Electronic Supporting Information

Synthesis and functionalization of pure-phase NU-901 for enhanced CO_2 adsorption: The influence of zirconium salt and modulator on topology and phase purity

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Abstract: The synthesis of NU-901, a microporous Zr_6-based MOF with scu topology often contains NU-1000 **csq** phase impurities. This work demonstrates that the use of certain Zr-salts and carboxylic acid modulators affect the formation of phase impurities. Phase-pure NU-901 was solvothermally synthesized and functionalized with amines through the use of solvent-assisted linker incorporation (SALI) resulting in more than double the typical CO_2 adsorption capacity of NU-901.

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Experimental Procedures

All reagents were purchased from commercial sources and used without further purification. H_4TBAPy was synthesized following modified published procedure.[1-3]

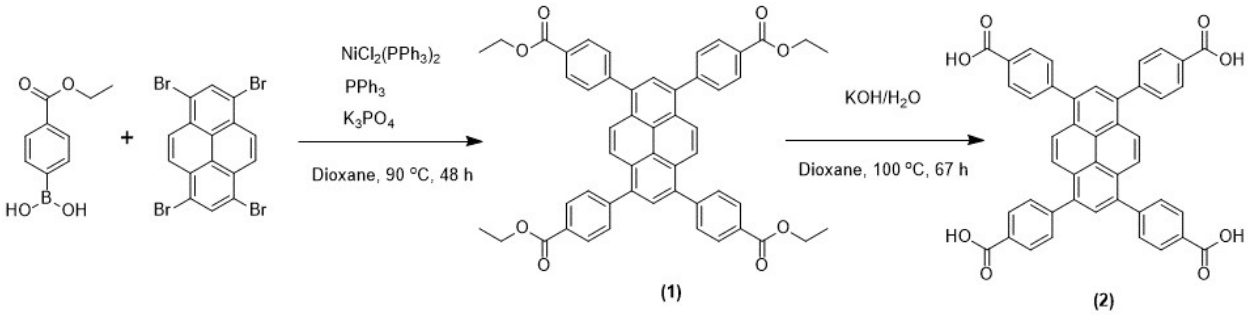
^{1}H-NMR spectra were recorded on Varian FT-NMR spectrometer (300 MHz) and data were analysed with iNMR software. Samples (~10 mg) were digested using ~60 µL of D_2SO_4 and 600 µLof DMSO-d_6

Powder X-ray diffraction (PXRD) data were measured at room temperature on a STOE-STADIMP powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuKα1 radiation, λ = 1.54056 Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. The activated powder was sandwiched between two Kapton foils and measured in transmission geometry in a rotating holder. Intensity data from 2 to 30 degrees two theta were collected over a period of 15 min. The instrument was calibrated against a NIST Silicon standard (640d) prior to the measurement. PXRD data were also measured on a Rigaku Miniflex 600 diffractometer at 30kV, 15mA (CuKα1 radiation, λ = 1.54056 Å) with a scan speed of 5°/min and a step size of 0.05 in 2θ at room temperature

Nitrogen isotherm measurements were carried out on a Micromeritics Tristar II 3020 or ASAP 2420 at 77 K. Samples were activated at 120 °C for 16 h under vacuum on Micromeritics Smart VacPrep instrument and outgas rate below 0.05 mmHg/min was achieved.

Carbon dioxide isotherm measurements were carried out on a Micromeritics 3G flex at 273K, 283K, and 293K through the use of water-ethylene glycol automated cooling system. Samples were activated at 120 °C for 16 h under vacuum on Micromeritics Smart VacPrep instrument and outgas rate below 0.05 mmHg/min was achieved. Isotherms were fitted using non-linear leas-squares fitting to either a single-site Langmuir or viral equations. The Clausius-Clapeyron equation was employed to calculate the isosteric heat of adsorption (Q_{st}).[4]

Scanning electron micrographs (SEM) images were taken using a Hitachi SU8030 at the EPIC facility (NUANCE Center-Northwestern University). EDS line scans were also obtained on the same instrument. Samples were activated and coated with OsO_4 to ~9 nm thickness in a Denton Desk III TSC Sputter Coater before imaging.



Preparation of tetraethyl 4,4′,4″,4‴-(pyrene-1,3,6,8-tetrayl)tetrabenzote TBAPyOEt$_4$ (1):

2.7 L of 1,4-dioxane was added to 12-liter reactor and purged with argon for 1.5 h using a high-efficiency sparger. While argon is still purging stirring the dioxane, 50 g of tetrabromopyrene, 84.3 g of 4-ethoxycarbonylphenylboronic acid, 247 g of K_3PO_4, 6.30 g of $NiCl_2(PPh_3)_2$ and 5.10 g PPh_3 were added into the reactor. The system was sealed and purged argon additional 5 min before, heating to 90 °C for 48 h. The reaction was quenched with 2 L of water and filtered. The resulting solid was washed with 1 L water twice and with 2 L of acetone. Desired product on the filter was taken into chloroform by washing with 6x500 mL hot chloroform on the frit. The volume of the solution was

reduced to 1.5 L by evaporating the chloroform and the product is precipitated with 3 L of methanol. The solid product was collected via filtration and dried in vacuum oven at 70 °C for 12 h resulting in a 45 g, 59% yield (see Fig S1 for ^{1}H NMR).

Preparation of tetraethyl 4,4′,4″,4‴-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid or H_4TBAPy (2):

45 g of **1** and 5 L of dioxane were added to a 12-liter reactor with a mechanical stirrer. The solution of 70.6 g of potassium hydroxide and 4 liters of water was prepared in a 4-liter Erlenmeyer flask and added to the reaction flask. The resulting suspension was refluxed with rigorous stirring for 67 h. A clear solution should be seen after the reaction. Concentrated hydrochloric acid was added slowly through an addition funnel into the reaction (dropwise) while stirring until a pH of 1 was achieved. Vacuum filtration was used to filter the yellow precipitate. The resulting solid was suspended in 1 L water via sonication and filtered, and washed with additional 1 L of water. The powder dried on the filter for 4 h under vacuum to remove excess of water and then dissolved in boiling DMF (1 L) followed by precipitation with DCM (3 L). The resulting yellow solid was collected via filtration and washed with additional 1 L of DCM and dried under vacuum at 120 °C for 36 h resulting in a 36 g, 93% yield (see Fig S2 for ^{1}H NMR).

NU-1000: $ZrOCl_2.8H_2O$ (98 mg, 0.3 mmol) and 4-aminobenzoic acid (2.7 g, 22 mmol) were mixed in 8 mL of DMF in an 8-dram vial and ultrasonically dissolved. The clear solution was incubated in an oven at 80 ^{0}C for 1 h. After cooling down to room temperature H_4TBAPy (40 mg, 0.06 mmol) was added and sonicated for 10 min. The yellow suspension was placed in a pre-heated oven at 100 ^{0}C for 18 h. After cooling down to room temperature, yellow polycrystalline material was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh dimethlyformamide (DMF) three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-1000 was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h. The yellow powder was suspended in 12 mL DMF and 0.5 mL of 8 M aqueous HCl was added to a 8-dram vial and heated in an oven at 100^{0}C for 18 h. After cooling to room temperature, the powder was isolated by centrifugation and washed with DMF three times (10 mL each) and acetone three times (10 mL each). NU-1000 was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h. (yield: ~40 mg).

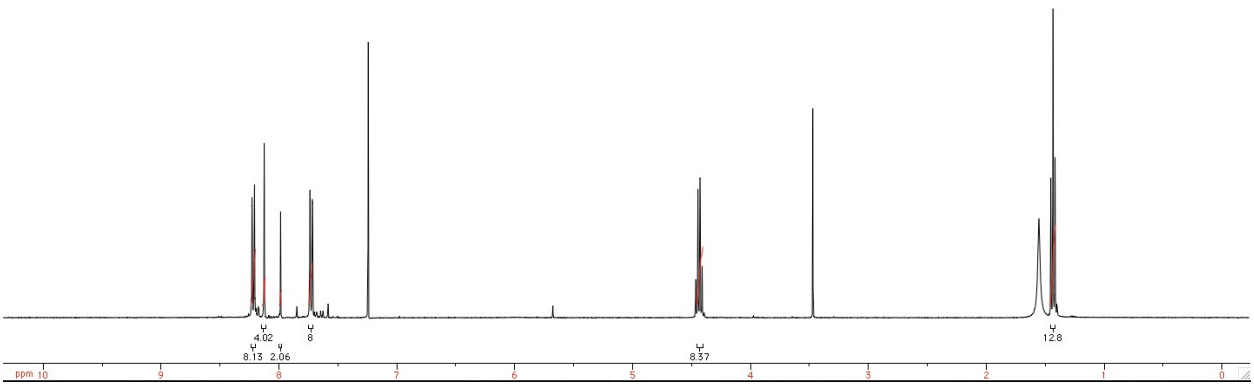


Figure S1. ^{1}H NMR spectrum of digested TBAPyOEt$_4$ in C*D*Cl$_3$.

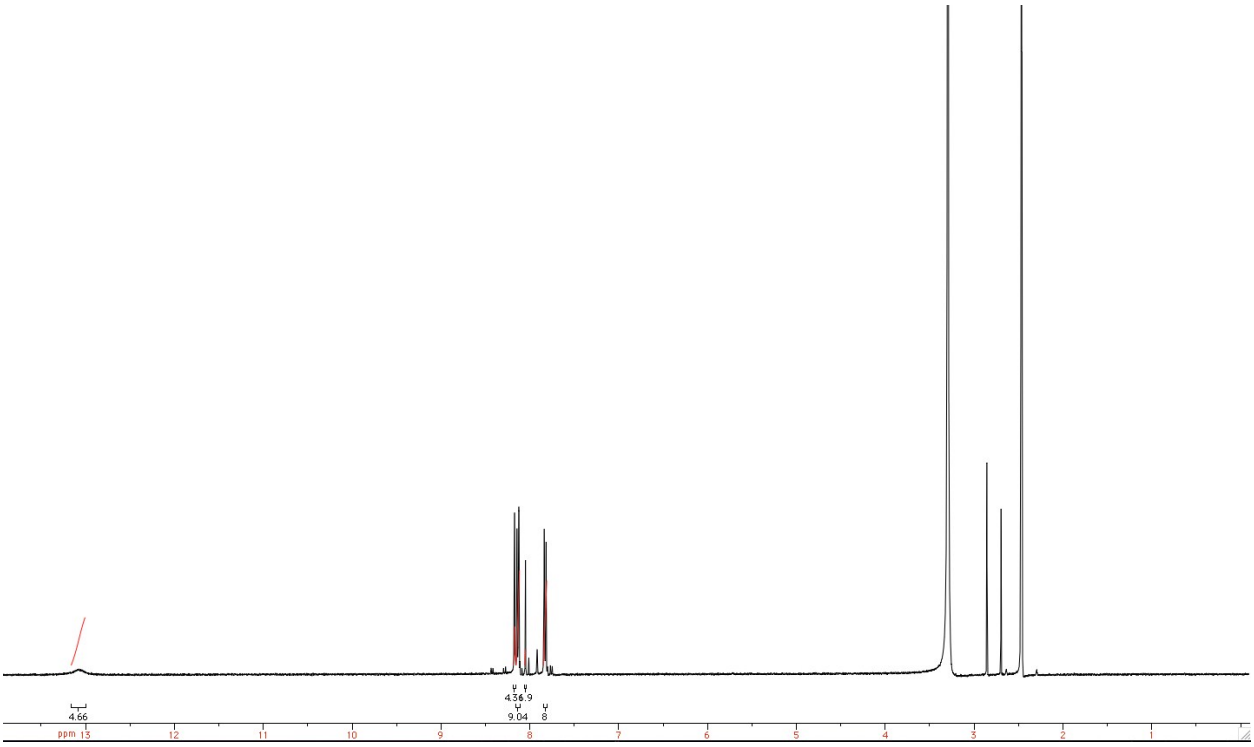


Figure S2. ^{1}H NMR spectrum of digested H_4TBAPy in d_6-DMSO.

