SUPPORTING INFORMATION

Pore-filling contamination in metal-organic frameworks

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S1 Computational Details

For each MOF studied in this work, cif files were obtained from the Cambridge Crystallographic Data Centre (CCDC). After removing solvent molecules and/or disordered atoms, the remaining structures were optimised using a classical mechanics treatment within the forcite module of Materials Studio 7.0.¹ The optimisation was carried out using the Universal Force Field² with the unit cell parameters and copper paddlewheels bond lengths constrained to match their experimental values.

To calculate the theoretical BET surface areas, GCMC simulations were carried out using the Multi-Purpose Simulation Code (MUSIC) of Snurr et al.^{3,4} Input fugacities for each simulation were calculated using the Peng-Robinson equation of state.⁵ Simulations included random translation and rotation moves, as well as, energy biased insertion and deletion moves. Each simulation involved an equilibration stage of $6x10^6$ steps followed by a production stage of $9x10^6$ steps for each pressure point. Errors in the adsorbate loading were calculated by separating the production steps into 18 equally sized blocks. In all MOFs, the errors in the adsorbate loading were found to be smaller than the symbol sizes and have been removed from the adsorption isotherms for clarity. In this work, the frameworks were treated as rigid species with their atoms fixed in their crystallographic or geometry optimised coordinates. For the framework atoms, Lennard-Jones parameters were taken from the DREIDING force field⁶ or the Universal Force-Field for those which were missing from DREIDING. The adsorbate in this work was treated as a rigid three-site species, where two nitrogen atoms were bound to a non-interacting and dimensionless centre of mass atom. The Lennard-Jones parameters and partial charges for the N₂ molecules were taken from the TraPPE force-field.⁷ All Lennard-Jones interactions were calculated with a cut-off distance of 15.0 Å, and N₂-N₂ interactions were handled using the Ewald method.⁸ Previous work has shown that N₂-MOF electrostatic

interactions play a minor role in the adsorption of N_2 and as such, were not included.⁹ All BET surface areas were calculated using the consistency criteria devised by Rouquerol *et al.*¹⁰ surface areas were calculated by the Poreblazer toolkit of Sarkisov and Harrison¹¹¹¹¹¹¹¹. The probe in this work consisted of a spherical nitrogen site whose parameters were taken from the TraPPE force-field. A list of simulation parameters used in this work can be found in the table below.

Site σ (Å) ε(K) Force-Field q С 3.47 47.86 N/A DREIDING 0 3.03 48.19 N/A DREIDING Η 2.85 7.65 N/A DREIDING Cu 3.114 UFF 2.516 N/A N (Adsorbate) TraPPE 3.31 36.00 -0.482 TraPPE COM (Adsorbate) 0.0 0.0 0.964

Table S1. A list of the LJ parameters used in this work to compute the Lennard-Jones and coulombic interactions.

S2 Pore size distributions of the investigated MOFs.

Pore size distributions (PSD) were calculated using the method outline by Gelb and Gubbins.¹² This method uses a Monte-carlo scheme to determine the largest sphere that encompasses a random point in space, without overlapping with any framework atoms. By iterating this process at various points across the simulation cell, a PSD profile can be recorded. In this work, PSDs were recorded using the Poreblazer toolkit of Sarkisov and Harrison.



Figure S1. Pore size distributions of each investigated MOF with nbo topology.



Figure S2. Pore size distributions of each investigated MOF with rht topology.

<u>NOTT-101</u>



Figure S3. The simulated N2 isotherm for NOTT-101 from GCMC simulations.



Figure S4. Rouquerol consistency plot for NOTT-101. A maximum at $p/p_0 = 0.0296$ was observed.



Figure S5. The BET plot for NOTT-101. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $2x10^{-4} \le p/p_0 \le 0.031$. A C value of 3544 was calculated.

PCN-16



Figure S6. The simulated N2 isotherm for PCN-16 from GCMC simulations.



