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Effect of Functional Group (Fluorine) of Aromatic Thiols on Electron Transfer at the Molecule−Metal Interface

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Abstract: Electron transfer at the molecule−metal interface of self-assembled monolayers of 1,1′;4′,1″-terphenyl-4″-thiol (BBB) and its partially fluorinated counterpart (BFF: *p*-thiophenyl-nonafluorobiphenyl) on Au(111) is investigated by core-hole clock spectroscopy. Ultrafast electron transfer at the BBB/Au(111) interface in the low-femtosecond regime (on the same time scale as the C 1s core-hole lifetime, ∼6 fs) was observed. In contrast, for BFF/Au(111), the interface electron transfer was forbidden during the core-hole decay. This strongly suggests that fluorination of phenyl rings significantly enhances the localization of the excited electrons in the LUMO.

Introduction

Electron transfer at the molecule−substrate interface is important for technological applications such as biocatalysis,[1,2] electrochemistry,[3] photodiodes,[4,5] solar-energy conversion,[6,7] and, more recently, molecular electronics.[8−10] Intensive efforts have focused on the design and investigation of a variety of chemically bonded molecule−substrate interfaces that do not mask the molecule's electronic signature and favor ultrafast interface electron transfer, including sulfur−metal (usually S−Au bond),[11,12] carbon−silicon,[13,14] and metal−carbon π bonds.[15,16] Recently, Dadosh et al.[17] demonstrated that the electron transfer from molecules to metal substrates depends critically on the delocalization of the molecular orbitals and their connection to the metallic contacts: adding localizing groups (e.g., an oxygen atom at the center or a methylene group near the S−Au contacts) to the fully conjugated molecule (4,4′-biphenyldithiol) strongly interferes with the conjugated aromatic system and suppresses the overall conductance through the molecule. Functional molecular electronic devices such as molecular diodes can be realized by introducing different functional groups; however, these may inevitably modify the delocalization of the molecular orbitals and affect the electron transfer from molecule to electrode. In this Article, the effects of functional groups (fluorine in our case) on the electron transfer from the self-assembled monolayer of aromatic thiols to Au(111) substrates are investigated. Two aromatic thiol molecules are studied: 1,1′;4′,1″-terphenyl-4″-thiol (BBB) with fully conjugated lowest-unoccupied-molecular-orbital (LUMO); and its partially fluorinated counterpart (BFF: *p*-thiophenyl-nonafluorobiphenyl), in which the LUMO is mainly localized on the two fluorinated phenyl rings, as shown in Figure 1. Ultrafast electron transfer at the BBB/Au(111) interface in the low-femtosecond regime (∼6 fs) was observed. In contrast, for BFF/Au(111), the fluorination of phenyl rings significantly enhances the localization of excited electrons in the LUMO, thereby reducing the interface electron-transfer rate.

The ultrafast interface electron-transfer dynamics (in femtosecond time scale) is probed by the element specific synchrotron-based soft X-ray spectroscopy method, which has been referred to as core-hole clock spectroscopy.[18−26] This method has been

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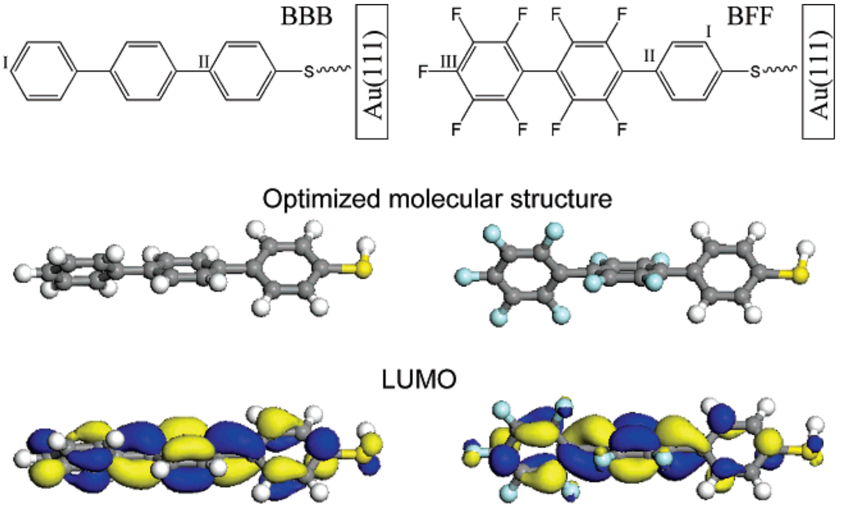