MOF synthesis with $ZrO(NO_3)_2$: $ZrO(NO_3)_2$ (69 mg, 0.3 mmol) and benzoic acid (2.7 g, 22 mmol) were mixed in 8 mL of DMF in an 8-dram vial and ultrasonically dissolved. The clear solution was incubated in an oven at 80 ^{0}C for 1 h. After cooling down to room temperature H_4TBAPy (40 mg, 0.06 mmol) was added and sonicated for 10 min. The yellow suspension was placed in a pre-heated oven at 100 ^{0}C for 18 h. After cooling down to room temperature, yellow polycrystalline material was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-1000/NU-901 was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~58 mg).

MOF synthesis with $Zr(acac)_4$: $Zr(acac)_4$ (acac = acetyl acetonate) (146 mg, 0.3 mmol) and benzoic acid (2.7 g, 22 mmol) were mixed in 8 mL of DMF in an 8-dram vial and ultrasonically dissolved. The clear solution was incubated in an oven at 80 ^{0}C for 1 h. After cooling down to room temperature H_4TBAPy (40 mg, 0.06 mmol) was added and sonicated for 10 min. The yellow suspension was placed in a pre-heated oven at 100 ^{0}C for 18 h. After cooling down to room temperature, yellow polycrystalline material was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-1000/NU-901 was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~58 mg).

Synthesis of NU-901-BA-NH_2: $Zr(acac)_4$ (97 mg, 0.2 mmol) and 4-aminobenzoic acid (3.02 g, 22 mmol) were mixed in 8 mL of DMF in an 8-dram vial and ultrasonically dissolved. The clear solution was incubated in an oven at 80 ^{0}C for 1 h. After cooling down to room temperature H_4TBAPy (40 mg, 0.06 mmol) was added and sonicated for 10 min. The yellow suspension was placed in a pre-heated oven at 100 ^{0}C for 18 h. After cooling down to room temperature, yellow polycrystalline material was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with

fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-901 was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~30 mg).

HCl-activation of NU-901-BA-NH_2: The yellow powder was suspended in 12 mL DMF and 0.5 mL of 8 M aqueous HCl was added to a 8-dram vial and heated in an oven at 100^{0}C for 18 h. After cooling to room temperature, the powder was isolated by centrifugation and washed with DMF three times (10 mL each) and acetone three times (10 mL each). NU-901-HCl was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h, and then activated at Micromeritics Smart VacPrep instrument as described above (yield: ~20 mg HCl activated NU-901).

Synthesis of NU-901-BA-$NHCH_3$: $Zr(acac)_4$ (acac = acetyl acetonate) (97 mg, 0.2 mmol) and 4-(methylamino)benzoic acid (3.32 g, 22 mmol) were mixed in 15 mL of DMF in an 8-dram vial and ultrasonically dissolved. The clear solution was incubated in an oven at 80 ^{0}C for 1 h. After cooling down to room temperature H_4TBAPy (40 mg, 0.06 mmol) was added and sonicated for 10 min. The yellow suspension was placed in a pre-heated oven at 100 ^{0}C for 18 h. After cooling down to room temperature, yellow polycrystalline material was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-901-BA-$NHCH_3$ was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~35 mg).

Synthesis of NU-901-BA-$N(CH_3)_2$: $Zr(acac)_4$ (acac = acetyl acetonate) (97 mg, 0.2 mmol) and 4-(dimethylamino)benzoic acid (3.63 g, 22 mmol) were mixed in 15 mL of DMF in an 8-dram vial and ultrasonically dissolved. The clear solution was incubated in an oven at 80 ^{0}C for 1 h. After cooling down to room temperature H_4TBAPy (40 mg, 0.06 mmol) was added and sonicated for 10 min. The yellow suspension was placed in a pre-heated oven at 100 ^{0}C for 18 h. After cooling down to room temperature, yellow polycrystalline material was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-901-BA-$N(CH_3)_2$ was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~40 mg).

Synthesis of NU-901-SALI-BA-$NHCH_3$: NU-901-HCl (14 mg, 0.007 mmol) was added to a solution of 4-(methylamino)benzoic acid (28 mg, 0.185 mmol) dissolved with 5 mL of DMF to a 8-dram vial and ultrasonically agitated. The vial was incubated in an oven at 65 ^{0}C for 18 h. After cooling down to room temperature, the yellow suspension was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-901-SALI-BA-$NHCH_3$ was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~14 mg).

Synthesis of NU-901-SALI-isonic: NU-901-HCl (14 mg, 0.007 mmol) was added to a solution of isonicotinic acid (23 mg, 0.187 mmol) dissolved with 5 mL of DMF to a 8-dram vial and ultrasonically agitated. The vial was incubated in an oven at 65 ^{0}C for 18 h. After cooling down to room temperature, the yellow suspension was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-901-SALI-isonic was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~14 mg).

Synthesis of NU-901-SALI-nico: NU-901-HCl (7 mg, 0.003 mmol) was added to a solution of nicotinic acid (12 mg, 0.094 mmol) dissolved with 5 mL of DMF to a 8-dram vial and ultrasonically agitated. The vial was incubated

in an oven at 65 ^{0}C for 18 h. After cooling down to room temperature, the yellow suspension was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-901-SALI-nico was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~6 mg).

Synthesis of NU-901-SALI-BA-3,5-NH_2: NU-901-HCl (14 mg, 0.007mmol) was added to a solution of 3,5-diaminobenzoic acid (25 mg, 0.164 mmol) dissolved with 5 mL of DMF to a 8-dram vial and ultrasonically agitated. The vial was incubated in an oven at 65 ^{0}C for 18 h. After cooling down to room temperature, the yellow suspension was isolated by centrifuge (5 min, 7500 rpm) and solvent exchanged with fresh DMF three times (10 mL each) followed by methanol three times (10 mL). Yellow polycrystalline NU-901-SALI-BA-3,5-NH_2 was collected by centrifugation and dried in a vacuum oven at 80 ^{0}C for 1 h (yield: ~14 mg).

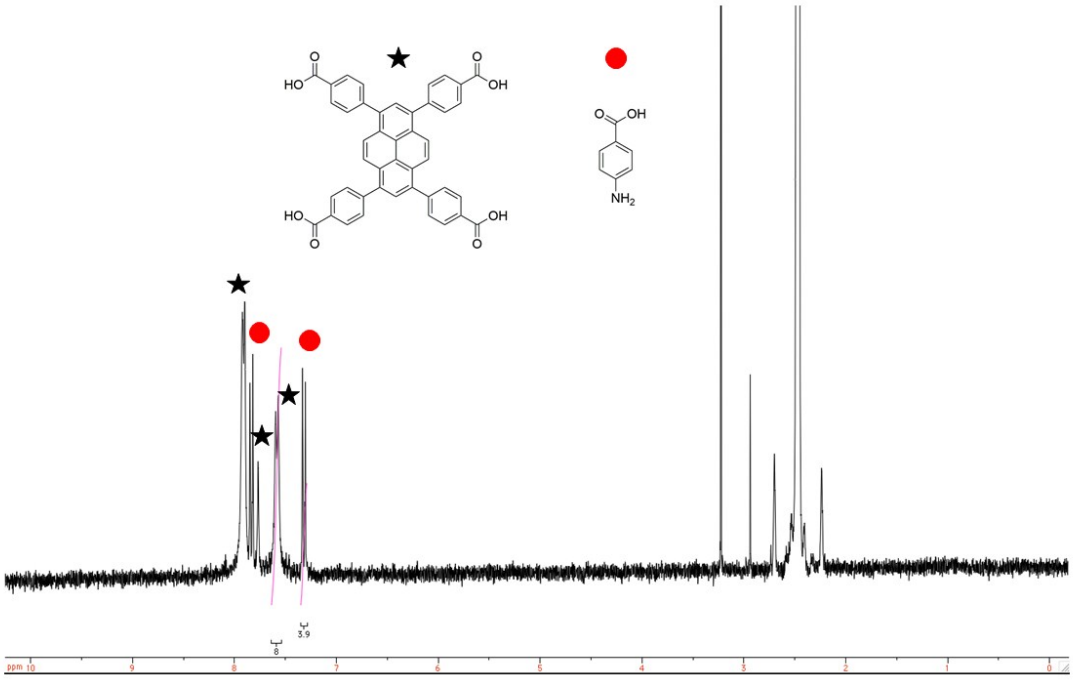


Figure S3. ^{1}H NMR spectrum of digested NU-901-BA-NH_2 in d_6-DMSO.

