Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supplementary Information
for
Modeling diffusion of nanocars on a Cu (110) surface

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1. Simulation configurations

In addition to this document DFT optimized geometries for all nine molecules used in this study are provided in the format of an xyz file. Furthermore, LAMMPS[1] data files containing atomic positions for the molecules and the Cu (110) surface, as well as exemplary LAMMPS[1] input files for both molecular dynamics (MD) and transition state theory (TST) calculations are also provided.

2. Force field parameters

All molecules were assumed to be rigid and the Cu (110) surface atom positions were fixed during all simulations (including both MD and TST). Only vdW interactions between the molecule and surface were considered using a Lennard-Jones potential with a cut-off radius of 12.5 Å as implemented in LAMMPS[1] software package. The force field parameters were adopted from Universal Force Field (UFF)[2] and Lorenz-Berthelot mixing rules were applied. For classical MD simulations the parameters were used without change, however, for TST simulations all mixed parameters were scaled by 10 (see Table 1 below for all parameters used).

Table 1: Simulation parameters used in this study to calculate vdW energy using a Lennard-Jones potential. All parameters are for pairs of atoms where the epsilon values are in kcal/mol and sigma values are in Å.

	MD		**TST**	
Element Pair	**Epsilon** (kcal/mol)	**Sigma** (Å)	**Epsilon** (kcal/mol)	**Sigma** (Å)
Cu - B	0.15	3.376	1.5	3.376
Cu - C	0.115	3.272	1.15	3.272
Cu - H	0.074	2.842	0.74	2.842
Cu - N	0.093	3.187	0.93	3.187
Cu - O	0.087	3.116	0.87	3.116

3. Calculating diffusion coefficients from rigid body Molecular Dynamics simulations

For each molecule, the center of mass was calculated at every 1 ps and was used to calculate mean squared displacement (MSD) to estimate the diffusion coefficient. The MSD is calculated using the relation below:

$$MSD = \langle (x - x_0)^2 \rangle = \frac{1}{N} \sum_{i}^{N} [x_n(t) - x_n(0)]^2 \qquad Eq.1$$

where N is the number of particles to be averaged (in our case since there is only one molecule N becomes 1), $x_n(0)$ is the reference position, and $x_n(t)$ is the position at time t. Calculating MSD with respect to different reference times, we can plot MSD vs τ *(see Fig 1a)*. Repeating this for multiple runs to improve sampling we can then get an average MSD vs τ and using Einstein's relation we can calculate self-diffusion coefficient using the relation below:

$$MSD = (2nD)\tau + b \qquad Eq.2$$

where n is the dimensionality of motion, D is the self-diffusion coefficient, τ is the time delta, and b is the constant to the linear fit (see Figure 1b). For each molecule 1D self-diffusion coefficients in $[001]$ and $[1\bar{1}0]$ directions (corresponding to x and y axes in the MD simulations) were calculated (see Fig 1 – 5 below).

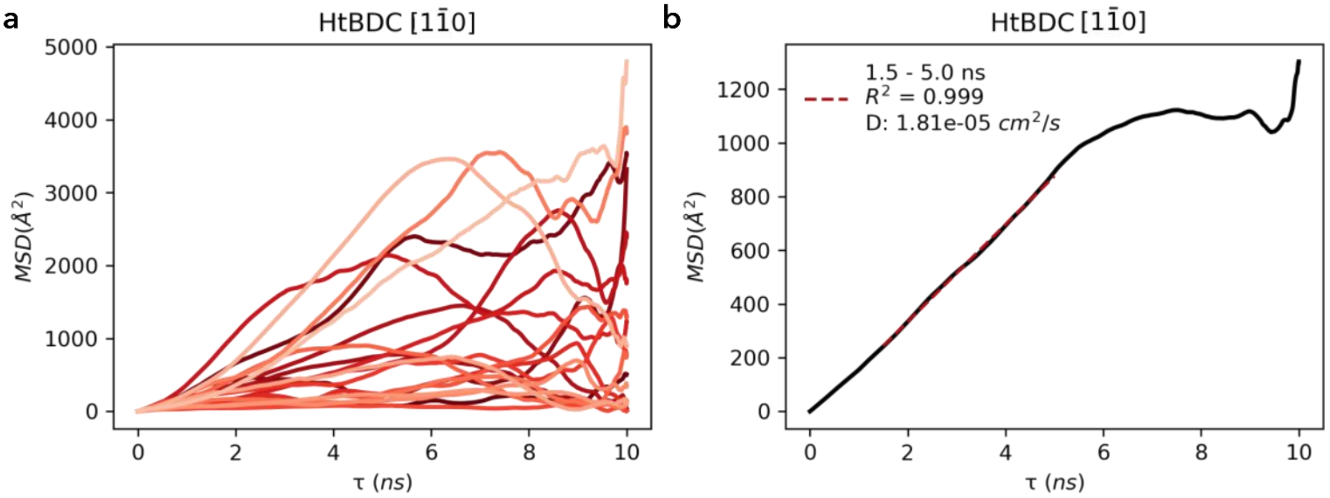

Fig 1: (a) Mean squared displacement (*MSD*) vs time delta (τ) for 20 molecular dynamics simulations in $[1\bar{1}0]$ direction for HtBDC molecule. (b) Average of all *MSD* vs τ curves and a linear fit between 1.5 ns – 5.0 ns to calculate self-diffusion coefficient. The R-squared value for the fit as well as the diffusion coefficient are given in the legend.

