

## Computer modeling of 2D supramolecular nanoporous monolayers self-assembled on graphite

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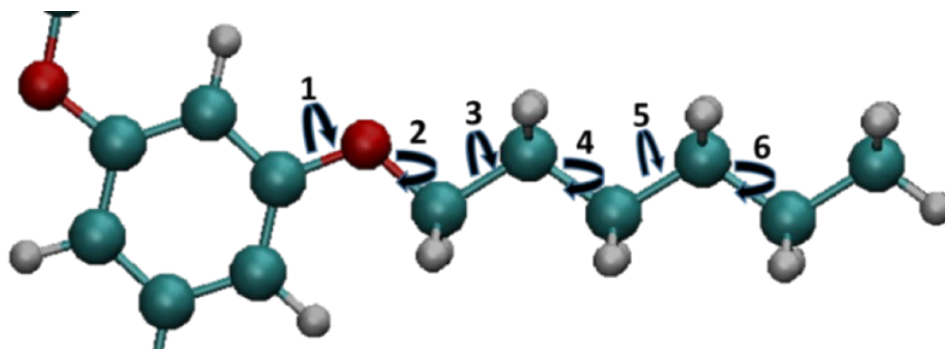
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### 1. Visual representation of the dihedral angles D1-D6.



The numbers 1-6 correspond to the rotation axes of the dihedrals D1-D6:

D1: CC-OC

D2: CO-CC

D3: OC-CC

D4-D6: CC-CC

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## 2. Setup of Molecular Dynamics simulations.

All MD simulations were performed using the NAMD2<sup>1</sup> code running on a 24 Intel Xeon E5-2620 processors Linux machine. To speed the calculation, the length of hydrogen bonds in the adlayer and the positions of the carbon atoms in the bulk graphite were fixed, allowing the use of a 1 fs time step. Calculations were performed in the *NVT* canonical ensemble using a velocity-rescaling thermostat. Periodic boundary conditions (PBC) were implemented in all directions. In the direction perpendicular to the basal graphite plane, the simulation cell size was chosen sufficiently large to neglect the effects of PBC's in this direction. In the direction parallel to the basal graphite plane the commensurability of simulation cell, graphite, and TSB3,5-C6 monolayer was assured by the parameters  $(k_1, k_2)$  described in the main text. All simulations were run for a period of 6 ns of equilibration ( $6 \times 10^6$  steps), followed by an additional 6 ns production runs used for averaging

All particle-particle interactions are modeled and defined in the CHARMM General Force Field (CGenFF).<sup>2,3</sup> Bonded internal molecular degrees of freedom considered are (i) the two-body stretch (bond), (ii) the three-body bend (angle and Urey-Bradley) and (iii) the four-body torsion (dihedral). The molecular geometric parameters  $b_0, \theta_0, s_0,$  and  $\delta,$  as well as atomic partial charges were determined from *ab initio* calculations using the Gaussian 09 code going up to the 2<sup>nd</sup> order Møller–Plesset (MP2) theory<sup>4,5</sup> using Pople's 6-31g(d,p) basis set.<sup>5,6</sup> The elastic force constants  $k_b, k_\theta, k_{UB}, k_\chi,$  and the dihedral multiplicity  $n$  were obtained from the CGenFF.

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The non-bonded terms (the Lennard-Jones (12-6) potential and the Coulomb potential) were calculated for both inter- and intra-molecular interactions. Lennard-Jones nonbonded parameters were taken from the CGenFF literature.<sup>2,3</sup> Lorentz-Berthelot mixing rules were employed for Lennard-Jones interactions between different atoms. For intra-molecular (non-bonded) terms, the standard “1-4 scaling”, with scaling factor equal 0.4 has been used.<sup>7,8,9,10</sup> For all 1-5 atom pairs and beyond, we fully accounted for both non-bonded potential energies, up to the cutoff distance for pair separation set at 12 Å (with a linear rollover at 10 Å). Particle Mesh Ewald (PME) summation for the electrostatic energy has not been employed. Instead we have used the NAMD2 option that forces the electrostatic energy to reach zero at the cutoff distance by way of an overall downward shift.

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