

NEXAFS Study of Fullerene Adsorbed on Aminothiophenol Self-Assembled Monolayer

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Controlling the microstructure of organic materials to nanometer scale has motivated scientific studies of molecular structure and molecular interactions on various surfaces. Among the various techniques for the preparation of ordered thin organic films, the self-assembled films provide the desired control of molecular order at the interface and also introduce various functional groups into the molecular systems with a high degree of control over the orientation of those groups. The adsorption of thiols onto gold surfaces has attracted considerable interest, as it has been shown that such adsorption can result in formation of well-organized self-assembled monolayer (SAM) [1]. The organothiol self-assembly on metal surface have attracted much interest in a facile manipulating of surface functionality. The SAM have successfully employed as components in molecular electronic devices. Self-assembly of aromatic thiols are particularly interesting due to the interaction of delocalized π orbital of phenyl ring.

The unique electronic, spectroscopic, and structural properties of fullerene and fullerene derivative are very useful to the various application of the material. C_{60} is characterized by the delocalized and highly degenerate orbitals due to π bonding and I_h symmetry. C_{60} is also served as an excellent electron acceptor in molecularly designed donor-acceptor systems, such as molecular photovoltaics [2]. Attachment of C_{60} to the tail groups of SAM provides discrete monolayers of C_{60} and also organized assembly where C_{60} will remain immobilized on the surface.

In this study, the adsorbed state of C_{60} on SAM was examined by NEXAFS spectroscopy. 4-aminothiophenol was used as SAM. The aminothiophenol SAM was prepared by immersing the gold coated Si substrate to 1 mM solution in ethanol for 24 h. The aminothiophenol SAM was cleaned with ethanol and dipped further in 1 mM C_{60} solution in benzene and kept for 24 h. The SAMs thus formed were washed with benzene, ethanol, and dichloromethane. C_{60} multilayer was formed by dropping benzene solution to gold coated substrate and drying in air. NEXAFS measurements were performed at BL13 of Hiroshima Synchrotron Radiation Center.

C K-edge NEXAFS spectra were measured for C_{60} , aminothiophenol SAM and C_{60} adsorbed aminothiophenol SAM. Since NEXAFS spectrum of C_{60} adsorbed SAM includes contribution of aminothiophenol, the component of C_{60} in the C_{60} -SAM was obtained by subtraction of aminothiophenol SAM spectrum from C_{60} -SAM spectrum. The obtained difference spectrum shows similar feature as C_{60} spectrum, but shows peak shifts and peak broadening compared with C_{60} spectrum. Particularly, LUMO peak is shifted to higher photon energy and overlapped with LUMO+1 peak. A higher photon energy shift of LUMO is observed at C_{60} adsorbed on 11-amino-1-undecane thiol SAM [3]. The results suggest that C_{60} is chemisorbed on amino thiolate SAM by hybridization between N Pz of amino group and π^* orbital of C_{60} .

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