

Photoelectron Spectroscopy to Probe the Mechanism of Electron Transfer through Oligo(phenylene vinylene) Bridges

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The valence spectra of monolayers of ferrocene oligo(phenylene vinylene) (OPV) methyl thiols deposited on gold have been collected using synchrotron radiation. These spectra reveal the relative positions of the gold Fermi level, the highest occupied molecular orbital of ferrocene, and an upper limit for the highest occupied molecular orbital of OPV. The onset of ejected electrons from ferrocene occurs 0.2 eV below the Fermi level of gold, and the onset of ejected electrons from OPV occurs at least 0.8 eV below the Fermi level of gold. The difference between these values implies a hole injection barrier from ferrocene to OPV of at least 0.6 eV. Such a large injection barrier rules out a hopping mechanism for electron transfer between gold and ferrocene through OPV.

Electron transfer through monolayers deposited on metal surfaces has been studied for a number of years. Knowledge gained from these studies has been relevant to biosensing¹ and to devices such as organic light-emitting diodes (OLEDs).² More recently, applications in molecular electronics have been suggested. An understanding of electron transfer and electron transport through organic molecules linked to metal contacts is imperative for this opportunity to be exploited fully.

Recently, an unusual distance dependence was observed in the interfacial electron-transfer rate constants for electron transfer between ferrocene and gold through an oligo(phenylene vinylene) (OPV) bridge.³ Rate constants do not rapidly decay as expected for a tunneling process as the electron-transfer distance is increased by using longer phenylene vinylene oligomers to link ferrocene and gold. This unexpected result can be explained two ways: (i) the mechanism is single-step tunneling, but the tunneling is sufficiently fast that it is not rate-limiting, so the electron transfer is adiabatic, or (ii) the mechanism is hopping rather than single-step tunneling. Such a hopping mechanism has recently been reported in other systems.^{4–6} In addition to the distance dependence of the rate constants, the experimental activation energy is also relevant when considering a mechanism. In the case of ferrocene oligo(phenylene vinylene) monolayers on gold, an activation energy of 0.25 eV was observed for the electron-transfer reaction.³ If the highest occupied or lowest unoccupied molecular orbital (HOMO or LUMO) of phenylene vinylene is within 0.25 eV of the HOMO of ferrocene, then hopping is a possible mechanism. If both of the phenylene vinylene energy levels are farther separated from the HOMO of ferrocene, hopping can be ruled out. Gold electrodes have previously been used to inject holes into the valence band of poly(phenylene vinylenes) in OLEDs.⁷ Thus, hole hopping through the OPV HOMO is an important mechanism to consider in the current system. To distinguish between

hopping and single-step tunneling mechanisms, detailed information about the electronic structure of the interfacial system is necessary.

Photoelectron spectroscopy (PES) is an established method of determining the energies of states occupied by valence electrons in thin solid films. Most studies on organic films reported to date involve multilayers that are either spin-coated or deposited *in situ* by condensation from the vapor. Fewer studies have been done on organic monolayers. The smaller number of molecules in a monolayer makes the signal from photoemitted electrons weak when compared with that from thicker layers. In addition, strong photoemission from the underlying metallic electronic states can mask the less intense signal from the monolayer. The use of synchrotron radiation rather than He lamp emission for such studies minimizes both of these difficulties; the high intensity of synchrotron radiation maximizes the signal from the small number of molecules in a monolayer, and the tunability of synchrotron radiation allows the contribution from the underlying metallic states to be minimized. Alkanethiol^{8,9} and benzenethiol¹⁰ self-assembled monolayers on gold have been studied previously by both ultraviolet photoelectron spectroscopy and angle-resolved ultraviolet photoelectron spectroscopy to answer questions about the structure and orientation of such monolayers.

The quest for electronically functional organic materials has prompted many studies of energy level alignment at the interface between organics and metals; these studies have been reviewed by Ishii et al.¹¹ In particular, the electronic structures of multilayers of oligo(phenylene vinylenes) on gold^{12–14} and calcium¹⁵ have been reported.

