Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Aligned macroporous monoliths with intrinsic microporosity via a frozen-solvent-templating approach

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Experimental

Preparation of aligned porous monoliths

For preparation of CC13 and PIM-1 monoliths, CC-13 solution in chloroform (200 mg cm^{-3}) and PIM-1 solution in chloroform (100 mg cm^{-3} and 200 mg cm^{-3}) were directionally frozen in liquid nitrogen and then freeze dried in a freeze dryer CoolSafe CS 100-9 Pro for 24 hours. The CC13 and PIM-1 were synthesized according to the previously reported procedures, respectively.[21,24]

For preparation of HKUST-1 monolith, the precursors $Cu(CH_3COO)_2 \cdot H_2O$ and 1,3,5-benzenetricarboxylic acid (BTC) were purchased from Sigma-Aldrich and used as received. Typically, a solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.1 mmol) in DMSO (0.5 cm^3) was added to a solution of BTC (0.07 mmol) in DMSO (0.5 cm^3). The solution was kept at room temperature or heated to 80 ^oC for 1, 2, and 24 hours (later the 24 hours used as the typical condition) before freezing. After this, the solution was directionally frozen and submerged in liquid nitrogen for 1 minute to fully freeze the solution. The frozen samples were then placed into a VIRTIS ADVANTAGE freeze dryer for 48 hours to remove the DMSO. *For the post-treatment,* the freeze-dried HKUST-1monolith was placed in a glass vial containing DMSO or ethanol (6 cm^3) which was then placed in a Teflon liner within an autoclave. The autoclave was placed in a furnace at 120°C for 24 hours.

Sample Characterizations

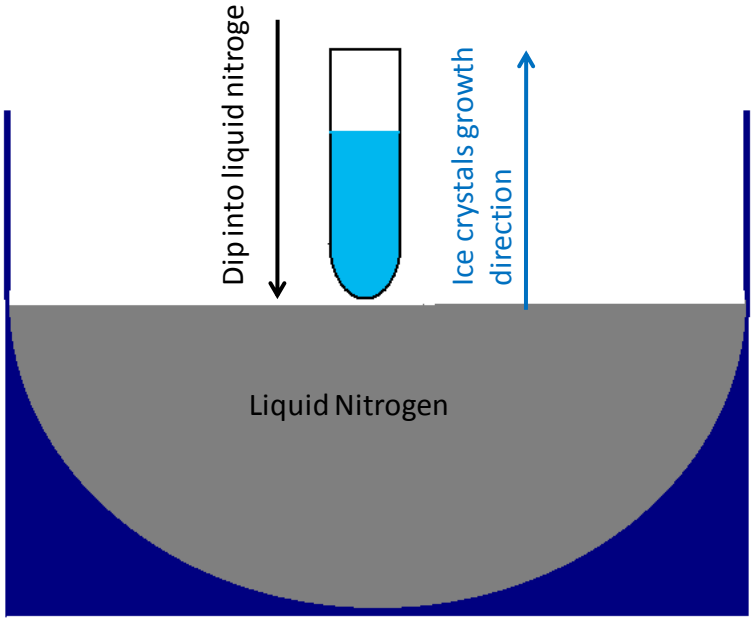
The morphologies were observed by a Hitachi S-4800 SEM equipped with an EDX detector. The samples were coated with gold using a sputter-coater (EMITECH K550X) for 2 minutes at 25 mA before imaging. The BET surface area and pore size by N_2 sorption at 77 K were measured using a Micromeritics ASAP 2420 adsorption analyzer. The micropore size

distributions were calculated by the non-local density functional theory (NLDFT) which is typically used for micropores. Mesopore size distributions were calculated by the Barrett-Joyner-Halenda BJH method from the desorption data. Samples were degassed for 10 h at 120 °C for HKUST-1 samples before N_2 sorption analysis. For the cage and PIM samples, the degassing was performed at 100 ^{o}C for 48 hours. The pore volume and macropore distribution were determined using Hg intrusion porosimetry (Micromeritics Autopore IV 9500) in the pressure range of 0.10- 60000 psia. PXRD data were collected on a Panalytical X'Pert Pro Multi-Purpose Diffractometer in high-throughput transmission geometry. Cu anode operated at 40 kV and 40 mA. Samples were pressed into the well of aluminium plate. The PXRD patterns were collected over 5-50° 2θ with a scan time of 40 minutes. Compression test was conducted using an Instron 4204 with a 1 kN loading cell and cylindrical samples (30 mm height × 4.6 mm diameter).

Video Description for Liquid Adsorption of HKUST-1 Monoliths

<u>Movies S1:</u> "Fast dye motion in aligned pores"

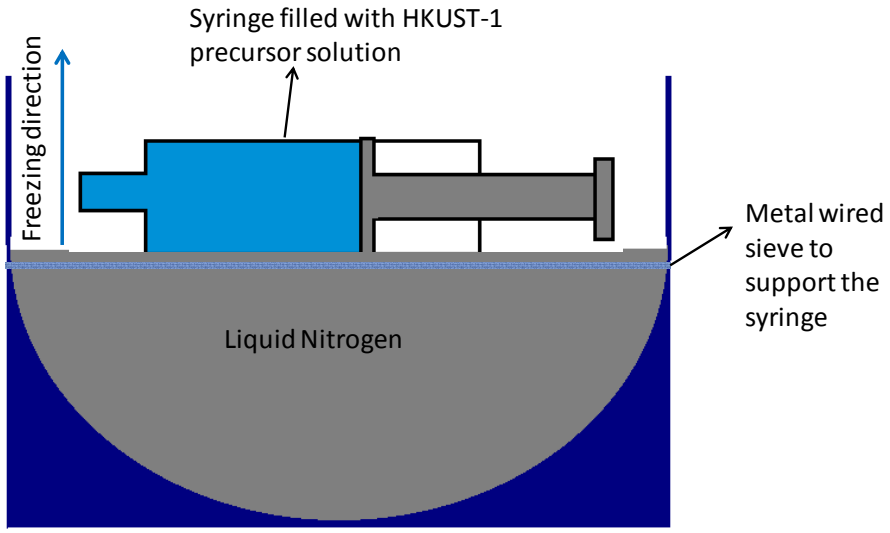
This HKUST-1 monolith was prepared by the directional freezing (as shown in the diagram below) and freeze drying procedure. This monolith contained well-defined aligned porous structure. As shown in the video, a cylindrical monolith is placed in a glass vial. The aligned direction is from bottom upwards. A solution of Rhodamine B in heptane (red colour) is added into the glass vial. It can be clearly seen that the liquid is drawn up into the monolith immediately. The monolith becomes dark purple once absorbing the red heptane solution. With the continue addition of heptanes solution, the interface is moving up rapidly until the whole monolith become dark purple.



