

Supplementary Information

for

**Green and Rapid Mechanochemistry of High-
Porosity NU- and UiO-type Metal-Organic
Frameworks**

EXPERIMENTAL SECTION

Synthesis of acetate metal cluster $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CH}_3\text{COO})_{12}]_2$ (cluster 1)

Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CH}_3\text{COO})_{12}]_2$ was prepared according to literature method.¹ Zr (IV) propoxide (% 70 wt. % 1-propanol solution) (1 g, 3.05 mmol) and acetic acid (3.50 mL) (1:20 ratio) were mixed in a sealed beaker and left at RT overnight. Microcrystalline powder was collected by filter suction, washed gently with acetic acid and dried in air. Isolated yield: 0.825 g. The same procedure was used for preparing of up to 50 g of the acetate cluster. Fig. S3.

Synthesis of methacrylate metal cluster $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CH}_2\text{C}(\text{CH}_3)\text{COO})_{12}]$ (cluster 2)

Synthesis of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_2\text{H}_3\text{COO})_{12}$ was prepared according to literature method.² 1 mL solution of Zr (IV) propoxide (% 70 wt. % 1-propanol solution) (0.73 g, 2.22 mmol) was added to 1 mL methacrylic acid (11.8 mmol). The mixture was left overnight, volume reduced to half by evaporation and microcrystals started to precipitate. Solvents were completely removed under vacuum and resulting white powder analyzed by PXRD, FTIR-ATR and TGA. Fig S1.

Synthesis of DMF methacrylate metal cluster $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CH}_2\text{C}(\text{CH}_3)\text{COO})_{12}(\text{DMF})_4]$ (cluster 3)

40 mg of methacrylate cluster and 20 μL DMF were milled in PTFE (Teflon) jar (10 mL) with two stainless steel balls (1.38 mg each) for 5 min. at 25 Hz. The resulting product was analyzed by PXRD, FTIR-ATR and TGA. The crystals suitable for single crystal XRD were obtained by dissolution of **2** (30 mg) in minimal volume of DMF. The resulting solution was left for three days at RT, after which the prismatic crystals of **3** were harvested by filtration and washed with minimal portion of cold DMF. Fig S2.

Milling synthesis of NU-901 from the methacrylate cluster 2

0.042 g of H_4TBAPY was added to one half of PTFE milling vessel, followed by 100 μL of DMF and 2 stainless steel balls (7 mm diameter). **2** (0.055 g) was added to another part of the vessel, the vessel was snapped carefully and placed in the MM400 mixer mill. The reaction mixture was milled for 60 minutes on 30 Hz oscillation rate. After the milling was stopped, the product was scraped from the vessel, washed with 1 mL of DMF and dried in air, to yield 100 mg of yellow product. The BET surface of the activated product was 1165 m^2/g .

Milling synthesis of NU-901 from the acetate cluster 1

H_4TBAPY (53 mg) and cluster **1** (56.7 mg) were placed each in a separate halves of a PTFE milling vessel (14 mL). 60 μL of DMF was added to a half containing the ligand, the vessel was snapped together and the reaction mixture was milled for 90 minutes using MM400 mixer mill with 30 Hz oscillation rate and two stainless steel balls each weighing 1.4 g. The milling was stopped after 45 minutes for sampling and immediately continued for another 45 minutes. Both samples, the one from 45 minutes and the one from 90 minutes milling show peaks

characteristic for the NU-901 MOF in PXRD. After the milling was finished, the yellow solid product was isolated and washed with 1 mL of DMF to give finally 130 mg of the purified sample. The activated sample has a BET surface of 1610 m²/g. Aging in DMF vapors did not result in formation of NU-901 product.

Synthesis of NU-901 by accelerated aging in DMF vapors from Zr₆-benzoate cluster

The solid reactants Zr₆-benzoate cluster (150 mg, 0.056 mmol) and H₄TBAPY (76 mg, 0.112 mmol) were briefly ground manually in an agate mortar for 5 minutes. The mixture was then dispersed in a Petri dish, placed in a sealed chamber along with a container of DMF. The reaction mixture was left to stand at 45°C without any further mixing. NU-901 sample was synthesized by this method within two days. The resulting product was washed with DMF, filtered and dried to give a total amount of 110 mg, before subjected to further analysis. The sample has a BET surface of 1250 m²/g.

Synthesis of NU-901 by accelerated aging in DMF vapors from Zr₆-methacrylate cluster 2

The solid reactants Zr₆-methacrylate cluster (**2**) (95 mg, 0.056 mmol) and H₄TBAPY (76 mg, 0.112 mmol) were briefly ground manually in an agate mortar for 5 minutes. The mixture was then dispersed in a Petri dish, placed in a sealed chamber along with a container of DMF. The reaction mixture was left to stand at 45°C without any further mixing. Although NU-901 sample was successfully synthesized in a two days' period, a small amount of unreacted cluster **2** was still being observed. Thus, the resulting product was purified by washing with DMF, and then filtered and dried to give 130 mg of pure product, before subjected to further analysis.

Milling Synthesis of UiO-67 from Zr₆-methacrylate cluster 2

The optimized LAG reaction was achieved in a PTFE (Teflon) 14 mL jar, using two 1.4 g stainless steel balls and a Retsch MM400 or the Insolido Technologies IST500 mixer mill operating at 30 Hz. The solid reactants, Zr₆-methacrylate cluster (**2**) (170 mg, 0.1 mmol) and 4,4'-H₂BPA (145 mg, 0.6 mmol), were placed to the same part of the milling jar and gently mixed in a 1:6 molar ratio, followed by the addition of DMF in a one-pot, two-step procedure. In a total amount of 315 mg of solid reactants, 300 µL of DMF was initially added to the reaction mixture and the milling process was firstly conducted for 90 minutes. The reaction was then stopped and the mixture was analyzed via XRD measurement. The PXRD data collected at this point, revealed the formation of compound **3**, along with the appearance of the characteristic peaks of UiO-67 structure. The reaction mixture was then treated with the addition of an extra volume of DMF (+ 300 µL) and the milling was continued for another 90 minutes. By the end of the total milling time (180 min) and the addition of a total 600 µL of DMF, the pure form of UiO-67 structured was isolated and scraped off the jar walls, in the form of white crystalline powder. The final mixture was washed with DMF, centrifuged and dried in a vacuum oven for 30 minutes, to give 170 mg of pure product. Product was subjected to further analysis.

Synthesis of UiO-67 by accelerated aging in DMF vapors from Zr₆-meth cluster (2)

The solid reactants Zr₆-methacrylate cluster (**2**) (170 mg, 0.1 mmol) and 4,4'-H₂BPA (145 mg, 0.6 mmol) were briefly ground manually in an agate mortar for 2 minutes. The mixture was then dispersed in a Petri dish, placed in a sealed chamber along with a container of DMF. The reaction mixture was left to stand at 45°C without any further mixing. UiO-67 sample was synthesized by this method in a period of 7 days. The resulting product was washed with DMF, filtered and dried to give a total amount of 180 mg, before subjected to further analysis.

Gram-scale milling synthesis of UiO-67 from Zr₆-meth cluster 2

UiO-67 (1.2 g) was successfully isolated after 260 minutes of milling in a zirconia (ZrO₂) 50 mL vessel, using two 3.0 g zirconia balls and Spex 8000 mixer mill. Cluster **2** (1 g, 0.59 mmol) was mixed with 0.81 g (3.33 mmol) of 4,4'-H₂BPA, followed by the addition of 1.65 mL of DMF ($n=0.91$ mg/ μ L). The final mixture was washed, filtered and dried under vacuum.

Milling synthesis of UiO-67 from the Zr₁₂-acetate cluster 1

Optimized LAG assisted milling reaction of UiO-67 was performed in mixer mill at 25 Hz, with the milling duration of 90 min. Precursor **1** (89.5 mg, 0.032 mmol), biphenyl-4,4'-dicarboxylic (93.8 mg, 0.387 mmol) (molar ratio of 1:12) and 100 μ L DMF were placed into a PTFE (Teflon) jar (10 mL) with two stainless steel balls (1.38 mg each) and milled for 90 minutes. The resulting white powder was analyzed by PXRD, FTIR-ATR and TGA. Isolated: 150 mg.

Ex situ PXRD measurements were performed on a Panalytical Aeris (research edition) diffractometer with Cu K α radiation (40 kV, 7.5 mA) in Bragg Bretano geometry.

In situ PXRD experiments were performed at the High Resolution Powder Diffraction Beamline P02.1 (DESY, Hamburg) using an unfocused and collimated X-ray beam with the size of ca. 1 x 1 mm². The beamline is equipped with a PerkinElmer 2D area detector. The wavelength was determined with a NIST NSR 660a (LaB₆) standard to be 0.20743(3) Å (59.77 keV) and 0.20715(1) Å (59.853 keV), respectively. All 2D PXRD patterns were integrated using Fit2D.³ All *in situ* reactions were performed using a modified MM400 Retsch mill with 14 mL PMMA reaction jars, 2 stainless steel balls (each weighing 1.4 g) and at a milling frequency of 30 Hz.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were performed using a Shimadzu DTG-60H instrument, in range of 30-800 °C and in the air atmosphere, and, unless stated different, with 10 °C/min heating rate.

FTIR-ATR Analysis.

Fourier-transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) was performed using the Perkin-Elmer SpectrumTwo spectrometer equipped with diamond cell. The data was collected in the range of 4400 cm^{-1} to 500 cm^{-1} and with resolution of 4 cm^{-1} . The data was processed using a Spectrum software (version 10.5.3.738, 2016).

