

Fermi Level Alignment in Self-Assembled Molecular Layers: The Effect of Coupling Chemistry

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Photoelectron spectroscopy was used to explore changes in Fermi level alignment, within the π – π^* gap, arising from modifications to the coupling chemistry of conjugated phenylene ethynylene oligomers to the Au surface. Self-assembled monolayers were formed employing either thiol (4,4'-ethynylphenyl-1-benzenethiol or OPE-T) or isocyanide (4,4'-ethynylphenyl-1-benzeneisocyanide or OPE-NC) coupling. The electronic density of states in the valence region of the two systems are nearly identical with the exception of a shift to higher binding energy by about 0.5 eV for OPE-NC. Corresponding shifts appear in C(1s) spectra and in the threshold near E_F . The lack of change in the optical absorption suggests that a rigid shift of the Fermi level within the π – π^* gap is the major effect of modifying the coupling chemistry. Qualitative consideration of bonding in each case is used to suggest the influence of chemisorption-induced charge transfer as a potential explanation. Connections to other theoretical and experimental work on the effects of varying coupling chemistries are also discussed.

Introduction

Electronic coupling effects at the semiconductor–metal interface have long been recognized as a critical issue in inorganic semiconductor device physics,¹ making it no surprise that their impact on transport and injection in organic electronic device structures is also a main theme.^{2–4} These effects are even more evident in nanoscale junctions, relevant for envisioned molecular electronics applications, where details of coupling to specific molecular levels become pertinent.^{5–10} The goal of producing nonlinear transport characteristics derived from the molecular electronic structure is often masked by effects induced at the contacts as evidenced, for instance, in the observation of asymmetric I – V characteristics in symmetric molecules due to asymmetric electrode coupling.^{11,12} In addition, many model systems for testing concepts in molecular electronics involve self-assembled monolayers (SAM) that employ strong linking groups, such as thiol–gold, to control surface bonding. Significant electronic interactions and hybridization effects operative in this strong chemisorption regime further serve to enhance the importance of understanding the details of interface coupling in molecular electronic systems.

Several factors control interfacial coupling at metal–organic interfaces. One of these is the energetic separation between the

molecular levels important for transport and the Fermi level/levels of the contacts. A second component is the strength of the coupling between these levels, which depends on the energetic overlap but also may hinge on factors such as orbital symmetry and localization. Techniques such as ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES) provide direct access to information on energetics and band alignment while investigation of level broadening or time-domain (lifetime) studies, via time-resolved photoemission or other measurements are required to interrogate coupling strength.¹³

This contribution provides a study contrasting and comparing two different linking chemistries for SAMs of phenylene ethynylene oligomers on gold. Photoelectron spectroscopy was employed to investigate energetic alignment for SAMs coupled via thiol linking groups versus linking with isocyanide chemistry, along with complementary optical absorption and reflection–absorption infrared spectroscopy (RAIRS). We will suggest a rationalization for the results based on the disparate bonding/chemisorption processes in these two systems.

In the following sections, experimental procedures will be described, followed by experimental results from photoelectron spectroscopy studies of thiol versus isocyanide coupled molecules. Discussion of these results, with a brief review of previous findings for thiol-coupled SAMs, will focus on simple models for the bonding in each case and the influence this has

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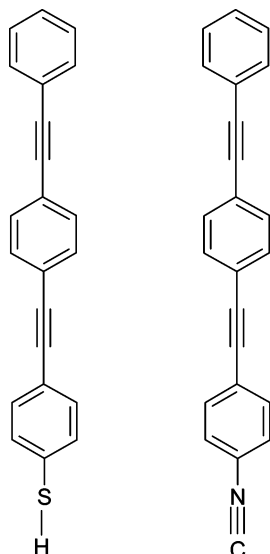


Figure 1. Schematic representations of (left) 4,4'-ethynylphenyl-1-benzenethiol (OPE-T) and (right) 4,4'-ethynylphenyl-1-benzeneisocyanide (OPE-NC).

on electronic level alignment. We will also discuss connections to related theoretical and experimental studies.

Experimental Methods and Procedures

Synthesis. The isocyanide product was synthesized using the classical palladium–copper cross-coupling protocol.¹⁴ The first step involved the reaction of 4-ethynylaniline with 1-bromo-4-(phenylethynyl) benzene¹⁵ to give the monosubstituted aniline derivative 4-[[4-(phenylethynyl)ethynyl]] aniline. The final product, 4,4'-ethynylphenyl-1-benzeneisocyanide (OPE-NC), was obtained by conversion of the amine group to the isocyanide following a modified literature procedure.¹⁶

The thiolated analogue, 4,4'-ethynylphenyl-1-benzenethiol (OPE-T), was synthesized as described previously.¹⁷ Schematic representations of 4,4'-ethynylphenyl-1-benzenethiol (OPE-T) and 4,4'-ethynylphenyl-1-benzeneisocyanide (OPE-NC) are provided in Figure 1.

SAM Growth Protocols. Monolayers were grown on polycrystalline Au that were prepared by evaporation of 200 nm of Au onto a 20 nm Cr adhesion layer on a Si (100) substrate. All films were cleaned prior to SAM formation by exposure to ultraviolet/ozone (Jelight Corporation)¹⁸ for 15–20 min, rinsed in 18.2 MΩ cm H₂O, and dried under a stream of ultrapure nitrogen.

