Metal–organic nanosheets formed via defect–mediated transformation of a hafnium metal–organic framework

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1 Adsorption Measurements and Calculations

1.1 Measurements

N₂ adsorption isotherms were carried out at 77 K on a Micromeritics 3Flex gas adsorption analyser. Samples were degassed in situ under vacuum at 120 °C for 20 h using the internal turbo pump. Warm and cold free-space correction measurements were performed by using ultrahigh purity He gas (grade 5.0, 99.999% purity). Ultrahigh purity N₂ (i.e. 99.9992%) was provided by Air Products.

1.2 Molecular Simulation

The simulated adsorption of N₂ was investigated using grand canonical Monte Carlo (GCMC) simulations performed in the multi-purpose code RASPA. We used an atomistic model of the hcp UiO-67 MOF structure for which the framework atoms were kept fixed at the crystallographic positions. We used the standard Lennard-Jones (LJ) 12-6 potential to model the interactions between the framework and fluid atoms. In addition, a Coulomb potential was used for N₂/N₂ interactions. The parameters for the framework atoms were obtained from the UFF or Dreiding force field and N₂ was modelled using the TraPPE potential with charges placed on each atom and at the centre of mass (Supporting Table 1). The Lorentz-Berthelot mixing rules were employed to calculate fluid/solid LJ parameters, and LJ interactions beyond 12.8 Å were neglected. The Ewald sum method was used to compute the electrostatic interactions. Up to 80,000 Monte Carlo cycles were performed, the first 50% of which were used for equilibration, and the remaining steps were used to calculate the ensemble averages. Monte Carlo moves consisted of insertions, deletions, displacements, and rotations. In a cycle, \( N \) Monte Carlo moves are attempted, where \( N \) is defined as the maximum of 20 or the number of adsorbates in the system. To calculate the gas-phase fugacity we used the Peng-Robinson equation of state. Geometric surface areas were calculated by rolling a 3.681 Å diameter sphere, which corresponds to a nitrogen molecule, across the surface of the material.

Supporting Table 1: Lennard-Jones parameters for MOF atoms and the N₂ molecule.

|        | \( \sigma (\text{Å}) \) | \( \epsilon/k \text{(K)} \) | \( \sigma (\text{Å}) \) | \( \epsilon/k \text{(K)} \) | \( q (\text{e}) \) |
|--------|-----------------|----------------|-----------------|----------------|----------------|
| UFF    |                 |                 |                 |                 |                |
| C{\text{MOF}} | 3.431           | 52.838          | 3.472           | 47.856          |                |
| N{\text{MOF}} | 3.261           | 34.722          | 3.262           | 38.949          |                |
| H{\text{MOF}} | 2.571           | 22.142          | 2.846           | 7.648           |                |
| Hf{\text{MOF}} | 2.798           | 36.262          | N/A             | N/A             |                |
| Dreiding|                 |                 |                 |                 |                |
| TraPPE |                 |                 |                 |                 |                |
| N{\text{N}}_2 | 3.310           | 36.000          | -0.482          |                |                |
| N{\text{com}} | 0                | 0               | 0.964           |                |                |
Supporting Fig. 1: Calculated and experimental N$_2$ adsorption isotherms for hcp UiO-67 (presented on a linear scale).

Supporting Fig. 2: N$_2$ adsorption isotherm for hcp UiO-67 (presented on a logarithmic scale).
Supporting Fig. 3: Non-local density functional theory (NLDFT) pore size distribution for hcp UiO-67.
Supporting Fig. 4: Effect of varying the synthesis temperature on the product formed for the hcp UiO-67. At 130 °C and above hcp UiO-67 forms. At 120 °C an unknown phase forms, and below that no significant reaction occurs, leaving just ligand.

Supporting Fig. 5: Restacking of hxl UiO-67. On washing at elevated temperatures in DMF hxl and the residual ligand restack to form hcp UiO-67. This process occurs gradually on soaking in room temperature DMF. This reaction does not occur through simply annealing the hxl UiO-67.
2  \textit{in situ} synthesis analysis

Full pattern analysis of powder patterns was performed using the Pawley method within the Topas Academic software to determine lattice parameters\textsuperscript{98}. The peak shape was allowed to vary freely throughout the refinement. The background was modelled using a combination of a broad Gaussian function, to account for the scattering due to the apparatus and solvent, and a freely refining Chebyshev polynomial. An additional broad Gaussian peak was used to model the small angle scattering present early in the reaction. Additional peaks due to the instrumental background and undissolved ligand were modelled as Gaussians, with width and intensity freely refining. Selected patterns were also refined using the Rietveld method in order to quantify phase fractions.