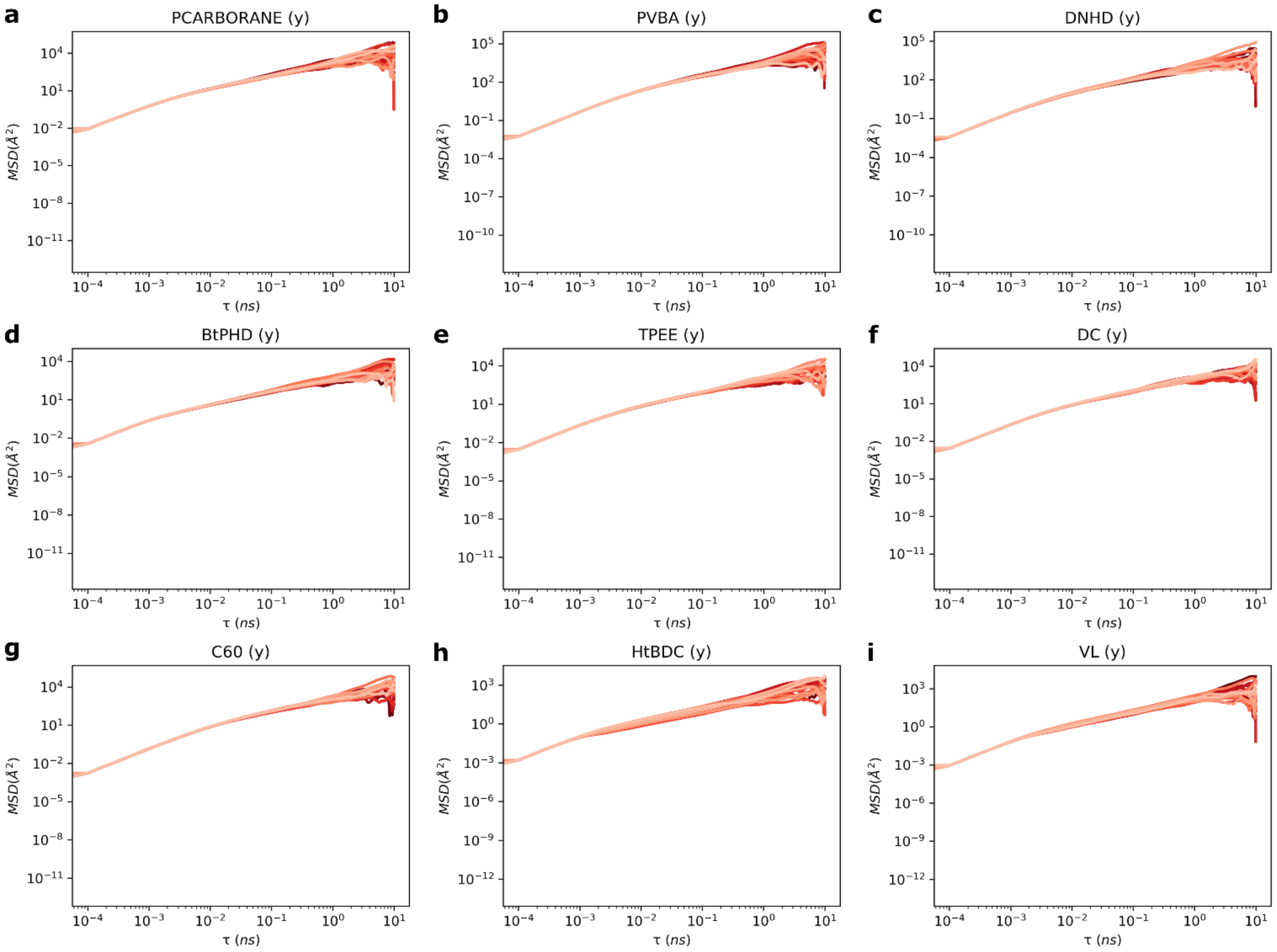

Fig 2: Log mean squared displacement (*MSD*) vs log time delta (τ) for 20 molecular dynamics simulations in $[1\bar{1}0]$ direction. Molecule names are given in the title.

