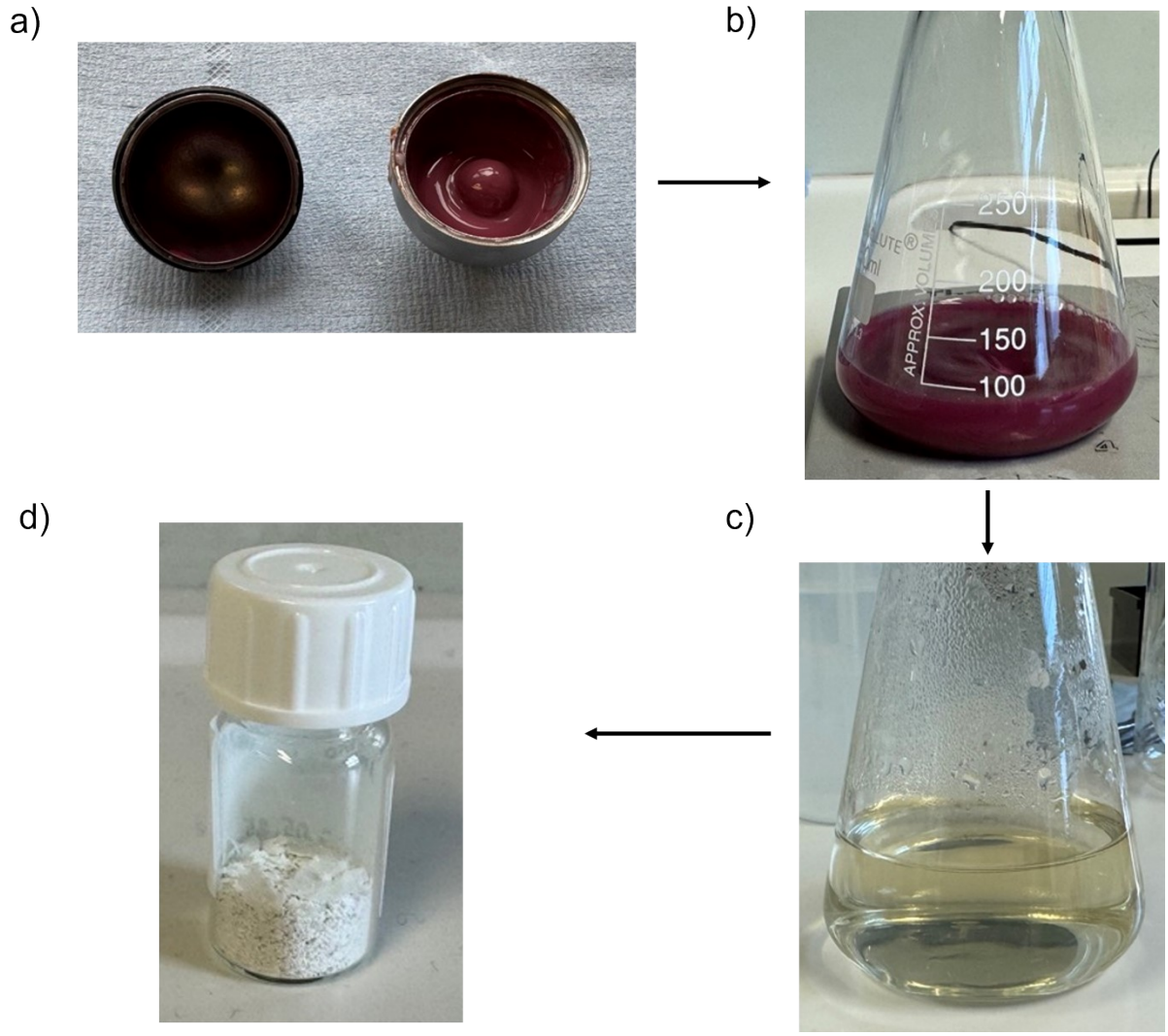

Figure S17. Workflow for decolorization: a) red textile polyester/PET after depolymerization reaction with NaOH, b) product mixture with activated carbon powder after heating, c) product mixture after the filtration, d) isolated Na_2TP after water evaporation, washing, and drying.

BET Surface Area Report

BET Surface Area: 777.7039 ± 1.2940 m²/g
Slope: 0.005592 ± 0.000009 g/cm³ STP
Y-Intercept: 0.000006 ± 0.000000 g/cm³ STP
C: 1011.248369
Qm: 178.6511 cm³/g STP
Correlation Coefficient: 0.9999958
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)	1/[Q(p°/p - 1)]
0.009917692	164.9272	0.000061
0.020891140	173.8681	0.000123
0.029150391	178.0261	0.000169
0.039733933	181.8965	0.000227
0.051487062	184.9619	0.000293

Figure S18. BET report from the nitrogen adsorption measurement for fcu UiO-66 (bottle LAG TEA/H_2O).

BET Surface Area Report

BET Surface Area: 733.8013 ± 0.7358 m²/g
Slope: 0.005921 ± 0.000006 g/cm³ STP
Y-Intercept: 0.000011 ± 0.000000 g/cm³ STP
C: 534.000181
Qm: 168.5660 cm³/g STP
Correlation Coefficient: 0.9999985
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)	1/[Q(p°/p - 1)]
0.021490122	159.0123	0.000138
0.032087223	164.6214	0.000201
0.039664296	167.7973	0.000246
0.051541462	171.9143	0.000316
0.078340951	178.9515	0.000475

Figure S19. BET report from the nitrogen adsorption measurement for hcp UiO-66 (bottle LAG H_2O).

BET Surface Area Report

BET Surface Area: 804.3785 ± 1.4370 m²/g
Slope: 0.005406 ± 0.000010 g/cm³ STP
Y-Intercept: 0.000006 ± 0.000000 g/cm³ STP
C: 962.485301
Qm: 184.7787 cm³/g STP
Correlation Coefficient: 0.9999952
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)	1/[Q(p°/p - 1)]
0.009896400	169.9167	0.000059
0.020734042	179.2728	0.000118
0.029353146	183.9039	0.000164
0.039981724	187.9527	0.000222
0.051493682	191.1655	0.000284

Figure S20. BET report from the nitrogen adsorption measurement for fcu UiO-66 (textile LAG TEA/H_2O).

BET Surface Area Report

BET Surface Area: 807.5308 ± 1.1570 m²/g
Slope: 0.005379 ± 0.000008 g/cm³ STP
Y-Intercept: 0.000011 ± 0.000000 g/cm³ STP
C: 478.776212
Qm: 185.5028 cm³/g STP
Correlation Coefficient: 0.9999969
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)	1/[Q(p°/p - 1)]
0.020746233	173.0236	0.000122
0.028643726	178.0629	0.000166
0.039466207	183.5207	0.000224
0.051564900	188.3780	0.000289
0.078074240	196.4232	0.000431

Figure S21. BET report from the nitrogen adsorption measurement for hcp UiO-66 (textile LAG H_2O).

References

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3) Brunauer, S., Emmet, P. H., Teller, E. Adsorption of Gases in Multimolecular Layers. J. Amer. Chem. Soc., 60 (1938) 309 – 319.