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Electronic Supplementary Information (ESI)

Widely Tunable Persistent Micelle Templates via Homopolymer Swelling

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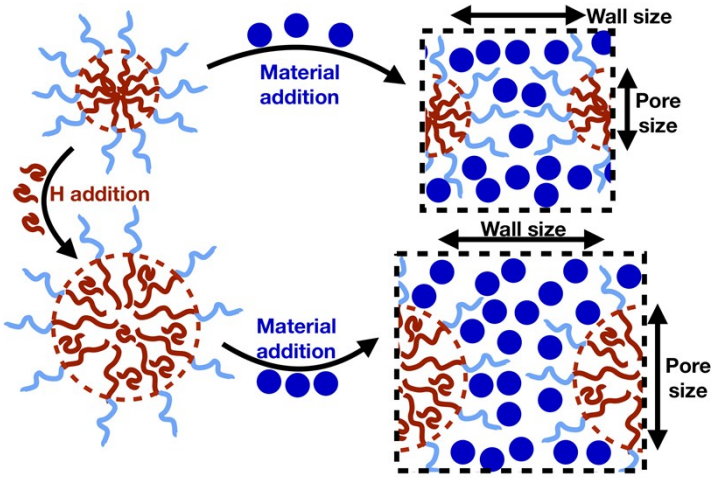

Scheme S1. Homopolymer, **H**, was added to swell micelle cores and thus to adjust the template dimension of the future pore size. The subsequent addition of material precursors (sol-gel chemistry) within and in between the micelle coronas establish the wall thickness.

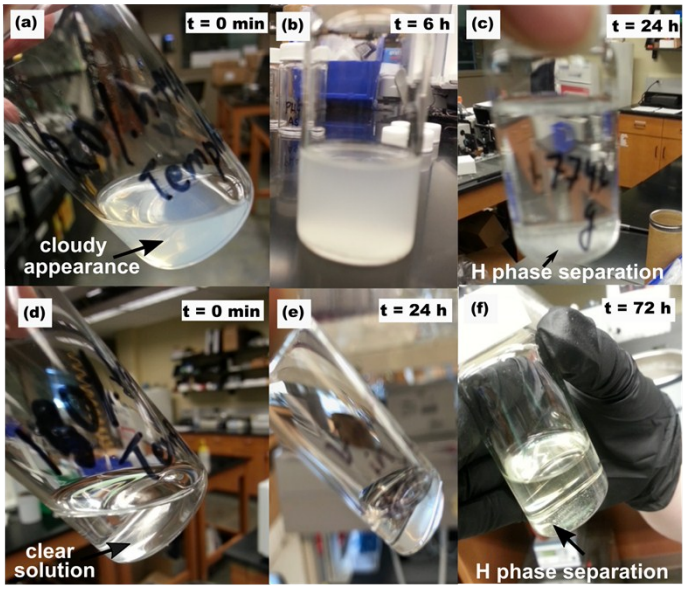

Fig. S1. Photograph of **OH1** with 150 wt% **H** in MeOH (a-c) as compared to EtOH (d-e) at different time points. The polymer and homopolymer solutions in MeOH were turbid even after heating to 50 °C (a) and remained turbid for 6 hours (b) until complete phase separation of **H** after ~1 day at RT (c). In contrast, the same components dissolved in EtOH led to a clear solution (d) and remained so for 1 day of storage at RT (e), eventually leading to **H** phase separation after 3 days (f).

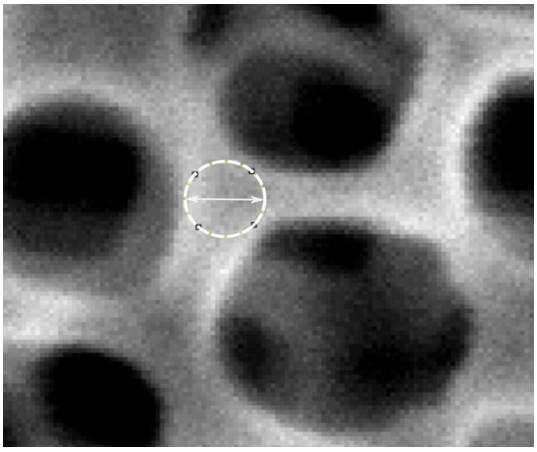

Fig. S2. Depiction of wall thickness measurement method. The diameter of the largest inscribed circle between pores was repeatedly measured in different locations to derive statistical metrics of wall thickness.