Nitrogen adsorption-desorption measurements

Nitrogen adsorption and desorption isotherm measurements were performed on a Micromeritics Tristar II at 77K. All gases used were Ultra High Purity Grade 5 gases from Airgas Specialty Gases. Prior to measuring the nitrogen adsorption-desorption isotherms, the materials were activated as described below.

Scanning electron microscopy (SEM)

SEM micrographs were collected using JEOL JSM-7000F Field Emission Scanning Electron Microscope. Samples were not coated with conductive layer.

Activation of UiO-67 and NU-901 samples

Samples were shipped to Northwestern University as wet powders containing a minimal amount of DMF. Each sample (≈ 60 mg each) was then soaked in 12 mL of acetone in a 15 mL polypropylene centrifuge tube. After soaking for 3 hours, the MOF sample was centrifuged and the acetone was removed using a Pasteur pipette. 12 mL of fresh acetone was then added to the MOF sample in the 15 mL polypropylene centrifuge tube. The sample was allowed to soak in the fresh acetone for 3 hours before repeating centrifugation and removal of solvent. Finally, 12 mL of fresh acetone was added to the MOF sample in the 15 mL polypropylene centrifuge tube and allowed to soak for 18 hours before repeating centrifugation and removal of solvent. The sample was then placed in a vacuum oven set at 80 $^{\circ}\text{C}$ for 6 hours to remove the majority of the acetone in the sample. Lastly, the MOF was thermally activated under ultra-high vacuum at 120 $^{\circ}\text{C}$ for 18 h on a Micromeritics Smart VacPrep instrument.

HCl activation of NU-901

Prior to the solvent exchange activation procedure described above, sample of NU-901 were also subject to HCl activation using the same procedure commonly used for NU-1000 and described in the literature.⁴ This procedure is performed to remove any monotopic ancillary ligands (benzoic acid, acetic acid etc) that may be coordinated to the four remaining sites on the eight-connected Zr_6 -node of these MOFs.

Nerve agent simulant hydrolysis experiments

Hydrolysis reactions were analysed by in-situ ^{31}P NMR measurement at room temperature. Tested catalyst (1.5 μmol) was loaded into a vial, followed by the addition of 1 mL of 0.4 M

N-ethylmorpholine solution (0.05 mL *N*-ethylmorpholine, 0.9 mL water/0.1 mL D₂O). The resulting suspension was sonicated for 5 min to disperse homogeneously. 4 μL (25 μmol) of DMNP was added to mixture solution and swirled. The reaction mixture was then transferred to an NMR tube and the NMR spectrum was immediately measured.

Crystallographic Section:

Single crystal X-ray study of **1**

As the structure of cluster **1** differs from the recently published one, we solved and refined the structure of **1** from single crystal prepared by slow evaporation of a mixture of Zr(propoxide)₄ and acetic acid (1:20 molar ratio). Diffraction measurements were performed on an Oxford Diffraction Xcalibur Nova R (microfocus Cu tube) at 118 K. Data reduction was performed using the program package CrysAlisPRO.⁵ The structures were solved using SHELXT⁶ and refined with SHELXL-2014⁷ contained in WinGX v2014.1⁸ program package. The non-H atoms were treated anisotropically, whereas the aromatic H atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. We used PLATON SQUEEZE method⁹ to account for the large solvent-accessible voids in the structural model. The cif file contains both the unsqueezed data (the '_shelx_hkl_file' block) and the corrections for solvent (the '_shelx_fab_file' block). CCDC 1830216 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. The crystallographic data for **1** are listed in Table S1.

Single crystal X-ray study of **3**

Crystal and molecular structure of **3** was determined by single crystal X-ray diffraction. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation.¹⁰ The data sets were collected using the ω scan mode over the 2θ range up to 54°. The structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively.¹¹ The structural refinement was performed on F^2 using all data. The hydrogen atoms not involved in hydrogen bonding were placed in calculated positions and treated as riding on their parent atoms [C-H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$; C-H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$]. The hydroxyl hydrogen atoms were located from the electron difference map and refined isotropically with the O-H distance restrained to 0.95(1) Å. The crystallographic data are listed in Table S1. All calculations were performed using the WINGX crystallographic suite of programs.¹²

CCDC 1837734 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

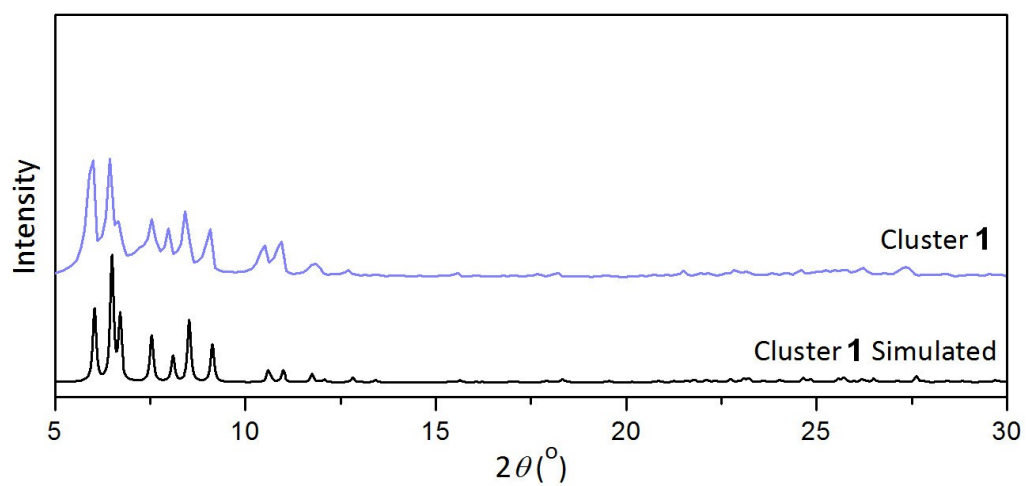


Figure S1. PXRD patterns for cluster 1. $\lambda = 1.54 \text{ \AA}$.

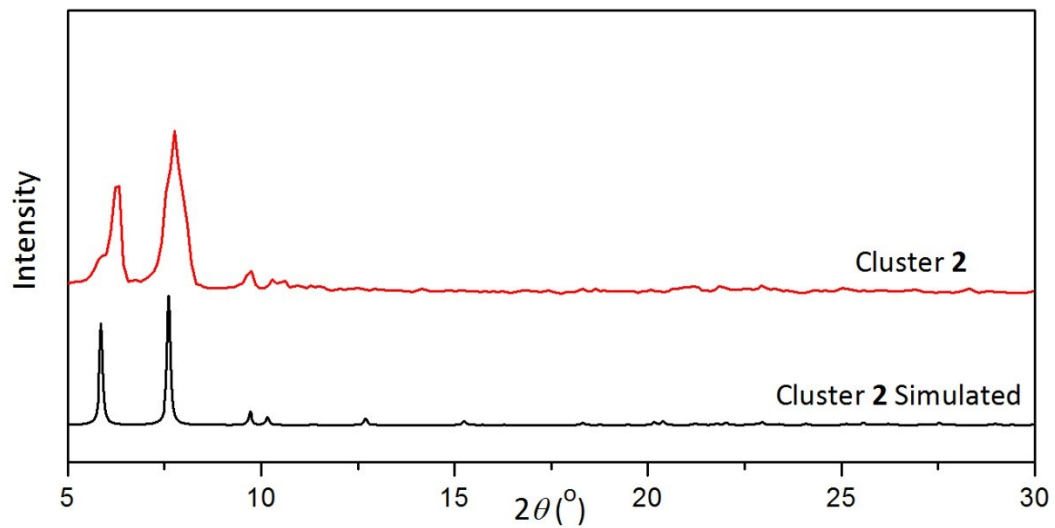


Figure S2. PXRD patterns for cluster **2**. $\lambda = 1.54 \text{ \AA}$.

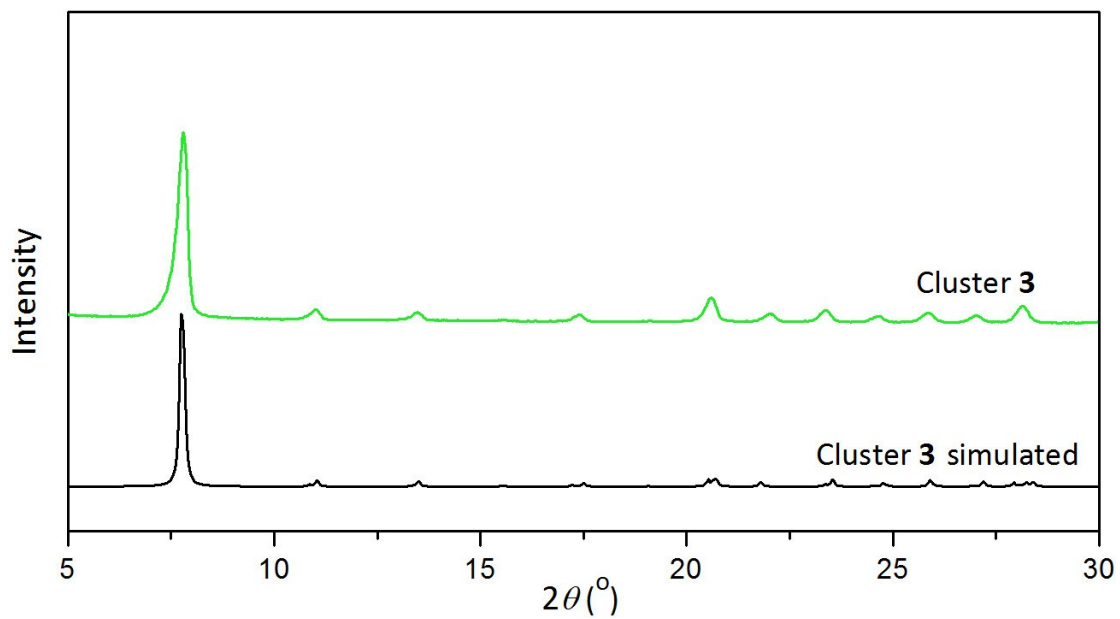


Figure S3. PXRD patterns for cluster **3** obtained by milling of **2** in the presence of DMF. $\lambda = 1.54 \text{ \AA}$.

