

Understanding Nucleation And Self-Assembly Of Large Organic Molecules On An Insulating Surface

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We used non-contact atomic force microscopy (NC-AFM) and theoretical simulations to study the adsorption, diffusion, film stability, de-wetting, and desorption of functional organic molecules on bulk insulating surfaces at a range of different temperatures. Our results focus on the importance of molecular mobility and flexibility in order to provide insight into the mechanisms that drive self-assembly in these systems.

Two functionalised molecules, 1,3,5-tri-(4-cyano-4,4 biphenyl)-benzene (TCB) and 1,4-bis(cyanophenyl)-2,5-bis(decyloxy)benzene (CDB), were deposited and annealed on the KCl(001) substrate at temperatures between 300K to 440K and imaged using NC-AFM. CDB self-assembled structures were observed to grow from step edges, while TCB self-assembled structures grew as islands on the terrace and from step edges. Complementary theoretical calculations using van der Waals corrected DFT-D3 were used to study the adsorption of single such molecules on the KCl (001) surface and to investigate the difference in growth mechanism. Using a genetic algorithm an empirical force field was parameterised for each molecule, which were used in conjunction with molecular dynamics (MD) to study the diffusion of individual CDB and TCB molecules on terraces and at step edges. The results demonstrate that the conformational flexibility of the CDB molecule allows it to interact strongly with steps and kinks, where nucleation and subsequently cluster growth occurs. In contrast, the rigid TCB molecule is unable to adapt to step edges and kinks with a significant entropy loss upon adhesion on step edges, leading to different monolayer growth modes. Minimum energy monolayer structures were deduced from NC-AFM data and their stability was investigated in MD simulations. Our results compare well to experimental NC-AFM observations of film stability.