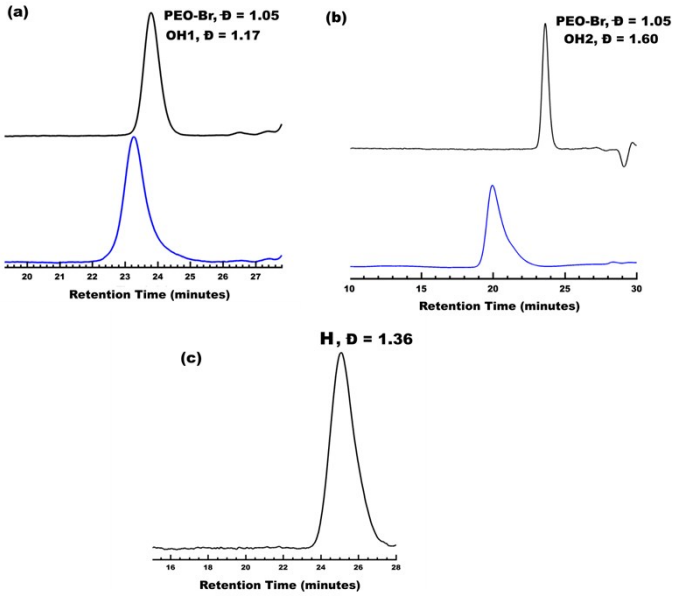

Fig. S3. GPC elugrams for the synthesis stages of polymers **OH1** (a), **OH2** (b), and **H** (c).

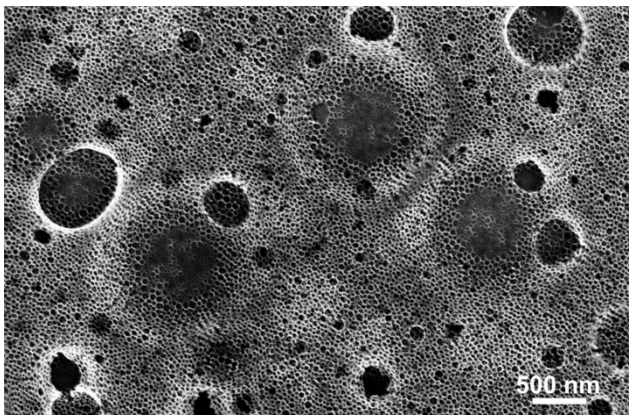

Fig. S4. SEM image of sample made using **OH1 with** 500 wt% **H** and MeOH, exhibiting large voids (black) attributed to phase separation of **H**.

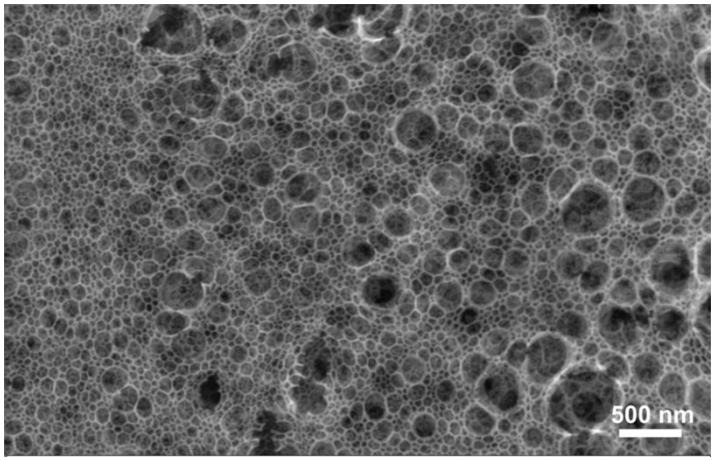

Fig. S5. SEM image of sample made using **OH1** with 800 wt% **H** and EtOH showing large voids (black) attributed to phase separation of **H**.

