

Complete Series of Mono-Halogenated Isorecticular Metal-Organic Frameworks: Synthesis and the Importance of Activation Method

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Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction experiments were carried out using a PANalytical Empyrean™ diffractometer equipped with a PIXcel-3D detector operating in scanning line detector mode with an active length of 4 utilizing 255 channels. The diffractometer is outfitted with an Empyrean Cu LFF (long fine-focus) HR DK386079 XRD tube operated at 45 kV and 40 mA and Cu K-alpha radiation ($\lambda_{\alpha} = 1.5418704 \text{ \AA}$) was used for diffraction experiments. Experiments were conducted in continuous scanning mode with the goniometer in the theta-theta orientation. Incident beam optics included the Fixed Divergences slit with Anti-scatter slit PreFIX module, with a $1/16^{\circ}$ divergence slit and a $1/8^{\circ}$ anti-scatter slit, as well as a 10 mm fixed incident beam mask and a Soller slit (0.04 rad). Divergent beam optics included a P7.5 anti-scatter slit, a Soller slit (0.04 rad), and a Ni Beta filter. The samples were typically dry and ground into a fine powder, applied to a low background sample holder and mounted to a bracket flat sample stage. In a typical experiment, data was collected via a continuous scan in the range of 3° - 70° (2θ) with a step-size of 0.131° and a scan time of 90 seconds per step. Raw data was then evaluated using the X'Pert HighScore Plus™ software V 3.0.0 (PANalytical, The Netherlands).

Low Pressure Porosimetry

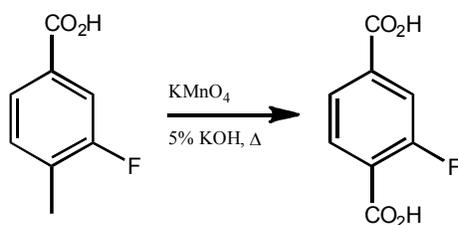
N_2 isotherms were collected at 77 K and 292 K. These experiments were carried out via the method of gas adsorption manometry using a Quadrasorb-SI™ (Kr/MP) automated surface area and pore size analyzer (Quantachrome Instruments, USA). The data were evaluated using the QuadraWin™ software V.5.02 (Quantachrome Instruments, USA). N_2 (UHP, $\geq 99.999\%$) and He (UHP, $\geq 99.999\%$) were purchased from Matheson Tri-Gas and used as received without further purification. Prior to adsorption analysis all samples were outgassed for extended periods under dynamic turbomolecular pump vacuum and heating profiles described in the activation protocols. Outgassing was achieved using a MasterPrep™ 6-station degasser in vacuum mode with CN616 control software (Quantachrome Instruments, USA). Upon completion of the degas/heat profile, the samples were backfilled with dry N_2 (UHP). Data was analyzed with Quantachrome QuadraWin software. Multipoint BET surface areas were calculated from 10 points spaced between $P/P_0 = 0.005$ and 0.075 . Ambient temperature adsorption Isotherms were collected from $P/P_0 = 0.01 - 1.00$. P_0 was set to 760 mmHg.

Synthesis

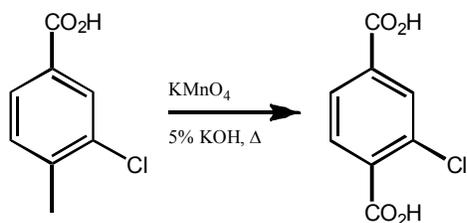
All chemicals were purchased from Sigma-Aldrich or Alfa-Aesar and used as received. Dichloromethane, Chloroform, and Anhydrous N,N-dimethylformamide, were purchased from Sigma-Aldrich, and dried over 4A molecular sieves. IRMOF-1 was synthesized from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and terephthalic acid in DMF/water as reported in the literature.¹ NMR spectra were obtained on a 500 MHz Varian Inova spectrometer, and reported in parts per million, referenced from residual solvent peaks (d_6 -DMSO: 2.49 ppm for ^1H , 39.5 ppm for ^{13}C). The following abbreviations are used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; b, broad. Elemental analysis data was obtained by Columbia Analytical Services.

