

## Molecular Chain Effect of Aromatic Self-Assembled Monolayers Measured in Soft X-Ray Stimulated Ion Desorption

Shin-ichi Wada<sup>1,2\*</sup>, Mai Ogawa<sup>1</sup>, Ryosuke Koga<sup>1</sup>, Jumpei Kajikawa<sup>1</sup>,  
Hironori Hayashita<sup>1</sup>, Kenichiro Tanaka<sup>3</sup>, and Atsunari Hiraya<sup>1,2</sup>

<sup>1</sup>Department of Physical Science, Hiroshima Univ., Higashi-Hiroshima 739-8526, Japan

<sup>2</sup>HSRC, Hiroshima Univ., Higashi-Hiroshima 739-0046, Japan

<sup>3</sup>XFEL Division, Japan Synchrotron Radiation Research Institute, Sayo, 679-5198, Japan

### 1 Introduction

Inner shell excitation of a specific atom in a molecule by soft X-ray irradiation can induce site-selective chemical bond breaking due to spatial localization of core electrons. Self-assembled monolayers (SAMs) consist of end functional groups, molecular chains and thiol groups, and so far, we have investigated site-selective photostimulated ion desorption (PSID) in the end functional group of methyl-ester terminated aliphatic thiol SAM (MHDA : Au-S(CH<sub>2</sub>)<sub>15</sub>-COOCH<sub>3</sub>) [1]. Differently from insulating aliphatic chain, it is known that aromatic thiols show high conductivity due to its delocalized  $\pi$  conjugation [2]. Furthermore, from previous studies, it is considered that site-selectivity and yield in PSID strongly depend on molecular environment [1]. In this study, we have studied two types of methyl ester terminated aromatic thiols, MP0 (Au-SC<sub>6</sub>H<sub>4</sub>COOCH<sub>3</sub>) and MP1 (Au-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COOCH<sub>3</sub>), in order to discuss how molecular chains affect PSID in their end functional groups. Chemicals used in this study are illustrated in Fig. 1. Both of MP0 and MP1 have a phenyl groups as molecular chains and additional insulating methylene group (-CH<sub>2</sub>-) is absent for MP0, while it is inserted between phenyl and thiol groups of MP1.

### 2 Experiment

The experiment was performed at the beamline BL7A of KEK-PF. During measurements, the experimental chamber had a base pressure of  $1 \times 10^{-9}$  Torr. Near edge X-ray absorption fine structure (NEXAFS) was recorded in TEY mode by measuring a sample drain current. The TEY spectra were measured at 20° incident angle from

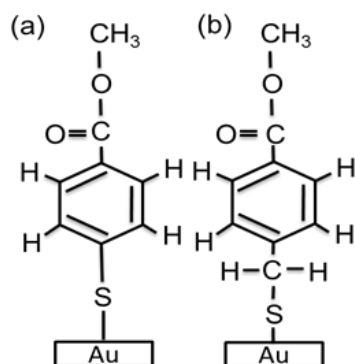


Fig. 1: Chemical structure of target molecules: (a) MP0 and (b) MP1 SAMs.

the sample surface. Partial ion yield (PIY) spectra were measured using TOF mass spectrometer system. All spectra were normalized to the incident photon flux monitored with a gold-coated mesh. SAMs used in this study were prepared by immersing Au coated Si substrates in 1mM ethanol solution of target molecules at room temperature during one day.

### 3 Results and Discussion

Fig. 2 shows the TEY and PIY spectra for MP0 in C 1s region. All peaks in the spectrum can be assigned based on a building-block method using Refs. 1 and 3. The C 1s  $\rightarrow \sigma^*(\text{O-CH}_3)$  excitation located on the shoulder around the photon energy of 289 eV overlaps  $2\pi^*(\text{C=C})\text{:C-H}$  excitation. Obvious desorption of  $\text{CH}_n^+$  ( $n = 0\sim 3$ ) ions, however, indicates that the site-selective ion desorption of  $\text{CH}_n^+$  is promoted by the resonant excitation to the  $\sigma^*(\text{O-CH}_3)$  unoccupied orbital.

Fig. 3 shows the fragmentation patterns of  $\text{CH}_n^+$  ions desorbed from MP0 and MP1 at the C 1s  $\rightarrow \sigma^*(\text{O-CH}_3)$

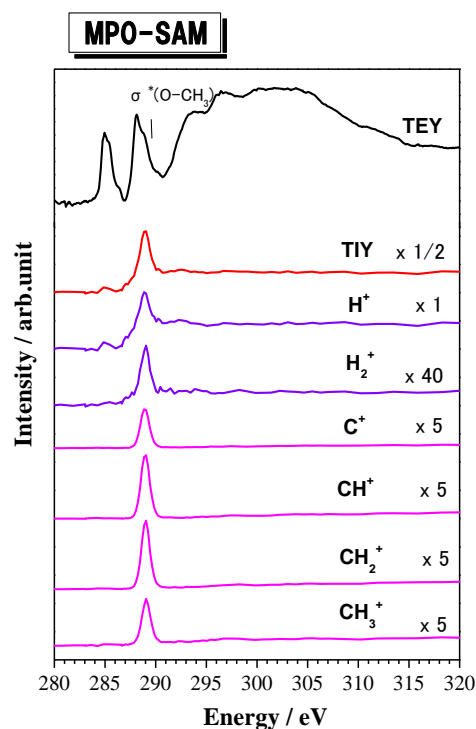


Fig. 2: TEY and PIY spectra measured for MP0 in C 1s region.

excitations, together with the result of MHDA for easy comparison. Here is noted that  $\text{CH}_n^+$  ions come from the fragmentation of  $\text{CH}_3^+$  ions after leaving substrate molecules (SAM molecules). The more internal energy for  $\text{CH}_3^+$  ions in desorbing becomes high, the more C-H bonds would break. The internal energy of desorbed  $\text{CH}_3^+$  ions from aromatic thiol SAMs (MP0 and MP1) becomes higher than that from the aliphatic thiol SAM (MHDA). Moreover, MP0 indicates more pronounced production of fragment ions in comparing with MP1. Based on these results, it can be considered that ion yield and site-selectivity of desorbed ions from different conductivity environments are strongly attributed to charge transfer rates between SAM molecules and metal surfaces.

#### References

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\* swada@sci.hiroshima-u.ac.jp

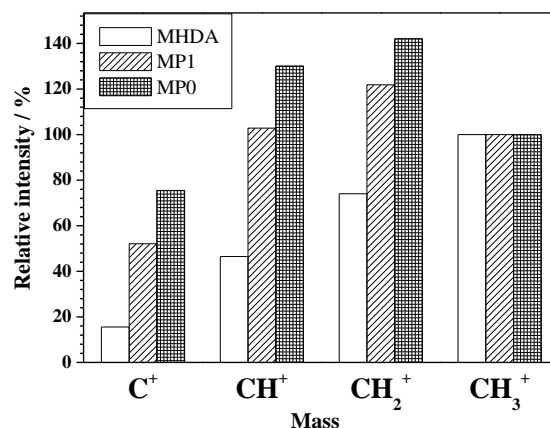


Fig. 3: Fragmentation ratio of desorbed  $\text{CH}_n^+$  ( $n = 0\sim 3$ ) ions by the  $\text{C } 1s \rightarrow \sigma^*(\text{O-CH}_3)$  excitations of MP0 and MP1 aromatic SAMs and MHDA aliphatic SAM.