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Structure of a Functionalized Oxacarbocyanine / Saponite Clay Nanofilm

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Introduction: Nanoscale functionalized organic films are of technological importance, for example in the case of dye molecules, where assembly into well ordered thin films produces desirable optical properties for miniaturized devices. Dilute aqueous suspensions of smectite clay particles, which have elementary platelets 1 nm thick and from 50-3000 nm across and a variable surface charge, are well suited to enhance the ordering of such thin organic films [1]. A number of investigations into clay-organic films assembled at aqueous surfaces are being pursued at present, but direct structural information at the molecular scale is being achieved in only a few instances [2-4]. We have used x-ray reflectivity to characterize monolayer films of oxacarbocyanine (OXA), a dye molecule, and saponite clay particles assembled on silicon substrates, comparing the structural order to OXA films assembled on Si without the clay.

Methods and Materials: Langmuir-Blodgett films of dioctadecyloxacarbocyanine on silicon were prepared by assembly at surface pressures of 20 mN/m either on a pure water subphase, or on an 0.005 wt% aqueous suspension of Saponite clay (CMS Source Clay SapCa-2, origin Ballarat, California, USA). X-ray reflectivity measurements were performed on 20 mm long wafers in air, using an x-ray wavelength 1.155 Å.

Results: Both samples were found to have rough surfaces, with the specular reflection progressively broadened along the rocking curve at large q values. Similar behavior has been observed for bare silicon surfaces [5], and thus the base roughness we observe is probably characteristic of the substrates. This roughness produced some ambiguity in the analysis of the reflectivity curves. Nevertheless, x-ray reflectivities measured from the films showed clear oscillations which can be directly related to the length scales of the regions occupied by the clay and dye molecules. The experimental reflectivities are shown in Figure 1(a). The Si/OXA film data exhibit minima that arise from interference between x-rays reflecting from the air-OXA and OXA-Si interfaces. The data can be fit by a smoothly varying density dependence at the interface, as shown in Figure 1(b). A second length scale is evident in the data from the Si/saponite/OXA film, and successful models show a well defined 1.4 nm thick region between the substrate and OXA. This region is slightly thicker than the 0.9 nm thickness of an exfoliated clay particle, and is also less dense, indicating a partial coverage perhaps accompanied by slight tipping of the clay sheets. However, a layer more than one clay particle thick is ruled out by the data. Both with and without the saponite, the OXA molecules at the surface seem disordered, with no observable difference in OXA organization between the two. Dashed lines in Figure 1(a) and (b) demonstrate the differences between our experiment and idealized film structures, in which the saponite particles perfectly tile the surface, and the OXA molecules stand straight up and are densely packed. In such models, the minima in the reflectivity are shifted to lower q since the straightened molecules define a thicker film.

Our observations demonstrate that the clay particles lie between the OXA and the substrate in a fairly well defined single layer, and that the OXA molecular tails do not stand straight from the surface. Future efforts will be directed towards improving the substrate roughness, and characterizing the structure of these and similar films.

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References:

[1] R. A. Schoonheydt, Clays and Clay Minerals **50** (2002) 411.
[2] S. Takahashi *et al*, Chemical Physics Letters **352** (2002) 213.
[3] B. Struth *et al*, Phys. Rev. Lett. **88** (2002) 25502.
[4] A. Madsen *et al*, Phys. Rev. E **64** (2001) 61406.
[5] A. Gibaud *et al*, Phys. Rev. Lett. **74** (1995) 3205.

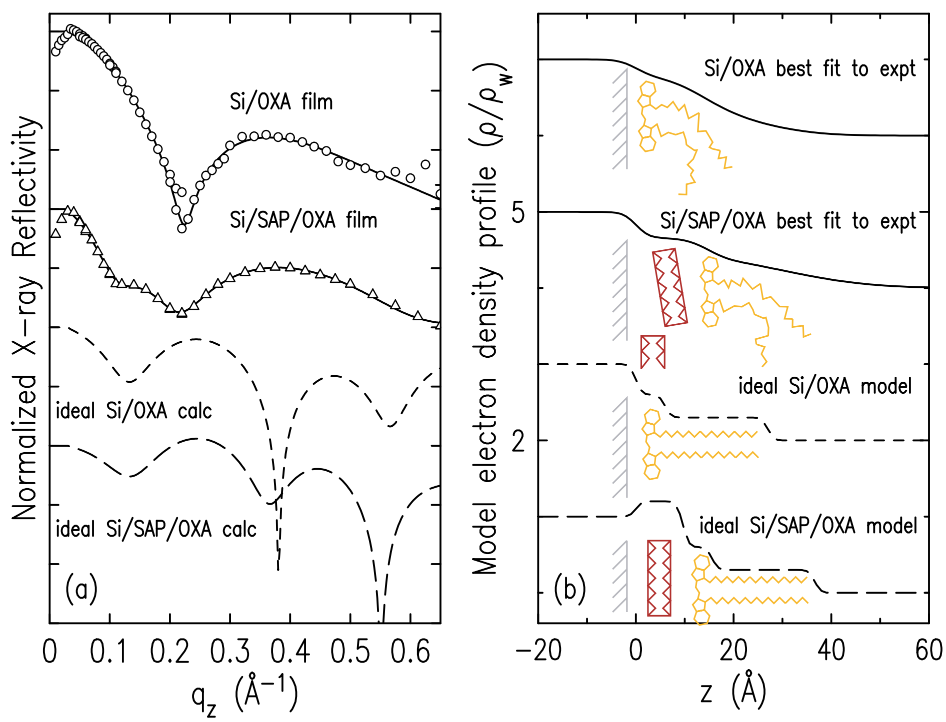

Figure 1. (a) Fresnel-normalized reflectivity data for silicon/OXA film (circles) and silicon/saponite/OXA film (triangles). (Data are offset along a logarithmic axis.) Solid lines are calculated for the best fit model profiles. Short and long dash lines are calculated for idealized films where the OXA molecules are well ordered with straight hydrocarbon tails. (b) Model real-space electron density profiles (normalized to the substrate density ρ_w). Solid lines correspond to the experimental data, and dashed lines to idealized films, as depicted in the schemes.