Supercritical CO_2 Drying

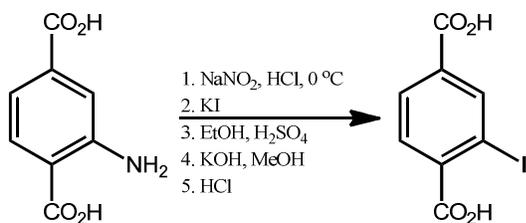
Freshly prepared MOF samples were soaked in EtOH dried over 4A molecular sieves for 5 days, and during that period of time it was replaced 4 times. These samples were transferred to a Tousimis Samdri®-PVT-3D critical point drier. The chamber was then cooled to $-10\text{ }^\circ\text{C}$ and filled with liquid CO_2 . The chamber was sealed, and held below $10\text{ }^\circ\text{C}$ for 20 minutes and then liquid CO_2 was allowed to flow through the chamber for 10 minutes. This process was repeated three additional times. The chamber was then sealed and heated to $40\text{ }^\circ\text{C}$ at which point the liquid CO_2 became supercritical. The sample were held for 30 minutes under supercritical conditions, and then the CO_2 was slowly released from the chamber over a period of 18 h.



2-Fluoroterephthalic acid: 3-fluoro-4-methylbenzoic acid (1.0 g, 5.7 mmol) and of KMnO_4 (3.42 g, 21.4 mmol) were dissolved in aqueous KOH solution (35 mL, 5%) and the solution was refluxed for 4 hours. The solution was then allowed to cool to room temperature and was stirred overnight and filtered. The filtrate was diluted with water (25 mL) and acidified with conc. HCl to pH 1. The white precipitate was collected by filtration, washed with water, and dried in vacuo (100 mtorr) to afford 2-fluoroterephthalic acid as a white powder (0.66 g, 56% yield). NMR (d_6 -DMSO) ^1H : 13.54 (2H, bs), 7.95 (1H, t, $J = 7.6$ Hz), 7.82 (1H, dd, $J = 8.1$ Hz, 1.5 Hz), 7.72 (1H, dd, $J = 11.0$, 1.5 Hz). ^{13}C : 165.5 (d, $J = 2.3$ Hz), 164.4 (d, $J = 2.8$ Hz), 161.6 (s), 159.6 (s), 136.4 (d, $J = 7.9$ Hz), 132.2 (s), 125.0 (d, $J = 3.7$ Hz), 123.2 (d, $J = 10.7$ Hz), 117.3 (d, $J = 23.7$ Hz)



2-Chloroterephthalic acid: 3-chloro-4-methylbenzoic acid (1.0 g, 6.5 mmol) and KMnO_4 (3.16 g, 19.8 mmol) were dissolved in aqueous KOH solution (30 mL, 5%) and the solution was refluxed for 4 h. The solution was then allowed to cool to room temperature and was stirred overnight and filtered. The filtrate was diluted with water (25 mL) and acidified with conc. HCl to pH 1. The white precipitate was collected by filtration, washed with water, and dried in vacuo (100 mtorr) to afford 2-chloroterephthalic acid as a white powder (0.9 g, 75% yield). NMR (d_6 -DMSO) ^1H : 13.60 (2H, bs), 7.96 (1H, d, $J = 1.5$ Hz), 7.93 (1H, dd, $J = 8.1$ Hz, 1.5 Hz), 7.86 (1H, d, $J = 7.8$). ^{13}C : 163.4, 162.5, 133.2, 132.1, 129.4, 128.7, 127.4, 125.8