Figure S7. Rouquerol consistency plot for PCN-16. A maximum at $p/p_0 = 0.0296$ was observed.



Figure S8. The BET plot for PCN-16. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $2x10^{-4} \le p/p_0 \le 0.030$. A C value of 4142 was calculated.



Figure S9. The simulated N_2 isotherm for NOTT-102 from GCMC simulations.



Figure S10. Rouquerol consistency plot for NOTT-102. A maximum at $p/p_0 = 0.0395$ was observed.



Figure S11. The BET plot for NOTT-102. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $4x10^{-5} \le p/p_0 \le 0.039$. A C value of 1822 was calculated.

<u>PCN-46</u>



Figure S12. The simulated N2 isotherm for PCN-46 from GCMC simulations.



Figure S13. Rouquerol consistency plot for PCN-46. A maximum at $p/p_0 = 0.0395$ was observed.



Figure S14. The BET plot for PCN-46. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $2x10^{-4} \le p/p_0 \le 0.039$. A C value of 2500 was calculated.



Figure S15. The simulated N_2 isotherm for NOTT-112 from GCMC simulations.



Figure S16. Rouquerol consistency plot for NOTT-112 A maximum at $p/p_0 = 0.0395$ was observed.



Figure S17. The BET plot for NOTT-112. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $2x10^{-4} \le p/p_0 \le 0.039$. A C value of 600 was calculated.

PCN-61



Figure S18. The simulated N₂ isotherm for PCN-61 from GCMC simulations.



Figure S19. Rouquerol consistency plot for PCN-61. A maximum at $p/p_0 = 0.0395$ was observed.



Figure S20. The BET plot for PCN-61. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $2x10^{-4} \le p/p_0 \le 0.039$. A C value of 682 was calculated.



Figure S21. The simulated N_2 isotherm for NOTT-119 from GCMC simulations.



Figure S22. Rouquerol consistency plot for NOTT-119. A maximum at $p/p_0 = 0.099$ was observed.



Figure S23. The BET plot for NOTT-119. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $4x10^{-3} \le p/p_0 \le 0.099$. A C value of 71 was calculated.

<u>NOTT-116</u>



Figure S24. The simulated N2 isotherm for NOTT-116 from GCMC simulations.



Figure S25. Rouquerol consistency plot for NOTT-116. A maximum at $p/p_0 = 0.08$ was observed.



Figure S26. The BET plot for NOTT-116. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $8 \times 10^{-3} \le p/p_0 \le 0.08$. A C value of 144 was calculated.



Figure S27. The simulated N₂ isotherm for NU-111 from GCMC simulations.



Figure S28. Rouquerol consistency plot for NU-111. A maximum at $p/p_0 = 0.08$ was observed.



Figure S29. The BET plot for NU-111. Using the consistency criteria, the monolayer capacity and surface area were determined from a linear range between $0.019 \le p/p_0 \le 0.08$. A C value of 191 was calculated.

MOF	p/p ₀ range	BET C value	R ² value
NOTT-101	0.0002 - 0.031	3544	1.000
PCN-16	0.0002 - 0.030	4142	1.000
NOTT-102	0.00004 - 0.039	1822	0.9999
PCN-46	0.0002 - 0.039	2500	1.000
NOTT-112	0.0002 - 0.039	600	0.9996
PCN-61	0.0002 - 0.039	682	0.9999
NOTT-119	0.00004 - 0.099	71	0.9935
NOTT-116	0.008 - 0.08	144	0.9991
NU-111	0.019 - 0.08	191	0.9997

Table S2. Summary of BET linear fitting parameters for each investigated MOF



Figure S30. Comparison of the simulated and experimental N₂ isotherms of NOTT-119 at 77 K. Whilst the experimental isotherm is type-IV in shape, each generic force-field is found to predict a type-Ib isotherm.

