Postsynthetic Ligand Exchange as a Route to Functionaliation in 'Inert' Metal-Organic Frameworks

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SUPPORTING INFORMATION

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General Methods for Metal-Organic Frameworks Experiments.

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded by a Varian FT-NMR spectrometer (400 MHz for ^{1}H/ 100 MHz for ^{13}C). Carbon nuclear magnetic resonance spectroscopy was fully decoupled by broad band decoupling. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d= doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz).

General Methods for Aerosol Time-of-Flight Mass Spectrometry Experiments.

Dry UiO materials were aerosolized using sonication and were drawn into an ATOFMS where they were accelerated to their terminal aerodynamic velocity.[1] The particles pass through two continuous-wave diode pumped 532 nm lasers beams (Crystal Laser, Reno, NV) positioned 6 cm apart. By measuring the time difference between the scatter pulses from these two lasers, the velocity of the particles can be determined. The characteristic speed and the known distance of the two scattering lasers are used to determine the aerodynamic diameter of each particle using a calibration curve generated by know-size polystyrene latex sphere particles (PSL, Inviterogen), as well as set the time for firing a pulsed 266-nm Nd:YAG desorption/ionization laser (Nd:YAG, Quantel, Newbury, UK, Ultra CFR) at ~1 mJ

(~10^8 W/cm^2). The laser pulse ablates the particle and generated ions are detected using a dual polarity reflection time of flight mass spectrometer, and mass spectra of the positive and negative ions along with the individual particle size information are saved for data analysis.[1] UiO-66 classifications were assigned by identifying the presence of the ions CN^- (m/z -26), Br^- (m/z -79 and -81), or both in the negative ion spectrum of the particle. Typical spectra of UiO-66-NH_2, UiO-66-Br, and UiO-66-(Br)(NH_2) are given in Figures S1-S3, respectively. Particles with no negative ion spectra were removed from this analysis. Rates of ATOFMS particle sampling were repoted in Hz, and mass spectra of approximately 2000 particles were collected for each UiO-66 variant. The hierarchical clustering (HC) algorithm was used to cluster and group the mass spectra which were then calssified manually.[2]

Experimental Procedures for Ligands Synthesis.

Caution! Organic azides are potentially explosive materials – proper safety precautions should be employed.

Dimethyl 2-azidoterephthalate. A solution of sodium nitrite (285 mg, 4.1 mmol) in H_2O (5 mL) was added dropwise to a solution of dimethyl 2-aminoterephthalate (356 mg, 1.7 mmol), H_2O (5 mL), and conc. HCl (5 mL) at 0 ˚C. After stirring for 30 min, the mixture was then added dropwise to a stirred solution of sodium azide (130 mg, 10 mmol) in H_2O (5 mL) at 0 ˚C. After the addition was complete, the reaction mixture was warmed to room temperature and stirred overnight. The

resulting precipitate was collected by vacuum filtration, washed with cold water, and dried under reduced pressure to yield dimethyl 2-azidoterephthalate (271 mg, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz) 7.89-7.87 (2H, m), 7.81 (1H, dd, J = 8.1 and 1.4 Hz), 3.96 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.4, 140.5, 134.6, 132.0, 126.4, 125.5, 121.0, 53.0, 52.9. HR-ESI-TOFMS *m/z* calcd. for $C_{10}H_9N_3NaO_4$ $[M+Na]^+$: 258.0485, found $[M+Na]^+$: 258.0486.

2-Azido-1,4-benzenedicarboxlyic acid. Dimethyl 2-azidoterephthalate (118 mg, 0.5 mmol) was dissolved in 3 mL of THF and 3 mL of a 4% KOH aqueous solution was added dropwise. The mixture was stirred at room temperature overnight. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with 1.0 M HCl aqueous solution at 0 ˚C. The precipitate was collected by filtration, and washed with water and hexane. The desired compound was obtained by air drying (76 mg, 73%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (1H, d, J = 8.3 Hz), 7.76-7.74 (2H, m); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 166.6, 139.5, 135.2, 131.8, 126.0, 121.8, 121.7. HR-ESI-TOFMS *m/z* calcd. for $C_8H_4N_3O_4$ $[M-H]^-$: 206.0207, found $[M-H]^-$: 206.0209.

Dimethyl 2-hydroxyterephthalate.[3] A solution of sodium nitrite (670 mg, 9.7 mmol) in H_2O (6.2 mL) was added dropwise to a solution of dimethyl 2-aminoterephthalate (1.34 g, 6.4 mmol), H_2O (6.2 mL), acetic acid (12.4 mL) and conc. HCl (1.5 mL) at 0 ˚C. After stirring for 30 min, the reaction mixture was warmed to room temperature and stirred 30 min more. Urea (150 mg) was added for quenching the remained

sodium nitrite. The reaction mixture was added dropwise to 40 mL of 10% H_2SO_4 aqueous solution. And the mixture was stirred at 100 ^oC for 1 h. After removing solvent by evaporation, the mixture was cooling with ice bath. The resulting precipitate was collected by vacuum filtration, washed with cold water, and dried under reduced pressure to yield dimethyl 2-azidoterephthalate (600 mg, 22%). ^1H NMR ($CDCl_3$, 400 MHz) 7.87 (2H, d, *J* = 8.3 Hz), 7.60 (1H, s), 7.49 (2H, d, *J* = 8.3 Hz), 3.96 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 165.9, 161.2, 136.3, 130.0, 119.6, 118.8, 115.6, 52.6, 52.4.

2-hydroxy-1,4-benzenedicarboxlyic acid.[4] Dimethyl 2-hydroxyterephthalate (105 mg, 0.5 mmol) was dissolved in 3 mL of THF and 3 mL of a 4% KOH aqueous solution was added dropwise. The mixture was stirred at room temperature overnight. Once conversion was complete (by TLC), THF was removed by evaporation and the mixture was acidified with 1.0 M HCl aqueous solution at 0 ˚C. The precipitate was collected by filtration, and washed with water and hexane. The desired compound was obtained by air drying (73 mg, 80%). ^1H NMR (400 MHz, DMSO-d_6) δ 7.85 (1H, d, *J* = 8.1 Hz), 7.42 (1H, d, *J* = 8.1 Hz), 7.41 (1H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.8, 167.0, 161.2, 137.5, 131.3, 120.3, 120.2, 118.4, 117.4.

2,5-Dihydroxy-1,4-benzenedicarboxlyic acid.[5] Diethyl 2,5-dihydroxyterephthalate (1.5 g, 5.9 mmol) was poured in 45 mL of water and NaOH (0.65 g, 16.3 mmol) was added to solution. The mixture was stirred at 85 ˚C for overnight. Once conversion

was complete (by TLC), the solution was acidified with conc. HCl to pH 1. The precipitate was collected by filtration, and washed with water. The desired compound was obtained by air drying (1.1 g, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.25 (2H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.0, 152.7, 120.0, 118.0.

Experimental Procedures for MOFs Exchange.

UiO-66, UiO-66-NH$_2$, UiO-66-Br Synthesis. UiO-66, UiO-66-NH$_2$, and UiO-66-Br were prepared and activated previously described.[6]

Exchange Experiment between UiO-66-NH$_2$ and UiO-66-Br. UiO-66-NH$_2$ (ca. 29 mg, 0.1 mmol equiv. of –NH$_2$) and UiO-66-Br (ca. 35 mg, 0.1 mmol equiv. of –Br) were placed in a dram vial either without solvent or with 2 mL of solvent ($CHCl_3$, MeOH, DMF, or H_2O). The mixture was incubated for 5 days. After cooling down (if the sample was incubated above room temperature), the mixture was centrifuged and the solvent decanted. The solid was washed with 3×10 mL of MeOH, isolated by centrifugation, and dried under vacuum for at least 6 hours before ATOFMS analysis.

Solid-Liquid Postsynthetic Exchange Experiment between UiO-66-Br and NH$_2$-BDC. Dimethyl 2-aminoterephathalate (42 mg, 0.2 mmol) was dissolved in THF (2 mL) and aqueous 4% KOH solution (2 mL). The solution was stirred at room temperature overnight. The THF was removed by evaporation and the remaining aqueous phase was neutralized to pH 7 with 1 M HCl. This solution was added to

UiO-66-Br (ca. 70 mg, 0.2 mmol equiv. of –Br) and the mixture was incubated in a pre-heated oven (room temperature, 55 °C, or 85 °C) for 5 days. After cooling down, the mixture was centrifuged and the aqueous phase decanted. The solids were suspended in 10 mL of MeOH. After 24 h, the solid was centrifuged and the MeOH was decanted and combined with the original aqueous phase. This MeOH soaking step was repeated two more times (24 h each). The solid phase was finally dried under vacuum for 6 h at 100 °C, digested with a 48% HF, and used for ^{1}H NMR analysis. The mixed of aqueous/methanol solution was evaporated to dryness and the remaining residue was taken up in minimum volume of 1 M HCl. The acidified solution produced a solid that was collected by filtration and used for ^{1}H NMR analysis.

