Electronic Supplementary Material (ESI) for Nanoscale.

Atomic Layer Deposition Enables Multi-Modal Three-Dimensional Electron Microscopy of Isoporous Membranes

Assaf Simon,[a#] Zhenzhen Zhang,[b#] Clarissa Abetz,[b] Volker Abetz,[b,c]* Tamar Segal-Peretz[a]*

a Department of Chemical Engineering, Technion, Haifa-3200003, Israel

b Helmholtz-Zentrum Hereon, Institute of Membrane Research, Max-Planck-Str.1, 21502 Geesthacht, Germany

c Universität Hamburg, Institute of Physical Chemistry, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

#- the authors equally contributed to the paper

Segmentation of FIB-SEM tomography data and Pore Network Model Generation

The original data was loaded into Amira® (Thermo-Fischer), as a stack of '.tif' files. The voxel size was 2 nm x 2 nm x 5 nm. The data was segmented using an auto-thresholding algorithm with default parameters. The noise was reduced by applying a median filter, with default settings. The segmented data was then separated into individual pores using the separate objects algorithm, with parameters as shown in Figure S1.

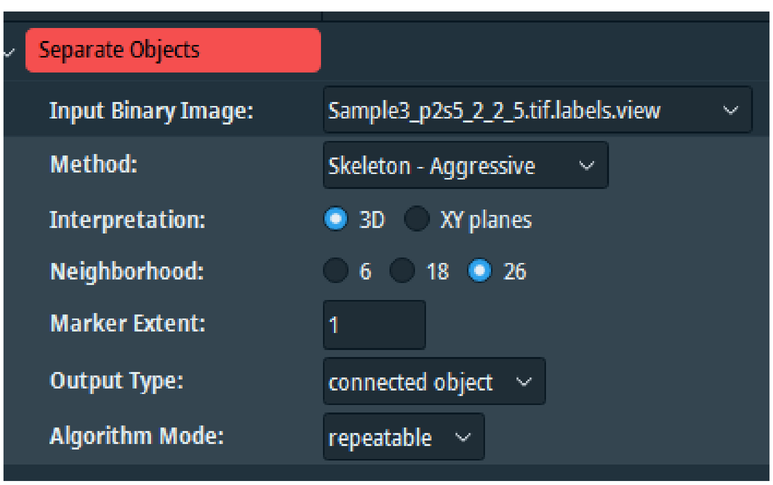


Figure S1 – Parameters for separate objects algorithm

Finally, the pore network model was generated using the "generate pore network" algorithm, which is part of the xPore® add-on to Amira®. The parameters were used as default, defining the flow direction on the y-axis. This process is illustrated in Figure S2.

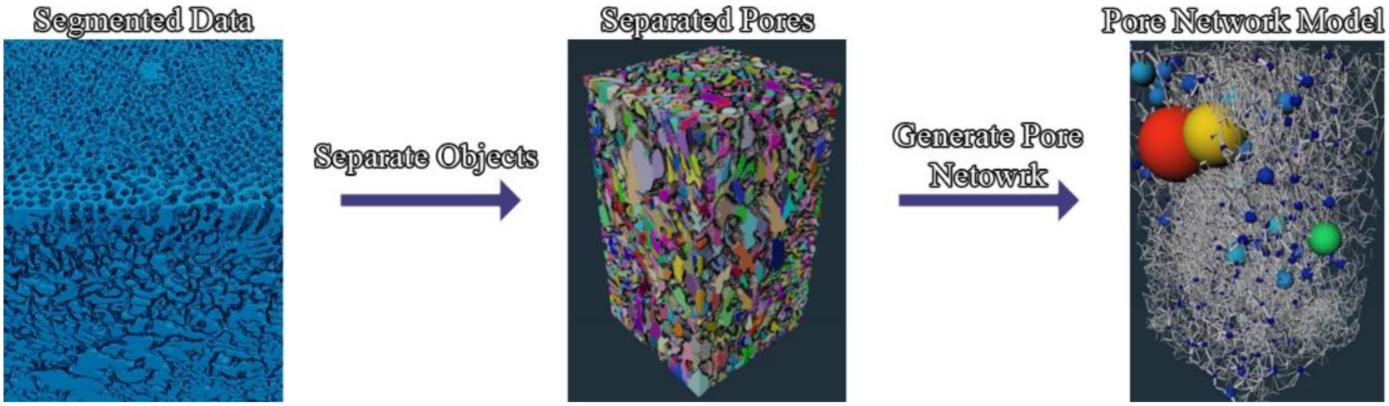


Figure S2 – Pore network analysis of FIB-SEM tomography data: The segmented data is separated into individual pores, then a pore network is generated by simulating a flow of pressurized water through the pores.