Site	σ (Å)	ε (K)	Force-Field
С	3.431	52.838	UFF
0	3.118	30.193	UFF
Н	2.571	22.142	UFF
Cu	3.114	2.516	UFF
C (sp ²)	3.550	35.226	OPLS
C (COOH)	3.750	52.838	OPLS
Н	2.420	15.097	OPLS
0	2.960	105.68	OPLS

Table S3. A list of simulation input parameters used for the OPLS and UFF force-fields.

S5 Volumetric surface area calculations

MOF	crystallographic density (g/cm ³)	UC/cm ³ (x10 ¹⁸)	Total surface area of UC (Å ²)	ASA (m ² /cm ³)	Method 2 PFC corrected SA (m ² /cm ³)
NOTT-101	0.683	86.4	2459 ± 13	2126 ± 11	1977
PCN-16	0.722	101	1976 ± 9	2002 ± 10	2001
NOTT-102	0.587	64.9	3693 ± 8	2397 ± 5	2066
PCN-46	0.618	82.5	2612 ± 7	2156 ± 6	2005
NOTT-112	0.503	9.66	19261 ± 18	1855 ± 2	1908
PCN-61	0.560	12.8	15020 ± 12	1916 ± 1	1943
NOTT-119	0.361	5.60	28792 ± 34	1614 ± 2	1615
NOTT-116	0.406	7.23	24077 ± 28	1745 ± 2	1754
NU-111	0.409	8.55	21772 ± 32	1863 ± 3	1849

Table S4. List of the calculated crystallographic densities, numbers of UC per cm^3 and UC ASA which are used to calculate volumetric surface areas for each investigated MOF.

UC = unit cell; ASA = accessible surface area; PFC = pore-filling contamination

S6 Pore filling contamination snapshots in each rht MOF

Colour Scheme: red = O, orange = Cu, white = H, grey = C, $green = N_2$ pore-filling contaminants

<u>NOTT-112</u>



Figure S31. Pore-filling contamination found inside the small (left), medium (middle) and large (right) pores of NOTT-112.

<u>PCN-61</u>



Figure S32. Pore-filling contamination found inside the small (left), medium (middle) and large (right) pores of PCN-61.

<u>NOTT-116</u>



Figure S33. Pore-filling contamination found inside the small (left), medium (middle) and large (right) pores of NOTT-116.

<u>NOTT-119</u>



Figure S34. Pore-filling contamination found inside the small (left), medium (middle) and large (right) pores of NOTT-119.



Figure S35. Pore-filling contamination found inside the small (left), medium (middle) and large (right) pores of NU-111.

S7 Accessibility of the hard-sphere probe vs soft GCMC N₂



Figure S36. Left - Image of the accessible surface area surrounding the triangle pore windows in PCN-61. Right – Image showing how the soft N₂ molecules from GCMC simulations can access regions that are inaccessible to the hard-sphere probe used in accessible surface area calculations.

The left image shows a triangular window found in the tetrahedral pores of each **rht** MOF. The purple spheres surrounding each framework atom represent accepted probe insertions that make up the accessible surface. In the centre of the triangular window, there is a discontinuity in the accessible surface area where the hard-sphere probe cannot access. Analysis of our GCMC simulation snapshots, reveals that the "softer" N_2 molecules can clearly access this region of the window (shown in the right image).

S8 Correlating the extent of PFC with pore size



Figure S37. Left – Plot of second largest cage diameter vs largest cage diameter in each of the nine investigated MOFs. The circles represent a single MOF with the size of each circle representing the magnitude of the deviation between the MOFs BET surface area and ASA. Filled circle = BET surface area > ASA, Open circle = BET surface area < ASA.

The plot on the left of Figure S37 shows very similar characteristics to a similar plot developed by Snurr and co-workers¹³ reinforcing that MOFs which possess a combination of different sized cages are more susceptible to the effects of pore-filling contamination. Furthermore, our results also agree with the findings in reference 13 that show MOFs containing large micropores and mesopores possess the largest deviations between their BET surface areas and ASAs.

S9 References

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