Solid-Liquid Postsynthetic Exchange Experiment between UiO-66-NH_2 and Br-BDC. 2-Bromoterephthalic acid (50 mg, 0.2 mmol) was dissolved in 4% KOH aqueous solution (2 mL). The solution was neutralized to pH 7 with minimum amount of 1 M HCl aqeous solution. This solution was added to UiO-66-NH_2 (ca. 57 mg, 0.2 mmol equiv. of –NH_2) and the mixture was incubated in a pre-heated oven (room temperature, 55 °C, or 85 °C) for 5 days. The mixture was centrifuged and the aqueous phase decanted. The solids were washed with 3×10 mL of MeOH, after which the solid was left to soak in 10 mL of MeOH. The solids were left to soak in MeOH for 3 days, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

Solid-Liquid Exchange Comparison Experiment between UiO-66, NH_2-BDC and Br-BDC. 2-Aminoterephathalic acid or 2-bromoterephthalic acid (18 mg or 25 mg, 0.1 mmol) was dissolved in 4% KOH aqueous solution (2 mL). The solution was neutralized to pH 7 with minimum amount of 1 M HCl aqeous solution. This solution was added to UiO-66 (ca. 28 mg, 0.1 mmol equiv. of benzene ring) and the mixture was incubated at room temparature for 12h, 1 day, 2 days or 5 days. The mixture was centrifuged and the aqueous phase decanted. The solids were washed with 3×10 mL of MeOH, after which the solid was left to soak in 10 mL of MeOH. The solids were left to soak in MeOH for 3 days, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

Exchanged UiO-66-N_3 and UiO-66-OH Synthesis. Dimethyl 2-azidoterephathalate (47 mg, 0.2 mmol) or dimethyl 2-hydroxyterephathalate (42 mg, 0.2 mmol) was dissolved in THF (0.1 M, 2 mL) and aqueous 4% KOH (2 mL). The solution was stirred at room temperature overnight, after which the THF was removed by evaporation. The aqueous phase was neutralized to pH 7 with minimum amount of 1 M HCl. UiO-66 (ca. 57 mg, 0.2 mmol) was placed in the aqueous solution. The mixture was incubated at room temperature for 1, 2, or 5 days. The mixture was centrifuged and the solvent decanted. The solids were washed with 3×10 mL of MeOH, after which the solid was left to soak in 10 mL of MeOH. The solids were left to soak in MeOH for 3 days, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

Hydrolysis of Diethyl 2,5-Dihydoxyterephathalte (2,5-$(OH)_2$-BDC). Diethyl 2,5-dihyroxyterephathalate (2.5 g, 10 mmol) was dissolved in THF (50 mL) and aqueous 4% KOH (50 mL). The solution was stirred at room temperature overnight, and the light brown solid was collect by filtration. The solid was washed 5 mL of ice water and 10 mL of THF. The desired dicarboxylated form was obtained by air drying (1.6 g, 82%).

Exchanged UiO-66-2,5-$(OH)_2$ Synthesis. 2,5-dihydroxyterephathalate (392 mg, 2 mmol) was dissolved in water (16 mL) and neutralized to pH 7 with minimum amount of 1 M HCl. UiO-66 (ca. 57 mg, 0.2 mmol) was poured in the aqueous solution. The mixture was incubated at room temperature for 5 days. The mixture was centrifuged and the solvent decanted. The solids were washed with 3×10 mL of MeOH, after which the solid was left to soak in 10 mL of MeOH. The solids were left to soak in MeOH for 3 days, and the solution was exchanged with fresh MeOH (10 mL) every 24 h. After 3 days of soaking, the solids were centrifuged and dried under vacuum.

UiO-66 room temperature synthesis and seeding effect. Terephthalic acid or 2-aminoterephthalic acid or 2-bromoterephthalic acid (0.1 mmol) was added to 3 mL of sat. $NaHCO_3$ solution. And the solution was neutralized to around pH 7 with minimum amount of 1M HCl. After adding $ZrCl_4$ (0.1 mmol, 23 mg) to solution, the mixture was sonicated for 5 minutes. The solution was incubated at room

temperature for 5 days. The solid was washed with MeOH (10 mL) three times and dried under vacuum. For test seeding effect, 1 mg of UiO-66 was added to solution after sonication. Other procedure was same with room temperature synthesis.

UiO-66-OH and UiO-66-2,5-(OH)$_2$ direct synthesis. 2-Hydroxyterephthalic acid or 2,5-dihydroxyterephthalic acid (0.175 mmol), $ZrCl_4$ (0.175 mmol, 41 mg), and DMF (4 mL) was placed in a Teflon lined autoclave and heated at oven (85 ^oC, 100 ^oC, 120 ^oC, and 150 ^oC) for 24h. The solid was then isolated by centrifugation and washed with MeOH (10 mL) for three times. After washing, the solids were centrifuged and dried under vacuum.

Digestion and Analysis by ^1H NMR. Approximately 10 mg of UiO-66 material was dried under vacuum at 100 ^oC and digested with sonication in 580 μL of CD_3OD or DMSO-d_6 and 20 μL of HF (48% aqueous solution). For the exchanged UiO-66-N_3, the sample was dried under vacuum at room temperature.

Mass Spectrometry Analysis. Electrospray ionization mass spectrometry (ESI-MS) was performed using a ThermoFinnigan LCQ-DECA mass spectrometer and the data was analyzed using the Xcalibur software suite. Approximately 5 mg of the sample was digested with sonication in 1 mL of MeOH and 10 μL of HF (48% aqueous solution).

Thermal Analysis. Approximately 10-15 mg of exchanged UiO-66 series was used for

TGA measurements, after BET analysis (activated). Samples were analyzed under a stream of N_2 using a TA Instrument Q600 SDT running from room temperature to 800 °C with a scan rate of 5 ^{o}C/min. For samples containing N_3-BDC, a smaller sample size (4 mg) was used and the instrument was placed behind a safety shield.

PXRD Analysis. Approximately 20-30 mg of UiO-66 series was dried at 120 ^{o}C prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Ka (l = 1.5418 Å), with a scan speed of 3 sec/step, a step size of 0.02^{o} in 2θ, and a 2θ range of 5-55^{o}. For the N_3-functionalized UiO-66 case, the sample was dried under vacuum at room temperature.

BET Surface Area Analysis. Approximately 50 mg of exchanged UiO-66 was evacuated on a vacuum line for overnight at room temperature. The sample was then transferred to a pre-weighed sample tube and degassed at room temperature on an Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. The sample tube was re-weighed to obtain a consistent mass for the degassed exchanged UiO-66. BET surface area (m^2/g) measurements were collected at 77 K by N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using volumetric technique.

Scanning Electron Microscopy. Approximately 5 mg of UiO-66 material was evacuated on a vacuum line overnight at room temperature. Half of the sample was

then transferred to carbon black on a sample holder disk. The sample was coated using a Cr-sputter coating to preventing the image from being too bright. A Philips XL30 ESEM instrument was used for acquiring images using a 5 kV-30 kV energy source under vacuum. Around 18000× scale images were collected.

Dynamic Light Scattering. Dynamic Light Scattering (DLS) size distribution was performed using a Zeta Sizer from Malvern. 5 mg of UiO-66 material was placed in 995 μL of water (0.5 wt% water solution) and the sample was sonicated for 1 min. Approximately 100 μL of sample solution was transferred to disposable cuvette cell to acquire the measurements.

Experimental Procedure for Dry Aerosol Generation.

Approximately 100 mg of dry UiO material was placed in a 1 L volumetric flask. Aerosol was generated by constant sonication using a Bransonic 3510R-MTH sonicator. ~1-2 lpm of dry N_2 flowed into the volumetric flask carrying the MOF into a dilution chamber (~7900 cm^3). A constant 1 lpm was brought into the ATOFMS for analysis at ~10-12 Hz. Between sample runs the dilution chamber was purged with dry N_2 until no aerosol particles were observed (<0.001Hz).

Hierarchical Clustering (HC) Analysis

Clustering is used to reduce the volume of data into a much more manageable size. HC analysis groups similar mass spectra into clusters. Clusters are formed based on manual identification of the cluster's average mass spectrum and the dot product of

all spectra in the cluster. Clusters were finalized once further divisions of clusters had no significant impact on the average spectrum (i.e. all spectra in the cluster were identical). The final clusters were identified as described above into UiO-66 containing CN^-, Br^-, or both.[2]

ATOFMS Size Distributions

The ATOFMS measured aerodynamic diameter (d_{va}) can provide useful complimentary information on the UiO-66 particle types. The ATOFMS size distributions were found to be similar across all UiO-66 variants. This suggests that the exchange of ligands did not significantly vary the size of a single particle, which ranged from 1.3 – 4.0 μm with an average mode at 1.94 ± 0.04 μm (Figure S5). Using scanning electron microscopy (SEM), the UiO particles have been estimated to be ~100 nm,[7] and by PXRD and the Debey-Scherrer equation, to be ~400 nm.[8] It should be noted that the measurement of d_{va} by ATOFMS assumes a spherical particle shape, which is not the case for UiO-66 (square bipyramidal) and may account for the notable difference in particle size determined by ATOFMS.

