Electronic Supplementary Information for

Effects of MOF linker rotation and functionalization on methane uptake and diffusion

Shuwen Yue[1], Changhwan Oh[1,2], Aditya Nandy[1,3], Gianmarco G. Terrones[1], and Heather J. Kulik[1,3*]

[1]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

[2]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

[3]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

*email: hjkulik@mit.edu

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Table S1. Bond lengths and angles for functional groups implemented in the functionalization code. All bond lengths are in Å and angles in °. N_{rot} is the number of rotations at a given angle that are necessary to complete the functional group. Bond lengths and angles were determined from gas-phase geometry optimizations of monofunctionalized benzene-1,4-dicarboxylic acid (BDC). All calculations were carried out using TeraChem v1.9[1] with the B3LYP[2-4] global hybrid functional and the empirical D3 dispersion[5] correction using Becke–Johnson damping.[6] All calculations used the LACVP* basis set, which consists of the LANL2DZ effective core potential[7, 8] for Br and I and the 6-31G* basis set for all other atoms.

functional group	C-X bond length	X-Y bond length	C-X-Y bond angle	N_{rot}, rotation angle about C-X bond
CH_3	X = C, 1.52	Y = H, 1.09	110	2, 120
CN	X = C, 1.44	Y = N, 1.17	180	--
NH_2	X = N, 1.38	Y = H, 1.02	120	1, 180
NO_2	X = N, 1.49	Y = O, 1.25	122.5	1, 180
CF_3	X = C, 1.51	Y = F, 1.36	112	2, 120
OH	X = O, 1.36	Y = H, 1.03	100	--
SH	X = S, 1.82	Y = H, 1.34	100	--
F	X = F, 1.37	--	--	--
Cl	X = Cl, 1.80	--	--	--
Br	X = Br, 2.03	--	--	--
I	X = I, 2.23	--	--	--

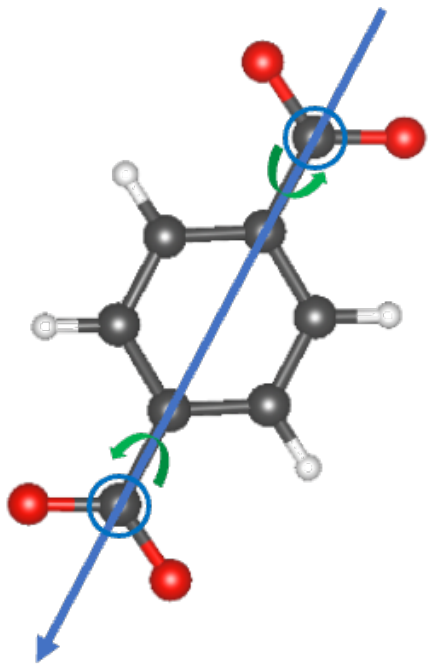

Figure S2. Rotation axis for the carboxylic acid linker (here terephthalic acid). The two rotating C–C bonds are shown with green arrows. The carboxylic acid, which is connected to the metal SBU, is identified from the connectivity matrix generated by the MOF analysis code. The O atoms connected to the metal atom are identified and the two C atoms (blue circles) connected to these O atoms are used to build the rotation axis (blue arrow). The directional vector of the rotation axis is calculated by subtracting the coordinates of these two C atoms, and the reference point is defined as any one of these C atoms.

