Modelling Of Supramolecular Network Deposited On A Semiconductor Surface

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ABSTRACT

We investigated the self-assembly mechanisms and electronic properties of highly-symmetric organic molecules based on a substituted 1,2,5-tri(4-phenyl)benzene core[1], deposited on a passivated boron-doped Si(111)-$\sqrt{3}$x$\sqrt{3}$*R30°* surface, by using *ab-initio* calculations, empirical molecular dynamics and metadynamics. The electronic properties of the isolated molecules in vacuo have been calculated using GAUSSIAN03 software. The different molecular conformations have been optimized assuming the highest symmetry group (D3h) for all the molecules. Very similar electronic properties (HOMO-LUMO gap, Mülliken charge distribution, vertical ionization potential, adiabatic electronic affinity) have been observed for the different molecules, despite the presence of various terminations (such as H, bromine, iodine, biphenyl, cyanobiphenyl, phenylpyridin, iodobiphenyl). The minor variation in the electronic properties does not explain the large differences observed in the experimental STM images of supramolecular networks [1,2]. Next, combination of empirical molecular dynamics using DLPOLY software and metadynamics using the PLUMED plugin with the MM3 molecular force field have been undertaken for the cyanobiphenyl substituted molecule, by using the results of *ab-initio* calculations as input for the molecular structure. The first simulations allowed us to reconstruct a very similar network with that observed on the STM images. By calculating the ratio of interaction molecule-network and molecule-surface, we highlight the influence of Van der Waals interactions for the stability of the supramolecular network. Current molecular dynamics simulations focus on the monolayer vs. bilayer assembly mechanisms in order to explain the structural differences of the network between a single and a double deposition of the molecule visible on STM images.

REFERENCES

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