Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Electronic Supplementary Information (ESI)

Supermolecular building layer approach for gas separation and storage applications: the eea and rtl MOF platforms for CO_2 capture and hydrocarbons separation

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1. Materials and general procedures

The organic ligands used in this study, 5-(isonicotinamido)isophthalic acid (H_2L1) and 5-(nicotinamido)isophthalic acid (H_2L2), were synthesized from isonicotinic acid and nicotinic acid, respectively, with 86 and 91% yields. Other ligands, H_2L3-H_2L5, were prepared as outlined on the following pages. All reagents were obtained from commercial sources and used without further purification, unless otherwise noted.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400, 500 and 600 MHz instruments. Chemical shifts for ^1H NMR spectra are reported in ppm (δ, relative to TMS) using DMSO residual peak ($\delta = 2.50$ ppm) in DMSO-d_6 as an internal standard and for ^{13}C NMR spectra solvent peaks at 39.52 ppm, and for solutions in $CDCl_3$ solvent peaks at 7.26 and 77.16 ppm, respectively. For solutions in D_2O, methyl signal of sodium salt of 3-(trimethylsilyl)propanesulfonic acid was used as a reference; $\delta = 0$ ppm for ^1H NMR and $\delta = -2.04$ ppm for ^{13}C NMR spectra.[1]

Powder X-ray diffraction (PXRD) measurements were carried out at room temperature on a PANalyticalX'Pert PRO diffractometer 45kV, 40mA for CuKα ($\lambda = 1.5418$ Å), with a scan speed of 1.0° min^{-1} and a step size of 0.02° in 2θ.

High resolution dynamic thermogravimetric analysis (TGA) were performed under a continuous N_2 flow and recorded on a TA Instruments hi-res TGA Q500 thermogravimetric analyzer with a heating rate of 5 °C per minute.

Low pressure gas adsorption measurements were performed on 3Flex Surface Characterization Analyzer (Micromeritics) at relative pressures up to 1 atm. The cryogenic temperatures were controlled using liquid argon baths at 87 K, respectively. The bath temperature for the CO_2 adsorption measurements was controlled using an ethylene glycol/H_2O re-circulating bath.

High pressure gas adsorption studies were performed on a magnetic suspension balance marketed by Rubotherm (Germany).

2. Synthesis of the ligands

2.1 Synthesis of H_2L1

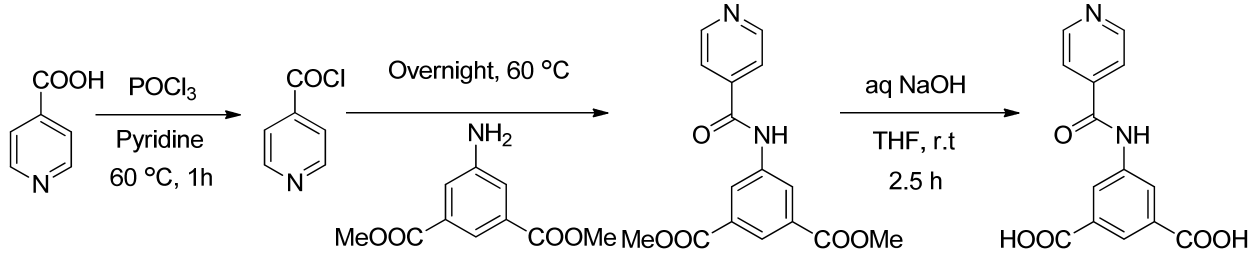


Fig. S1. Synthetic scheme of ligand H_2L1.

Dimethyl 5-(isonicotinamido)isophthalate

This compound was prepared following the reported method.[2]
To a pyridine solution of isonicotinic acid (5 g, 40.6 mmol in 25 ml pyridine) at room temperature, 2 ml of phosphoryl chloride (21.4 mmol, 0.5 equiv) was added and the mixture was heated at 60 ºC for 1 hour. Then dimethyl 5-aminoisophthalate (8.5 g, 40.6 mmol, 1 equiv) was added portionwise for few minutes, and heating continued for 7 h at the same temperature. Then water was carefully added (up to total vol. ± 250 ml) and the solids were filtered out. The crude product was washed thoroughly with DI water, then 2 x 20 ml ethanol and dried on air at suction. White solid was obtained, 11.36g (89%). ^1H NMR (400 MHz, DMSO-d_6): δ= 10.9 (bs, 1H), 8.82 (m, 2H), 8.71 (d, *J*= 1.5 Hz, 2H), 8.23 (t, *J*= 1.5 Hz, 1H), 7.91 (m, 2H), 3.91 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ= 165.2 (Cq), 164.4 (Cq), 150.4, 141.2 (Cq), 139.6 (Cq), 130.7 (Cq), 124.9, 124.8, 121.6, 52.6.

5-(Isonicotinamido)isophthalic acid

Dimethyl 5-(isonicotinamido)isophthalate (1.57 g, 5 mmol) was suspended in aq. NaOH [2.4 g, 60 mmol, 6 equiv in H_20 (50 ml)], then THF (15ml) was added to give clear solution, and the mixture was stirred at room temperature for 2.5 h. Then it was diluted with 40 ml diethyl ether, the phases were separated, and aq. phase was acidified with aq HCl. The product was collected via filtration, washed thoroughly with DI water, acetone and dried on air at suction to yield 1.393 g of the reddish solid (97%). ^1H NMR (400 MHz, DMSO-d_6): δ= 13.3 (bs, 2H), 10.8 (bs, 1H), 8.81 (dd, *J* = 1.5, 4.5 Hz, 2H), 8.66 (d, *J* = 1.5 Hz, 2H), 8.23 (t, *J* = 1.5 Hz, 1H), 7.91 (dd, *J* = 1.5, 4.5 Hz, 2H).^{13}C NMR (100 MHz, DMSO-d_6): δ= 166.5 (Cq), 164.4 (Cq), 150.4, 141.4 (Cq), 139.4 (Cq), 131.8 (Cq), 125.5, 124.8, 121.6.

2.2 Synthesis of H_2L2

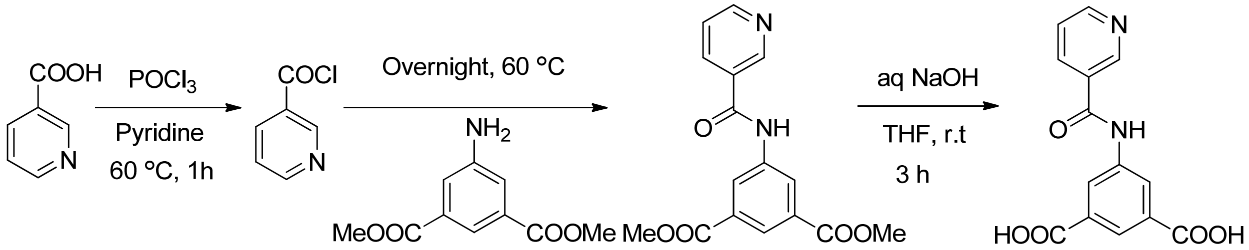


Fig. S2. Synthetic scheme of ligand H_2L2.

Dimethyl 5-(nicotinamido)isophthalate

A similar procedure as for dimethyl 5-(isonicotinamido)isophthalate was followed but using nicotinic acid instead. White solid was obtained (5.92g, 92%). ^{1}H NMR (600 MHz, DMSO-d_6): δ= 10.8 (bs, 1H), 9.15 (m, 1H), 8.78 (m, 1H), 8.70 (d, *J*= 1.3, 2H), 8.34 (m, 1H), 8.22 (m, 1H), 7.59 (m, 1H), 3.91 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d_6): δ= 165.2 (Cq), 164.4 (Cq), 152.5, 148.8, 139.9 (Cq), 135.5, 130.6 (Cq), 129.9 (Cq), 124.65, 124.63, 123.5, 52.6.

5-(Nicotinamido)isophthalic acid

A similar procedure as for 5-(isonicotinamido)isophthalic acid was followed. White solid was obtained (1.42 g, 99 %). ^{1}H NMR (600 MHz, DMSO-d_6): δ= 13.3 (bs, 2H), 10.8 (bs, 1H), 9.15 (m, 1H), 8.78 (m, 1H), 8.66 (d, *J*= 1.4, 2H), 8.34 (m, 1H), 8.23 (t, *J*= 1.5, 1H), 7.59 (m, 1H) (in agreement with the reported data[3]) ^{13}C NMR (150 MHz, DMSO-d_6): δ= 166.5 (Cq), 164.4 (Cq), 152.4, 148.8, 139.6 (Cq), 135.6, 131.7 (Cq), 130.1 (Cq), 125.2, 124.7, 123.6.

2.3 Synthesis of H_2L3

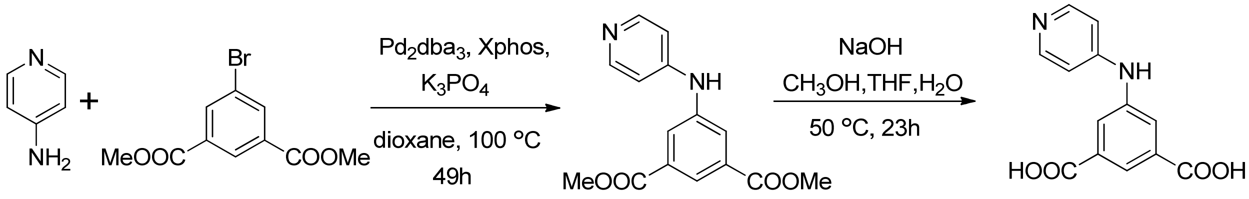


Fig. S3. Synthetic scheme of ligandH$_2$L3.

Dimethyl 5-(pyridin-4-ylamino)isophthalate

This compound was prepared following the reported general method.[4]

An oven-dried Schlenk tube was charged with a mixture of 4-aminopyridine (0.54 g, 5.5 mmol), dimethyl 5-bromoisophthalate (1.365 g, 5 mmol), grounded K_3PO_4 (1.5 g, 7.0 mmol), Xphos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, 192 mg, 0.4 mmol, 8 mol%), Pd_2dba_3 (92 mg, 0.1 mmol, 2 mol%) and dry dioxane (15 ml, stored over CaH_2), then stirred at 100 ºC for 49 h under Ar. After 49 h the mixture was cooled, and upon cooling solidified. It was sonicated in diluted aq HCl/EtOAc mixture to give two clear phases, that were separated and the organic phase was discarded. The aq. phase was neutralized with $NaHCO_3$ to give the precipitate that was collected via filtration, washed with water and dried at suction overnight to give 0.68 g of a cream solid that was taken into the next step without further purification.

5-(Pyridin-4-ylamino)isophthalic acid

Crude dimethyl 5-(pyridin-4-ylamino)isophthalate (0.68 g) was dissolved in 40 ml THF/ MeOH (1/1), then 20 ml aq NaOH (6 eq, 14.6 mmol, 0.58 g) was added. The reaction was kept at 50 ºC for 23 h. The mixture was concentrated with a rotary evaporator to remove the organic solvents, and then diluted with DI water (75 ml). It was washed once with EtOAc (discarded). The aq. phase was acidified with aq. HCl, a white precipitate was collected via centrifugation (6000 rpm, 3 min). Centrifugation was repeated twice with water, then the compound was suspended in EtOH and the mixture concentrated with a rotary evaporator. The residue was dried in the vacuum oven at 40 ºC overnight to give a white solid (0.32 g, 25 % in 2 steps). ^{1}H NMR (500 MHz, D_2O/NaOH): δ= 8.15 (d, *J*= 5.5, 2H), 8.00 (s, 1H), 7.80 (s, 2H), 6.98 (d, *J*= 5.5, 2H). ^{13}C NMR (125 MHz, D_2O/NaOH): δ= 175.5, 152.2, 149.9, 140.5, 138.4, 124.9, 124.5, 110.3.

2.4 Synthesis of H_2L4

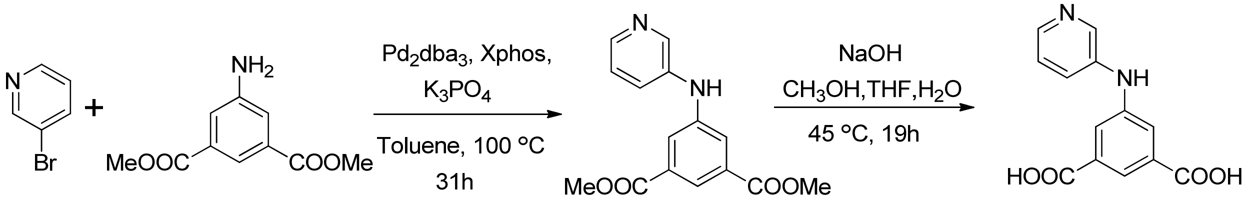


Fig. S4. Synthetic scheme of ligand H_2L4.

Dimethyl 5-(pyridin-3-ylamino)isophthalate

An oven-dried Schlenk tube was charged with a mixture of 3-bromopyridine (0.8 g, 5.0 mmol), dimethyl 5-aminoisophthalate (1.15 g, 5.5 mmol), grounded K_3PO_4 (1.5 g, 7.0 mmol), Xphos (192 mg, 0.4 mmol, 8 mol%), Pd_2dba_3 (92 mg, 0.1 mmol, 2 mol%) and dry toluene (10 ml, stored over CaH_2), then stirred at 100 ºC for 31 h under Ar following the general procedure. The crude reaction mixture was filtered through Celite with an aid of EtOAc and CH_2Cl_2, concentrated and purified by flash column chromatography using using 5% EtOAc/hexane to 100% EtOAc to yield the title compound as an off-white solid (0.83 g, 57 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.45 (m, 1H), 8.26 (m, 2H), 7.91 (s, 2H), 7.50 (m, 1H), 7.26 (m, 1H), 6.29 (bs, 1H), 3.94 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 166.3, 143.3, 143.2, 141.2, 138.6, 132.0, 125.0, 124.2, 123.4, 122.0, 52.6.