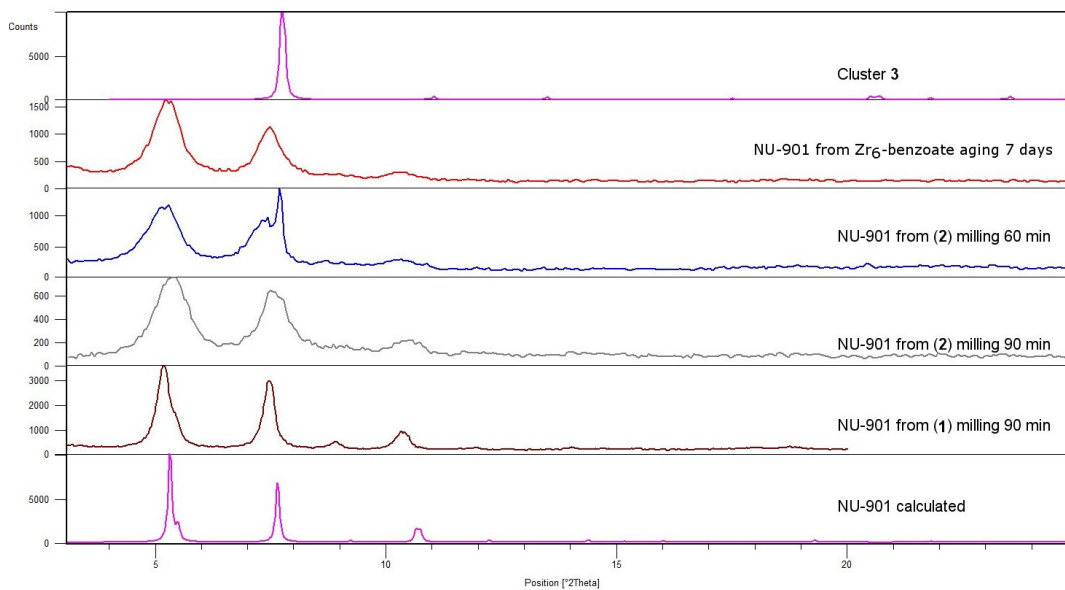


Figure S4. PXRD patterns for selected samples in LAG (DMF) synthesis of NU-901 MOF from different preorganized clusters. While the milling synthesis of NU-901 from benzoate cluster was not successful, the NU-901 with a BET surface of 1250 m²/g was synthesized by aging of the pre-milled (**Zr₆_benzoate**):H₄**TBAPY** (1:2 molar ratio) reaction mixture in DMF vapors for 3-7 days at 45 °C, second PXRD from top. In the LAG from precursor **2**, the formation of cluster **3** is clearly visible in the sample isolated after 60 minutes milling, and the pure product was gained only after thorough washing with DMF (gray, third PXRD from bottom). $\lambda = 1.54 \text{ \AA}$.

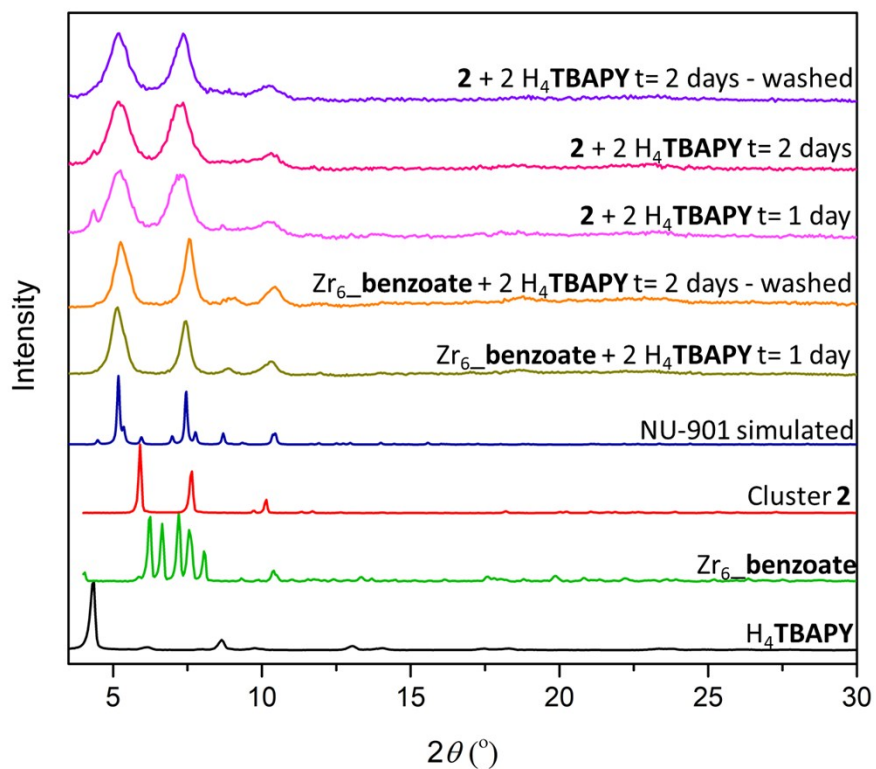


Figure S5. PXRD patterns for selected samples in aging synthesis of NU-901 MOF from different preorganized clusters. While the milling synthesis of NU-901 from benzoate cluster was not successful, the NU-901 with a BET surface of 1250 m²/g was synthesized by aging of the pre-milled **Zr₆-benzoate**:**H₄TBAPY** (1:2 molar ratio) reaction mixture in DMF vapors for 7 days at 45 °C. The aging procedures were inefficient for the NU-901 syntheses from cluster **1**. $\lambda = 1.54 \text{ \AA}$.

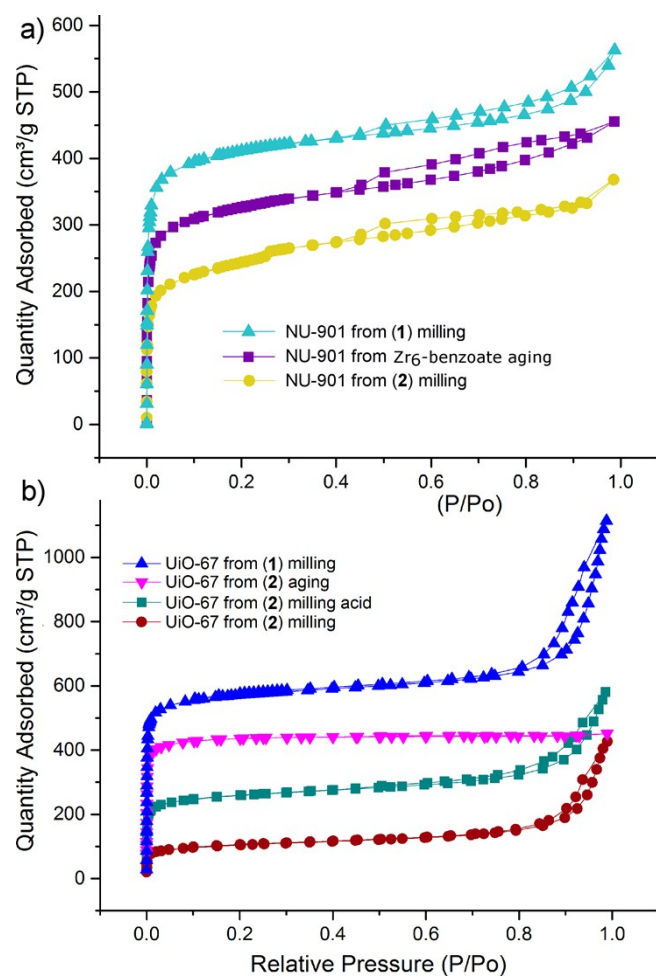


Figure S6. N_2 sorption isotherms at 77 K for: a) NU-901 samples from LAG syntheses and after HCl activation using Zr₆-benzoate, **1** or **2** as a precursor; (b) UiO-67 MOF materials prepared by LAG syntheses.