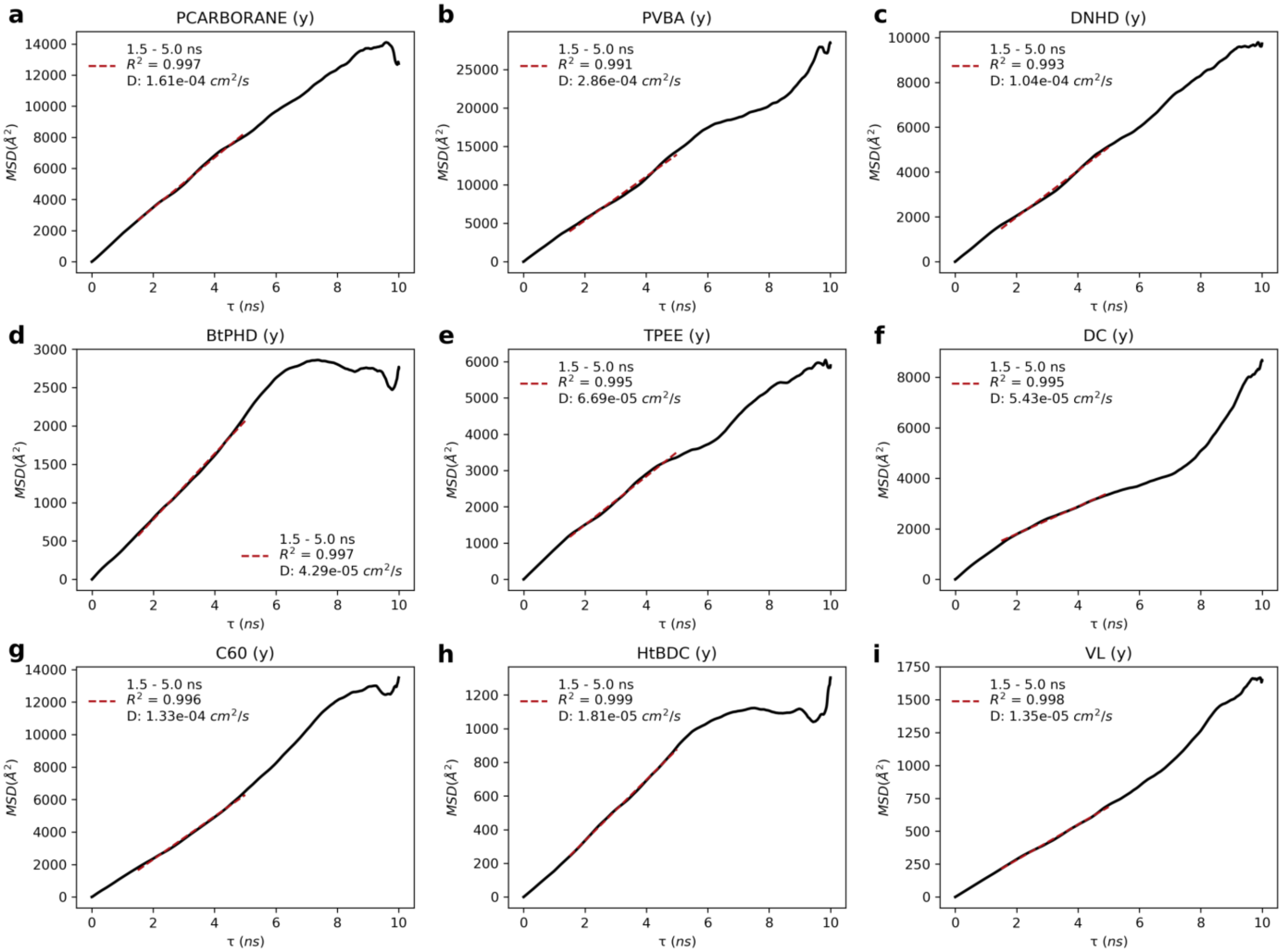

Fig 3: Averaged mean squared displacement (*MSD*) vs time delta (τ) for 20 molecular dynamics simulations in $[1\bar{1}0]$ direction. A linear fit between 1.5 ns – 5.0 ns was used to calculate self-diffusion coefficient. The R-squared value for the fit as well as the diffusion coefficients are given in the legend and the molecule names are given in the title.