SAMs of OPE-NC were grown in an argon purged drybox (<1 ppm O₂, <0.5 ppm H₂O) in a ~0.5 mM solution in dichloromethane (CH₂Cl₂, Aldrich). CH₂Cl₂ was distilled over calcium chloride under nitrogen. The films were allowed to incubate for 24 h. OPE-T films were grown in a 2:1 ratio of CH₂Cl₂/anhydrous ethanol. After removal from solution the substrates were rinsed with CH₂Cl₂ in the drybox. Reflection–absorption infrared spectroscopy (RAIRS) data were acquired on samples grown concurrently with those used in the UPS investigation to ensure monolayer quality.

Exposure of some films to ambient conditions or high concentrations of O₃ was also performed to investigate the stability of isocyanide-coupling to oxidation effects. Ozone exposure was accomplished by placing samples in the UV/O₃ cleaner after it had been run for 10–15 min to build the ozone concentration.

Characterization Techniques. Samples were introduced into the UPS analysis chamber via a fast entry load lock immediately after rinsing with solvent and removal from the drybox. The

excitation source for photoelectron spectroscopy was a linearly polarized He I (21.22 eV) line source. Light was incident at 45° from the sample normal and photoelectrons were collected at normal emission with a 180° hemispherical electrostatic analyzer operated with a 3 eV pass energy to produce an overall resolution of about 100 meV. The energy scale is referenced to the Au Fermi level (E_F) of the substrate for all spectra. X-ray photoelectron spectroscopy studies of core levels were performed in a separate UHV chamber with a high sensitivity Kratos AXIS 165 XPS spectrometer.¹⁸

Absorption spectra in the UV–visible range were acquired using a Perkin-Elmer Lambda Bio20 UV–visible spectrometer from solutions of approximately 10^{−5} mol/L in CH₂Cl₂.¹⁸ RAIR spectra of monolayers and the isolated molecule (in KBr) were obtained using a BioRad FTS 7000 Series spectrometer and a variable-angle, specular reflectance accessory (VeeMax, Pike Technologies) at a sampling angle of 75° relative to the surface normal.¹⁸

Results

Stability of Isocyanide-Coupled Monolayers. Oxidation-related effects in isocyanide-coupled monolayers were studied to determine their potential influence on measurements of band alignment. Representative spectra from a fresh OPE-NC monolayer and two examples of oxidized samples are provided in Figure 2a. Changes due to oxidation are readily observable in UP spectra of OPE-NC on Au. Similar spectral shifts, of about 0.7 eV to lower binding energy, and broadening are observed after exposing the film to either the ambient for 6 days (solid line in Figure 2a) or to a high concentration of O₃ for 30 s (dotted spectrum in Figure 2a). We note that the direction of the oxidation-induced binding energy shift is opposite to that which occurs between fresh thiol-coupled to fresh isocyanide-coupled monolayers, discussed below. These results provide a means of clearly identifying problematic samples.

RAIRS data corresponding to the O₃ exposed sample is provided in Figure 2b, along with infrared data for a fresh sample. We note that Stapleton and co-workers have given a detailed analysis of the structure and bonding of OPE-NC interaction with Au previously, and we use their notation here.¹⁹ Data from an oxidized sample shows a distinct peak at 2270 cm^{−1}, absent in the fresh monolayer. This peak is assigned to the $\nu(\text{N}=\text{C}=\text{O})$ associated with oxidation of R–NC to R–NCO.¹⁹ Comparable RAIR data were obtained from films left in the ambient laboratory for 6 days. Photoelectron spectra of fresh OPE-NC exposed to the ambient for less than 5 min were reproducible and RAIR data showed no discernible $\nu(\text{NCO})$ peak at 2270 cm^{−1}. Exposure to strongly oxidizing O₃ required about 1 h for the initial growth of $\nu(\text{NCO})$ intensity. No changes were observed in photoelectron spectra of isocyanide-coupled monolayers stored in 10^{−10} mbar for 1 week.

Photoelectron Spectroscopy Results: Fermi Level Alignment. Typical UPS data from SAMs formed using thiol-based linking chemistry and isocyanide coupling are provided in Figure 3a. Data from the two systems are nearly identical with respect to observed bands, intensities, and degree of attenuation of the Au substrate contribution. These similarities are consistent with similar structure in the monolayers, such as packing and tilt, for the different linking chemistries.

The origins of the spectral features have been discussed previously for the thiol-coupled system.^{20,21} Photoelectron spectra are dominated by intensity from molecular levels associated with the aromatic phenyl ring system. These levels are not dramatically affected, to within the level discernible by UPS,