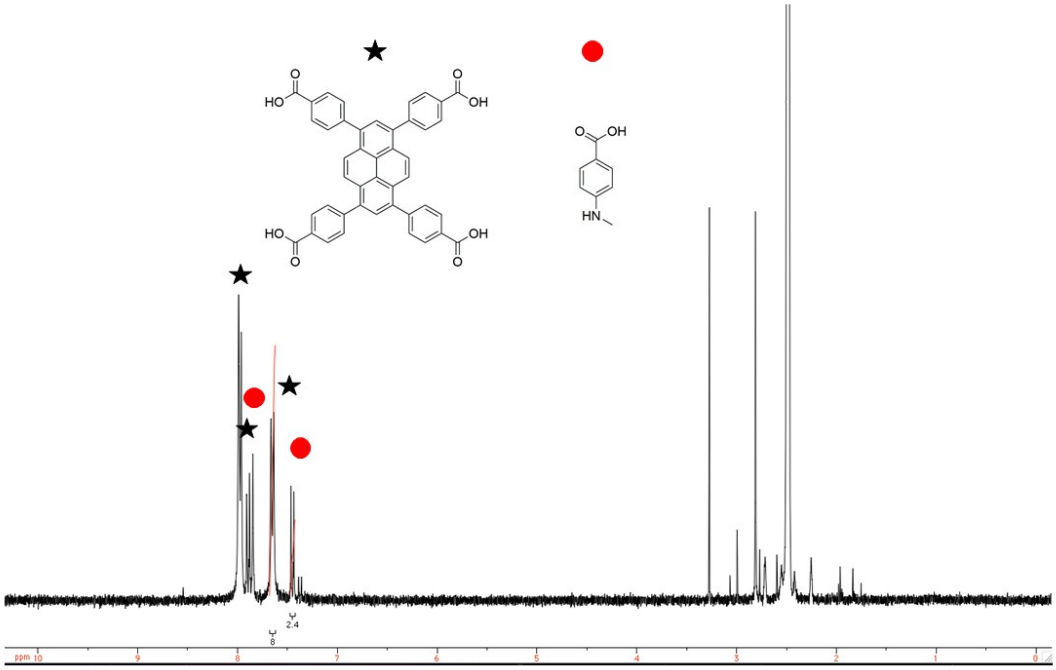


Figure S4. ^{1}H NMR spectrum of digested NU-901-BA-NHCH$_3$ in d_6-DMSO.

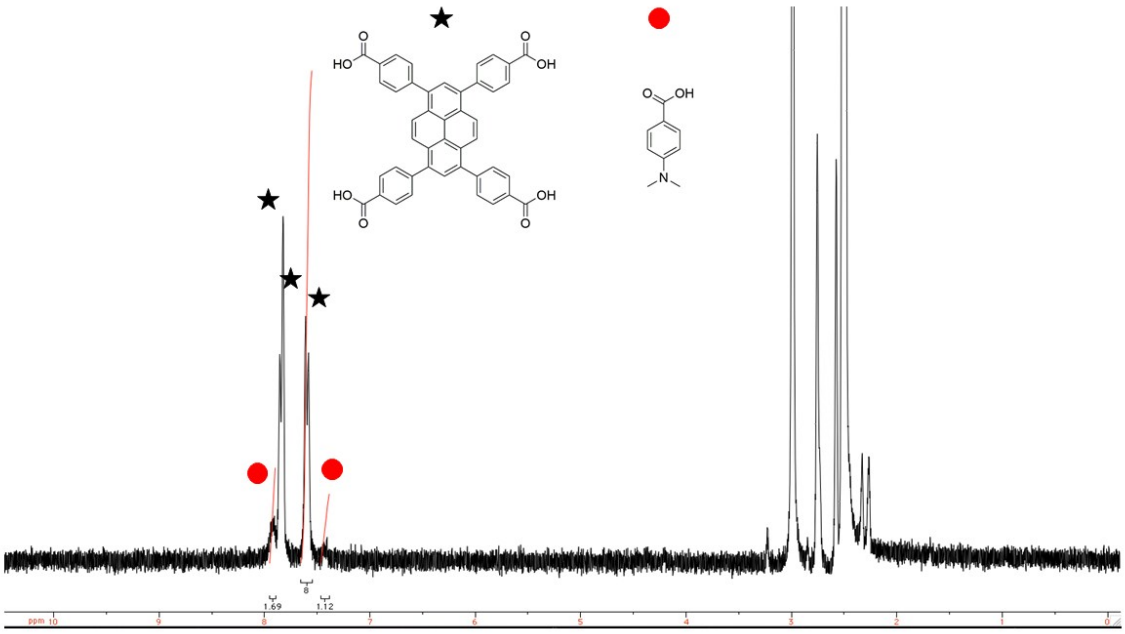


Figure S5. ^{1}H NMR spectrum of digested NU-901-BA-N(CH$_3$)$_2$ in d_6-DMSO.

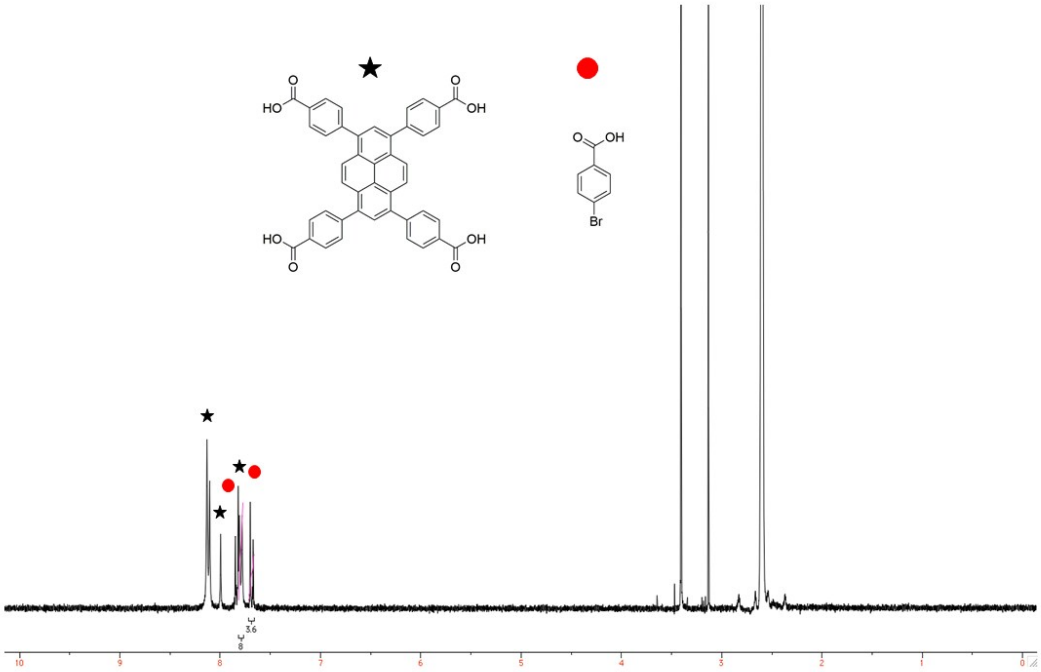


Figure S6. ^{1}H NMR spectrum of digested NU-901-BA-Br in d_6-DMSO.

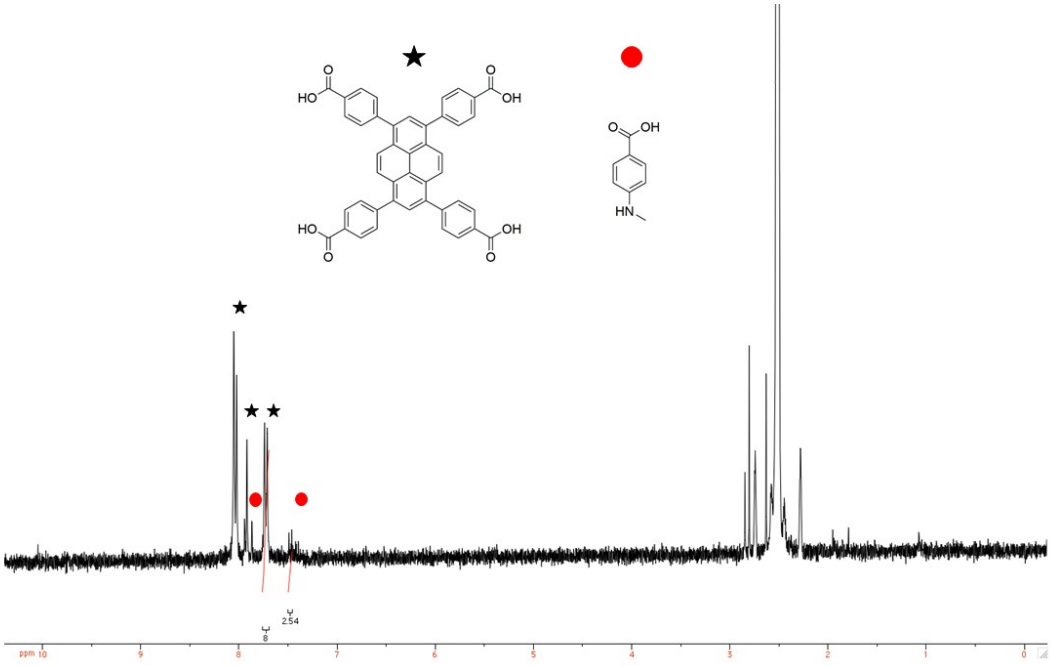


Figure S7. ^{1}H NMR spectrum of digested NU-901-SALI-BA-NHCH$_3$ in d_6-DMSO.

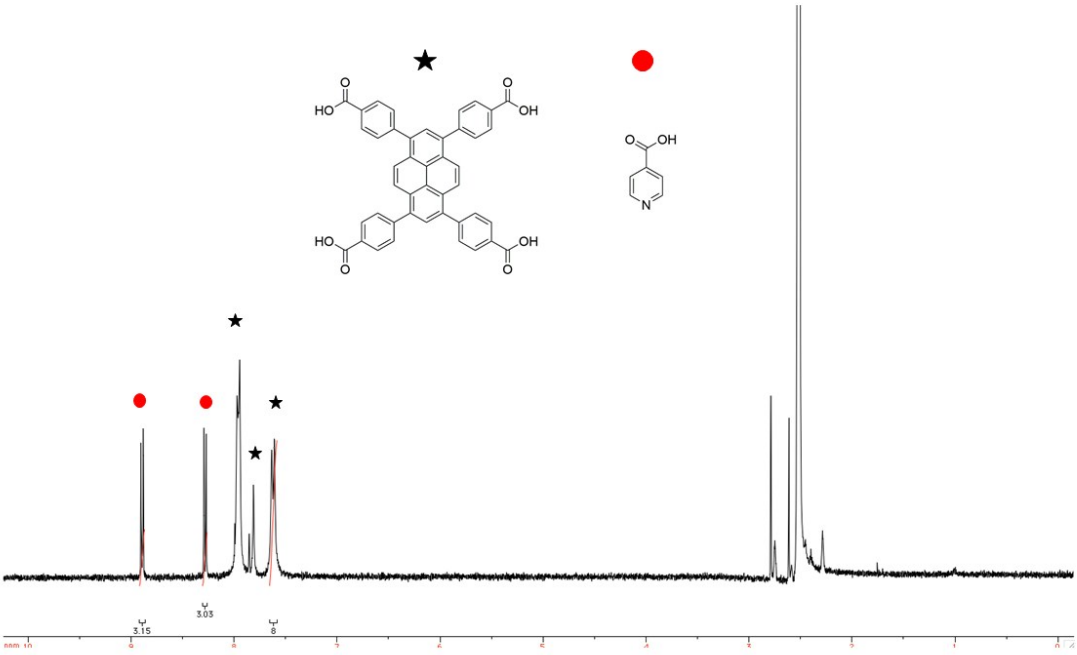


Figure S8. ^{1}H NMR spectrum of digested NU-901-SALI-isonic in d_6-DMSO.