<u>Movie S2:</u> "Slow motion perpendicular to aligned direction"

This HKUST-1 monolith was prepared by directional freezing with the precursor solution contained in a plastic syringe. As shown in the diagram below, a metal sieve is placed near the top of liquid nitrogen. The syringe is placed onto the sieve in the way shown in the diagram. As illustrated by the freezing direction, the ice crystals grow in that direction. Liquid nitrogen is added from the side to allow the solution in the syringe is fully frozen. After freeze drying, aligned porous monolith is produced. From the video, it is clear that the red solution (Rhodamine B in heptanes) can only be absorbed very slowly into the monolith. This is because the aligned pores are parallel to the solution surface. Comparing with the video shown in "Fast dye motion in aligned pores", this video demonstrates that the aligned pores are important to allow fast flow of liquid phase, hence much high mass transport.

Please Note: The videos cannot be submitted in the RSC manuscript submission system.


Syringe filled with HKUST-1
precursor solution
Freezing direction
Metal wired
sieve to
support the
syringe
Liquid Nitrogen

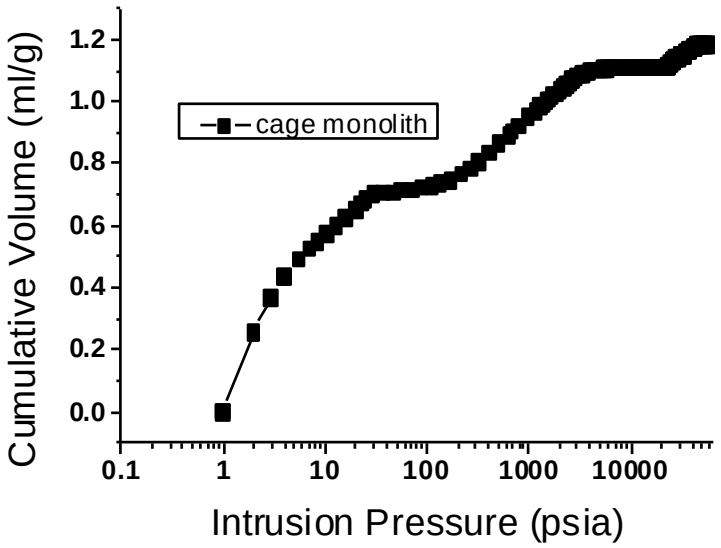


Figure S1. The graph shows the cumulative intrusion volume curve versus the increasing intrusion pressure for the cage compound CC13 monolith. The large intrusion volume from the pressure < 30 psia corresponds to the large pores around 100 μm. The intrusion volume at high pressure is contributed from the small pores as shown in Fig. 2C.

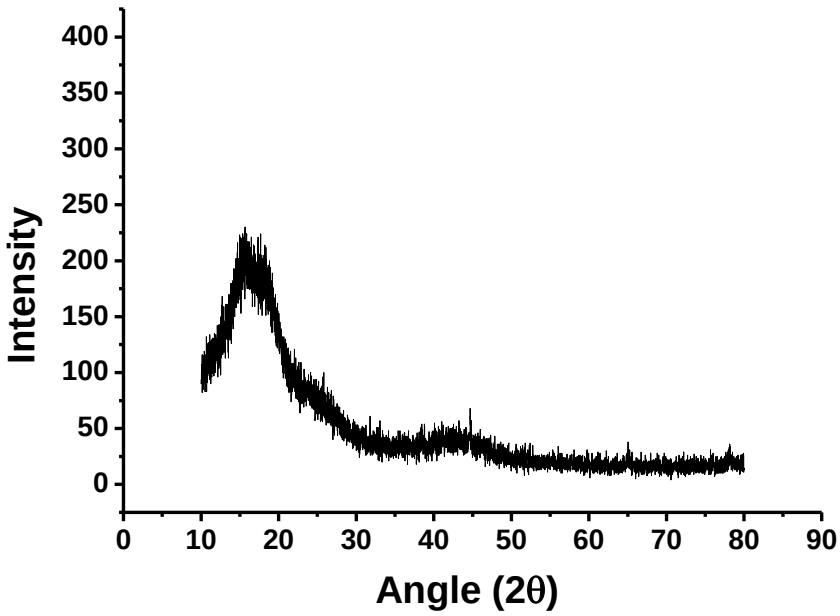


Figure S2. The powder x-ray diffraction (PXRD) pattern of the freeze-dried CC13 monolith. This shows that the monolith is close to an amorphous material.

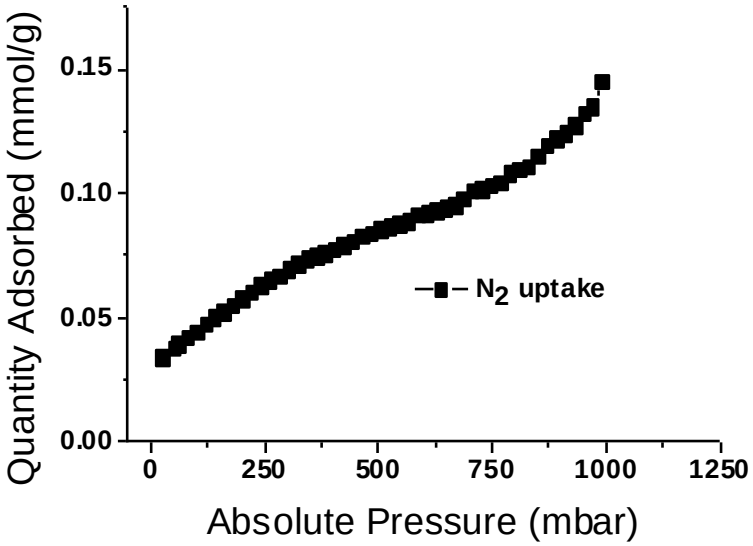


Figure S3. The N_2 uptake of the freeze-dried CC13 monolith that was re-dissolved in $CHCl_3$ and freeze-dried again, measured at 77 K. This shows the freeze-dried material is nearly N_2 non-porous.