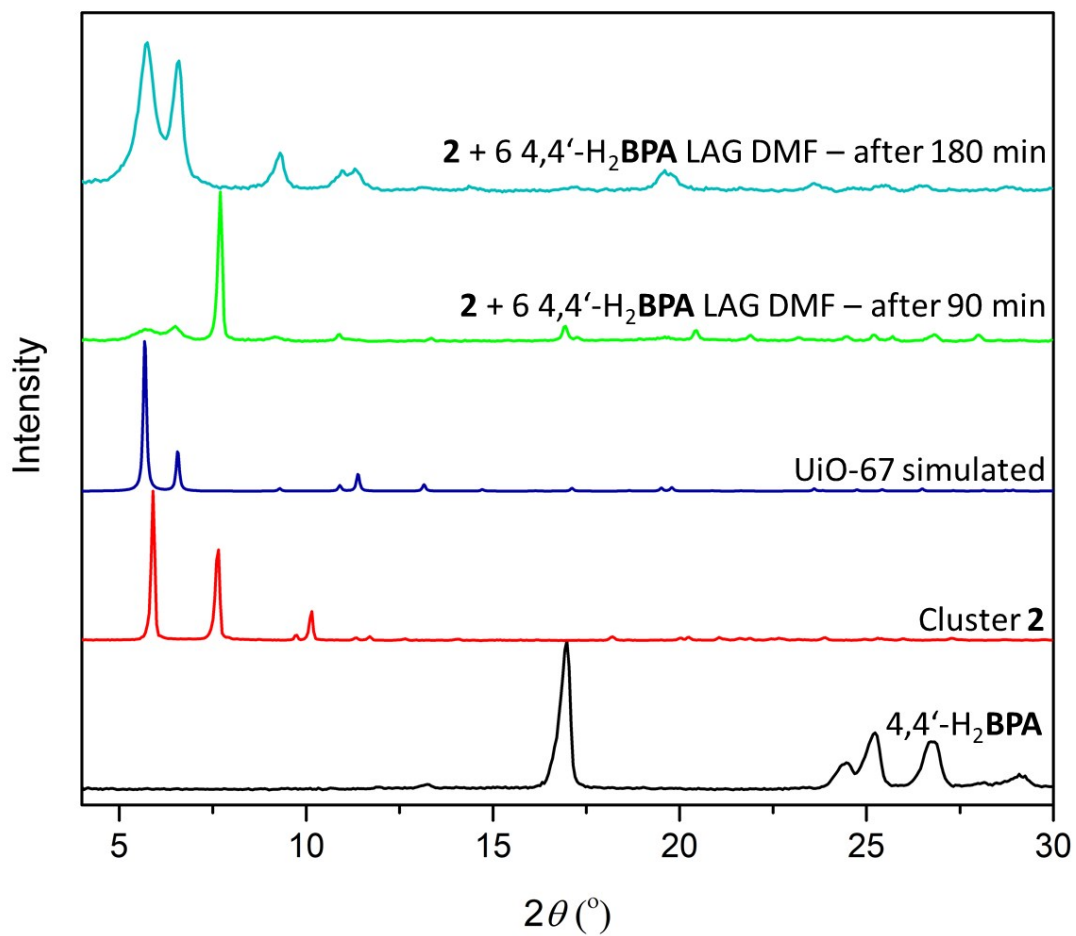


Figure S7. PXRD patterns for selected samples in milling synthesis of UiO-67 from cluster 2. The UiO-67 simulated pattern (blue) corresponds to the CSD code WIZMAV. $\lambda = 1.54 \text{ \AA}$.

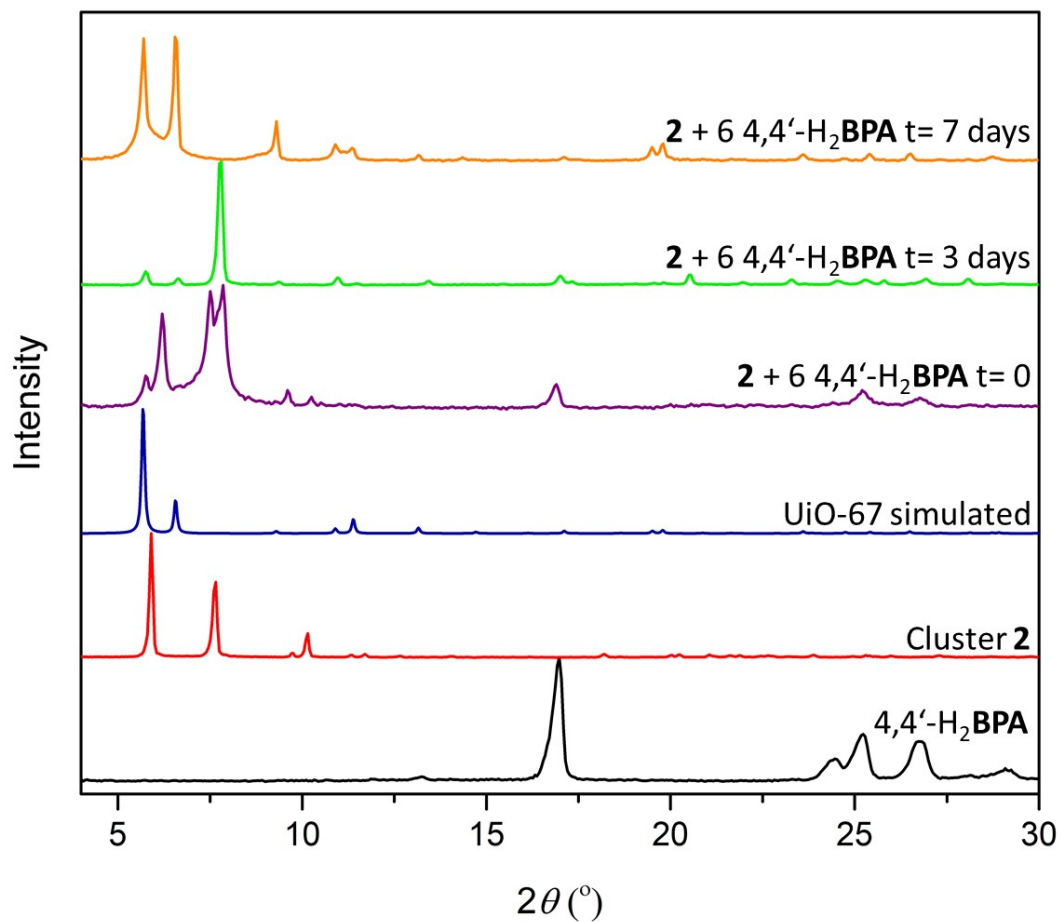


Figure S8. PXRD patterns for UiO-67 synthesis by accelerated aging in DMF vapors (45°C). $\lambda = 1.54 \text{ \AA}$. Both **Zr₆-benzoate** cluster and cluster **1** proved inefficient for the aging syntheses of UiO-67.

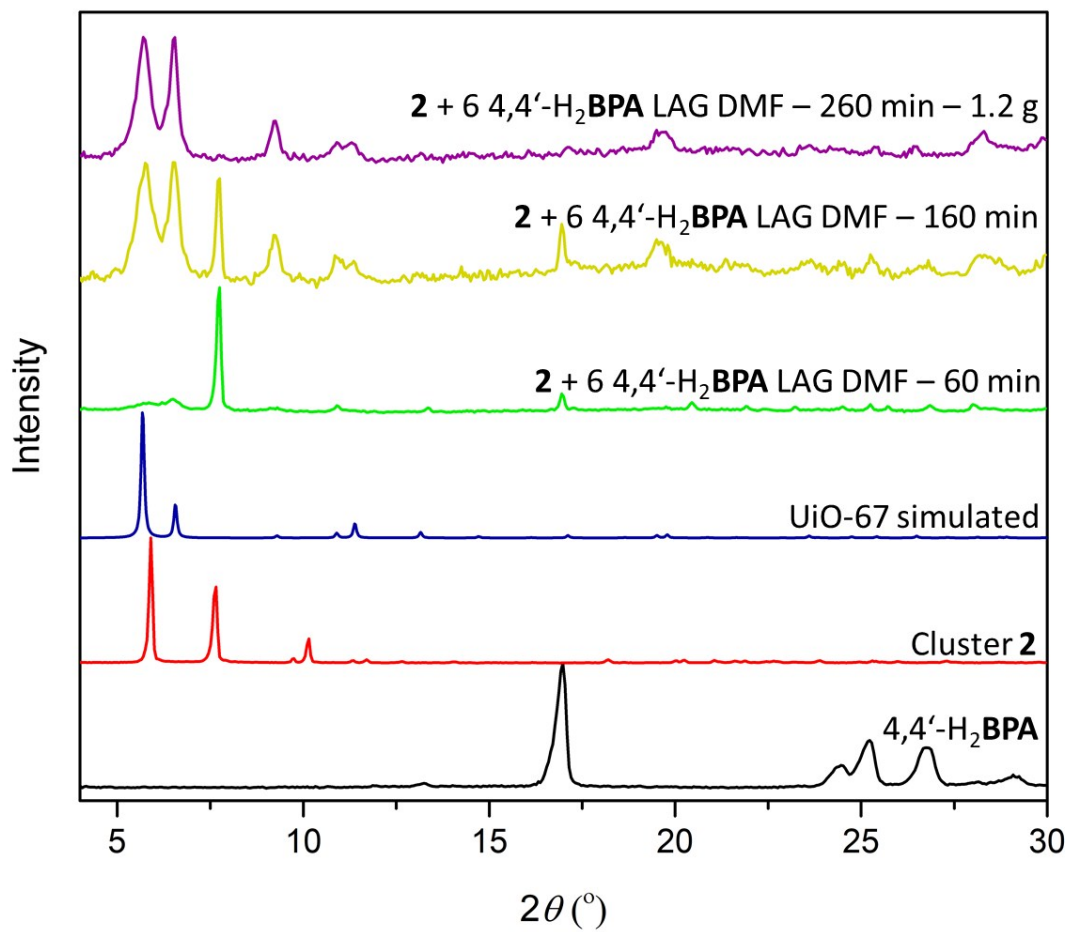


Figure S9. PXRD patterns for the gram-scale production of UiO-67 from cluster 2. $\lambda = 1.54 \text{ \AA}$.