5-(Pyridin-3-ylamino)isophthalic acid

Dimethyl 5-(pyridin-3-ylamino)isophthalate (0.83 g, 2.9 mmol) was dissolved in 40 ml THF/MeOH (1/1), and 20 ml aq NaOH (6 eq, 14.6 mmol, 0.58 g) was added. The reaction was kept at 45 ºC for 19 h. The mixture was concentrated on a rotary evaporator to remove the organic solvents, and then diluted with DI water (75 ml). It was washed once with EtOAc (discarded). The aq. phase was acidified with aq. HCl, a white precipitate was collected via centrifugation (6000 rpm, 3 min). Centrifugation was repeated twice with water, then the compound was suspended in EtOH and the mixture concentrated on a rotary evaporator. The residue was dried in the vacuum oven at 40 ºC overnight to give the white solid (0.53 g, 71 %). ^{1}H NMR (500 MHz, D_2O/NaOH): δ= 8.25 (m, 1H), 8.01 (m, 1H), 7.87 (s, 1H), 7.68 (s, 2H), 7.56 (m, 1H), 7.29 (m, 1H). ^{13}C NMR (125 MHz, D_2O/NaOH): δ= 174.3, 141.6, 140.1, 139.5, 137.9, 137.0, 124.2, 124.0, 121.6, 119.9.

2.5 Synthesis of H_2L5

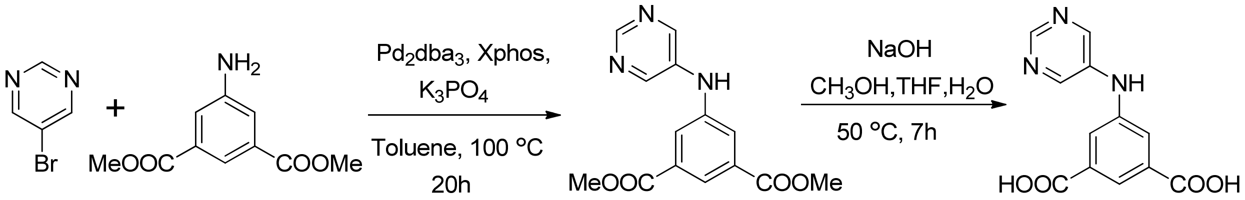


Fig. S5. Synthetic scheme of ligand H_2L5.

Dimethyl 5-(pyrimidin-5-ylamino)isophthalate

An oven-dried Schlenk tube was charged with a mixture of 5-bromopyrimidine (0.8 g, 5.0 mmol), dimethyl 5-aminoisophthalate (1.15 g, 5.5 mmol), grounded K_3PO_4 (1.5 g, 7.0 mmol), Xphos (192 mg, 0.4 mmol, 8 mol%), Pd_2dba_3 (92 mg, 0.1 mmol, 2 mol%), and dry toluene (10 ml, stored over CaH_2), then stirred at 100 ºC for 20 h under Ar, following the general procedure. The crude reaction mixture was filtered through Celite with an aid of EtOAc and CH_2Cl_2, concentrated and purified by flash column chromatography using ethyl acetate to yield the title compound as a white solid (0.71 g, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.85 (s, 1H), 8.66 (s, 2H), 8.31 (s, 1H), 7.94 (d, *J* = 1.2 Hz, 2H), 6.63 (bs, 1H), 3.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 165.9 (Cq), 151.0, 145.8, 141.6 (Cq), 137.8 (Cq), 132.4 (Cq), 124.8, 123.0, 52.7.

5-(Pyrimidin-5-ylamino)isophthalic acid

Dimethyl 5-(pyrimidin-5-ylamino)isophthalate (0.7 g, 2.4 mmol) was dissolved in 40 ml THF/MeOH (1/1), and 20 ml aq NaOH (6 eq, 14.6 mmol, 0.58 g) was added. The reaction was kept at 50 ºC for 7 h. The mixture was concentrated with a rotary evaporator to remove the organic solvents, and then diluted with DI water (75 ml). It was washed once with EtOAc (discarded). The aq. phase was then acidified with aqueous HCl, and the precipitate was collected via filtration. It was washed thoroughly with DI water, CH_2Cl_2, dried at suction, followed by vacuum oven at 40 ºC overnight to give a yellow solid (0.58 g, 92 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 13.2 (bs, 2H), 8.96 (s, 1H), 8.76 (s, 1H), 8.64 (s, 2H), 8.00 (t, *J*=1.4 Hz, 1H), 7.84 (d, *J* =1.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ= 166.5 (Cq), 150.9, 145.6, 142.8 (Cq), 137.5 (Cq), 132.5 (Cq), 122.1, 120.6.

Copies of NMR spectra

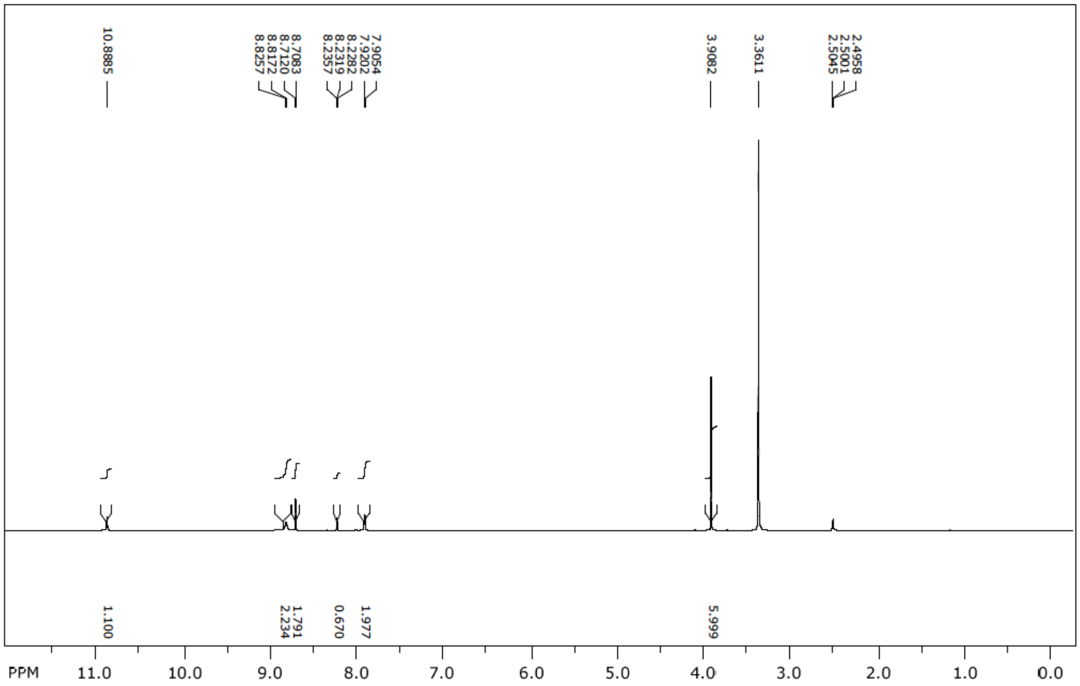


Fig. S6a ^{1}H NMR spectrum of dimethyl 5-(isonicotinamido)isophthalate (DMSO-d_6, 400 MHz).

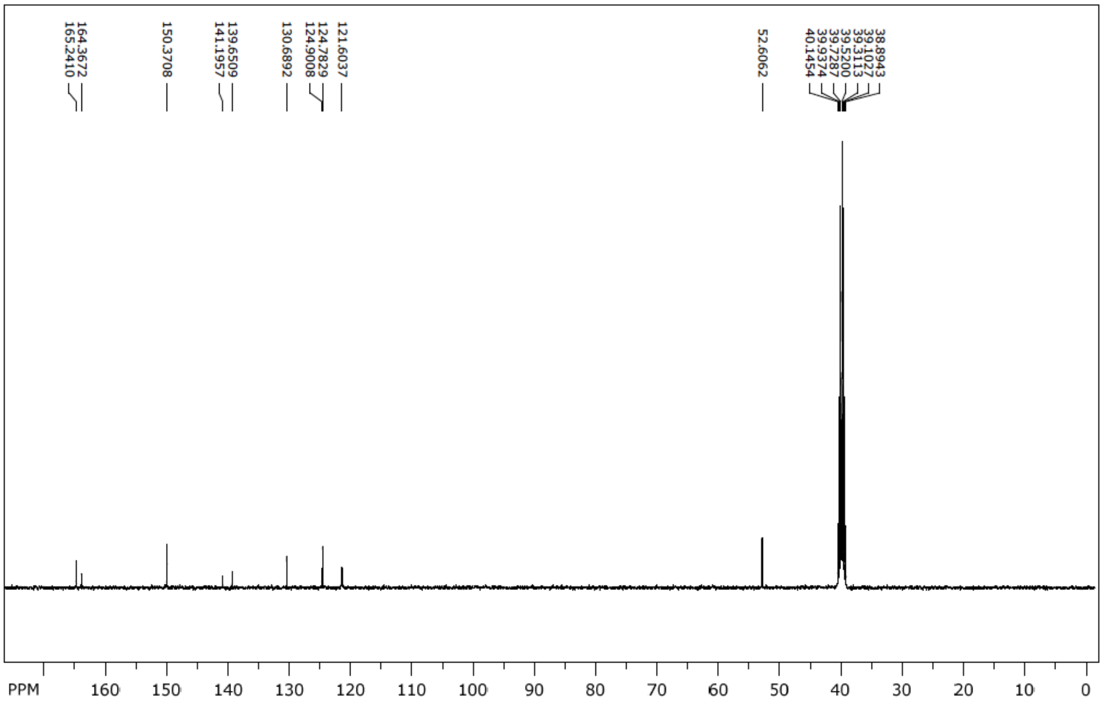


Fig. S6b ^{13}C NMR spectrum of dimethyl 5-(isonicotinamido)isophthalate (DMSO-d_6, 100 MHz).

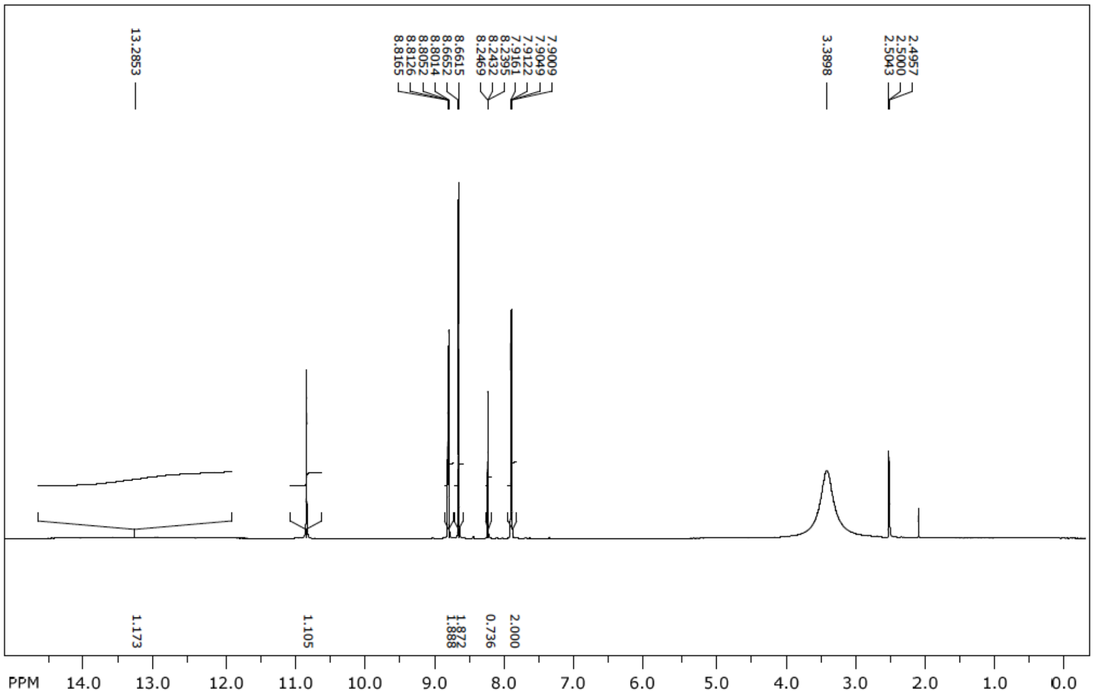


Fig. S6c ^{1}H NMR spectrum of 5-(isonicotinamido)isophthalic acid (DMSO-d_6, 400 MHz).

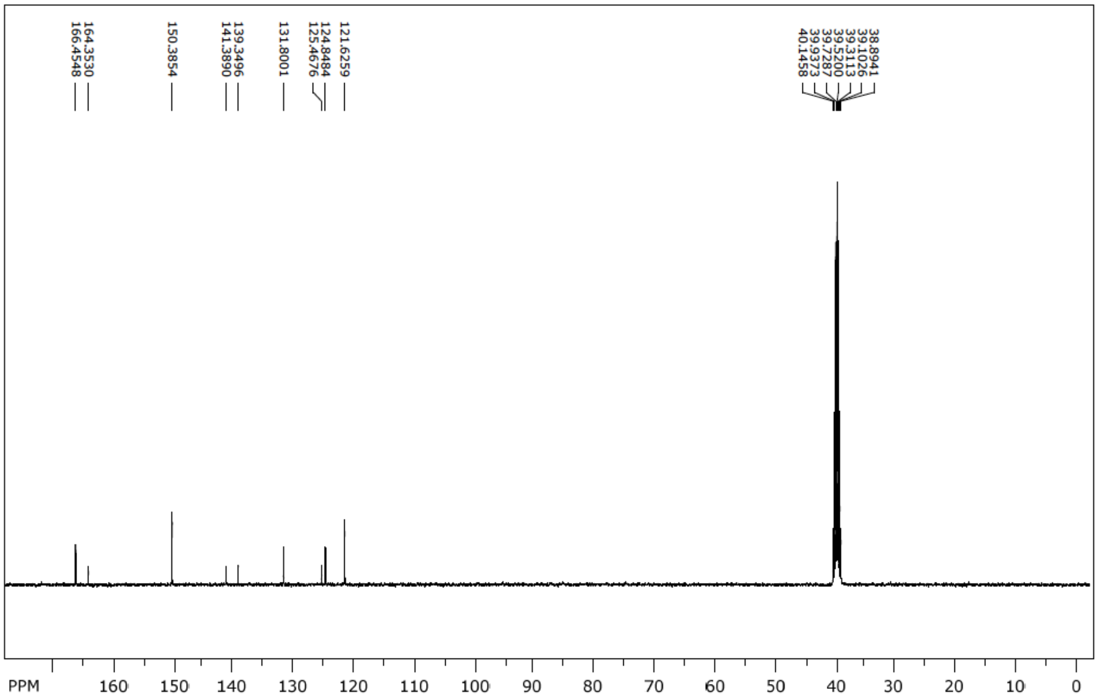


Fig. S6d ^{13}C NMR spectrum of 5-(isonicotinamido)isophthalic acid (DMSO-d_6, 100 MHz).