Figure 1. Schematic drawings of structures of BBB/Au(111) and BFF/Au(111) samples, and corresponding optimized molecular structures and calculated lowest-unoccupied-molecular-orbital (LUMO) of both molecules. Dark gray spheres represent the C atoms, white spheres are for the H atoms, green spheres are for the F atoms, and yellow spheres are for the S atoms. Three different chemically shifted carbon sites are highlighted in the schematic drawings. Site I: C(H) sites at which carbon atoms link to one H atom. Site II: C(C) sites at which carbon atoms link to three other C atoms. Site III: C(F) sites at which carbon atoms link to one F atom.

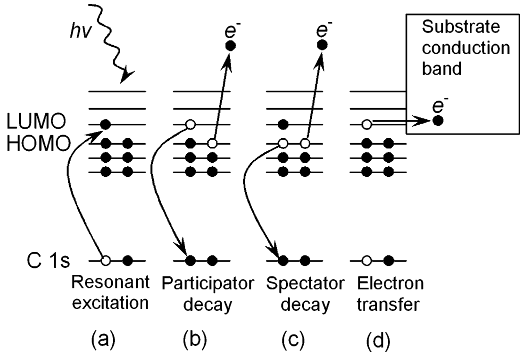

Figure 2. Schematic overview of the working principle of the core-hole clock spectroscopy. (a) A core level electron (C 1s in our case) is resonantly excited into adsorbate unoccupied molecular orbital (LUMO). In the core-hole lifetime (6 fs for C 1s core-hole), this excited electron can either (b) participate in the decay process leading to a one-hole final state (participator decay), or (c) be passive as a spectator leading to a two-hole-one-electron final state (spectator decay), or (d) directly transfer to substrate conduction band if the molecular orbital strongly couples with substrate density-of-states.

used to investigate electron transfer at S/Ru(0001),[18] CO/Ru-(0001),[22] and Ar/Ru(001)[23] interfaces in the sub-femtosecond or attosecond time scale, and has recently been extended to the study of sub-3-fs interface electron transfer for an aromatic adsorbate on $TiO_2(110)$.[19] The working principle of this synchrotron-based soft X-ray spectroscopy method is summarized in Figure 2. Core-hole clock spectroscopy monitors the decay events [participator or spectator decay as shown in Figure 2b and c, respectively] of the core-excited state involving the resonantly excited electron in an unoccupied molecular orbital [Figure 2a] upon the absorption of a photon with energy of $h\nu$. If the resonantly excited electron localizes in the unoccupied molecular orbital, the core-hole decays through the participator or spectator channels, and hence a particular valence band state or HOMO level of the molecule is enhanced at a certain photon energy (so-called "resonant enhancement"). If this molecular orbital is delocalized over many atomic centers, that is, strongly coupled to the substrate, a transfer of the excited electron to the substrate [Figure 2d] competes with the decay process that takes place during the core-hole lifetime (in our case, 6 fs for C 1s),[27] thereby reducing the resonant peak intensity. By monitoring the intensity changes in the resonant peaks, the interface electron transfer on the low-femtosecond or sub-femtosecond time scale can be evaluated using the core-hole lifetime as an internal reference clock.

Experimental Section

Synthesis details of *p*-thiophenyl-nonafluorobiphenyl (BFF) and 1,1′;4′,1″-terphenyl-4″-thiol (BBB) molecules will be reported elsewhere.[28] Monolayers of BFF and BBB molecules were formed by spontaneous adsorption of their thioacetate forms (*p*-acetylthiophenyl-nonafluorobiphenyl for BFF and 1,1′;4′,1″-terphenyl-4″-acetylthio for BBB) on Au(111)/mica substrates (SPI, USA). In all cases, the Au-(111)/mica samples were immersed in 3 mL of 1×10^{-4} M solutions in an N_2 environment for 48 h, using tetrahydrofuran (THF) as the solvent and 10 μL of 25% ammonia solution as the deprotection reagent to remove the acetyl protection groups. After growth, the samples were thoroughly rinsed using THF and immediately transferred into an ultrahigh-vacuum (UHV) chamber with a base pressure of 1.0×10^{-10} Torr. The photoemission and X-ray absorption experiments were carried at SINS beamline of Singapore synchrotron light source.[29,30] The X-ray absorption measurements were performed in total electron yield (TEY) mode with a photon energy resolution of 0.1 eV. The TEY signal, which is measured via the drain current from the sample, consists of all electrons escaping from the specimen as a result of the cascade process initiated by the absorption of each photon.[31] All photoemission (PES)

