Doctoral Thesis

Atomic force microscopy of organic nonlinear optical molecules at the gas-liquid and gas-solid interface

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Atomic force microscopy of organic nonlinear optical molecules at the gas-liquid and gas-solid interfaces

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Abstract

The structure and intermolecular forces of the surface of organic materials showing high nonlinear optical susceptibilities were investigated.

The first part of the dissertation is devoted to Langmuir and Langmuir Blodgett (LB) films, which are defined as monolayers floating at the air-liquid interface and multilayers deposited on a solid substrate, respectively.They were studied during the whole formation process. Organic components with high hyperpolarizabilities (chromophores), determined by Electric-Field Induced Second Harmonic generation experiments (EFISH) and calculated theoretically by a semi-quantum mechanical method, were attached to hydrocarbon chains to form LB molecules. The obtained floating films and the layers transferred onto a solid substrate were investigated by force methods and optical microscopy. The LB structure was simulated and predicted theoretically by force field techniques.The unit cell of 2-docosylamino-5-nitropyridine (DCANP) and 2-(21'-docosenyl)-amino-5-nitropyridine (VECANP) was determined experimentally by high resolution microscopy. The film formations, particularly the macro- and micromolecular structures of the different material phases, are theoretically and experimentally explained. The order of the 2-dimensional solid-liquid phase transitions was determined for each LB-film. We observed deterioration of the transferred monolayers on solid. The air humidity modified the crystalline structures of the LB films and provoked holes.

A special atomic force microscope to image the Langmuir films floating at the air-water interface in high resolution was constructed for the first time. The results presented here show that the tip of the underwater atomic force microscope stays in feedback for each Langmuir film type, but only very stable films, with a second order liquid-solid phase transition, could be imaged. Molecular resolution of arachidic acid and nitropyridine films floating at the air-liquid interface are also presented in this work.

Stable Langmuir and Langmuir Blodgett film of molecules with very high hyperpolarizability coefficients (N-nitrostilbene derivatives) were fabricated for the first time and are presented in this dissertation. The macroscopic domain structure and its formation were studied by optical microscopic techniques (absorption enhanced contrast and second harmonic generation) as well as by scanning force techniques (2-dimensional surface pressure / area diagram measurement, atomic force microscopy (AFM)). The films show a first order solid-liquid phase transition. The solid phase is crystalline and noncentrosymmetric. The crystalline domains were very stable and could be transferred onto a solid substrate without modifying their macroscopic and microscopic structures. The transferred and floating monolayers show a large second harmonic intensity, about ten times larger than that of DCANP. The second harmonic could be observed by unassisted visual inspection alone. The monolayers could not, however, be superposed.

In the second part of this work, some previously developed organic nonlinear optical crystals (2-cyclooctylamino-5-nitropyridine (COANP), and 4-N,N-dimethyl-stilbazolium tosylate (DAST)) were investigated by AFM. In contrast to previously used optical methods, scanning force microscopy allows the observation of local effects. Growth surfaces as well as cleaved surfaces were measured. It was observed that the external layers of crystals having predominantly van der Waals binding forces, and to a smaller extent also the ionic crystals, are deformed and dissolved by the humidity in the air. On cleaved surfaces, the monomolecular layer can be observed and the thickness determined: in the case of DAST, both of the layers consisting alternatively of two different molecules could be distinguished. High resolution imaging was possible as well. The AFM results allow the determination of some of the intermolecular forces in organic crystals, and the observation of the unit cells, the dimensions of which are in good agreement with the ones determined by X-rays.

The last part of this dissertation presents some results obtained by atomic force microscopy on nonlinear optical polymer. The material was stable enough to image the macroscopic topography of the surface and to obtain a high resolution of the molecular structure. No difference in the topography was observed between electrically poled and unpoled polymers.