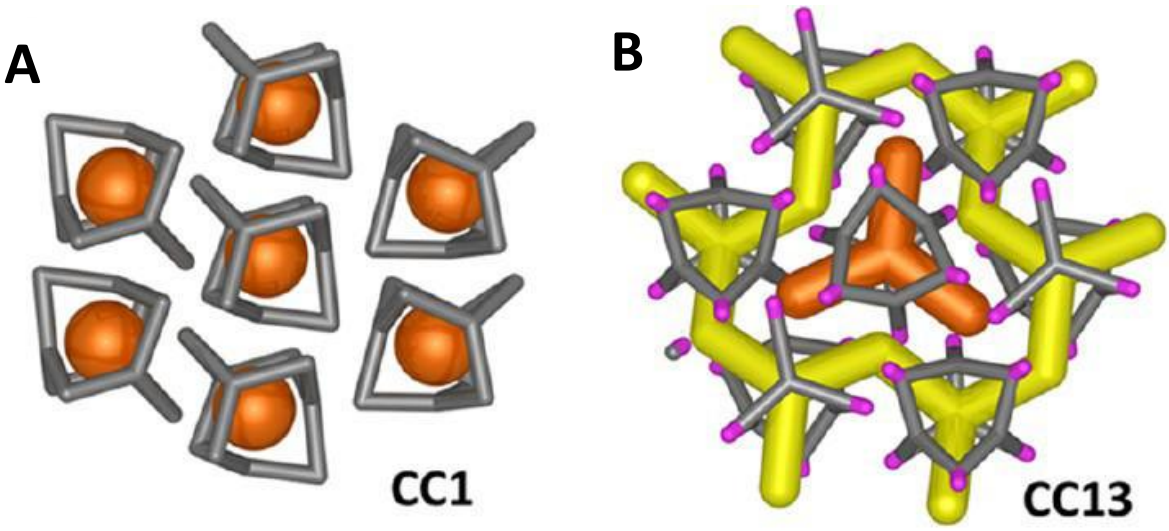


Figure S4. Schematic low-energy crystal packings for (A) CC1 (hydrogens on vertices) and (B) CC13 (dimethyl vertices). The structures are adapted from J. Am. Chem. Soc. 2014, 136, 1438.

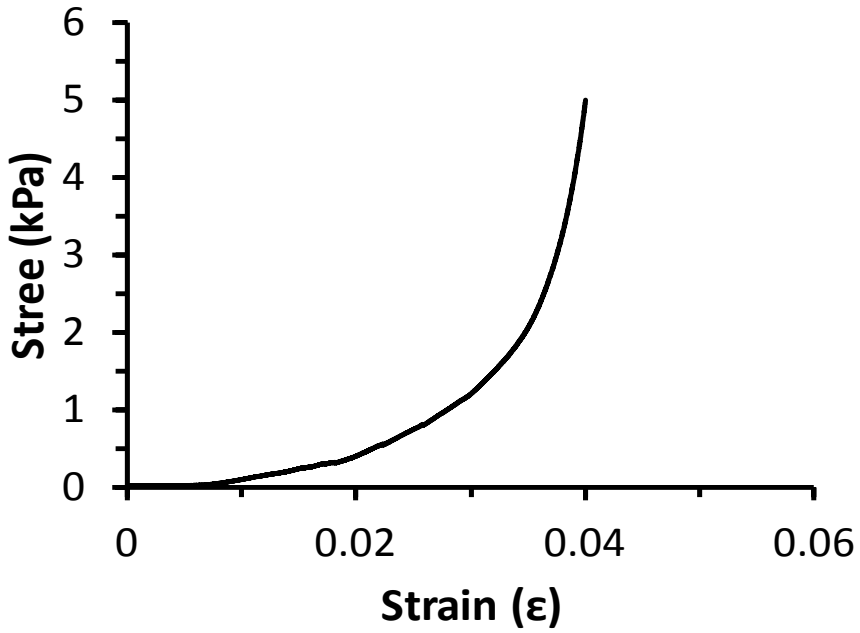


Figure S5 (A) The mechanical stability of the PIM-1 monolith (prepared from 200 mg cm^{-3} $CHCl_3$ solution) as evaluated by compression test. The Young module was calculated to be 33 KPa.

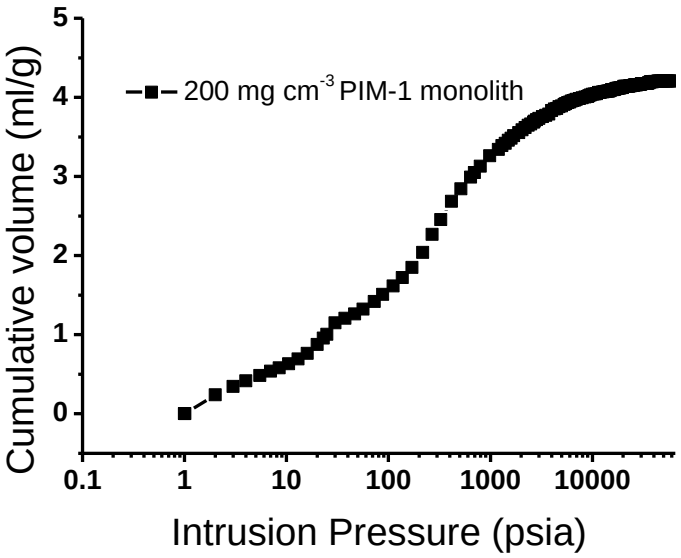


Figure S6. This graph shows the intrusion cumulative volume change with the intrusion pressure for the PIM-1 monolith prepared from 200 mg cm^{-3} chloroform solution, as measured by Hg intrusion porosimetry.

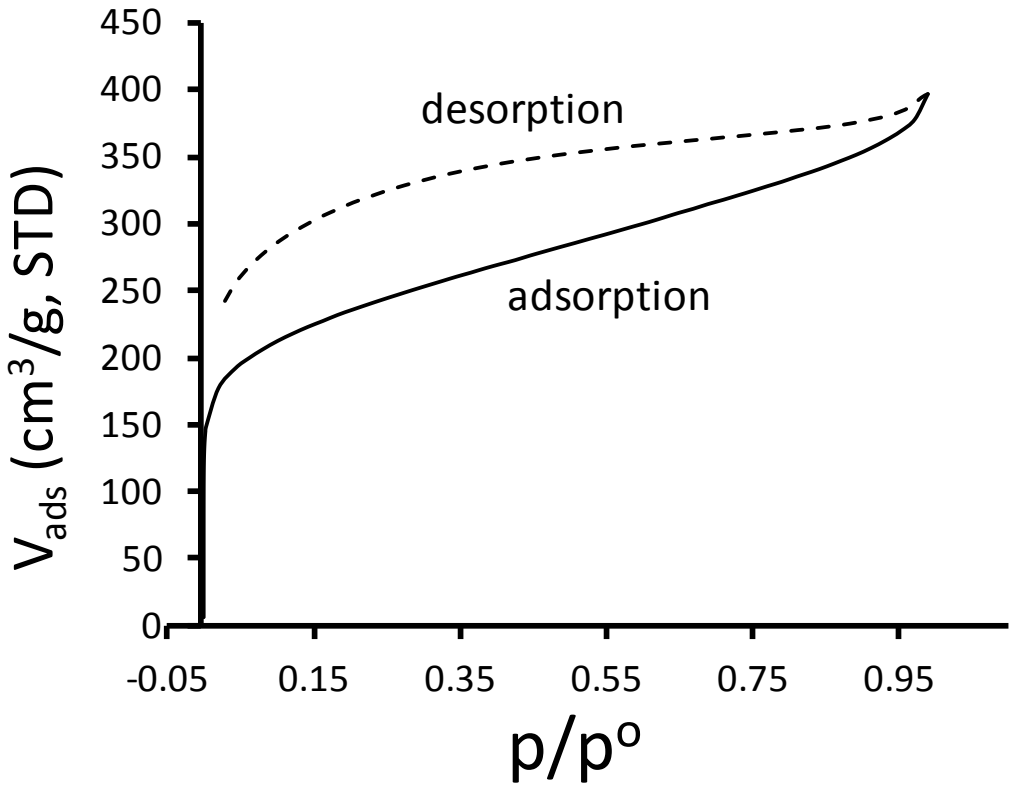


Figure S7. The isothermal curve by N_2 sorption for PIM-1 monolith of 20 wt%. This material shows a BET surface area of 766 m^2 g^{-1} and a pore volume of 0.61 cm^3 g^{-1} at P/P0 = 0.9912.

