## SUPPLEMENTARY INFORMATION

## Exploiting hydrophobicity and hydrophilicity in nanopores as a design principle for "smart" MOF microtanks for methane storage

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Note: *CIFs for screened MOFs can be downloaded from <u>https://github.com/tobacco-mofs/tobacco\_3.0</u>* 

## S1. Simulation details.



**Fig.S1**. Force field parameters used for all the components relevant to our simulations. The parameters  $\varepsilon$  and  $\sigma$  correspond to the well depth and the location of the repulsion core in a Lennard Jones potential, whereas q was the electrostatic charge in a Coulomb potential. For graphene oxide (hydrophilic pore model) and graphene (hydrophobic pore model) only a representative piece of the material containing all the relevant atom types in the model is presented.

Grand canonical Monte Carlo (GCMC) simulations were perfomed using the simulation code RASPA. Intermolecular interactions were described according to the parameters detailed in Fig. S1. These parameters are assigned according to the Universal force field (UFF) and the TraPPE force fields. A cutoff of 12.8 Å was used for dispersion interactions, and Ewald summation was used to calculate elsctrostaic interactions beyond 12 Å. Lorentz-Berthelot mixing rules were used to obtain cross-interaction parameters.

Simulations were run for 2,000 cycles for equilibration, and 5,000 additional cycles for calculating statistical averages. Each cycle corresponds to either 20 or N moves Monte Carlo moves (whichever is higher) where N is equal to the number of molecules in the simulation supercell. Monte Carlo moves were translation, insertion, deletion, and identity swap for all adsorbates, plus rotation for methanol and DMB, plus biased insertion for DMB (using a Rosenbluth factor of 0.1848. The fugacity of methane, methanol and DMB in the implicit gas phase was calculated using the corresponding Peng Robinson equation of state.

**Table S1.** Textural properties for hydrophobic (graphene = Gr) and hydrophilic (graphene oxide = GrO) pore models.

Chemistry	Н	S.A.	Hydrophilic	Void	Largest	Shortest
	(Å)	$(m^2/cm^3)$	groups $(n/Å^3)$	fraction	Pore	Pore
					Dimension	Dimension
					(Å)	(Å)
Gr	8.2	2540	0.000	0.59	4.8	4.8
GrO	8.2	3350	0.006	0.46	4.8	1.4
Gr	12.2	1700	0.000	0.74	8.8	8.8
GrO	12.2	2250	0.004	0.64	8.8	5.4
Gr	16.2	1290	0.000	0.79	12.8	12.8
GrO	16.2	1690	0.003	0.72	12.8	9.4
Gr	28.0	750	0.000	0.89	24.6	24.6
GrO	28.0	980	0.002	0.84	24.6	21.2



**Fig. S2.** Snapshots for hydrophilic graphene oxide (top row) and hydrophobic graphene (bottom row) pore models. C = black, O = red, H = w hite.



**Fig.S3**. Simulated (pure component) methane adsorption isotherms in hydrophobic graphene (left) and hydrophilic graphene oxide (right) pore models at different interlayer separation H. Methane pressure in the bulk was varied up to 100 bar. Color code for isotherms for different interlayer separations is given to the side.



**Fig. S4**. Simulation snapshots when methane pressure is 100 bar for methane/methanol mixture adsorption in hydrophilic graphene oxide (top row) and in hydrophobic graphene (bottom row) pores. Methane is shown in yellow and methanol in green. Pore colors follow the same convention as in Fig. S4.



**Fig. S5**. Schematic of stable and metastable adsorbed (core *c* and shell *s*) and fluid (*f*) phases during loading and storing stages. *During the loading stage* all three phases are equilibrated with each other (they are all stable) according to the loadings of methane (*n*) and methanol (*m*) given by the mixture isotherms. The chemical potential of methane ( $\mu_{CH4}$ ) and methanol ( $\mu_{MeOH}$ ) are respectively equal across the three phases. *During the storing stage* the chemical potential of methane in the fluid phase changes from "high pressure" to "low pressure" (( $\mu_{CH4}$ )<sub>H</sub> to ( $\mu_{CH4}$ )<sub>L</sub>) while the chemical potential of methanol remains essentially unchanged. The equilibrium composition of the adsorbed shell phase does not change with change in methane chemical potential. Thus, the adsorbed shell is in equilibrium with both the fluid phase (( $\mu_{CH4}$ )<sub>L</sub>) and "high pressure" core adsorbed phase (( $\mu_{CH4}$ )<sub>H</sub>). The core adsorbed shell phase becomes trapped in a metastable state because is no longer in equilibrium with the fluid phase. However, since the core adsorbed phase is not in direct contact with the fluid phase, the only way for it to equilibrate with the fluid phase is for methane to diffuse into and through the shell adsorbed phase. However, in the described scenario, this should not happen because the shell adsorbed phase is stable without methane in it.



**Fig. S6.** Mixture isotherms showing the sensitivity of the "sealing" effect to the polarity of the functional groups when using methanol as sealant. Each panel is analogous to the results for these systems in Fig. 4. The percentage indicate the bond dipole moment for the O-H group in graphene oxide compared to the dipole corresponding to the O and H charges assigned based on the TraPPE force field.



**Fig. S7**. Simulated methane/DMB adsorption isotherms at 298 K in hydrophobic graphene (top row) and hydrophilic graphene oxide (bottom row) pore models at different interlayer separation H. Methane partial pressure was varied while keeping DMB partial pressure equal to the vapor pressure of liquid DMB at this temperature (43863 Pa).



**Fig. S8**. Simulation snapshots when methane pressure is 100 bar for methane/DMB mixture adsorption in hydrophilic graphene oxide (top row) and in hydrophobic graphene (bottom row) pores. Methane is shown in yellow and DMB in blue. Pore colors follow the same convention as in Fig. S4.



**Fig. S9.** Screening for methane adsorption loadings in constructed ~2000-MOF database. Sealant partial pressure was set equal to the vapor pressure of liquid sealant at 298 K. a-d) methane/methanol adsorption. e-h) methane/DMB adsorption. i-l) methane/methanol adsorption when MOF atomic charges are artificially "turned off." m-p) methane/DMB adsorption when MOF atomic charges are artificially "turned off."



**Fig. S10.** Average methane loadings (a-d) and methanol molar percentages (e-h) for various combinations of MOF pore size and functionality. Each square represents a pore size-functionality combination. The color of each square is given according to the color bar scale on top of each plot. The LPD quantiles correspond to LPD values between 3.8 and 31.1 Å. The maximum charge magnitude in the functional group increases from left to right. The methane pressures are 40 bar (a,e), 60 bar (b,f), 80 bar (c,g) and 100 bar (d,h).



**Fig. S11.** Simulation snapshots obtained at a 100 bar methane pressure in candidate MOF for the microtank shell. To the left, Fig. 10 from the main text is reproduced. To the right: adsorbed methanol is shown to hydrogen-bond with amino groups. C: gray, H: white, N: blue, O: red, Zr: cyan, Methanol: yellow stick-models.