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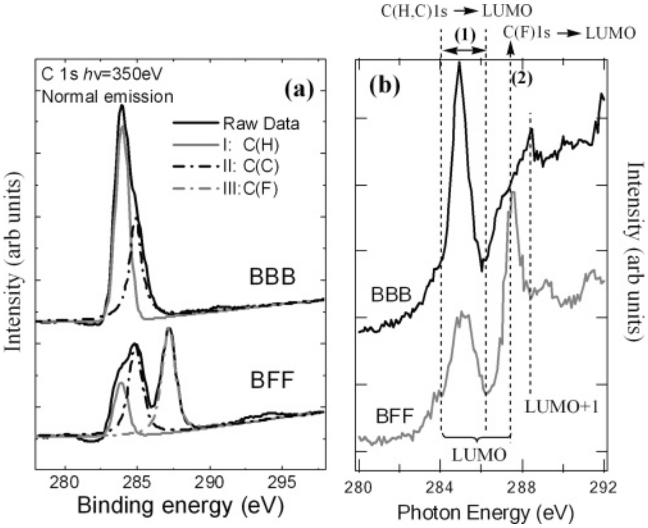

Figure 3. (a) High-resolution C 1s spectra of BBB/Au(111) and BFF/Au(111) samples (relative to Fermi level of Au substrate) recorded at a photon energy of 350 eV, and corresponding C K-edge X-ray absorption spectra for (b) BBB/Au(111) and BFF/Au(111).

and X-ray absorption spectra (XAS) were taken at normal emission at room temperature. The photon energies were calibrated using the position of Au ($4f_{7/2}$) line excited by first- and second-order light. The intensities of the spectra were normalized to the total incoming photon flux measured with a gold mesh. The quantum-chemical calculations for free neutral BBB and BFF thiol molecules were performed using DMol(3).[32−35]

Results and Discussion

Figure 3a shows the high resolution C 1s spectra for the BBB/Au(111) and BFF/Au(111) samples taken at an incident photon energy of 350 eV. The C 1s spectrum of BBB/Au(111) [upper part of Figure 3a] is fitted with two peaks at binding energies of 284.0 eV (peak I) and 284.7 eV (peak II), respectively, using the standard XPS fitting method of Shirley background subtraction followed by fitting the envelope with mixed Gaussian−Lorenztian functions. Peak I is assigned to excitation at C(H) sites (site I in Figure 1), and peak II is assigned to excitation at C(C) sites (site II). Because only 1 out of 18 carbon atoms is linked to an S atom for each molecule, the contribution to the C 1s spectrum at C(S) site was neglected in the fitting procedure. For BFF/Au(111) [lower part of Figure 3a], an additional peak III at higher binding energy of 287.0 eV was observed and assigned to excitation at C(F) sites (site III).[36] These three main chemically shifted carbon sites are highlighted in the schematic drawings of both molecules in Figure 1. The C *K*-edge X-ray absorption spectra of the BBB/Au(111) and BFF/Au(111) samples are shown in Figure 3b, which measures the unoccupied electronic density-of-states as a function of incoming photon energy.[31] A strong absorption peak (1) is seen at ∼284.8 eV for BBB/Au(111) in Figure 3b. This spectrum is in good agreement with that previously for BBB monolayer on Au,[37] and peak 1 is attributed to the C 1s → π_1*(LUMO) resonance at C(H, C) site orbitals. For BFF/Au(111) [Figure 3b], two strong resonances are observed at ∼284.7 eV [peak 1] and ∼287.6 eV [peak 2], respectively. The intensity of peak 2 is much higher than that of peak 1. In a detailed inner-shell electron energy loss spectroscopy (EELS) study of a series of $C_6H_xF_{6-x}$ molecules (fluorinated benzene derivatives),[38] two C 1s → π_1*(LUMO) resonant peaks were observed in EEL spectra; the lower-energy resonant peak was assigned to the resonance at C(H) sites, and the higher-energy one to the resonance at C(F) sites. As such, we assign peak 1 to the C 1s → π_1*(LUMO) resonance at C(H, C) sites, and peak 2 to the resonance at C(F) sites (see details in the Supporting Information). It is worth noting that both resonant peaks [peaks 1 and 2] are due to excitation from C 1s at different sites [C(H, C) and C(F) sites] to the same LUMO of BFF molecule.