Self-assembled monolayers of oligo(phenylene vinylene) methyl thiols containing between one and four phenylene vinylene repeat units were prepared on gold substrates as previously described.^{3,16,17} In anticipation of complex spectra, a number of other monolayers were also prepared for study by PES. These include pentadecanethiol, nonanethiol, hexadecanethiol, ferrocene carboxyl-linked nonanethiol, and oligomers

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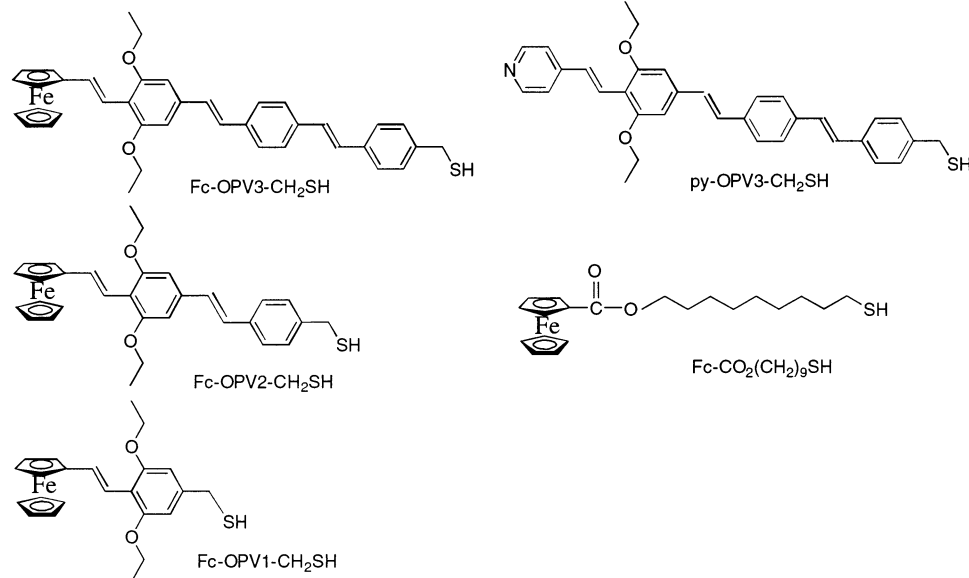


Figure 1. Structures of thiols.

of phenylene vinylene methyl thiol terminated with pyridine rather than ferrocene. Figure 1 shows the structures of these molecules.

Photoelectron spectra were collected using beamline 8-1 at the Stanford Synchrotron Radiation Laboratory. Spectra were collected with a base pressure in the ultra-high-vacuum (UHV) chamber of 2×10^{-10} Torr. A hemispherical analyzer (Physical Electronics) was used to detect the kinetic energy of ejected electrons. Binding energies are referenced to the gold Fermi level. In cases where the Fermi edge was not visible, peaks due to Au 4f_{5/2} and Au 4f_{7/2} electrons were used to determine its position. (These Au 4f electrons have binding energies of 87.6 and 83.9 eV, respectively, below the Fermi level.) Spectra were collected using incident radiation in the energy range of 50–140 eV; however, because of the high photoionization cross sections of the gold 5d electrons, the most useful spectra were taken at 130 eV, near the Cooper minimum for these gold electrons.¹⁸

Figure 2 shows the valence band spectra of bare gold¹⁹ and of two phenylene vinylene oligomers that are the same aside from having different terminal groups. One oligomer is terminated by ferrocene, the other by pyridine. The Fermi edge of gold is visible in the bare gold spectrum, along with photoemission of 5d electrons in the 1–10 eV range. An axis break shows emission from gold 4f electrons as well. Curve fits confirm that the position of the Fermi edge is separated from the positions of the Au 4f_{5/2} and Au 4f_{7/2} electrons by 87.6 and 83.9 eV, respectively, as expected. Deposition of a monolayer containing ferrocene attached to gold by three phenylene vinylene units (Fc-OPV3) changes the valence band considerably. The 1–10 eV region is dramatically different: a sharp spectral feature at low binding energy is notable. Emission of gold 4f electrons, although still visible, has been attenuated. The third spectrum in Figure 2 shows the effect of terminating OPV with pyridine rather than with ferrocene. Attenuation of the gold 4f electrons is the same; however, the 1–10 eV region of the valence band spectrum is quite different. There is an absence of sharp spectral features at low binding energy; instead, there is a gradual onset. Figure 3 shows spectra for a number of other monolayers, including alkanethiols, ferrocene alkanethiols, and other ferrocene-terminated oligomers of phenylene vinylene.