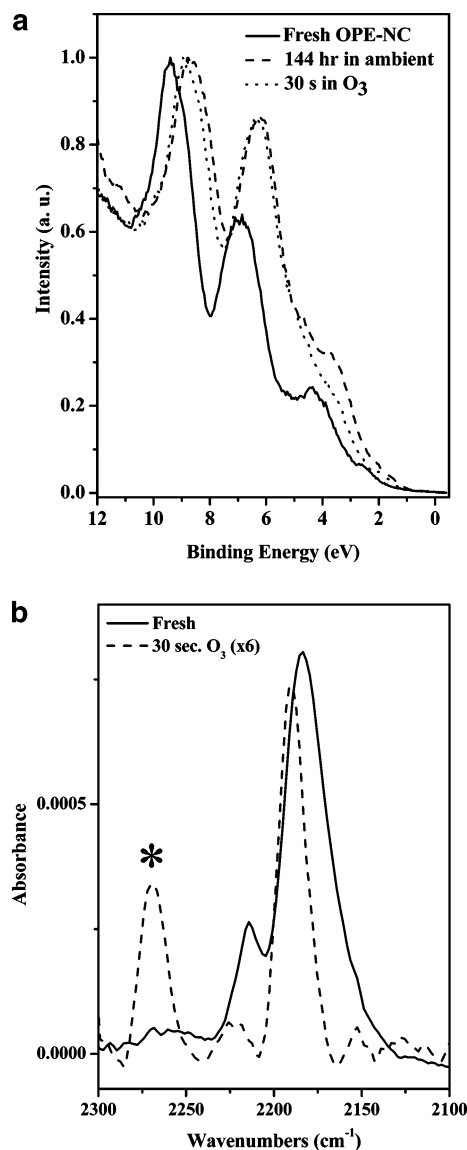


Figure 2. (a) Ultraviolet photoelectron spectra of a monolayer of OPE-NC on Au acquired fresh from solution (solid line), after 6 days in the ambient (dashed line), and exposed to high concentration of O_3 for 30 s. (dotted line). (b) RAIR spectrum of corresponding fresh monolayer and after 30 s. O_3 exposure. Peak corresponding to R–NCO at 2270 cm^{-1} is shown with *.

by the change in coupling group. Intensity associated with the sulfur–Au interaction at the interface is not evident for the three-ring oligomers examined here because photoelectron attenuation effects mask interfacial information from the approximately 2-nm-thick film. This is also true for the isocyanide-coupled monolayers.

Intensity below 5 eV, at about 9 eV and 6 to 7 eV, arises predominantly from C–C and C–H σ bonding levels on the phenyl rings. Contributions to the photoelectron intensity from π levels occur primarily in the range from 5 eV up to E_F . The structure at 3.9 eV for the thiol-coupled system (or 4.4 eV in the case of isocyanide) is associated with π orbitals, derived from benzene e_{1g} levels that remain largely localized on individual phenyl rings, with little weight along the backbone of the oligomer. Intensity from $C\equiv C$ π bonds also contributes in this region. Coupling of the phenyl rings leads to a splitting of the second of the twofold degenerate e_{1g} levels of benzene to form bonding, at about 1.9 eV (thiol) and 2.4 eV (isocyanide), levels and antibonding levels around 5 eV. The bonding

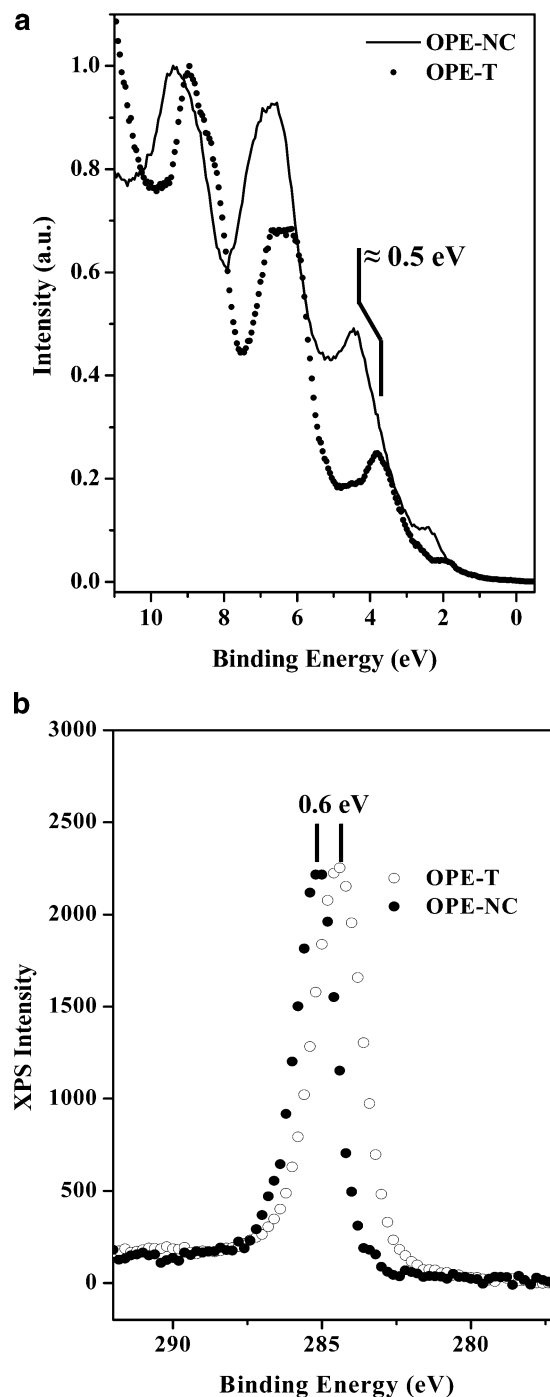


Figure 3. (a) Ultraviolet photoemission spectra of monolayers of OPE-T (plus) and OPE-NC (solid line) on polycrystalline Au. (b) Shift in the C(1s) core level for OPE-T (plus) and OPE-NC (solid line).

contribution cannot be located precisely because of large intensity in the band around 6.5 eV associated with molecular orbitals derived from $1a_{2u}$ and $2e_{2g}$ benzene levels.

The major difference evident in the photoelectron spectra from the two monolayers is a rigid shift by approximately 0.5 eV toward larger binding energy (relative to E_F) for the isocyanide spectrum. A comparison of C(1s) core level spectra, provided in Figure 3b, also indicates a shift of ~ 0.5 eV in the isocyanide-coupled system, further suggesting a rigid shift of all electronic levels associated with the change in coupling chemistry.