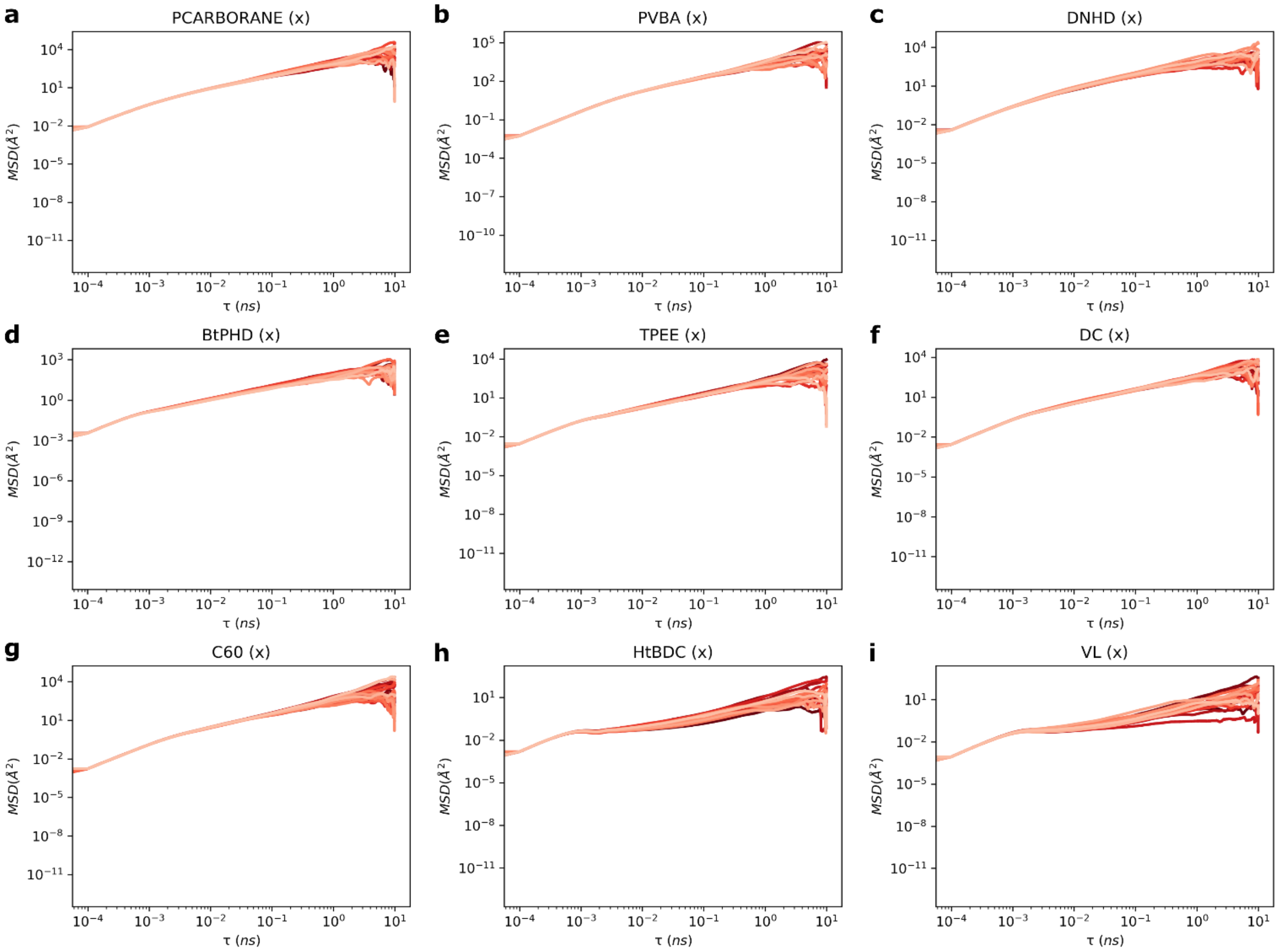

Fig 4: Log mean squared displacement (*MSD*) vs log time delta (τ) for 20 molecular dynamics simulations in $[001]$ direction. Molecule names are given in the title.

