Electronic Relaxation Process in Fluorinated Aromatic Monolayers Studied by Core-Excited Ion Desorption

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Core-electrons are localized to each atom in the molecule, and their binding energy varies depending on the types of element and the surrounding chemical environment. Therefore, by selecting the energy of the incident light, it is possible to selectively excite the inner-shell electrons of specific atoms in the molecule. After core resonant excitation, various reaction pathways occur (Figure. 1). Desorbed ions include site selective ion desorption (red arrow) and non-selective ion desorption through energy redistribution within the molecule (blue arrow). In the case of surface molecules, these reactions compete with energy deactivation by charge transfer to substrate (green arrow), so the faster the charge transfer to the substrate occurs, the more the slower reactions are suppressed. Site non-selective ion desorption is slower than site selective ion desorption. So, we tried to evaluate the charge transfer rate from the site selectivity of ion desorption.

Measurements of near edge X-ray absorption fine structure (NEXAFS) were performed at the beamline BL-13 of HiSOR, and time of flight (TOF) mass spectroscopy was measured at the beamline BL-2B of KEK-PF. NEXAFS spectra around the C K-edge were recorded in total electron yield (TEY) mode by measuring a sample drain current. TOF spectra were measured with pulse selector [1] in the hybrid mode operation at PF.

Figure. 2 shows the schematic drawings of self-assembled monolayers (SAMs) used in this study. SAMs were prepared by immersing Au substrates into 1.0 mM ethanol solutions of MBB (HSC₆H₄C₆H₄COOCH₃), MBF (HSC₆F₄COOCH₃), and MFB (HSC₆H₄C₆F₄COOCH₃). It has been reported that these samples have different charge transfer rate [2]. All samples have methyl ester groups as terminal groups at topmost surfaces, and conductive phenyl rings as molecular chains.

Figure 3 shows the NEXAFS spectra measured for MBF and MFB changing the incident angle. NEXAFS spectra show features derived from fluorine substitution, especially in the peak



Figure 1. Reaction pathways after core resonant excitation.



Figure 2. Molecular structures of SAMs used in this study; MBB, MBF, and MFB SAMs.

splits of the first (~285eV) and second peaks(~288eV). From the intensity of first peaks, MBF and MFB were estimated to be oriented at 74° and 69° from the surfaces, respectively. Even though the orientation angles of MBF and MFB are almost the same, the ion fragmentation in MFB is more intense than that in MBF in terms of its CH_n^+ (n=0-3) ion desorption yield. These ions are produced by further fragmentation of CH_3^+ due to the excess energy it has when it is desorbed from the terminal group. The excess energy in MFB is estimated to be higher than that in MBF. We estimated the ratio of site selective vs. non-selective processes by reproducing the ion fragmentation pattern by adding together the site selective and non-selective model fragmentation patterns. As a result, selective:non-selective ratios were 0.81:0.19 for MBF and 0.98:0.02 for MFB. The results show non-selective ion desorption in MFB is faster than that in MBF because energy deactivation by charge transfer to substrate in MFB is faster than that in MBF. This result is consistent with the charge transfer rate in MBF and MFB (MBF: ~8.8fs, MFB: ~6.6fs) [2]. Therefore, the difference in conductivity depending on the fluorine substitution position was evaluated from the site selectivity of ion desorption.

REFERENCES

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Figure 3 TEY spectra for (a)MBF and (b)MFB. The angles in the figure are the incident angles from the sample surfaces. MBF and MFB were estimated to be oriented at 74° and 69° from the surfaces, respectively.