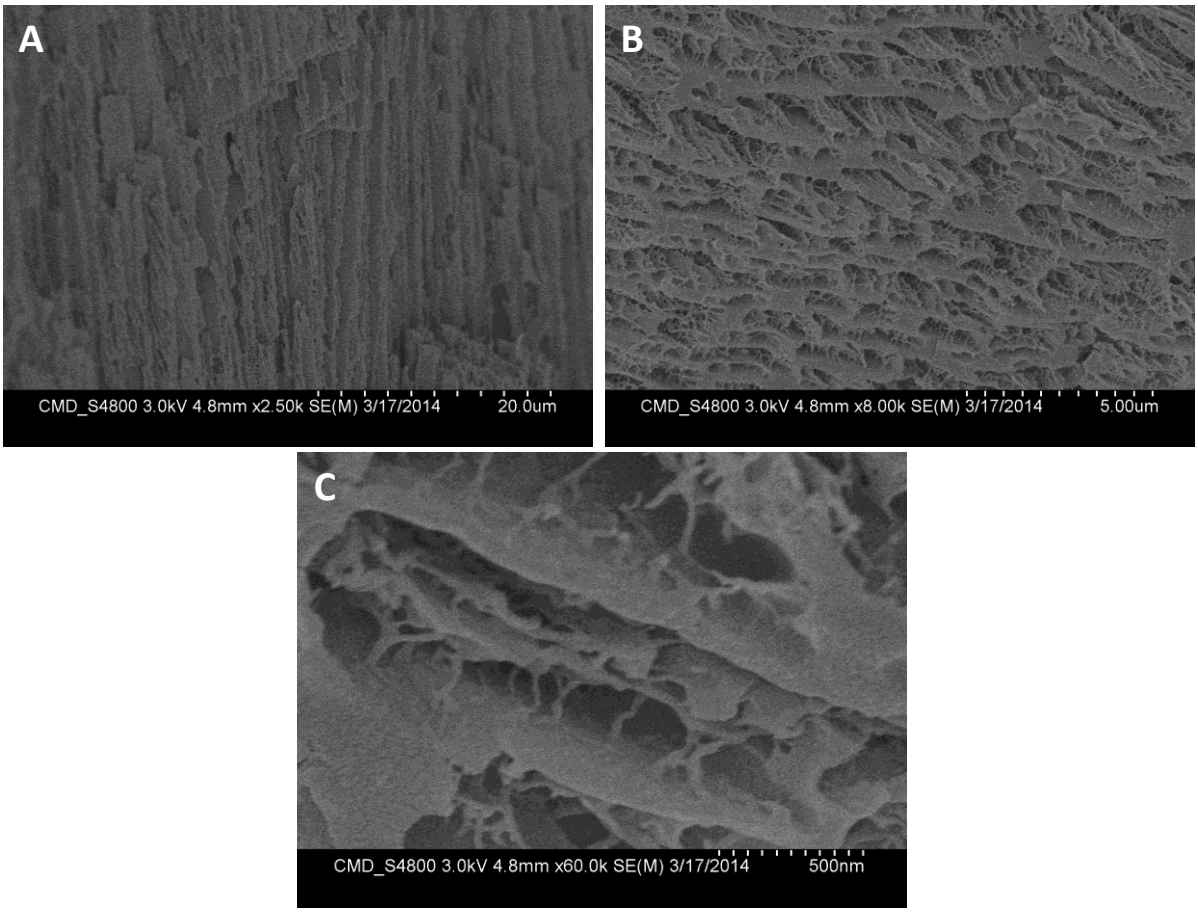


Figure S8. The SEM images at different magnifications show the pore structure of aligned PIM-1 monolith prepared from 100 mg cm^{-3} $CHCl_3$ solution.

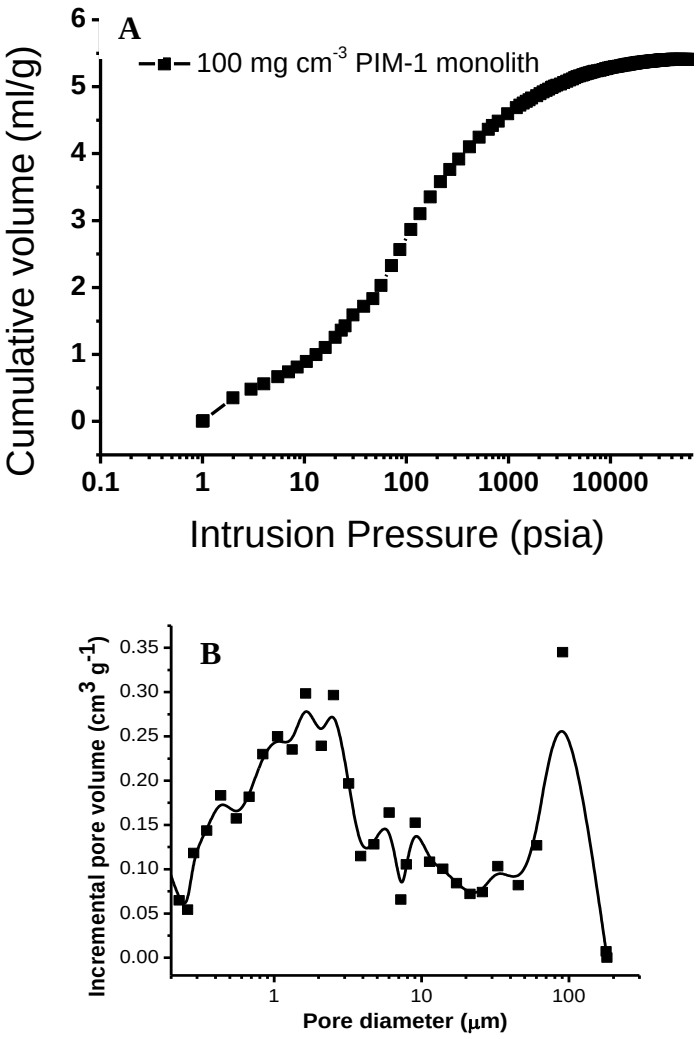


Figure S9. The characterization data by Hg intrusion porosimetry for the PIM-1 monolith prepared from 100 mg cm^{-3} chloroform solution. (A) The cumulative volume versus intrusion pressure; (B) The macropore size distribution based on the incremental pore volume versus pore diameter.