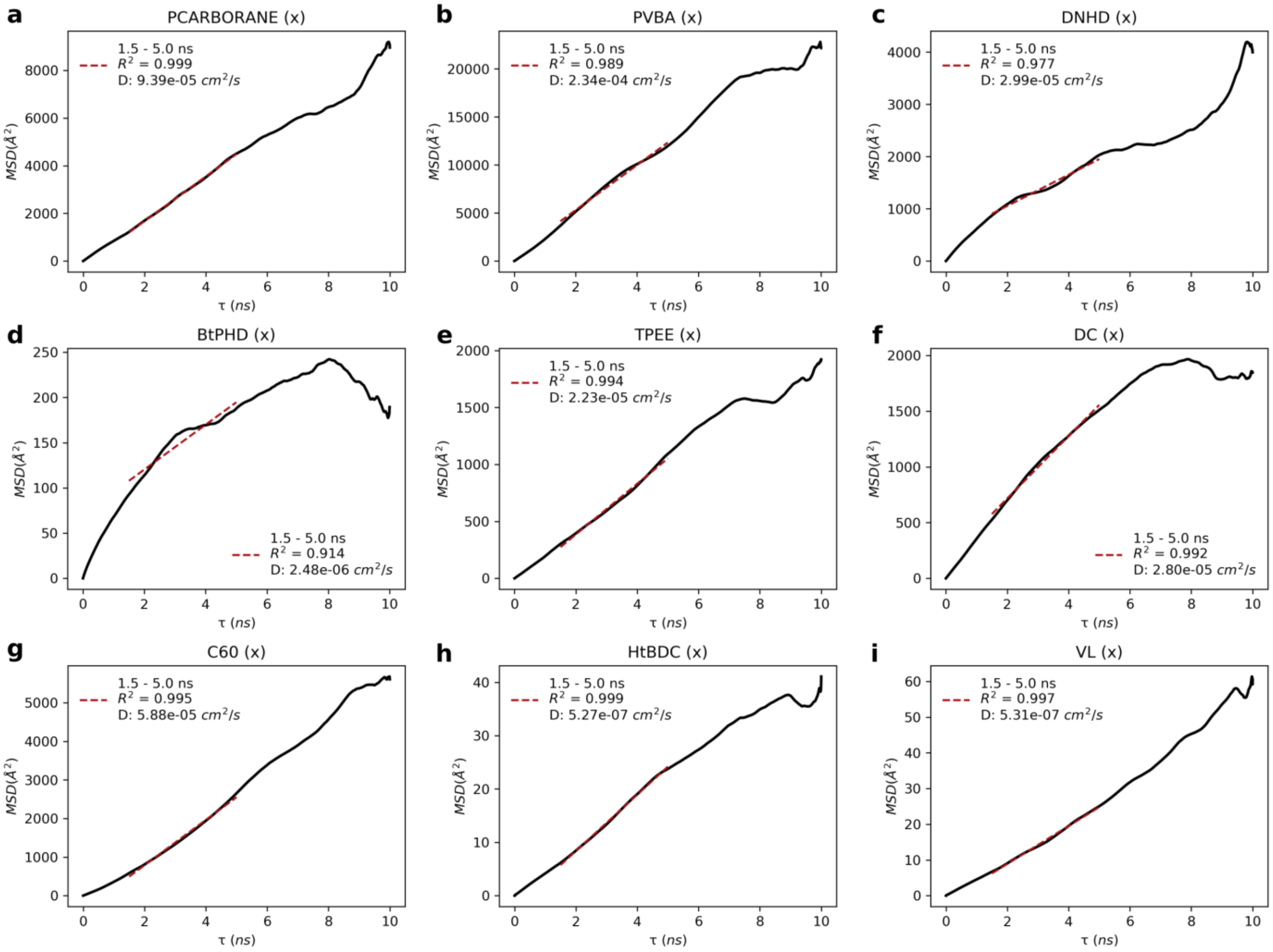

Fig 5: Averaged mean squared displacement (*MSD*) vs time delta (τ) for 20 molecular dynamics simulations in $[001]$ direction. A linear fit between 1.5 ns – 5.0 ns was used to calculate self-diffusion coefficient. The R-squared value for the fit as well as the diffusion coefficients are given in the legend and the molecule names are given in the title.

4. Transition state theory

As the diffusion of large molecules are quite slow and time scales cannot be achieved with classical MD simulations, we further increased adsorption energy by increasing LJ epsilon parameter of the surface atom and employed umbrella sampling and weighted histogram analysis method (WHAM)[3] to calculate free energy barriers for diffusion. We developed a Python wrapper for the WHAM implementation by Grossfield et al.[4] for this study which is freely available on GitHub.[5]

For the umbrella sampling, we divided the orthogonal unit cell of a Cu (110) surface (3.597 x 2.543 Å) using 0.1 Å grid spacing with two additional grid points on the edges of the cell resulting in 29 points in $[1\bar{1}0]$ and 39 points in $[001]$ directions (1131 total). For each point on the surface, we placed the molecule at that point and constrained its motion in $[1\bar{1}0]$ and $[001]$ directions in separate simulations using a spring with a constant of 200 kcal/mol. The motion in the direction perpendicular to the surface was not constrained.

For a given direction, periodic free energy barriers were calculated for each parallel pathway. For $[1\bar{1}0]$ direction 39 parallel paths were considered with 29 points in each path. For each of these paths the transition state energy was estimated and for given direction overall transition state energy was calculated using a Boltzmann average.

Using one dimensional transition state theory, hopping rate between these points were calculated using the equation below:

$$k_{A\to B} = \kappa \sqrt{\frac{k_B T}{2\pi M}} \times \frac{e^{-\beta F(q^*)}}{\int e^{-\beta F(q)} dq} \qquad Eq. 3$$

where $k_{A\to B}$ is hopping rate from state A to B, κ is transmission coefficient, k_B is Boltzmann constant, T is temperature, M is mass of the molecule, $F(q)$ is free energy at position q where * denotes the transition state position and $\beta = 1/k_B T$.[6] In this study the transmission coefficient κ was assumed to be 1. After calculating hopping rate, self-diffusion coefficient can be estimated using the relation below:

$$D_S = \frac{1}{2n} \times k_{A\to B} \times \lambda^2 \qquad Eq. 4$$

where n is dimensionality and λ is hopping length. As diffusion coefficient was calculated separately for each direction, dimensionality was taken as 1.