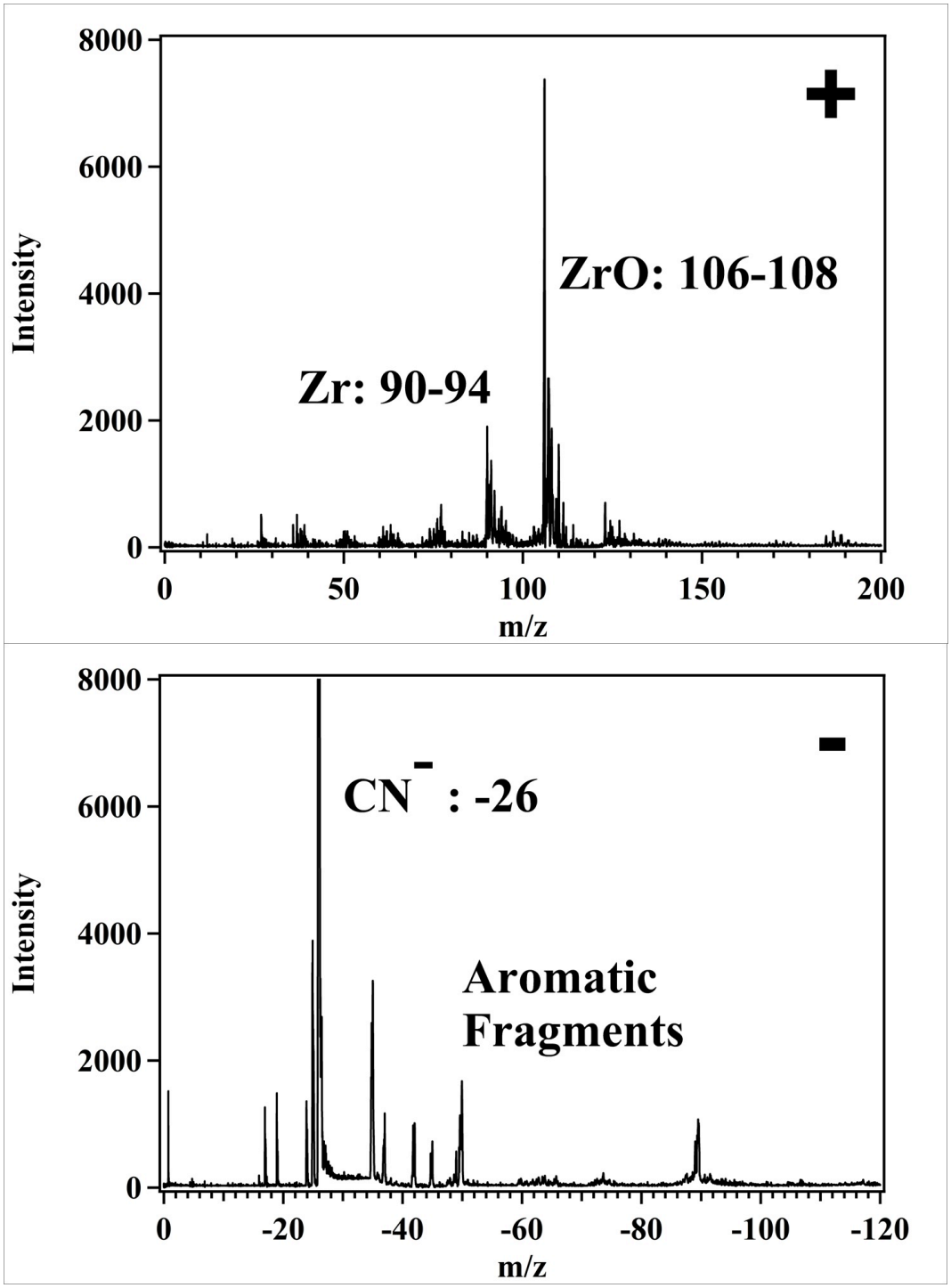


Fig. S1 Aerosol time-of-flight mass spectrometry positive ion (top) and negative ion (bottom) mass spectra of UiO-66-NH_2.

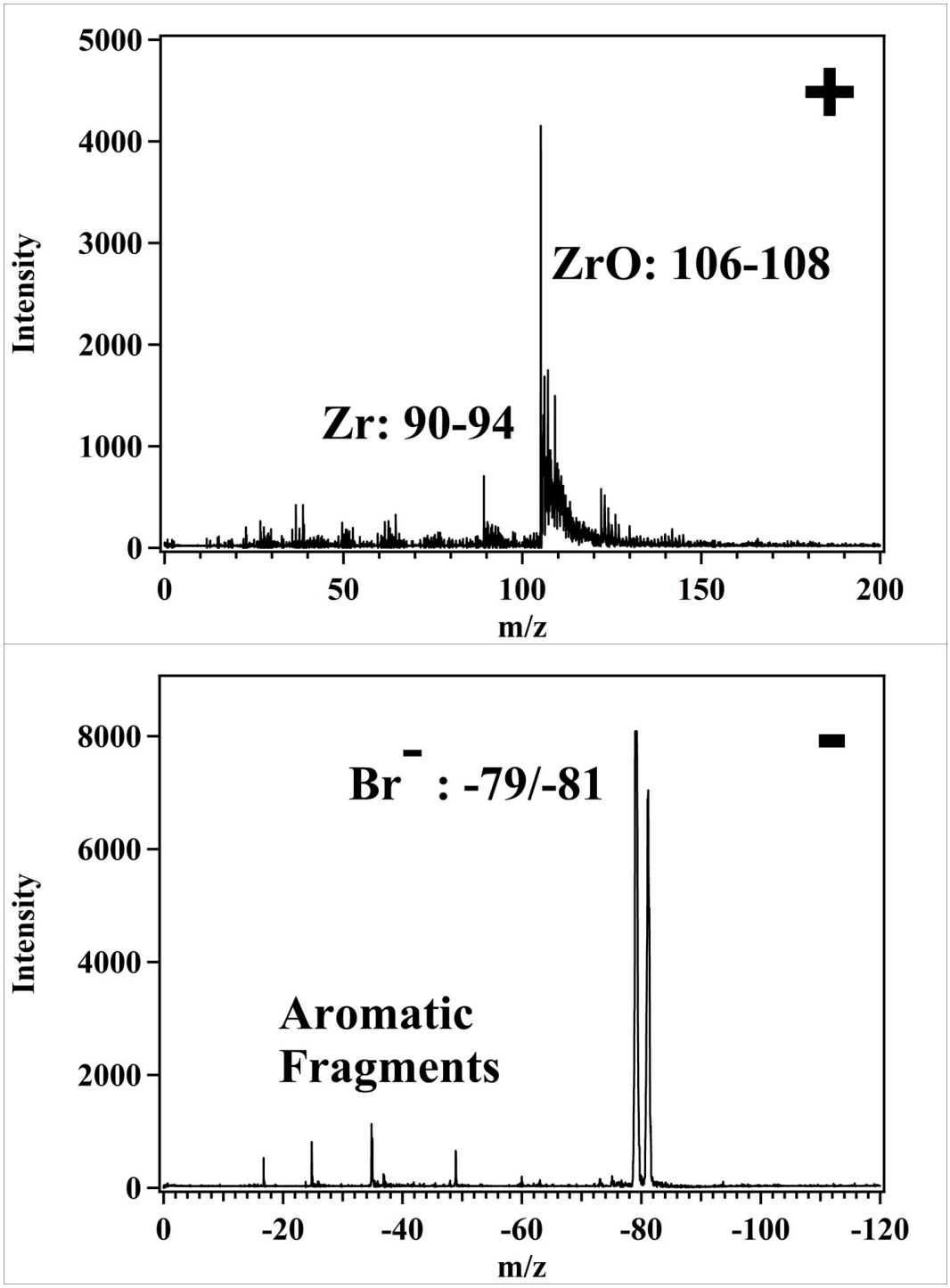


Fig. S2 Aerosol time-of-flight mass spectrometry positive ion (top) and negative ion (bottom) mass spectra of UiO-66-Br.

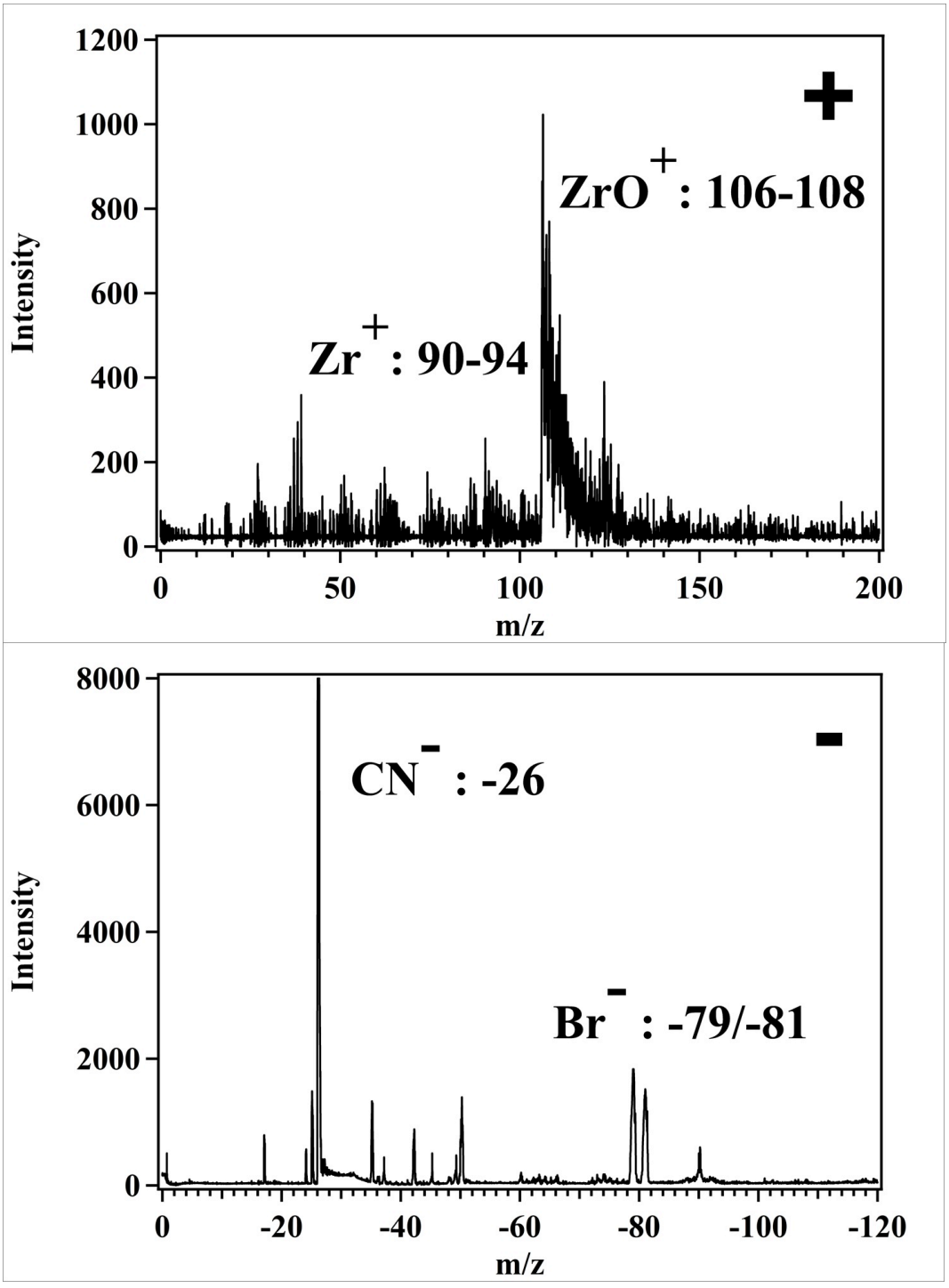


Fig. S3 Aerosol time-of-flight mass spectrometry positive ion (top) and negative ion (bottom) mass spectra of exchanged UiO-66-(Br)(NH_2).