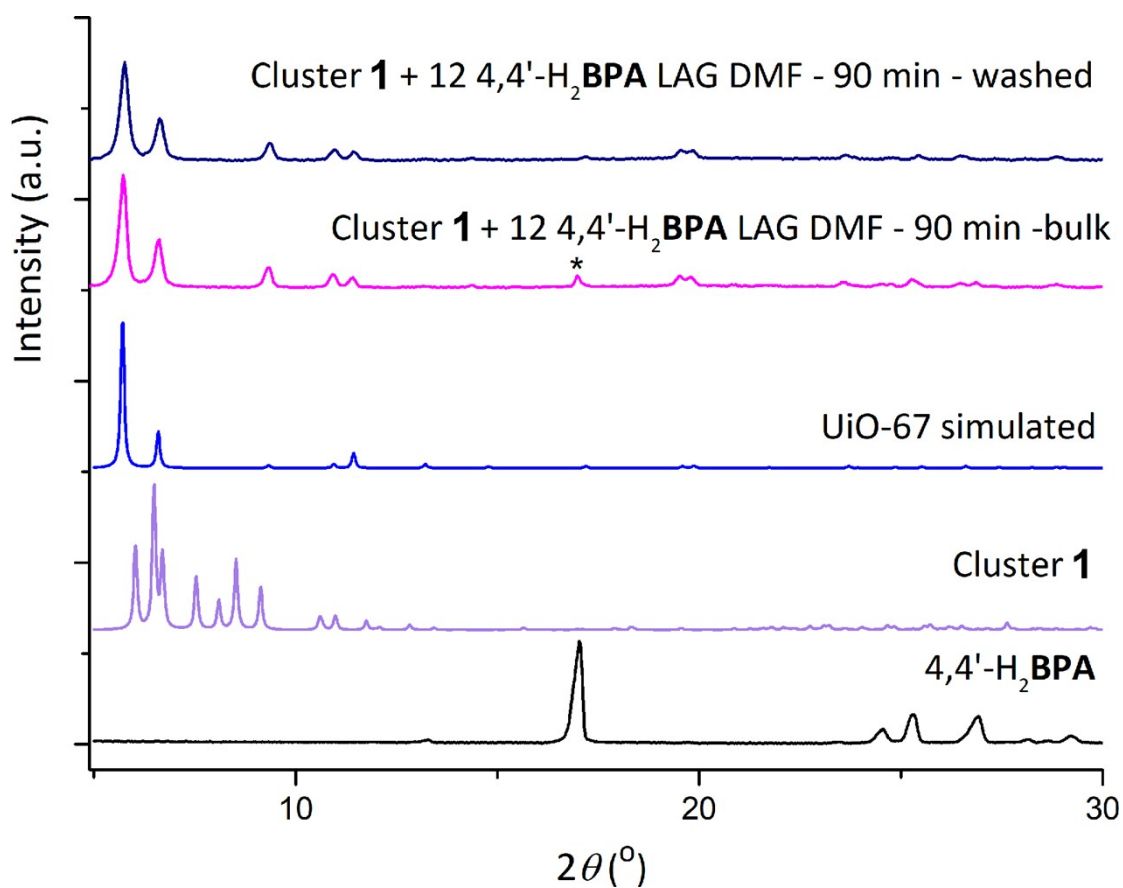


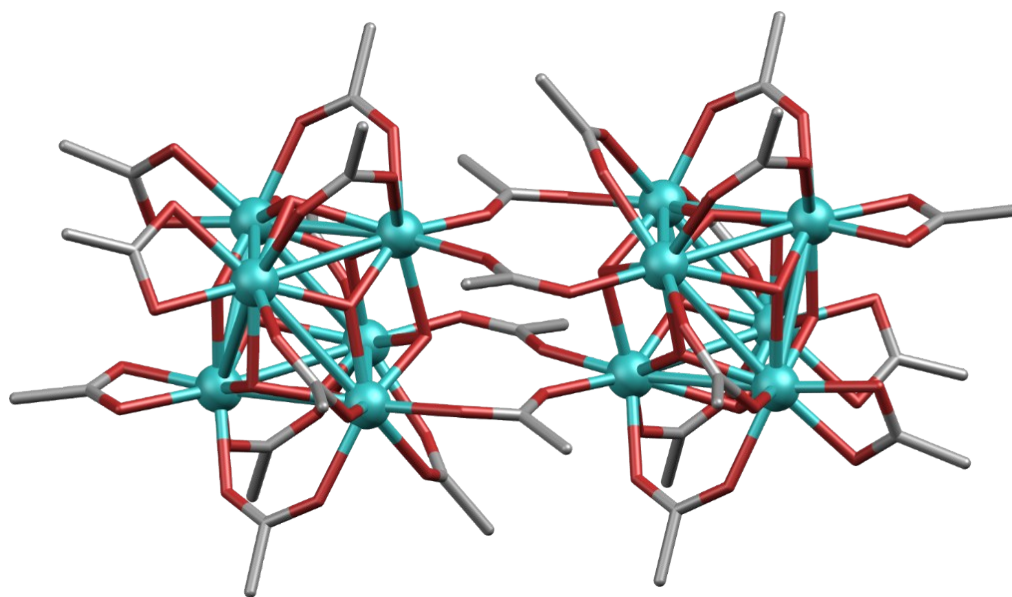
Figure S10. PXRD patterns for the milling synthesis of UiO-67 from cluster **1**. $\lambda = 1.54 \text{ \AA}$. Bragg maximum corresponding to 4,4'-H₂BPA in the bulk sample is highlighted with asterisk. UiO-67 obtained from **1** has a BET surface of 2250 m²/g.

Crystallographic tables and figures

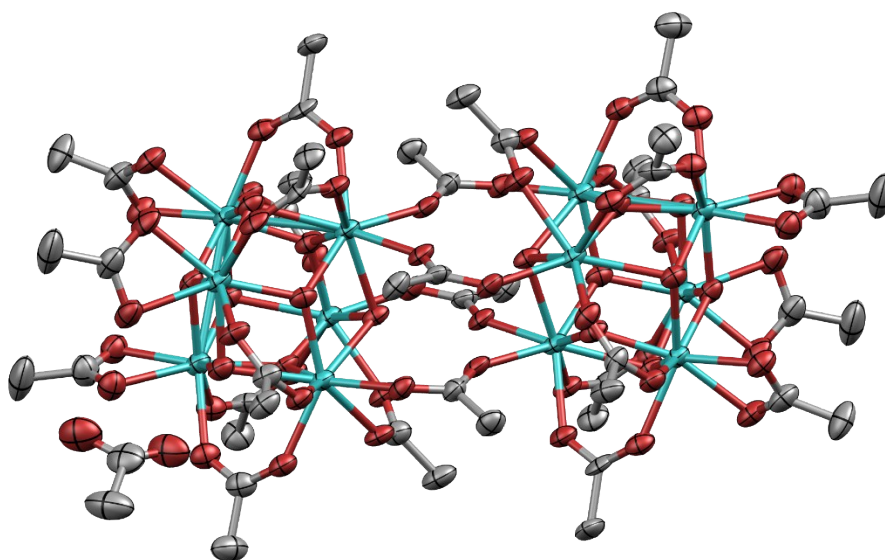
Table S1. Crystal data and summary of experimental details for clusters **1** and **3**.

	1	3
Empirical formula	C _{51.20} H _{86.40} O _{71.20} Zr ₁₂	C ₆₀ H ₉₂ N ₄ O ₃₆ Zr ₆
Formula weight	2935.84	1992.69
Temperature	118(2) K	150.0(2)
Wavelength	1.54184 Å	0.71073 Å
Crystal system	Triclinic	Tetragonal
Space group	<i>P</i> -1	<i>I</i> -4
Unit cell dimensions	<i>a</i> = 12.5793(8) Å, <i>α</i> = 116.322(6)° <i>b</i> = 15.7491(8) Å, <i>β</i> = 93.693(6)° <i>c</i> = 16.7679(13) Å, <i>γ</i> = 106.969(5)°	<i>a</i> = 16.0037(4) <i>b</i> = 16.0037(4) <i>c</i> = 16.2833(13)
Volume	2774.1(3) Å ³	4170.5(4)
<i>Z</i>	1	2
Density (calculated)	1.757 g/cm ³	1.587 g/cm ³
Absorption coefficient	9.685 mm ⁻¹	0.806 mm ⁻¹
<i>F</i> (000)	1443	2016
Crystal size	0.3 x 0.2 x 0.1 mm ³	0.32 × 0.21 × 0.11 mm ³
<i>θ</i> range for data collection	3.018 to 58.928°	3.964 to 26.993°
<i>hkl</i> range	-13, 12; -17, 17; -17, 18	-20, 20; -20, 20; -19, 20
Reflections collected	17266	18520
Independent reflections	7922	4543
Completeness	99.5%	99.6%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Number of restraints / parameters	17 / 625	1 / 249
Goodness-of-fit	0.996	0.969
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> _{obs} = 0.0657, <i>wR</i> _{obs} = 0.1595	<i>R</i> _{obs} = 0.0163, <i>wR</i> _{obs} = 0.0386
<i>R</i> indices [all data]	<i>R</i> _{all} = 0.0962, <i>wR</i> _{all} = 0.1855	<i>R</i> _{all} = 0.0188, <i>wR</i> _{all} = 0.0389
Largest diff. peak and hole	2.048 and -0.888 e·Å ⁻³	0.228 and -0.209 e·Å ⁻³

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR = \{\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(|F_o|^4)]\}^{1/2}$ and $w = 1 / [\sigma^2(F_o^2) + (0.1019P)^2]$ where $P = (F_o^2 + 2F_c^2) / 3$



a)



b)

Figure S11. a) Stick representation of molecular structure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CH}_3\text{COO})_{12}]_2$ (cluster **1**); and b) ORTEP view of **1** with displacement ellipsoid plots at the 50 % probability level. Hydrogen atoms are omitted for clarity sake

