

## Ultrafast Electron Transfer from Oligo(*p*-phenylene-ethynylene)thiol to Gold

Li Wang,<sup>†\*</sup> Wei Chen,<sup>†</sup> Chun Huang,<sup>‡</sup> Zhi-Kuan Chen,<sup>‡</sup> and Andrew T. S. Wee<sup>\*†</sup>

*Department of Physics, National University of Singapore, Singapore 117542, and Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore*

*Received: November 9, 2005; In Final Form: December 12, 2005*

The electron transfer dynamics of oligo(*p*-phenylene-ethynylene) (OPE) SAM on Au(111) was studied by resonant photoemission spectroscopy. The ultrafast electron transfer from OPE molecules to Au substrate was clearly observed. The time scale for this charge transfer is much less than 6 fs, the core-hole lifetime for C 1s. This strongly suggests that there is an intense interfacial electronic coupling between OPE molecules and the Au substrate.

Oligo(*p*-phenylene-ethynylene) (OPE) and its derivatives have attracted an enormous amount of attention as one of the most promising systems in molecular electronics.<sup>1</sup> They have exhibited negative differential resistance,<sup>2</sup> bistable conductance,<sup>3</sup> and rectification.<sup>4</sup> Understanding the electron-transfer process between OPE and supporting material is central to explaining these novel properties.<sup>5</sup>

Although there are many investigations of OPE, most of them focus on synthesis of its derivatives,<sup>6</sup> *I*–*V* measurements,<sup>7</sup> and electronic structural properties.<sup>8</sup> There are few reports on the electron-transfer process between OPE molecules and metals,<sup>9</sup> especially the electron-transfer dynamics. Resonant photoemission spectroscopy (REPES) provides a feasible method to monitor electron transfer occurring in the less-than-3-femtosecond (fs) time scale.<sup>10</sup> This letter reports the first experimental evidence for the presence of ultrafast electron transfer in OPE molecules chemisorbed on gold and the time scale for this transfer process by REPES technique.

OPE molecules of 4,4'-bis(phenylethynyl)-benzenethiol were synthesized in the way described in ref 11. OPE self-assembled monolayers (SAMs) were prepared on atomically flat Au(111)/mica substrates (SPI, USA), using methods known to give densely packed monolayers. The Au(111)/mica samples were immersed in 3 mL THF solution of OPE's thioacetate forms [4,4'-bis(phenylethynyl)-benzenethioacetate] with the concentration of  $1 \times 10^{-5}$  M in N<sub>2</sub> environment for 48 h, using 10  $\mu$ L of 25% ammonia solution as de-protection reagent to generate the free OPE thiol molecules. After growth, the SAM was immediately transferred to an ultrahigh vacuum chamber with a typical base pressure of  $1.0 \times 10^{-10}$  Torr. The photoemission and X-ray absorption experiments were carried on the beamline surface, interface, and nanostructure science (SINS) of Singapore synchrotron light source.<sup>12</sup> SINS uses a modified dragon-type monochromator covering the energy range 50–1200 eV. The emitted photoelectrons were measured using a hemispherical analyzer with seven channels (Omicron EAC200–125). The

X-ray absorption measurements were performed in total-yield mode with the photon energy resolution of 0.1 eV. All photoemission (PES) and X-ray absorption spectra (XAS) were taken at normal emission at room temperature.

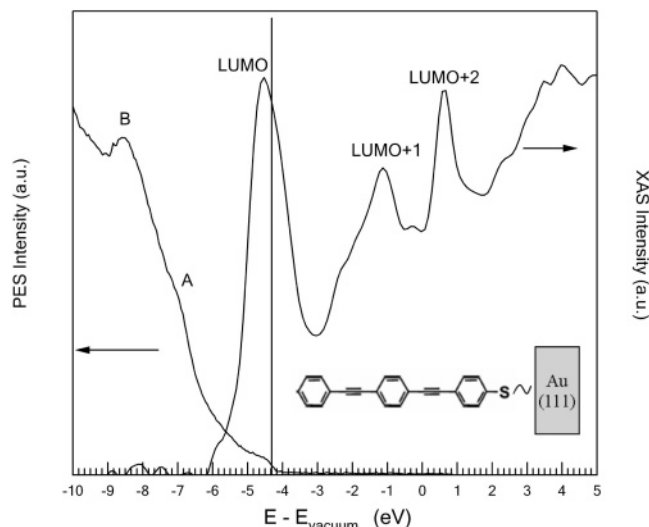
Figure 1 shows the electronic structure of OPE SAM/Au measured by the combination of the valence band spectrum taken at the incident photon energy of 60 eV (the left curve), and the C 1s XAS spectrum (the right curve) at the same energy scale. The vacuum level is used as the common energy reference. Two features labeled as A and B are observed in the occupied state, which is consistent with a previous report.<sup>8</sup> Moreover, the work function for OPE SAM/Au is measured to be about 4.35 eV by the cutoff method and is very close to the previous value.<sup>8</sup> Three sharp peaks are present in the C 1s XAS spectrum. The previous study on C<sub>60</sub> reveals that the resonances in the XAS spectrum well represent the unoccupied states.<sup>13</sup> Therefore, the three peaks observed here are assigned to the lowest unoccupied molecular orbital (LUMO), LUMO+1, and LUMO+2, respectively. Note that the LUMO is situated at  $\sim 0.2$  eV below the Fermi level. This is an effect of the core hole produced in XAS, which leads to energy shifts to higher binding energies.<sup>14</sup>