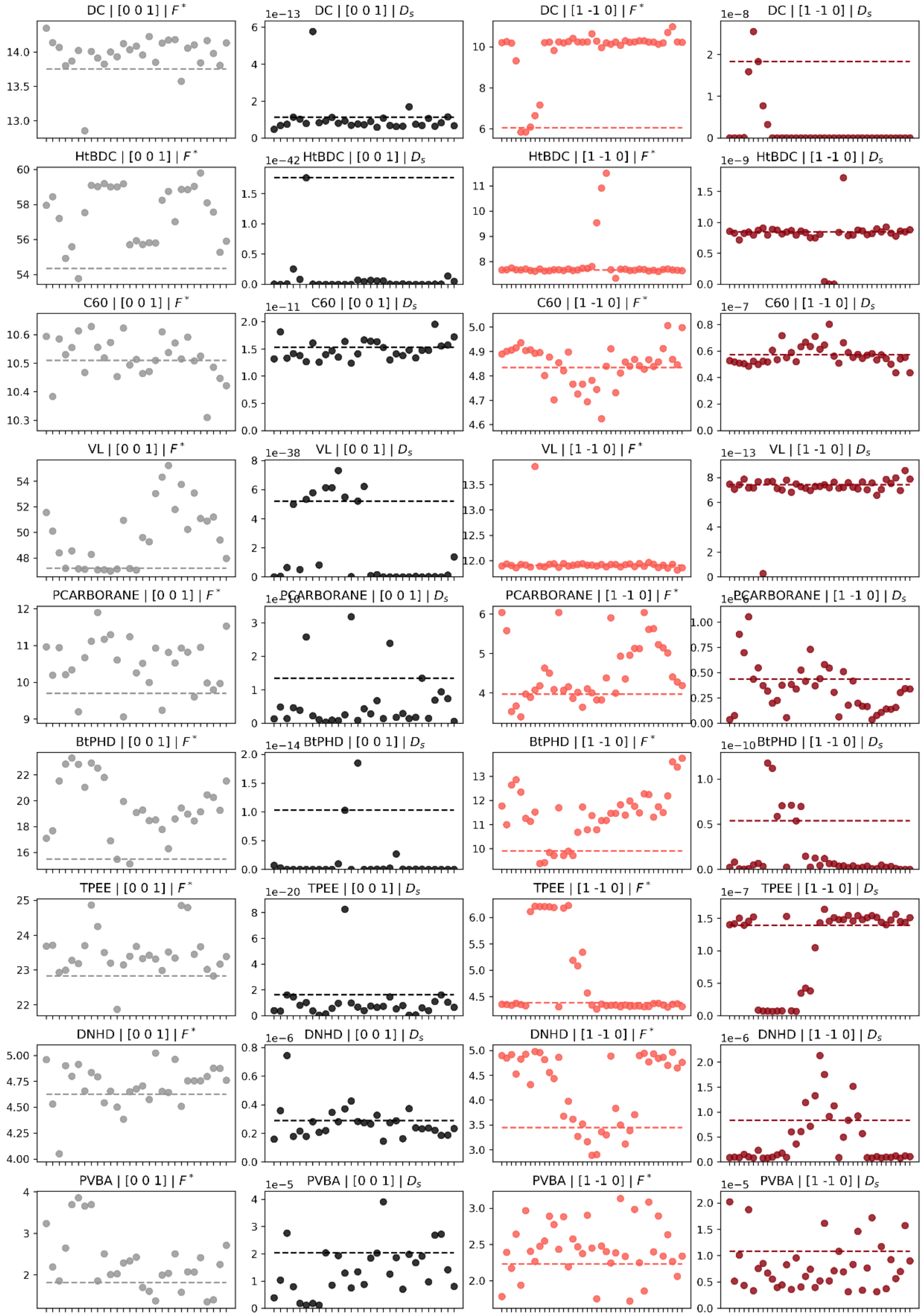

Fig 6: Free energy barriers and self-diffusion coefficients for each molecule and each umbrella sampling paths for the two primary crystallographic directions. Red and blue points correspond to results for $[001]$, and $[1\bar{1}0]$ directions, respectively. The dashed line represents the Boltzmann averaged value for the overall diffusion in that direction. The molecule name, crystallographic direction and variable names are given in the title.

5. Elevation weighted density

As discussed in the paper, we calculated elevation weighted density for each molecule according their orientation with respect to the surface. This calculation was done by counting the number of atoms within a selected cut off-distance (1 Å) as we discretely move up from the surface (with a step size of 0.05 Å) until we reach a distance of 12 Å (see Fig 7).