Calculation of permeability (k) and tortuosity factor (τ)

The program calculates the permeability factor (k) and the pore tortuosity (τ) for the pore network model. Permeability is computed as follows: We assume that we are in a laminar flow regime. Mass conservation in steady-state, each pore must obey:

i. $\sum_{i \to j} q_{ij} = 0$ (Continuity equation)

Under laminar flow, the relation between flow (q) and conductance (g) is linear:

ii. $q_{ij} = g_{ij} \times (P_i - P_j)$

Each channel between two pores i and j is assumed as cylindrical with a radius of r_{ij} and length of l_{ij}, therefore, we can calculate:

iii. $g_{ij} = \frac{\pi}{8\mu} \times \frac{r_{ij}^4}{l_{ij}}$ (Poiseuille law)

Where μ is the fluid viscosity.

These equations combined lead to a system of linear equations, which are solved numerically. The total flow rate Q is computed by:

iv. $Q = \sum g_{ij} \times (P_i - P_j)$

The permeability coefficient k is calculated from Darcy's law:

v. $$k = \frac{Q}{\Delta P} \times \frac{\mu L}{A}$$

Where ΔP is the pressure drop through the membrane's volume, A is the average cross-sectional area, and L is the average length of the pores.

The tortuosity is computed as follows. Based on the theoretical permeability factor computed previously, the velocity is calculated in each channel and the tortuosity is computed as:

vi. $$\tau = \frac{\sum_{i=0}^{n} \|v_i\|}{\sum_{i=0}^{n} \|vx_i\|}$$

Where v_i is the velocity of the fluid through channel i , vx_i is the projection of the velocity along the flow direction of the fluid passing through channel i and n is the number of channels.

Calculation of permeability (k) based on the experimental data

We performed the experimental water permeance measurements following our previous report.[1] Briefly, we used the dead-end mode with a home-made automatic testing device at a transmembrane pressure (Δp) of 1 bar at room temperature. The volume change ΔV was measured gravimetrically for time slots Δt of 1-3 min for 2 h. The effective membrane area A was 1.77 cm^2. These studies were carried out by employing ultrapure water with an electrical conductivity of ≈ 0.055 µS cm^{-1} and a density of 0.998 g cm^{-3} at room temperature (20-22 °C). A minimum of 3 samples were measured. We calculated the water permeance (J) by normalizing the flux with the transmembrane pressure, as below equation:

$$J = \frac{\Delta V}{A \Delta t \Delta p}$$

Under the assumption that the resistance of the spongy substructure of the membrane is negligible and only the cylindrical ordered selective layer of the membrane mainly hinders the permeance, Darcy's law can be used to calculate the permeability of membranes based on experimental data, as shown in the following equation

$$k = \frac{J\, 4\mu L}{N \pi d^2}$$

Where J is the water permeance (L $m^{-2}h^{-1}bar^{-1}$), N is the number of surface pores per unit area, d is the pore diameter determined based on SEM surface images, μ is the water viscosity (8.9×10^{-4} Pa s at 25 °C) and L is the length of the selective layer.

According to the top surface and cross-sectional SEM images of membranes (Figure S3), 75A membrane had a pore diameter d of 18.5 nm, pore number density N of 2.521×10^{14} m^{-2} and average length of selective layer L of 217 nm. The water permeance $J = 672.1 \pm 33$ L $m^{-2}h^{-1}bar^{-1}$.

