Electronic Supplementary Information (ESI)

Sub-nanometer Pore Formation in Single-Molecule-Thick Polyurea Molecular-Sieving Membrane: a Computational Study

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S1. Force field (FF): energy expressions and parameters.

A parametrization of the interaction energy E based on the OPLS-AA FF[1-2] is used for the Monte Carlo (MC) conformation search presented in this work. The functional form is expressed as follows.

$$E = E^{\text{bonding}} + E^{\text{nonbonding}} = E^{\text{bond}} + E^{\text{angle}} + E^{\text{torsion}} + E^{\text{coulomb}} + E^{\text{vdW}}.$$

Bond stretching (E^{bond}) $\quad E_{bond} = \sum_{bond} \frac{K_r}{2}(r - r_{eq})^2$

Angle bending (E^{angle}) $\quad E_{angle} = \sum_{angle} \frac{K_\theta}{2}(\theta - \theta_{eq})^2$

Torsion (E^{torsion}) $\quad E_{torsion} = \sum_{torsion} \frac{V1}{2}[1 + \cos(\phi)] + \frac{V2}{2}[1 + \cos(2\phi)] + \frac{V3}{2}[1 + \cos(3\phi)]$

Non-bonding ($E^{\text{Coulomb}} + E^{\text{vdW}}$) $\quad E_{non-bonding} = \sum_i \sum_j \left[\frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{ij}\left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right)\right] f_{ij}$

where $f_{ij} = 0.5$ for 1-4 interactions and 1.0 otherwise; $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$.

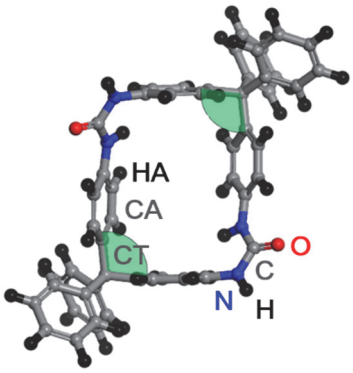

Figure S1. OPLS-AA FF types: TPU

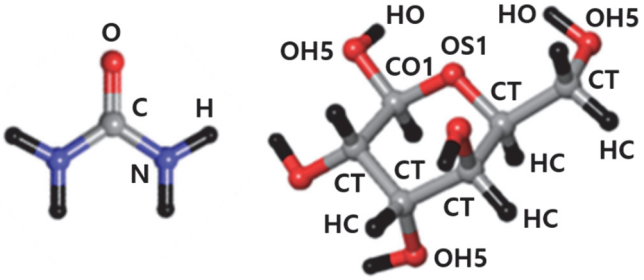

Figure S2. OPLS-AA FF types: urea and glucose

Table S1. Generalized Born (GB) solvation parameter: initial van der Waals (vdW) radii

*solvent molecule (water) probe radius = 1.40 Å

FF type	CT	CA*	CA	C	N	O	HA	H
σ (Å)	1.8	1.77	1.82	1.875	1.64	1.49	1.25	1.2075

FF type: urea	N	C	O	H
σ (Å)	1.64	1.875	1.49	1.2075

FF type: glucose	CT	CO1	OS1	OH5	OH5*	HC	HO
σ (Å)	1.8	1.8	1.48	1.47	1.54	1.25	1.2075

Table S2. FF parameter: Non-bonding (vdW)

FF type	CT	CA	C	N	O	HA	H
σ (Å)	3.500	3.550	3.750	3.250	2.960	2.420	0.000
ε (kcal/mol)	0.066	0.070	0.105	0.170	0.210	0.030	0.000

FF type	N	C	O	H
σ (Å)	3.250	3.750	2.960	0.000
ε (kcal/mol)	0.170	0.105	0.210	0.000

FF type	CT	CO1	OS1	OH5	HC	HO
σ (Å)	3.500	3.500	2.900	3.120	2.500	0.000
ε (kcal/mol)	0.066	0.066	0.140	0.170	0.030	0.000

Table S3. FF parameter: Non-bonding (atomic charges)

FF type: TPU	CT	CA*	CA	CA	C	N	O	HA	H
Attached FF type	–CA –CA –CA	–CA –CA –CT	–CA –CA –HA	–CA –CA –N	–N –N –O	–CA –C –H	–C	–CA	–N
q (|e|)	0.460	-0.115	-0.115	0.107	0.766	-0.473	-0.616	0.115	0.291