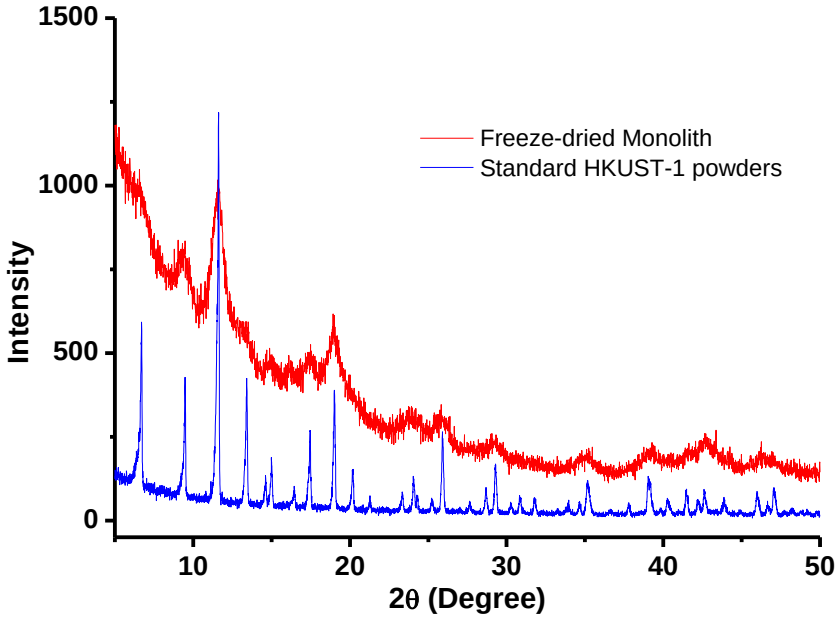


Figure S10. The PXRD pattern of the freeze-dried monolith prepared from the DMSO solution of room temperature. Compared to the standard HKUST-1 powders, synthesized by the solvothermal synthesis in ethanol/water mixture at 150 ^{o}C.

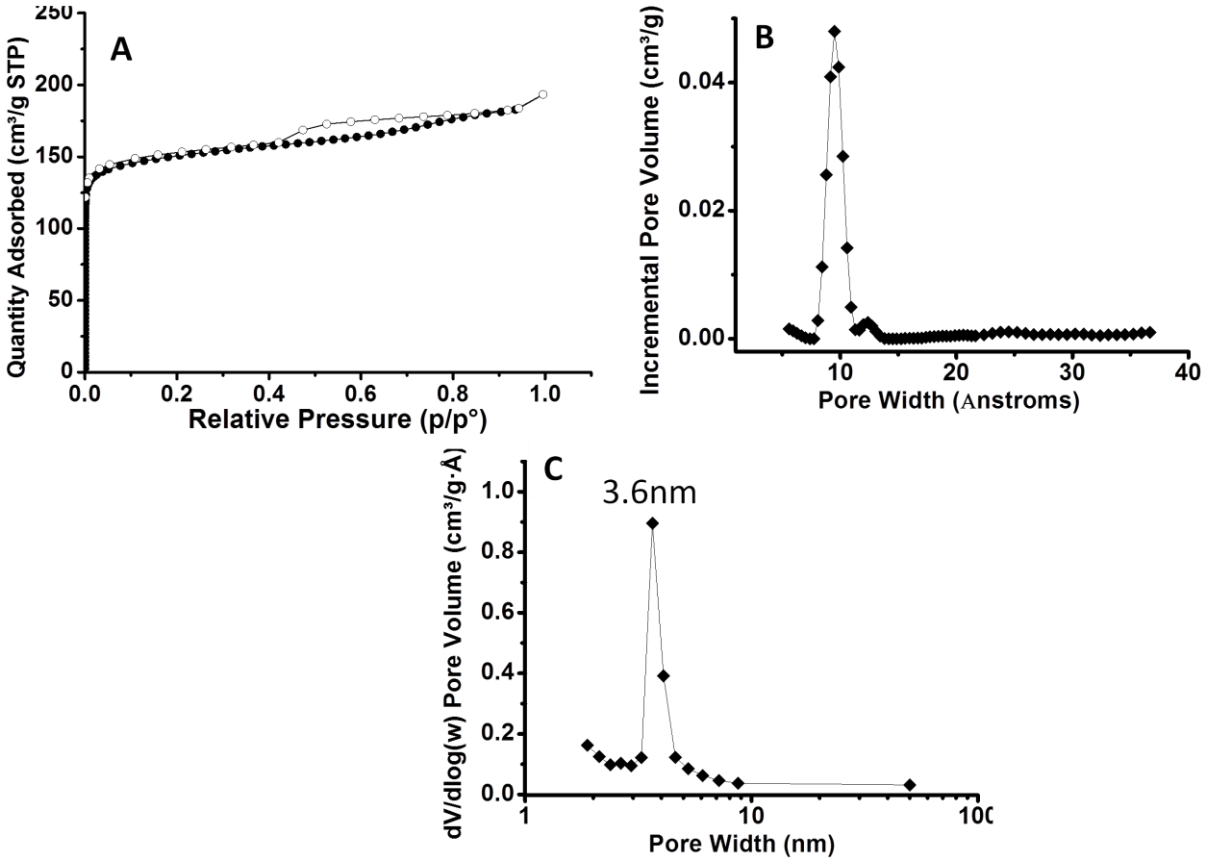


Figure S11. N_2 sorption data for the freeze-dried monolith prepared from the precursors-DMSO solution of room temperature. No further treatment performed. (A) The isothermal curves. (B) The micropore size distribution calculated by the NLDFT method, suitable for micropores. (C) The mesopore size distribution calculated by the BJH method from the desorption data, suitable for mesopores. Surface area = 660 m^2 g^{-1}; Mesopore volume = 0.113 cm^3 g^{-1}; Micropore volume = 0.218 cm^3 g^{-1}.