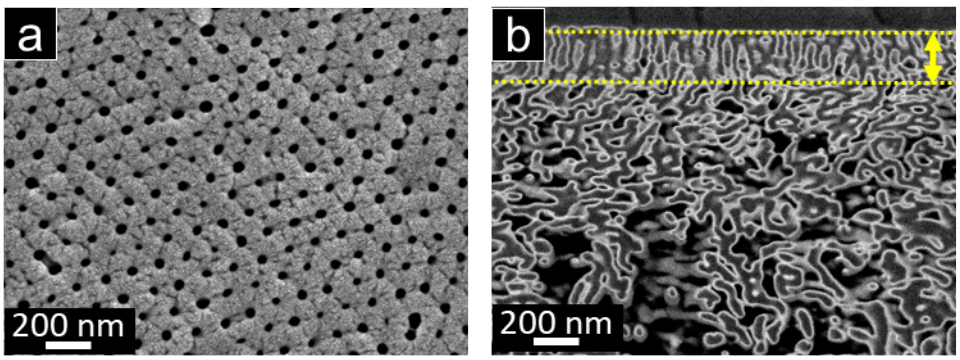


Figure S3 - The representative SEM images of 75A membrane top surface (a) and cross-section (b).

TEM Tomography Analysis

To analyze the pore's deviation from a straight line, 13 select pores were randomly chosen from along an A25 membrane's cross-section, as can be seen in Figure S4. The geometry of the pores was investigated throughout a sufficient amount of slices to account for the whole circumference (the modified pores have an average pores size of ~20nm). As each slice is 2.08 nm thick, 10 slices were considered to be adequate. The observed cross-section is a view of the selective layer, after simple segmentation, to improve the clarity. The pores' geometry was recorded throughout the 10 slices and monitored throughout the whole circumference, as is demonstrated in Figure S5 & Figure S6. For reference, a dashed line representing a straight orientation was plotted as well.