Resonant enhancement occurs when the photoemission intensity for a particular valence band state or HOMO level of the molecule is enhanced at certain photon energies (in our case, the C 1s → π_1*(LUMO) absorption threshold photon energy).[18−20] In our experiment, the resonant enhancement was detected by collecting a set of valence band spectra with photon energy ranging from 280 to 290 eV across the C 1s → π_1*(LUMO) absorption threshold as shown in Figure 3b. The well-pronounced peak at the low binding energy side in the spectra, which appears to move linearly in energy as the photon energy was swept, is assigned to the C 1s core level excited by second-order light ($2h\upsilon$).[26] At resonance, a very small resonantly enhanced peak (peak a) with binding energy lower than 4 eV was observed for the BBB/Au(111) sample [Figure 4a], which showed roughly linear dispersion with the incident photon energy. In comparison, three strong resonantly enhanced peaks (peaks b, c, and d) near the valence band edge were observed for BFF/Au(111) as shown in Figure 4b when the photon energy was swept across the absorption threshold (287.6 eV) of C 1s → π_1*(LUMO) resonance at C(F) sites. The selected spectra at resonant regime for BBB/Au(111) and BFF/Au(111) were rearranged as a function of kinetic energy as shown in Figure 4c and d according to the equation:[39]

$$E_{\text{kinetic}} = h\upsilon - E_{\text{binding}} - \phi$$

where $h\upsilon$ is the incident photon energy, and ϕ is the work function of the electron analyzer (spectrometer), which is measured as 4.2 eV for our system. It is obvious that the kinetic energies of these resonantly enhanced peaks are constant and independent of the incident photon energy, indicating that the enhancements observed here most likely originate from the spectator decay processes.[20]

The intensity of the resonant peaks (sum of all of the resonant peaks) is strongly affected by the interface electron transfer. If the excited electron can transfer from the LUMO of the molecule to the conduction band of the metal substrate during the core-hole lifetime, the core-hole will decay through the normal Auger process, thereby reducing the intensity of the resonant peaks.[18−20] In this experiment, we compare the intensities of the resonant peaks for both BBB and BFF molecules at the C 1s → π_1*(LUMO) resonance threshold to study how the fluorination of phenyl rings affects the interface electron transfer. As shown

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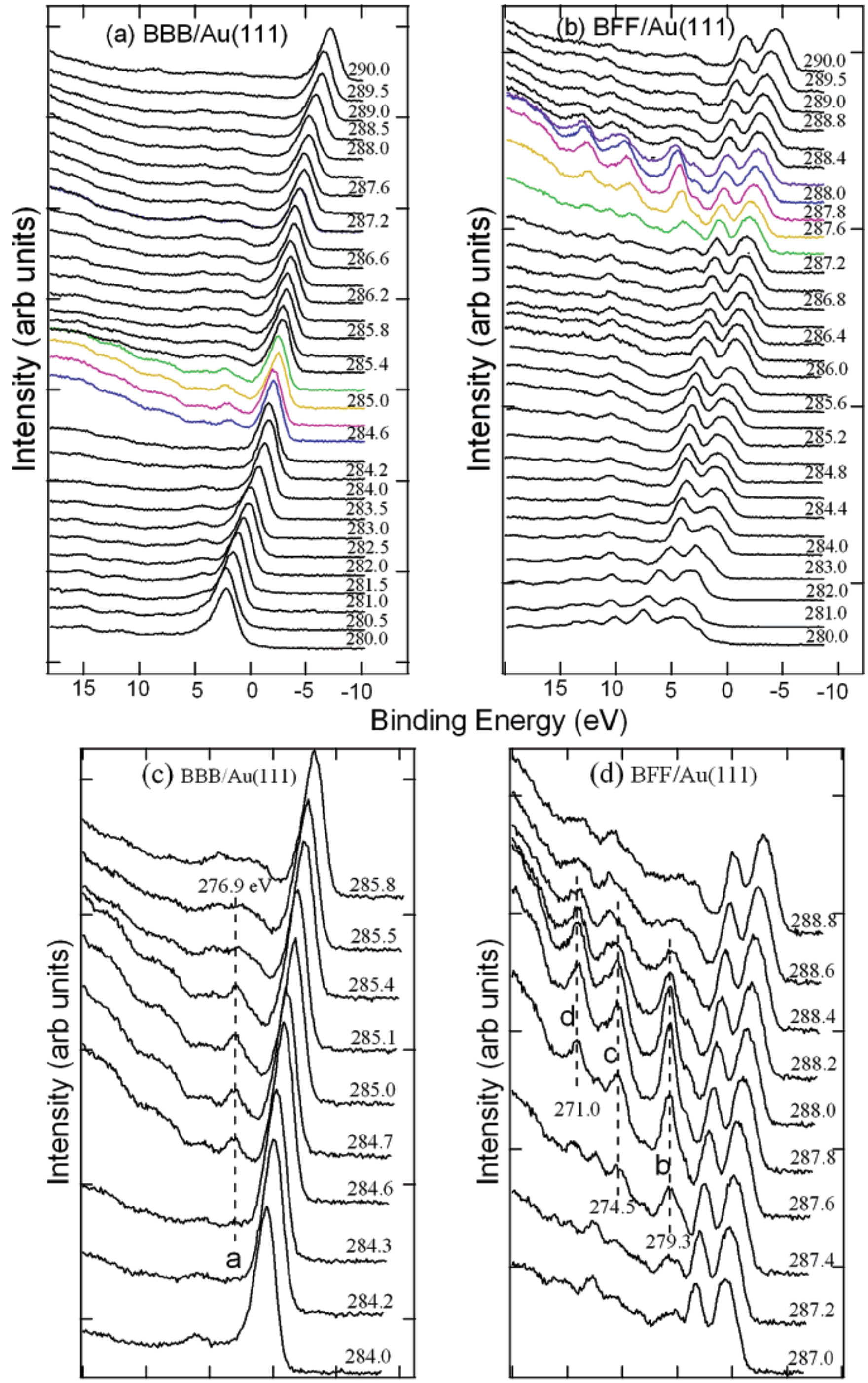