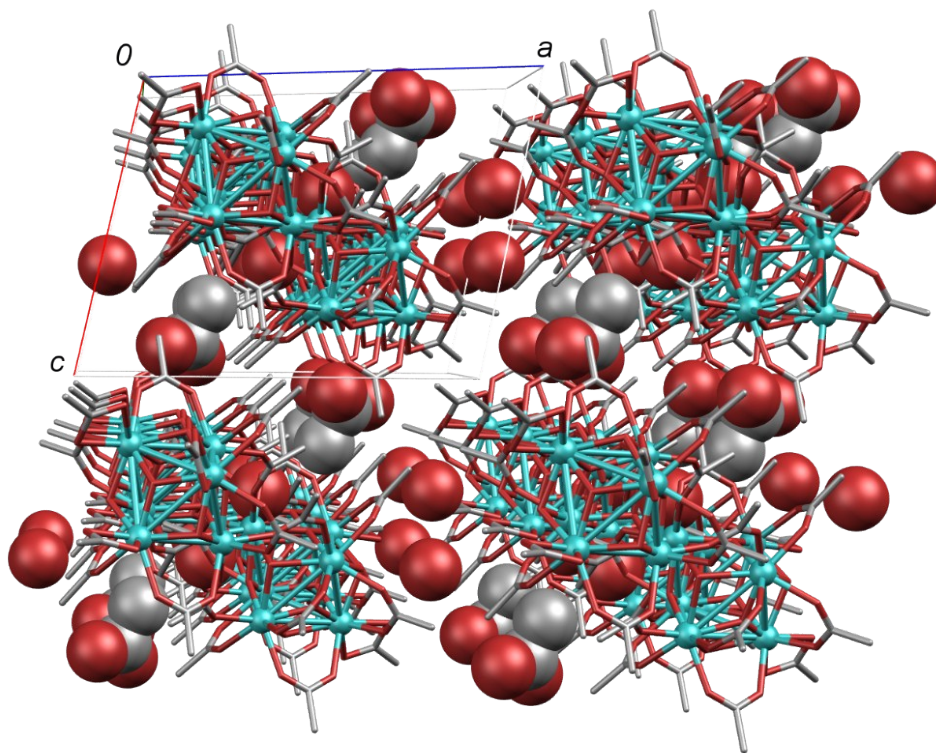
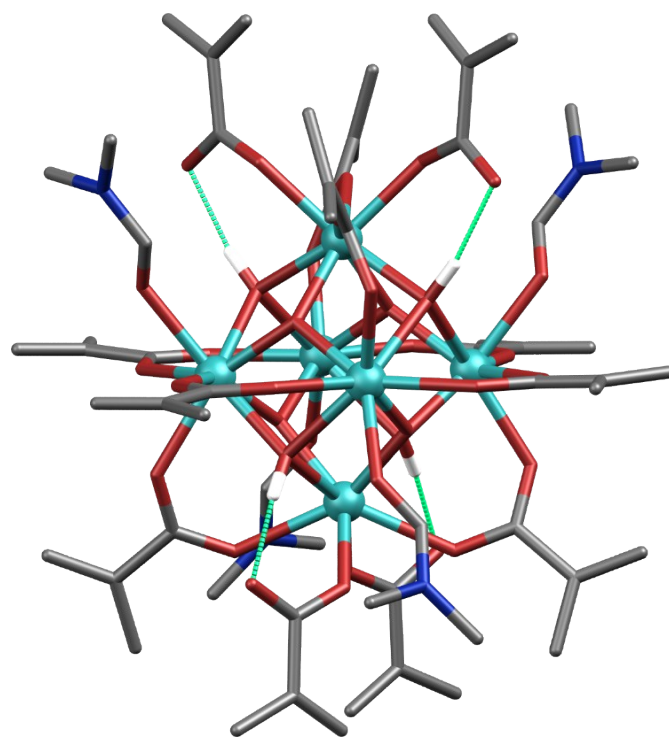
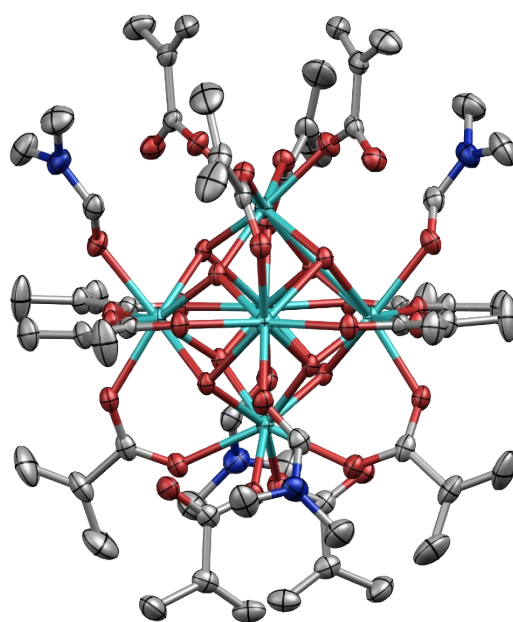


Figure S12. Crystal packing of cluster **1** viewed down the *b*-crystallographic axis.



(a)



(b)

Figure S13. a) Molecular structure of cluster **3**. Intramolecular O–H···O hydrogen bonds are denoted with green stippled lines; b) ORTEP view of **3** with displacement ellipsoid plots at the 50 % probability level.

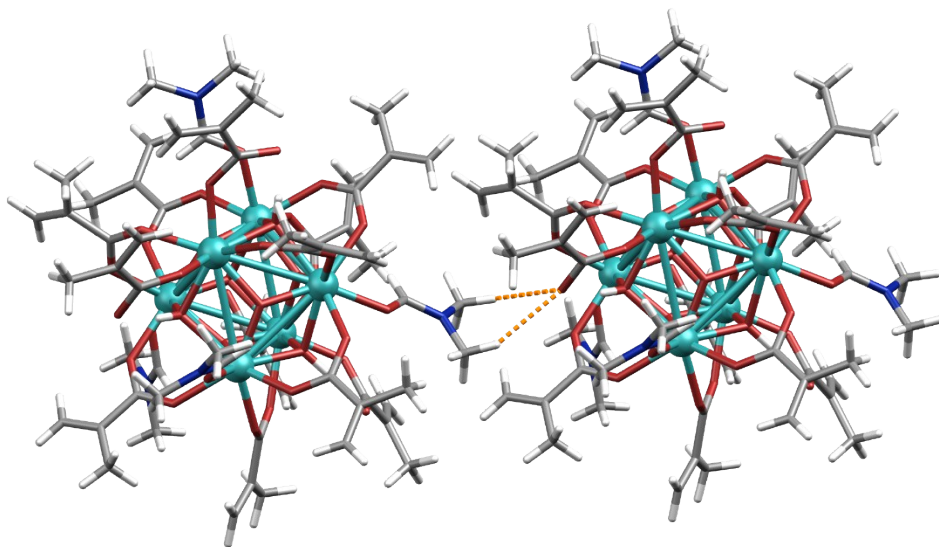


Figure S14. Stabilization of the crystal structure of **3** is conducted over C–H···O interactions between the coordinated DMF molecule and methacrylate carboxyl group of the other cluster molecule. C–H···O bonds are denoted with an orange stippled lines.

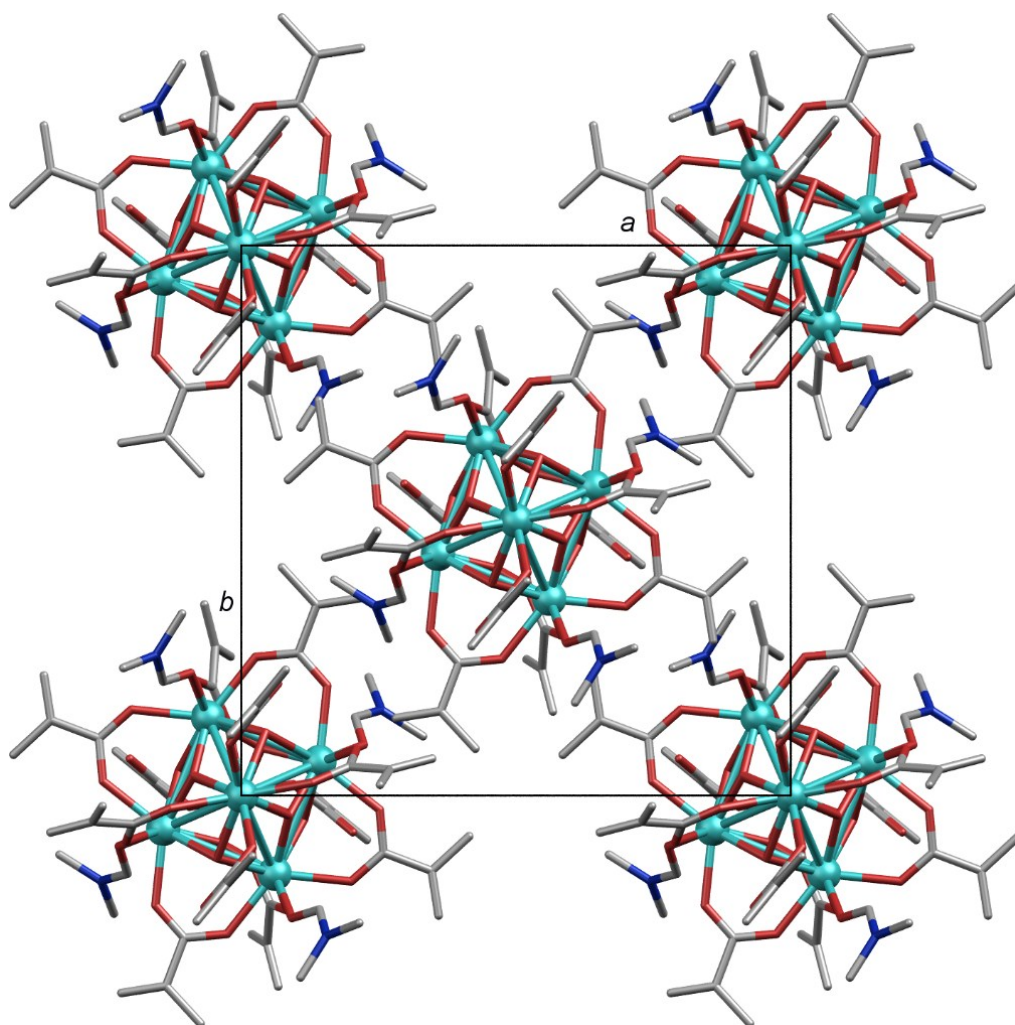


Figure S15. Crystal packing of **3** viewed down the c-crystallographic axis.