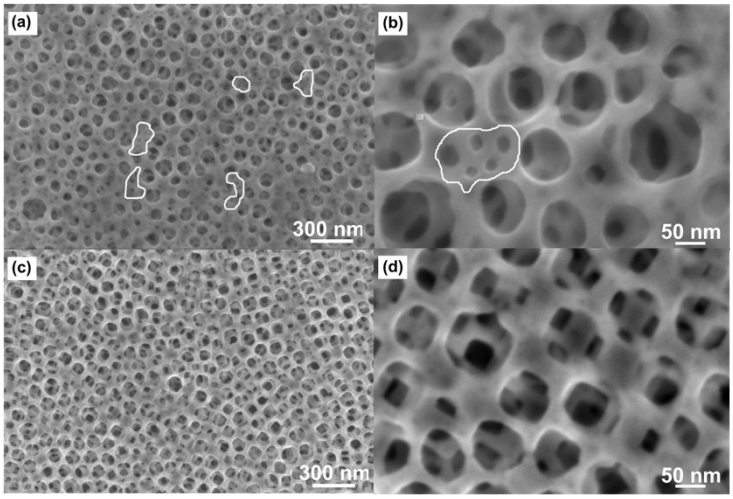

Fig. S6. SEM image of samples prepared using **OH2** with 200 wt% **H** processed from either MeOH (a-b) or EtOH (c-d). Secondary pores were only found in samples processed from MeOH and were indicated with white lines (a-b).

Table S1. Statistical measurements on sample series prepared **OH1+H** in EtOH.

Samples (wt%H_M:T)†	SEM Mean pore diameter ± error-of mean (nm)‡	Pore diameter standard deviation (nm)‡	SEM Mean wall-thickness ± error-of mean (nm)‡	Wall-thickness standard deviation (nm)‡	SAXS d-spacing (nm)‡
0 wt%_1.04	16.3±0.3	3.19	10.7±0.2	2.3	25.3
0 wt%_1.36	16.8±0.4	3.58	12.1±0.2	2.4	26.6
0 wt%_1.47	16.6±0.3	3.33	13.2±0.3	2.9	27.1
0 wt%_1.59	16.9±0.4	4.00	12.6±0.2	2.3	27.7
0 wt%_1.70	16.3±0.4	4.37	12.2±0.2	2.1	28.4
0 wt%_1.79	16.0±0.4	3.85	12.9±0.4	2.7	28.8
0 wt%_1.88	16.0±0.4	3.84	13.0±0.3	2.6	29.3
0 wt%_1.96	16.9±0.4	4.11	13.3±0.4	2.8	29.7
0 wt%_2.14	17.0±0.4	3.52	14.6±0.2	2.0	30.7
60 wt%_0.30	---	---	---	---	29.3
60 wt%_0.36	---	---	---	---	29.9
60 wt%_0.44	25.4±0.6	6.12	10.80±0.5	5.3	31.1
60 wt%_0.49	25.0±0.3	3.21	11.45±0.3	3.4	32.1
60 wt%_0.54	---	---	---	---	33.1
60 wt%_0.62	25.1±0.4	3.67	11.34±0.3	2.7	35.1
60 wt%_0.68	25.8±0.6	5.85	12.67±0.4	4.3	35.2
60 wt%_0.75	25.2±0.3	3.31	12.31±0.3	3.1	37.1
60 wt%_0.82	25.4±0.5	5.31	12.75±0.3	3.3	38.0
60 wt%_0.88	25.4±0.4	3.88	13.45±0.3	2.7	38.1
60 wt%_0.95	25.7±0.4	3.67	13.99±0.3	3.4	38.4
60 wt%_1.08	25.9±0.5	5.04	14.08±0.4	3.8	38.9
60 wt%_1.14	25.4±0.4	4.21	16.30±0.4	3.9	40.5
60 wt%_1.20	25.5±0.4	4.33	15.77±0.3	3.4	41.9
60 wt%_1.26	25.6±0.5	5.16	14.34±0.3	2.7	43.3
60 wt%_1.34	26.2±0.5	4.93	15.61±0.4	3.5	44.8
60 wt%_1.41	---	---	---	---	46.3
60 wt%_1.48	26.8±0.4	4.02	17.10±0.4	4.2	48.3
200 wt%_0.67	32.2±0.6	6.18	14.87±0.2	1.9	43.8
200 wt%_0.72	31.3±0.6	5.67	14.58±0.3	2.9	46.2
200 wt%_0.83	32.2±0.6	6.07	15.18±0.5	5.1	46.7
200 wt%_0.91	31.7±0.7	6.76	16.65±0.6	5.9	47.7
200 wt%_0.96	30.2±0.4	4.02	17.21±0.3	3.3	49.4
200 wt%_1.00	29.3±0.7	3.46	17.61±0.4	3.9	49.9
200 wt%_1.08	27.9±0.6	6.05	12.98±0.4	1.9	52
200 wt%_1.13	---	---	---	---	43.3
200 wt%_1.16	---	---	---	---	56.9