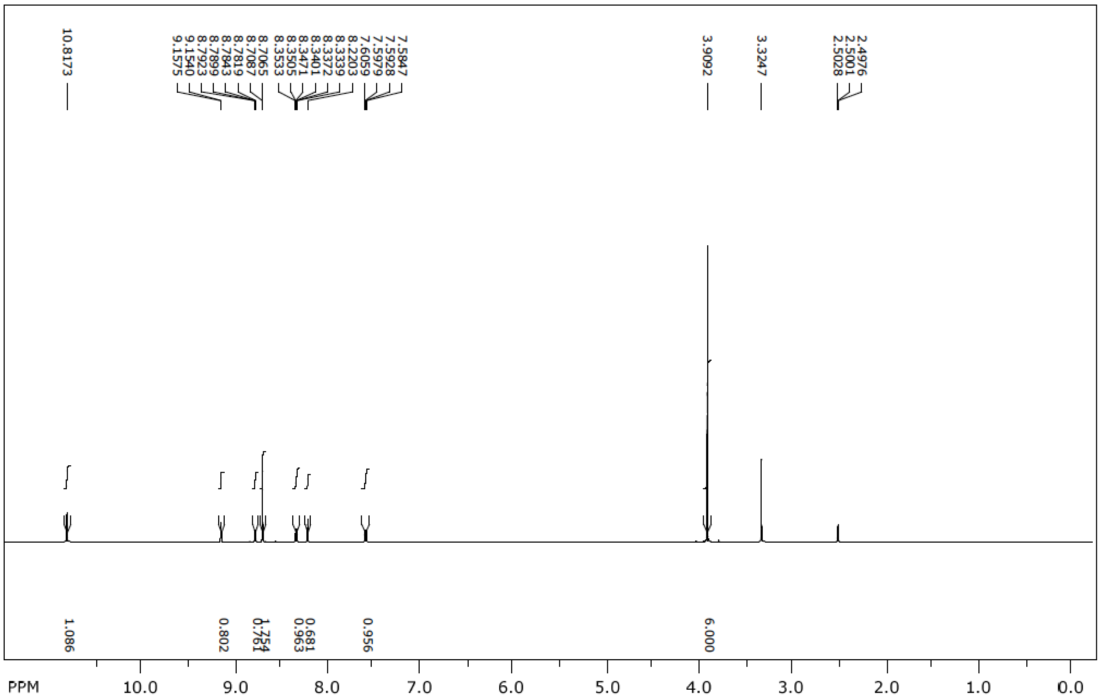


Fig. S6e ^{1}H NMR spectrum of dimethyl 5-(nicotinamido)isophthalate (DMSO-d_6, 600 MHz).

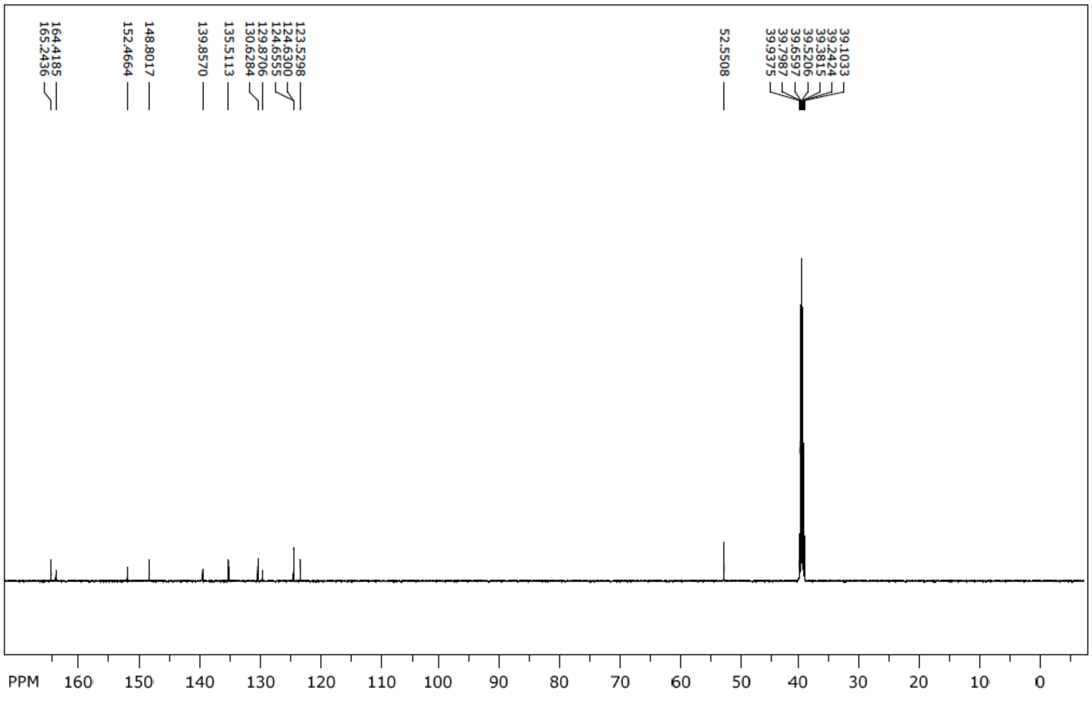


Fig. S6f ^{13}C NMR spectrum of dimethyl 5-(nicotinamido)isophthalate (DMSO-d_6, 150 MHz).

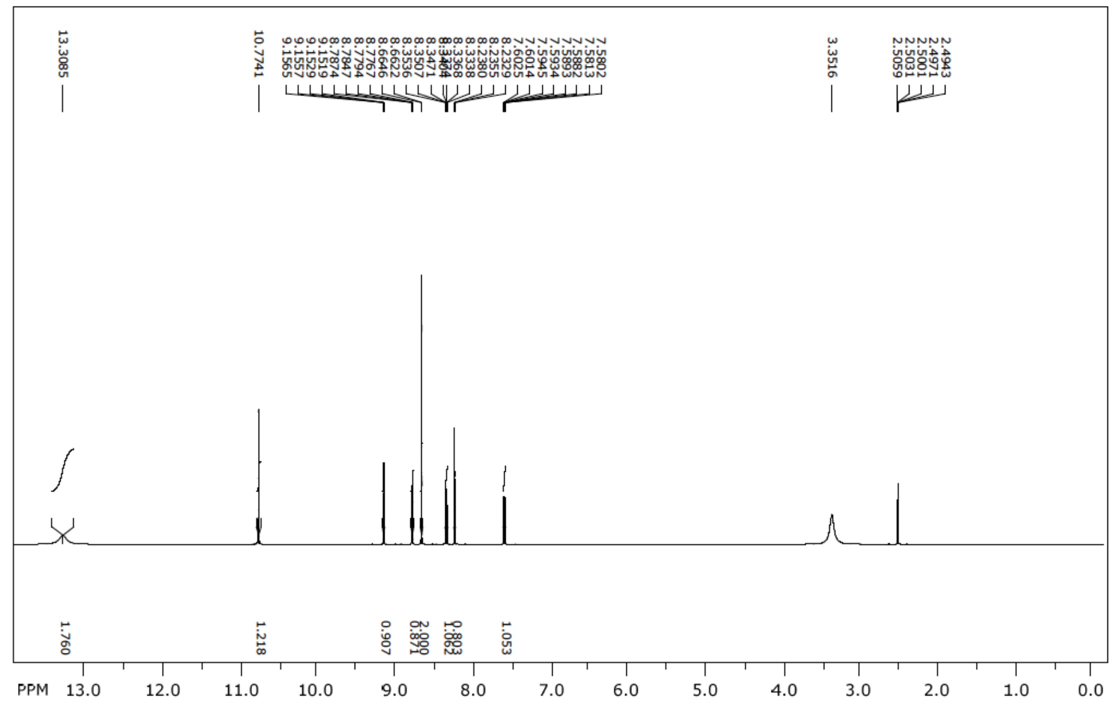


Fig. S6g ^{1}H NMR spectrum of 5-(nicotinamido)isophthalic acid (DMSO-d$_6$, 600 MHz).

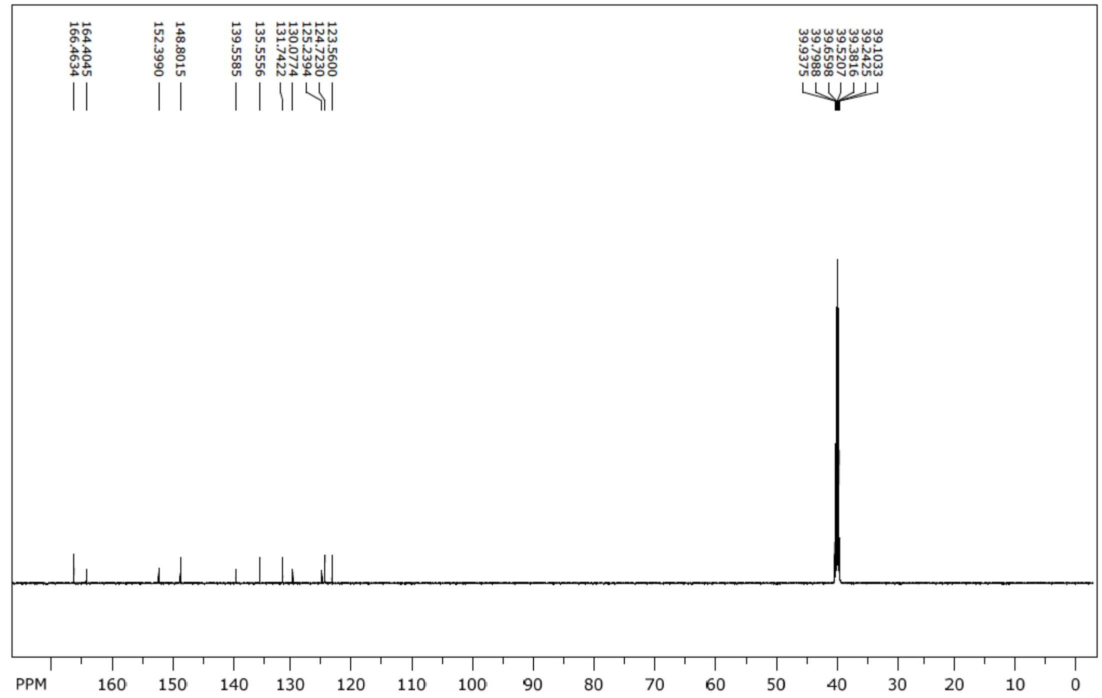


Fig. S6h ^{13}C NMR spectrum of 5-(nicotinamido)isophthalic acid (DMSO-d$_6$, 150 MHz).

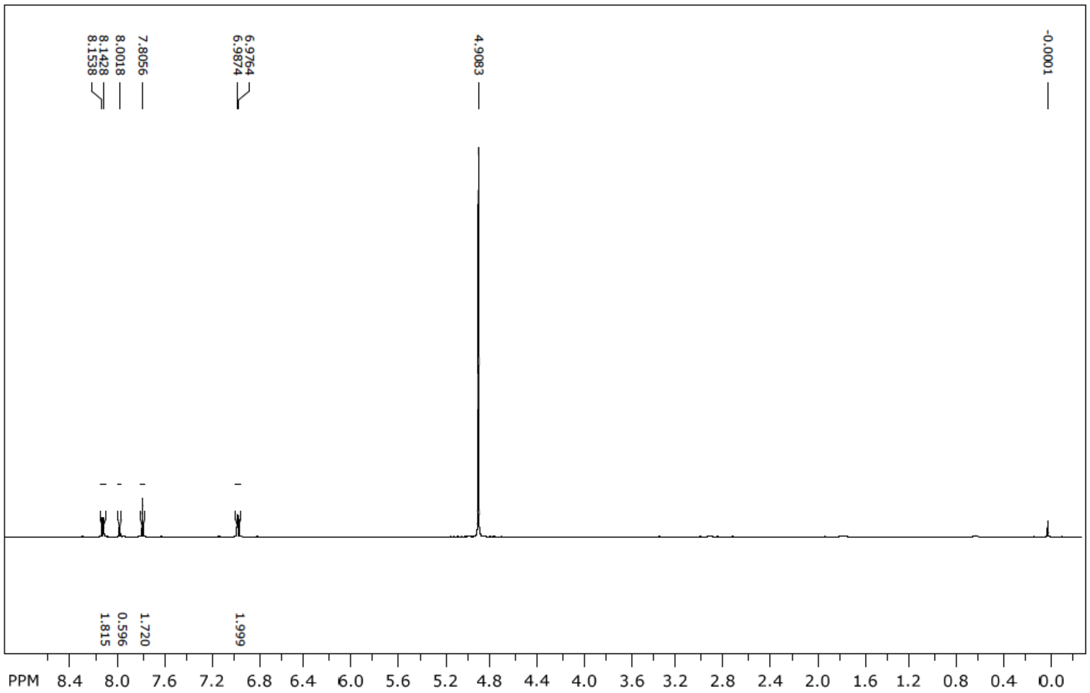


Fig. S6i ^{1}H NMR spectrum of 5-(pyridin-4-ylamino)isophthalic acid (D_2O/NaOH, 500 MHz).