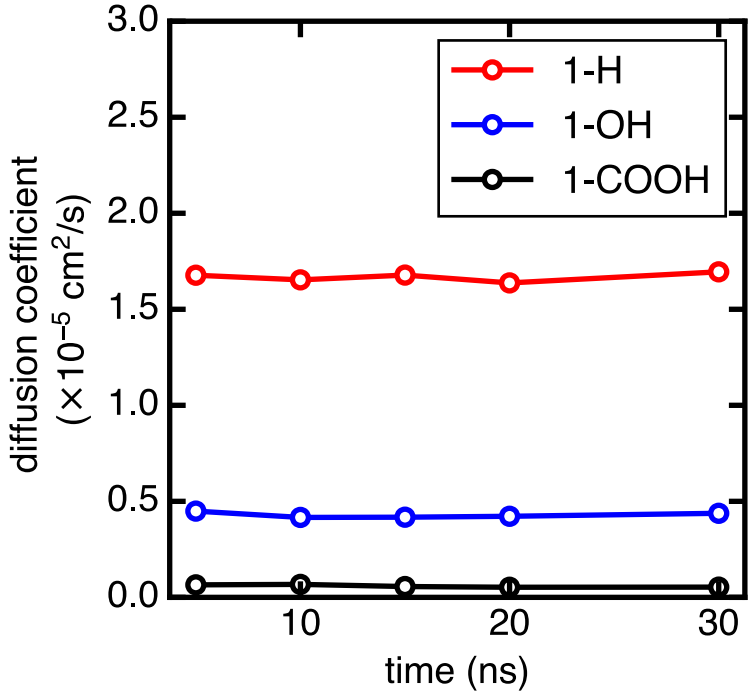

Figure S3. Diffusion coefficient of methane (in cm^2/s) calculated at simulation time up to 30 ns for three functional groups: H, OH, and COOH each mono-functionalized on unrotated BDC linkers. These functional groups are representative of the span of pore sizes in the entire set of UiO-66 derivatives studied for diffusivity of methane. Diffusion coefficients are obtained following the protocol described in the Methods section in the main text. Each line represents only one simulation trajectory.

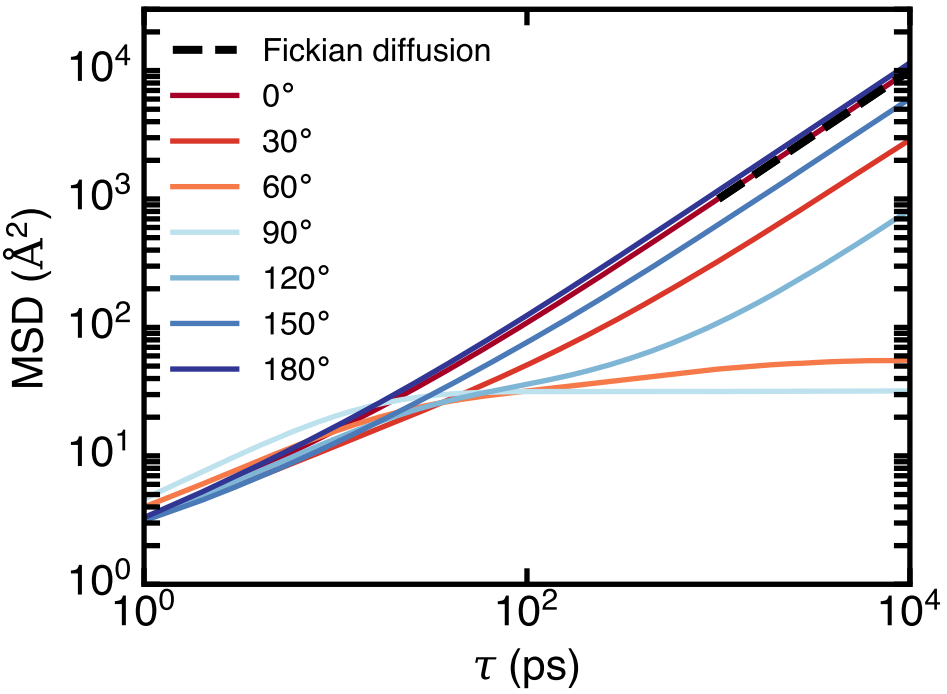

Figure S4. Mean-squared displacement (MSD) of methane (Å^2) over lag time τ (ps) in UiO-66 with 1-H functionalized (i.e., unfunctionalized) BDC linkers rotated at 7 discrete angles. Lines represent the average of 3 independent 30 ns trajectories. The dashed black line represents the τ region where the slope MSD/τ is fit to determine the diffusion coefficient following the procedure described in the Methods section. The diffusion coefficient is only evaluated for rotamers (0°, 30°, 120°, 150°, 180°) where the slope MSD/τ ~1, defined as the Fickian diffusion regime and represented by the slope of the dashed black line. All other rotamers (60°, 90°) are assigned a diffusion coefficient of 0 to signify the regime as sub-diffusive.