† Sample naming "wt%H_M:T" corresponds to homopolymer **H** loading represented as a weight percent followed by the material-to-template ratio as described in the experimental procedures.

‡ SEM and SAXS measurements were used to quantify in-plane sample dimensions. SAXS was performed on aged films and SEM was performed on calcined films.

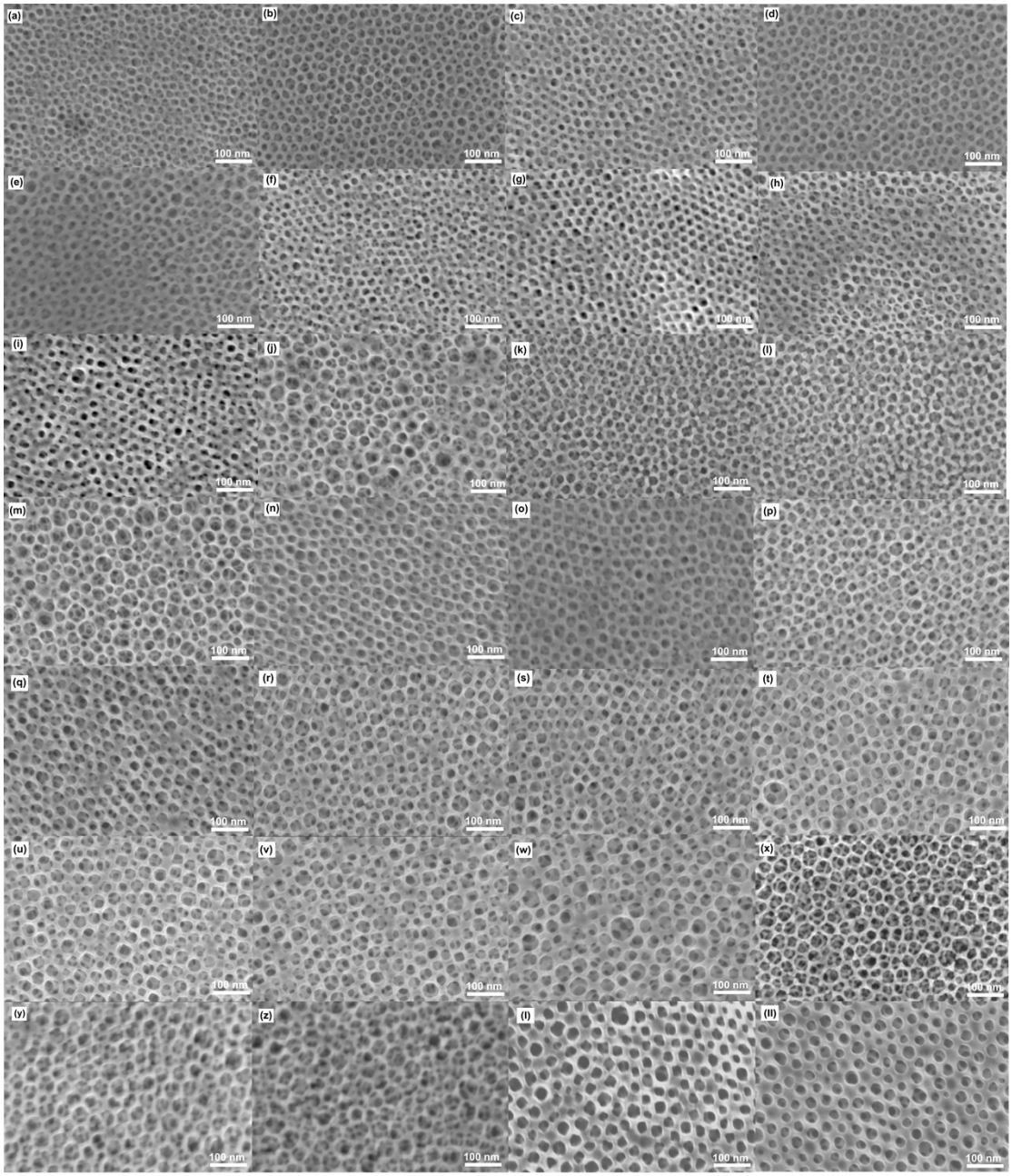

Fig. S7. SEM images of porous nanomaterial series derived from **OH1** with 0 (a-i), 60 (j-w) or 200 wt% **H** (x-II) prepared using EtOH. Each series at constant wt%H had variable material-to-template ratios (M:T): 1.04 (a), 1.36 (b), 1.47 (c), 1.59 (d), 1.70 (e), 1.79 (f), 1.88 (g), 1.96 (h), 2.14 (i), 0.44 (j), 0.49 (k), 0.62 (l), 0.68 (m), 0.75 (n), 0.82 (o), 0.88 (p), 0.95 (q), 1.08 (r), 1.14 (s), 1.20 (t), 