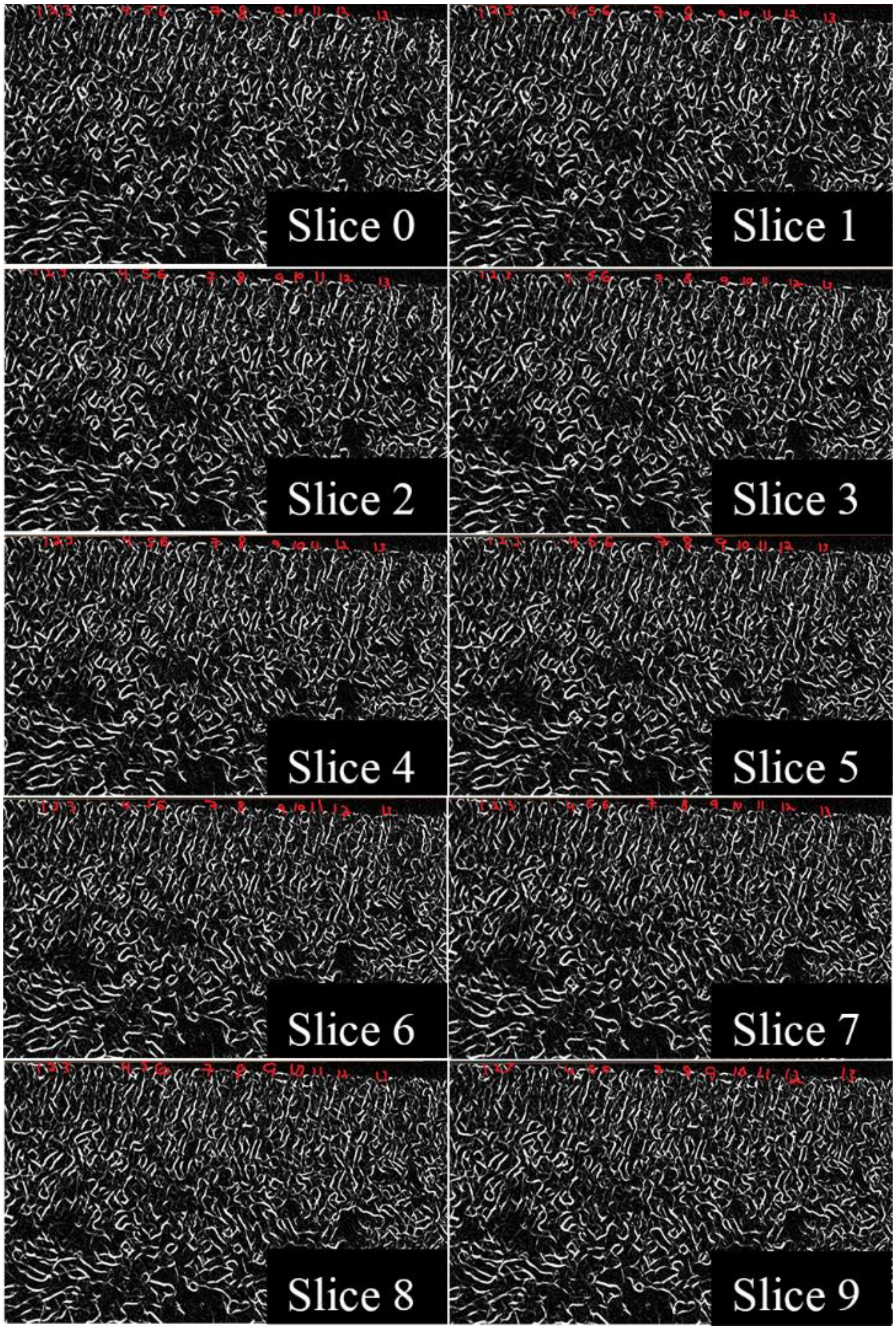


Figure S4 – TEM tomography pore geometry analysis: slices 0-9, each slice is 2.08 nm thick. Pores are numbered arbitrarily (1-13) and monitored throughout the circumference.