FF type: urea	N	C	O	H
Attached FF type	–C –H –H	–N –N –O	–C	–N
q (|e|)	-0.959	0.878	-0.616	0.414

FF type: glucose	CT	CT*	CO1	CT	OS1	OH5	HC	HC	HC	HO
Attached FF type	–CT –C* –OH5 –HC	–CT –CT –OS1 –HC	–CT –OS1 –OH5 –HC	–CT –OH5 –HC –HC	–CT –CO1	–C* –HO	–CT	–CT*	–CO1	–OH5
q (|e|)	0.205	0.170	0.365	0.145	-0.400	-0.683	0.060	0.030	0.100	0.418

Table S4. FF parameter: Bond stretching

FF type: TPU	CA-CA	CA-CT	CA-HA	CA-N	N-C	O-C	N-H
r_0 (Å)	1.400	1.510	1.080	1.404	1.335	1.229	1.010
K_r (kcal/mol Å^2)	938	634	734	720	980	1140	868

FF type: urea	N-H	N-C	C-O
r_0 (Å)	1.010	1.335	1.229
K_r (kcal/mol Å^2)	868	980	1140

FF type: glucose	CT-CO1	CT-CT	CT-OH5	CT-OS1	CT-HC	CO1-OH5	CO1-OS1
r_0 (Å)	1.525	1.529	1.421	1.422	1.090	1.410	1.399
K_r (kcal/mol Å^2)	510	536	710	670	680	750	740
FF type: glucose	CO1-HC	OH5-HO					
r_0 (Å)	1.097	0.967					
K_r (kcal/mol Å^2)	720	1160					

Table S5. FF parameter: Angle bending

FF type: TPU	CA-CA-CA	CT-CA-CA	CA-CA-HA	CA-CA-N	CA-N-C	CA-N-H
θ_o (°)	120.000	120.000	120.000	119.019	121.965	118.236
K_θ (kcal/mol deg^2)	126	140	70	140	130	90
FF type: TPU	N-C-N	N-C-O	C-N-H			
θ_o (°)	111.917	122.900	119.800			
K_θ (kcal/mol deg^2)	180	160	70			

FF type: urea	N-C-N	O-C-N	H-N-C	H-N-H
θ_o (°)	111.917	122.900	119.800	120.000
K_θ (kcal/mol deg^2)	180	160	70	70

FF type: glucose	CT-CT-CT	CT-CT-CO1	CT-CT-OS1	CT-CT-OH5	CT-CO1-OH5	CT-CO1-OS1
θ_o (°)	112.700	111.100	107.885	111.453	110.760	109.707
K_θ (kcal/mol deg^2)	116.7	140	190	180	180	180
FF type: glucose	CO1-CT-OH5	CT-OS1-CO1	OS1-CO1-OH5	CO1-CT-HC	CT-CO1-HC	OS1-CO1-HC
θ_o (°)	109.420	112.107	108.760	109.540	111.650	105.754
K_θ (kcal/mol deg^2)	180	180	230	90	90	120
FF type: glucose	OH5-CO1-HC	CT-CT-HC	OS1-CT-HC	OH5-CT-HC	HC-CT-HC	CT-OH5-HO
θ_o (°)	111.660	110.700	108.988	109.390	107.800	108.535
K_θ (kcal/mol deg^2)	110	75	110	120	66	130
FF type: glucose	CO1-OH5-HO					
θ_o (°)	107.660					
K_θ (kcal/mol deg^2)	140					

Table S6. FF parameter: Proper torsion (Improper torsion or out-of-plane bending not shown)

FF type: TPU	*-CA-CA-*	*-CA-CT-*	CA-CA-N-C	CA-CA-N-H
V_1 (kcal/mol)	0.000	0.000	1.001	0.000
V_2 (kcal/mol)	3.625	0.043	0.850	0.978
V_3 (kcal/mol)	0.273	0.000	0.000	0.000
FF type: TPU	CA-N-C-N	CA-N-C-O	N-C-N-H	O-C-N-H
V_1 (kcal/mol)	0.549	0.000	0.000	0.000
V_2 (kcal/mol)	1.908	0.040	2.567	2.450
V_3 (kcal/mol)	0.000	0.000	0.000	0.000

FF type: urea	N-C-N-H	O-C-N-H
V_1 (kcal/mol)	0.000	0.000
V_2 (kcal/mol)	2.567	2.450
V_3 (kcal/mol)	0.000	0.000