UV–visible spectroscopy data from free thiol- and isocyanide-coupled molecules are shown in Figure 4. The spectra are

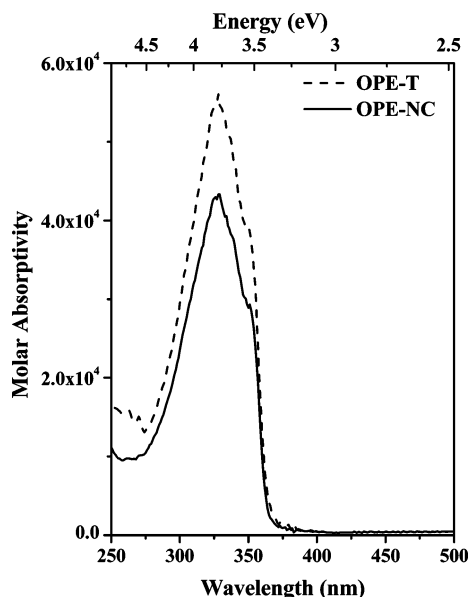


Figure 4. Ultraviolet-visible spectra of 1×10^{-5} mole/liter solutions of OPE-T (dashed line) and OPE-NC (solid line) in CH_2Cl_2 .

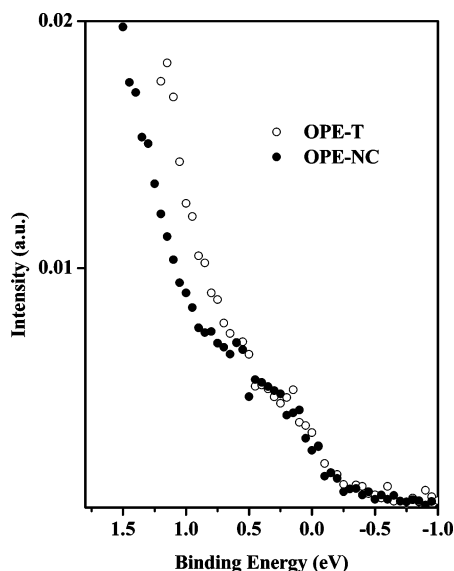


Figure 5. (a) Photoelectron spectra OPE-T (open circle) and OPE-NC (solid circle) for the region near the Fermi level showing the shift in threshold associated with the change in coupling.

nearly identical, exhibiting an absorption thresholds at 370 nm (3.3 eV) and $\pi-\pi^*$ (S_0 to S_1) transition absorbance maxima at 328 nm (3.8 eV). Changing the coupling group clearly thus does not modify the $\pi-\pi^*$ band gap of the free molecule and the same should hold for the adsorbed system. If we make the reasonable assumption of similar excitonic effects, then the transport gap will be the same for both coupling chemistries. Thus, to first order, the predominant influence of the isocyanide-coupling group is a shift of the Fermi level, relative to the thiol-coupled case, within the $\pi-\pi^*$ band gap of the conjugated oligomer, increasing the barrier to hole injection and decreasing the barrier to electron injection.

Similar differences between thiol and isocyanide bonded systems are evident close to the Fermi level. Figure 5 provides a comparison of the region close to E_F for spectra that have been normalized to each other within 0.1 eV of E_F . This provides an indication of the difference in the shape of the threshold emission for the two coupling chemistries. The threshold in the

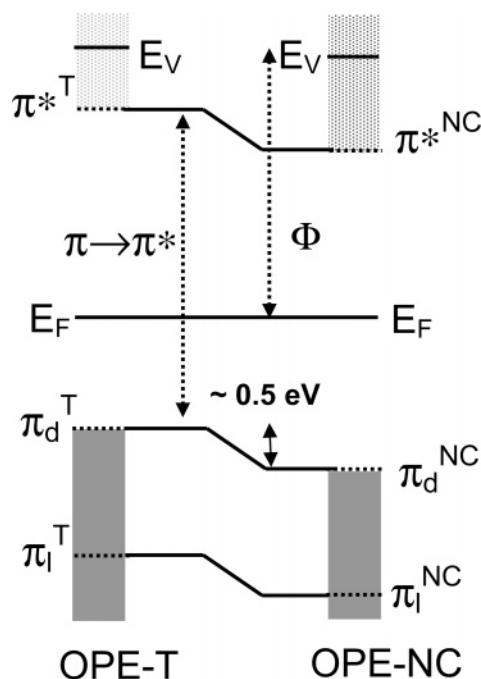


Figure 6. Schematic diagram of the relative alignment for thiol-coupled OPE compared to isocyanide coupling. E_V represents the vacuum level, Φ is the surface work function, π_d signifies the delocalized π levels, and π_l identifies localized π levels.

isocyanide system is shifted by several tenths of an electronvolt to larger binding energy; consistent with the shift observed in the other molecular levels. This appears to be slightly smaller than the shift in the other electronic bands but varies somewhat with the details of the normalization chosen.

Discussion

Chemisorption and Charge-Transfer Effects. Figure 6 provides a schematic representation of the relative Fermi level alignment for the two different coupling chemistries derived from the experimental results discussed above. This section will present simple ideas, based on qualitative pictures of bonding for the two coupling groups to the Au surface, with the goal of suggesting an explanation for the observed shift in the Fermi level from thiol to isocyanide coupling. This is not intended to provide a complete picture of the bonding and quantitative account for observed energy level shifts. The goal is to introduce a framework within which to consider how chemisorption could lead to the observed differences. Results from calculations for free molecules, using density functional based methods, are provided to aid in developing and supporting the ideas. These calculations employed density functional theory within the local density approximation as implemented with DMol3 package of Materials Studio (Accelrys).¹⁸ The geometry of the molecules was first optimized using Materials Studio Forcite.¹⁸

The calculations for the thiol radical and isocyanide OPE indicate that the molecular ionization potentials of the three A_2 symmetry π levels, giving rise to the prominent peak at around 4 eV for both chemistries, differ by less than 0.1 eV for the two cases in the gas phase. (As discussed below, the thiol species adsorbs as a radical after abstraction of the hydrogen.) Differences in the ionization energy alone thus cannot explain the shift observed between the two chemisorbed species. This suggests that we consider differences in bonding as an alternative factor contributing to the changes in band alignment for these two linking chemistries.