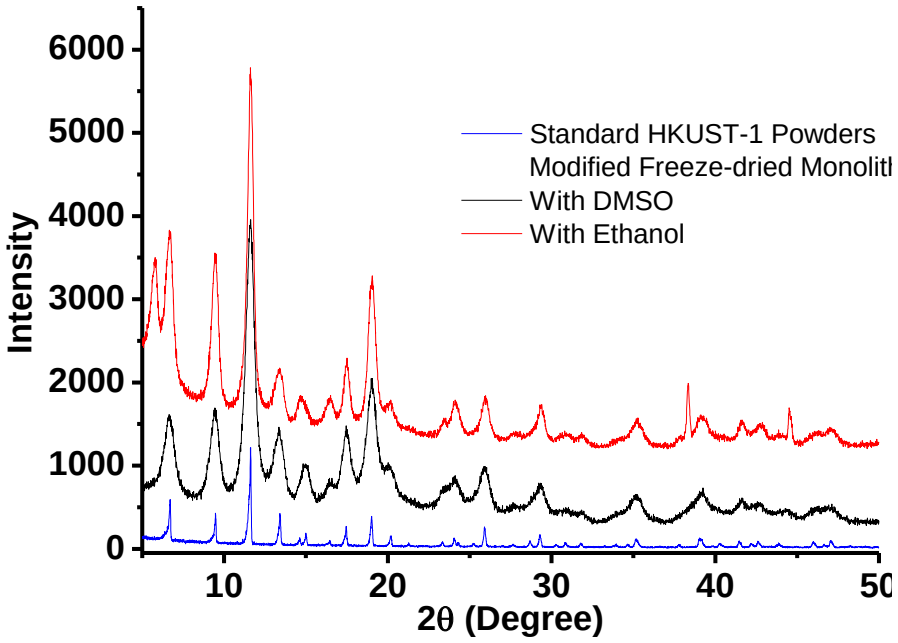


Figure S12. The PXRD patterns for the freeze-dried monolith (by directionally freezing the DMSO solution of room temperature) further treated with DMSO or ethanol. The treatment temperature was 120 ^{o}C for 48 hrs in glass vial within autoclave. The PXRD patterns are similar to that of standard HKUST-1 powders. Compared with Fig. S10, it is clear the treatment has improved the crystalline quality.

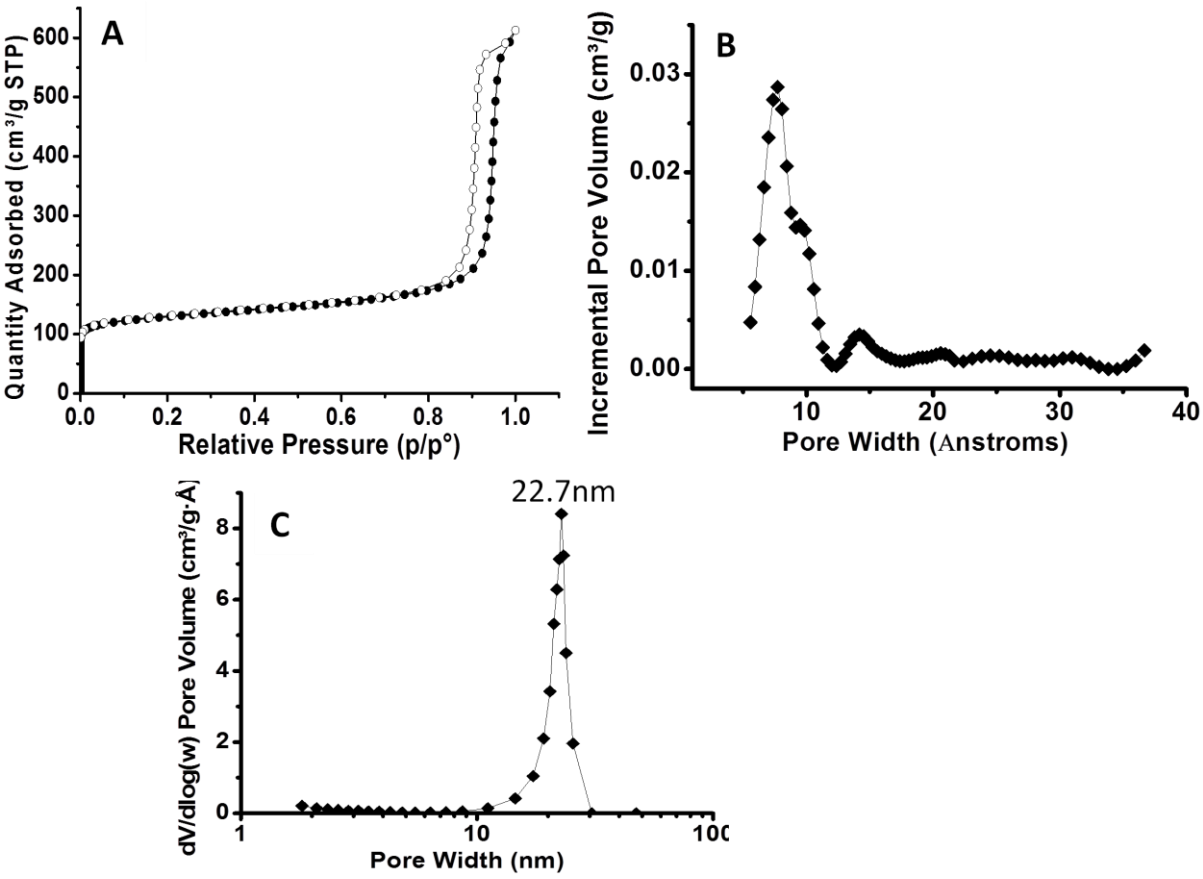


Figure S13. The N_2 sorption data for the freeze-dried monolith (from DMSO solution of room temperature) further treated with ethanol (120 ^{o}C, 48 hours). (A) The isothermal plot. (B) The micropore size distribution calculated by the NLDFT method. C) The meospore size distribution calculated by the BJH method from the desorption data. Surface area = 484 m^2 g^{-1}, mesopore volume = 0.711 cm^3 g^{-1}, micropore volume = 0.134 cm^3 g^{-1}.

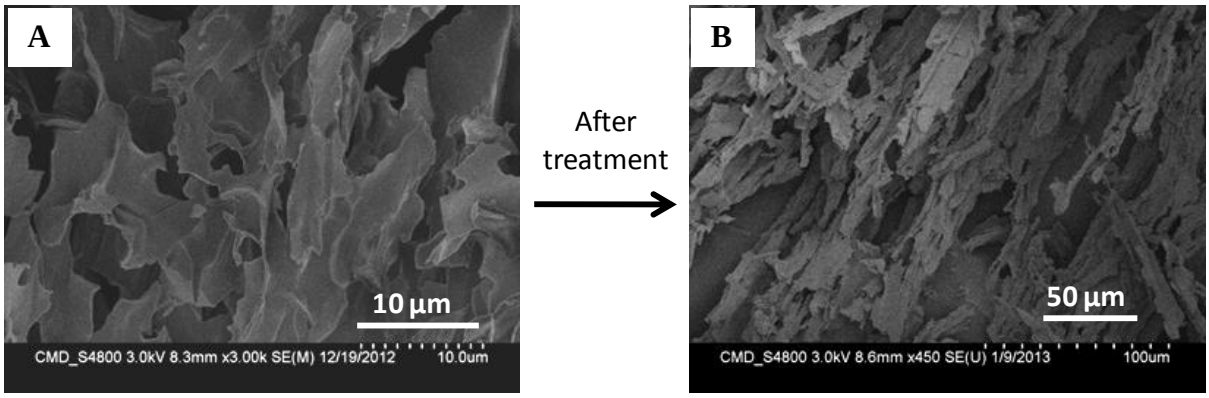


Figure S14. The SEM images of the freeze-dried monolith (from DMSO solution of room temperature) and after further treatment with ethanol. The post-treatment still produced an aligned porous monolith. The relevant PXRD patterns are shown in Fig. S10 and Fig. S12.