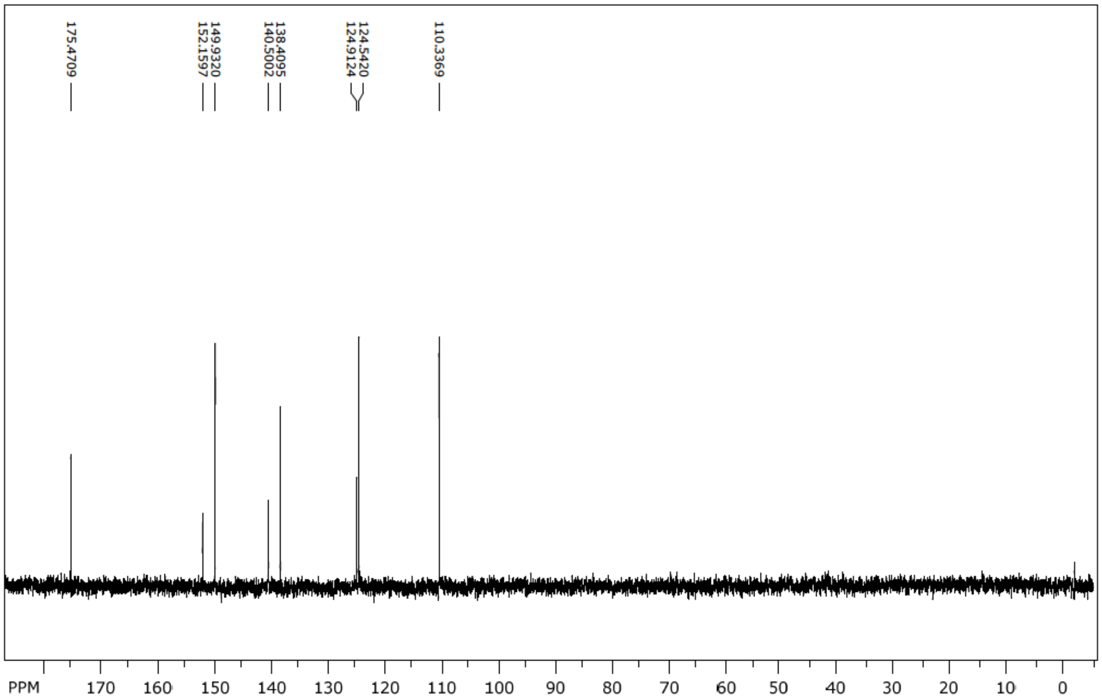


Fig. S6j ^{13}C NMR spectrum of 5-(pyridin-4-ylamino)isophthalic acid (D_2O/NaOH, 125 MHz).

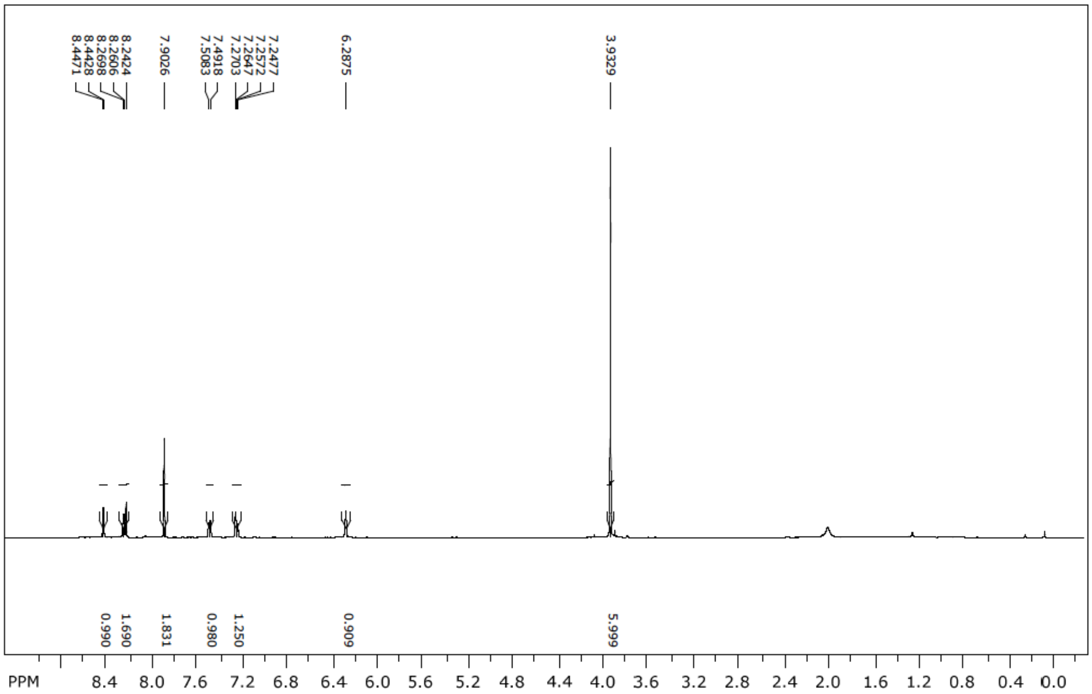


Fig. S6k ^{1}H NMR spectrum of dimethyl 5-(pyridin-3-ylamino)isophthalate (CDCl$_3$, 500 MHz).

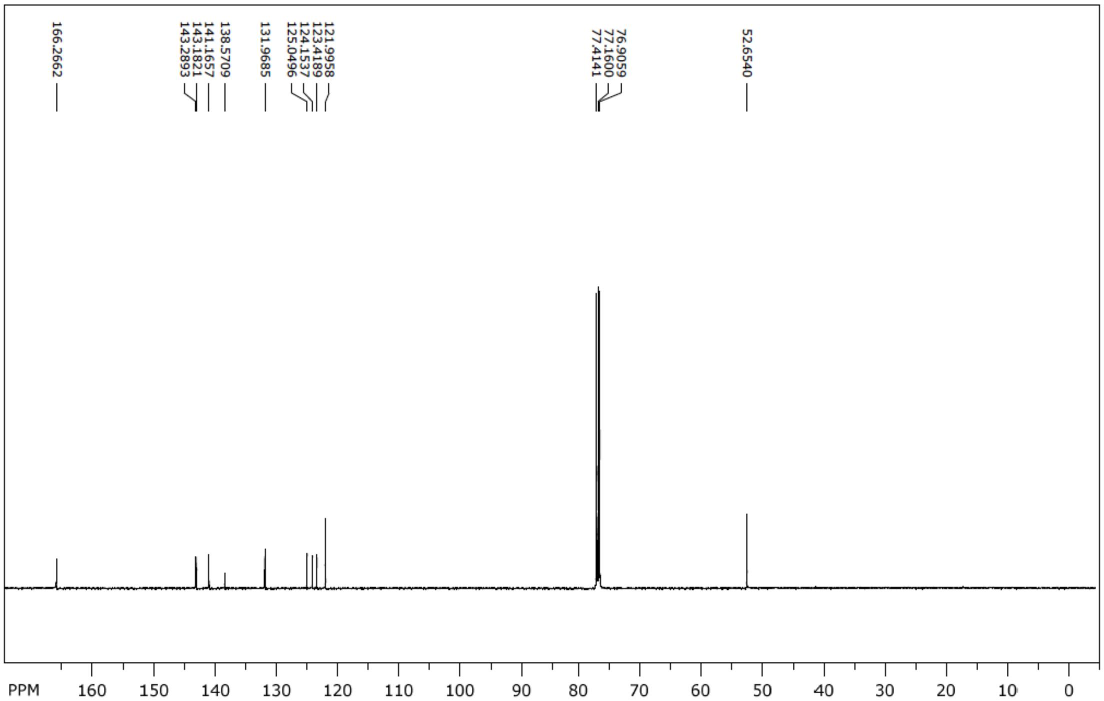


Fig. S6l ^{1}H NMR spectrum of dimethyl 5-(pyridin-3-ylamino)isophthalate (CDCl$_3$, 125 MHz).

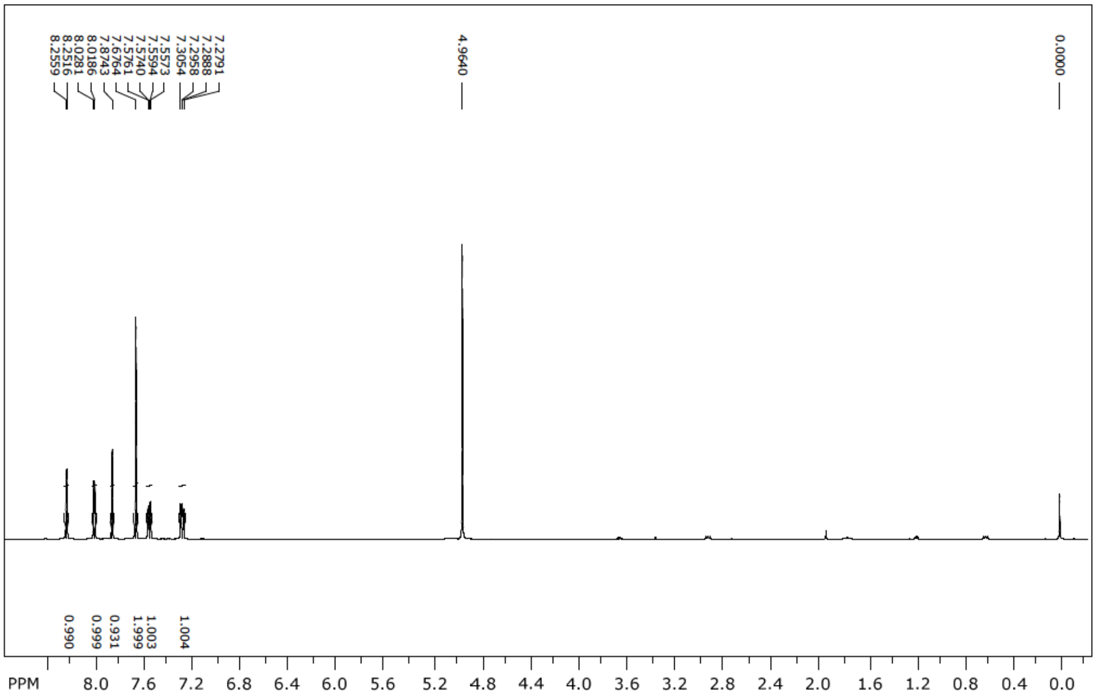


Fig. S6m ^{1}H NMR spectrum of 5-(pyridin-3-ylamino)isophthalic acid (D_2O/NaOH, 500 MHz).

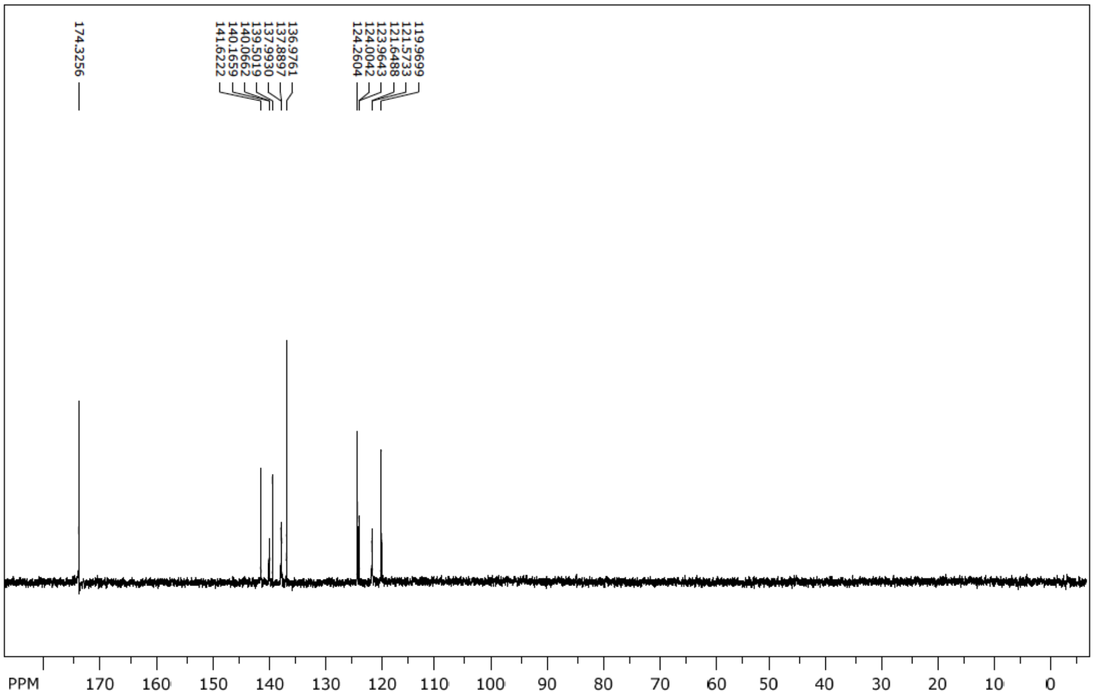


Fig. S6n ^{13}C NMR spectrum of 5-(pyridin-3-ylamino)isophthalic acid (D_2O/NaOH, 125 MHz).

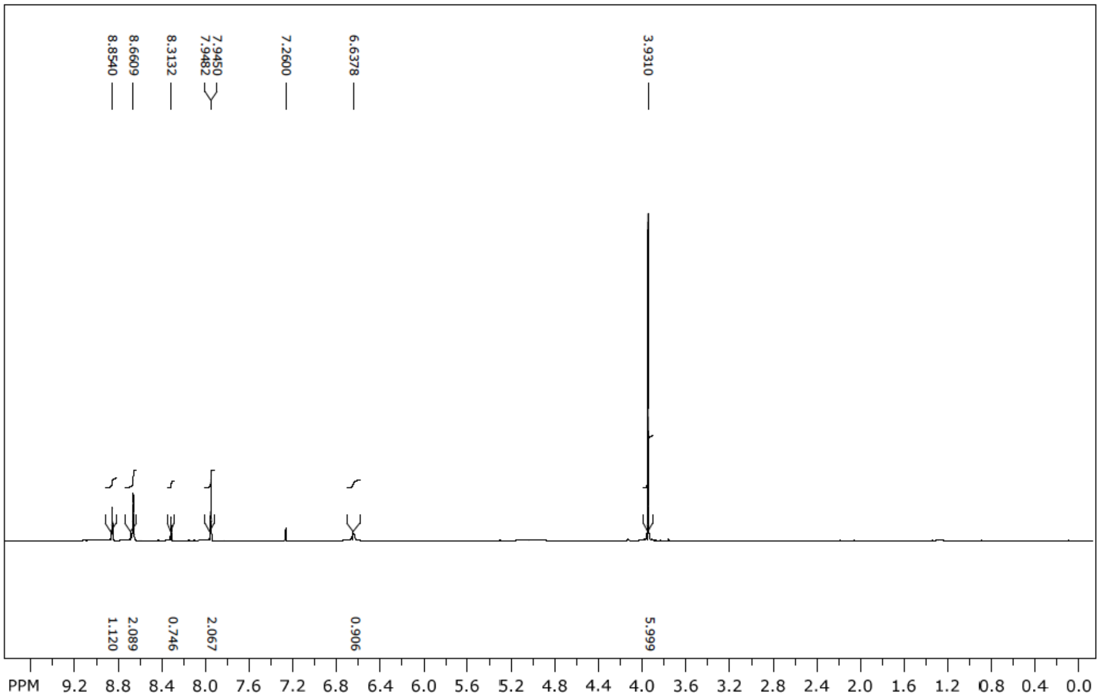


Fig. S6o ^{1}H NMR spectrum of dimethyl 5-(pyrimidin-5-ylamino)isophthalate ($CDCl_3$, 400 MHz).