UPS studies of thiol-bound phenylene–ethynylene oligomers, coupled with complementary investigation of the unoccupied levels using two-photon photoelectron spectroscopy (2PPES),^{20,21} led to a qualitative picture with Fermi level alignment controlled by chemisorption-induced Au-to-S charge transfer at the molecule–substrate interface. That work combined information on occupied and unoccupied molecular levels to indicate a Fermi level shift of about 0.6 to 0.7 eV from mid-gap of the organic system. UPS/IPES studies of similar organic molecules without thiol coupling, such as anthracene, indicate a mid-gap position for the Fermi level, as do studies of polymers such as PPV and related oligomers.^{22–24} The shift of the Fermi level toward the occupied levels that occurs with thiol-coupling is then attributed to Au-to-molecule (primarily Au-to-S) charge transfer^{20,21} and the concurrent formation of a dipole. For simplicity, the “interfacial” region is assumed to consist of the coupling group, with associated Au-to-S charge transfer, and resulting dipole and aromatic portion of the molecule is assumed to lie essentially outside this dipole region. The magnitude of the charge transfer in this region, and the corresponding dipole, determines the shift with respect to the Au Fermi level of the molecular levels associated with the phenylene ethynylene component. This picture is a simplification and detailed changes in charge transfer/polarization that occur upon thiol (or isocyanide) coupling throughout the oligomer and coupling group must be determined through self-consistent calculations. However, it provides an adequate starting point for our discussion.

Previous theoretical work is consistent with this picture, indicating charge transfer from the Au surface to the thiol-coupled molecule.^{5,25,26} Bonding in thiol-based systems involves the loss of hydrogen, forming a radical with a half-filled, predominantly S (3p)-derived orbital.^{26–29} Interaction with Au d/p levels leads to partial refilling of this level. This charge transfer creates a dipole component directed from the molecule to the substrate, raising the potential on the molecule as outlined in theoretical work by Xue et al.⁵ and Piccinin et al.²⁶ DFT-based calculations for benzenedithiol coupled to Au electrodes found Au-to-molecule charge transfer with an accompanying increase in the electrostatic potential on the molecule of between 0.8 and 1.2 eV in the region of the phenyl ring. This is about a factor of 2 larger than the value of 0.6–0.7 eV estimated for thiol-coupled OPE based on UPS/2PPES. However, the calculations were performed on di-thiol species coupled at two Au electrodes, whereas the UPS measurements of necessity involve Au–thiol coupling at only one interface.

This chemisorption-induced interface dipole picture then requires reduced metal-to-molecule charge for the isocyanide group compared to the thiol-coupling case to explain the observed shift. To understand this, we consider a frontier molecular orbital (FMO) picture often used to describe the CO–metal surface, metal–carbonyl systems, and isocyanide–ligand based chemistry. Two dominant contributions to the CO–metal (or NC, NC[−]) bonding interaction^{30–34} are emphasized. Sigma donation from the lone pair orbital on carbon (5σ) to unoccupied metal levels is coupled with back-donation from occupied metal levels to unoccupied π* (2π*) molecular orbitals. In the case of CO, σ donation and π* back-donation are comparable.^{30,32} Cyanide-derived systems generally display a stronger tendency for σ interaction.^{30,35,36}

A low-lying (energetically), half-filled 5σ orbital is a signature of free, neutral CN, resulting in an effective acceptor, while CN[−] displays a high lying, doubly occupied 5σ level and is an efficient donor to the metal surface.^{35,36} Interaction/charge transfer between the conjugated oligomer and the isocyanide

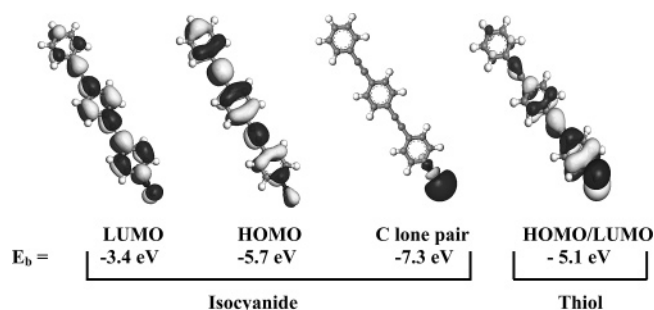


Figure 7. Wave function plots for the HOMO, HOMO-1, and carbon lone pair orbitals of the free isocyanide molecule resulting from density functional calculations.

group will reduce the acceptor character, leading to an interaction with the Au surface between extremes of CN and CN[−].