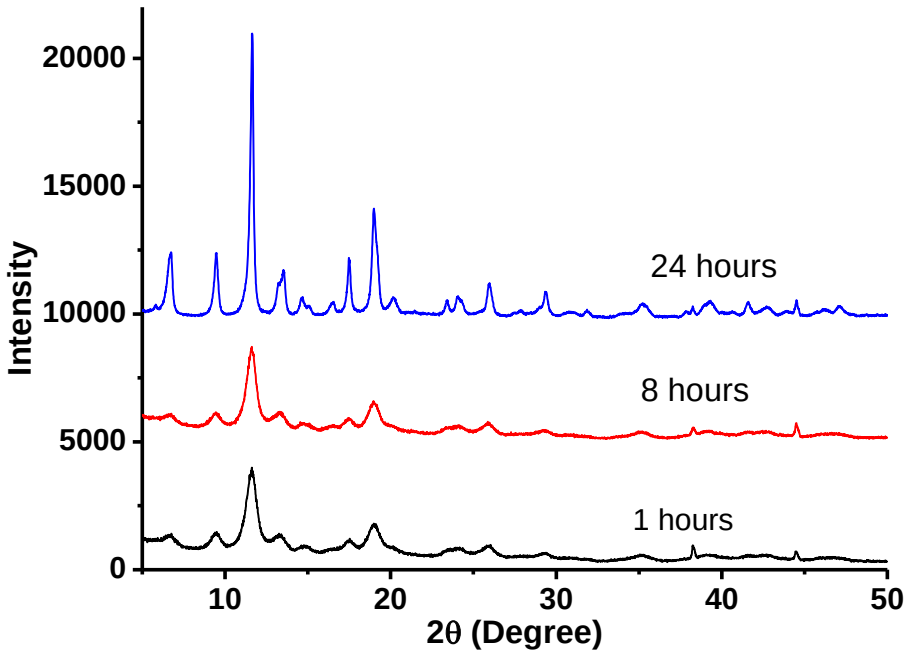


Figure S15. Effect of heating DMSO solution before freezing on the monoliths' crystallinity. Before freezing, the DMSO precursor solution was heated at 80 ^{o}C for different time periods (1, 2, and 24 hours). The resulting freeze-dried monoliths show improved PXRD patterns with the increasing heating time. During the heating period, the dark green solution in a glass vial with lid was heated in a furnace preset at 80 ^{o}C. A 24 hours study at room temperature did not show crystallinity improvement over solution time before freezing.

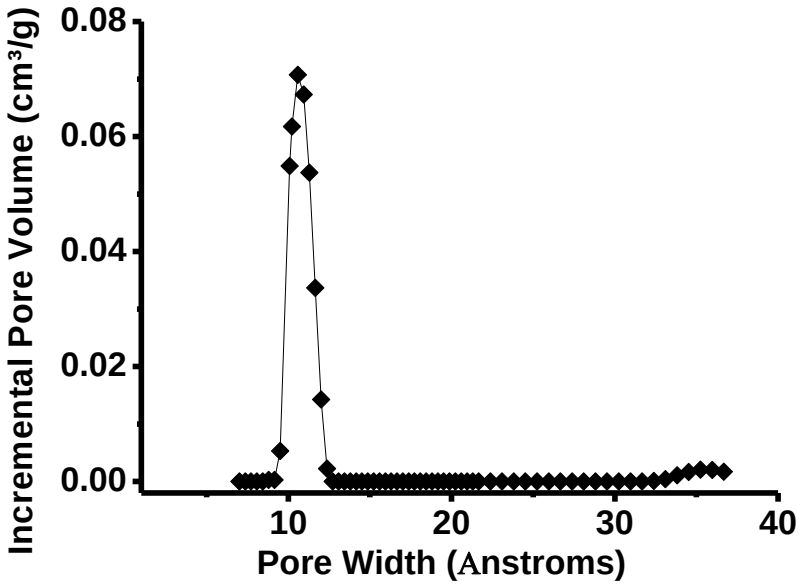


Figure S16. The micropore size distribution based on the N_2 sorption data calculated by the NLDFT method for the freeze-dried monolith from heated DMSO solution at 80 ^{o}C for 24 hours.

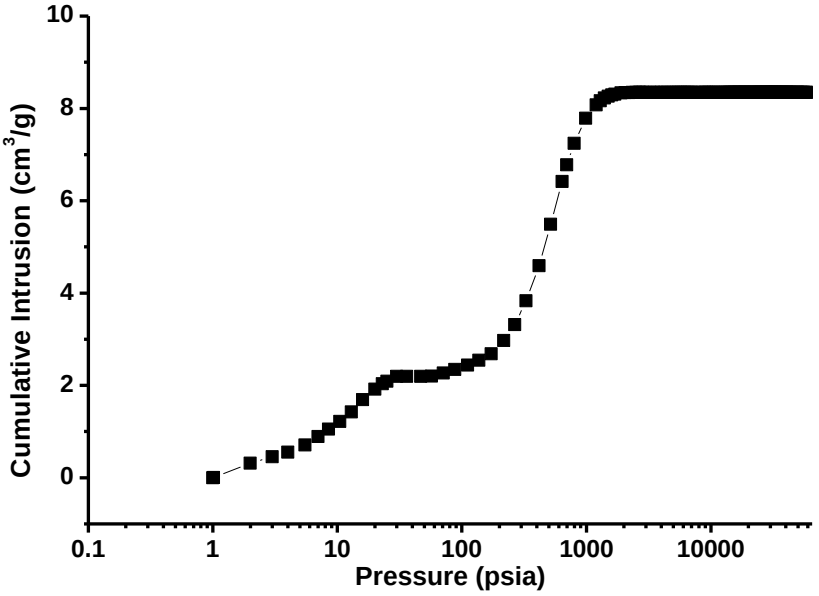


Figure S17. Cumulative Hg intrusion graph for the freeze-dried monolith from heated DMSO solution at 80 ^{o}C for 24 hours.