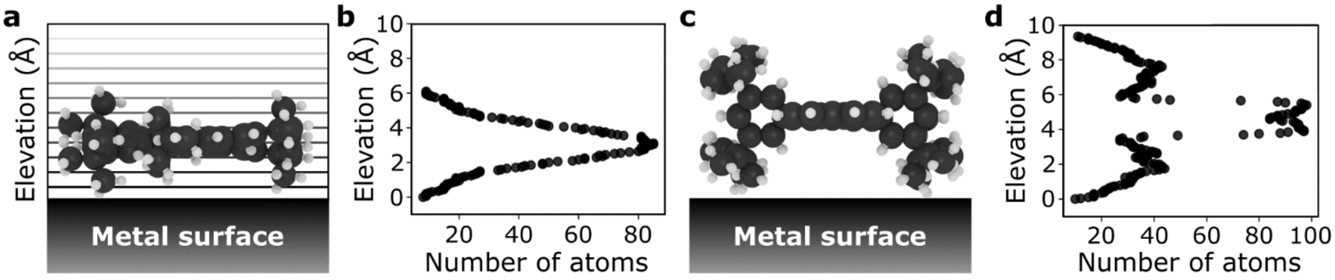

Fig 7: (a) Elevation weighted density calculation schematic for HtBDC. Starting from the bottom most part of the molecule, number of atoms are counted with 0.05 Å discrete steps and using a cut-off radius of 1 Å. (b) Plot of number of atoms with increasing elevation from the surface, i.e. elevation weighted density curve. (c) Side view of VL molecule on metal surface. (d) Elevation weighted density curve for VL molecule.

The resulting distance vs number of atoms graphs are plotted for each molecule in Fig 8 below. In order to calculate a scalar value from the curves in Figure 8, each point from *z=0* to *z=12* was scaled exponentially to reach zero at *z=12*, where *z* is the elevation in Å. An exponential decay equation was used for the scaling and the constants were chosen to make sure the scaling reaches to zero at the cut-off radius. The elevation weighted density equation form is given below:

$$\sum_{i=0}^{s\times r_c} N_{i/s}\left[a(1-b)^{i/s}\right] \tag*{$Eq.5$}$$

where r_c is the cut-off radius taken as 12 Å, $N_{i/s}$ is the number of atoms for a given elevation $z = i/s$, *a*, and *b* are the constants of the exponential decay equation which were taken as 0.376 and 0.4, respectively. *s* is the scaling factor that is used to adjust the step size of the increase in elevation. For this study an *s* value of 20 was used corresponding to a step size of 0.05 Å. $N_{i/s}$ is determined by counting the atoms at that elevation ($z = i/s$) within a cut-off radius of 1 Å. Furthermore, we calculated Spearman's rank correlation coefficients and p-values between elevation weighted densities and MD and TST results as implemented in scipy Python package. Results are given in Table 2 below.

Table 2 Spearman's rank correlation coefficient and p-values between elevation weighted density and parameters calculated using MD and TST simulations. D [0 0 1] and D [1 -1 0] indicate diffusion coefficients for MD and TST results. E(vdW) is the average vdW interaction energy during MD simulations in kcal/mol. F* [0 0 1] and F* [1 -1 0] are free energy barriers of diffusion calculated with umbrella sampling.

		rho	**p**
MD	**D [0 0 1]**	-0.917	0.001
	D [1 -1 1]	-0.917	0.001
	E (vdW)	-0.783	0.013
TST	**D [0 0 1]**	-0.883	0.002
	D [1 -1 0]	-0.733	0.025
	F* [0 0 1]	0.883	0.002
	F* [1 -1 1]	0.733	0.025