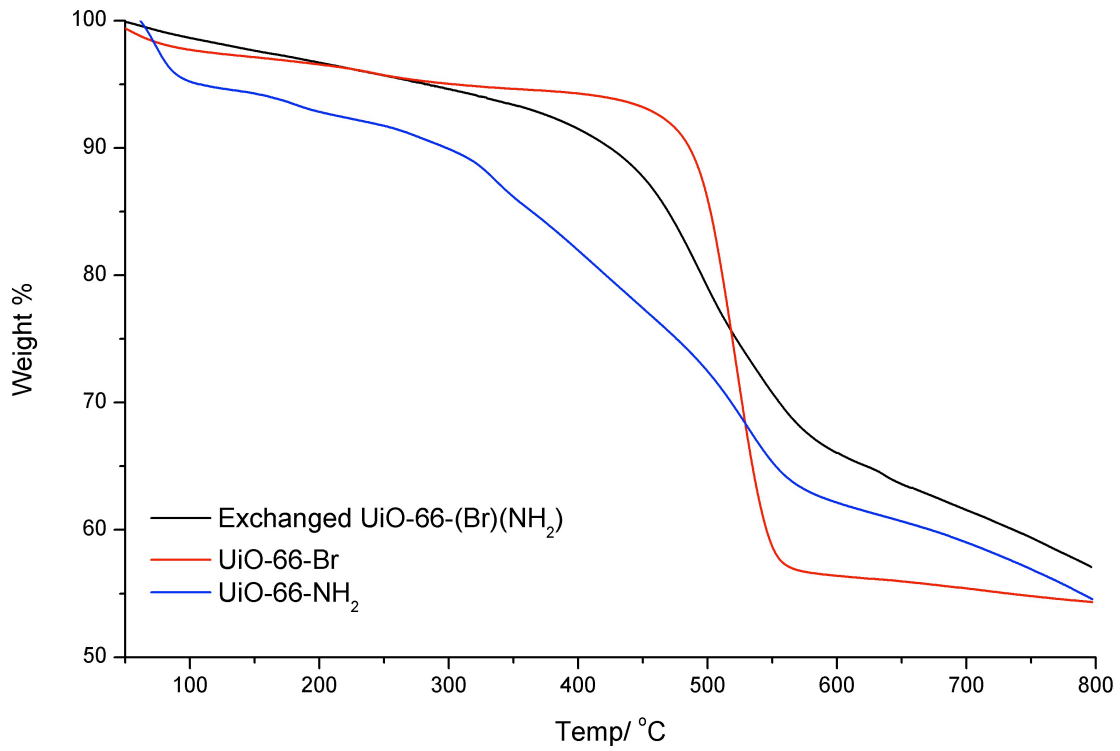


Fig. S4 Thermogravimetric analysis of activated (100 °C for 2 h under vacuum line) UiO-66-NH_2, UiO-66-Br, and exchanged UiO-66-(Br)(NH_2) (sample was exchanged at 85 °C in water for 5 days).

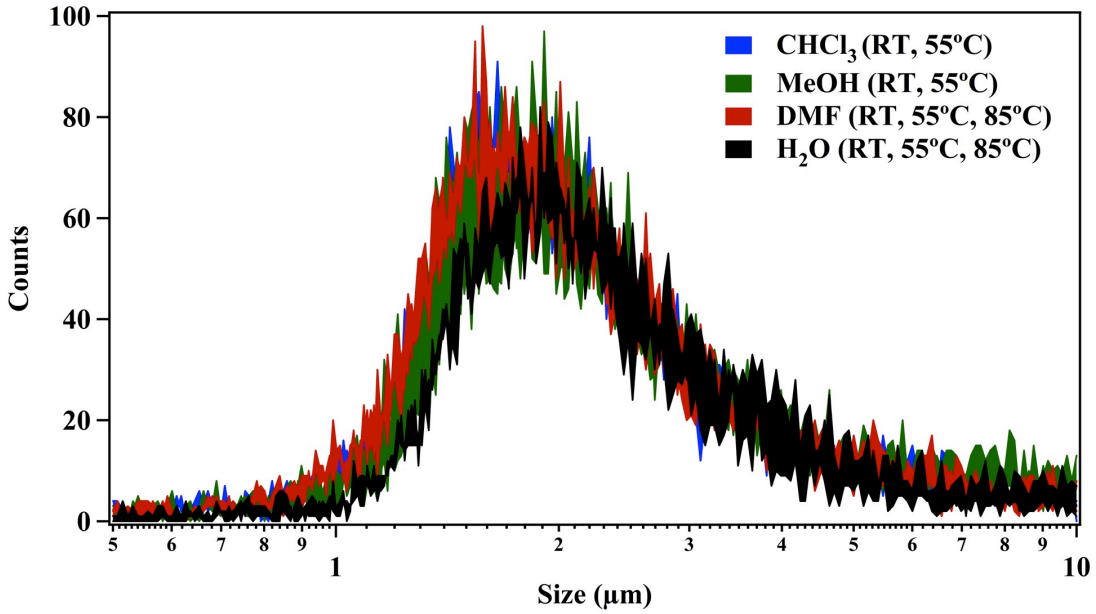
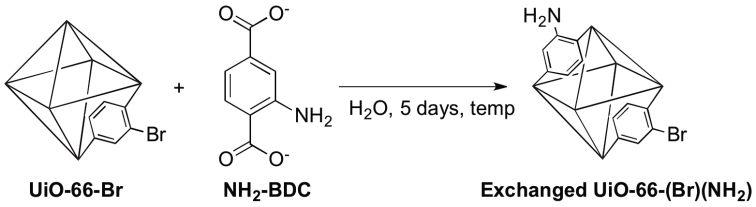
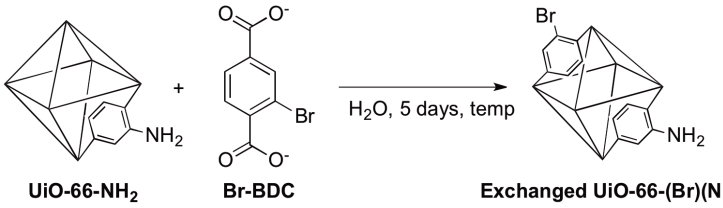


Fig. S5 ATOFMS size distributions of all UiO-66 variants grouped by solvent.



UiO-66-Br **NH_2-BDC** **Exchanged UiO-66-(Br)(NH_2)**

Temperature	**RT**	**55 °C**	**85 °C**
NH_2-BDC : Br-BDC in solid phase	**0.1 : 1 (9%)**	**1.7 : 1 (63%)**	**3.1 : 1 (76%)**



UiO-66-NH_2 **Br-BDC** **Exchanged UiO-66-(Br)(NH_2)**

Temperature	**RT**	**55 °C**	**85 °C**
NH_2-BDC : Br-BDC in solid phase	**3.6 : 1 (22%)**	**2.0 : 1 (33%)**	**1.3 : 1 (43%)**

Fig. S6 Postsynthetic exchange (PSE) of UiO-66-Br with NH_2-BDC (top) and UiO-66-NH_2 with Br-BDC (bottom). The solid phase samples were digested with HF and analyzed by ^{1}H NMR to obtain the ligand exchange ratio (percentages listed reflect percent of newly incorporated ligand).