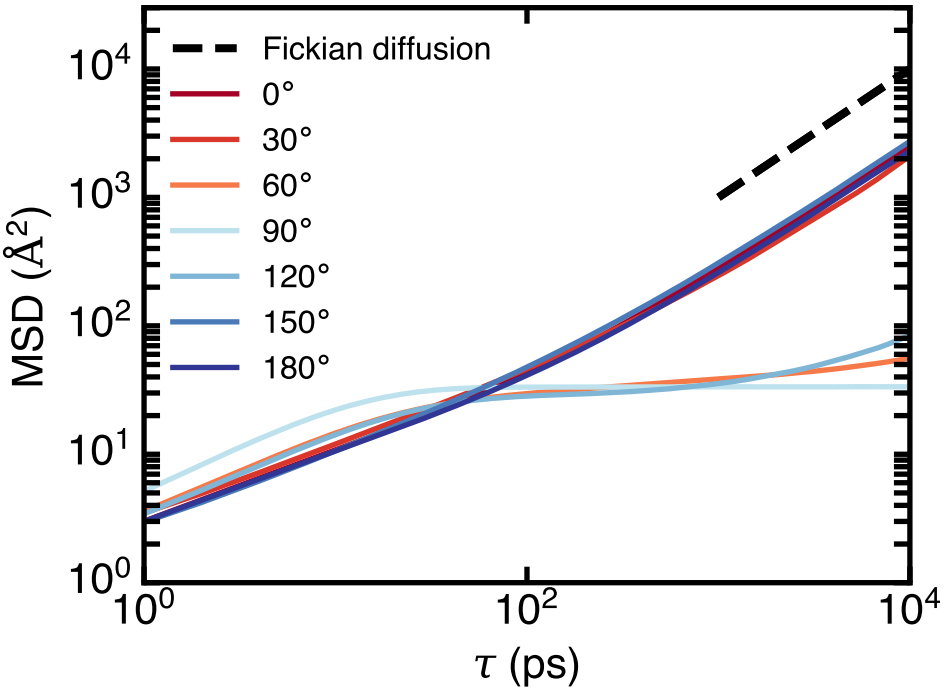

Figure S5. Mean squared displacement (MSD) of methane (Å^2) over lag time τ (ps) in UiO-66 with 1-OH functionalized BDC linkers rotated at 7 discrete angles. Lines represent the average of 3 independent 30 ns trajectories. The dashed black line represents the τ region where the slope MSD/τ is fit to determine the diffusion coefficient following the procedure described in the Methods section. The diffusion coefficient is only evaluated for rotamers (0°, 30°, 150°, 180°) where the slope MSD/τ ~1, defined as the Fickian diffusion regime and represented by the slope of the dashed black line. All other rotamers (60°, 90°, 120°) are assigned a diffusion coefficient of 0 to signify the regime as sub-diffusive.

