Torsional Angle Dependence of Ultrafast Charge Transfer in Biphenyl Monolayers

K. Yoshioka[a], J. Yamada[a], A. Niozu[a], and S. Wada[a,b]

[a]*Department of Physical Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[b]*Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima 739-0046, Japan*

Keywords: π-conjugated system, core-hole clock.

Introduction

In recent years, the application of organic molecules in the field of molecular electronics, such as organic semiconductors and molecular devices, has attracted considerable interest [1]. The evaluation of the conductivity of organic molecules is an important issue for their use in those applications. Among organic molecules, aromatic systems with π-electrons exhibit excellent electrical conductivity [2]. Therefore, the purpose of this study is to investigate the effect of the degree of π-conjugation of the molecules on the electrical conductivity. To investigate this, we evaluated the molecular conductivity by observing the charge transfer process that occurs when inner-shell electrons are excited by soft X-ray irradiation.

Experiment

In this study, Auger electron spectroscopy (AES) measurements were performed at HiSOR BL-13 to observe charge transfer processes. The experimental chamber is equipped with a circular hemisphere electron energy analyzer, and the pressure is $\sim 10^{-10}$ torr at room temperature.

The samples are self-assembled monolayers (SAMs) of biphenyl thiol molecules on Au substrates. The molecular structures are shown in Figure 1. The molecules have different torsional angles by the introduction of methyl groups, which result in different degrees of π-conjugation. As a reference system, MHDA molecule composed of a highly insulating aliphatic chain was employed. The molecules have methyl ester groups as the tail group, which are resonantly excited in the AES measurements.

In observing the charge transfer process, we focus on the oxygen atom in the methyl ester group at the end group. For the characterization of the prepared SAMs, we evaluated the orientation of the molecules by soft X-ray absorption spectroscopy varying X-ray incidence angles.
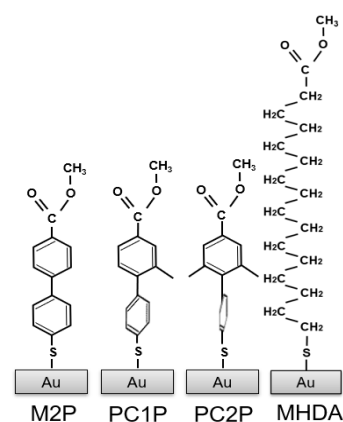

Figure 1. Overview diagram of each sample molecule.

Results and Discussion

We compared soft X-ray absorption spectra at different incidence angles. As an example, the spectra of M2P SAM is shown in Figure 2. A clear polarization dependence was observed in the absorption intensities of the peaks for the transitions of π^*(C=C) orbital (about 285 eV) and the π^*(C=O) orbital (about 289 eV). The intensities of those peak increases with increasing incident angle, indicating that the molecules in the SAMs are arranged in nearly upright orientations.

We investigated the charge transfer process that occurs when the oxygen atoms at the tail group are inner-shell excited to the π^* (C=O) orbital. The charge transfer
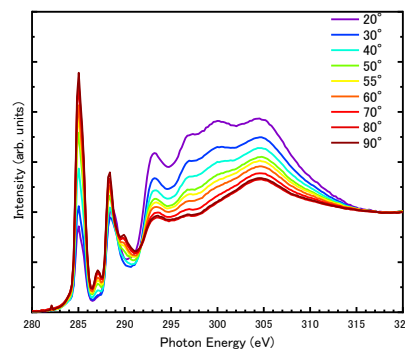

Figure 2. The soft X-ray absorption spectra of M2P SAM at different incidence angles.

process competes with the pure-resonant Auger decay, and Auger electrons with different kinetic energies are emitted in those processes. Therefore, by decomposing the measured AES spectra into the charge transfer component and the resonant Auger component, the charge transfer time can be evaluated. The fitting results are shown in Figure 3. Here, for the spectra of the pure-resonant Auger electrons, we used the data of the MHDA SAM at the photon energy of the $\pi^*(C=O)$ transition. For the spectra of the normal Auger electrons emitted when charge transfer occurs, the data at the energy of the $\sigma^*(C-O)$ transition was used.

An evident admixture of the normal Auger electrons was observed in the case of M2P SAM, indicating that a charge transfer occurred within the core-hole lifetime. Table 1 shows the charge transfer time τ_{CT} calculated with the following equation [3] using the normal Auger electron yield ratio P_{CT} obtained from there fitting results and the core-hole lifetime τ_{CH} (O: about 4 fs).

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

The results show that M2P SAM has the highest yield ratio of normal Auger electrons and the shortest charge transfer time. For, PC1P and PC2P SAMs, the yield ratio of normal Auger electrons decreased due to torsion, and the charge transfer times were PC1P: 52 fs and PC2P: 63 fs. These results suggest that torsion decreases the degree of π-conjugation, making the charge transfer less likely to occur.
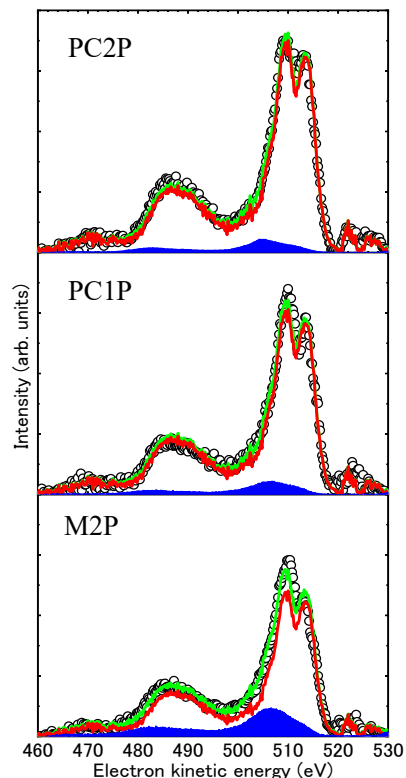

Figure 3. The fitting results of AES spectra for each sample SAMs. (The black dot: The experimental data, The green line: The fitting results, The red line: The data of pure-resonant Auger electrons, The blue area: The data of normal Auger electrons.)

Table 1. The yield ratio of normal Auger electrons and the charge transfer times obtained from AES spectra.

	M2P	PC1P	PC2P
The yield ratio of normal Auger electrons P_{CT}	0.18	0.07	0.06
Charge-transfer time τ_{CT}	19 fs	52 fs	63 fs

Conclusion

In this study, we observed the charge transfer that occurs when SAMs of biphenyl molecular systems with different torsion angles due to the addition of methyl groups by Auger electron spectroscopy with soft X-rays. The charge transfer time was evaluated by using the core-hole clock method for the Auger spectra. The obtained charge transfer times are M2P: 19 fs, PC1P: 52 fs, and PC2P: 63 fs. The results indicate that torsion decreases the π-conjugation and slows down the charge transfer between the molecule and the substrate.

REFERENCES

1. A. Asyuda, R. O. de la Morena, E. Sauter, K. Turner, K. McDonald, M. Buck, M. Zharnikov: J. Phys. Chem. C, **124**, 25107 (2020).
2. A. Asyuda, A. Wiesner, X. Wan, A. Terfort, M. Zharnikov: J. Phys. Chem. C, **124**, 24837 (2020).
3. P. A. Bruhwiler, O. Karis, N. Martensson: Rev Mod Phys, **74**, 703 (2002).