

Characterization of self-assembled monolayers of methyl-ester terminated naphthalenethiol

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Core-electron excitations by soft X-ray radiation possess several unique properties that differ from those of valence excitations. Core-excitation energy depends on the element and its chemical environment, which allows selective excitation of a specific atom in a molecule. In general, core excitation is followed by Auger decay on a time scale of a few femtoseconds, resulting in final states with large excess energy. Thereafter, the excited molecule follows a rich variety of relaxation pathways, e.g. desorption of ion and neutral species and charge transfer within the molecule.

An interesting phenomenon that reflects the selective nature of core excitation is site-selective bond breaking of molecules, i.e. the so-called “molecular scalpel” [1,2]. In particular, it has been reported that highly site-selective bond scission can be achieved in self-assembled monolayers (SAMs) of molecules absorbed on metal surfaces [1,2]. Furthermore, our recent experiments on aliphatic and aromatic SAMs have suggested that the degree of site-selective bond scission depends on the molecular structure of backbone between the excitation site and the metal substrate. This implies the key role of energy transfer between the excitation site and the substrate for the manifestation of site-selective bond scission. To corroborate this picture, a systematic experimental study about the fragmentation dynamics dependent on the molecular structure is helpful.

In this study, we investigated the ion desorption dynamics of SAMs of methyl-ester terminated naphthalenethiol molecules. The SAM samples were prepared by immersing Au substrates in 1.0 mM ethanol solution of the sample molecules for 24 hs. We characterized the prepared SAM samples by near-edge X-ray absorption fine structure (NEXAFS) measurements. The experiment was performed at the BL 13 of HiSOR. The C K-edge NEXAFS spectra were measured by the total electron yield (TEY) method via the sample drain current. The measurements were performed at different incident beam angles, and polarization dependence of the NEXAFS intensity was investigated. The obtained NEXAFS spectra (Fig. 1) show peaks corresponding to excitations to individual unoccupied molecular orbitals and provided precise values of their excitation energies. In addition, the spectra exhibit a clear polarization dependence, which supports the formation of well-oriented SAMs on the substrate.

The measurements of desorbed ions were performed at BL 2B of photon factory (PF) in KEK. PF was operated in the hybrid operation mode, and the single-bunch component of the X-ray beam was skimmed and used in the experiment. Partial ion yield (PIY) spectra were recorded with a time-of-flight ion spectrometer. The PIY of CH_n^+ ($n=0,1,2,3$) ions showed a prominent enhancement at the $\text{C } 1s(\text{OCH}_3) \rightarrow \sigma^*(\text{O}-\text{CH}_3)$ resonant excitation, which have been observed in previous experiments on methyl-ester terminated SAMs [1,2]. From the PIY spectra, we evaluated the degree of site-selective desorption by analyzing the relative yield of CH_n^+ ions. The degree of site-selectivity for the present molecule with naphthalene backbone was evaluated to be between those for molecules with benzene and biphenyl (with two benzene rings) backbones. The present results corroborate the correlation between the molecular conductivity and the site selectivity in ion desorption.

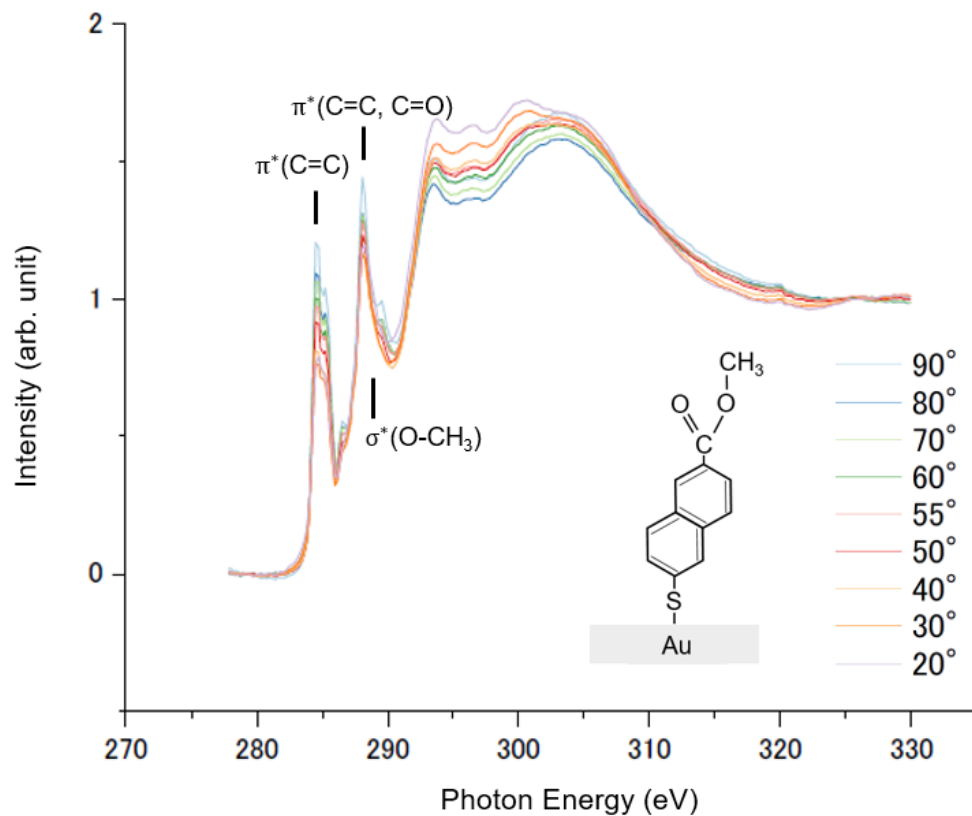


FIGURE 1. TEY spectra for methyl-ester terminated naphthalenethiol SAMs. The spectra exhibit peaks corresponding to excitations to individual π^* and σ^* orbitals. The spectra show a clear polarization dependence, which supports the formation of ordered SAMs on the Au substrate.

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