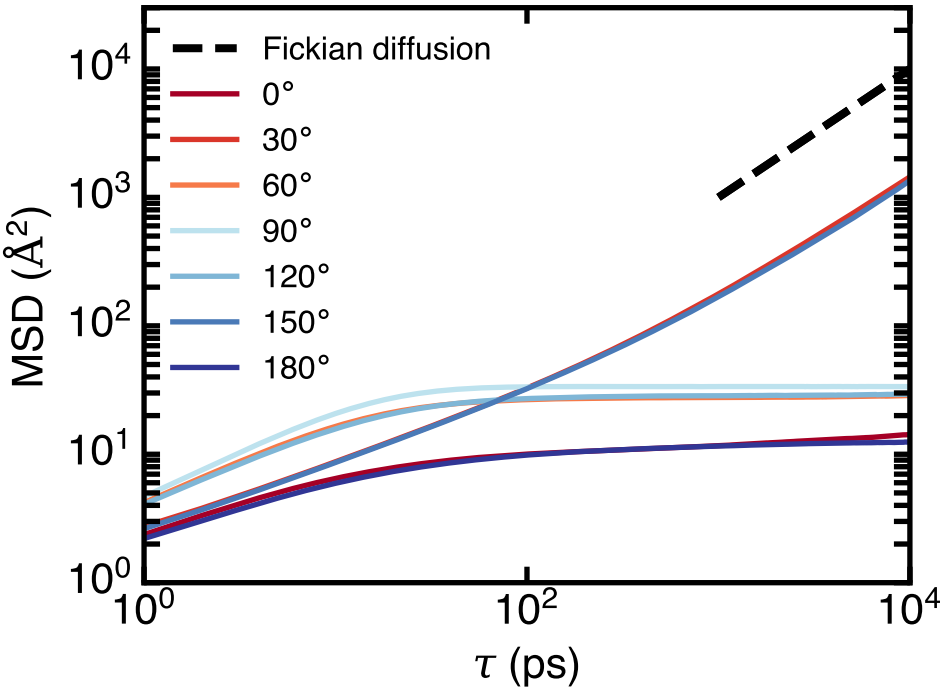

Figure S6. Mean squared displacement (MSD) of methane (Å^2) over lag time τ (ps) in UiO-66 with 2-OH functionalized BDC linkers rotated at 7 discrete angles. Lines represent the average of 3 independent 30 ns trajectories. The dashed black line represents the τ region where the slope MSD/τ is fit to determine the diffusion coefficient following the procedure described in the Methods section. The diffusion coefficient is only evaluated for rotamers (30°, 150°) where the slope MSD/τ ~1, defined as the Fickian diffusion regime and represented by the slope of the dashed black line. All other rotamers (0°, 60°, 90°, 120°, 180°) are assigned a diffusion coefficient of 0 to signify the regime as sub-diffusive.