1.26 (u), 1.34 (v), 1.48 (w), 0.67 (x), 0.72 (y), 0.83 (z), 0.96 (I), and 1.00 (II). Sample statistical metrics derived from similar images are presented in **Table S1**.

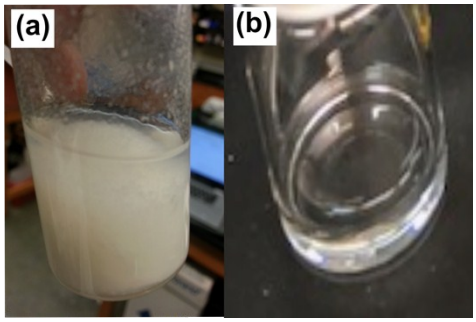

Fig. S8. Photograph of **OH1** with 200 wt% **H** in EtOH with either 3.5 wt% water (a) or 1.8 wt% water (b). The turbidity of (a) indicates phase separation of **H**.

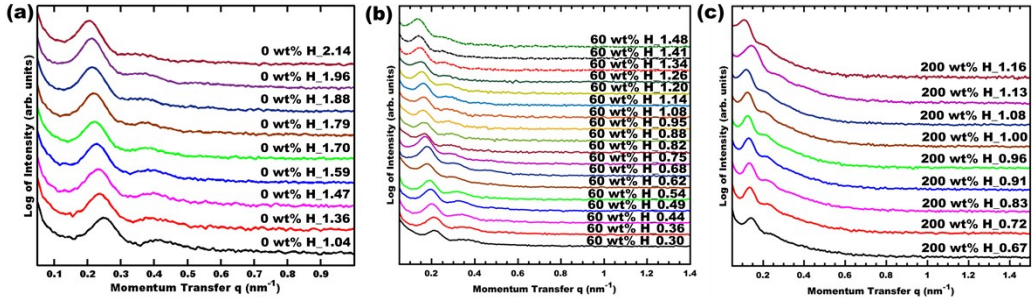

Fig. S9. SAXS data of material series prepared by precursor titration into **OH1** micelle templates with either 0 wt% (a), 60 wt% (b), and 200 wt% (c) of **H**. SAXS was performed on spin coated, aged films.

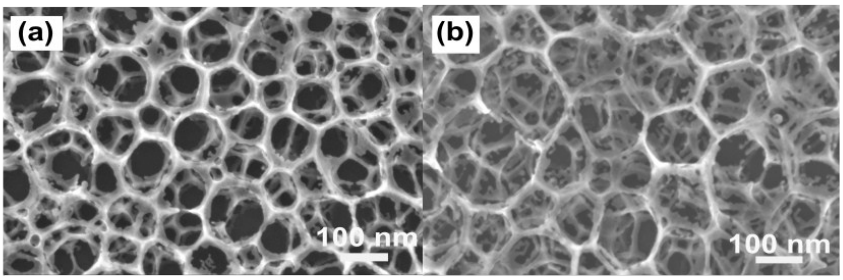

Fig. S10. SEM images of macroporous materials derived from **OH2** in EtOH with **H** loadings of 250 wt% (a) and 350 wt% (b).