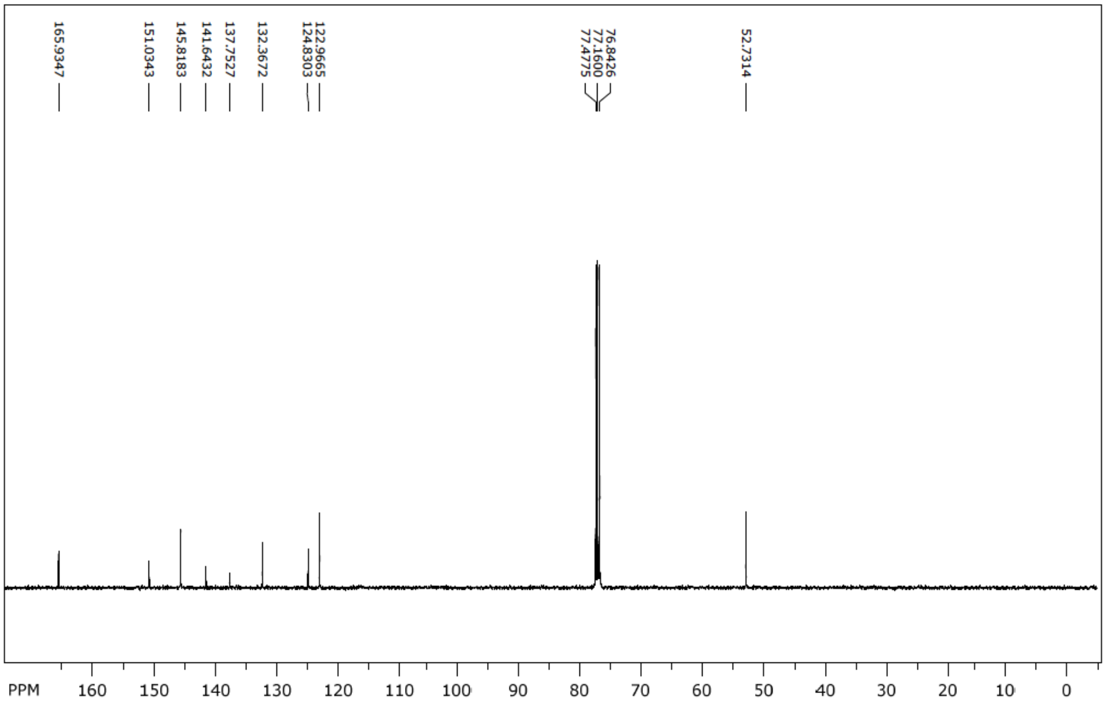


Fig. S6p ^{13}C NMR spectrum of dimethyl 5-(pyrimidin-5-ylamino)isophthalate ($CDCl_3$, 100 MHz).

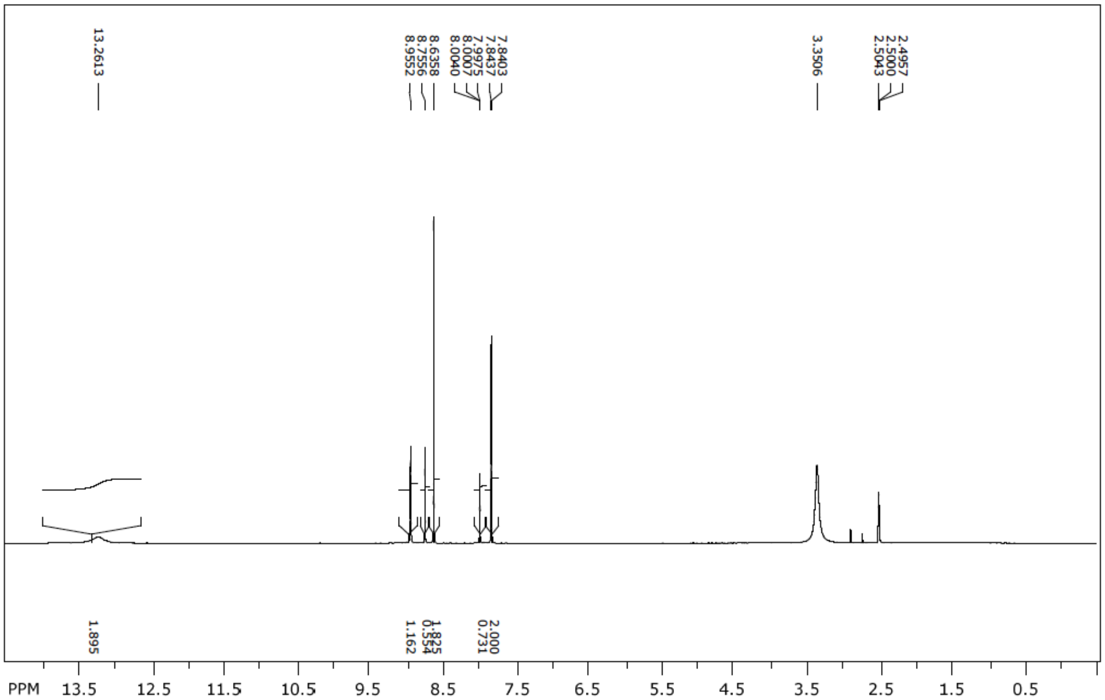


Fig. S6q ^{1}H NMR spectrum of 5-(pyrimidin-5-ylamino)isophthalic acid (DMSO-d$_6$, 400 MHz).

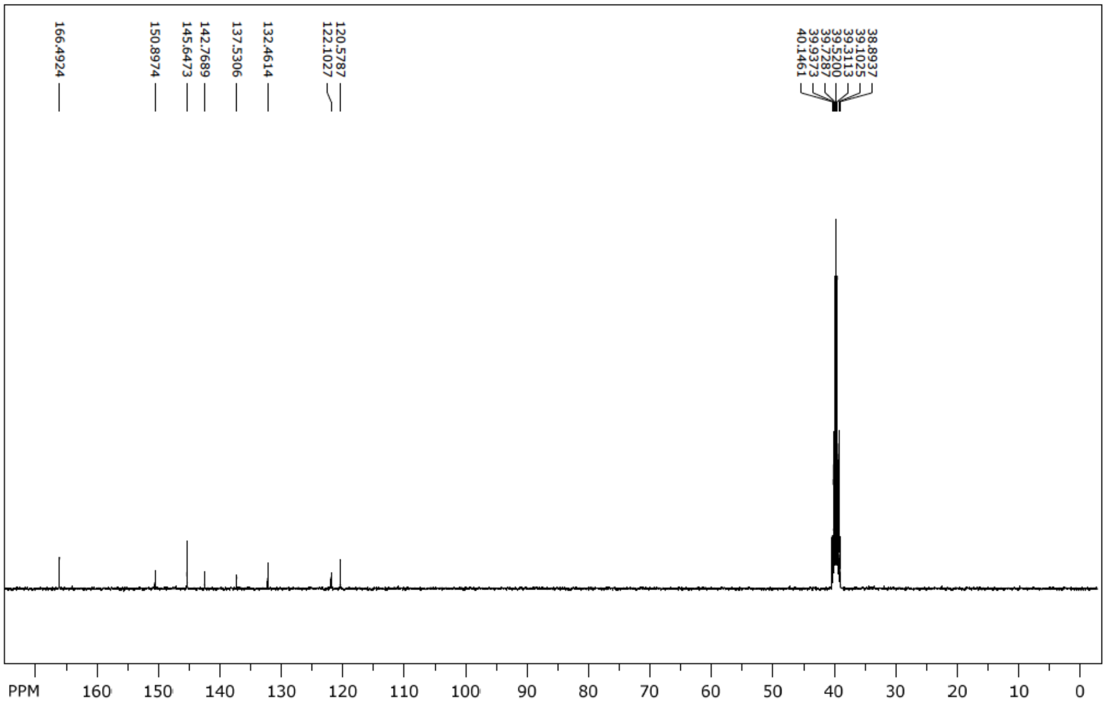


Fig. S6r ^{13}C NMR spectrum of 5-(pyrimidin-5-ylamino)isophthalic acid (DMSO-d$_6$, 100 MHz).

3. Synthesis of Metal Organic Frameworks

3.1 Synthesis of eea-MOF-4 (1)

A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (23.3 mg, 0.1 mmol) and H_2L1 (28.6 mg, 0.1 mmol) in 2 mL of N,N-dimethylacetamide (DMA) was prepared in a 20 mL scintillation vial. To this was added 100 µL of conc. HOAc and then the mixture was sonicated for 20 min. The mixture was sealed and heated to 115°C for 48h. The green block crystals obtained were filtered and washed with DMA. The as-synthesized material was determined to be insoluble in H_2O and common organic solvents.

3.2 Synthesis of eea-MOF-5 (2)

A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (23.3 mg, 0.1 mmol) and H_2L2 (28.6 mg, 0.1 mmol) in 2 mL of N,N-dimethylacetamide (DMA) was prepared in a 20 mL scintillation vial. To this was added 100 µL of conc. HOAc and then the mixture was sonicated for 20 min. The mixture was sealed and heated to 115°C for 48h. The green block crystals obtained were filtered and washed with DMA. The as-synthesized material was determined to be insoluble in H_2O and common organic solvents.

3.3 Synthesis of rtl-MOF-2 (3)

A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (4.65 mg, 0.02mmol) and H_2L3 (5.16 mg, 0.02mmol) in 1.5 mL of N,N-dimethylformamide (DMF) and 0.5 ml of ethanol was prepared in a 20 mL scintillation vial. To this was added 100 µL of water and then the mixture was sonicated for 20 min. The mixture was sealed and heated to 85°C for 24h. The green sheet crystals obtained were filtered and washed with DMF. The as-synthesized material was determined to be insoluble in H_2O and common organic solvents.

3.4 Synthesis of rtl-MOF-3 (4)

A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (4.65 mg, 0.02mmol) and H_2L4 (5.16 mg, 0.02mmol) in 1.5 mL of N,N-dimethylformamide (DMF) and 0.5 ml of ethanol was prepared in a 20 mL scintillation vial. To this was added 100 µL of water and then the mixture was sonicated for 20 min. The mixture was sealed and heated to 85°C for 24h. The green sheet crystals obtained were filtered and washed with DMF. The as-synthesized material was determined to be insoluble in H_2O and common organic solvents.

3.5 Synthesis of rtl-MOF-4 (5)

A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (4.65 mg, 0.02mmol) and H_2L4 (5.16 mg, 0.02mmol) in 1.5 mL of N,N-dimethylformamide (DMF) and 0.5 ml of ethanol was prepared in a 20 mL scintillation vial. To this was added 200 µL of water and then the mixture was sonicated for 20 min. The mixture was sealed and heated to 85°C for 24h. The green sheet crystals obtained were filtered and washed with DMF. The as-synthesized material was determined to be insoluble in H_2O and common organic solvents.

4. Single Crystal X-ray Data

	rtl-MOF-2	**rtl**-MOF-3	**rtl**-MOF-4
Empirical formula	$C_{13}H_8 CuN_2O_4$	$C_{13}H_8CuN_2O_4$	$C_{12}H_7CuN_3O_4$
Formula weight	319.76	319.75	329.75 g.mol^{-1}
Temperature, Wavelength	150(2) K, 1.54178 Å		
Crystal system, space group	Monoclinic, $P2_1/c$		
Unit cell dimensions	a = 11.573(1) Å, b = 12.429(2) Å, c = 14.425(2) Å β = 102.10(2)°	a = 12.5824(6) Å, b = 11.7081(7) Å, c = 14.7356(7) Å β = 114.99(1)°	a = 12.599(1) Å, b = 11.852(1) Å, c = 14.594(1) Å β = 115.37(2)°
Volume	2028.8(4) Å^3	1967.5(2) Å^3	1969.0(2) Å^3
Z, Calculated density	4, 1.044 g.cm^{-3}	4, 1.079 g.cm^{-3}	4, 1.082 g.cm^{-3}
θ range for data collection	3.91° to 65.84°	3.88° to 60.04°	5.02° to 62.43°
Limiting indices	-6<=h<=13, -12<=k<=14, -16<=l<=16	-14<=h<=13, -12<=k<=13, -14<=l<=16	-14<=h<=14, -13<=k<=13, -16<=l<=15
Reflections collected / unique	10664 / 3369 [R(int) = 0.0245]	9375 / 2820 [R(int) = 0.0303]	24370 / 3115 [R(int) = 0.0392]
Completeness	95.6%	96.7 %	99.4 %
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	3369 / 0 / 181	2820 / 0 / 181	3115 / 0 / 181
Goodness-of-fit on F^2	1.288	1.138	1.185
Final R indices [I>2σ(I)]	R_1 = 0.0430, wR_2 = 0.1487	R_1 = 0.0467, wR_2 = 0.1212	R_1 = 0.0529, wR_2 = 0.1363
R indices (all data)	R_1 = 0.0460, wR_2 = 0.1514	R_1 = 0.0493, wR_2 = 0.1224	R_1 = 0.0541, wR_2 = 0.1369
Largest diff. peak and hole	0.757 and -0.474 e.A^{-3}	0.500 and -0.367 e.A^{-3}	0.602 and -0.627 e.A^{-3}

	eea-MOF-4	**eea**-MOF-5
Empirical formula	$C_{14}H_7CuN_2O_5$	$C_{14}H_7CuN_2O_5$
Formula weight	349.78	349.78
Temperature, Wavelength	150(2) K, 1.54178 Å	
Crystal system, space group	Hexagonal, R-3m	Hexagonal, R-3c
Unit cell dimensions	a = 18.785(1) Å, b = 18.785(1) Å, c = 37.823(2) Å	a = 18.295(5) Å, b = 18.295(5) Å, c = 69.430(3) Å
Volume	11558(1)	20124(1) $Å^3$
Z, Calculated density	18, 0.897 $g.cm^{-3}$	6, 1.027 $g.cm^{-3}$
θ range for data collection	2.96 to 66.47°	3.07 to 66.33°
Limiting indices	-20<=h<=22, -16<=k<=21, -44<=l<=44	-18<=h<=0, 0<=k<=21, 0<=l<=82
Reflections collected / unique	11190 / 2462 [R(int) = 0.0309]	3893 / 3893 [R(int) = 0.0000]
Completeness	98.2 %	98.6 %
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2462 / 3 / 125	3893 / 42 / 212
Goodness-of-fit on F^2	1.659	0.969
Final R indices [I>2σ(I)]	$R_1 = 0.0589$, $wR_2 = 0.2171$	$R_1 = 0.0709$, $wR_2 = 0.1917$
R indices (all data)	$R_1 = 0.0693$, $wR_2 = 0.2213$	$R_1 = 0.1016$, $wR_2 = 0.2074$
Largest diff. peak and hole	0.645 and -0.362 $e.A^{-3}$	1.510 and -0.503 $e.A^{-3}$