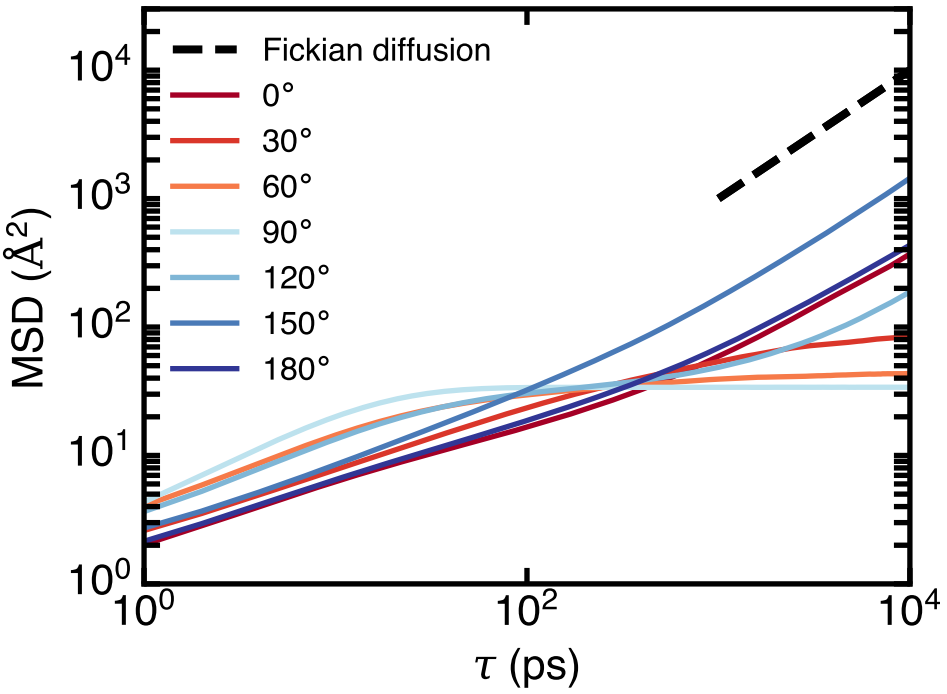

Figure S7. Mean squared displacement (MSD) of methane (Å^2) over lag time τ (ps) in UiO-66 with 1-COOH functionalized BDC linkers rotated at 7 discrete angles. Lines represent the average of 3 independent 30 ns trajectories. The dashed black line represents the τ region where the slope MSD/τ is fit to determine the diffusion coefficient following the procedure described in the Methods section. The diffusion coefficient is only evaluated for rotamers (0°, 120°, 150°, 180°) where the slope MSD/τ ~1, defined as the Fickian diffusion regime and represented by the slope of the dashed black line. All other rotamers (30°, 60°, 90°) are assigned a diffusion coefficient of 0 to signify the regime as sub-diffusive.

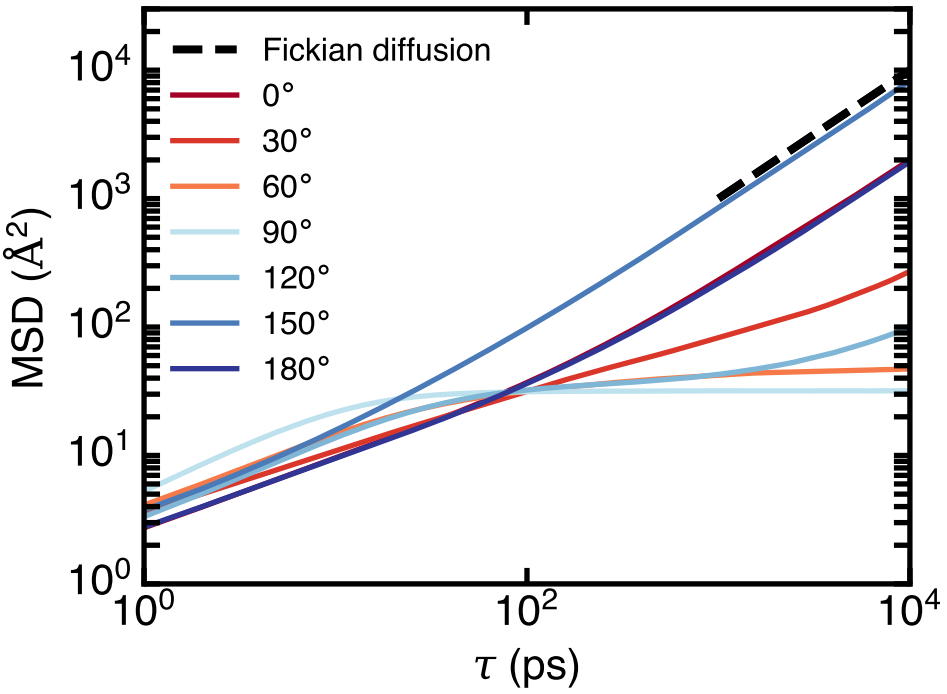

Figure S8. Mean squared displacement (MSD) of methane (Å^2) over lag time τ (ps) in UiO-66 with 1-Cl functionalized BDC linkers rotated at 7 discrete angles. Lines represent the average of 3 independent 30 ns trajectories. The dashed black line represents the τ region where the slope MSD/τ is fit to determine the diffusion coefficient following the procedure described in the Methods section. The diffusion coefficient is only evaluated for rotamers (0°, 30°, 150°, 180°) where the slope MSD/τ ~1, defined as the Fickian diffusion regime and represented by the slope of the dashed black line. All other rotamers (60°, 90°, 120°) are assigned a diffusion coefficient of 0 to signify the regime as sub-diffusive.