Electronic structure calculations provide information on the effects of interaction between the oligomer and CN group. Calculations were also performed for the radical formed by H abstraction from the thiol molecule for comparison. The absolute energies, gaps, and so forth from these calculations will not be correct but they should allow examination of the relative level ordering and occupancies of molecular orbitals on the isocyanide molecule and comparisons between the two molecules. Wave function plots for the highest occupied level and the lowest unoccupied level of the isocyanide OPE are provided in Figure 7, along with the lone pair orbital on the terminal carbon atom. The highest occupied half-filled level of the thiol-based molecule is also shown. The 5σ (carbon lone pair) orbital is filled, as in CN[−], so significant donation into this level will not occur (broadening due to interaction could, in principle, shift weight above the Fermi level). However, the 5σ level lies at a relatively deep binding energy, below levels with π character on both the oligomer and the CN group, so a picture of the isocyanide group as purely CN[−] is not correct. The implication of ordering with the π levels above the 5σ for the FMO-based model is unclear but previous work suggested that repulsion from the like-symmetry, higher lying occupied π levels would further reduce the tendency for back-donation to π* orbitals on the molecule increasing the influence of molecule-to-metal σ bonding.³⁷

The doubly occupied highest occupied molecular orbital (HOMO) of OPE-NC is close in energy to the half-filled radical level for the thiol case, whereas the LUMO of OPE-NC is significantly higher in energy. Following Piccinin, et al., the Au Fermi level will lie slightly above the half-filled thiol radical level.²⁶ This is well removed from the lowest unoccupied molecular orbital (LUMO) on OPE-NC, reducing the tendency for charge donation into empty isocyanide-coupled molecular levels.

The preceding discussion suggests factors that could lead to a tendency for 5σ donation to the Au surface to dominate chemisorption of isocyanide-coupled OPE, with weaker back-donation to the molecule. This dominant contribution of σ donation to gold, palladium, and transition-metal surfaces in interactions with aryl isocyanides has been postulated in a number of previous studies.^{33,34,37,38} In addition, the degree of covalent character in the bonding can play an important role in driving the difference between thiol coupling and isocyanide coupling.

In contrast to early studies, recent theoretical work has suggested that the isocyanide (cyanide)–metal interactions are dominantly covalent in character.³⁹ In this case, no substantial charge transfer is expected and effects associated with dipole formation are reduced. The validation of these qualitative

considerations requires a detailed examination of the bonding for OPE-NC or analogous systems.

Xue et al. performed computational studies of the effect of varying coupling in single molecule junctions and presented a qualitatively similar picture.⁵ Calculations for benzenedithiol and dibenzenedithiol indicated charge transfer from the Au surface and an increase in the electrostatic potential on the molecule once coupling to the electrodes was included. In contrast, calculations for isocyanide coupling show reduced charge transfer. The main effect appears as charge rearrangement in the Au–CN region reminiscent of the polarization of σ levels that occurs during CO bonding. There is a small additional electron barrier after coupling but virtually no charge transfer onto the phenyl ring or increase in the electrostatic potential on the molecule.⁵ Theoretical work exploring the adsorption of H–NC on Ni also suggested a very slight electron transfer to the metal surface upon chemisorption.⁴⁰

Support for this picture is provided by surface infrared studies of the isocyanide vibrational modes. The N≡C stretching mode, $\nu(\text{N}\equiv\text{C})$, exhibits a small increase from about 2120 cm^{-1} for the “free” molecule (in KBr) to about 2180 cm^{-1} for the molecule bound to the Au surface. A blue shift of the frequency upon adsorption is often noted in the literature as evidence of predominant σ donation in the bonding, whereas π^* back-donation is associated with a red shift of the stretch frequency. The σ orbitals are weakly antibonding so that pulling charge from these levels strengthens the C≡N bond and increases $\nu(\text{N}\equiv\text{C})$, whereas back-donation into the π^* level, which is also antibonding, weakens the bond and produces a red-shift.^{34,39,41} In a study of CN^- and CO bonding to transition-metal clusters, Ample et al. theoretically established a correlation between σ donation to the metal and an increase in $\nu(\text{N}\equiv\text{C})$, while a frequency decrease occurred when back-donation dominated the bonding.³⁰ The work by Stapleton et al. also concluded that the bonding of the isocyanide oligomer has predominant σ character on Au, while more π back-donation is found for adsorption on Pd.¹⁹ As a final note, however, we caution that additional factors, such as Pauli exclusion or “wall” effects, modification to molecular dipoles, and details of the electric field in the surface region should also be considered in interpreting the frequency shift that occurs upon chemisorption.^{42–47}

Further supporting evidence may be present in the measured work functions for the two systems. At the simplest level, reduced Au-to-molecule charge-transfer associated with the isocyanide coupling group should lead to a reduction in the work function for this case. The measured monolayer work function values are 4.2–4.3 eV for thiol coupling, compared to 4.1 eV for isocyanide. This does suggest a reduction for the isocyanide, but it is close to experimental uncertainty and, as in the case of the intensity near E_F (Figure 5), smaller than the shift observed in the HOMO and C(1s) peaks. The total work function is determined, however, from contributions in addition to charge rearrangement in the coupling region, including charge rearrangement/dipole formation within the phenylene ethynylene portion of the molecule which may differ for the two coupling chemistries. A quantitative explanation of the correlation between level shifts versus the work function is beyond this simple discussion and requires a self-consistent theoretical treatment for the adsorbed system.

In summary, the difference in band alignment for the two coupling chemistries is suggested to arise in large part due to different charge transfer and electrostatic potentials in the near-surface region. This difference in potential is associated with different charge transfer onto the molecule from the gold, and

corresponding dipoles, associated with the two coupling groups. The molecular levels on the oligomer are then shifted *with reference to the substrate Fermi level* upon changing from thiol to isocyanide coupling chemistry. The rigid shift of all levels is a strong indication that different interfacial electrostatics, charge transfer and dipole formation, is the origin, and not chemical bonding to specific levels.

