Supplementary Information

Gel-Based Morphological Design of Zirconium Metalorganic Frameworks

Bart Bueken,^a Niels Van Velthoven,^a Tom Willhammar,^{b,c} Timothée Stassin,^a Ivo Stassen,^a David A. Keen,^d Gino V. Baron,^e Joeri F. M. Denayer,^e Rob Ameloot,^a Sara Bals,^b Dirk De Vos,^{a,*} and Thomas D. Bennett^{f,*}

^a Centre for Surface Chemistry and Catalysis, Department M²S, KU Leuven, Celestijnenlaan 200F p.o. box 2461, 3001 Heverlee, Belgium

^b EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

^c Department of Materials and Environmental Chemistry, Berzelii Center EXSELENT on Porous Materials, Stockholm University, S-106 91 Stockholm, Sweden

^d ISIS Facility, Rutherford Appleton Laboratory, Harwell Campus, Didcot, Oxon OX11 0QX, United Kingdom

^{e.}Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium.

^f Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom

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Oil-drop granulation setup for monolithic UiO-66 spheres

A schematic overview of the in-house constructed oil-drop granulation setup is provided in Figure S0. The setup consists of a perfusor pump (Braun; Figure S0, a) which dispenses gel droplets at a fixed flow rate of 3 mL·h⁻¹ from a 3 mL syringe (BD Luer Lock) into a glass hopper (Figure S0, b and right panel) containing an immiscible silicone oil (Roger Coulon M1028/50). The end of the dispensing needle was blunted to form perfectly spherical gel droplets. A gear pump (Modelcraft #F3007; Figure S0, e) pumps the silicone oil throughout the setup at a constant flow rate, transporting the gel droplets through a 16 m polytetrafluoroethylene (PTFE) tube, which is submerged in a hot oil bath at 150 °C (Figure S0, c). The average residence time of the gel droplets undergo a temperature-induced syneresis. Subsequently, the hardened monolithic spheres exit the PTFE tube and are captured in a Schott bottle (Figure S0, d) which has been modified to allow easy recovery of the spheres from the bottom of the vessel. The residual silicone oil is then recirculated by the gear pump to the glass hopper.



Figure S0. Oil-drop granulation setup. Left & Middle: Schematic representation (left) and image (middle) of the setup used to prepare monolithic UiO-66 spheres. (a) perfusor pump; (b) hopper (b); (c) PTFE tube in oil bath; (d) Recovery of spheres in modified Schott bottle; (e) gear pump (e). Right: Close-up of the glass hopper (b) and dispensing needle (a), showing one gel droplet forming on the needle and one gel droplet suspended in the hopper.

Additional images of UiO-66 monoliths



Figure S1. UiO-66 monolithic xerogels. (a) millimetre-sized xerogel particles obtained after drying. (b) Transparent, mudcracked film obtained after drying a gel film coated on a glass petri dish (scale bar = 100 μ m). (c-f) Optical images of transparent xerogel particles obtained after crushing particles as in (a) (scale bars = 200 μ m). (g-h) Scanning electron micrographs of xerogel particles (scale bars = 50 μ m (g); 200 μ m (h)).



Figure S2. Various monolithic aerogels. (a) UiO-66. (b) UiO-67. (c) UiO-66-NH₂.

Pair Distribution Functions



Figure S3. Pair distribution functions. Top: Pair distribution functions (PDFs; D(r) vs. r) for a microcrystalline UiO-66 sample (black) and a monolithic xerogel of UiO-66 (red; Table S1, entry 10). The main peaks, at interatomic distances of 2.33 Å, 3.75 Å and 4.89 Å, correspond to UiO-66's intracluster Zr-O and Zr-Zr (adjacent and diagonal, respectively) atom pairs, while those at greater interatomic distances can be attributed to correlations between atoms in neighbouring clusters. Bottom: Recorded structure factors S(Q) used to generate the PDFs by Fourier transformation for the microcrystalline UiO-66 sample (black) and the UiO-66 xerogel (red).

Pore size distributions



Figure S4. Pore size distribution. (a) Mesopore size distribution obtained from the Barrett-Joyner-Halenda (BJH) model applied to the N_2 physisorption isotherms displayed in Figure 4, c. Hierarchical mesopores can be found in the UiO-66 xerogel (red diamonds) and aerogel (blue triangles). Note that in microcrystalline UiO-66 (black circles), no mesopores are observed. (b) Micropore size distribution obtained from the Tarazona Non-Local Density Functional Theory model applied to the N_2 physisorption isotherms displayed in Figure 4, c, illustrating the presence of micropores characteristic for UiO-66, with pore widths of 6 Å and 8 Å.¹

Thermogravimetric analyses



Figure S7. Thermogravimetric plots for UiO-66 gels. Thermogravimetric plots for UiO-66 xerogel (red) and aerogel (blue) (both prepared from Table S1, entry 10). For the xerogel, an average of 11 linkers per Zr_6 -cluster is found, while the aerogel has an average of 11.8 linkers per cluster, possibly due to unremoved H₂bdc.

Mercury intrusion experiments



Figure S6. Low pressure mercury intrusion (up to 0.2 MPa) of monolithic xerogel. In this range, mercury intrusion is fully reversible, and represents filling of interparticle voids, as well as filling of surface defects (e.g. cracks) and the dilatometer.