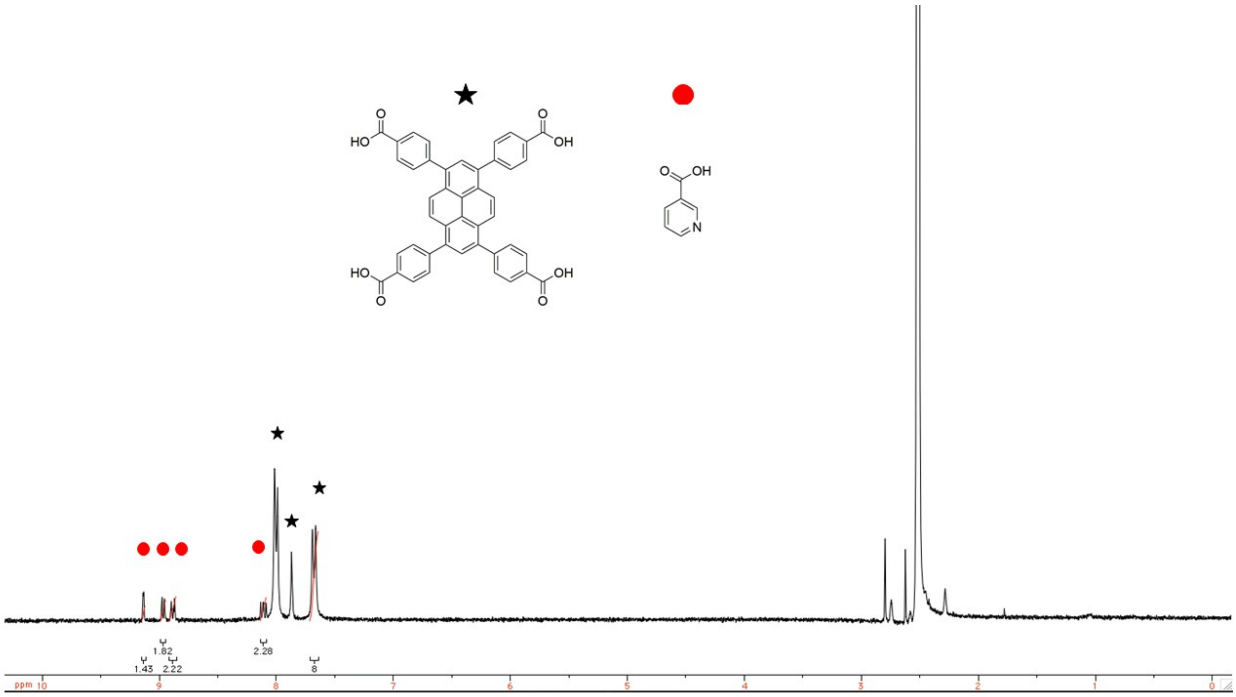


Figure S9. ^{1}H NMR spectrum of digested NU-901-SALI-nico in d_6-DMSO.

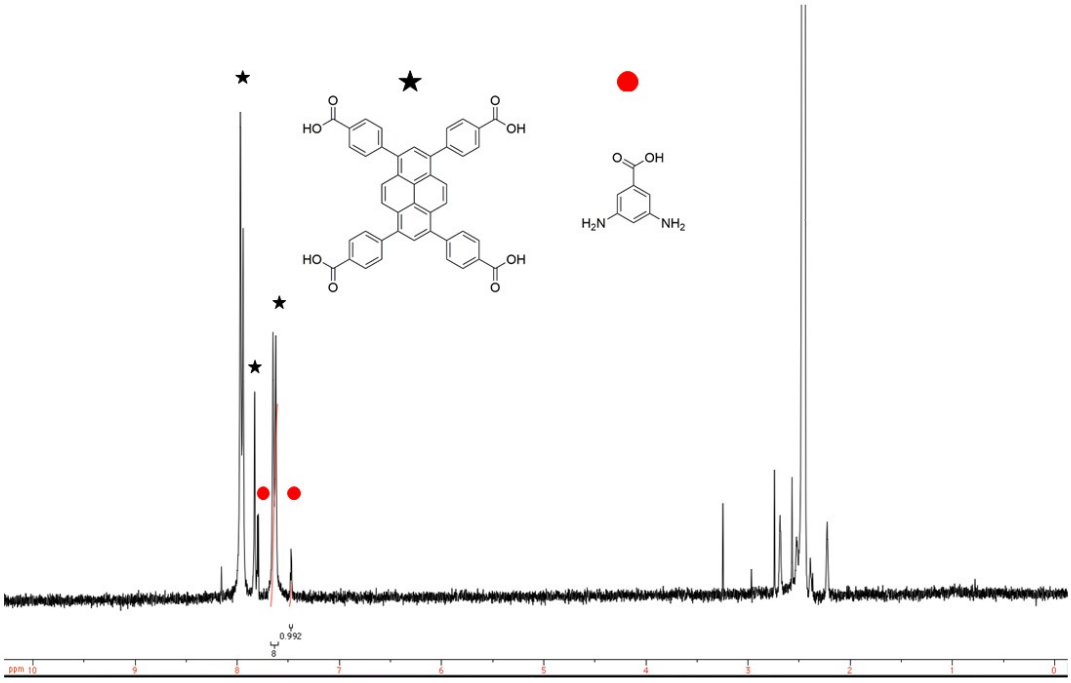


Figure S10. ^{1}H NMR spectrum of digested NU-901-SALI-BA-3,5-NH_2 in d_6-DMSO.

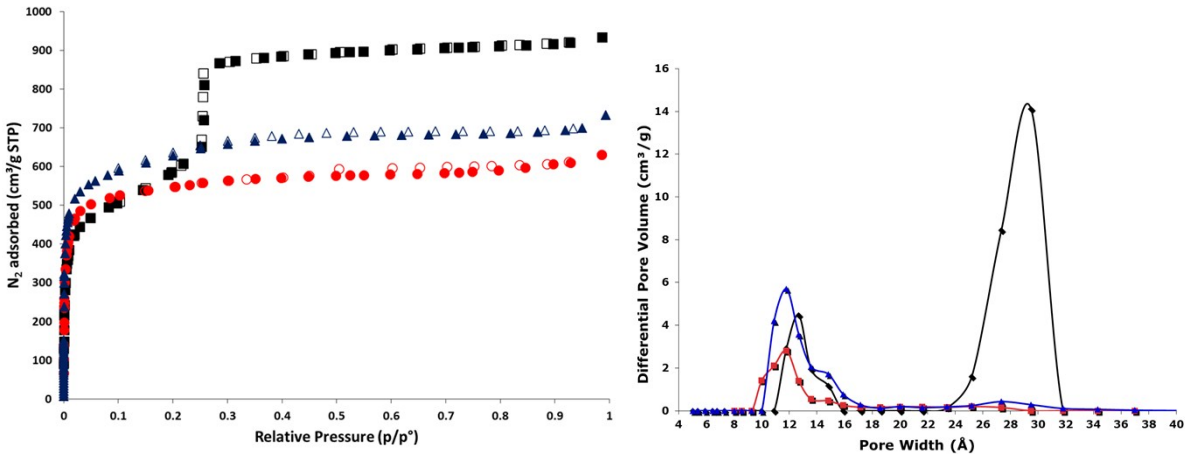


Figure S11. N_2 isotherms of NU-1000 (black squares), NU-901-BA-NH_2 (red circles), and NU-901-HCl (blue triangles). Adsorption = filled, desorption = empty markers.

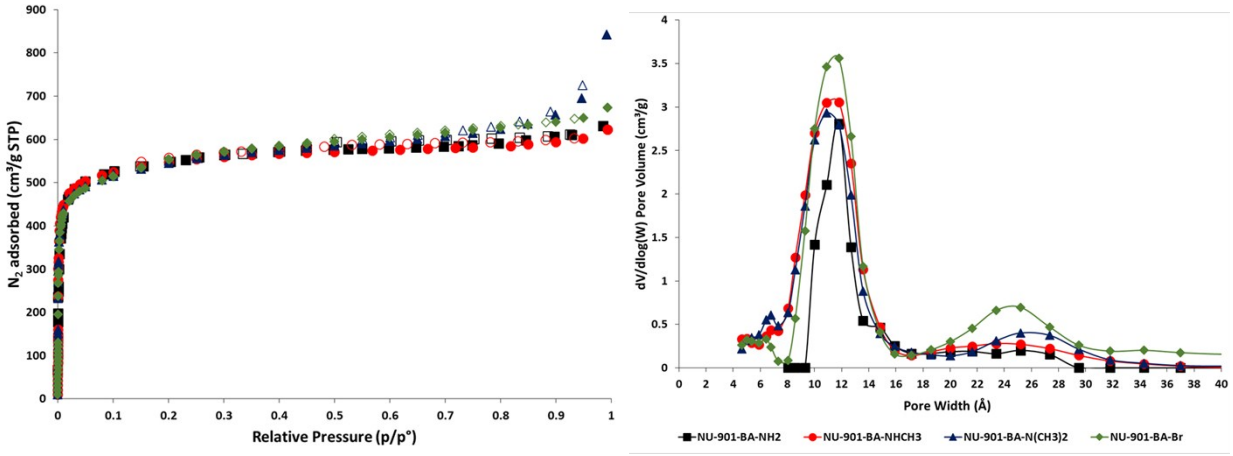


Figure S12. N_2 isotherms of NU-901-BA-NH_2 (black squares), NU-901-BA-$NHCH_3$ (red circles), NU-901-BA-$N(CH_3)_2$ (blue triangles), and NU-901-BA-Br (green diamonds) synthesized through *de novo* MOF synthesis. Adsorption = filled, desorption = empty markers.

