

XAFS Study of 17,19-Hexatriacontadiyne Monolayers on Au(111)

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Introduction

Conjugated alkadiyne 17,19-hexatriacontadiyne (HTDY) molecules physisorbed on a graphite (0001) surface form self-assembled columns or lamellae with their carbon planes parallel to the surface. Each column is converted into a single sheet of sashlike polydiacetylene (PD) -*atomic sash* (AS)- upon UV irradiation[1,2]. The AS molecules having one-dimensional π electronic systems serve for a detailed study on organic nanowires and it is desirable to construct the AS nanowires on alternative surfaces including semiconductors and metals. We have recently reported that HTDY forms flat-lying columns in a monolayer prepared by a wet process on Au(111)[3]. However, it was also revealed that the products obtained by UV irradiation on HTDY/Au(111) are somewhat different from those on HTDY/graphite (0001). In this work, we intend to study the nature of the products and a possible cause of the difference in the reaction using carbon K-edge X-ray absorption fine structure (C K-NEXAFS).

Experimental

XAFS measurement was performed at a soft X-ray beam line BL-7A of Photon Factory in Institute of Materials Structure Science. A flame-annealed Au(111) surface cooled in pure acetone was immersed into an HTDY acetone solution for a short period of time and subsequently rinsed with the pure solvent. The monolayer was irradiated with UV light from a deuterium lamp. After each specimen was introduced into a UHV chamber, C K-edge NEXAFS spectra were measured at 1×10^{-6} Pa with a partial electron yield method using a microchannel plate. The spectra were collected at three X-ray incidence angle: grazing (GI), magic angle (MI), and normal incidence (NI).

Results & Discussion

In Fig. 1(a), we show the polarization dependent C K-edge NEXAFS spectra of HTDY on Au(111) before UV irradiation. A peak dominantly observed in a NI spectrum, which corresponds to the σ_{CC}^* resonance, indicates that the carbon zigzag plane of the HTDY molecule is parallel to the surface (flat-on orientation). Another peak assigned to the M^* resonance proves that there exists a mixing of the σ_{CH}^* or pseudo- π^* orbitals of the alkyl chains with metal d-bands, which is consistent with the flat-on orientation and the soft mode of the CH stretching

vibration observed by infrared reflection absorption spectroscopy[3]. The peak position of the π^* resonance for the monolayer is almost the same as that for a multilayer. This means that there is little mixing between the π^* orbital of HTDY in the monolayer and the metal d-bands. Changes occurring in the GI spectrum upon UV irradiation are shown in Fig. 1(b). The polarization dependence of the spectra is diminished and the π^* resonance shifts to a lower energy. These results indicate that the molecular orientation becomes random owing to the formation of oligomeric species resembling red phase PDs in LB films[4].

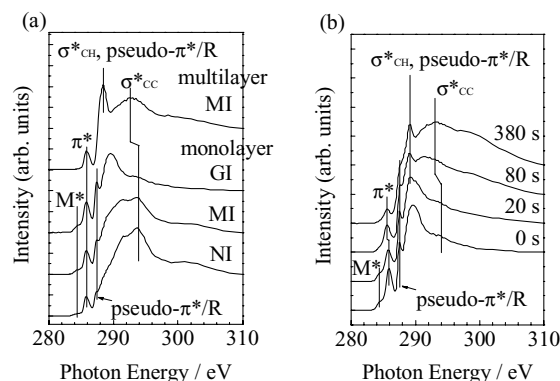


Fig. 1 (a) C K-edge NEXAFS spectra for a mono- and a multilayer of HTDY on Au(111); GI, MI, and NI mean grazing, magic angle, and normal incidence of X-ray, respectively. (b) Changes of C K-edge NEXAFS spectra (GI) for an HTDY monolayer on Au(111) upon UV irradiation.

References

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