2-Iodoterephthalic acid: A solution of NaNO_2 (4.75 g, 68.8 mmol) in H_2O (40 mL) was added dropwise to an ice bath cooled suspension of 2-aminoterephthalic acid (5.00 g, 27.7 mmol) in H_2O -conc. HCl (166 mL, V:V, 1:1) mixture over a period of 30 min. The solution was stirred for an additional 30 min. while being cooled in an ice bath, and was then poured into a solution of KI (27.5 g, 166 mmol) in water (250 mL), and the resulting reaction mixture was stirred at room temperature overnight. NaHSO_3 was then added in portions until the dark color of the solution was discharged, and the resulting yellow product was collected by filtration, washed with water, and recrystallized from 1:1 (V:V) H_2O :acetone (130 mL). This product was washed with CHCl_3 (100 mL) and dried in vacuo to afford crude 2-iodoterephthalic acid (5.2 g, 65% yield). Of this crude product, 4.0 g (14 mmol) were dissolved in anhydrous EtOH (100 mL) with concentrated H_2SO_4 (2 mL), and the solution was refluxed overnight. The reaction mixture was then cooled to room temperature, and poured into water. The sticky precipitate was collected by filtration, and then purified by flash chromatography on silica gel with dichloromethane. This product was dissolved in saturated KOH in MeOH (65 mL) and stirred at room temperature overnight. This solution was concentrated to dryness, and the residue was dissolved in water, and acidified to pH 1 with concentrated HCl. The resulting white precipitate was collected by filtration, washed with water, and dried in vacuo (100 mtorr) to afford 2-iodoterephthalic acid (2.54 g, 41% yield overall). NMR (d_6 -DMSO) ^1H : 13.52 (2H, bs), 8.41 (1H, d, $J = 1.4$ Hz), 7.98 (1H, dd, $J = 8.0$ Hz, 1.6 Hz), 7.76 (1H, d, $J = 7.8$ Hz). ^{13}C : 164.9, 162.4, 138.7, 138.3, 131.5, 127.7, 126.7, 92.3.

IRMOF-2-F: 2-fluoroterephthalic acid (0.152 g, 0.836 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.84 g 2.8 mmol) were dissolved in DEF (50 mL), and the mixture was heated at 95 °C in a 100 mL capped glass jar for 29 h in an oven. The DEF was decanted hot, and replaced with hot DMF immediately. The cubic crystals were dislodged from the sides of the jar while hot, and the DMF was replaced with fresh, hot DMF and the capped jar was returned to the 95 °C oven for 10 minutes. The mixture was then allowed to cool to room temperature, and the crystals were pipetted into a 20 mL scintillation vial, and activated as described in the main text. The product was then heated at 125 °C for 14 h at 10 mtorr to afford activated IRMOF-2-F (0.0764 g, 34% yield). EA (measured): C: 33.55 H: 2.06 N 0.35 (Calc.) C: 34.99 H: 1.10 N: 0.0