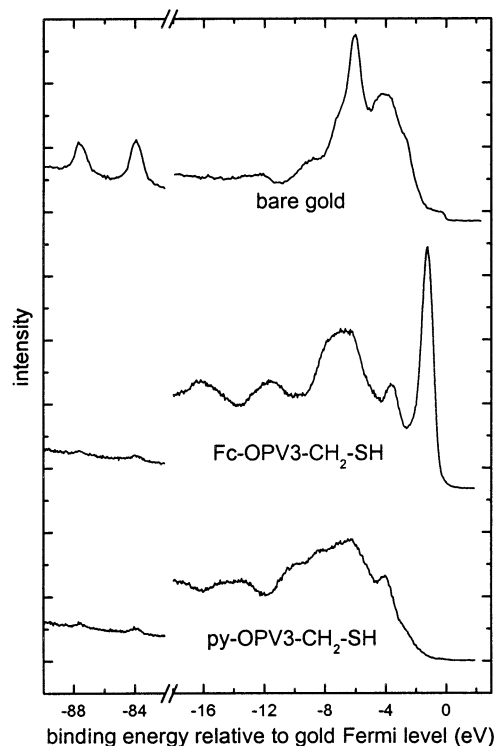


Figure 2. PES valence band spectra taken at $h\nu = 130$ eV of bare gold, Fc-OPV3-methyl thiol monolayers on gold, and pyridine-OPV3-methyl thiol monolayers on gold. The comparison of the two differently substituted OPVs shows which bands arise from ferrocene and which bands arise from conjugated hydrocarbons such as those of OPVs. However, pyridine also is a conjugated hydrocarbon, so the bands are not due solely to OPV.

In the Fc-OPV3-methyl thiol spectrum in Figure 1, the sharp feature closest to the gold Fermi level has an onset at -0.2 eV. This feature is due to the ionization of ferrocene to ferrocenium. It reveals the position of the ferrocene HOMO in this interfacial system. The similarities among the Fc-OPV spectra in Figures 2 and 3 and the Fc-CO₂(CH₂)₉SH spectrum in Figure 3 suggest that these valence band spectra are dominated by the electronic structure of ferrocene rather than by the electronic structure of the bridges (i.e., OPVs or alkanes). To obtain information about the energy levels in OPV, it is

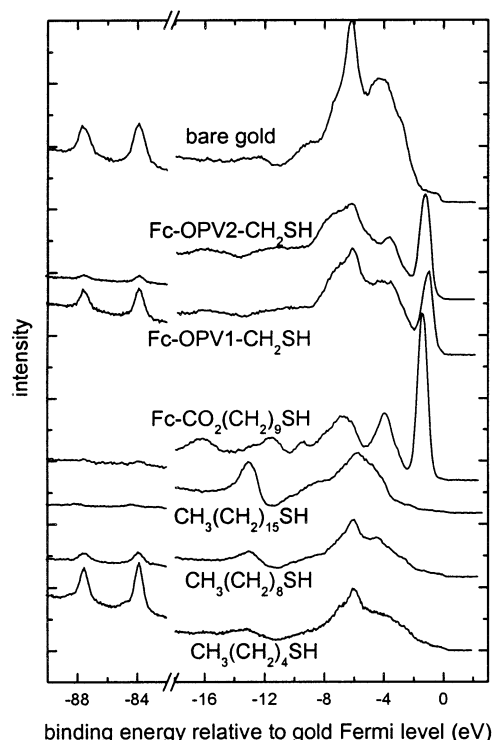


Figure 3. PES valence band spectra of bare gold and of a number of different adsorbates on gold, including alkanethiols of different lengths, ferrocene alkanethiol, and ferrocene oligo(phenylene vinylene) of different lengths.

useful to look at a spectrum of a monolayer containing OPV without ferrocene. A pyridine-terminated OPV3 thiol was available for this purpose.¹⁷ The pyridine-OPV3 monolayer spectrum reinforces the idea that many of the peaks in the Fc-OPV3 monolayer spectrum are due to the ferrocene part of the molecule. The pyridine-OPV3 spectrum has a gradual onset at -0.8 eV and is otherwise featureless in the 0 to -2 eV range. It is clear that the low binding energy ferrocene peak is not obscuring any OPV bands that would have otherwise been observable.²⁰