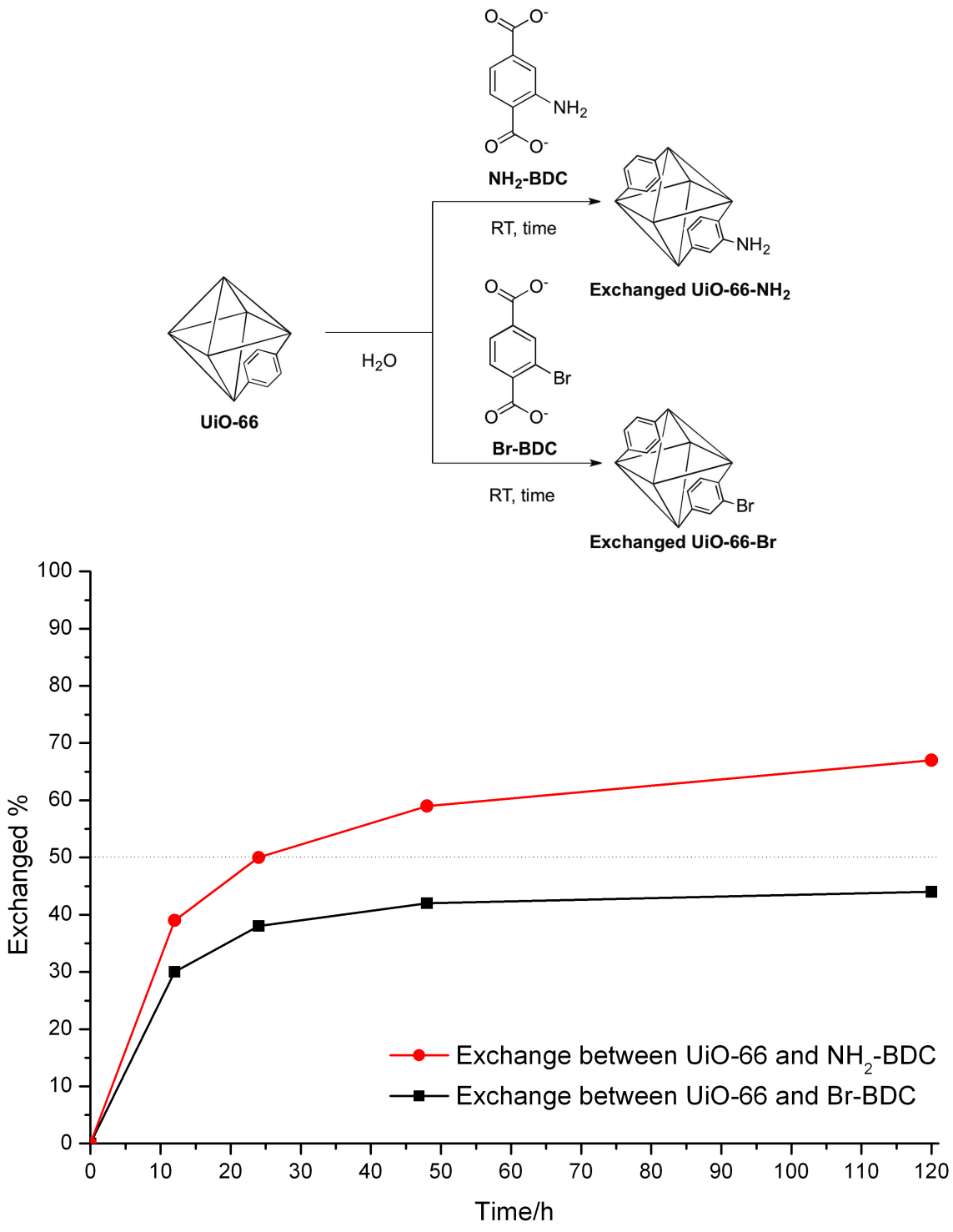


Fig. S7 Postsynthetic exchange (PSE) of UiO-66 with NH_2-BDC and Br-BDC for comparison.

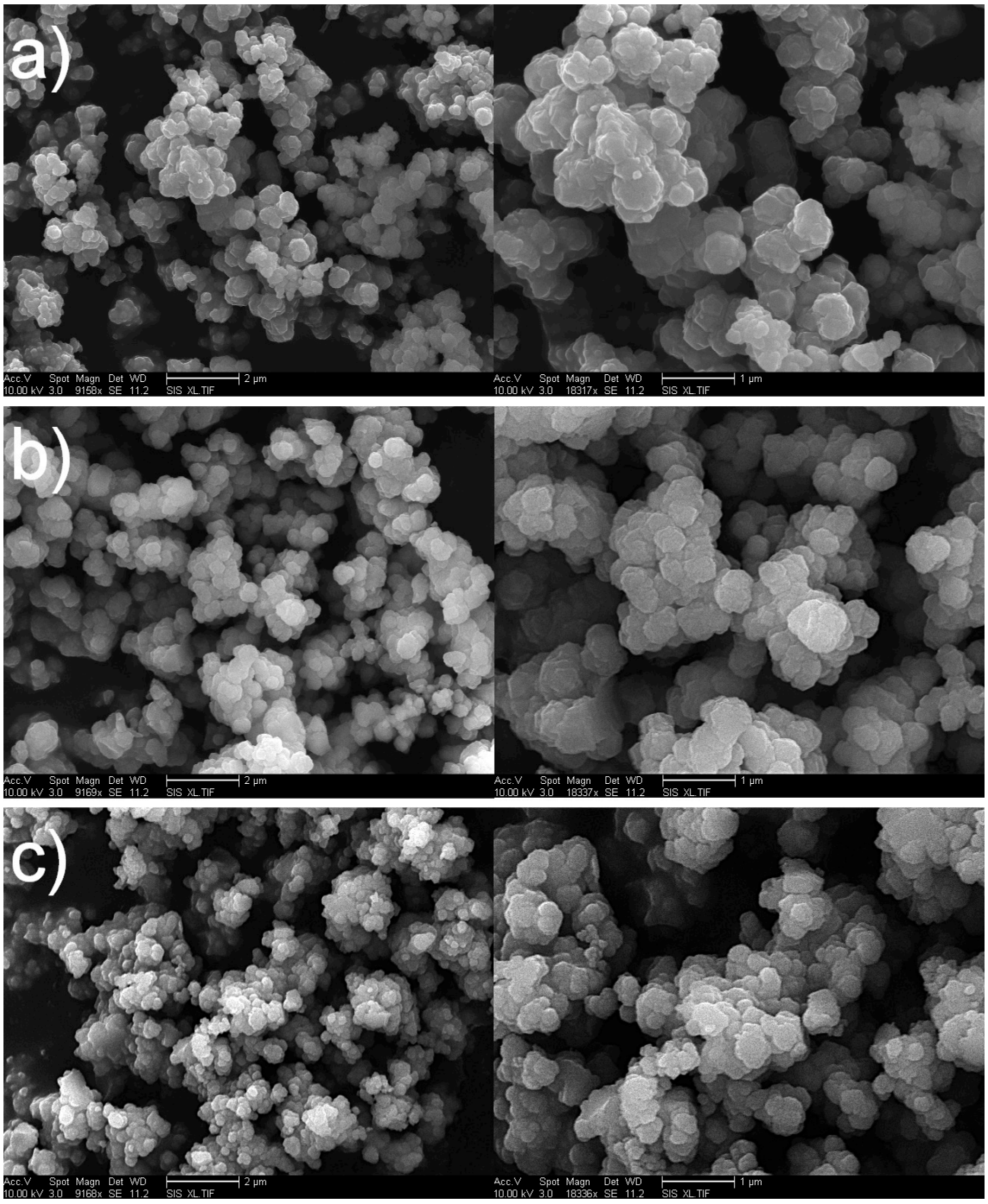


Fig. S8 Scanning electron microscopy (SEM) images of exchanged UiO-66-(Br)(NH_2) in solid-liquid system; a) room temperature incubation, b) 55 ^oC incubation, c) 85 ^oC incubation.

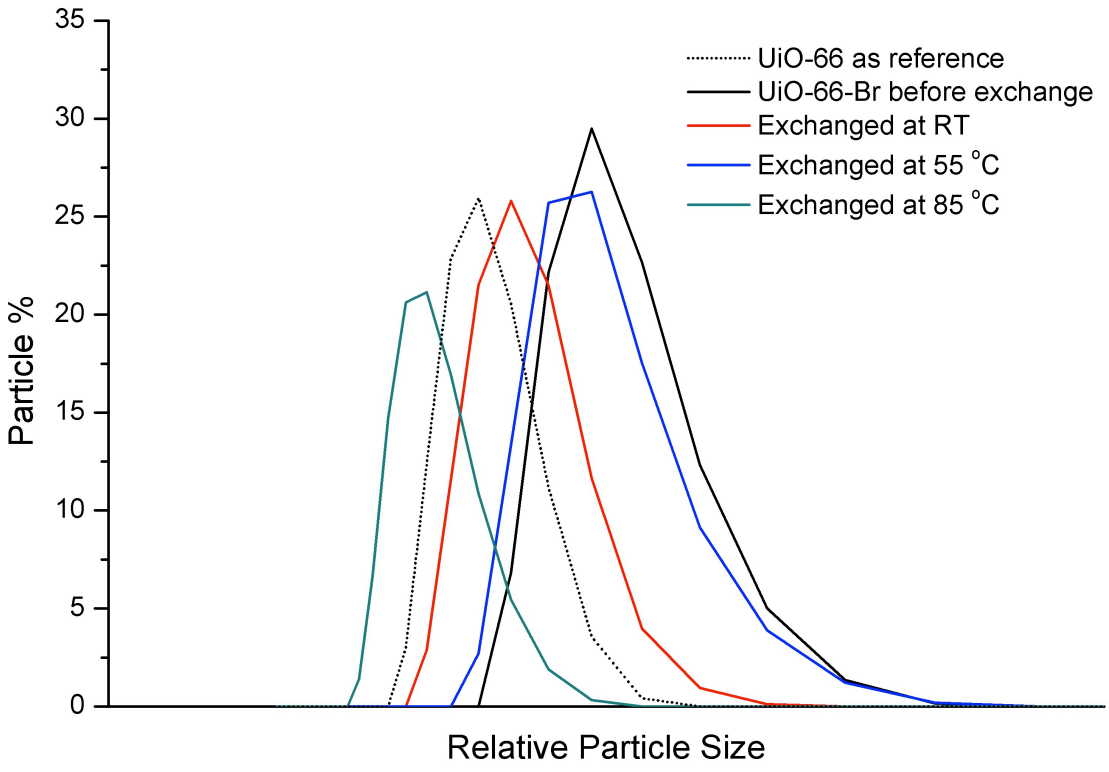


Fig. S9 Dynamic light scattering (DLS) size distribution of exchanged UiO-66-(Br)(NH_2) in solid-liquid system.