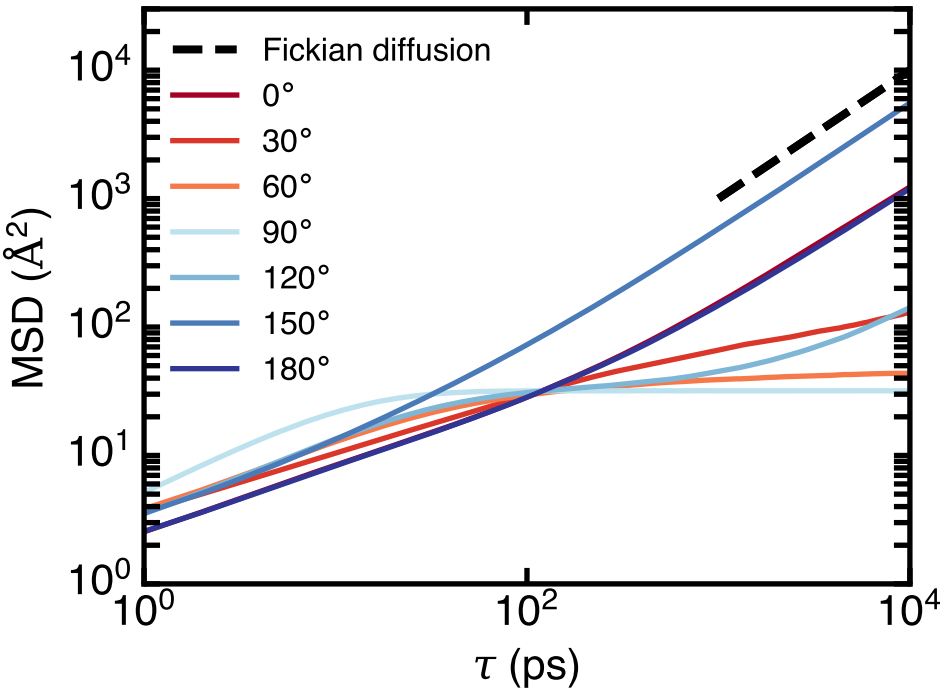

Figure S9. Mean squared displacement (MSD) of methane (Å^2) over lag time τ (ps) in UiO-66 with 1-Br functionalized BDC linkers rotated at 7 discrete angles. Lines represent the average of 3 independent 30 ns trajectories. The dashed black line represents the τ region where the slope MSD/τ is fit to determine the diffusion coefficient following the procedure described in the Methods section. The diffusion coefficient is only evaluated for rotamers (0°, 150°, 180°) where the slope MSD/τ ~1, defined as the Fickian diffusion regime and represented by the slope of the dashed black line. All other rotamers (30°, 60°, 90°, 120°) are assigned a diffusion coefficient of 0 to signify the regime as sub-diffusive.