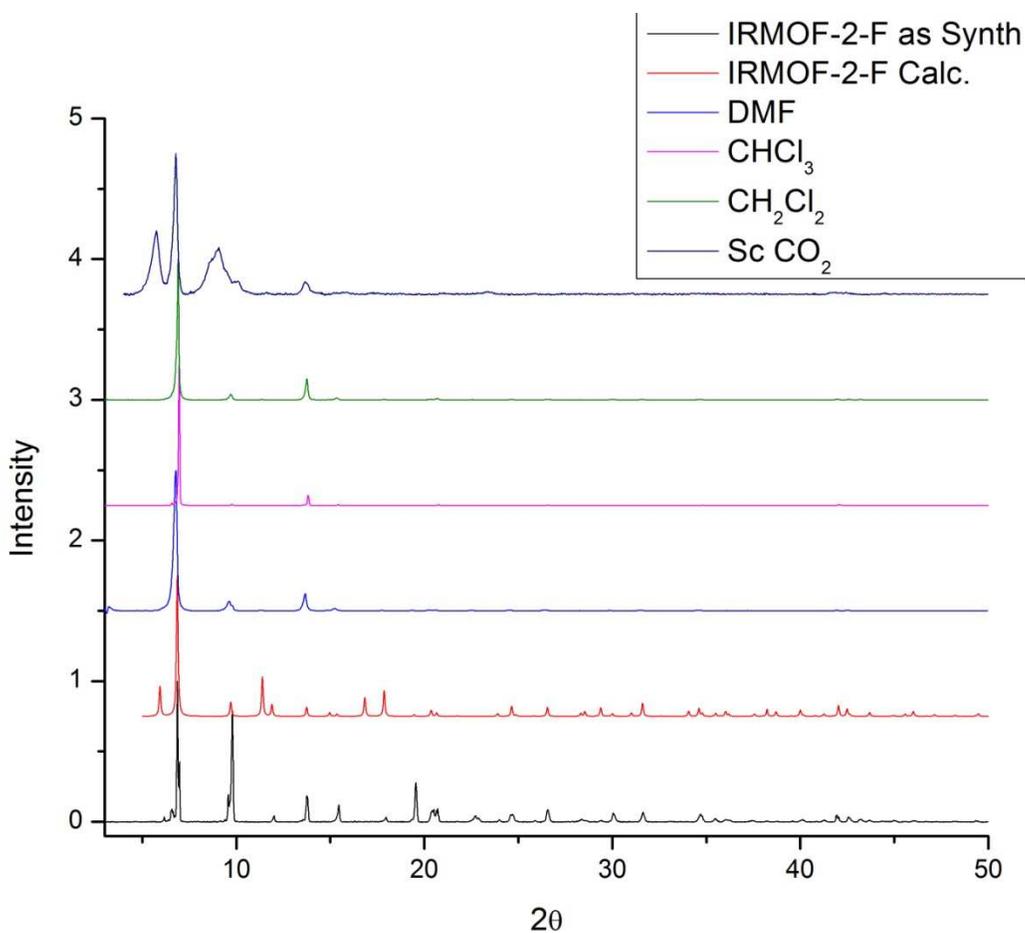


Fig. S1 PXRD patterns of IRMOF-2-F as synthesized, after activation with CH_2Cl_2 , CHCl_3 , and DMF, and calculated for IRMOF-2-Br

IRMOF-2-Cl: 2-chloroterephthalic acid (0.165 g, 0.823 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.84 g 2.8 mmol) were dissolved in DEF (50 mL), and the mixture was heated at 95 °C in a 100 mL capped glass jar for 41 h in an oven. The DEF was decanted hot, and replaced with hot DMF immediately. The cubic crystals were dislodged from the sides of the jar while hot, and the DMF was replaced with fresh, hot DMF and the capped jar was returned to the 95 °C oven for 10 minutes. The mixture was then allowed to cool to room temperature, and the crystals were pipetted into a 20 mL scintillation vial, and activated as described in the main text. The product was then heated at 125 °C for 14 h at 10 mtorr to afford activated IRMOF-2-Cl (0.0764 g, 34% yield). EA (measured): C: 32.65 H: 2.21 N: 0.32 (calc.) C: 33.01 H: 1.04 N: 0.0