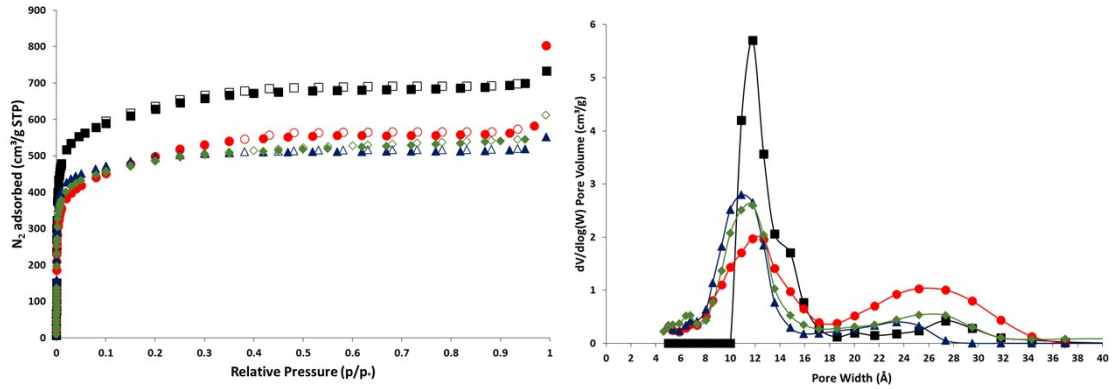


Figure S13. N_2 isotherms (left) and pore size distribution (right) of NU-901-HCl (black squares), NU-901-SALI-isonic (red circles), NU-901-SALI-nico (blue triangles), and NU-901-SALI-BA-3,5-NH_2 (green diamonds). Adsorption = filled, desorption = empty markers.

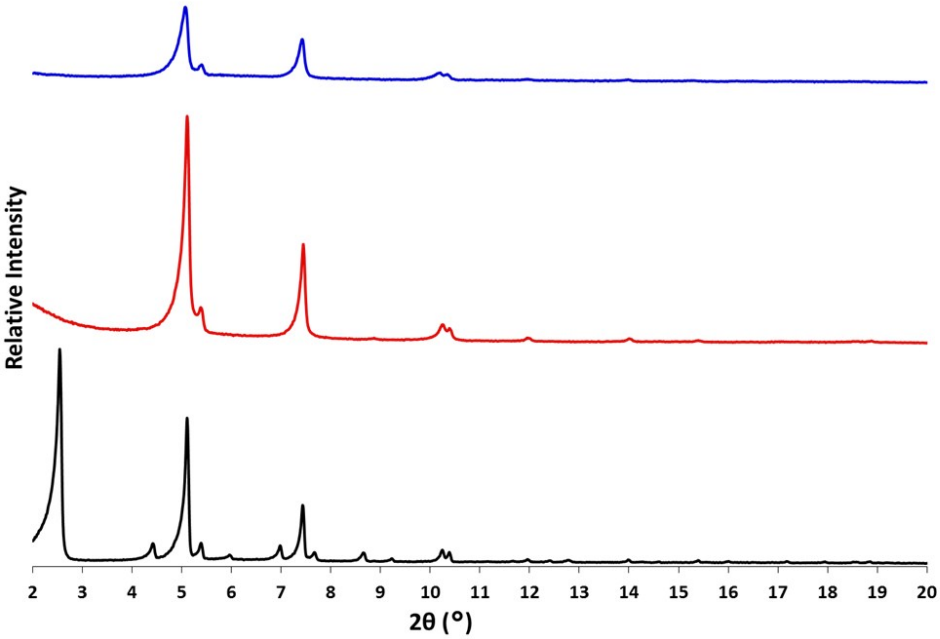


Figure S14. PXRD patterns of NU-1000 (bottom), NU-901-BA-NH_2 (middle), and NU-901-HCl (top).

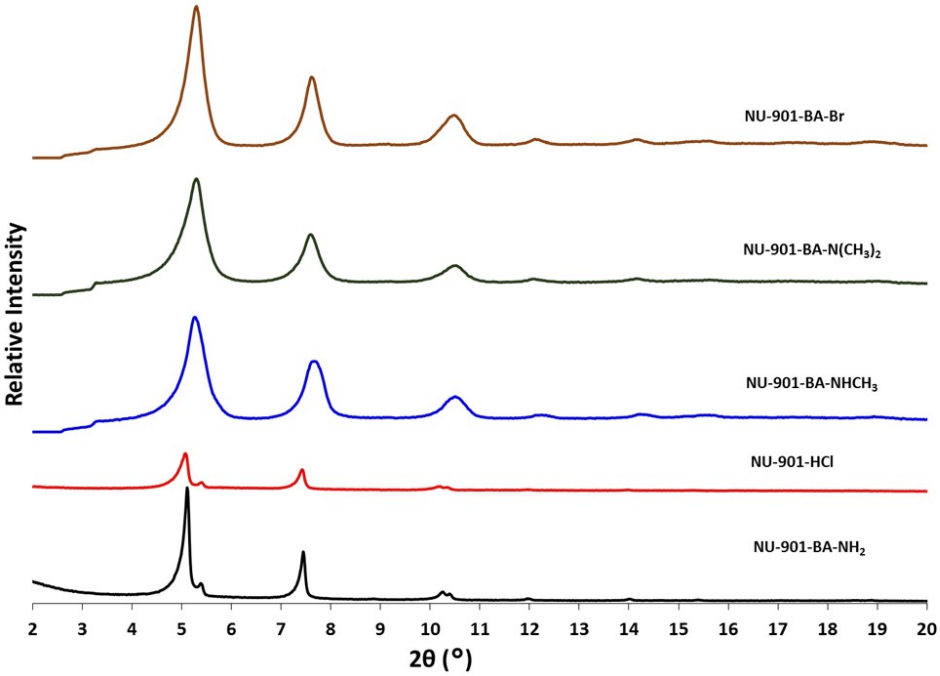


Figure S15. PXRD patterns of NU-901-BA-NH_2, NU-901-HCl- NU-901-BA$NHCH_3$, NU-901-$N(CH_3)_2$, and NU-901-BA-Br.

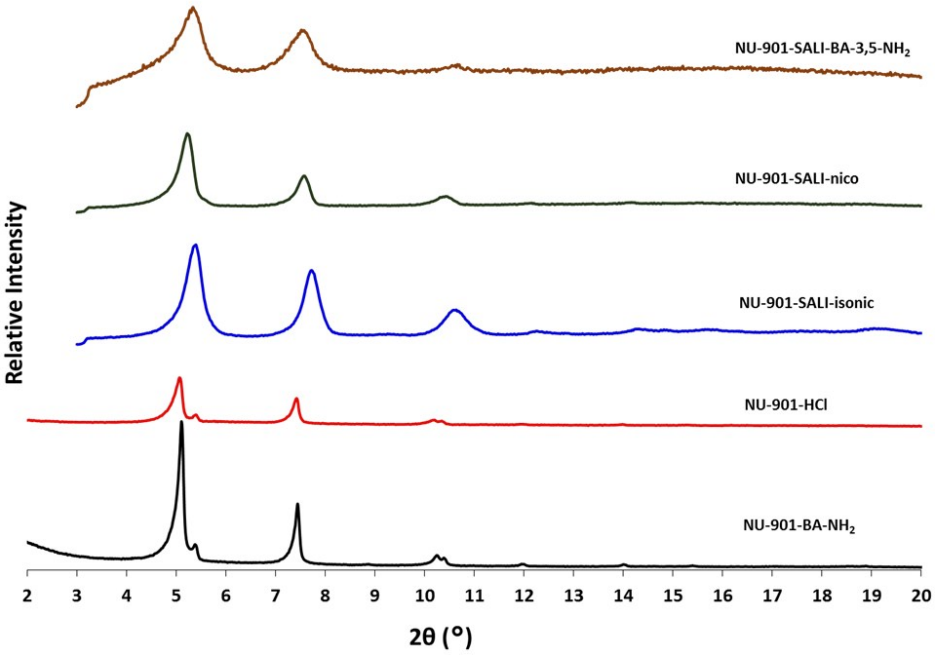


Figure S16. PXRD patterns of NU-901-BA-NH_2, NU-901-HCl- NU-901-SALI-isonic, NU-901-SALI-nico, and NU-901-SALI-BA-3,5-NH_2.