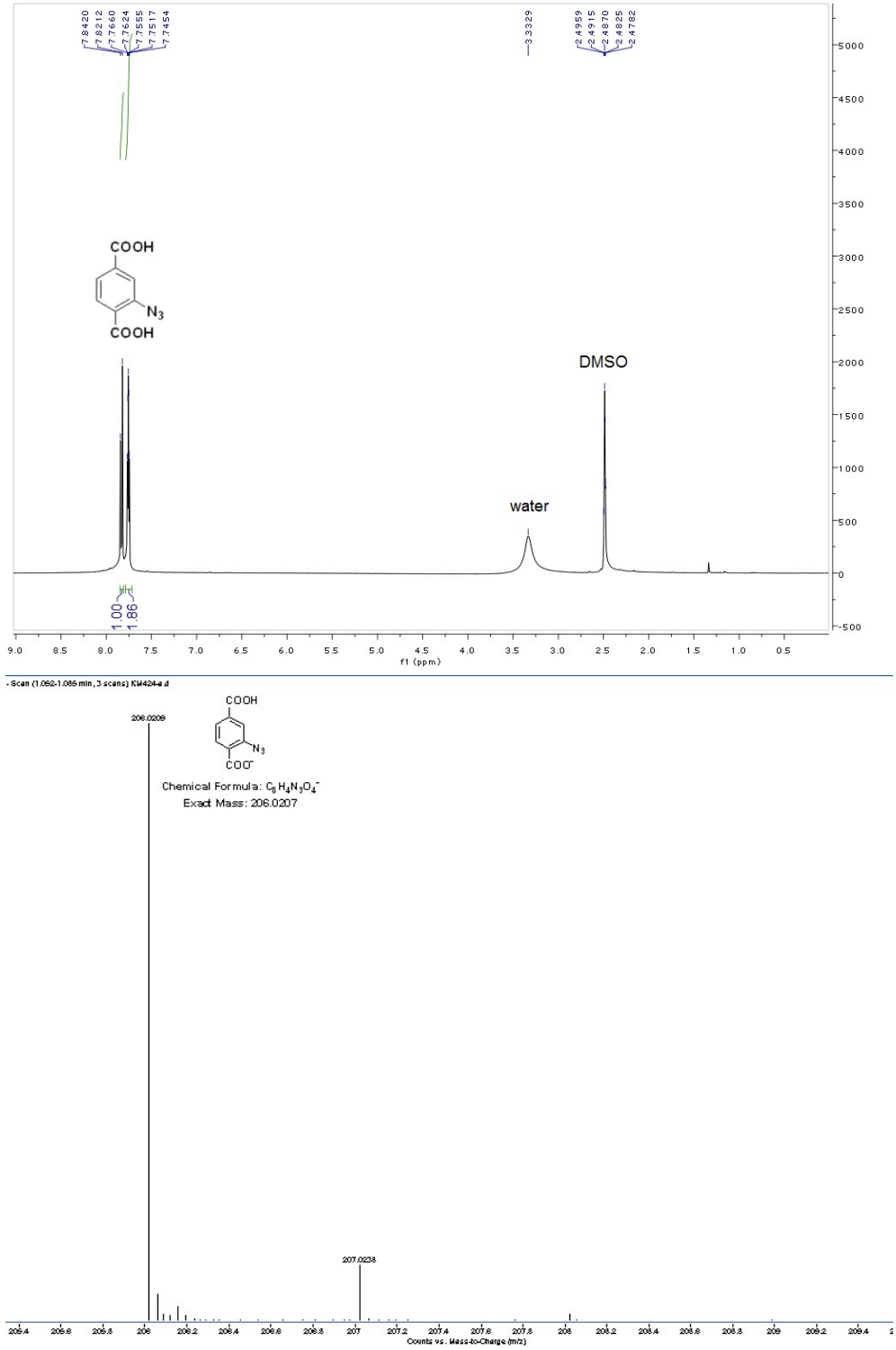


Fig. S10 ^{1}H NMR (top) and HR-MS (bottom) analysis of 2-azido-1,4-benzenedicarboxylic acid (N_3-BDC).

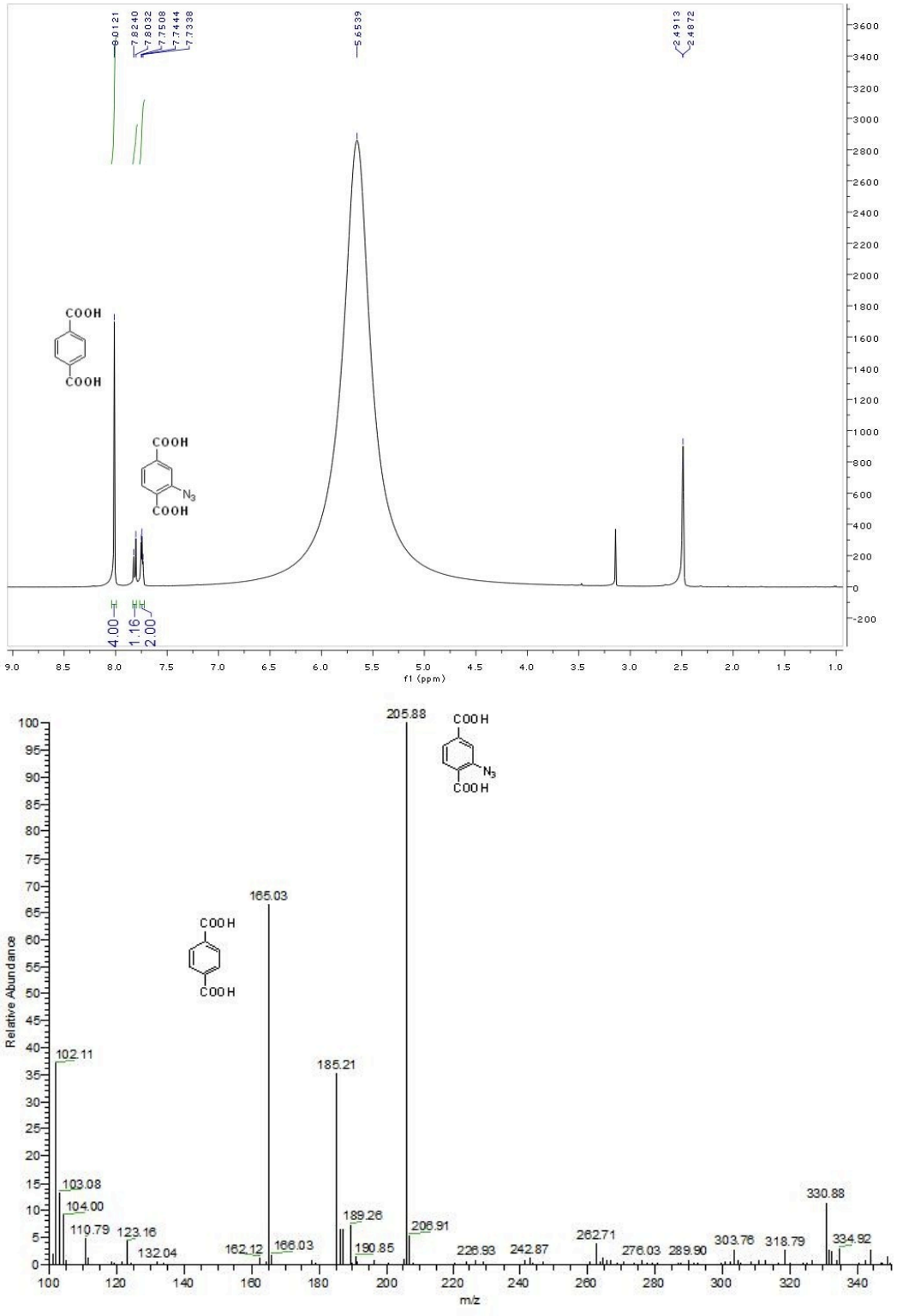


Fig. S11 ^{1}H NMR analysis and ESI-MS spectrum of exchanged UiO-66-N_3 after digestion.

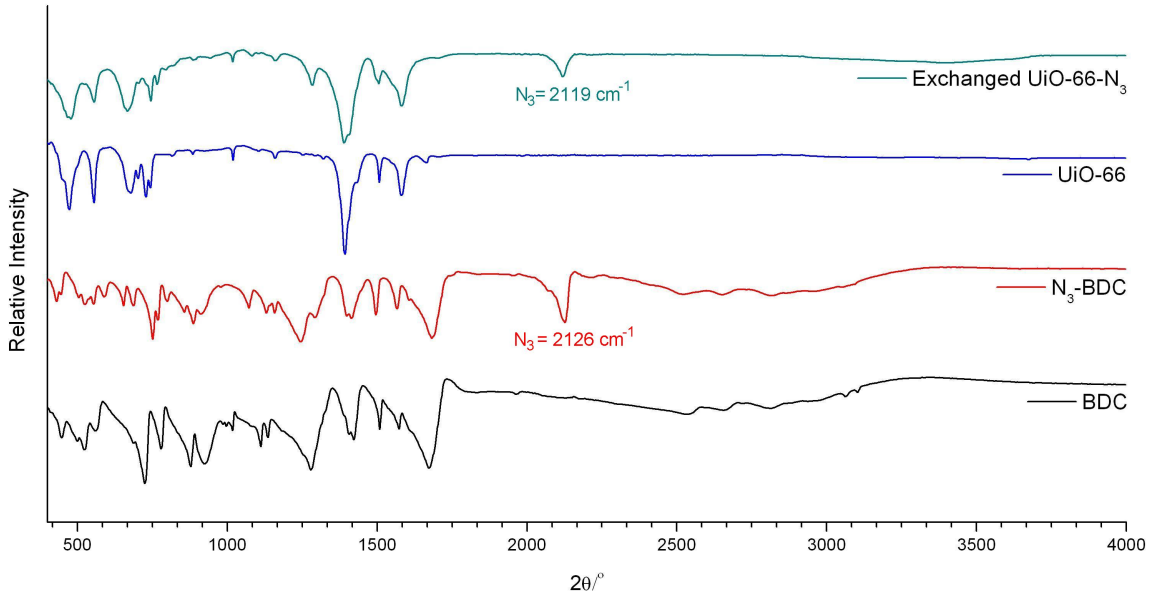


Fig. S12 Infrared spectrum (ATR-FTIR) of BDC ligand, N_3-BDC ligand, non-functionalized UiO-66 and exchanged UiO-66-N_3.