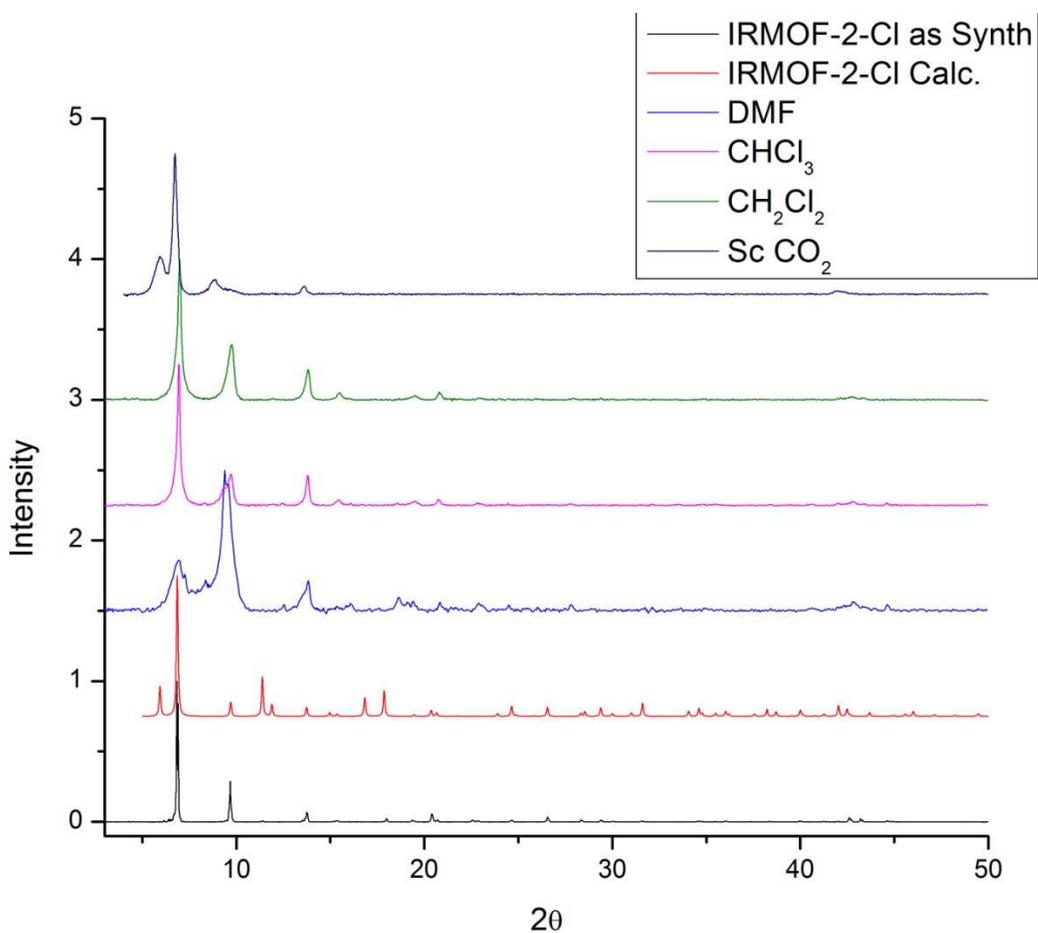


Fig. S2 PXRD patterns of IRMOF-2-Cl as synthesized, after activation with CH_2Cl_2 , CHCl_3 , and DMF, and calculated for IRMOF-2-Br

IRMOF-2-Br: 2-bromoterephthalic acid (0.165 g, 0.775 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.84 g 2.8 mmol) were dissolved in DEF (50 mL), and the mixture was heated at 95 °C in a 100 mL capped glass jar for 46 h in an oven. The DEF was decanted hot, and replaced with hot DMF immediately. The cubic crystals were dislodged from the sides of the jar while hot, and the DMF was replaced with fresh, hot DMF and the capped jar was returned to the 95 °C oven for 10 minutes. The mixture was then allowed to cool to room temperature, and the crystals were pipetted into a 20 mL scintillation vial, and activated as described in the main text. The product was then heated at 125 °C for 14 h at 10 mtorr to afford activated IRMOF-2-Br (0.1158 g, 45% yield). EA (measured): C: 29.25 H: 1.52 N: 0.26 (calc.) C: 28.64 H: 0.90 N: 0.0

