

FABRICATION AND PROPERTIES OF FULLERODENDRON THIN FILMS

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In the present study, we report the fabrication of Langmuir-Blodgett (LB) films and adsorption films of fullerene-functionalized dendrons, fullerodendrons ($C_{60}(\text{Gn-COOMe})$) ($n=0.5, 1.5, 2.5$), and investigate molecular arrangement within these thin films by X-ray reflectometry (XR). Additionally, the electrochemical properties of these films are investigated based on cyclic voltammetry, and the influence of fabrication methods, dendron generations, and terminal groups is compared and discussed.

Figure 1 shows the π -A isotherms of $C_{60}(\text{Gn-COOMe})$ at the air/water interface. In the case of $C_{60}(\text{G0.5-COOMe})$ and $C_{60}(\text{G1.5-COOMe})$, the occupied area per molecule is less than the expected value for a fullerene moiety, suggesting that molecules were either, at least, partially offset or accumulated in Langmuir film. As for $C_{60}(\text{G2.5-COOMe})$, the occupied area is significantly larger than the expected one. This indicates that bulky dendritic moiety disturbs closed packing of fullerene moieties and controls the occupied areas per molecule.

The LB films possessed well-ordered structure, although the adsorption method led random orientation of molecules. As to $C_{60}(\text{G2.5-COOMe})$, the LB film took two-layer structure in which the fullerene moieties were at air side and the dendron moieties were at substrate side (Fig.2 and Fig.3). On the other hand, $C_{60}(\text{G1.5-COOMe})$ leads four-layer structure consisting of double layer of molecules, and fullerene moieties exist in interior layers of the LB films. With increasing generation of dendron, the monolayer formation ability at the air/water interface as amphiphilic molecule strengthens and the amphiphilic property becomes superior to the fullerene-fullerene attractive interaction that prevents the monolayer formation. Furthermore, in the case of $C_{60}(\text{G0.5-COOMe})$ and $C_{60}(\text{G1.5-COOMe})$, the reduction peak of LB film remained even after UV light irradiation. On the contrary, the peak of $C_{60}(\text{G2.5-COOMe})$ LB film disappeared, indicating that molecular arrangement in the films affects to electrochemical property.

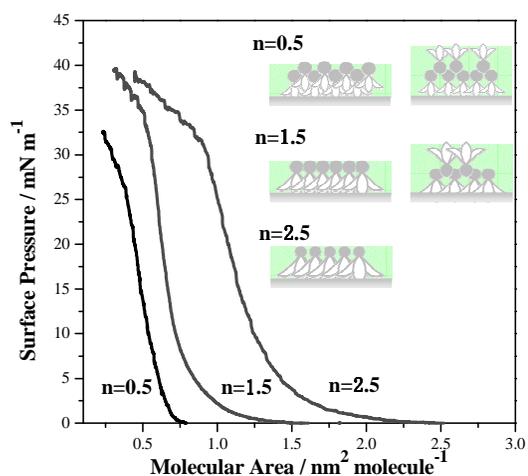


Fig. 1. π -A isotherms of $C_{60}(\text{Gn-COOMe})$ ($n=0.5, 1.5, 2.5$) on a water subphase and schematic representation of estimated molecular arrangements

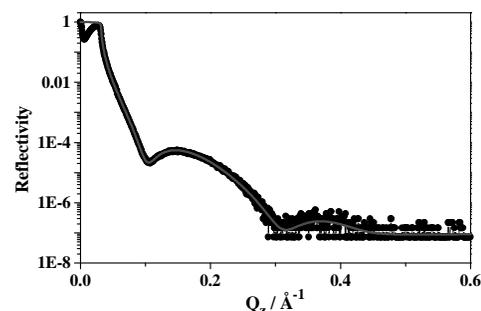


Fig. 2. XR curves of LB films of $C_{60}(\text{G2.5-COOMe})$ at air/silicon interface. The closed circles are experimental data and solid lines are the optimum fitting curves.

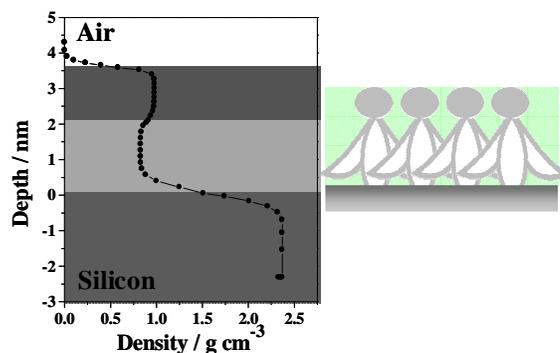


Fig. 3. Depth profile of LB films of $C_{60}(\text{G2.5-COOMe})$ and schematic illustration of molecular arrangements at air/silicon interface.