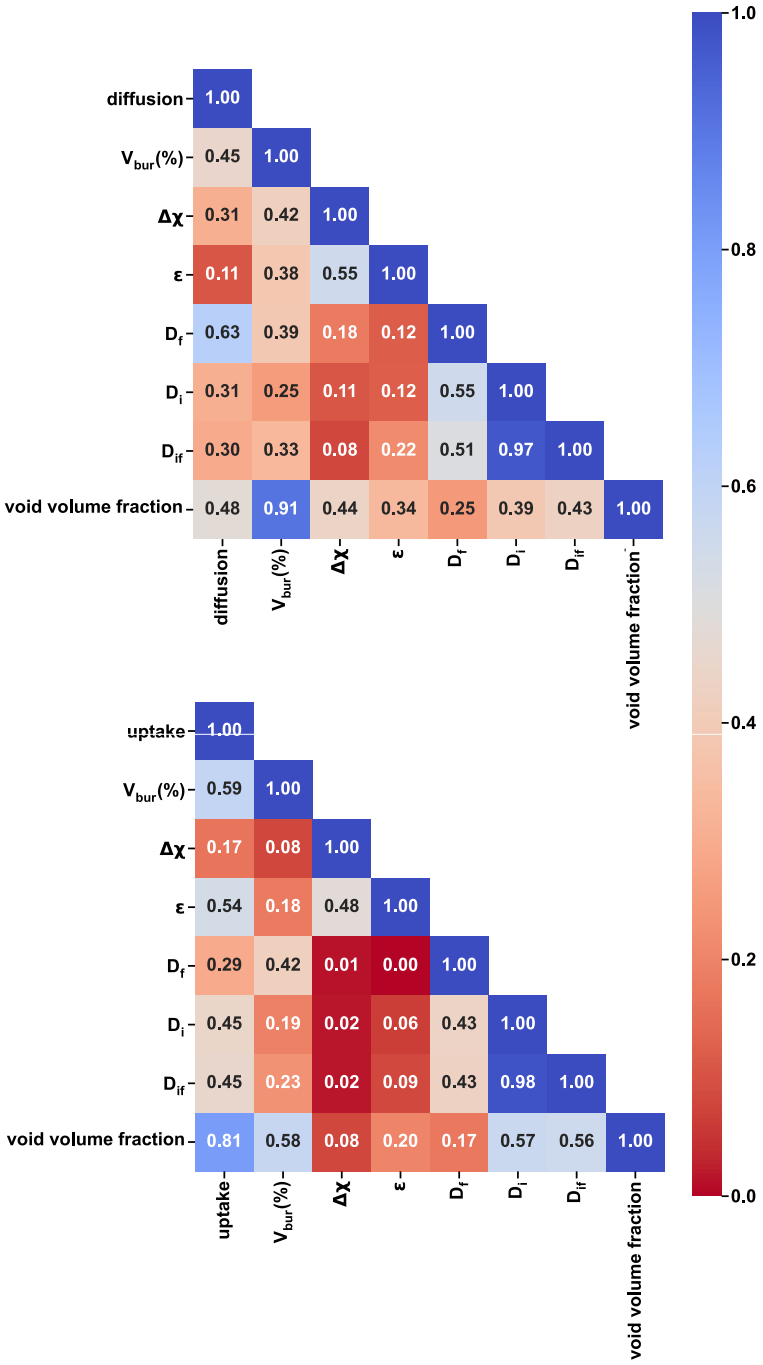

Figure S10. Lower triangular matrix of Pearson's correlation coefficients (absolute value) for geometric and chemical features along with methane diffusion (top) and uptake (bottom) at 298K and 65 bar. Only the diagonal of the matrix has a trivial value of 1.0. Features used here are buried volume (%V_{bur}) of the functional groups, electronegativity difference ($\Delta\chi$) of the two atoms most distant from the BDC ring, Lennard-Jones well depth parameter ε of the atom the most bond paths from the BDC carbon, largest free sphere (D_f), largest included sphere (D_i), largest included sphere along the free sphere path (D_{if}), and void volume fraction. The features for uptake and diffusion have different correlation values due to the difference in data set sizes (i.e., 5 functional groups for diffusion versus 13 for uptake).