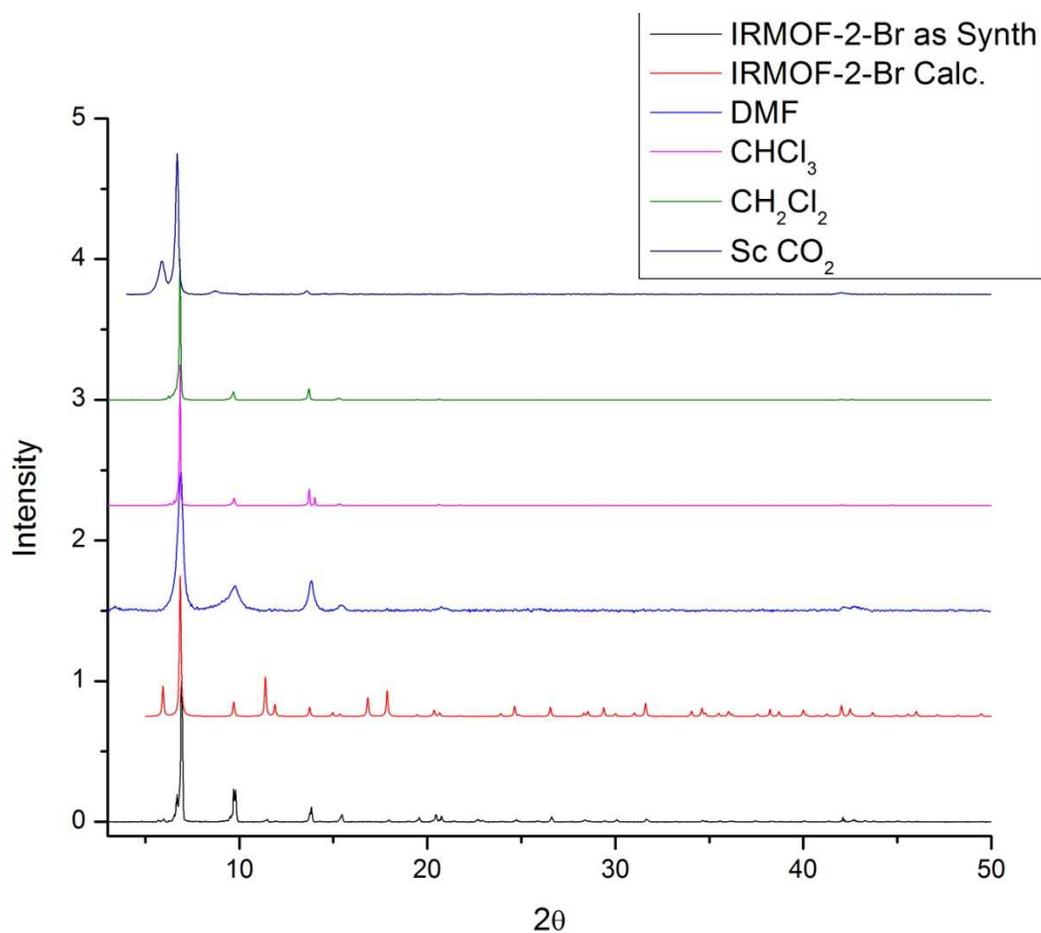


Fig. S3 PXRD patterns of IRMOF-2-Br as synthesized, after activation with CH_2Cl_2 , CHCl_3 , and DMF, and calculated for IRMOF-2-Br

IRMOF-2-I: 2-iodoterephthalic acid (0.24 g, 0.82 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.84 g 2.8 mmol) were dissolved in DEF (50 mL), and the mixture was heated at 95 °C in a 100 mL capped glass jar for 21 h in an oven. The DEF was decanted hot, and replaced with hot DMF immediately. The cubic crystals were dislodged from the sides of the jar while hot, and the DMF was replaced with fresh, hot DMF and the capped jar was returned to the 95 °C oven for 10 minutes. The mixture was then allowed to cool to room temperature, and the crystals were pipetted into a 20 mL scintillation vial, and activated as described in the main text. The product was then heated at 125 °C for 14 h at 10 mtorr to afford activated IRMOF-2-I (0.1042 g, 33% yield). EA (measured): C: 25.93 H: 2.32 N: 0.29 (calc.) C: 25.12 H: 0.79 N: 0.0