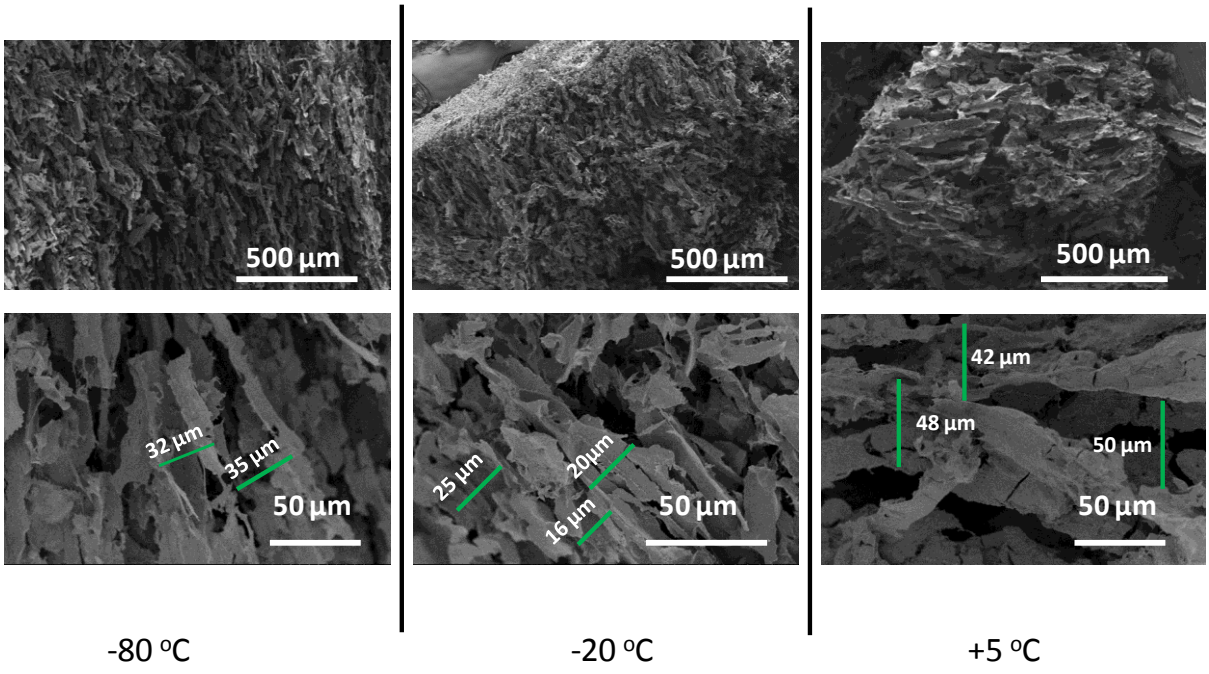


Figure S18. Effect of freezing temperature on the macropore structure of the freeze-dried monoliths. The precursor-DMSO solution was heated at 80 ^{o}C and then frozen at different temperatures. The SEM images show the structure of each sample at two magnifications. The top images have the same sized scale bars. Some pores are marked in the bottom images. Because the aligned pores are highly interconnected, it is very difficult to identify the well-defined pores. But these images can show there is effect of freezing temperature on the size of aligned macropores. It is quite obvious that the pore sizes are bigger when the freezing temperature was 5 ^{o}C while the difference between the freezing temperatures of -80 ^{o}C and –20 ^{o}C is not significant.

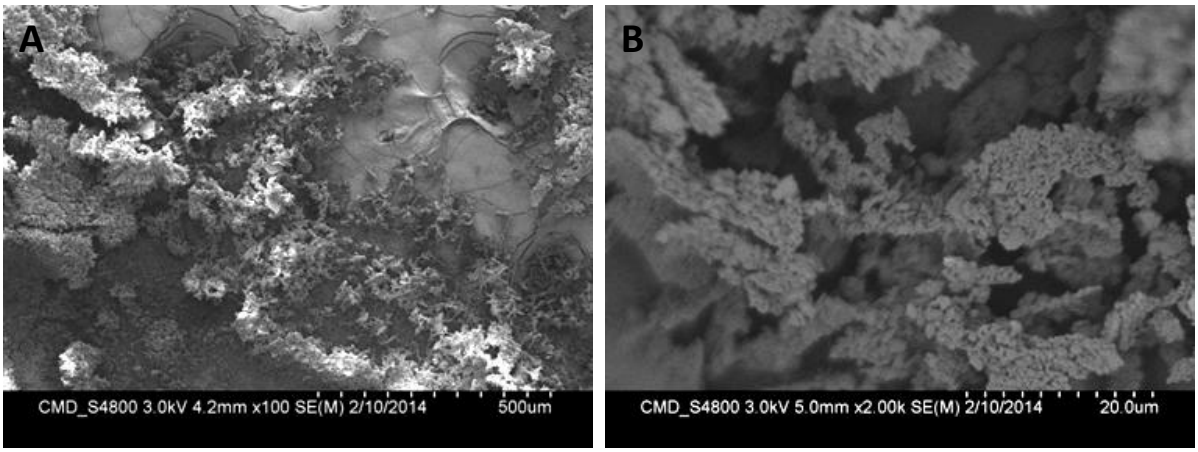


Figure S19. The SEM images (A & B) show the structure of the product after directional freezing and freeze drying of a HKUST-1 particle suspension in water. The HKUST-1 particles were firstly prepared by solvothermal synthesis with ethanol/water as solvent. The process did not produce a monolith, but aggregated powders.

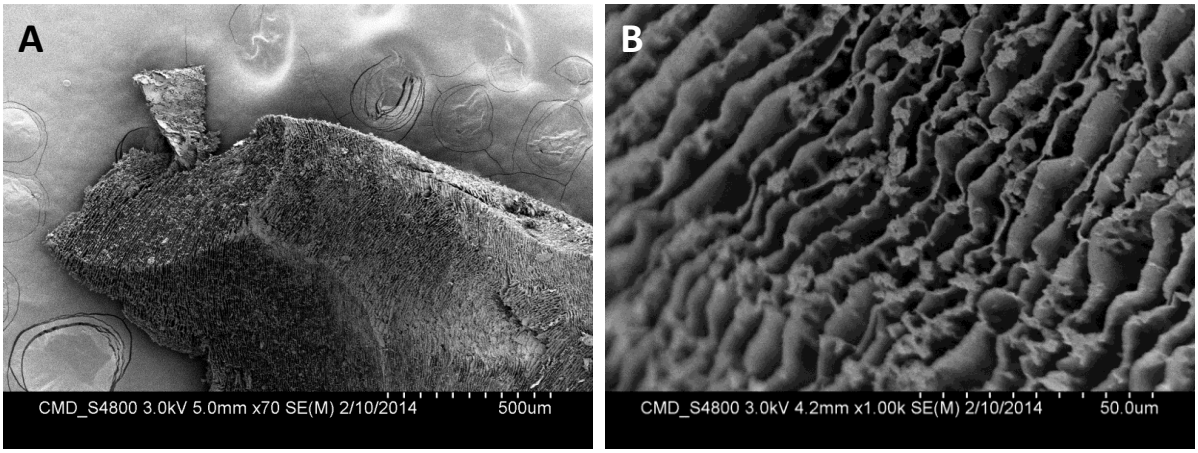


Figure S20. The SEM images show the monolith (A) and the aligned macroporous structure (B) produced by directional freezing and freeze drying of a HKUST-1 particle suspension in aqueous PVA solution. The HKUST-1 particles were suspended (15 wt%) in 5 wt% aqueous poly(vinyl alcohol) (Mw 10K) solution. However, this only produced a composite monolith, not a MOF monolith as formed by the freeze-drying approach from the precursor solution.