FF type: glucose*	CT-CT-CT-CT	CT-CT-CT-OS1	CT-CT-CT-OH5	CT-CT-CT-HC
V_1 (kcal/mol)	0.567	0.627	-0.477	0.000
V_2 (kcal/mol)	-0.075	-0.310	0.000	0.000
V_3 (kcal/mol)	0.200	0.273	0.000	0.150
FF type: glucose*	CT-OS1-CT-CT	CT-OS1-CT-HC	CT-OS1-CO1-OH5	OS1-CT-CT-OH5
V_1 (kcal/mol)	0.062	0.000	-0.704	1.518
V_2 (kcal/mol)	-0.011	0.000	-0.904	0.000
V_3 (kcal/mol)	0.280	0.370	0.000	0.000
FF type: glucose*	OH5-CT-CT-OH5	OS1-CT-CT-HC	OH5-CT-CT-HC	CT-CT-OH5-HO
V_1 (kcal/mol)	3.780	0.000	0.000	0.292
V_2 (kcal/mol)	0.000	0.000	0.000	-0.283
V_3 (kcal/mol)	0.000	0.234	0.234	0.436
FF type: glucose*	OS1-CT-OH5-HO	HC-CT-OH5-HO		
V_1 (kcal/mol)	-0.553	0.000		
V_2 (kcal/mol)	-1.344	0.000		
V_3 (kcal/mol)	0.342	0.194		

*CT = CO1 in the torsion FF

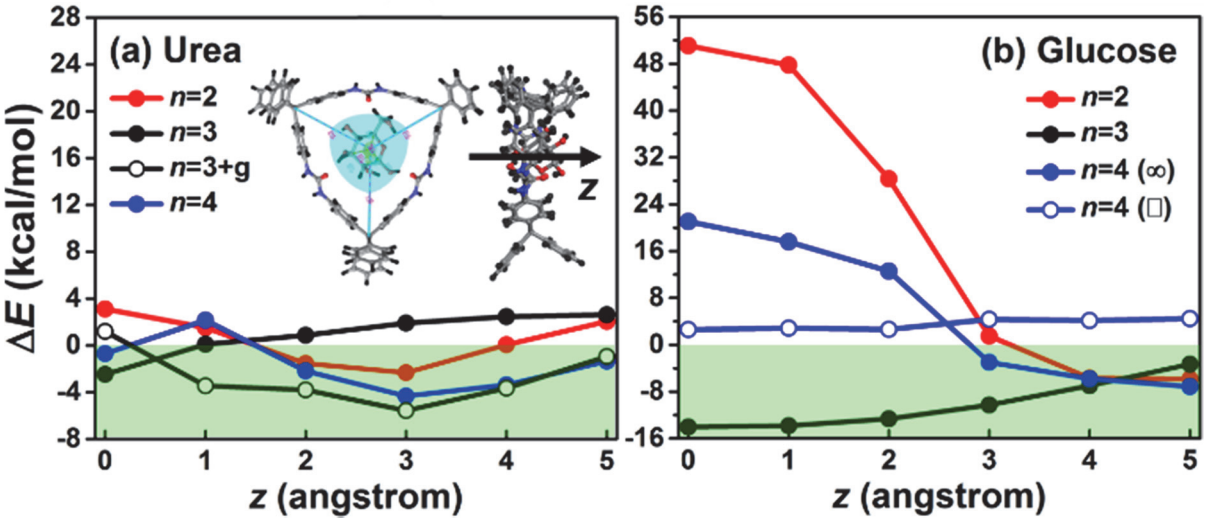

Figure S3 (complementary to Fig. 3 of the main article). Translocation energy profiles for (a) urea (zoomed in twice in the y axis) and (b) glucose entering dimeric (red), trimeric (black), and tetrameric (blue) pores by 1 Å vertically to the entrance (z = 0) with multiple constraints (inset, light blue). Since each pore is rather symmetric, only the positive half of translocation coordinate (z = 0-5 Å) is shown. Profiles for urea entering trimer occupied by glucose (black, open mark) and for glucose entering high-energy square-shape tetramer (blue, open mark) are also shown. The most stable structures at key distances (mostly at the pore center, z = 0) are shown in Fig. 4-6 of the main article.

REFERENCES

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(2) Kaminski, G. A.; Friesner, R. A.; Tirado-Rives, J.; Jorgensen, W. L. *J. Phys. Chem. B* **2001**, *105*, 6474.