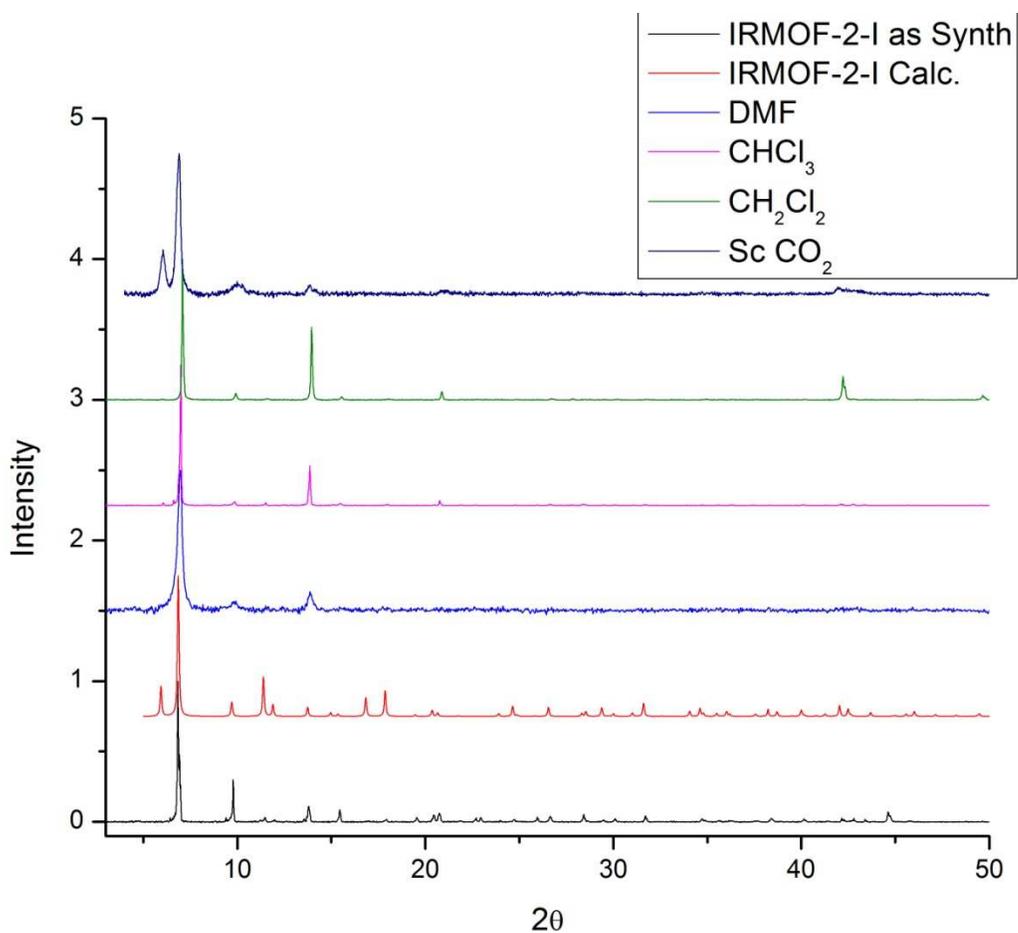


Fig. S4 PXRD patterns of IRMOF-2-I as synthesized, after activation with CH_2Cl_2 , CHCl_3 , and DMF, and calculated for IRMOF-2-Br

Pore size Distributions

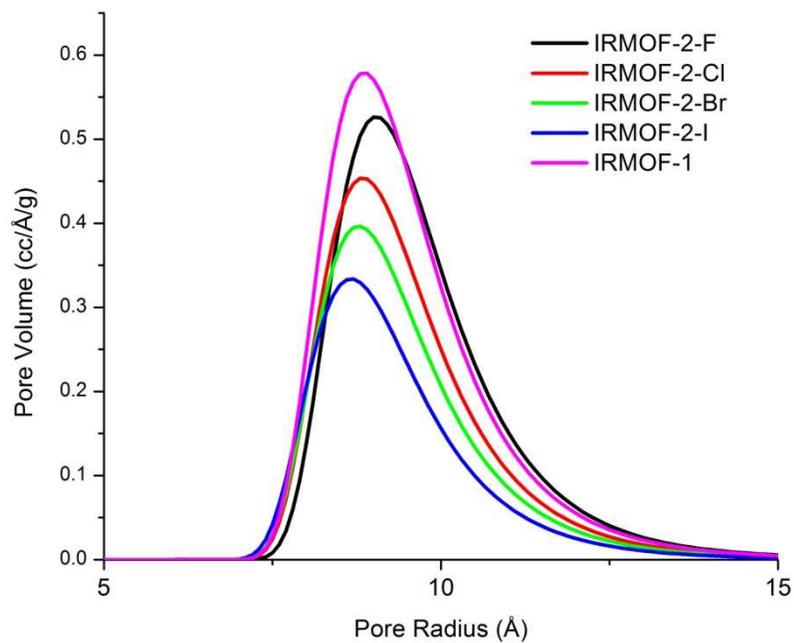


Fig. S5 Pore size distributions for the IRMOF-2-X series and IRMOF-1 calculated with the Dubinin-Ashtakhov method