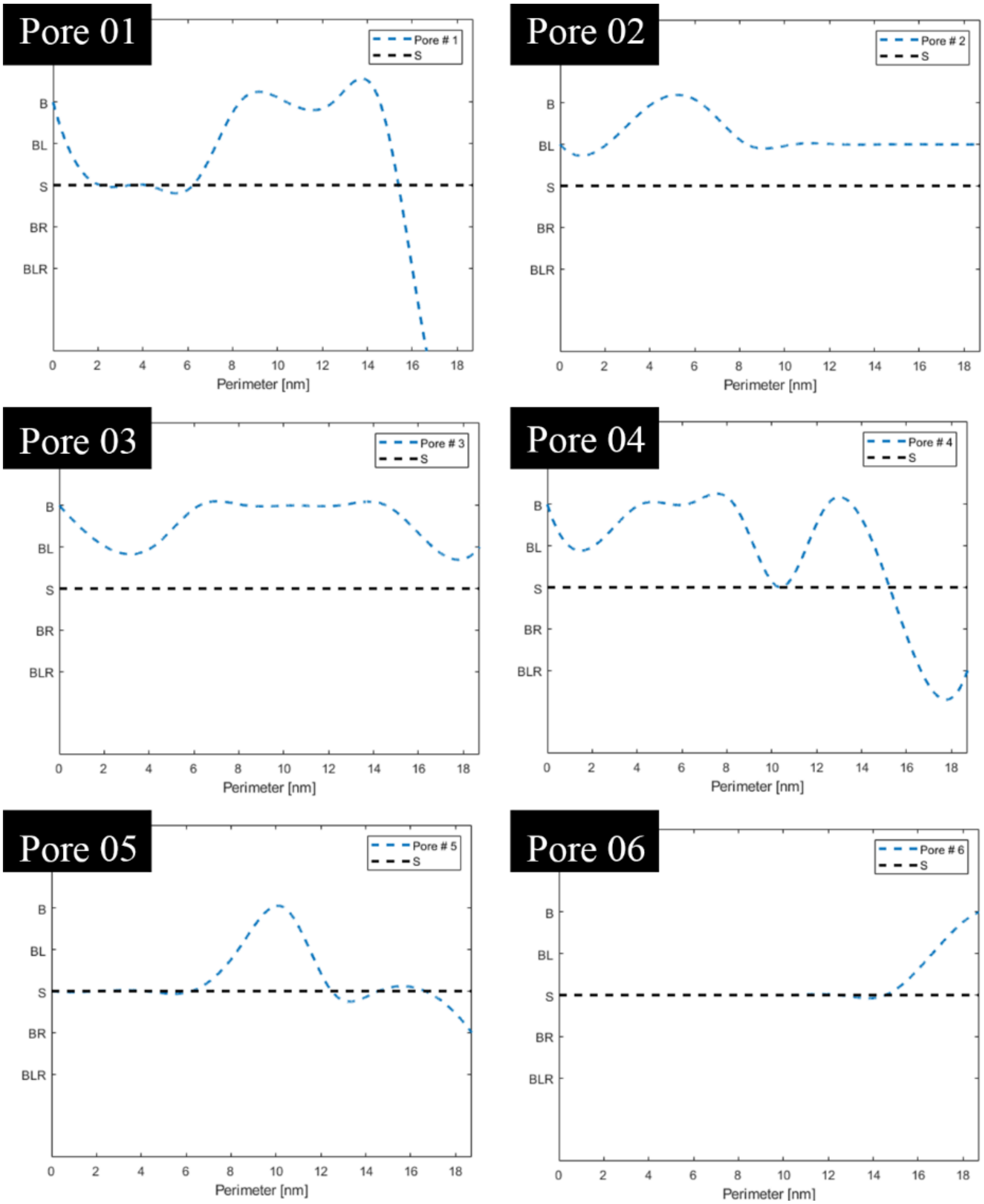
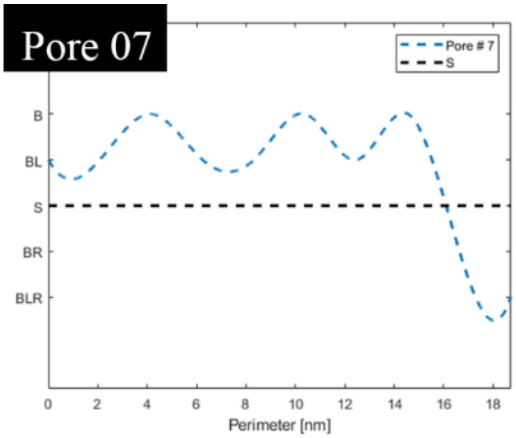
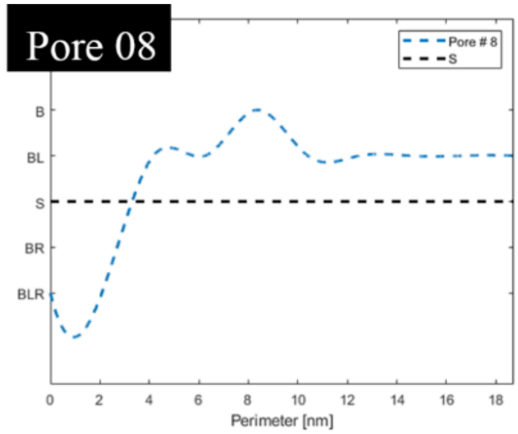
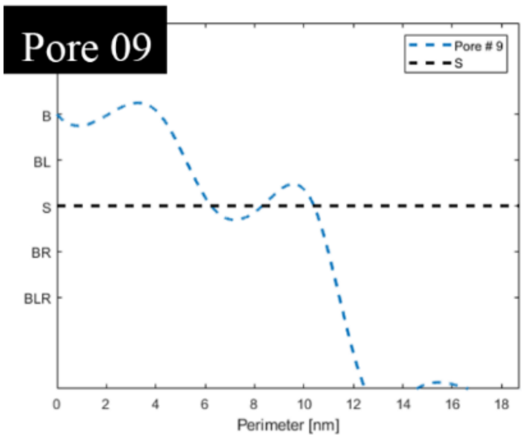
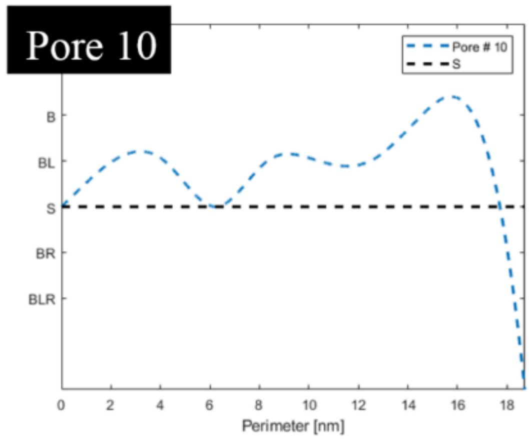