Initially the kinetics of the four distinct phases: SAXS scattering, UiO-67, hcp UiO-67 and ligand were modelled using the model proposed by Gualtieri\textsuperscript{99}:

\[
\alpha = \frac{A}{1 + \exp \left\{-\left(\frac{t-a}{b}\right)^a\right\}} \left\{1 - \exp \left[-(k_g t)^N\right]\right\}, \tag{1}
\]

\(A\) is a normalisation factor, \(N\) is the dimensionality of crystal growth, \(k_g\) is the rate constant of crystal growth and \(a\) and \(b\) are constants related to nucleation. The induction time is dependent on the nucleation process and so is determined by constants \(a\) and \(b\). This five parameter fit was found to over-parameterise the time evolution, and so a reduced functional form was used,

\[
\alpha = A \left(1 - \exp \left[-k_g(t - t_i)\right]\right)^d. \tag{2}
\]

Where \(A\) and \(k_g\) have equivalent meaning, but the induction time is explicitly accounted for by the constant \(t_i\). \(t_f\) as discussed in the main text is \(t_f = \frac{1}{k_g}\). Both functional forms were unable to account for the growth of hcp UiO-67.

| parameter | SAXS         | fcu UiO-67      |
|-----------|--------------|-----------------|
| \(A\)     | 3.75 (11)    | 1.059 (8) \times 10^{-5} |
| \(t_i\) (min) | -2.2 (9) | 88.0 (3)         |
| \(d\)     | 1.27 (8)     | 0.69 (2)        |
| \(k_g\) (min\(^{-1}\)) | 0.0257 (8) | 0.0203 (5)      |

Supporting Table 2: Fitted crystal growth parameters for fcu UiO-67 and the SAXS intensity. Parameters defined as in Eqn.\textsuperscript{2} \(t = 0\) refers to the start of the powder diffraction measurements rather than the first mixing of the samples.
Supporting Fig. 6: A 2D ‘film plot’ showing all the PXRD data collecting during the \textit{in situ} synthesis of hcp UiO-67 at 150°C. Key features and peaks are marked.
Supporting Fig. 7: Pawley refinement of in situ PXRD data for the final time point measured. Orange tick marks indicate the fcu phase and green tick marks highlight the hcp phase.
Supporting Fig. 8: Evolution of refined lattice parameters and peak widths for the hcp and fcu phases during synthesis. Errors (1σ) shown as light colour background. (a) fcu UiO-67 a, (b) fcu UiO-67 peak width, (c) hcp UiO-67 a, (d) hcp UiO-67 c, (e) hcp UiO-67 peak width.
3 Powder diffraction analysis

All refinements were carried out using Topas Academic 4.1. The background was modelled using a combination of a broad Gaussian function and a freely refining Chebyshev polynomial (nine parameters, except for hxl, for which seven parameters was sufficient). A small quantity of unreacted ligand was modelled as a single Gaussian peak with width and intensity freely refining. In order to account for the anisotropic broadening observed in the hxl UiO-67 due to reduced order in the c direction, an additional Gaussian size broadening term was also included in the refinement with its orientational dependence modelled using fourth order spherical harmonics. A small impurity peak was detected in the hcp phase and fitted separately as a Gaussian. This broadening corresponded to a size of approximately 40(5) nm. Rietveld refinements were carried out from the DFT optimised structural models, with the position and isotropic displacement parameter of Hf atoms allowed to refine. The observed discrepancies in the low Q peak intensities, particularly acute for hxl UiO-67, are likely due to the presence of large quantities of disordered guests, as often observed in porous materials. We were not able to crystallographically identify the guests through structural modelling, but structural envelopes derived from difference Fourier maps showed that residual electron density was primarily present within the pores. Although for fcu UiO phases there is uncertainty over the proton configuration, this uncertainty is eliminated for hcp because the two oxygens which are facing each other cannot be protonated (c.f. Ref. S12), and so we did not introduce additional disorder into the structure.
Supporting Table 3: Atomic coordinates from Rietveld refined model of hcp UiO-67(Hf)

| Radiation       | λ = 0.826168 Å          |
|-----------------|-------------------------|
| Formula         | C_{63}H_{43}Hf_{6}O_{29}|
| M (g mol⁻¹)     | 2334.91                 |
| Z               | 4                       |
| Crystal System  | Hexagonal               |
| Space Group     | P\text{6}_3/mmc         |
| a (Å)           | 19.015(4)               |
| c (Å)           | 43.491(18)              |
| V (Å³)          | 13617.7(8)              |

