Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics. This journal is © the Owner Societies 2015

Supplementary information

Observation and modeling of the conformational molecular structures driving the self-assembly of tri-adamantylbenzene on Ag(111)

Bastien Calmettes, Nicolas Estrampes, Christophe Coudret and Roland Coratger¹

CEMES/CNRS and Université Paul Sabatier 29, rue J. Marvig BP 94347 31055 Toulouse, France

Thomas J. Roussel and Jordi Faraudo

Institut de Ciència de Materials de Barcelona Consejo Superior de Investigaciones Científicas. (ICMAB-CSIC). Campus de la UAB, 08193 Bellaterra, Spain.

This supplementary information document includes: Molecular Dynamics (NAMD) supplementary information:

- construction of a cluster of 79 TAB molecules
- PME representation using VMD
- Room temperature MD

Monte Carlo(SANO) supplementary information:

- Radial pair correlation function (g(r))

¹ Corresponding author

Molecular Dynamics (NAMD) supplementary information:

We have performed Molecular Dynamics calculations using the NAMD software, 1 version 2.9 running in parallel on a local cluster. The equations of motion were solved with a 2 fs time step. The constant temperature (300K) ensemble (NVT) was controlled using the Langevin thermostat with a relaxation constant of 1 ps⁻¹.

The model for the TAB molecules was based on the CHARMM force field, designed for biomolecular simulations. To our knowledge, TAB molecule has not been previously simulated entirely within the selected force field, however it has been successfully employed for simulations of Adamantane.^{2, 3} The intramolecular and intermolecular parameters were determined taking advantage of the automation the CHARMM General Force Field (CGenFF,^{4,5,6} in its version number of the interface 0.9.7.1 and the force field 2b8), which provides the atom typing and assignment of parameters and charges by analogy with sub-functional groups (i.e. the Adamantane). When CGenFF is guessing some parameters by analogy, penalties are addressed and were less than 20 meaning fairly analogue, and quite reliable. Input files are available upon request.

We first minimized the freestanding molecule, then, the atomic structure once adsorbed on a Ag(111) surface made of four layers. Fig. 1 below shows the partial charge distribution based on CGenFF parameterization, which appears consistent with the previous model OPLS. Molecule-surface parameters are equivalent since they were transposed for both force fields (OPLS-AA and CHARMM).



Figure 1: TAB molecule with (CGenFF) partial charges represented in color scale (e-).

Then we have built a cluster of 79 TAB molecules for an intermolecular distance of 14,6 Å in an hexagonal lattice (Fig. 2: red and blue points). The contour of the cluster is following the morphology of the experimental one (red points). We have rotated the cluster by 7 degrees to obtain a better match with the experiment. Since the atomic resolution could not be reached experimentally, we started with the assumption that all the molecules were in the same orientation with one adamantane following the [1-10] direction of the substrate.



Figure 2: Initial configuration for modeling 79-TAB molecules cluster based on the experimental observation in a hexagonal distribution.

We have minimized the total potential energy using NAMD. The calculation performed after 10 ns of standard minimization are presented in Fig. 3. Interestingly, during the MD run of 20 ns at room temperature, we observe that not only the molecule can rotate on the surface, but also the adamantane groups also rotate.



Figure 3: Snapshot of a configuration taken after 20 ns of MD modelling.

The atomic detailed initial configuration is represented as spacefill in Fig. 2 (right) and in Fig. 3 (left) in ball and sticks, in the TAB0.3 conformation. Fig. 3 (right) represents the configurations after minimization of the potential energy. After minimization, one observes the rotation of the ADT functional groups, in general, one over three. The inset gives a better view of the rotated ADTs, which points out to the <111> direction. Most of the molecules have turned out to TAB1.2 (lateral) conformation.

One evaluates the reciprocal sum of the smooth particle-mesh Ewald method (PME), producing a smoothed electrostatic potential grid. ⁷



Figure 4: PME plot obtained from VMD (Visual Molecular Dynamics). The hexagonal lattice spacing is highlighted with the black lines, while the resulting hollows hexagonally distributed are emphasized in blue.

Obviously this calculation can not be directly compared to a STM imaging, but it reveals the nature of the hollows observed experimentally in the cluster. The PME representation tends to confirm the hypothesis that the observed experimental cluster is made of molecules with same orientation.

The molecules localized in the core of the cluster remain globally with the same orientation. Some in the contour tend to get in a closer-compact configuration by rotating slightly, as shown in the Fig. 4 below. This configuration could be obtained after a longer minimization time. We observe that some molecules have rotated keeping the hexagonal stacking but loosing the hexagonal lattice of hollows on the electrostatic potential density. Experimentally, one observes similarities in the contrast STM image where molecules are misaligned.



Figure 5: PME plot extracted from VMD. The substrate is not represented.

We have performed 20 ns run at fixed temperature 280K (NVT) using NAMD and the cluster rapidly converged to the following compact structure, like the one obtained in Fig. 7 of the main manuscript, although we observe many molecules TAB3.0, TAB2.1, TAB1.2 are found.



Figure 6: Snapshot of the final configuration of the 79TAB cluster obtained at 280K.

Monte Carlo(SANO) supplementary information:

Pair correlation function (g(r))

We have calculated the pair correlation function of the molecules using the only center of the benzene group and produced from 50 configurations taken along the final production MC runs at 280K.



Figure 7: Pair correlation functions for TAB0.3 and TAB1.2 extracted from Figs. 7 and 8 of the main manuscript.

(1) J. C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot,
R. D. Skeel, L. Kale and K. Schulten, *J. Comput. Chem.*, 2005, 26, 1781–1802.

(2) K. Vanommeslaeghe, E. Hatcher, C. Acharya, S. Kundu, S. Zhong, J. Shim, E. Darian, O. Guvench, P. Lopes, I. Vorobyov, A. D. MacKerell Jr., CHARMM General

Force Field: A Force field for Drug-Like Molecules Compatible with the CHARMM All-Atom Additive Biological Force Field, J. Comput. Chem. 2010, 31, 671-690.

(3) W. Yu, X. He, K. Vanommeslaeghe, A. D. MacKerell Jr., Extension of the CHARMM General Force Field to Sulfonyl-Containing Compounds and Its Utility in Biomolecular Simulations, *J. Comput. Chem.* **2012**, 33, 2451-2468.

(4) ParamChem interface: https://cgenff.paramchem.org

(5) K. Vanommeslaeghe, A. D. MacKerell Jr., Automation of the CHARMM General Force Field (CGenFF) I: bond perception and atom typing, J. Chem. Inf. Model. 2012, 52, 3144-3154.

(6) K. Vanommeslaeghe, E. P. Raman, A. D. MacKerell Jr., Automation of the CHARMM General Force Field (CGenFF) II: Assignment of bonded parameters and partial atomic charges, J. Chem. Inf. Model. 2012, 52, 3155-3168.

(7) A. Aksimentiev and K. Schulten. *Biophysical Journal*, **2005**, 88:3745-3761.