Organic molecules have high potential for thin film applications like organic solar cells (OSC), light emitting diodes (OLED) and thin film transistors (OTFT). In order to access their full potential, a deep molecular understanding of the systems is necessary, in particular of the initial growth and the formation of the first molecular layer, as this layer acts as a template for further growth.

In the field of molecular adsorption and thin films, the perylene derivative perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) was frequently and intensively studied within the last decades. Basically all geometric, electronic and optical properties of PTCDA thin films and monolayers on noble metal surfaces were investigated and are well understood. However, the growth itself was investigated only occasionally and qualitatively. Here we try to fill this gap of knowledge with a Low-Energy Electron Microscopy (LEEM) study. The growth of the first monolayer of PTCDA on Cu(001) is studied in-situ and in real-time (Fig. 1).

By analyzing size distributions of the islands within the aggregation regime and applying methods developed for atomic nucleation on surfaces [1, 2] we were able to determine the critical cluster size \( i \) for the formation of stable islands. This has been performed for different temperatures between 300 K and 350 K. The fact that values of \( i = 1 \) and \( i = 2 \) have been obtained for these temperatures enabled us to furthermore determine the interaction energies \( E_B^{(1)} \) and \( E_B^{(2)} \), which represent the diffusion barrier for individual molecules and the binding energy of a cluster of two molecules, respectively. For both energies we have determined relatively high values of \( E_B^{(1)} = (0.45 \pm 0.21) \) eV and \( E_B^{(2)} = (1.6 \pm 0.5) \) eV. They can be understood in terms of van der Waals and electrostatic interaction as well as hydrogen-bonding between neighboring molecules.

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