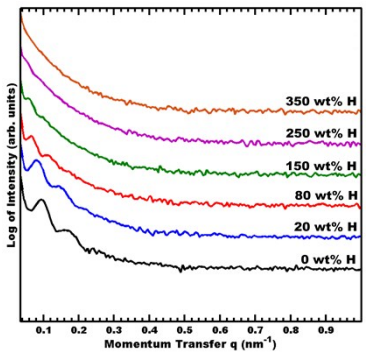

Fig. S11. SAXS data for templated materials prepared from **OH2** in EtOH as a function of **H** loading**.** SAXS was performed on spin coated, aged films.

PMT SAXS Modeling:

A previously derived geometric SAXS model[1] was used to 1) predict SAXS d-spacing for PMT titrations with constant pore size and variable material:template ratio, and 2) infer the pore and wall dimensions from measured SAXS data. In brief, this model relates the SAXS structure factor peak to an underlying micelle-to-micelle spacing. The micelle-to-micelle spacing has contributions from both the pores and walls. The material:template ratio is used to derive the relative volume fractions of the material and the template using a convolved density term β (unitless). These volume fractions enable deconvolution of the micelle-to-micelle spacing into pore and wall contributions. This approach was previously worked out with multiple structure factors including simple cubic, body centered cubic, face centered cubic, as well as an equilateral triclinic version to approximate paracrystals.[1] The equilateral triclinic model was selected for the short-range ordered samples here:

$$r = d_{m-m}\sqrt[3]{\frac{3\gamma}{4\pi}}\left(x\beta_{mct} + 1 + \frac{f_{corona}}{1-f_{corona}}\right)^{-1/3} \quad \text{(S1)}$$

where r is the pore radius, $d_{m\text{-}m}$ is the micelle-to-micelle spacing, γ is a unit cell shear parameter that is 1.0 or less, x is the material:template ratio, and f_{corona} is the polymer volume fraction for the corona block. Here $d_{m\text{-}m}$ is related to the $d_{spacing}$ with a constant structure factor, S:

$$S = \frac{d_{m-m}}{d_{spacing}} = \frac{qd_{m-m}}{2\pi} \quad \text{(S2)}$$

Lastly, the wall thickness was well fitted as a fraction, ε, of the $d_{m\text{-}m}$ spacing:[2]

$$Walls = \epsilon \cdot d_{m-m} \quad \text{(S3)}$$

PMT model parameter fitting was performed using least squares minimization. A range of M:T values consistent with the PMT model was identified on a log-log coordinate system. Fitting was constrained to the apparent PMT region using equations S1. The average pore size was calculated from SEM measurements and the S value was calculated using SAXS and SEM data

with equation S2. Lastly, the ε parameter was fitted to mean SEM wall measurements using equation S3.

Table S2. PMT Model fit parameters for 0 wt% **H**, 60 wt% **H**, and 200 wt% **H** compositions respectively, combining direct SEM measurements and data fitting.

Parameters	**0 wt% H**	**60 wt% H**	**200 wt% H**
Mean pore diameter (nm)	16.5	25.4	30.7
$f_{corona(PEO)}$ (vol%)[a]	33	33	33
S (unitless)	1.15	1.02	0.97
β convolved density (unitless)[b]	8.07	6.30	6.23
γ(unitless)[b]	1.00	1.00	1.00
ε (unitless)[b]	0.45	0.35	0.34

[a]Calculated from **OH1** composition and reported homopolymer densities.
[b]Determined using least squares minimization within the identified PMT window.

Table S3. Statistical measure of a series prepared using **OH2** with **H** processed from EtOH

H loading (wt%)	SEM Average Pore Diameter ±error-of mean (nm)†	Pore diameter standard deviation (nm) †	SAXS d-spacing (nm)†
20%	75.9±1.35	13.5	76.7
80%	79.9±1.45	14.5	98.2
250%	98±2.01¶ 153±2.24¶	18.4 8.4	#
350%	107±2.86¶ 159±1.81¶ 206±6.97¶	20.6 10.4 25.1	#

† SEM and SAXS measurements were used to quantify in-plane sample dimensions. SAXS was performed on aged films and SEM was performed on calcined films.
¶ Samples with multiple nominal pore sizes were subjected to the same quantification procedures after binning each measured value to one of the nominal distributions
# Peak of scattering intensity not observed, attributed to limit of q-range.

