

Position dependence in fluorine-substituted aromatic SAMs studied by X-ray photoemission and Auger electron spectroscopies

Hayate Inoue^a, Yuichiro Kodama^b, Yuri Ohura^a, Kakuto Yoshioka^a,
Shogo Tendo^c, Akinobu Niozu^d, Shin-ichi Wada^{a,b,e}

^aGraduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

^bSchool of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

^cNational Institute of Technology, Kochi College, Nankoku 783-8508, Japan

^dGraduate School of Humanities and Social Sciences, Hiroshima University, Higashi-Hiroshima 739-8524, Japan

^eResearch Institute for Synchrotron Radiation Science, Hiroshima University, Higashi-Hiroshima 739-0046, Japan

Keywords: Self-assembled monolayers (SAMs), X-ray photoemission spectroscopy, Auger electron spectroscopy.

In recent years, the development of organic materials for electronic and optoelectronic devices has attracted significant attention. To realize the industrial application of these materials, optimizing their charge transport properties is crucial. This requires elucidating intramolecular charge transfer dynamics. Consequently, research has focused on various organic molecules, particularly aromatic molecules where electron transfer is facilitated by π -conjugation. In particular, fluorine substitution has been suggested as a potential method for controlling charge transfer properties. For instance, it has been reported that asymmetric fluorine substitution within a molecule can induce diode characteristics.

In our previous study, we quantitatively evaluated charge transfer by tracking the relaxation process following soft X-ray core-level resonant excitation. We adopted self-assembled monolayers (SAMs) as a platform, where the photo-absorbing terminal groups are arranged at the outermost surface. By introducing a methyl ester group at the terminus, we were able to generate excited electrons at the terminal moiety through O 1s resonant excitation, allowing for the efficient observation of intramolecular charge transport processes. Using biphenyl SAMs with different fluorine substitution positions on Au substrates (as shown in Figure 1), we found that the charge transfer time for MFB was approximately 1 fs faster than that for MBF. However, the significance of this difference and the detailed mechanism behind it remain unclear. Therefore, in this study, we investigated the effect of fluorine substitution on the electronic states of the molecules using X-ray Photoemission Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) of the F 1s core level.

Two types of fluorine-substituted SAMs were prepared by immersing gold substrates in 1 mM ethanol solutions of each sample for 24 hours, followed by rinsing with ethanol. Near-edge X-ray absorption fine structure (NEXAFS), X-ray photoemission spectroscopy (XPS), and Auger electron spectroscopy (AES) measurements were performed on the prepared SAMs at HiSOR BL-13. All measurements were conducted at room temperature. NEXAFS measurements were carried out at the carbon and fluorine K-edges in the total electron yield (TEY) mode. The incidence angle of soft X-rays relative to the substrate surface was varied from 20° to 90° in 10° steps for the C K-edge, and set to 20°, 55°, and 90° for the F K-edge. For XPS measurements, the incident photon energy was set to 907 eV. The

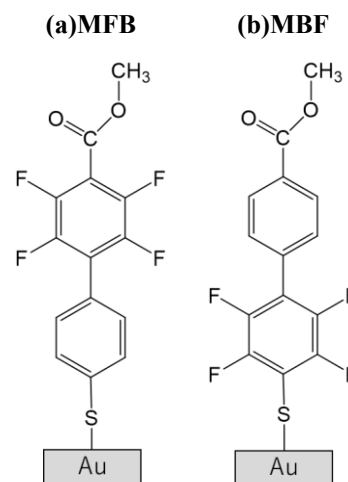


FIGURE 1. Schematic drawings of molecular structures of (a)MFB, and (b)MBF SAMs.

binding energy of the F 1s region was calibrated using the O 1s peak observed in the same spectrum. The reference binding energy of the O 1s peak was determined based on the Au 4f_{7/2} peak (84.0 eV) in a separately measured spectrum containing both O 1s and Au 4f peaks. AES measurements were performed at the following three excitation energies: (i) 696 eV, corresponding to the F 1s to π_1^* (C-F) resonant excitation where resonant Auger decay competes with the charge transfer process; (ii) 703 eV, which is sufficiently higher than the ionization potential (IP) to induce normal Auger decay; and (iii) 688 eV in the pre-edge region of the F K-edge to subtract the photoelectron component.

In the C K-edge NEXAFS spectra, π^* peaks were primarily observed in the photon energy region below the ionization potential (IP) (pre-edge region), while σ^* peaks were observed in the region above the IP (post-edge region). The absorption intensity of the π^* peak was maximized at an incidence angle of 90°, whereas that of the σ^* peak was maximized at 20°. These results indicate that both MFB and MBF molecules are oriented upright with respect to the gold substrates.

In the F K-edge region, π_1^* , σ^* , and π_2^* peaks were observed in this order from the lower photon energy side. This suggests that the π -conjugated structure extends to the vicinity of the fluorine atoms.

Next, in the XPS measurements, single-component F 1s peaks were observed at 686.4 eV for MFB and 685.6 eV for MBF, showing a chemical shift of approximately 0.8 eV. This difference in binding energy is attributed to the screening effect from the substrate resulting from the different fluorine substitution positions, as well as differences in the local chemical environment.

Comparing the AES spectra shown in Fig. 2, significant differences in spectral shape were observed in the 650–660 eV region. Specifically, the spectral intensity on the higher kinetic energy side, which corresponds to resonant Auger decay, was relatively lower for MBF compared to MFB. This suggests that the charge transfer process from a F atom is more dominant in MBF, indicating a faster charge transfer time. This result is consistent with the trend reported in previous studies, where the charge transfer time decreases as the excitation site becomes closer to the substrate [1].

This study demonstrates that AES measurements using F 1s excitation, in addition to the conventional O 1s excitation, are useful for evaluating intramolecular charge transfer dynamics. In the future, quantitative evaluation of charge transfer times in fluorine-substituted systems is expected to be achieved by performing Core-hole clock analysis using reference molecular systems where no charge transfer occurs.

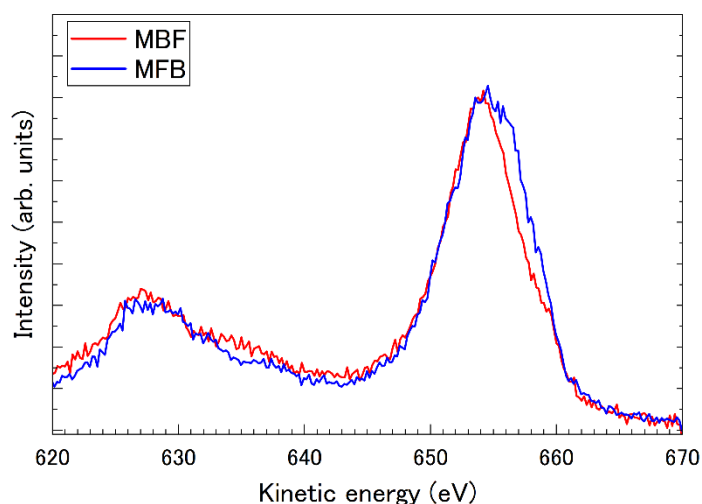


FIGURE 2. AES spectra of MBF (red) and MFB (blue).

REFERENCES

1. S. Tendo *et al.* Phys. Chem. Chem. Phys., **27**, 388 (2025).