Connections with Previous Work. Previous work, both experimental and theoretical, on the effects of different coupling groups provide an interesting context within which to consider these results. Connections with theoretical work by Xue et al. have been discussed already.⁵ We simply note here that those calculations also point toward a shift of the Fermi level away from the occupied levels and toward the LUMO when the linking group is modified from thiol to isocyanide. A similar result is apparent in simple cluster-based calculations.⁴⁸

A combined UPS and scanning tunneling microscopy (STM) study of terthiophene monolayers coupled to Au by thiol or selenol linkages correlated conductance behavior with density of states measured using photoemission.^{49,50} As in the case studied here, the change in coupling did not significantly modify the electronic structure of the terthiophene molecule, primarily leading to a shift in the relative position of the Fermi level. Thiol coupling produced an increased “hole-injection barrier” by about 0.2 eV. The reduced hole barrier for selenol-linked terthiophene was correlated with an increased apparent height of the molecules in STM, assumed to indicate an increased conductance through the selenol linkage. No discussion of potential origins of the change in barrier was provided.

Transport through isocyanide-coupled molecular systems was measured using both nanopore devices and STM.^{49,50} The STM study involved both thiol and isocyanide coupled molecular systems, but direct quantitative comparison of conductance was not provided. The separation between the HOMO level, identified in dI/dV spectra, and the Fermi level was found to decrease from 1.15 to 0.92 eV with the change from thiol to isocyanide coupling. This is opposite to the increase in separation between the π levels and E_F from thiol to isocyanide observed in this work. The origin of this discrepancy is unknown although it may arise from assumptions made for the electrostatic potential division between the two junctions, substrate–molecule and STM tip–molecule.^{51–53}

The influence of the coupling group was also examined in a conducting probe atomic force microscopy study of alkanes linked to Au via either thiol or N≡C groups.⁵⁴ Measurements of the conductivity as a function of alkane length indicated a small contact decrease in contact resistance for N≡C coupling than thiol, by about 10%. The UPS data presented here cannot provide a rationalization for this small change in the alkane system. However, additional work by the same group, but employing aromatic oligomers, has indicated a significantly increased contact resistance for isocyanide coupling. This is qualitatively consistent with the changes in electronic structure observed here, pointing to an increase in the interfacial barrier to hole injection for isocyanide coupling.⁵⁵

Summary

Modifications to the electronic structure near the Fermi level in self-assembled monolayers of phenylene ethynylene oligomers coupled to Au by either thiol or isocyanide groups were studied primarily using UPS. All valence electronic levels and the C(1s) core level exhibit a shift to higher binding energy by about 0.5 eV to 0.6 eV when the coupling group is changed from thiol to isocyanide. A shift in the threshold of several tenths

of an eV is also present. No change is evident in optical absorption from the molecule. Thus, the major effect of the coupling group appears to be a shift of the Fermi level within the band gap of the oligomer. Thiol coupling results in a Fermi level alignment about 0.5 eV closer to the occupied states (HOMO) than isocyanide coupling. An explanation for this change in Fermi level alignment was suggested based on qualitative pictures of the bonding to the Au surface in each case and the resultant charge transfer onto the molecule. Thiol bonding to Au leads to charge transfer from the *substrate to the molecule* resulting in a dipole field that shifts the Fermi level toward the HOMO. In the qualitative picture presented here, isocyanide coupling results in reduced charge transfer, possibly even transfer/polarization of carbon lone pair electrons *toward the gold surface*. Changing the coupling group from thiol to isocyanide degrades energetic alignment for hole injection into the π levels of the oligomer at the molecule–Au interface.