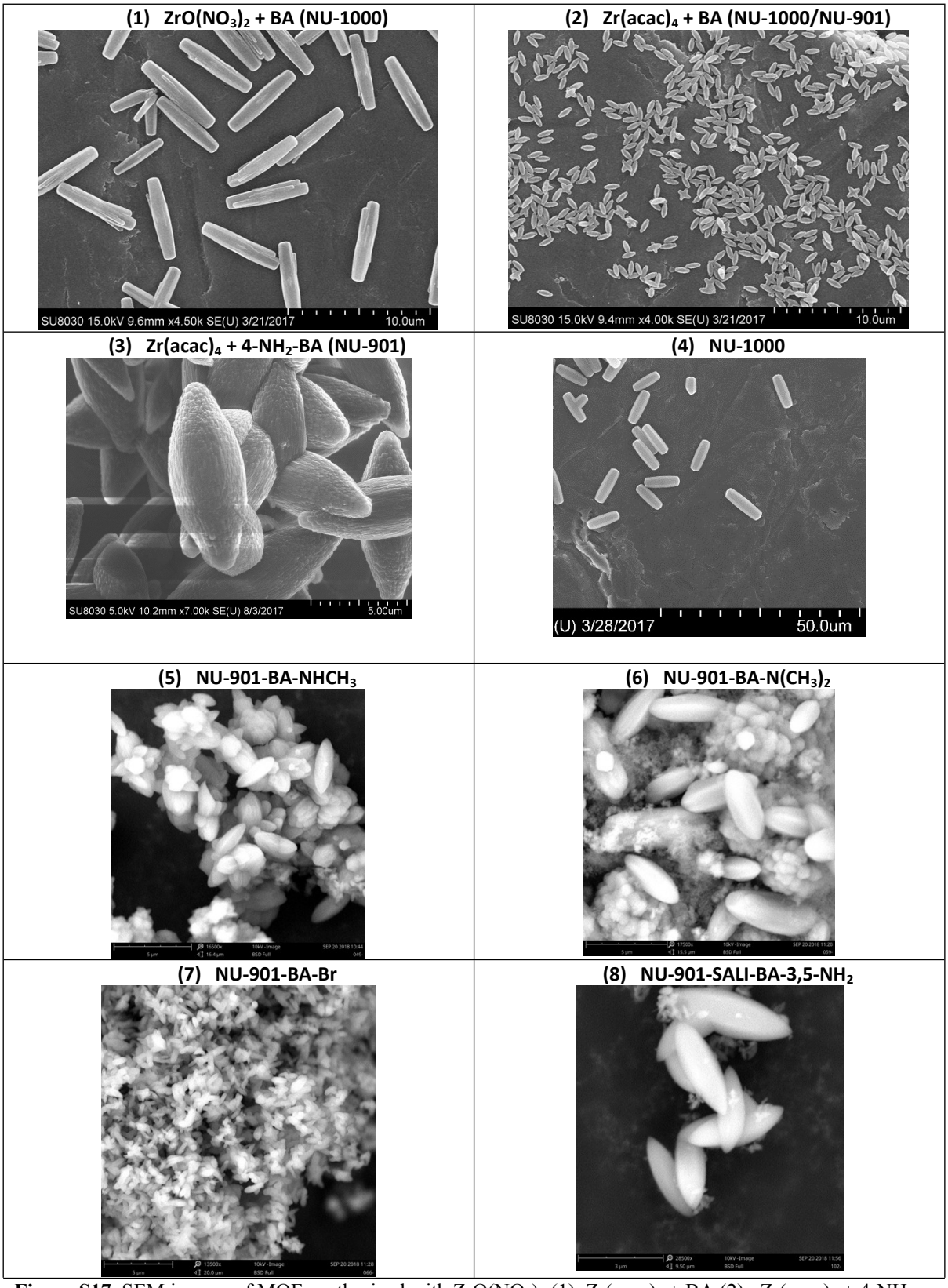


Figure S17. SEM images of MOF synthesized with $ZrO(NO_3)_2$ (1), $Zr(acac)_4$ + BA (2), $Zr(acac)_4$ + 4-NH_2-BA (3), NU-1000 (4), NU-901-BA-$NHCH_3$ (5), NU-901-BA-$N(CH_3)_2$ (6), NU-901-BA-Br (7), and NU-901-SALI-BA-3,5-NH_2 (8).

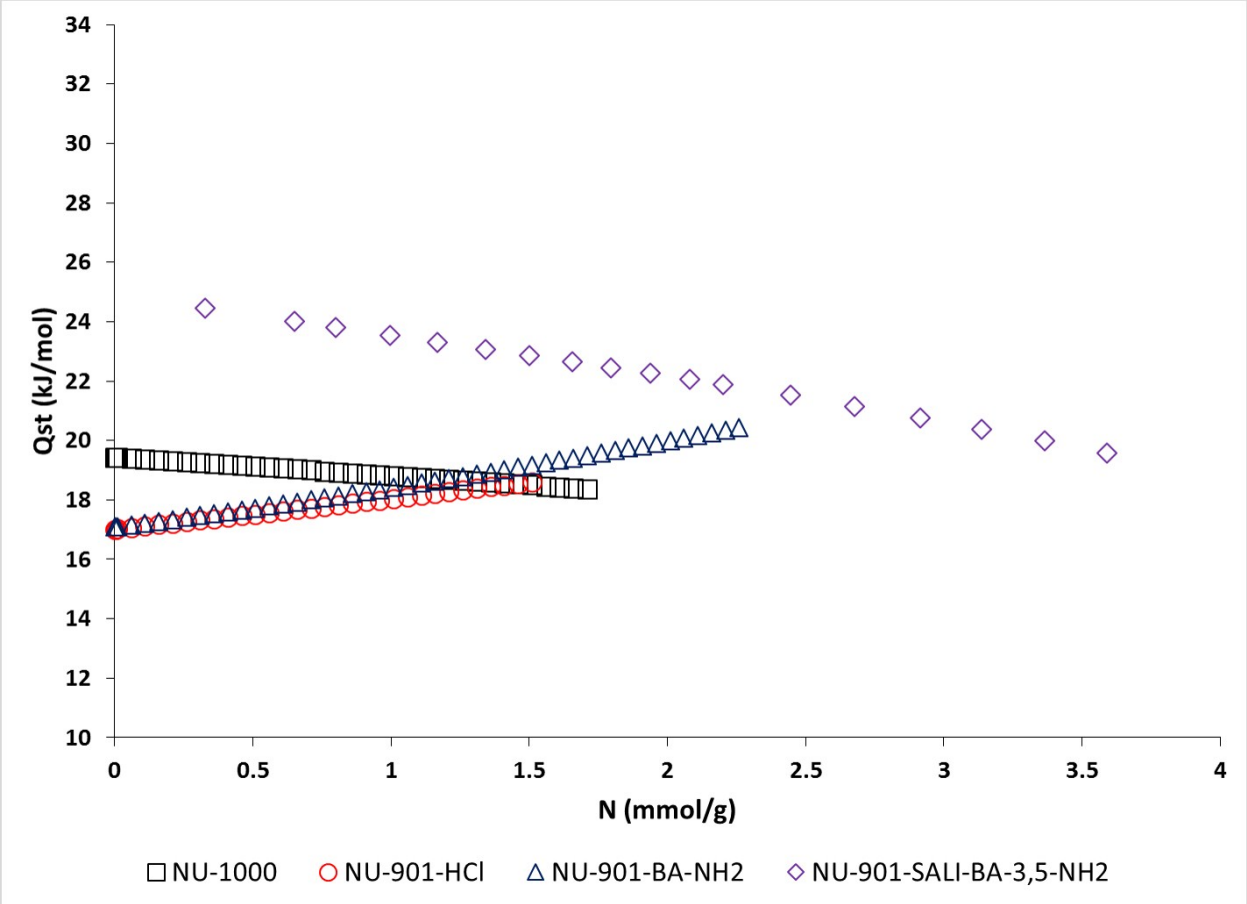


Figure S18. Plots of CO_2 isosteric heats of adsorption (Q_{st}) of NU-1000 (black squares), NU-901-HCl (red circles), NU-901-BA-NH_2 (blue triangles), and NU-901-SALI-BA-3,5-NH_2 (purple diamonds) calculated from single-site Langmuir model from CO_2 isotherms recorded at 273, 283, and 293 K.

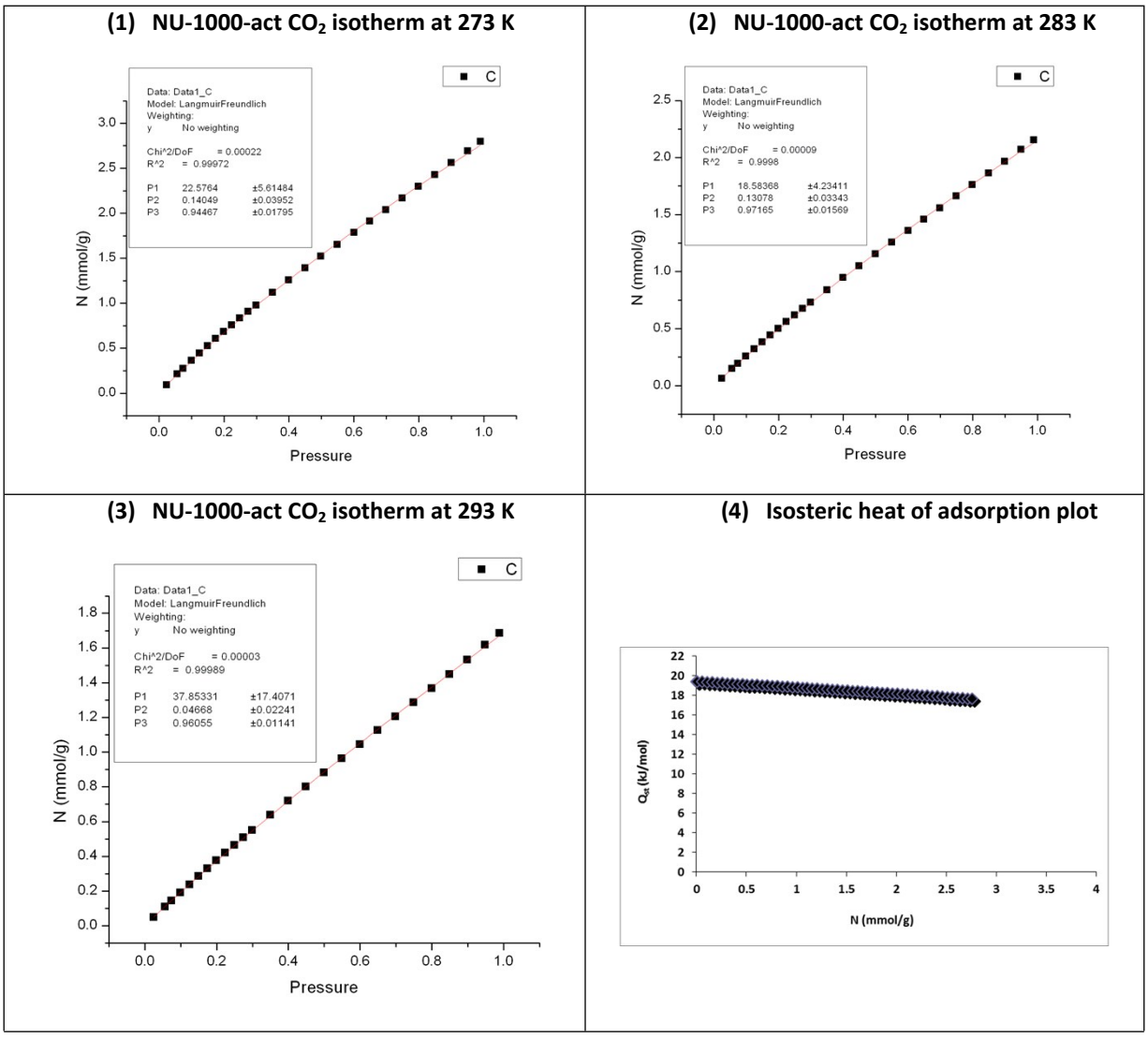


Figure S19. CO_2 adsorption curves, fitting and parameters for NU-1000-act at 273 K (1), 283 K (2), 293 K (3), and isosteric heat of adsorption (Q_{st}) calculated by the single-site Langmuir-Freundlich model (4).