FTIR-ATR Analysis

Fourier-transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) was performed using the Perkin-Elmer SpectrumTwo spectrometer equipped with diamond cell. The data was collected in the range of 4400 cm^{-1} to 500 cm^{-1} and with resolution of 4 cm^{-1} . The data was processed using a Spectrum software (version 10.5.3.738, 2016).

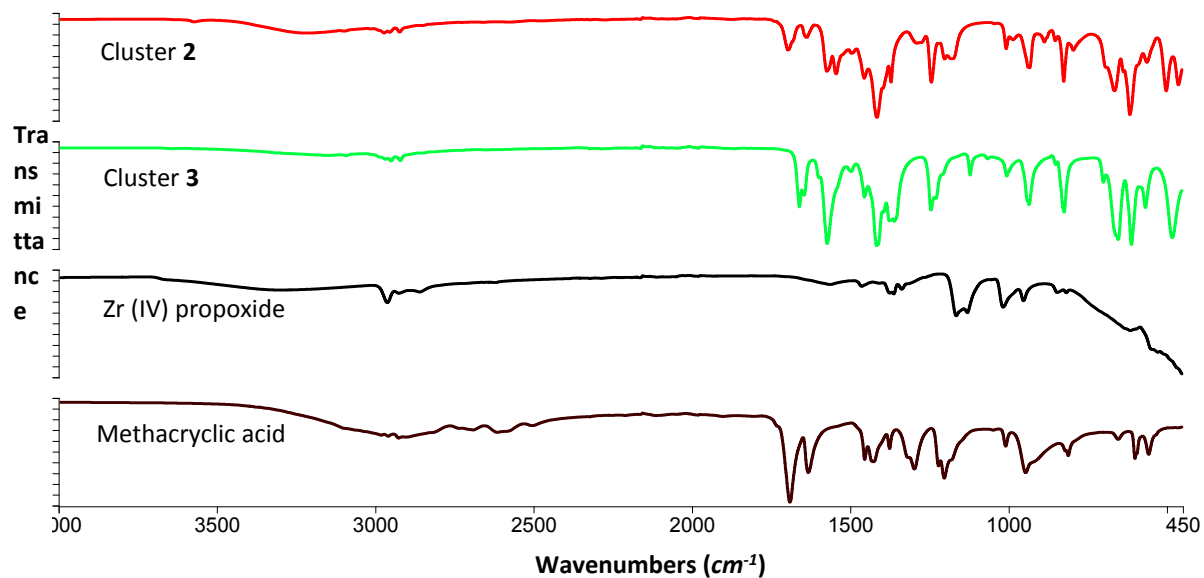


Figure S16. FTIR-ATR spectra for cluster 2 and cluster 3.

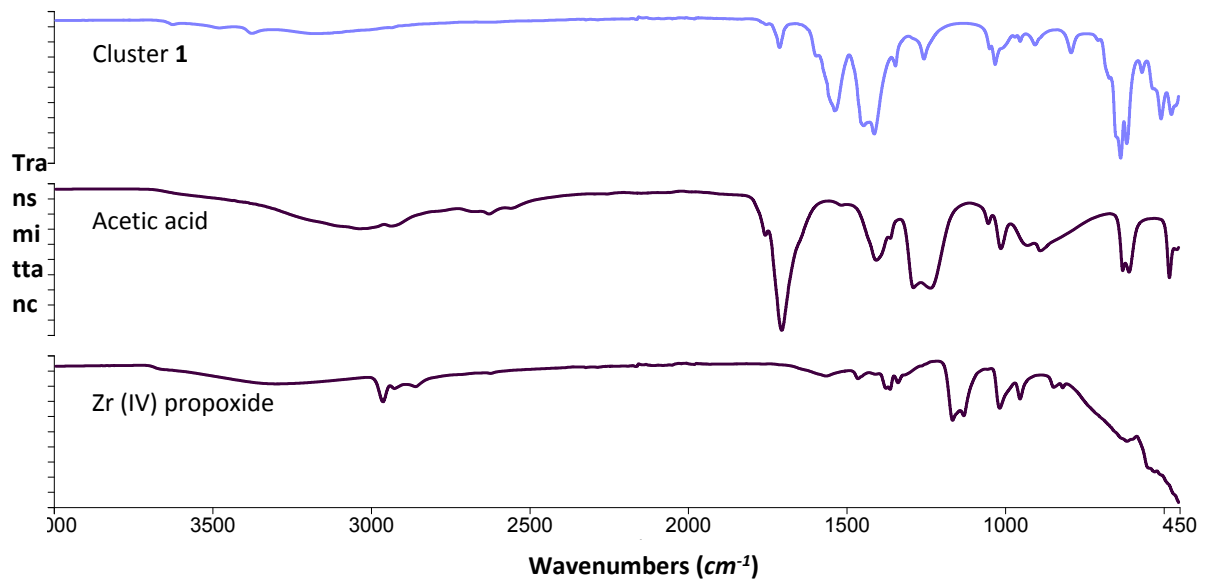


Figure S17. FTIR-ATR spectrum for cluster **1**.

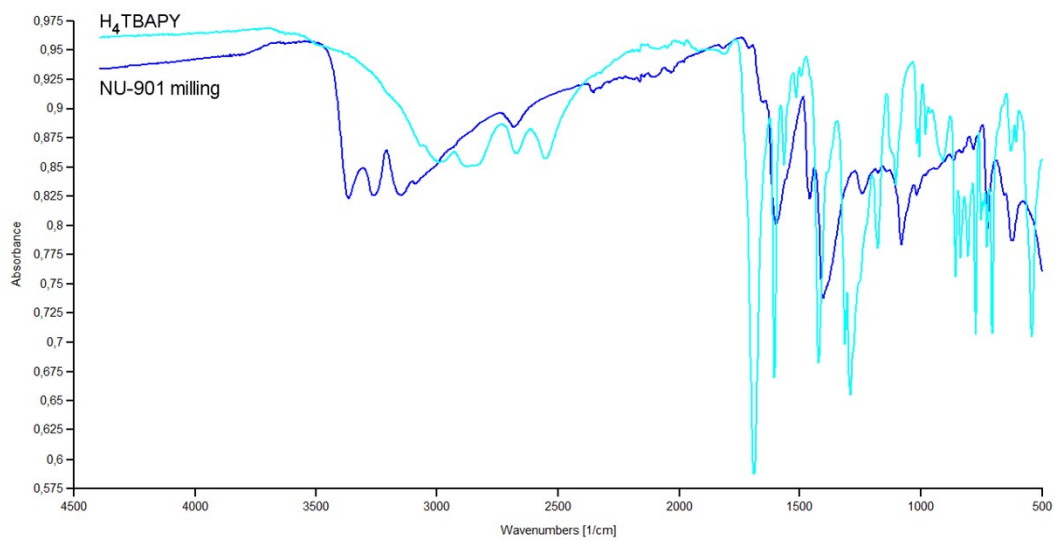


Figure S18. FTIR-ATR spectra for NU-901 prepared by LAG using DMF.

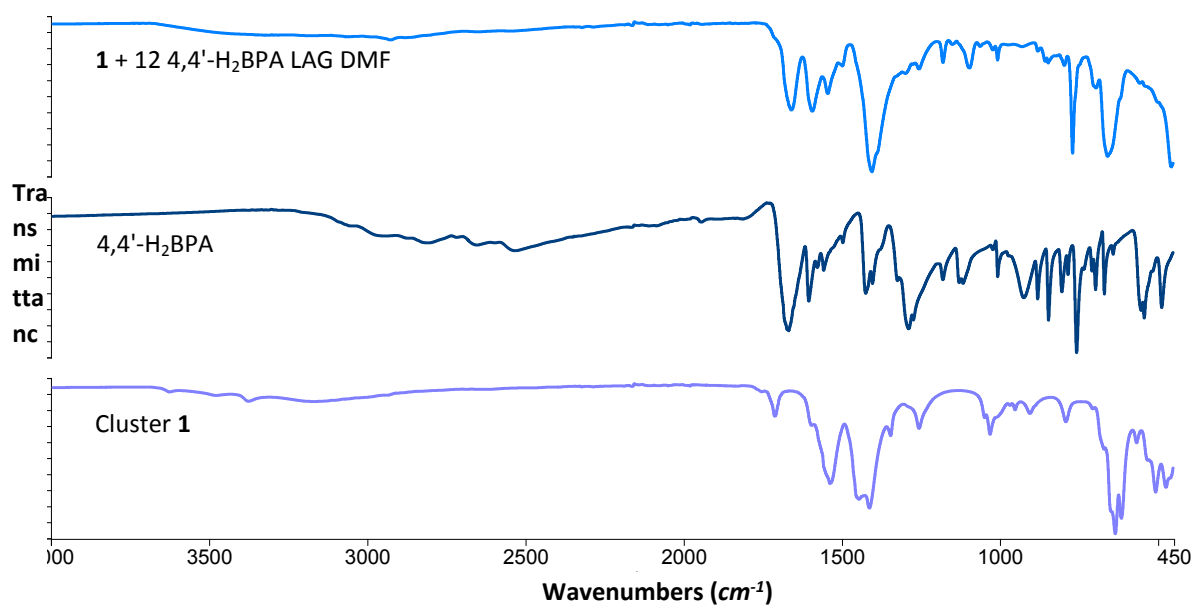


Figure S19. FTIR-ATR spectrum for UiO-67 prepared by LAG using DMF additive.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were performed using a Shimadzu DTG-60H instrument, in range of 30-800 °C and in the air atmosphere, and, unless stated different, with 10 °C/min heating rate.