5. Structural Figures

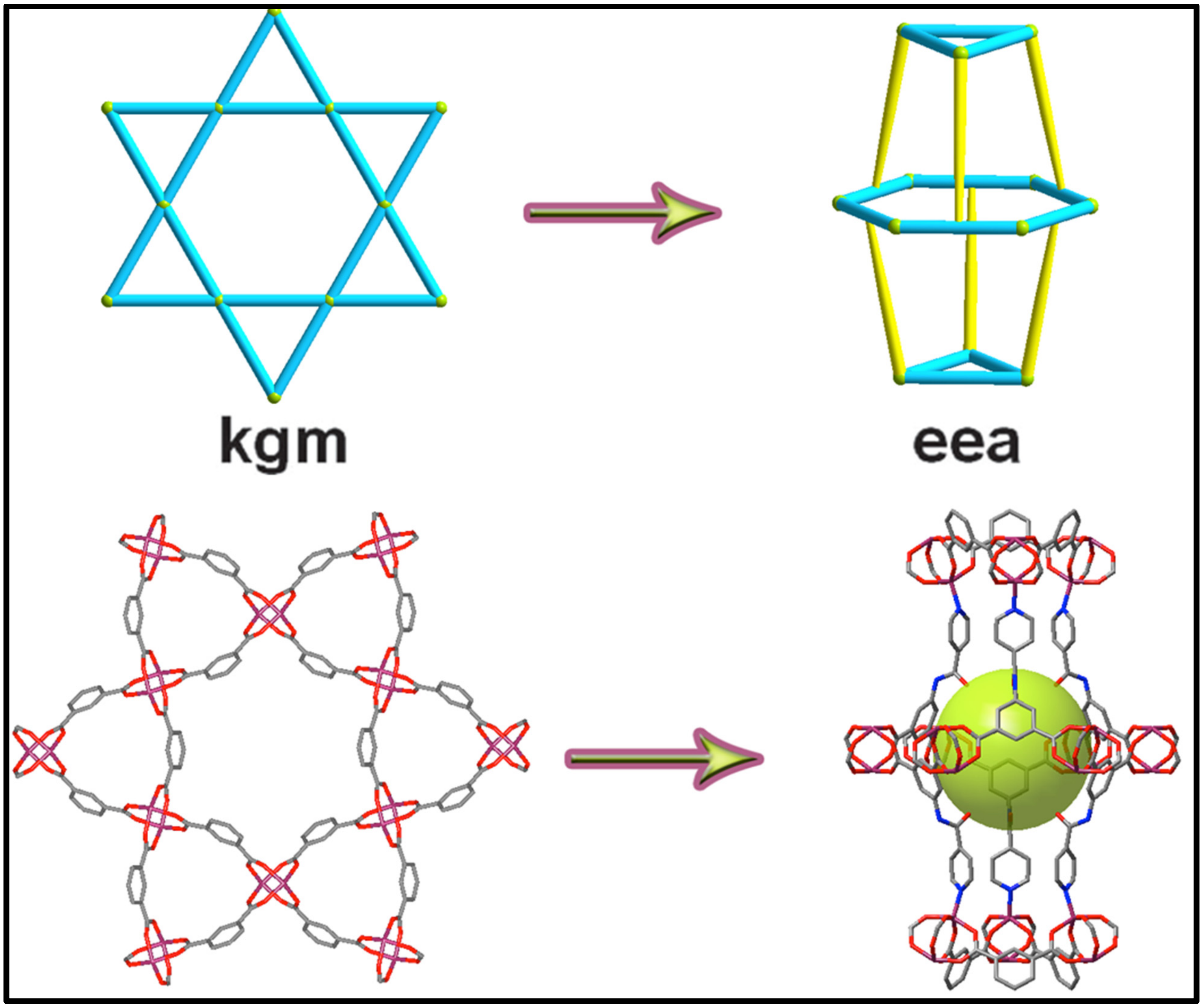


Fig. S7. Scheme representing the Kagomé lattice and the **eea** net (overhead). Layer of a **kgm**-MOF (bottom, left) and representation of **eea**-MOF-4 (botton, right). C = gray, O = red, N = blue, Cu = plum; H atoms are omitted for clarity.

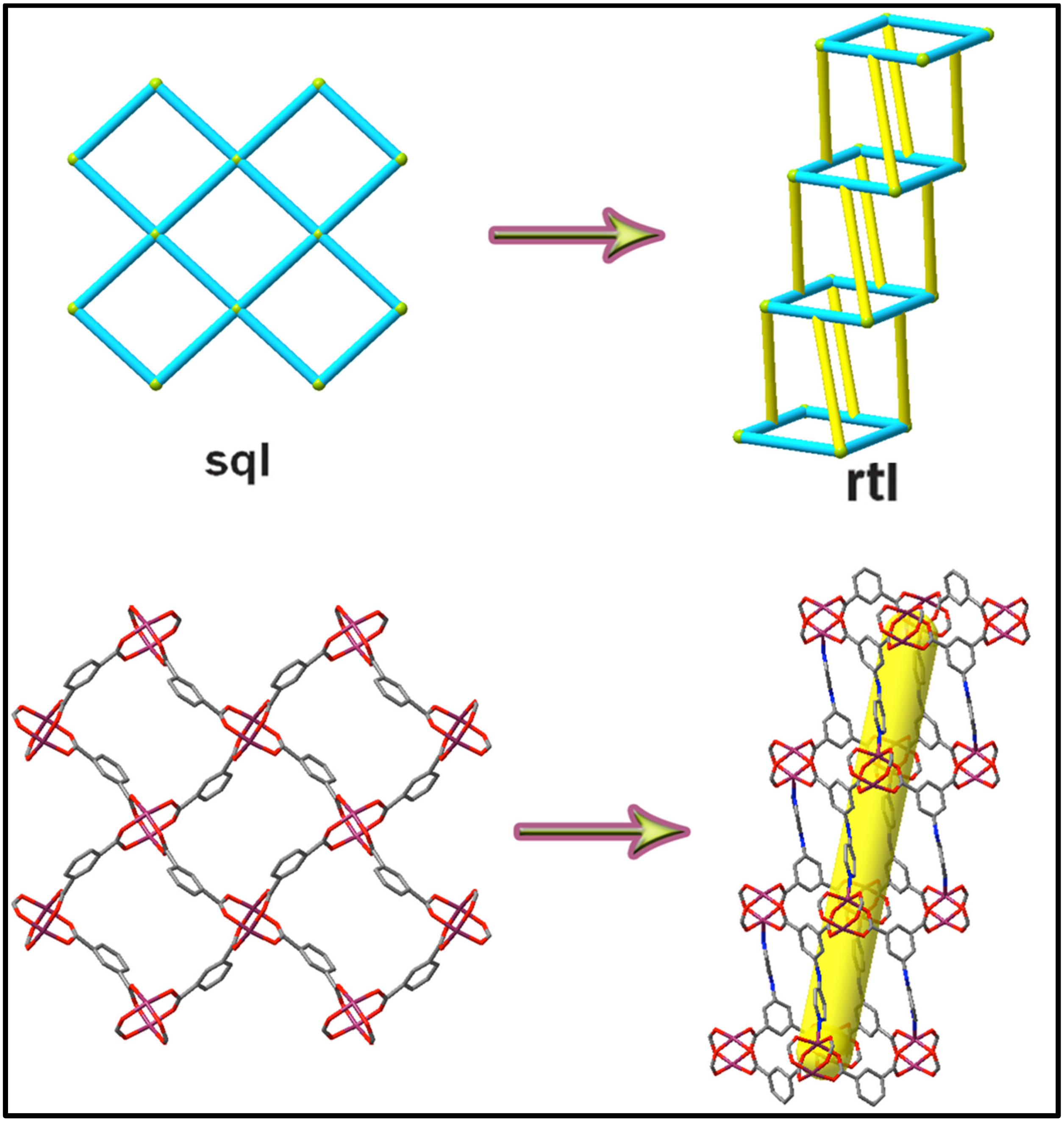
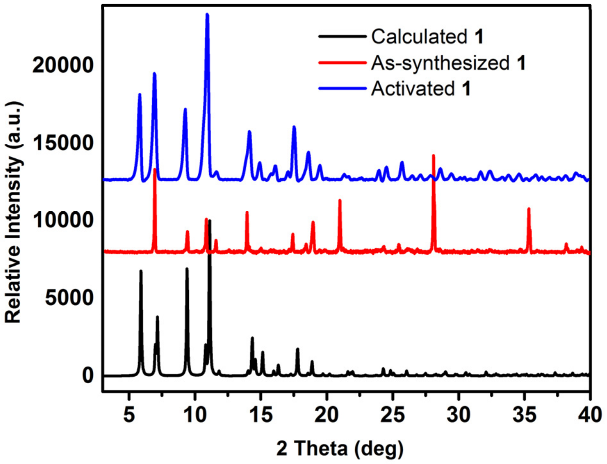


Fig. S8. Scheme representing the square-grid lattice and the **rtl** net (overhead). Layer of a **sql**-MOF (bottom, left) and representation of **rtl**-MOF-2 (botton, right). C = gray, O = red, N = blue, Cu = plum; H atoms are omitted for clarity.

6. Powder X-ray Diffraction Patterns and TGA Plots



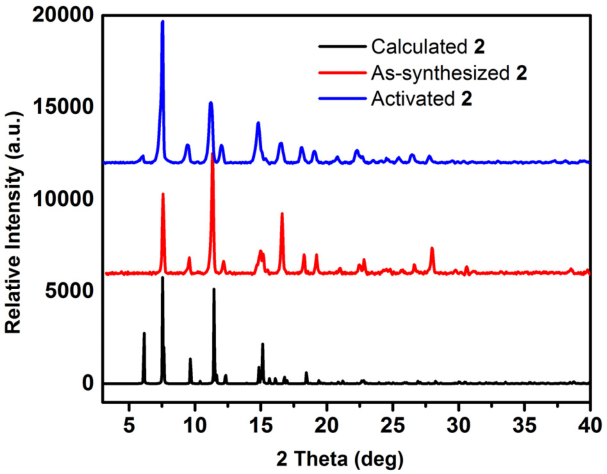


Fig. S9. PXRD patterns of the as-synthesized, calculated and activated compounds **1** and **2**, indicating the phase purity of as-synthesized and activated products.

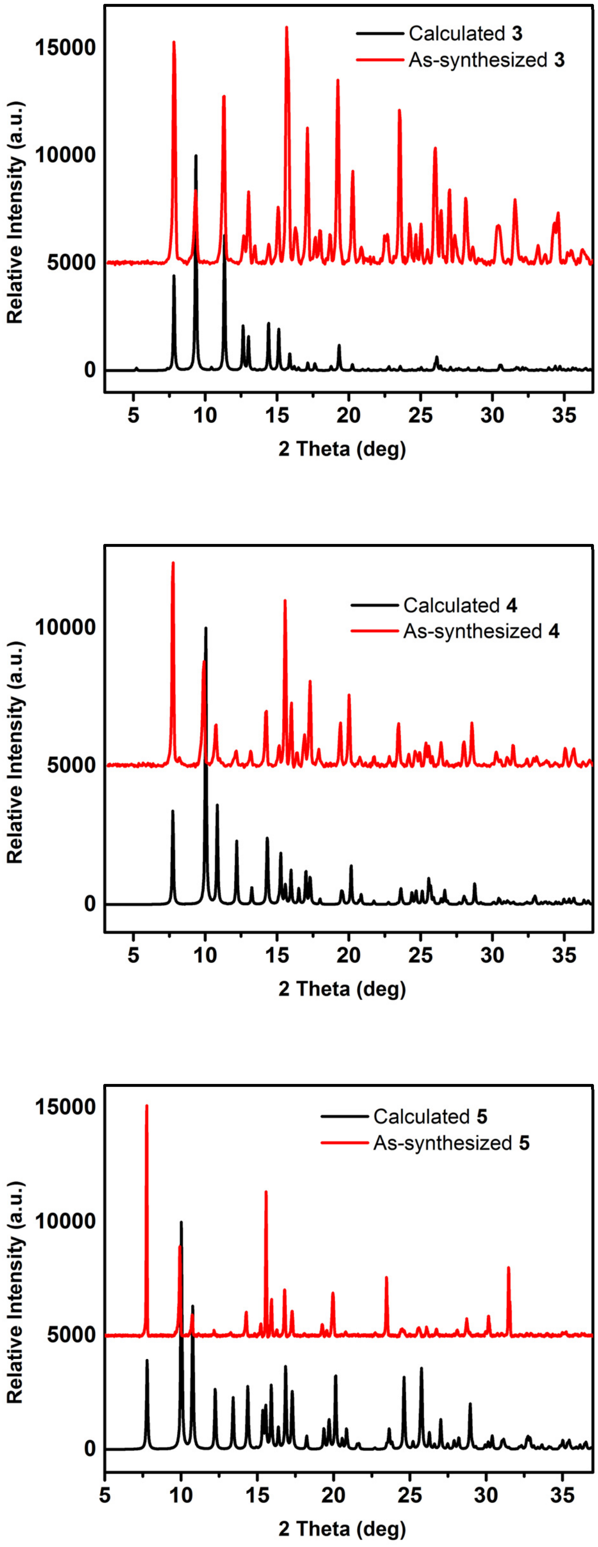


Fig. S10. PXRD patterns of the as-synthesized and calculated compounds **3**, **4** and **5**, indicating the phase purity of as-synthesized products.