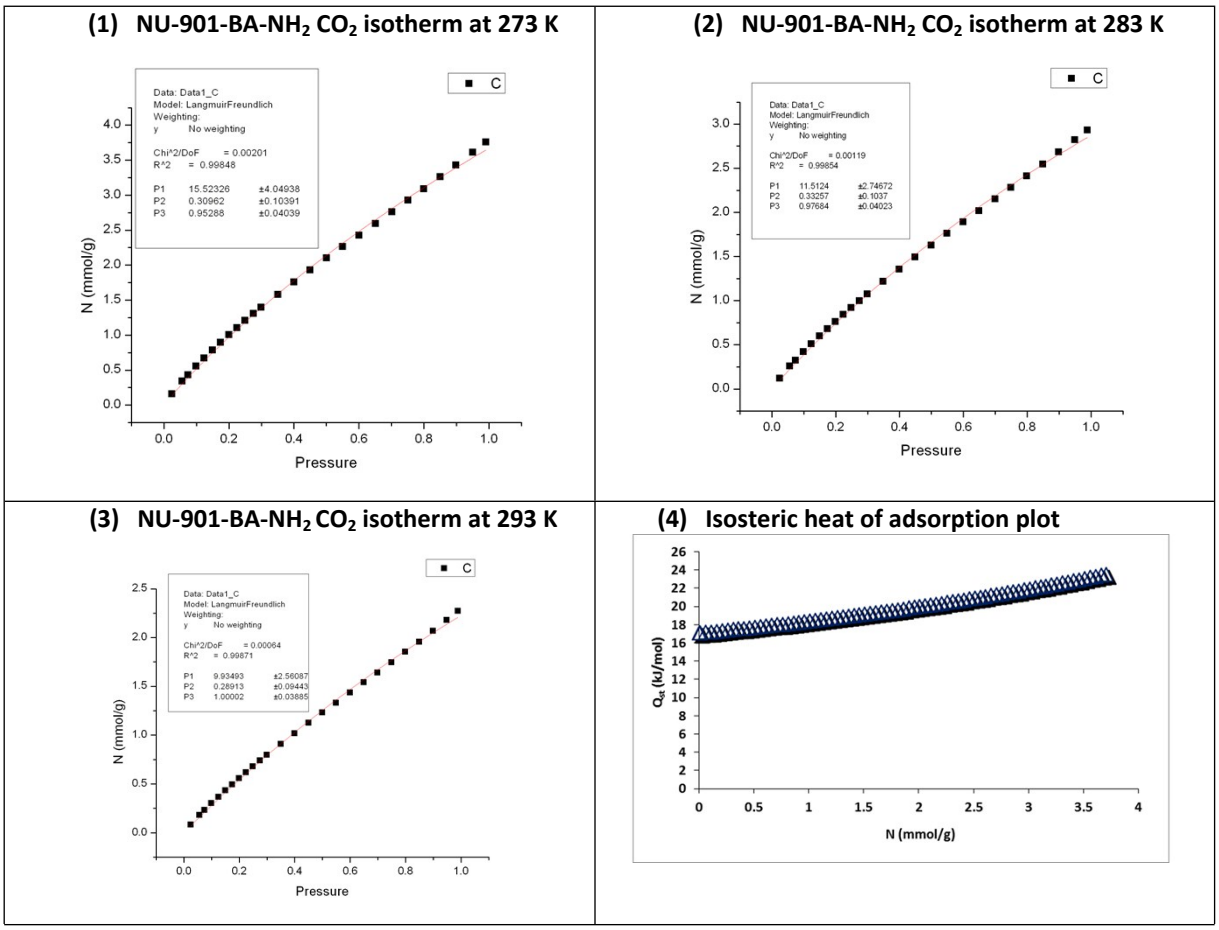


Figure S20. CO_2 adsorption curves, fitting and parameters for NU-901-BA-NH_2 at 273 K (1), 283 K (2), 293 K (3), and isosteric heat of adsorption (Q_{st}) calculated by the single-site Langmuir-Freundlich model (4).

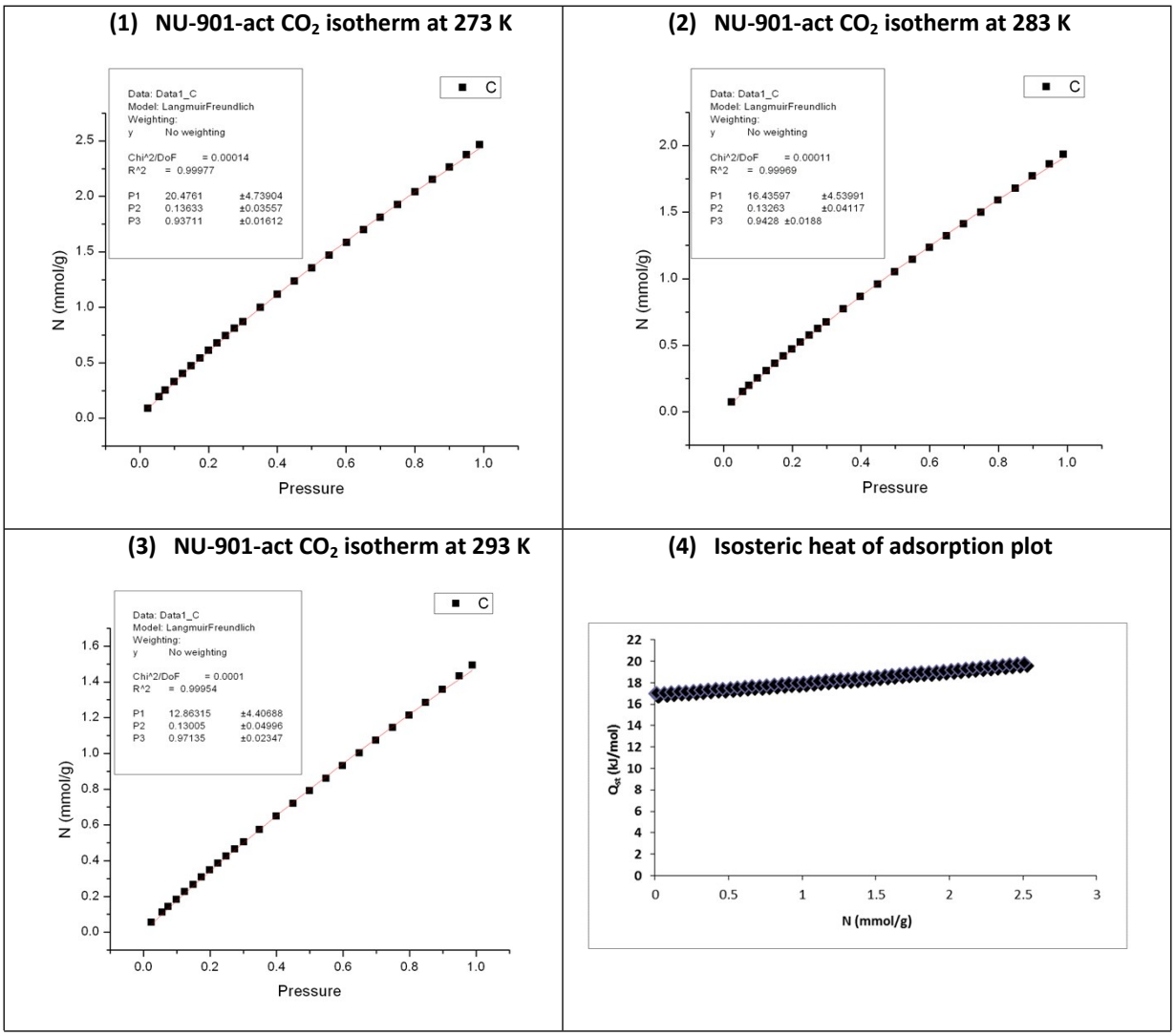
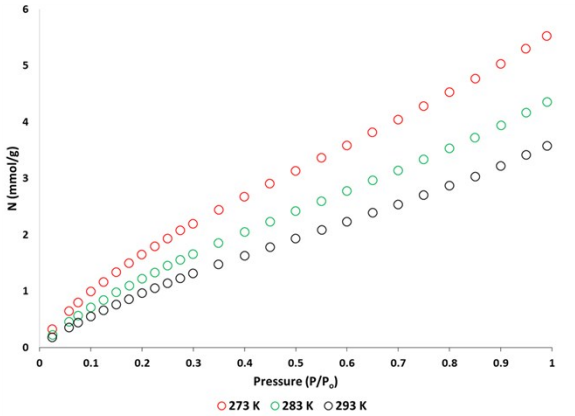
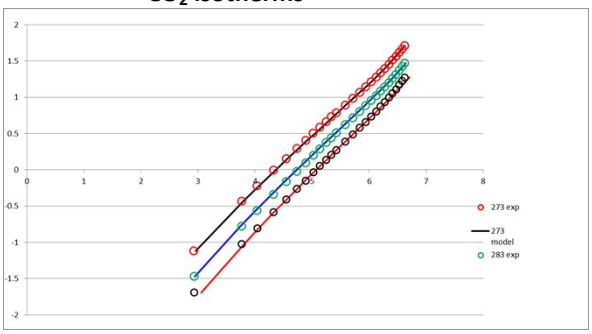


Figure S21. CO_2 adsorption curves, fitting and parameters for NU-901-act at 273 K (1), 283 K (2), 293 K (3), and isosteric heat of adsorption (Q_{st}) calculated by the single-site Langmuir-Freundlich model (4).

(1) NU-901-SALI-BA-3,5-NH_2 CO_2 isotherms



(2) Virial fitting of NU-901-SALI-BA-3,5-NH_2 CO_2 isotherms



(3) Virial equation fitting parameters

Zero coverage	-24.94120856
Total error	0.022329402

Power	a	b
0	-2999.904807	14.88422476
1	184.5161091	-0.059328286
2	-20.06554171	-0.093491874
3	3.931415014	0
4	1.640749118	0
5	-0.494271709	0
6	0.038440614	0
7	0	0

(4) Isosteric heat of adsorption plot

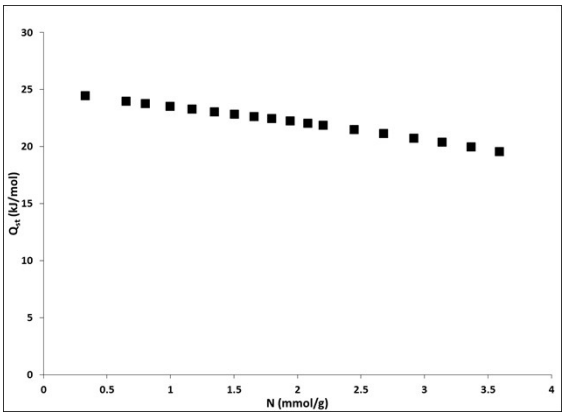


Figure S22. CO_2 adsorption curves (1), isotherm fitting (2), fitting parameters (3) and isosteric heat of adsorption (Q_{st}) calculated by the Virial equation (4) for NU-901-SALI-BA-3,5-NH_2 at 273 K, 283 K, 293 K.