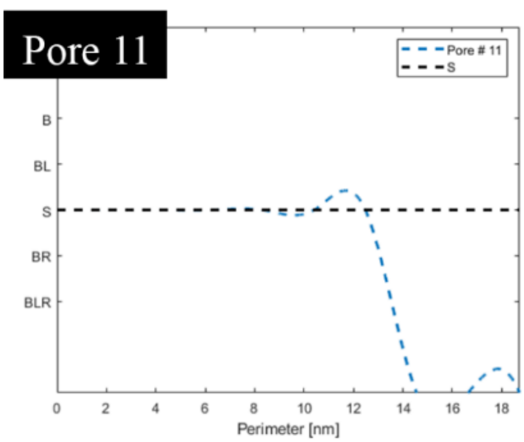
Figure S5 – TEM tomography pore profile analysis: pore geometry (Bent, Broken Left, Straight, Broken R, Broken Left-Right) vs. Perimeter of the pore. Pores 01-06.

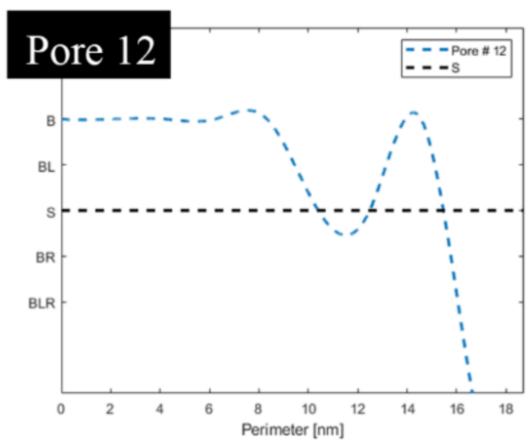

Pore 07
Pore # 7
S
B
BL
S
BR
BLR
0 2 4 6 8 10 12 14 16 18
Perimeter [nm]


Pore 08
Pore # 8
S
B
BL
S
BR
BLR
0 2 4 6 8 10 12 14 16 18
Perimeter [nm]


Pore 09
Pore # 9
S
B
BL
S
BR
BLR
0 2 4 6 8 10 12 14 16 18
Perimeter [nm]


Pore 10
Pore # 10
S
B
BL
S
BR
BLR
0 2 4 6 8 10 12 14 16 18
Perimeter [nm]


Pore 11
Pore # 11
S
B
BL
S
BR
BLR
0 2 4 6 8 10 12 14 16 18
Perimeter [nm]


Pore 12
Pore # 12
S
B
BL
S
BR
BLR
0 2 4 6 8 10 12 14 16 18
Perimeter [nm]

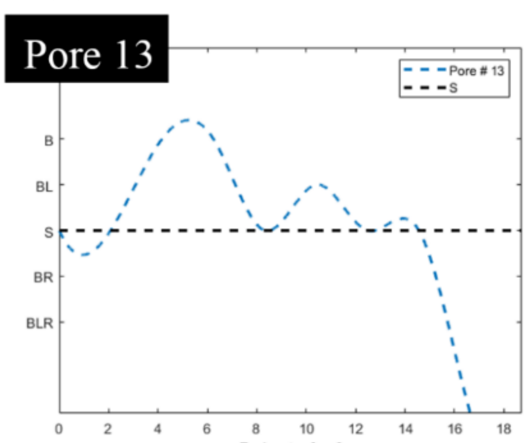

Pore 13
Pore # 13
S
B
BL
S
BR
BLR
0 2 4 6 8 10 12 14 16 18
Perimeter [nm]

Figure S6 - TEM tomography pore profile analysis: pore geometry (Bent, Broken Left, Straight, Broken R, Broken Left-Right) vs. Perimeter of the pore. Pores 07-13.

Reference:

(1) Zhang, Z.; Simon, A.; Abetz, C.; Held, M.; Höhme, A.-L.; Schneider, E. S.; Segal-Peretz, T.; Abetz, V. Hybrid Organic–Inorganic–Organic Isoporous Membranes with Tunable Pore Sizes and Functionalities for Molecular Separation. *Adv. Mater.* **2021**, *33* (48), 2105251. https://doi.org/10.1002/adma.202105251.