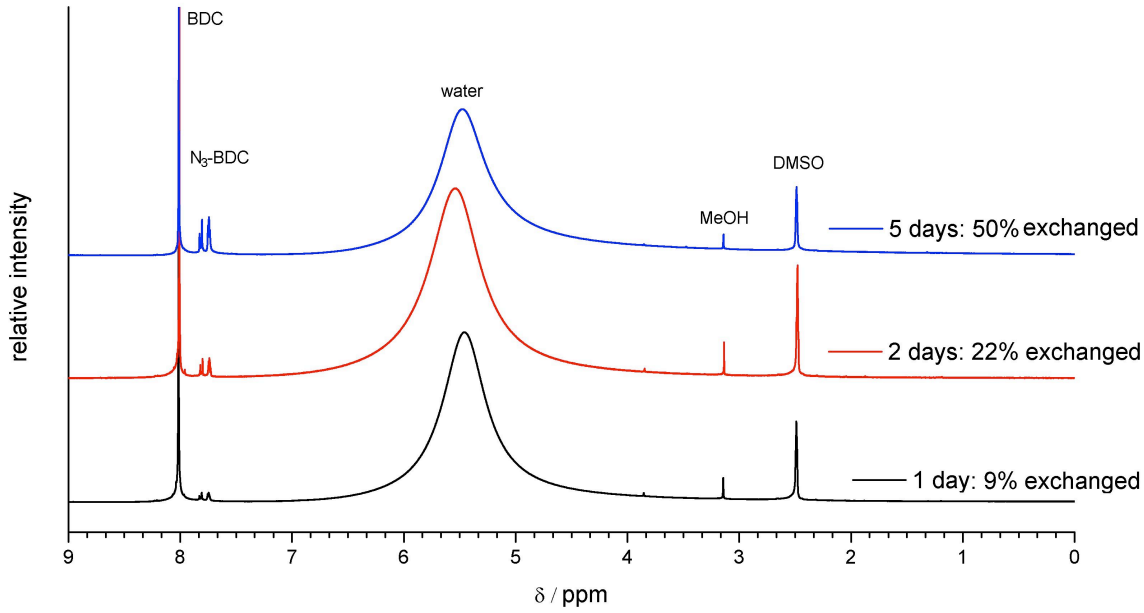


Fig. S13 ^{1}H NMR spectra of time dependent N_3-exchanged UiO-66.

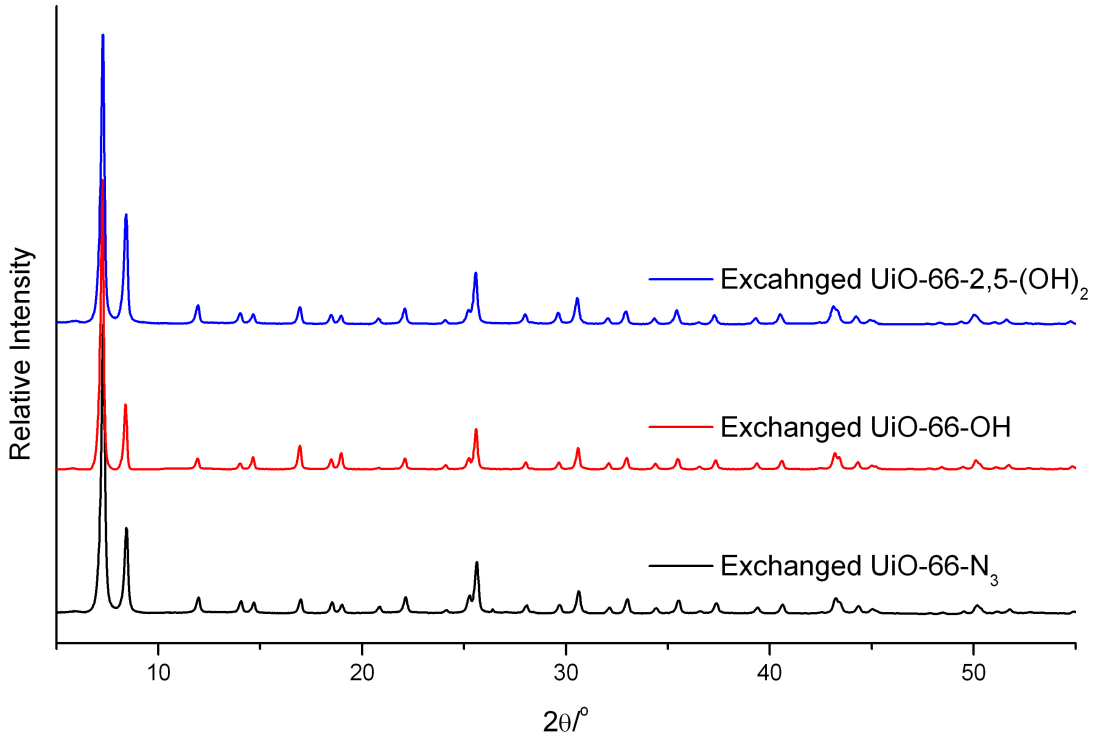


Fig. S14 Powder x-ray diffraction pattern of Exchanged UiO-66-N_3, Exchanged UiO-66-OH, and Exchanged UiO-66-2,5-$(OH)_2$.

Table S1 BET surface area of exchanged UiO-66

Exchanged UiO-66	BET (m^2/g)
UiO-66-50%-N_3	872 ± 96
UiO-66-50%-OH	1131 ± 59
UiO-66-40%-2,5-$(OH)_2$	922 ± 61

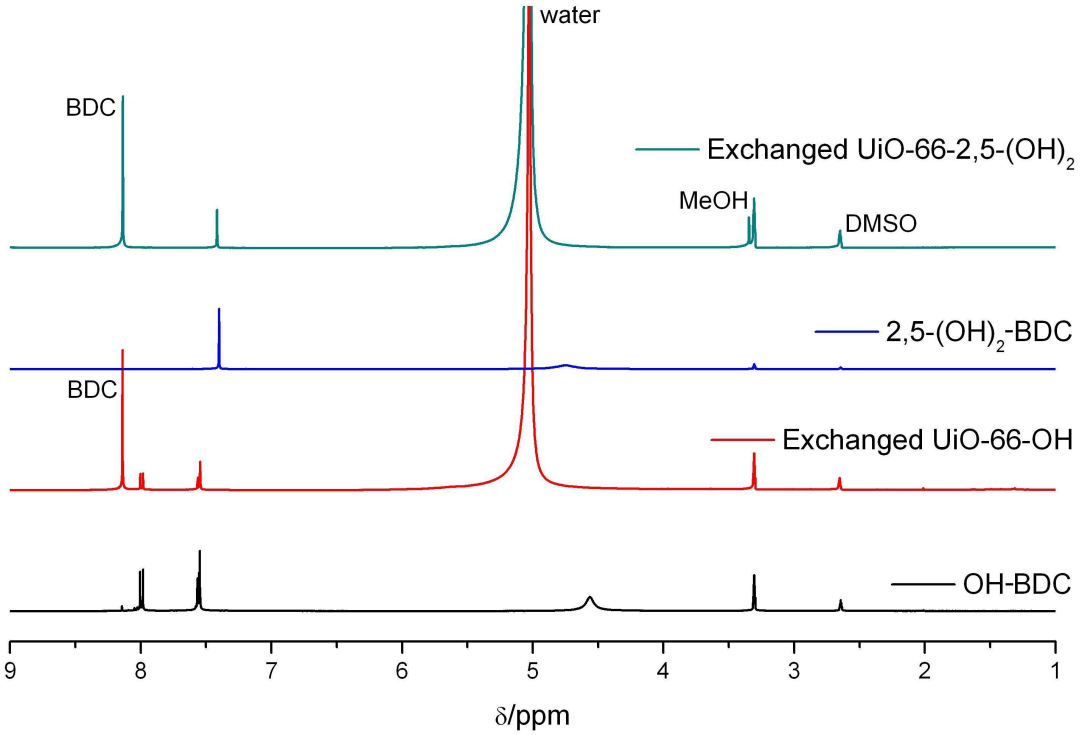


Fig. S15 ^{1}H NMR of OH-BDC, Exchanged UiO-66-OH, 2,5-$(OH)_2$-BDC and Exchanged UiO-66-2,5-$(OH)_2$. Mixed solvent of CD_3OD (400 μL) and DMSO-d_6 (200 μL) was used, and MOF were digested with extra 20 μL of HF solution.