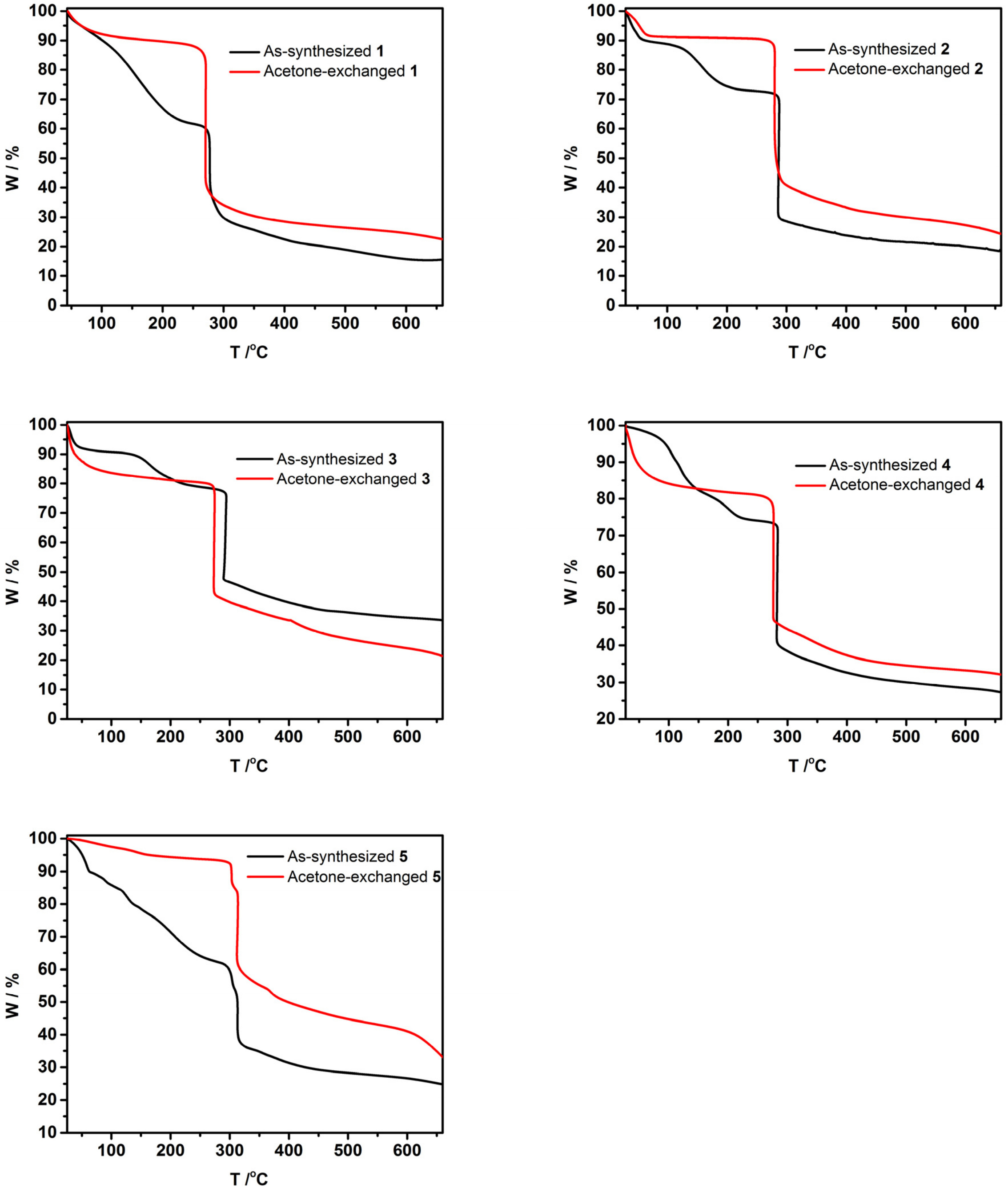


Fig. S11. TGA plots of as-synthesized and acetone-exchanged compounds **1, 2, 3, 4** and **5**.

7. Low-Pressure Gas Adsorption Measurements

Homogenous microcrystalline samples of **1** and **2** were activated by washing as-synthesized crystals with 3 x 20 mL of DMF followed by solvent exchange in acetone for 7 days. The solution was refreshed several times daily during this time period. In a typical experiment, 80 mg of each activated sample was transferred (dry) to a 12-mm large bulb glass sample cell and firstly evacuated at room temperature using a turbo molecular vacuum pump and then gradually heated to 55 °C for **1**, 85 °C for **2** (increasing at a rate of 1°C/min), held for 8 h and cooled to room temperature.

The determination of the isosteric heats of adsorption (Q_{st}) for H_2 and CO_2 was estimated by applying the Clausius-Clapeyron expression using the H_2 adsorption isotherms measured at 77 K and 87 K and the CO_2 isotherms measured at 258, 273, 288 and 298 K unless otherwise noted.

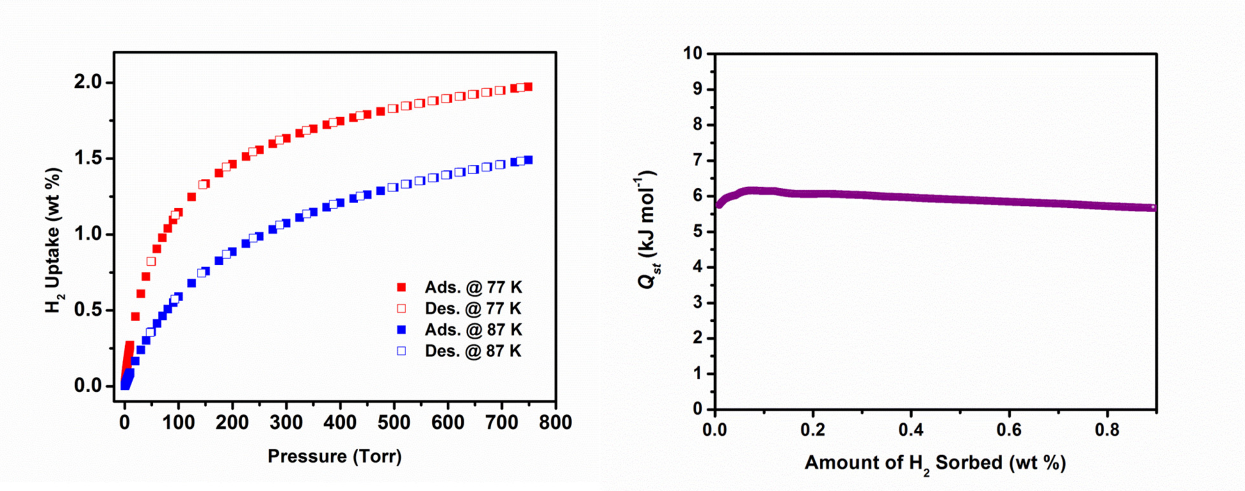


Fig. S12. H_2 adsorption data for data for compound **1**: fully reversible H_2 isotherms collected at 77 and 87K (left) and Q_{st} for H_2 calculated from the corresponding isotherms (right).

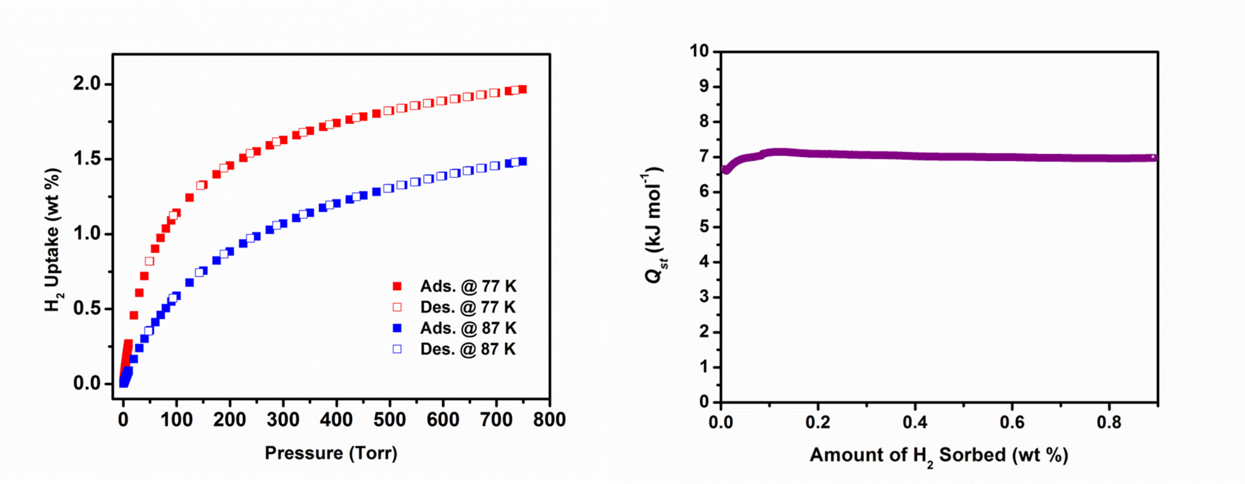


Fig. S13. H_2 adsorption data for data for compound **2**: fully reversible H_2 isotherms collected at 77 and 87K (left) and Q_{st} for H_2 calculated from the corresponding isotherms (right).

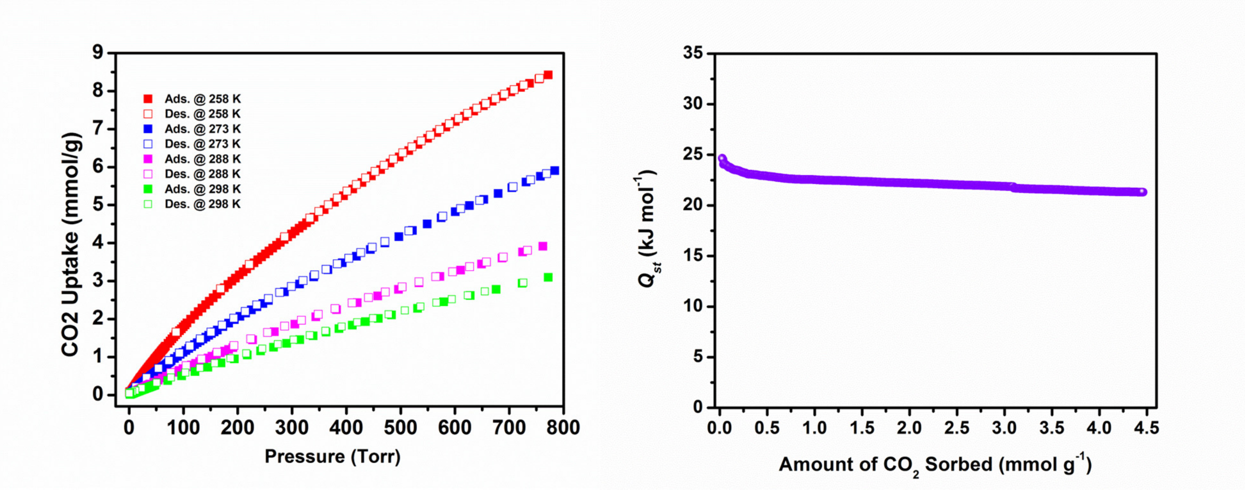


Fig. S14. CO_2 adsorption data for compound **1**: fully reversible variable temperature (VT) CO_2 isotherms (left) and *Q*st for CO_2 calculated from the corresponding isotherms (right).

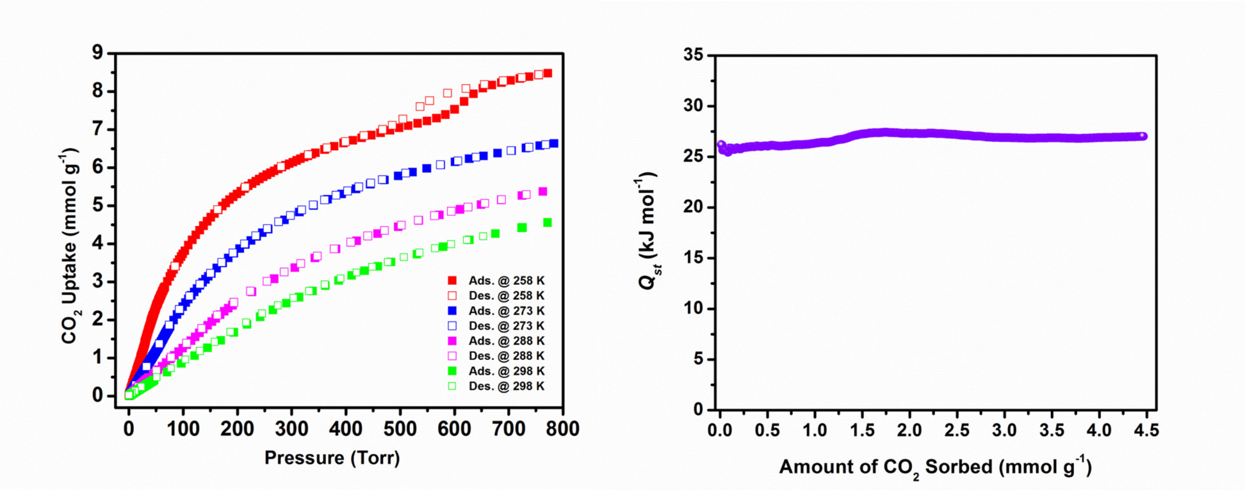


Fig. S15. CO_2 adsorption data for compound **2**: variable temperature (VT) CO_2 isotherms (left) and *Q*st for CO_2 calculated from the corresponding isotherms (right).