Figure 2 shows a series of REPES spectra of OPE SAM/Au for excitation energies in the region of the first resonance peak in the XAS spectrum. The intensities of the spectra were normalized to the total incoming photon flux measured with a gold grid. The photon energies and the binding energy scale were calibrated using the position of Au (4f<sub>7/2</sub>) photoelectric line excited by first- and second-order light. The peak located at the low binding energy side in the spectra, which appears to move linearly in energy with the excitation photon energy, corresponds to the C 1s core level photoionized by second-order light. Even though this C 1s peak is very prominent, an enhancement of particular valence band spectral features (as the dash line shows) is clearly observed when the excitation photon energy reaches the resonance. This behavior arises from participator decay process, which in a molecular solid is a major contribution to the resonant spectra in the low binding energy region, as long as the excited electron remains localized on the molecule probed.<sup>15</sup>

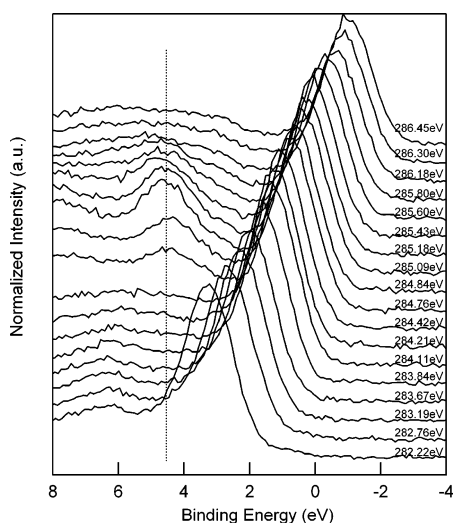
\* Corresponding authors. E-mail: phywl@nus.edu.sg; phyweets@nus.edu.sg

<sup>†</sup> National University of Singapore.

<sup>‡</sup> Institute of Materials Research and Engineering.



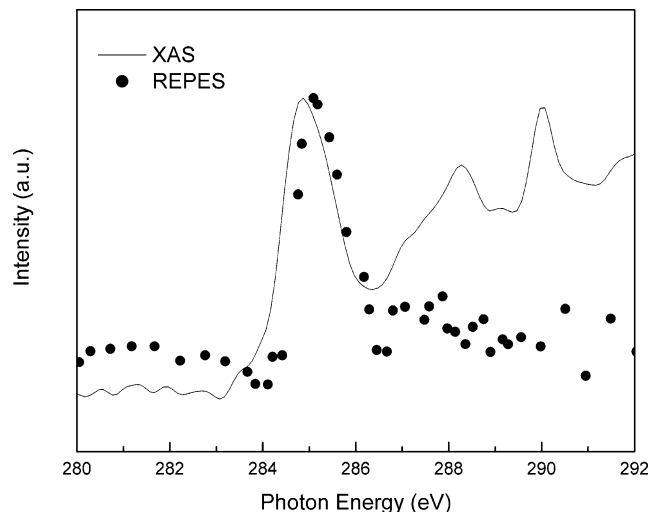
**Figure 1.** Electronic structure of OPE SAM/Au. The energy is referenced to the vacuum level. The vertical line represents the position of the Fermi level. The inset shows the schematic diagram for 4,4'-bis(phenylethynyl)-benzenethiolate on Au(111).



**Figure 2.** Series of RPES spectra of OPE SAM/Au across the first resonance in the XAS. The excitation energy is indicated on the right side of the graph.

The REPES intensities are obtained by subtracting the C 1s core level signal from the valence PES and then integrating the valence PES containing the resonant photoemission signal for the photon energies studied in the XAS. This allows one to probe the effect of placing the excited electron in different unoccupied states. Figure 3 gives the comparison of the REPES and the XAS spectra for OPE SAM/Au. Only a single peak was observed in the REPES spectrum. The peak position for the REPES is situated at 285.09 eV and is close to the first absorption peak in the XAS (284.87 eV). In contrast, the signals observed in the XAS for the LUMO+1 and LUMO+2 are completely quenched in the REPES.

For a core-excited system, the signal will decay exponentially via Auger process with a time constant given by the core-hole lifetime. REPES monitors only anticipator decay processes in which the excited electron takes part. If the particular unoccupied orbital to which the excited electron was promoted is coupled to unoccupied substrate states, the excited electron delocalizes into the substrate with the characteristic electron transfer time and competes with the decay process characterized by core-hole lifetime. If these two time scales are comparable, the



**Figure 3.** Comparison of REPES and XAS for OPE SAM/Au. The spectra were normalized on the intensity of the main peak.

REPES intensity serves as a fingerprint for the extent of excited electron localization. For very fast electron transfers, the REPES vanishes completely for the particular state.