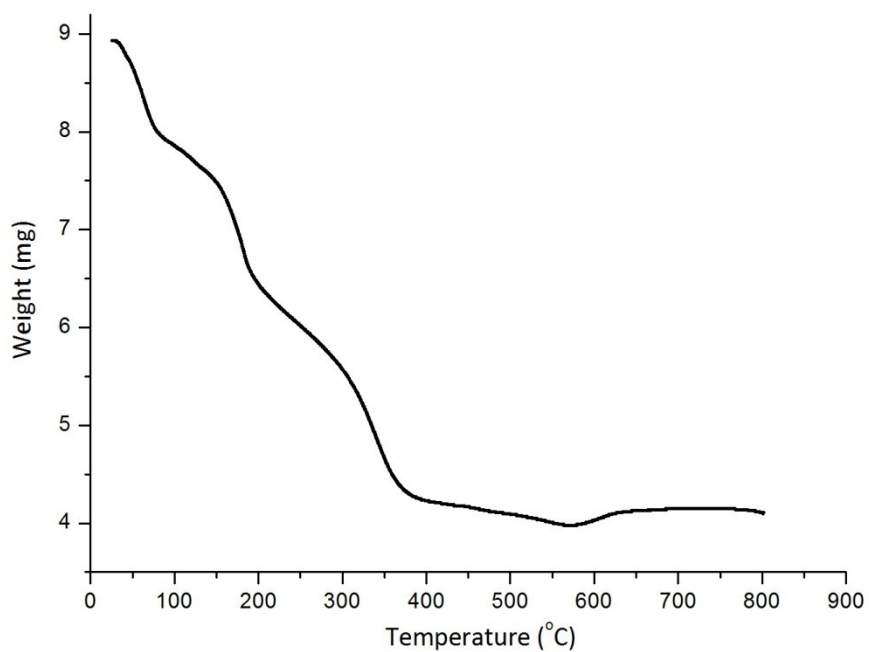


Figure S20. TGA graph of cluster **1**. Acetic acid and water loss was observed around 150 °C. Above this temperature mass loss of cluster **1** was observed. The mass above 390 °C is assumed as ZrO₂ (4.1 mg) and confirmed with PXRD.

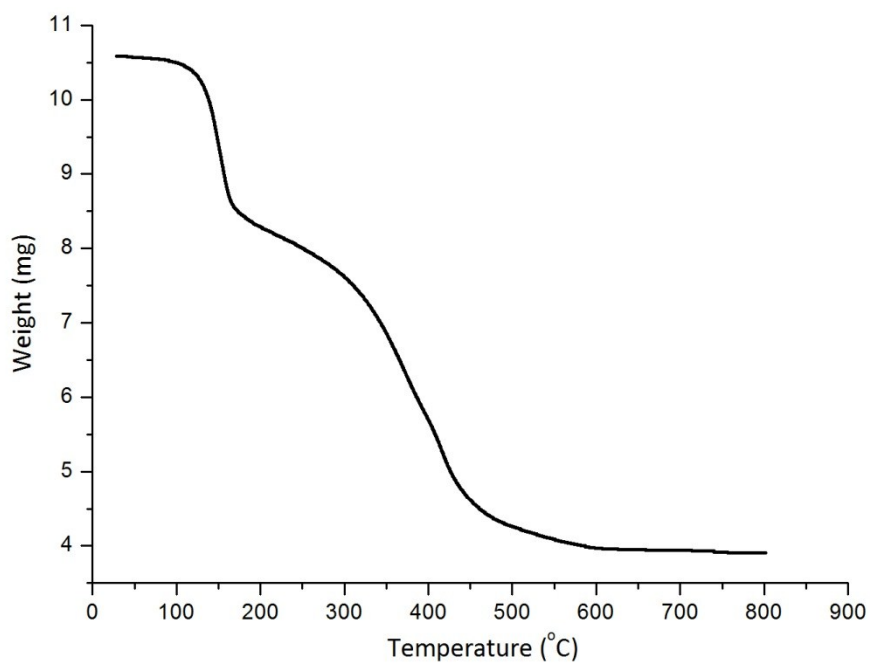


Figure S21. TGA graph of cluster **3** in air. The first step indicates DMF and methacrylic acid loss (1.93 mg, % 18.22). Mass loss of cluster **3** (4.75 mg, % 54.84) was observed around 300 °C. The mass above 500 °C is assumed as ZrO₂ (3.91 mg) and confirmed with PXRD.

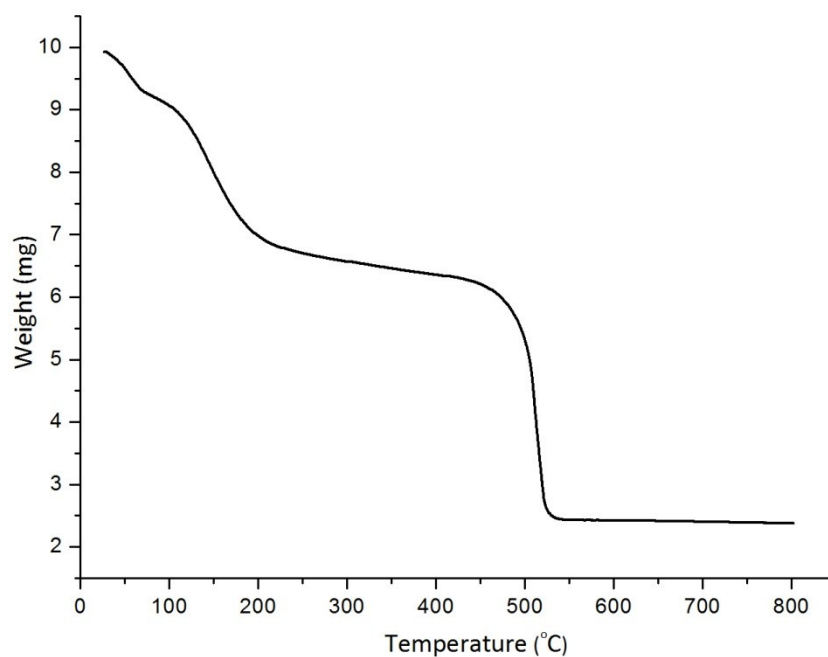


Figure S22. TGA graph of UiO-67. The solvent loss (%32.76, 3.27 mg) was observed near 50 °C followed by a drop at 250 °C. Mass loss was observed around 500 °C and above this temperature represents formation of ZrO_2 . Mw UiO-67(desolvated, $Zr_6O_6(BPDC)_n$): 2083, Mw for six 4,4'BPDC: 1453.38. During decomposition step of UiO-67, 4.32 mg ligand loss (% 64.3 exp., % 69.7 calc. $n = 5.53$ BPDC ligands) was observed. ZrO_2 residue was found as 2.38 mg (%23.84).

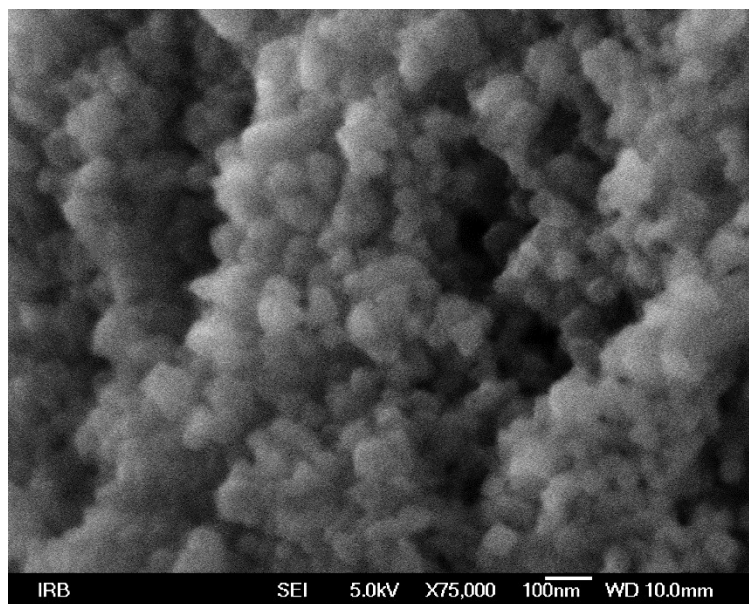


Figure S23. SEM micrograph of UiO-67 sample prepared from cluster **1** using described LAG procedure.

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