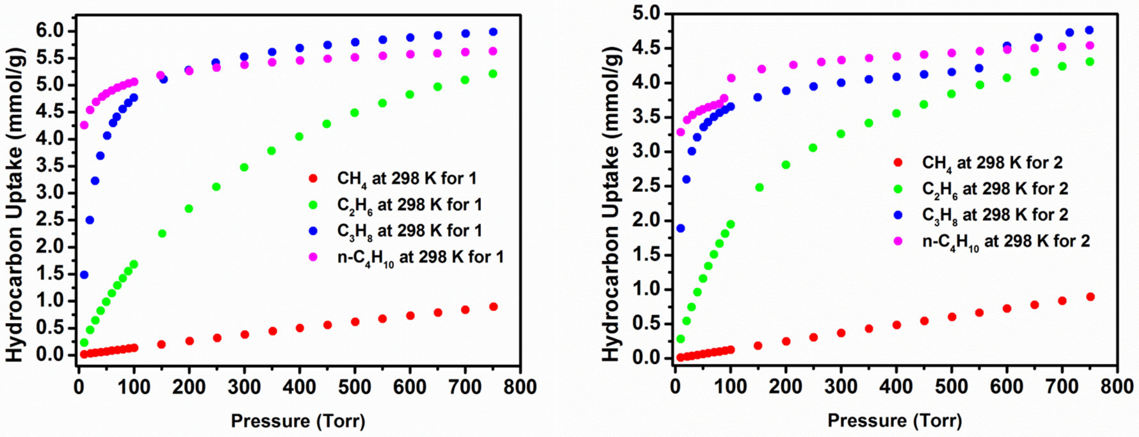


Fig. S16. Light hydrocarbon adsorption data for compound **1** (left) and compound **2** (right).

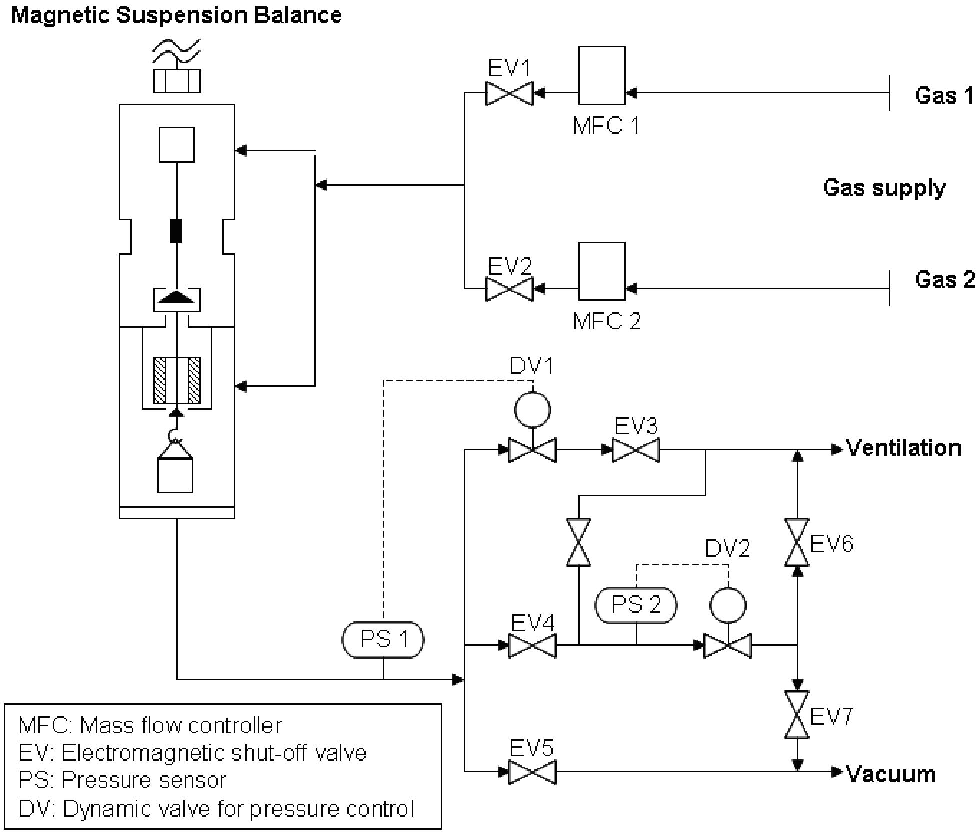
8. High-Pressure Gas Adsorption Measurements

Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany) (Scheme S1), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flow meters, and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere, and is able to perform adsorption measurements across a wide pressure range (i.e., from 0 to 20 MPa). The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount (Ω). Correction for the buoyancy effect is required to determine the excess and absolute adsorbed amount using equations 1 and 2, where Vadsorbent and Vss and Vadorbed phase refer to the volume of the adsorbent, the volume of the suspension system, and the volume of the adsorbed phase, respectively.

$$\Omega = m_{absolute} - \rho_{gas}(V_{adsorbent} + V_{ss} + V_{adsorbed-phase}) \tag{1}$$

$$\Omega = m_{excess} - \rho_{gas}(V_{adsorbent} + V_{ss}) \tag{2}$$

The buoyancy effect resulting from the adsorbed phase may be taken into account via correlation with the pore volume or with the theoretical density of the sample.



Scheme S1 Representation of the Rubotherm gravimetric-densimetric apparatus.

These volumes are determined using the helium isotherm method by assuming that helium penetrates in all open pores of the materials without being adsorbed. The density of the gas is determined using the Refprop equation of state (EOS) database and checked experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. Simultaneous measurement of adsorption capacity and gas-phase density as a function of pressure and temperature is therefore possible.

The pressure is measured using two Drucks high pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to each adsorption experiment, about 200 mg of sample is outgassed at 473 K at a residual pressure of 10^{-6} mbar. The temperature during adsorption measurements is held constant by using a thermostat-controlled circulating fluid.

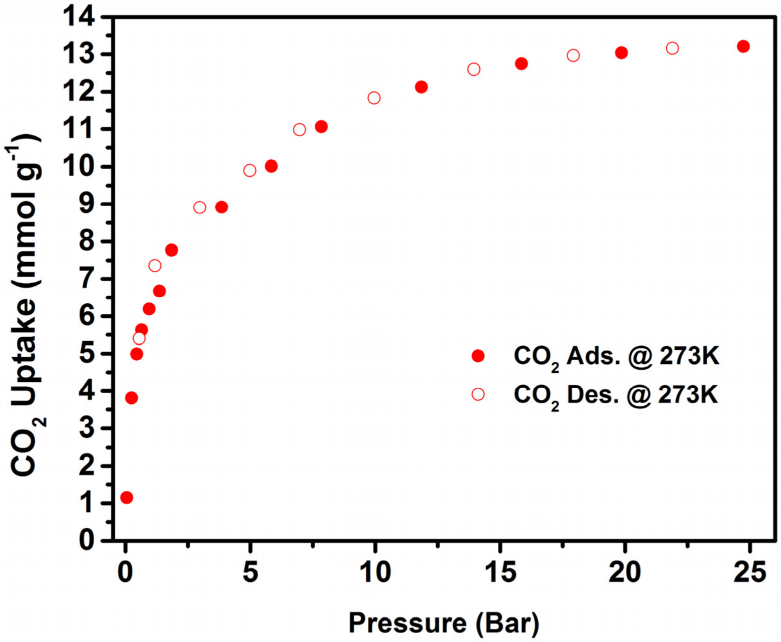


Fig. S17. Excess high pressure CO_2 adsorption data for compound **2**.

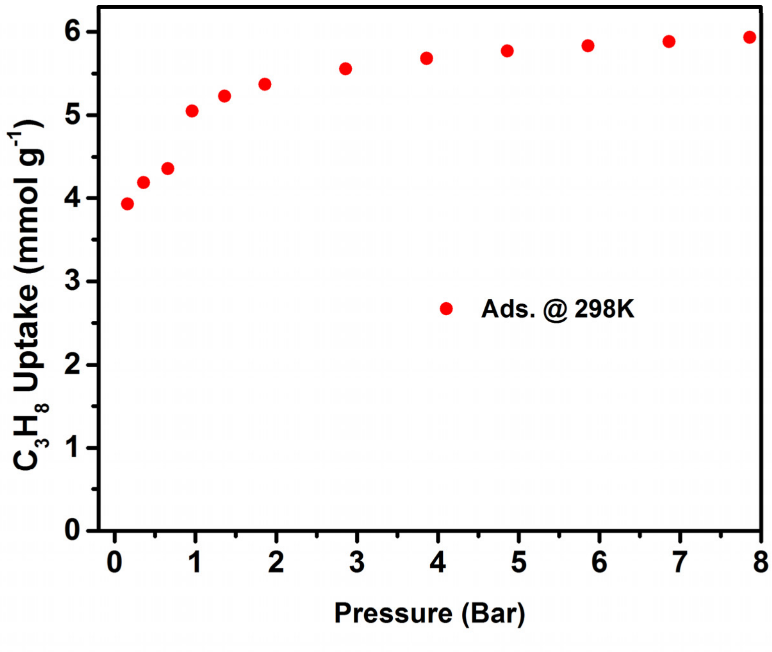


Fig. S18. Excess high-pressure C_3H_8 adsorption data for compound **2**.

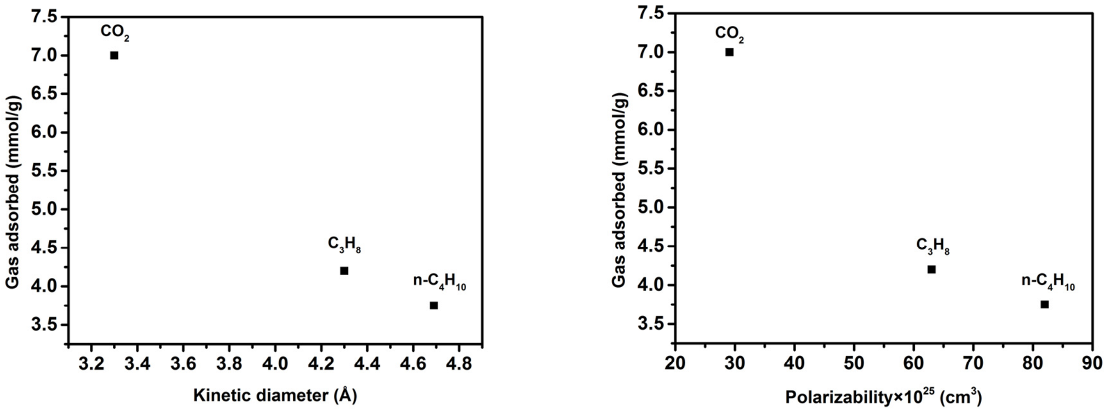


Fig. S19. Relationship of the gas adsorbed amount at the foot of the first plateau for CO_2, C_3H_8, n-C_4H_{10} with both the kinetic diameter (left) and the polarizability (right).

9. IAST Calculations

Prediction of multicomponent gas adsorption Ideal Adsorption Solution Theory (IAST)

The Ideal Adsorption Solution Theory (IAST) proposed by Mayer and Prausnitz (1965)[5] uses pure gas adsorption isotherms to predict the mixture adsorption equilibrium at the temperature of interest. For IAST application, the main condition to be fulfilled is the availability of (i) good quality single component adsorption data of different gases, and (ii) an excellent curve fitting model for such data (Chen and Sholl, 2007;[6] Bae et al., 2008[7]). In the current work, Toth model was used to fit the pure gas isotherms.
The most important equations used in the IAST calculation are listed hereafter:

$$f_i = x_i f_i^0(\pi) \tag{3}$$

$$\frac{\pi A}{RT} = \int_0^{f_i^0} n_i d \ln f_i \tag{4}$$

$$\frac{1}{n_t} = \sum_i \frac{x_i}{n_i^0} \tag{5}$$

$$S_{CO_2-i} = \frac{x_{CO_2} / x_i}{y_{CO_2} / y_i} \tag{6}$$

where f_i is the fugacity of component i in the gas phase; f_i^0 is the standard-state fugacity (i.e., the fugacity of pure component *i* at the equilibrium spreading pressure of the mixture, π); x_i and y_i are the mole fractions of component i in the adsorbed and gas phase, respectively; A is the surface area of the adsorbent; n_i is the number of moles adsorbed of pure component *i* (i.e., the pure-component isotherm); and n_i^0 is the number of moles adsorbed of pure component *i* at the standard-state pressure.
Equation 3 is the central equation of IAST, specifying the equality of the chemical potential of component *i* in the gas and the adsorbed phase (which is assumed to be ideal in the sense of Raoult's law). Equation 4 allows the calculation of the spreading pressure from the pure-component adsorption isotherm. The total amount adsorbed of the mixture, n_t, and the selectivity of CO_2 with respect to *i*, S_{CO_2-i}, are given by equations 5 and 6, respectively. The selectivity, S_{CO_2-i}, reflects the efficiency of CO_2 separation.

Toth Model for single gas adsorption fitting

In the current work, the Toth model was used to fit the pure gas isotherms and its simple formulation as expressed by equation 7 (Toth, 2002)[8]

$$n = n_s \frac{KP}{(1+(KP)^m)^{1/m}} \tag{7}$$

where n is the amount adsorbed, n_s is the amount adsorbed at saturation, P is the equilibrium pressure, K is the equilibrium constant, and m is a parameter indicating the heterogeneity of the adsorbent.

Table S1. CO_2 **-** Toth Parameter of **1**.

Qs	b	m
59.36171	0.07629	0.55181

Table S2. CH_4 **-** Toth Parameter of **1**.

Qs	b	m
14.96307	0.06826	0.8341

Table S3. N_2 **-** Toth Parameter of **1**.

Qs	b	m
220.13817	0.00105	1

Table S4. C_2H_6 **-** Toth Parameter of **1**.

Qs	b	m
8.75426	2.0652	0.8491

Table S5. C_3H_8 **-** Toth Parameter of **1**.

Qs	b	m
6.11416	27.97321	0.99501

Table S6. CO_2 **-** Toth Parameter of **2**.

Qs	b	m
5.83802	1.17642	2.06676

Table S7. CH_4 **-** Toth Parameter of **2**.

Qs	b	m
10.68472	0.08816	1.21768

Table S8. N_2 **-** Toth Parameter of **2**.

Qs	b	m
121.4341	0.00144	1

Table S9. C_2H_6 **-** Toth Parameter of **2**.

Qs	b	m
5.56844	4.4802	0.88889

Table S10. C_3H_8 **-** Toth Parameter of **2**.

Qs	b	m
4.2964	84.61637	0.82838

10. References

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