The observation of an intense peak in the REPES corresponding to the LUMO in the XAS, as shown in Figure 3, clearly reveals that the excited electron promoted to the LUMO is localized on the molecule. This is in good agreement with the fact that in the presence of the core hole, the LUMO is attracted to be about 0.2 eV below the Fermi level (shown in Figure 1), which means the decay of an electron residing in the LUMO to the Au substrate is forbidden. Similar energy forbidden transition was observed in the LUMO in bi-isonicotinic acid on TiO<sub>2</sub>.<sup>10</sup> However, for the electrons excited to the LUMO+1 or LUMO+2, transfers to the Au substrate are energetically feasible. In fact, the presence of these transfer processes with ultrafast transfer rate is confirmed by the vanishing REPES signal for these two states. The core-hole lifetime for the inner shell vacancy at C KLL is about 6 fs and weakly depends on the chemical environment.<sup>16</sup> Thus, the time scale for the decay of the electrons residing in the LUMO+1 or LUMO+2 to the Au substrate must be much less than 6 fs. During the core-hole lifetime, the back electron transfer process in which the electrons transfer from the gold substrate to the molecules is much slower since the Fermi level of Au(111) is below the unoccupied molecular orbitals of OPE.<sup>17</sup> The charge transfer across the molecule/Au interface is mainly dominated by the electron transfer from the molecules to the Au(111) as is observed here. The observation of this ultrafast electron transfer strongly suggests that there is an intense interfacial electronic coupling between OPE molecules and the Au substrate.

In conclusion, we observed the ultrafast electron transfer process from the LUMO+1 or LUMO+2 in OPE molecules to the Au substrate with a time scale of much less than 6 fs by resonant photoemission technique. This strongly suggests that the interfacial electronic coupling between molecules and support materials is crucial to the transport across a molecule/metal or semiconductor junction.

**Acknowledgment.** This work was supported by A\*STAR grant no. R-144-000-106-305.

## References and Notes

- (1) Kushmerick, J. G.; Allara, D. L.; Mallock, T. E.; Mayer, T. S. *MRS Bull.* **2004**, June, 396.

- (2) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.
- (3) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price Jr., D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss P. S. *Science* **2001**, *292*, 2302.
- (4) Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2000**, *77*, 1224.
- (5) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3015.
- (6) Yamaguchi, Y.; Tanaka, T.; Kobayashi, S.; Wakamlya, T.; Mat-subara, Y.; Yoshida, Z. *J. Am. Chem. Soc.* **2005**, *127*, 9332.
- (7) Kushmerick, J. G.; Holt, D. B.; Pollack, S. K.; Ratner, M. A.; Yang, J. C.; Shull, T. L.; Naciri, J.; Moore, M. H.; Shashidhar, R. *J. Am. Chem. Soc.* **2002**, *124*, 10654.
- (8) Zangmeister, C. D.; Robey, S. W.; van Zee, R. D.; Yao, Y.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 3420.
- (9) Kushmerick, J. G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. *Phys. Rev. Lett.* **2002**, *89*, 086802.
- (10) Schnadt, J.; Brühwiler, P. A.; Patthey, L.; O'Shea, J. N.; Södergren, S.; Odelius, M.; Ahuja, R.; Karis, O.; Bäessler, M.; Persson, P.; Siegbahn, H.; Lunell, S.; Mårtensson, N. *Nature* **2002**, *418*, 620.
- (11) Tour, J. M.; Jones II, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
- (12) Yu, X. J.; Wilhelmi, O.; Moser, H. O.; Vidyaraj, S. V.; Gao, X. Y.; Wee, A. T. S.; Nyunt, T.; Qian, H. J.; Zheng, H. W. *J. Elec. Relat. Phenom.* **2005**, *144*, 1031.
- (13) Kondo, D.; Sakamoto, K.; Takada, H.; Matsui, F.; Amemiya, K.; Ohta, T.; Uchida, W.; Kasuya, A. *Surf. Sci.* **2002**, *514*, 337.
- (14) Persson, P.; Lunell, S.; Brühwiler, P. A.; Schnadt, J.; Södergren, S.; O'Shea, J. N.; Karis, O.; Siegbahn, H.; Mårtensson, N.; Bäessler, M.; Patthey, L. *J. Chem. Phys.* **2000**, *112*, 3945.
- (15) Brühwiler, P. A.; Karis, O.; Mårtensson, N. *Rev. Mod. Phys.* **2002**, *74*, 103.
- (16) Coville, M.; Thomas, T. D. *Phys. Rev. A* **1991**, *43*, 6053.
- (17) Duncan, W. R.; Stier, W. M.; Prezhdo, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 7941.