Figure 4. Core-hole clock spectra of (a) BBB/Au(111) and (b) BFF/Au(111) with photon energy ranging from 280 to 290 eV as a function of binding energy, and selected spectra (c) and (d) at resonant regime as a function of kinetic energy. The color lines highlight the resonant regime.

in Figure 4c and d, the intensity of the resonantly enhanced peaks (sum of peaks b, c, and d) for the fluorinated BFF/Au(111) is about 20 times higher than that (peak a) of the unfluorinated BBB/Au(111). To explain the strong resonantly enhanced effects for BFF/Au(111), we refer to the resonant process shown in Figure 2c. At resonance, the C(F) 1s core level electron is excited to the LUMO on the 10-as (0.01 fs) time scale,[19,20] which is far shorter than any possible electron-transfer time. During the core-hole lifetime of C 1s (~6 fs), the excited electrons remain in the LUMO because the LUMO of BFF is localized mainly at the two fluorinated phenyl rings. This contrasts with the LUMO of BBB, which is well delocalized over the whole molecule with substantial weight on the S atom, as shown in Figure 1. This makes the lifetime of the excited electron in the LUMO of BFF longer than that of the C 1s core-hole, hence inducing the strong resonantly enhanced peaks (spectator decay) shown in Figure 4d. In comparison, the delocalized LUMO in BBB favors electron transfer from the LUMO to the conduction band of Au(111).[17] As such, the core-hole decays through the normal Auger process during the C 1s core-hole lifetime, thereby reducing the intensity of the resonant peak. Because a small resonantly enhanced peak (peak a, spectator decay) is observed in Figure 4c, this shows that a small portion of the excited electrons still reside in the LUMO after core-hole decay. Hence, the transfer of excited electron to Au(111) takes place on the same time scale as the core-hole decay process (6 fs), competes with the spectator decay event, and reduces the intensity of the resonantly enhanced peak shown in Figure 4c.

In conclusion, the electron transfers at BBB/Au(111) and BFF/Au(111) interfaces have been probed in the low-femtosecond regime by core-hole clock spectroscopy and X-ray absorption spectroscopy. Ultrafast electron transfer at the BBB/Au(111) interface takes place on the same time scale as the C 1s core-hole lifetime (about 6 fs), indicating that delocalized adsorbate frontier molecular orbitals (LUMOs and HOMOs) are desired to achieve ultrafast interface electron transfer. It is also found that fluorination of phenyl rings significantly enhances the localization of the excited electron in the LUMO and reduces the interface electron-transfer rate. This study opens the way for the specific design of functional groups in molecules to control charge transfer in applications such as molecular electronics.

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Supporting Information Available: Molecular calculation results, and detailed assignments for the PES, XAS spectra, and the resonantly enhanced peaks in the core-hole clock spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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