| Atom | x     | y     | z     | B_{eq} (Å²) |
|------|-------|-------|-------|-------------|
| Hf1  | 0.2075(6) | 0.6037(3) | 0.7888(2) | 1.76(14)*   |
| Hf2  | 0.4529(6) | 0.7265(3) | 0.8560(2) | 1.76(14)*   |
| H01  | 0.881903  | 0.553529 | 0.435925  | 2           |
| H02  | 0.032283  | 0.629898 | 0.517865  | 2           |
| H03  | 0.333333  | 0.666667 | 0.598642  | 2           |
| H04  | 0.032085  | 0.418032 | 0.209525  | 2           |
| H05  | 0.743282  | 0.160354 | 0.791180  | 2           |
| H06  | 0.747242  | 0.821639 | 0.368376  | 2           |
| H07  | 0.255046  | 0.946160 | 0.632873  | 2           |
| H08  | 0.164328  | 0.691905 | 0.750000  | 2           |
| H09  | 0.234989  | 0.469977 | 0.702682  | 2           |
| C01  | 0.902841  | 0.566957 | 0.327127  | 2           |
| C02  | 0.587650  | 0.412350 | 0.094188  | 2           |
| C03  | 0.355350  | 0.336441 | 0.328663  | 2           |
| C04  | 0.561496  | 0.438504 | 0.433311  | 2           |
| C05  | 0.612780  | 0.514255 | 0.446462  | 2           |
| C06  | 0.588600  | 0.050392 | 0.027552  | 2           |
| C07  | 0.793788  | 0.128608 | 0.829773  | 2           |
| C08  | 0.025360  | 0.512680 | 0.513884  | 2           |
| C09  | 0.660164  | 0.042179 | 0.807449  | 2           |
| C10  | 0.885674  | 0.266679 | 0.691912  | 2           |
| C11  | 0.703660  | 0.709656 | 0.649407  | 2           |
| C12  | 0.776999  | 0.066561 | 0.851075  | 2           |
| O01  | 0.657854  | 0.461615 | 0.395194  | 2           |
| O02  | 0.849314  | 0.292656 | 0.153020  | 2           |
| O03  | 0.894220  | 0.376484 | 0.305736  | 2           |
| O04  | 0.333333  | 0.666667 | 0.717673  | 2           |
| O05  | 0.615190  | 0.384810 | 0.162820  | 2           |
| O06  | 0.666667  | 0.333333 | 0.120859  | 2           |
| O07  | 0.263347  | 0.736653 | 0.803186  | 2           |
| O08  | 0.529775  | 0.182476 | 0.250000  | 2           |

Estimated standard errors are given in parentheses. * Hf displacement parameters constrained to be identical.
Supporting Table 4: Atomic coordinates from Rietveld refined model of hxl UiO-67(Hf)

| Atom  | x        | y        | z        | B(eq) (Å²) |
|-------|----------|----------|----------|------------|
| Hf1   | 0.7298(4)| 0.2703(4)| 0.0607(6)| 4.31(15)*  |
| Hf2   | 0.7948(7)| 0.3974(4)| 0.3174(5)| 4.31(15)*  |
| H01   | 0.2344   | 0.4688   | 0.8346   |            |
| H02   | 0.6667   | 0.3333   | 0.5219   |            |
| H03   | 0.0320   | 0.4187   | 0.3218   |            |
| H04   | 0.2572   | 0.4183   | 0.3233   |            |
| H05   | 0.1781   | 0.9252   | 0.4606   |            |
| H06   | 0.7447   | 0.0542   | 0.4581   |            |
| H07   | 0.8360   | 0.3073   | 0.2500   |            |
| H08   | 0.4376   | 0.8752   | 0.4382   |            |
| C01   | 0.6635   | 0.0188   | 0.3897   |            |
| C02   | 0.6647   | 0.8711   | 0.3919   |            |
| C03   | 0.9576   | 0.3401   | 0.8520   |            |
| C04   | 0.3818   | 0.2670   | 0.6467   |            |
| C05   | 0.2963   | 0.2902   | 0.0715   |            |
| C06   | 0.9334   | 0.2230   | 0.9296   |            |
| C07   | 0.4149   | 0.8299   | 0.4719   |            |
| C08   | 0.4329   | 0.0968   | 0.1127   |            |
| O01   | 0.1053   | 0.6228   | 0.6506   |            |
| O02   | 0.3333   | 0.6667   | 0.6922   |            |
| O03   | 0.3851   | 0.7701   | 0.5934   |            |
| O04   | 0.3333   | 0.6667   | 0.5181   |            |
| O05   | 0.5266   | 0.2633   | 0.3443   |            |
| O06   | 0.1802   | 0.6513   | 0.7500   |            |
| O07   | 0.7072   | 0.1505   | 0.4228   |            |
| O08   | 0.3434   | 0.8070   | 0.4887   |            |

Estimated standard errors are given in parentheses. * Hf displacement parameters constrained to be identical.