Because both Fc-OPV3-methyl thiol and pyridine-OPV3-methyl thiol have conjugated hydrocarbon groups that are not OPV-related (cyclopentadienyl and pyridine rings, respectively) it is not possible to attribute the onset of photoemission in either spectrum to an OPV HOMO. The gap between the Fc onset and the py-OPV onset does, however, give a lower limit for the difference in HOMO levels of ferrocene and OPV. Figure 4 shows an energy level diagram derived from the PES spectra. The ferrocene HOMO level and the upper limit of the OPV HOMO were determined by extrapolation to the baseline of a line tangent to each spectrum at 10% of the intensity of the first peak or shoulder. The gold Fermi level is taken as 0, the ferrocene HOMO is located 0.2 eV below the Fermi level, and the upper limit for the position of an OPV HOMO is 0.8 eV below the Fermi level. Subtraction results in a lower limit of 0.6 eV for the difference between the ferrocene HOMO and the OPV HOMO. From this result, we conclude that hole hopping is not the mechanism for electron transfer through oligo(phenylene vinylene) bridges between ferrocene and gold because the OPV and ferrocene HOMO levels are not aligned within the limits of the 0.25 eV activation energy for electron transfer that has been observed experimentally.³ This observation is not incompatible with hole injection by gold into the valence band of poly(phenylene vinylenes) in organic light-emitting

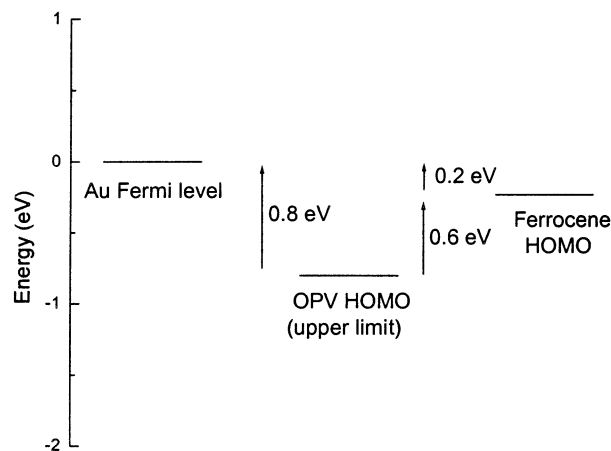


Figure 4. Energy level diagram derived from PES. The 0.6 eV minimum gap between the ferrocene HOMO and an OPV HOMO rules out electron hopping in this system.

diodes because of differing conjugation lengths, monomer substituents, deposition conditions, and interface dipole layers.

Hole injection into our OPVs has now been ruled out, but there remains the possibility that electron hopping through the OPV LUMO leads to the weak distance dependence of electron transfer. However, data from previous studies suggest that this is not the case. Cyclic voltammetry does not show peaks due to reduction of the OPV bridges in aqueous electrolyte.³ In addition, literature values for oligo(phenylene vinylene) LUMO positions suggest that electron transfer from ferrocene to OPV is uphill by at least 1.6 eV.^{3,4}

Photoelectron spectroscopy has proven to be a useful tool in distinguishing between two mechanisms of interfacial electron transfer. Identifying efficient molecular promoters of electrons over distances on the nanometer scale and understanding how such transport occurs continue to be an active and potentially useful area of research.

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prior to being loaded into the vacuum chamber and analyzed by UPS. As a result, they are not expected to be rigorously clean. Because they are used later in wet chemical soaks during self-assembled monolayer formation, depositing gold films in situ did not make sense. The gold films are sufficiently clean that the Fermi edge is visible.

(20) It is reasonable to assume that the dipole layer at the interface between gold and Fc-OPV3-methyl thiol is of essentially the same magnitude and direction as the dipole layer at the interface between gold and pyridine-OPV3-methyl thiol because the molecular structures are the same except for the terminal groups situated about 2 nm from the metal-organic interface. As a result, it is possible to compare energies in the two monolayers without explicitly finding a vacuum level shift that originates from interfacial dipole layers as described by Ishii et al. in ref 11.