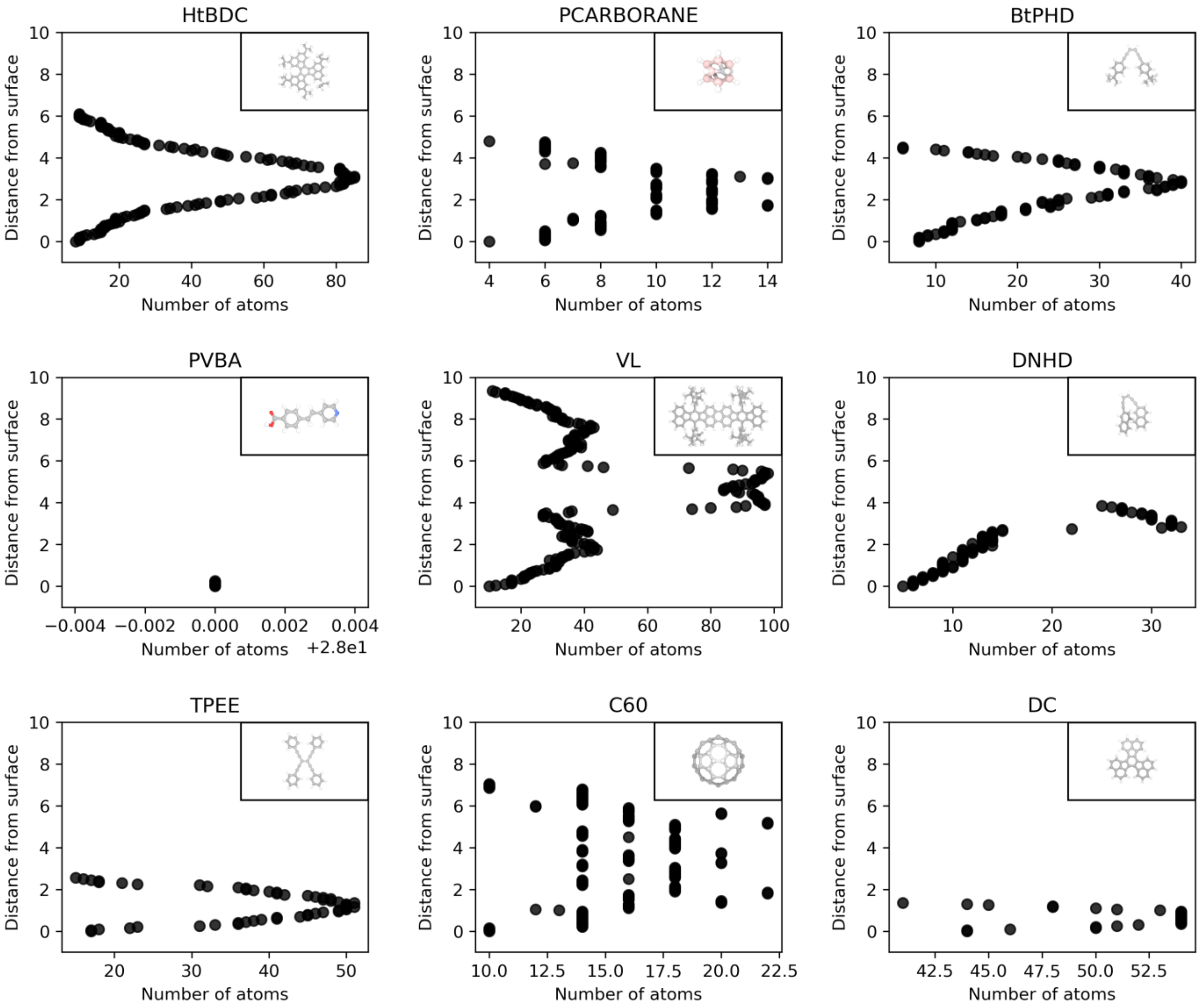

Fig 8: Elevation weighted density curves for the nine molecules used in this study.

6. MD and TST Results

The molecule names, molecular weights, elevation weighted densities and the resultds obtained from MD and TST calculations are presented in Table 3 below.

Table 3 Tabulated results for each molecule. MW is molecular weight in g/mol, EWD is elevation-weighted-density. D [0 0 1] and D [1 -1 0] indicate diffusion coefficients in cm^2/s for MD and TST results. E(vdW) is the average vdW interaction energy during MD simulations in kcal/mol. F* [0 0 1] and F* [1 -1 0] are free energy barriers of diffusion in kcal/mol calculated with umbrella sampling.

			MD			TST			
Molecule	**MW**	**EWD**	**D [0 0 1]**	**D [1 -1 0]**	**E(vdW)**	**D [0 0 1]**	**D [1 -1 0]**	**F* [0 0 1]**	**F* [1 -1 0]**
PCARBORANE	144.23	110.66	9.31E-05	1.57E-04	-9.27	1.67E-10	5.45E-07	9.70	3.96
PVBA	225.24	126.71	2.29E-04	2.94E-04	-17.03	2.09E-05	1.06E-05	1.82	2.23
DNHD	328.41	232.01	3.08E-05	1.04E-04	-16.79	3.20E-07	1.11E-06	4.63	3.45
BtPHD	340.50	322.72	2.36E-06	4.46E-05	-22.17	1.34E-14	7.24E-11	15.49	9.91
TPEE	428.52	408.99	2.30E-05	6.36E-05	-29.74	3.17E-20	1.43E-07	22.83	4.38
DC	450.53	406.61	2.70E-05	5.27E-05	-33.44	1.85E-13	1.83E-08	13.75	6.05
C60	720.64	217.93	6.14E-05	1.38E-04	-15.20	1.51E-11	5.77E-08	10.51	4.83
HtBDC	787.17	465.39	5.13E-07	1.84E-05	-28.07	1.23E-42	8.78E-10	54.33	7.66
VL	1401.98	503.15	5.38E-07	1.37E-05	-27.73	5.58E-38	7.39E-13	47.20	11.91

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