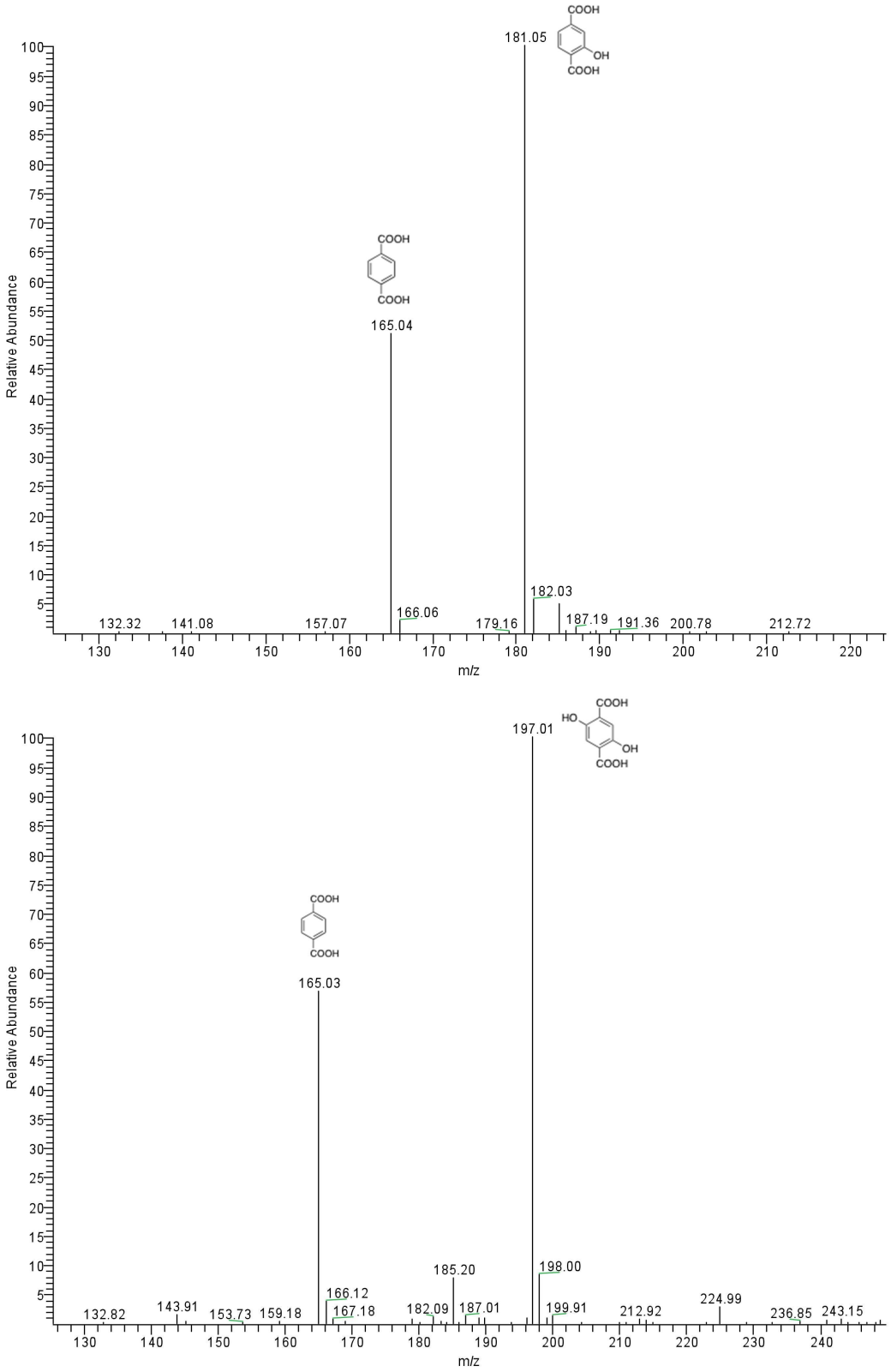


Fig. S16 ESI-MS of UiO-66-50%-OH (top) and UiO-66-40%-2,5-$(OH)_2$ (bottom) after digestion.

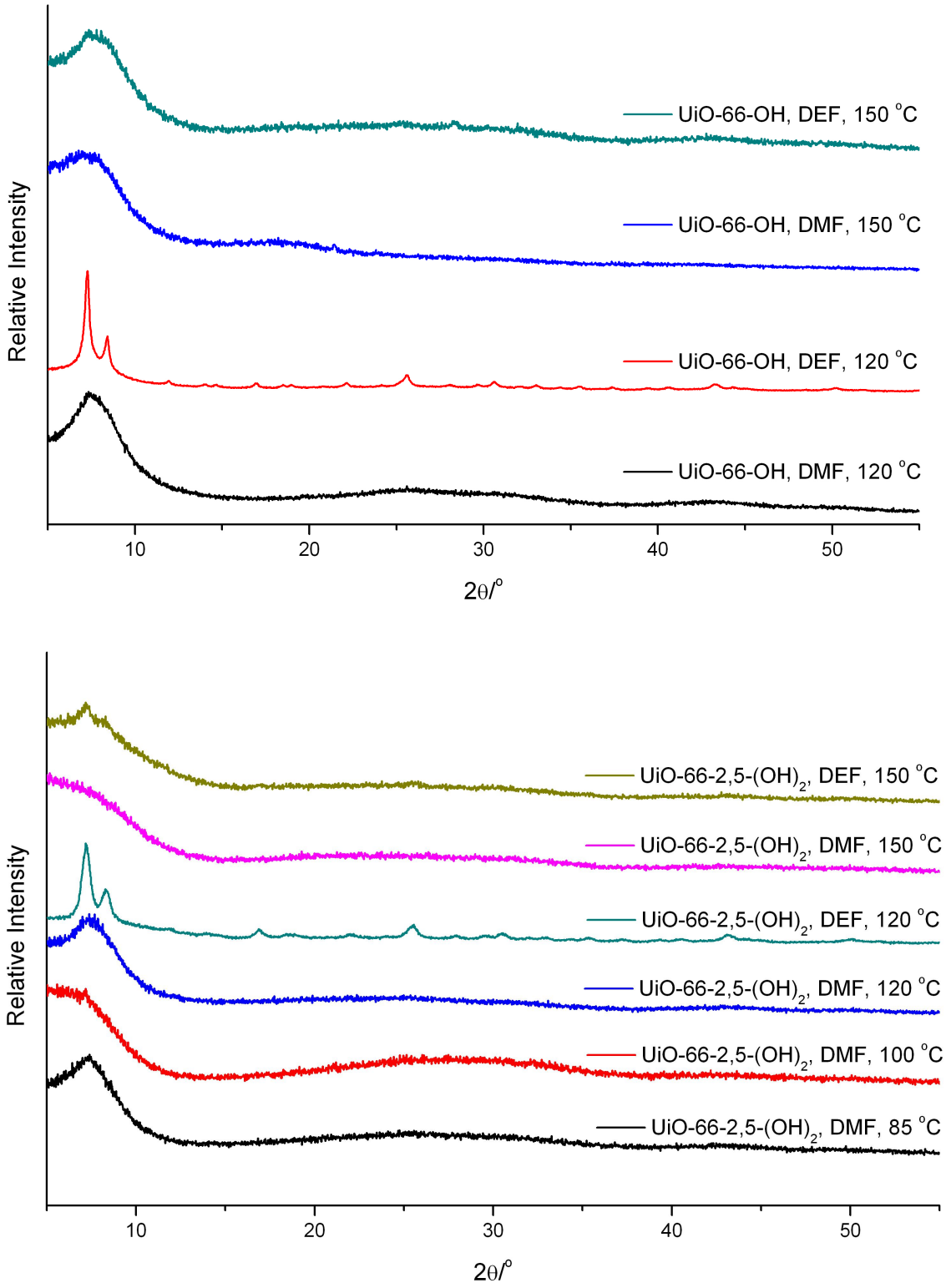


Fig. S17 Powder x-ray diffraction pattern of UiO-66-OH (top), and UiO-66-2,5-$(OH)_2$ (bottom) from direct synthesis.

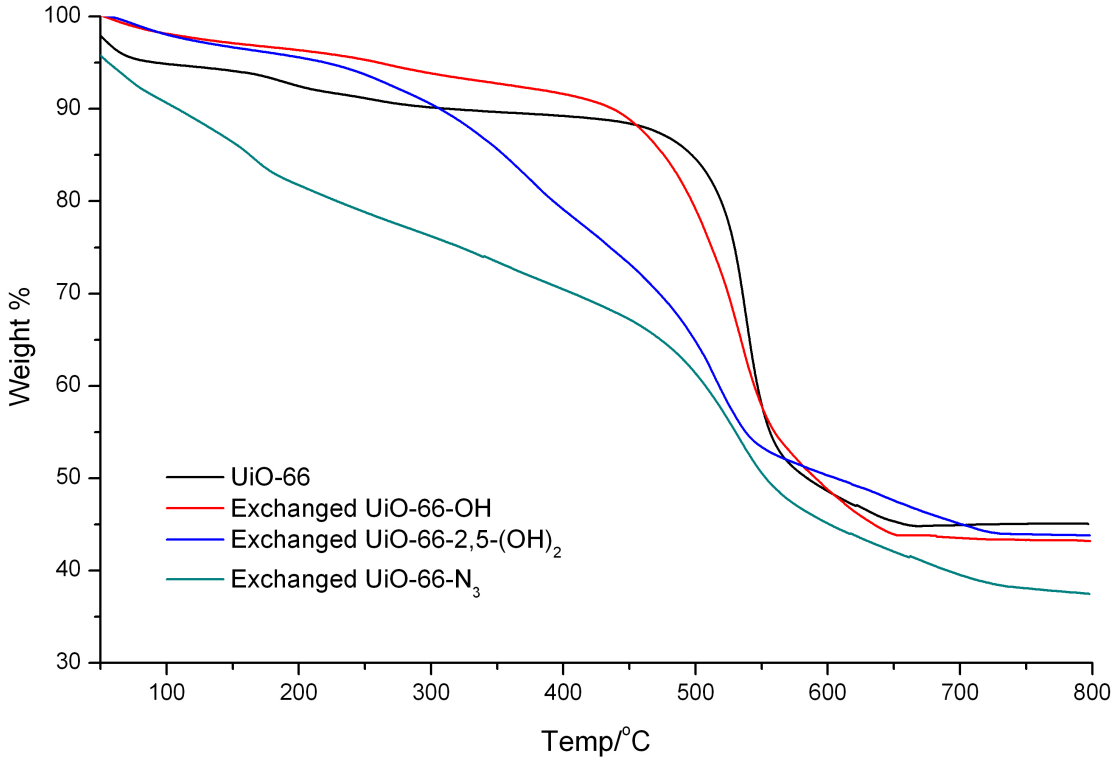


Fig. S18 Thermogravimetric analysis of activated non-functionalized UiO-66 and Exchanged UiO-66-OH/2,5-$(OH)_2$/N_3. Heating of azido containing MOF should be done with caution – this TGA analysis was performed on a small scale (4 mg) with a safety shielded.

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