Figure S7. High pressure mercury intrusion (0.1 - 200 MPa) of monolithic xerogel. In this range, mercury intrusion is fully irreversible, and represents a static compression of the mesopore voids found in the xerogel particles.

Nanoindentation experiments



Figure S8. Nanoindentation experiments on monolithic UiO-66 xerogels. Nanoindentation experiments were conducted on two xerogel samples (top curves = Sample 1; bottom curves = Sample 2; samples prepared from Table S1, entry 10). Left: Average elastic modulus (*E*) as a function of tip displacement into the monolith surface. Sample 1 showed an average *E* of 9.3 (±0.3) GPa, while for Sample 2 *E* averaged 10.5 (±0.5) GPa. Right: Load-displacement curves for the corresponding indentation experiments.



Figure S9. Optical microscopy of monolith nanoindentation. Optical microscopy images of xerogel particles (left: Sample 1 from Figure S8; right: Sample 2 from Figure S8) after nanoindentation. Each triangular mark corresponds to single load-displacement experiment using a Berkovich tip (scale bar = 50μ m).

Gelation of various Zr-MOFs



Figure S10. Gelation of various Zr-MOFs. Gels and xerogel monoliths of various Zr-MOFs based on Zr₆-clusters.





Figure S11. X-ray diffractograms of Zr-MOF (xero)gels. X-ray diffraction patterns of monolithic xerogels of functionalized UiO-66 analogues, UiO-67 and MOF-808. For NU-1000, the diffraction pattern represents that of an ethanol-exchanged gel, due to the insufficient sample amount produced in the drying stage, which precluded recording a diffraction pattern of the monolithic material. The diffractometer setup features a primary beam stop up to ~2.8 ° 20, masking NU-1000's first reflection at 2.6 ° 20. For MOF-801 (Zr-fumarate), the diffraction pattern of the xerogel shows a loss of crystallinity relative to that of the ethanol-exchanged gel.

Overview of UiO-66 gel syntheses

Table S1. Overview of UiO-66 gel syntheses. Influence of Zr source, reactant concentration (DMF:Zr ratio) and additives on the macroscopic outcome of UiO-66 syntheses (2 h, 100 °C). H_2O_{tot} = molar ratio of H_2O in ZrOCl₂·8H₂O and additionally supplied, relative to Zr; H_2O = molar ratio of added H_2O (pure and as HCl 37 wt% solution) to Zr; Cl_{tot} = molar ratio of Cl⁻ in Zr source and additionally added relative to Zr; HCl = molar ratio of added HCl to Zr; AA = molar ratio of added acetic acid to Zr; MP indicates the formation of a microcrystalline powder; FG describes a 'flowing' gellike, translucent to opaque suspension of moderate to high viscosity; NFG refers to a 'non-flowing', opaque gel for which the synthesis vessel can be turned upside down without the gel flowing downwards, see Figure 1, a). * = synthesized at 120 °C.

#	Outcome		DMF:Zr	H_2O_{tot}	H ₂ O	Cl _{tot}	HCI	AA
1	MP	ZrOCl ₂ ·8H ₂ O	1503	14.8	6.8	4	2.0	0.0
2	MP		620	14.2	6.2	3.8	1.8	3.5
3	FG		620	42.7	34.7	3.8	1.8	3.5
4	FG		388	14.3	6.3	3.8	1.8	0.0
5	FG		388	14.3	6.3	3.8	1.8	3.5
6	FG		388	42.9	34.9	3.8	1.8	3.5
7	FG		201	14.9	6.9	4	2.0	3.5
8	NFG		155	14.2	6.2	3.8	1.8	3.5
9	NFG		78	14.3	6.3	3.8	1.8	0.0
10	NFG		78	14.3	6.3	3.8	1.8	3.5
11*	NFG		78	14.3	6.3	3.8	1.8	3.5
12	NFG		78	37.4	29.4	2	0.0	3.5
13	NFG		78	8.0	0	2	0.0	3.5
14	NFG		65	34.0	26.0	9.5	7.5	0.0
15	NFG		39	14.2	6.2	3.8	1.8	3.5
16	MP		1501	1.0	1.0	4.0	0.0	0.0
17	MP	ZrCl4	621	14.3	14.3	4.0	0.0	3.5
18	MP		388	6.2	6.2	5.8	1.8	0.0
19	MP		388	6.3	6.3	5.8	1.8	3.5
20	MP		388	14.3	14.3	5.8	1.8	3.5
21	MP		388	40.0	40.0	5.8	1.8	3.5
22	FG		388	120.5	120.5	5.8	1.8	3.5
23	FG		388	241.1	241.1	5.8	1.8	3.5
24	MP		201	6.3	6.3	4.0	0.0	3.5
25	NFG		201	43.2	43.2	4.0	0.0	3.5
26	MP		155	14.2	14.2	4.0	0.0	3.5
27	NFG		86	37.0	37.0	4.0	0.0	3.5
28	/		78	0.0	0.0	4.0	0.0	3.5
29	MP		78	7.6	7.6	6.0	2.0	0.0
30	FG		78	19.0	19.0	4.0	0.0	3.5
31	NFG		78	57.0	57.0	4.0	0.0	3.5

References

1. Cavka, J. H. *et al.* A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. *J. Am. Chem. Soc.* **130**, 13850–13851 (2008).