

SELF-ASSEMBLED ORGANIC MONOLAYERS AS MOLECULAR SIEVES:
AB INITIO AND MOLECULAR DYNAMICS STUDIES

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ABSTRACT

We present the results of extensive fully atomistic Molecular Dynamics (MD) simulations of the self-assembled organic monolayer (SAOM) consisting of interdigitated molecules of 1,3,5-trisubstituted benzene substituted by alkoxy peripheral chains containing $n = 6, 8, 10, 12$, or 14 carbon atoms (TSB3,5- C_n or TSB35), deposited onto highly-ordered pyrolytic graphite (HOPG). We focus on the TSB3,5- C_6 and the TSB3,5- C_{10} systems. Our studies begin with the *ab initio* determination of the optimal electronic structure of the TSB35 molecule, from which we find the optimal lattice geometry, and reproduce experimental results for the TSB35 monolayer. The structure and functionality of the TSB35 monolayer as a “molecular sieve” is then explored through fully atomistic MD simulations where we find the monolayer to be stable and well-ordered around room and biological temperature. We construct probability distributions for dihedral angles and pore diameter to characterize order in the monolayer and the phase transitions that it undergoes. We then introduce guest organic molecules (e.g. benzene, pyrene, coronene) into the nanoporous host structure and observe how the stability of the TSB35 monolayer is affected by such additions.