

Ultrafast charge transfer through biphenyl and fluorene monolayers studied by core-hole clock spectroscopy

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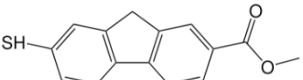
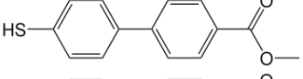
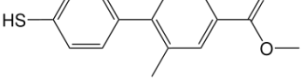
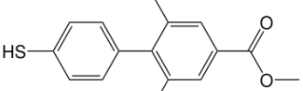
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Nanoscale charge transfer dynamics are crucial for fundamental physical chemistry and applications, such as nanoelectronics and photovoltaics. For these applications, it is crucial to understand the correlation between the molecular structure and charge transport properties. Although molecular conductance has been extensively studied using single-molecule conductance measurements [1], a notable disparity exists between these fundamental investigations of single-molecule junctions and their direct application in functional devices. The use of self-assembled monolayers (SAMs) is a potential solution to bridge this gap given their capacity to form functional devices, thus connecting the insights gained from fundamental studies to practical applications.

TABLE 1. Molecular structures and torsion angles of the molecules in SAMs.

Name	Structure	Torsion angle / °
MFL		0
MBP		0 [3]
MmBP		52
MdmBP		90

In this study, we investigated ultrafast charge transfer through self-assembled monolayers of biphenyl and fluorene molecules via resonant Auger electron spectroscopy (RAES) using the core-hole clock (CHC) technique [2]. In this approach, molecules are resonantly core-excited with soft X-rays, and the subsequent electron transfer is probed by monitoring Auger decay spectra. The thiolated derivatives of biphenyl and fluorene used in this study are listed in Table 1. The addition of methyl groups induces torsion between the two phenyl rings within the SAMs, resulting in a reduction in π -conjugation. MBP molecules are anticipated to adopt an almost planar conformation [3], similar to that observed in bulk solids. Conversely, the methyl-substituted thiolates (MmBP and MdmBP) are expected to exhibit twisted conformations owing to steric hindrance from the methyl groups. Density functional theory (DFT) calculations of the relaxed molecular geometries yielded torsion angles of 52° and 90° for MmBP and MdmBP molecules, respectively. These molecules have a methyl ester (COOCH₃) moiety as the tail group, which serves as the site resonantly excited

with soft X-rays in the CHC experiments.

The methylester-terminated biphenyl and fluorene derivatives were custom-synthesized by and purchased from Tokyo Chemical Industry Co., Ltd. (for MFL, MmBP, and MdmBP) and NARD Institute Ltd. (for MBP). The SAMs were formed by immersing the Au substrates in 1 mM ethanol (for MBP, MmBP, and MdmBP) and toluene (for MFL) solutions of the precursors at 30 °C for 24 h. After immersion, the SAM samples were rinsed with solvent and dried under a flow of N₂ gas. The SAM samples were characterized using near-edge X-ray fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS). NEXAFS, XPS, and RAES experiments were conducted at HiSOR BL13. NEXAFS spectra were collected at the C and O K-edges using the total electron yield mode. The XPS and RAES spectra were acquired at an X-ray incidence angle of 45° in the normal emission geometry using Omicron EA125 electron energy analyzer.

The C K-edge NEXAFS spectra showed several peaks corresponding to C 1s → π^* and C 1s → σ^* excitations. The polarization dependence of the π^* intensities indicated the orientational order of the molecules within the SAMs. The S 2p XPS spectra of the target SAMs confirmed sulfur species chemisorbed on Au. The NEXAFS and XPS spectra suggest the formation of ordered SAMs on the Au substrates.

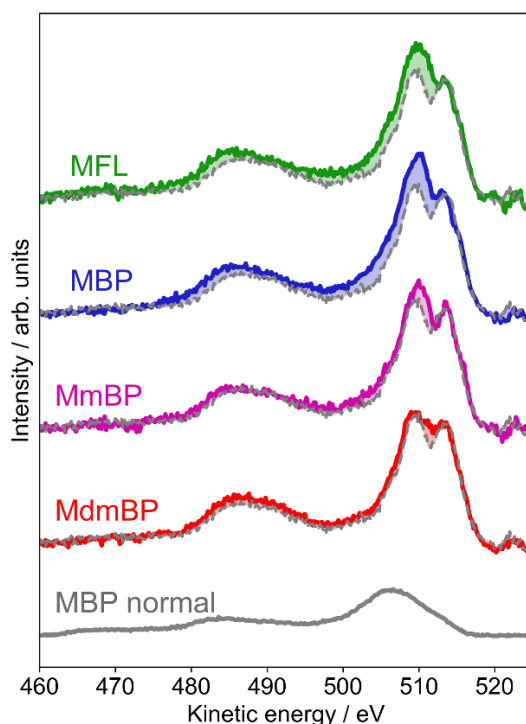


FIGURE 1. RAES spectra of MFL, MBP, MmBP, and MdmBP SAMs. The spectra were compared with the pure resonant spectrum recorded using the MHDA SAM and the normal Auger spectrum of the MBP SAM.

The RAES spectra at the O 1s → $\pi^*(\text{C}=\text{O})$ excitation are shown in Fig. 1. The spectra were compared with the pure resonant spectrum recorded with an MHDA (HS-(CH₂)₁₅-COOCH₃) SAM consisting of a long aliphatic chain, which was assumed to show no charge transfer contribution. The spectra for the MFL, MBP, and MmBP SAMs showed an increase in intensity corresponding to normal Auger decay, which indicates ultrafast charge transfer from the molecule to the Au substrate. For a quantitative analysis of the charge transfer dynamics, the RAES spectra were fitted with linear combinations of the normal Auger spectrum and the pure resonant Auger spectrum recorded with the MHDA SAM. The fitting analysis yielded charge transfer times of 16, 16, ~47, and ≥50 fs for the MFL, MBP, MmBP, and MdmBP SAMs, respectively. The CHC results demonstrate the conformational control of ultrafast charge transfer and suggest a negligible influence of the methylene bridge on the charge transfer dynamics.

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