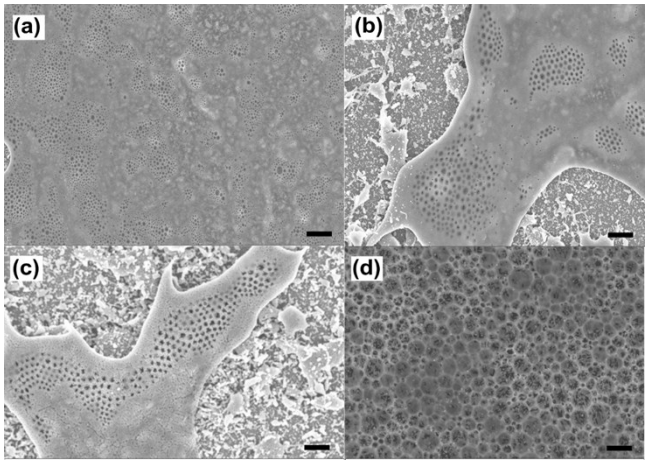

Fig. S12. SEM images of samples prepared with **OH2** and 1000 wt% **H** with various calcination conditions: 550 ºC for 1 hour (a), 600 ºC for 1 hour (b), 700 ºC for 1 hour (c) and 550 ºC for 12 hours. The aggressive heat treatments intended to produce interconnected porosity also sometimes led to film dewetting. All the scale bars are 1 μm.

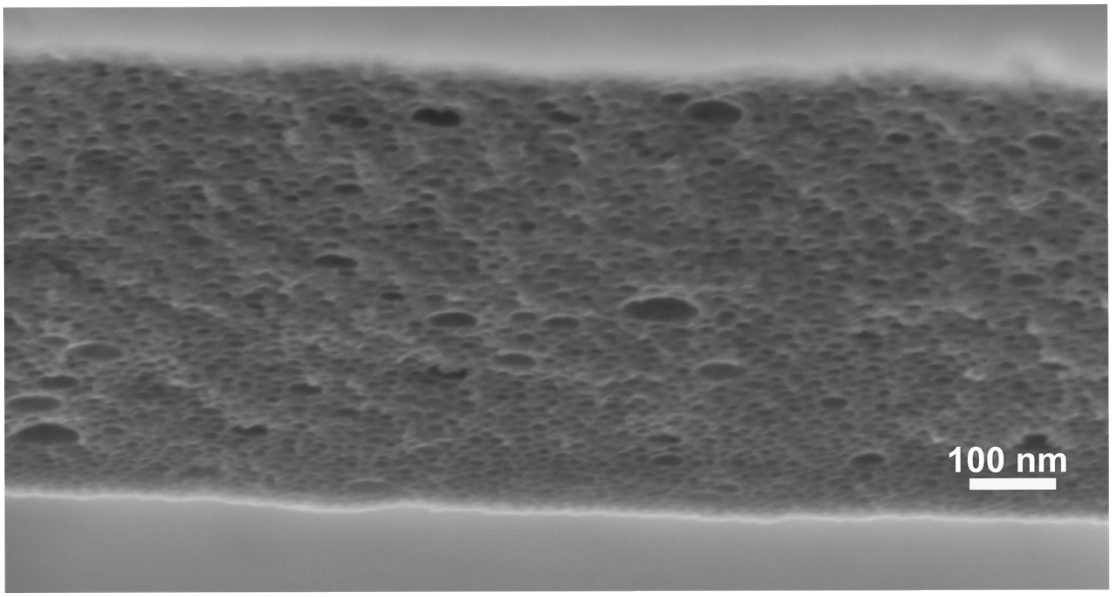

Fig. S13. Cross-sectional SEM image of a sample prepared using **OH1** with 0 wt% **H** from an EtOH solution. The mean out-of-plane pore size found with 6.1±0.1 nm with standard deviation of 1.4 nm.

References.

1. A. Sarkar and M. Stefik, *J. Mater. Chem. A,* 2017, **5**, 11840-11853.

2. K. A. Lantz, N. B. Clamp, W. van den Bergh, A. Sarkar and M. Stefik, *Small*, 2019, **15**, 1900393.