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References and Notes

- (1) Monch, W. *Surf. Sci.* **1994**, *300*, 928.
- (2) Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mater.* **1999**, *11*, 605.
- (3) Kahn, A.; Koch, N.; Gao, Y. *J. Polym. Sci. Polym. Phys.* **2003**, *41*, 2529.
- (4) Salaneck, W. R.; Stafstrom, S.; Bredas, J.-L. *Conjugated Polymers at Surfaces and Interfaces*; Cambridge University Press: Cambridge, 1996.
- (5) Xue, Y. Q.; Datta, S.; Ratner, M. A. *J. Chem. Phys.* **2001**, *115*, 4292.
- (6) Heurich, J.; Cuevas, J. C.; Wenzel, W.; Schon, G. *Phys. Rev. Lett.* **2002**, *88*.
- (7) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384.
- (8) Stokbro, K.; Taylor, J.; Brandbyge, M.; Mozos, J. L.; Ordejon, P. *Comput. Mater. Sci.* **2003**, *27*, 151.
- (9) Taylor, J.; Brandbyge, M.; Stokbro, K. *Phys. Rev. Lett.* **2002**, *89*.
- (10) Taylor, J.; Brandbyge, M.; Stokbro, K. *Phys. Rev. B* **2003**, *68*, 121101.
- (11) Reichert, J.; Ochs, R.; Beckmann, D.; Weber, H. B.; Mayor, M.; von Lohneysen, H. *Phys. Rev. Lett.* **2002**, *88*, 176804.
- (12) Weber, H. B.; Reichert, J.; Weigend, F.; Ochs, R.; Beckmann, D.; Mayor, M.; Ahlrichs, R.; von Lohneysen, H. *Chem. Phys.* **2002**, *281*, 113.
- (13) Zhu, X. Y. *Surf. Sci. Rep.* **2004**, *56*, 1.
- (14) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.
- (15) Maya, F.; Tour, J. M. *Tetrahedron* **2004**, *60*, 81.
- (16) Henderson, J. I.; Feng, S.; Bein, T.; Kubiak, C. P. *Langmuir* **2000**, *16*, 6183.
- (17) Tour, J. M. *Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture, and Programming*; World Scientific: Singapore, 2003.
- (18) Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.
- (19) Stapleton, J. J.; Daniel, T. A.; Uppili, S.; Cabarcos, O. M.; Naciri, J.; Shashidhar, R.; Allara, D. L. *Langmuir* **2005**, *21*, 11061.
- (20) Zangmeister, C. D.; Robey, S. W.; van Zee, R. D.; Yao, Y.; Tour, J. M. *J. Phys. Chem. B* **2004**, *108*, 16187.
- (21) Zangmeister, C. D.; Robey, S. W.; van Zee, R. D. *J. Am. Chem. Soc.* **2004**, *126*, 3420.
- (22) Salaneck, W. R.; Friend, R. H.; Bredas, J. L. *Phys. Rep.* **1999**, *319*, 232.
- (23) Veenstra, S. C.; Stalmach, U.; Krasnikov, V. V.; Hadzioannou, G.; Jonkman, H. T.; Heeres, A.; Sawatzky, G. A. *Appl. Phys. Lett.* **2000**, *76*, 2253.
- (24) Yannoulis, P.; Frank, K. H.; Koch, E. E. *Surf. Sci.* **1991**, *241*, 325.
- (25) Majumder, C.; Briere, T.; Mizuseki, H.; Kawazoe, Y. *J. Chem. Phys.* **2002**, *117*, 7669.
- (26) Piccinin, S.; Selloni, A.; Scandolo, S.; Car, R.; Scoles, G. *J. Chem. Phys.* **2003**, *119*, 6729.
- (27) Di Felice, R.; Selloni, A.; Molinari, E. *J. Phys. Chem. B* **2003**, *107*, 1151.
- (28) Schreiber, F.; Eberhardt, A.; Leung, T. Y. B.; Schwartz, P.; Wetterer, S. M.; Lavrich, D. J.; Berman, L.; Fenter, P.; Eisenberger, P.; Scoles, G. *Phys. Rev. B* **1998**, *57*, 12476.
- (29) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
- (30) Ample, F.; Curulla, D.; Fuster, F.; Clotet, A.; Ricart, J. M. *Surf. Sci.* **2002**, *497*, 139.
- (31) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772.
- (32) Gajdos, M.; Eichler, A.; Hafner, J. *J. Phys.: Condens. Matter* **2004**, *16*, 1141.
- (33) Guy, M. P.; Guy, J. T.; Bennett, D. W. *J. Mol. Struct.: THEOCHEM* **1985**, *23*, 95.
- (34) Murphy, K. L.; Tysse, W. T.; Bennett, D. W. *Langmuir* **2004**, *20*, 1732.
- (35) Daum, W.; Dederichs, F.; Muller, J. *Phys. Rev. Lett.* **1998**, *80*, 766.
- (36) Beltramo, G. L.; Shubina, T. E.; Mitchell, S. J.; Koper, M. T. M. *J. Electroanal. Chem.* **2004**, *563*, 111.
- (37) Guy, M. P.; Guy, J. T.; Bennett, D. W. *Organometallics* **1986**, *5*, 1696.
- (38) Joo, S. W.; Kim, W. J.; Yun, W. S.; Hwang, S.; Choi, I. S. *Appl. Spectrosc.* **2004**, *58*, 218.
- (39) Nelin, C. J.; Bagus, P. S.; Philpott, M. R. *J. Chem. Phys.* **1987**, *87*, 2170.
- (40) Yang, H.; Whitten, J. L. *J. Phys. Chem.* **1996**, *100*, 5090.
- (41) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1978.
- (42) Curulla, D.; Clotet, A.; Ricart, J. M.; Illas, F. *J. Phys. Chem. B* **1999**, *103*, 5246.
- (43) Mielczarski, J. A. *J. Phys. Chem.* **1993**, *97*, 2649.
- (44) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927.
- (45) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
- (46) Trenary, M. *Annu. Rev. Phys. Chem.* **2000**, *51*, 381.
- (47) Wasileski, S. A.; Weaver, M. J. *Faraday Discuss.* **2002**, *121*, 285.
- (48) Seminario, J. M.; De la Cruz, C. E.; Derosa, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 5616.
- (49) Patrone, L.; Palacin, S.; Bourgoin, J. P.; Lagoute, J.; Zambelli, T.; Gauthier, S. *Chem. Phys.* **2002**, *281*, 325.
- (50) Patrone, L.; Palacin, S.; Charlier, J.; Armand, F.; Bourgoin, J. P.; Tang, H.; Gauthier, S. *Phys. Rev. Lett.* **2003**, *91*, 096802.
- (51) Datta, S.; Tian, W. D.; Hong, S. H.; Reifenberger, R.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev. Lett.* **1997**, *79*, 2530.
- (52) Hong, S.; Reifenberger, R.; Tian, W.; Datta, S.; Henderson, J. I.; Kubiak, C. P. *Superlattices Microstruct.* **2000**, *28*, 289.
- (53) Tian, W. D.; Datta, S.; Hong, S. H.; Reifenberger, R.; Henderson, J. I.; Kubiak, C. P. *J. Chem. Phys.* **1998**, *109*, 2874.
- (54) Beebe, J. M.; Engelkes, V. B.; Miller, L. L.; Frisbie, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 11268.
- (55) Frisbie, C. D., personal communication.