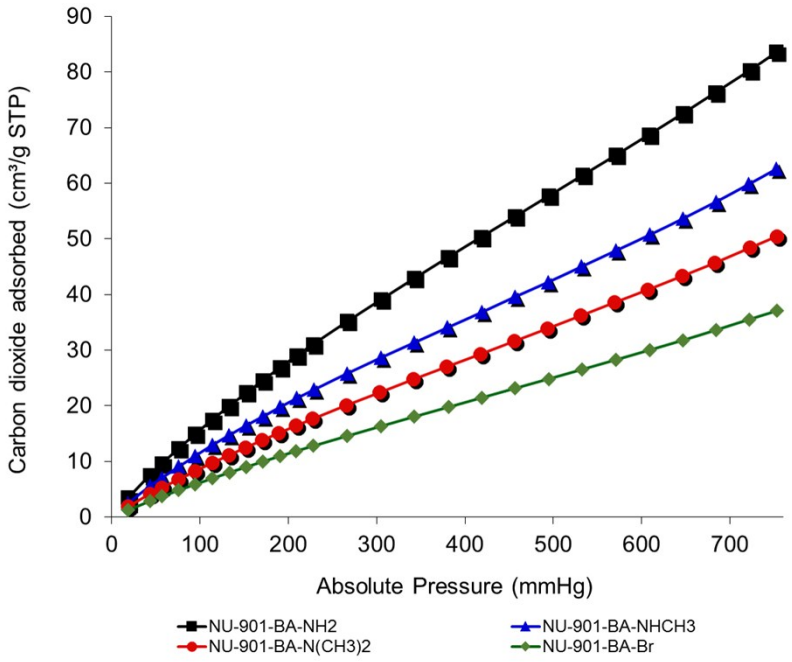


Figure S23. CO_2 adsorption curves of NU-901-BA-NH_2 (black squares), NU-901-BA$NHCH_3$ (blue triangles), NU-901-BA-$N(CH_3)_2$ (red circles), and NU-901-BA-Br at 273K.

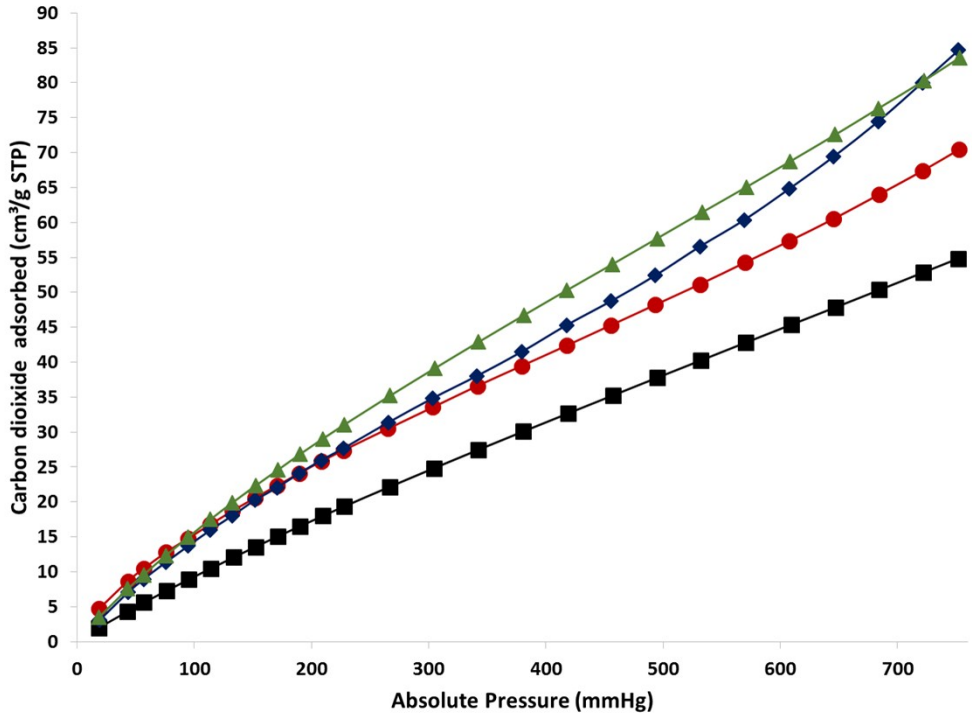


Figure S24. CO_2 adsorption curves of NU-901-HCl (black squares), NU-901-SALI-isonic (red circles), NU-901-SALI-nico (blue diamonds), and NU-901-BA-NH_2 (green triangles) at 273K.

DFT Calculations: Plane wave Density Functional Theory (DFT) calculations were done using the Quantum Espresso software package. Core electrons were approximated using PAW pseudopotentials with a 40/400 Ry corresponding wavefunction/electron density cutoff. The exchange and correlation was approximated using the Perdew–Burke-Ernzerhof (PBE) functional. All presented structures were geometry optimized with convergence thresholds of $10^{-5}/10^{-4}$ Ry for the energies/forces. All calculation included only the Γ-point due to size constraints.

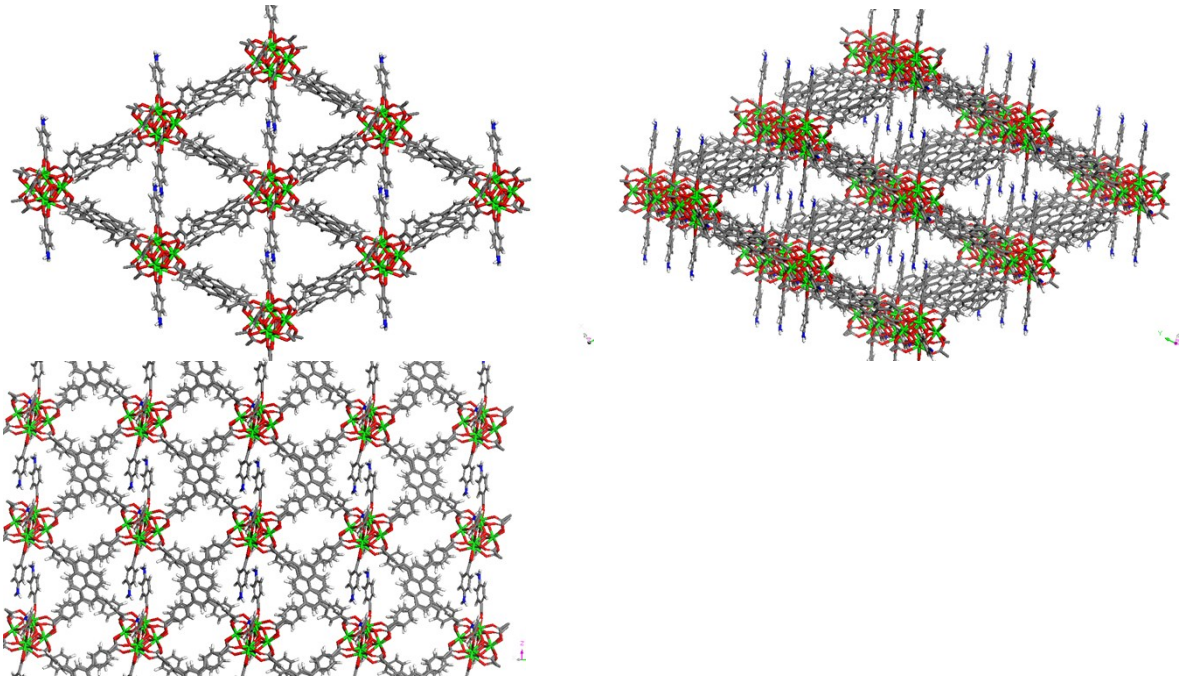


Figure S25. Optimized structures of NU-901-BA-NH_2.

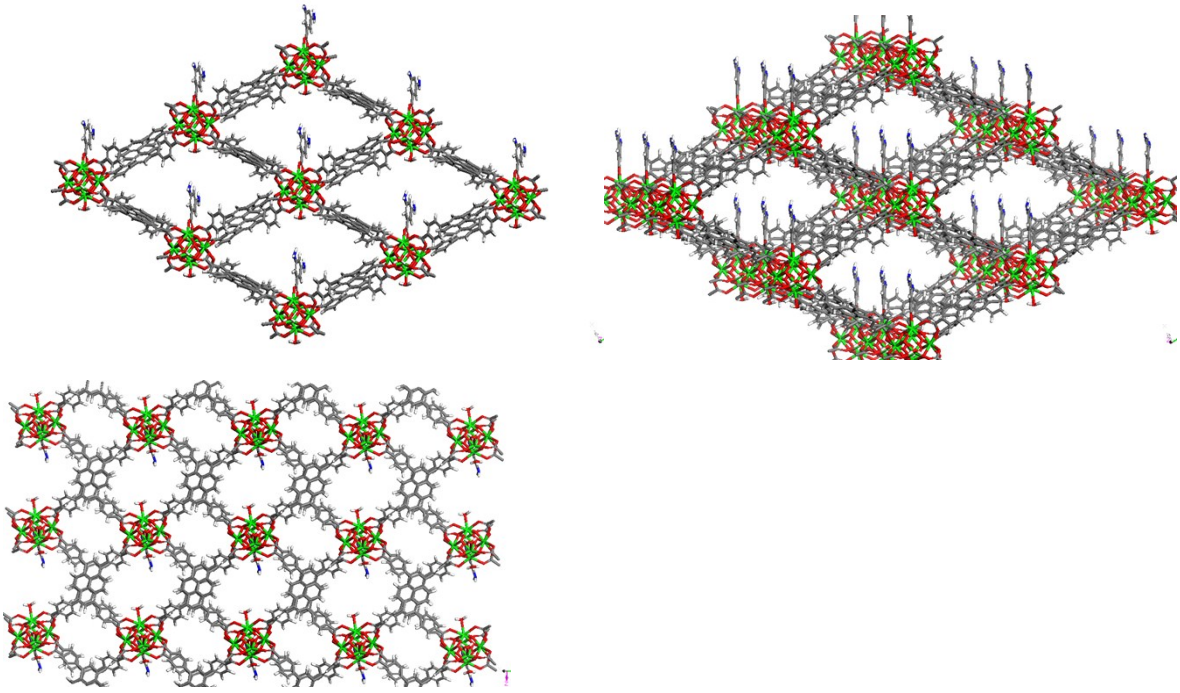


Figure S26. Optimized structures of NU-901-SALI-BA-3,5-NH_2.

References

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