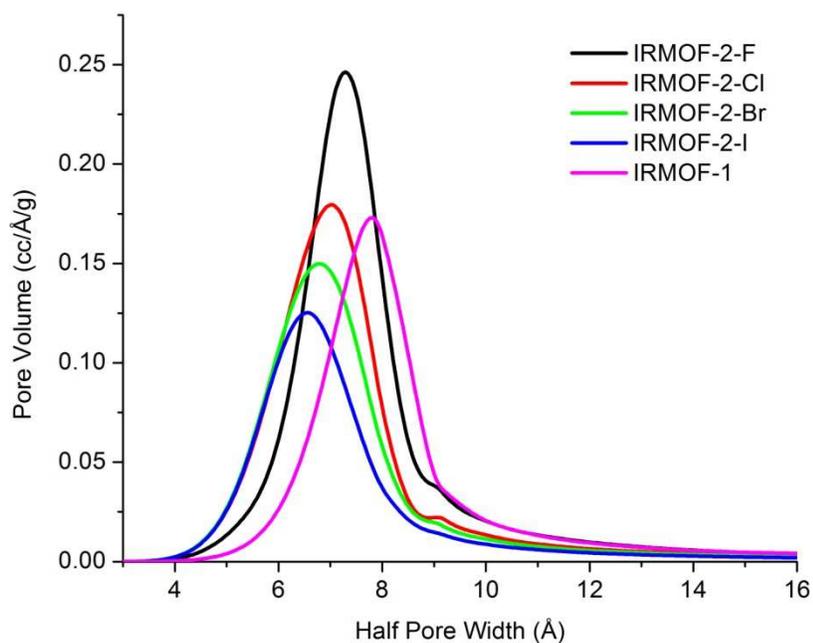


Fig. S6 Pore size distributions for the IRMOF-2-X series and IRMOF-1 calculated with the Satio-Foley method

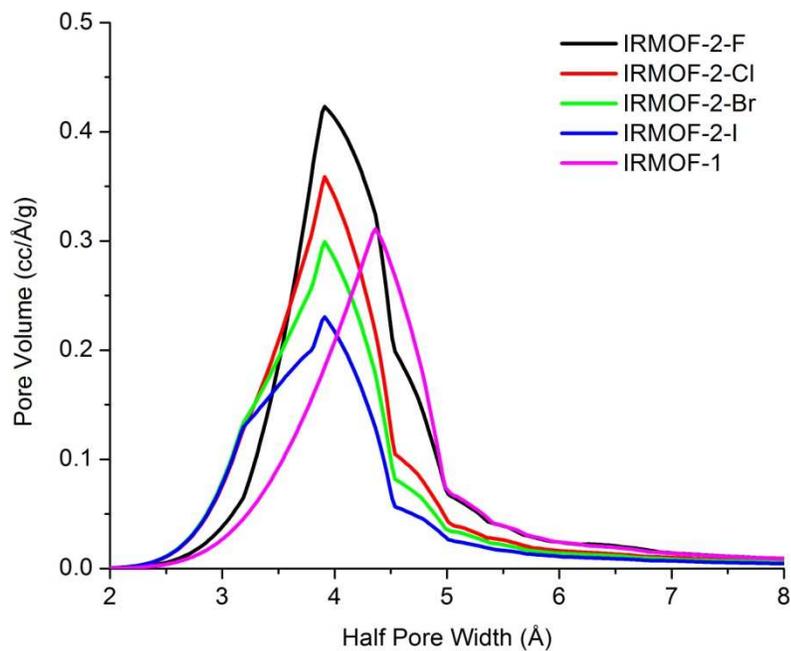


Fig. S7 Pore size distributions for the IRMOF-2-X series and IRMOF-1 calculated with the Horvath-Kawazoe method

- (1) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J Am Chem Soc* **2007**, *129*, 14176.