Fluorine substitution dependence of ultrafast electron transport in biphenyl monolayers induced by resonant core-excitations

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In recent years, the development of organic materials has attracted much attention in the field of electronic and optical devices. To realize industrial applications of organic materials, it is essential to optimize their electron transport properties and elucidate the correlation between molecular design and electron transport. For this reason, studies investigating the electron transport properties of various molecular systems have been actively conducted [1]. Among these studies, fluorine substitution has been suggested to control electron transport properties. As a method to evaluate electron transport properties, we focused on a technique to investigate the electron transport properties of molecules by observing the Auger decay process with electron transport after inner-shell resonance excitation using soft X-rays [2]. As a platform for this purpose, we focused on self-assembled monolayers (SAMs) where the end groups of molecules are located on the topmost surface of

FIGURE 1. Fluorine-substituted SAMs.

the substrate [3], which allows us to efficiently observe the electron transport from the end groups to the substrate. In this study, we investigated the effect of fluorine substitution positions on electron transport by measuring the kinetic energy of Auger electrons generated after soft X-ray irradiation for biphenyl SAMs with different fluorine substitution sites, as shown in Fig. 1.

Fluorine-substituted SAMs were prepared by immersing gold substrates in 1 mM ethanol solution of each sample for 24 hours and then rinsing with ethanol. Near-edge X-ray absorption fine structure (NEXAFS) and Auger electron spectroscopy (AES) measurements were performed on the prepared fluorine-substituted SAMs at HiSOR BL-13. NEXAFS measurements were performed in the carbon and oxygen K-edge regions, and the carbon K-edge region was measured in the range from 20° to 90° by changing the soft X-ray incidence angle by 10° (Fig. 2). The π* peak was mainly observed at photon energies lower than the ionization threshold (IP), while the σ* peak was observed at higher photon energies. The MFB and MBF molecules were found to be oriented perpendicularly to the gold substrate.

Next, AES measurements were performed on fluorine-substituted SAMs and insulating alkyl chain SAMs, where electron transport cannot occur. Fig. 2 shows the AES spectra of the carbonyl group when excited at 532 eV, which is the excitation energy from the oxygen 1s orbital to the π*(C=O) orbital, where the resonant
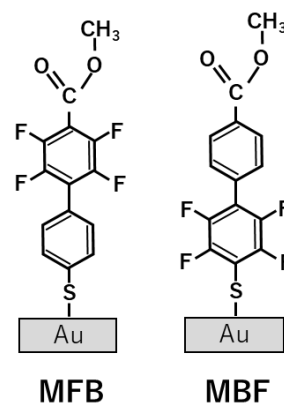
Auger decay and electron transport processes compete. The AES spectrum at 525 eV was used to subtract the photoelectron signal from the AES spectra at 532 eV and 540 eV. The 532 eV AES spectra of fluorine-substituted SAMs, shown as white circles in Fig. 2, are the pure resonance AES spectra of insulating alkyl chain SAMs, shown as yellow-green lines, and the equivalent Auger decay spectrum with electron transport, shown as gray lines. The AES spectrum at 532 eV of insulating alkyl chain SAMs was reproduced as shown in the red fitted line by fitting analysis using a linear combination of the pure resonance AES spectrum of insulating alkyl chain SAMs (yellow-green line) and the AES spectrum of normal Auger decay, which is equivalent to Auger decay with electron transport (gray line). To quantitatively compare the electron transport processes, the analysis was performed using the core-hole clock method, which determines the electron transport time with respect to the core-hole lifetime τ_{core}= 3.85 fs [4] for oxygen 1s from the fraction P of the normal Auger component.

$$\tau_{CT} = \tau_{CH} \frac{1-P_{CT}}{P_{CT}}. \tag{1}$$

The electron transport times were 15.7 ± 0.4 fs for MFB and 16.8 ± 0.4 fs for MBF, indicating that electron transport in MFB is about 1 fs faster. To discuss the results, we performed first-principles calculations of the lowest unoccupied molecular orbitals (LUMOs) involved in electron transport and found no clear difference in the LUMO shapes of the two molecules that could explain the difference in electron transport time. Since the molecular orbitals of the chemisorbed species are expected to change due to orbital hybridization with the Au substrate, a detailed understanding of each molecule would be obtained by performing first-principles calculations that consider the effect of the Au substrate.
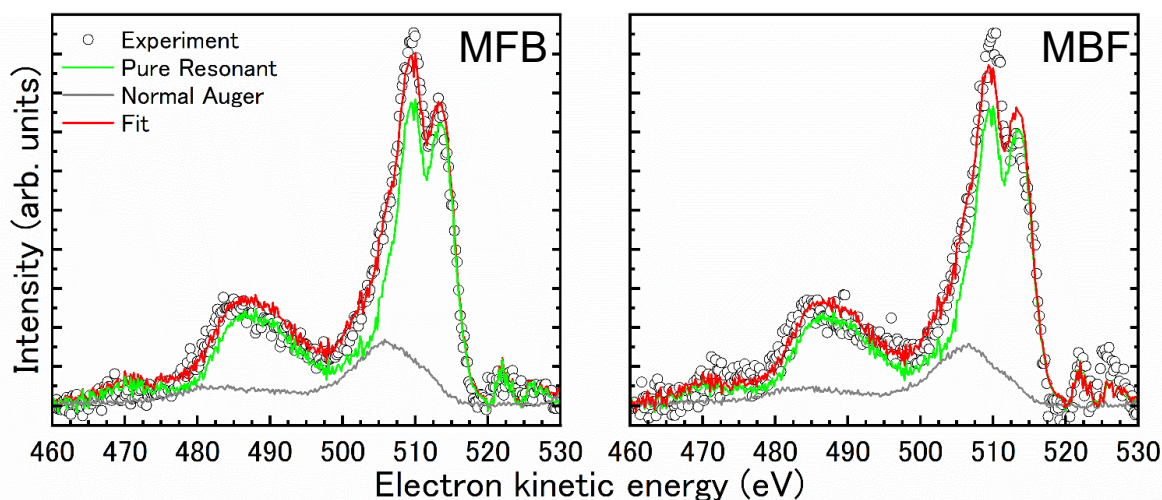

FIGURE 2. AES spectra (white circles) of MFB (left) and MBF (right). The fitted lines (red) are obtained by linear combination of the resonant Auger component (green) and the electron transport component (gray).

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