

Highlights

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Post-Deposition Wetting and Instabilities in Organic Thin Films by Supersonic Molecular Beam Deposition

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In this study, we discuss the formation and post-deposition instability of nanodrop-like structures in thin films of PDIF-CN₂ (a perylene diimide derivative with electron-transporting character – see Fig. 1a for a sketch) deposited via supersonic molecular beam deposition (SuMBD) technique on highly hydrophobic substrates. SuMBD technique was initially applied to check whether the huge kinetic energy of the depositing molecules could induce the superheating effect, thus preserving the occurrence of the crystallization processes during the PDIF-CN₂ film growth even keeping the substrate at room temperature. Surprisingly, we observe the formation of nanostructured thin films (with separated nano-drop structures see Fig. 1b) accompanied by the presence of a wetting instability in the condensate. This instability provides a remarkable evolution of the electron field-effect mobility and surface morphology of the film (see Fig. 1c) over a time scale of weeks or months. The role of the deposition rate on the characteristic lengths of organic nano-drops was studied by atomic force microscopy and the use of the height-height correlation function was effective to establish a link between morphological mechanism and growth. The nano-drops represent a metastable configuration for the freshly-deposited films and, for this reason, post-deposition wetting effects have been examined with unprecedented accuracy throughout one year. The observed time scales, from few hours to months, are related to the growth rate and characterize the thin films morphological reordering from three-dimensional nano-drops to a well-connected terraced film (see Fig. 1d). While the interplay between adhesion and cohesion energies favors the formation of 3D-mounded structures during the growth, the wetting phenomenon following the switching off of the molecular flux is found to be driven by an instability. A slow rate downhill process survives at the molecular flux shutdown and it is accompanied and maybe favored by the formation of a precursor layer composed of molecules with a dominant lying-down configuration. These results are supported by simulations based on a non-linear stochastic model, describing the instability phenomenon for both the growth and the post-growth evolution. To better reproduce the experimental data, it is needed to introduce a surface equalizer term characterized by a relaxation time taking into account the presence of a local mechanism of molecular correlation.

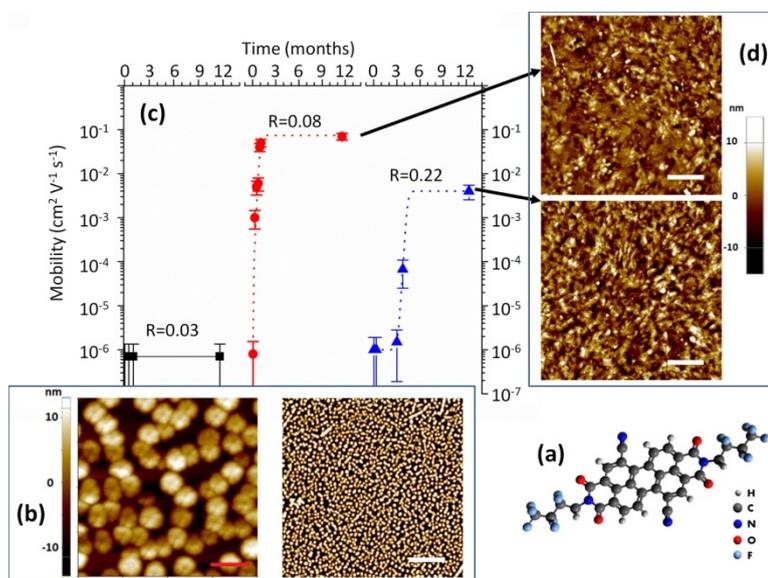


Fig. 1: (a) A sketch of the PDIF-CN₂ molecule. (b) 1x1 μm² and 5x5 μm² AFM images acquired just after the deposition using SuMBD on HMDS-treated SiO₂ at room temperature. The white and red markers are 1 μm and 250 nm, respectively. (c) Field-effect mobility values over time measured for PDIF-CN₂ films deposited at different deposition rates (R=0.03, 0.08, 0.22 nm/min). (d) 5x5 μm² AFM images of the film morphologies acquired after 1 year. At R=0.03 nm/min the nanostructured morphology and the field-effect mobility don't change with time.