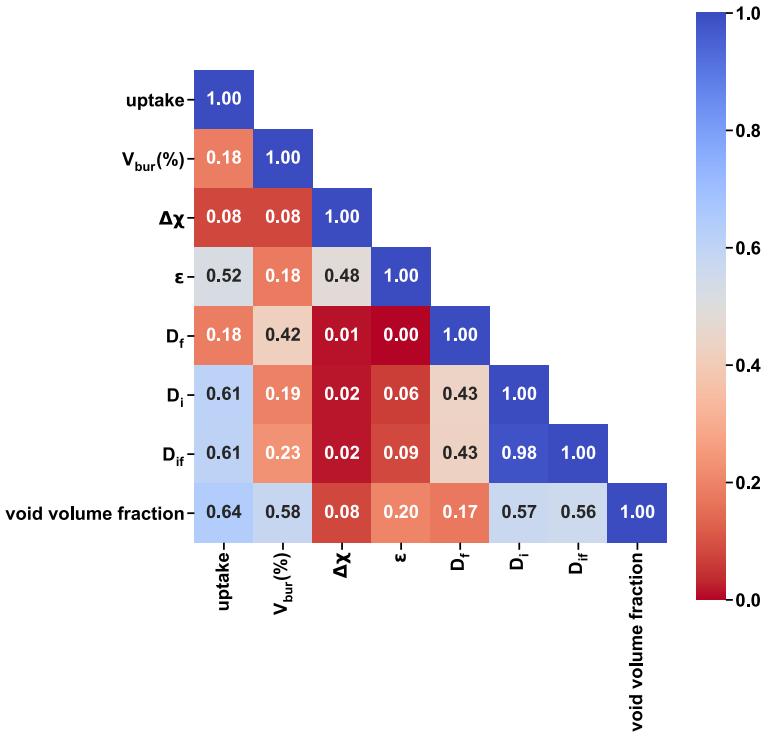

Figure S11. Lower triangular matrix of Pearson's correlation coefficients (absolute value) for geometric and chemical features along with methane uptake at 298K and 5.8 bar. Only the diagonal of the matrix has a trivial value of 1.0. Features used here are buried volume (%V_{bur}) of the functional groups, electronegativity difference ($\Delta\chi$) of the two atoms most distant from the BDC ring, Lennard-Jones well depth parameter ε of the atom the most bond paths from the BDC carbon, largest free sphere (D_f), largest included sphere (D_i), largest included sphere along the free sphere path (D_{if}), and void volume fraction.

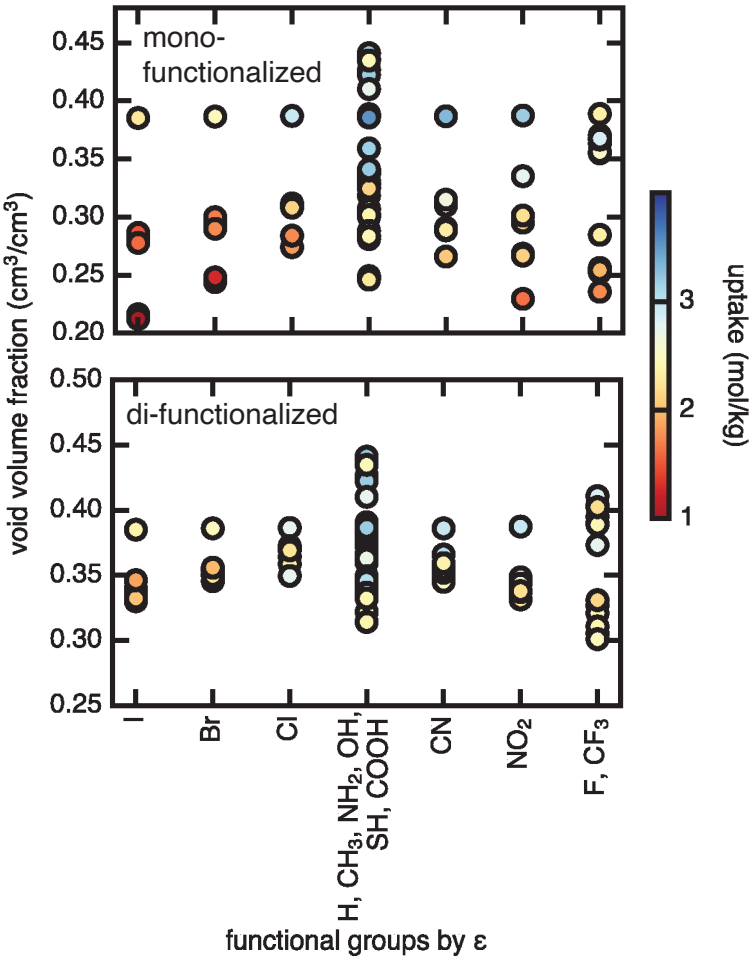

Figure S12. Methane uptake (in mol/kg) at 298 K and 5.8 bar, labeled by uptake according to the colorbar at right, in mono- and di-functionalized derivatives of UiO-66 as a function of two features: void volume fraction in cm^3/cm^3 (y-axis) and the Lennard-Jones potential well depth parameter ε (x-axis) of the functional group atom with the highest bond path from the terminal BDC carbon. The functional groups on the x-axis are ordered by decreasing ε from left to right, and functional groups that have the same ε are given the same x-axis position.

References

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