Supporting Table 5: Refined parameters for hcp and hxl UiO-67. Both refinements carried out in P6₃/mmc
Supporting Fig. 9: Pawley Refined PXRD patterns for activated hcp UiO-67(Hf). Top: full range, bottom: high Q region.
Supporting Fig. 10: Rietveld refined PXRD patterns for activated hcp UiO-67(Hf). Top: full range, bottom: high $Q$ region.
Supporting Fig. 11: Refined PXRD patterns for as-synthesised \textbf{hxl} UiO-67(Hf). Top: Pawley refinement, bottom: Rietveld refinement
Supporting Fig. 12: Difference density envelopes (at 3 Å) for as-synthesised hxl UiO-67(Hf). The additional density is primarily concentrated within the pores of the material, especially the small cages, indicating the presence of guests. Top: view along [001], bottom: view along [110].
Supporting Fig. 13: Geometric pore surface of hxl UiO-67 (calculated for a 1.84 Å probe, equivalent to \( N_2 \)) for hxl UiO-67(Hf). Both the infinite 1D channel and the small cage are visible. The small cage is formally disconnected from the channel for this probe radius, but will be accessible to guests through ligand rotations. Top: view along [001], bottom: view along [100].
Supporting Fig. 14: Diffraction patterns of isolated single sheets of hcp UiO-67 of different composition. The experimental powder diffraction data does not allow for discrimination between these models. The random stacking model was generated by sequentially adding layers of either single clusters (i.e. generating condensed clusters) or ligands and clusters at random. As only \((hk0)\) reflections are present, the experimental diffraction data is sensitive primarily to the projected electron density in the (001) plane. This is in large part responsible for the similarity of the diffraction patterns calculated from single layer sheets.
4 NMR of single sheets

A suspension of hxl UiO-67 nanosheets in MeOH was dried and 20 mg of the resultant powder was digested in 1M NaOH in D$_2$O, following the method of Shearer$^{13}$. $^1$H NMR spectra were collected on the resultant suspension and integration of the formate and bpdc$^{2-}$ ligand peaks gave a ratio of 0.21:1 formate:bpdc$^{2-}$ ratio.
Supporting Fig. 15: Solution $^1$H NMR spectrum of digested hxl UiO-67.
Supporting Fig. 16: Thermogravimetric analysis of hcp UiO-67. The ideal mass losses for hcp and non-defective fcu UiO-67 calculated for the desolvated frameworks are shown. TGA carried out under a flow of air at heating rate of 10 K min\(^{-1}\). Fractional mass loss is defined as \(\frac{m}{m_{\text{final}}} - 1\).
5 Atomic Force Microscopy

Samples for atomic force microscopy (AFM) were prepared by drop casting a dilute suspension of *hxl* UIO-67(Hf) prepared by sonication in MeOH of *hcp* UIO-67(Hf) onto freshly cleaved mica. AFM measurements were carried using an Agilent 5500 (Agilent Technologies) AFM in tapping mode (OTESPA-R3 tip).

Supporting Fig. 17: AFM surface topologies of *hxl* UIO-67 nanosheet. (a) AFM micrograph (b) height profile.
References

(S1) Frenkel, D.; Smit, B. *Understanding Molecular Simulation*; Academic Press, San Diego, USA, 2002.
(S2) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. *Mol. Simul.* 2016, 42, 81–101.
(S3) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* 1992, 114, 10024–10035.
(S4) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* 1990, 94, 8897–8909.
(S5) Potoff, J. J.; Siepmann, J. I. *AIChE J.* 2001, 47, 1676–1682.
(S6) Reid, R. C.; Pausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill Companies: New York, New York, USA, 1987.
(S7) Gómez-Gualdrón, D. A.; Moghadam, P. Z.; Hupp, J. T.; Farha, O. K.; Snurr, R. Q. *J. Am. Chem. Soc.* 2016, 138, 215–224.
(S8) Coelho, A. TOPAS - Academic: General Profile and Structure Analysis Software for Powder Diffraction Data., Version 4.1. 2007.
(S9) Gualtieri, A. F. *Phys. Chem. Miner.* 2001, 28, 719–728.
(S10) Yakovenko, A. A.; Wei, Z.; Wriedt, M.; Li, J.-R.; Halder, G. J.; Zhou, H.-c. *Cryst. Growth Des.* 2014, 14, 5397–5407.
(S11) Smeets, S.; McCusker, L. B.; Baerlocher, C.; Elomari, S.; Xie, D.; Zones, S. I. *J. Am. Chem. Soc.* 2016, 138, 7099–7106.
(S12) Piszczek, P.; Radtke, A.; Wojtczak, A.; Muzioł, T.; Chojnacki, J. *Polyhedron* 2009, 28, 279–285.
(S13) Shearer, G. C.; Chavan, S.; Bordiga, S.; Velle, S.; Olsbye, U.; Lillerud, K. P. *Chem. Mater.* 2016, 28, 3749–3761.