Orientation and Bonding of 4,4′-Biphenyldiisocyanide

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The orientation and bonding of 4,4′-biphenyldiisocyanide (BPDI) adsorbed by solution on Au(111) has been examined by polarization dependent photoemission and inverse photoemission. The highest occupied molecular orbital to lowest unoccupied molecular orbital gap for BPDI is about 10.8 eV, with the Fermi level nearly midgap. The electronic structure of isocyano-functionalized polyphenyls suggests that they are better dielectrics than thiol-functionalized polyphenyls.

Thiol-functionalized (H–S) molecules such as oligobenzenethiols and alkanethiols have received considerable attention because of their promise as materials for molecular electronics.1–19 Highly ordered molecular layers are sought, ideally with the long molecular axis along surface normal, perhaps aided by the thiol functional groups. In addition, voltage dependent hysteresis along the large conductance channels would provide additional device functionality. The reality of the thiol-functionalized molecules is that strong Au–S bonds often form but the bonding orientation of the long molecular axis is rarely along the surface normal. This can lead to a number of complications20,21 including imperfections and disorder within the molecular layer, not to mention polycrystalline molecular layers.

Nitrile22 and isocyano23–27 end groups offer an alternative means for attaching phenyl based molecules to metals. Furthermore, isocyano end groups appear to offer lower thermionic barriers to conduction.23–24 For these reasons we studied the orientation, bonding, and electronic properties of 4,4′-biphenyldiisocyanide (BPDI), adsorbed from solution on Au(111). We provide some comparisons with the results obtained from the related biphenyldimethylthiol.21

Light polarization dependent angle-resolved photoemission experiments were carried out using synchrotron radiation, dispersed by a 3 m toroidal monochromator, at the Center for Advanced Microstructure and Devices in Baton Rouge, LA, as described elsewhere.21,28 All angles (both light incidence angles as well as photoelectron emission angles) reported herein are with respect to the substrate surface normal. Because of the highly plane polarized nature of dispersed synchrotron light through the toroidal grating monochromator, large light incidence angles result in a vector potential parallel to the surface normal (p-polarized light), whereas smaller light incidence angles result in a vector potential residing more in the plane of the surface (s-polarized light). From a comparison of light incidence angle photoemission spectra, the irreducible group representation band symmetries can be assigned using formula (1)

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{PES}} \propto |\langle \Psi_f | A \cdot p + p \cdot A | \Psi_i \rangle|^2 \delta(E_F - E_i - h\nu) \quad (1)
\]

In this work, we applied the C\textsubscript{2v} point group to adsorbed BPDI, due to the symmetry reduction from the D\textsubscript{2h} point group of gas-phase BPDI. For the photoemission results reported here, the photoelectrons were collected normal to the surface (\(\mathbf{F} \); or \(k_0 = 0\)) to preserve the highest possible point group symmetry. This means that application of equation 1 to the selection rules in photoemission results in molecular orbitals of a\textsubscript{1} symmetry becoming enhanced in p-polarized light whereas b\textsubscript{1} and b\textsubscript{2} symmetry molecular orbitals are enhanced with increasing s-polarized light for adsorbed BPDI. Molecular orbitals of a\textsubscript{2} symmetry are forbidden.

The electronic structure of the unoccupied states was investigated using inverse photoemission spectroscopy (IPES). For the IPES studies, a Geiger–Müller detector with a CaF\textsubscript{2} window was used in conjunction with an Erdman–Zipf electron gun and the overall energy resolution in inverse photoemission was \(-400 \text{ meV. For both photoemission and inverse photoemission, binding energies are reported with respect to the substrate Fermi level (\(E - E_F\)), determined from spectra taken of clean gold and tantalum in intimate contact with the substrate.}

The Au(111) substrate surface was prepared by epitaxial growth on Si(111), and verified by X-ray diffraction to possess only the (111) peaks. Deposition of BPDI on the gold substrates was undertaken from solution. These molecular layers were prepared and assembled on gold following the recipe described by Kubiak and co-workers.26 After deposition, while still in the glovebox, each sample was placed in a sealed container under nitrogen. The sample was exposed to atmosphere only for a short period before placing the sample into the UHV chamber. No evidence was found for photodegradation, local photoinduced thermal desorption, and/or charging during the course of our measurements. For comparison, low coverages of 4,4′-biphenyldiisocyanide (BPDI) were adsorbed from the vapor on clean gold at 140 K. The 4,4′-biphenyldiisocyanide (BPDI) vapor was introduced into the UHV chamber through a standard leak valve.
The photoemission and inverse photoemission features can be assigned to biphenyldisocyanide molecular orbitals as summarized in Figure 1 and Table 1. The suppression of the Au substrate signal, as in previous studies, indicates that the biphenyldisocyanide film thickness exceeds the photoelectron mean free path of photoelectrons from the substrate (>3 nm thick). The calculated orbital energies are offset from experimental values, which cannot be attributed to the work function. Such offsets are common and have been observed in comparing photoemission with ground state theory of large molecular adsorbates such as adsorbed alkanethiols, metalloccenes, poly-(vinylidene fluoride), nido- and closo-carboranes, and many others. The difference between ground state theory and experiment may be a result of solid-state effects such as screening but can also occur in the comparison of gas-phase spectra with theory as well as electron spectroscopies, like photoemission, are final state spectroscopies. Final state effects due to photovoltaic charging are not evident in the studies here.

The experimental HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) gap can be extracted from combined photoemission and inverse photoemission spectra (inset to Figure 2). The experimental 10.8 eV gap, derived from the vertical HOMO–LUMO band positions, is in close agreement with the 10.0 eV gap expected from theory. Unlike biphenyldimethylthiol, which is clearly an n-type insulator on gold, biphenyldisocyanide is nearly perfectly compensated, because the position of the Fermi level is near the middle of the experimental HOMO–LUMO gap (inset to Figure 2). Nonetheless, from the observed paucity of states at the Fermi level, both biphenyldisocyanide and biphenyldimethylthiol are expected to be insulators. The electronic structure evident in photoemission and inverse photoemission for BPDI adsorbed on gold is characteristic of molecules perturbed by adsorption and the substrate, not altered by a true impurity doping effect. Though the relative placement of the molecular orbitals with respect to the Fermi level cannot be taken as an infallible guide as to the majority carrier, such band offset characteristics, nonetheless, have been shown to be consistent with some molecular electronic device characteristics.

The experimental HOMO to LUMO gap of about 10.8 eV for biphenyldisocyanide is substantially larger than the HOMO–LUMO gap for biphenyldimethylthiol similarly determined (7.8 eV). The theoretical HOMO–LUMO gaps are similar for both biphenyldisocyanide and biphenyldimethylthiol, at 10.65 and 10.33 eV, respectively. The difference between theory and experiment suggests that the charge donation from the metal substrate toward biphenyldimethylthiol is more significant than for biphenyldisocyanide, consistent with the differences in electron affinities between H and C=S– and C=N– groups.

Calculations to model the biphenyldisocyanide molecular orbitals were performed using the GAMESS ab initio package. A standard 6-31G(d) basis set was used, and all molecular geometries were optimized at this level. The starting geometries were obtained by assigning the molecule to the point group symmetry possible, after adsorption (C2v), does seem to be applicable to the data, as schematically shown in Figure 1.

For the BPDI films deposited from solution, the gold substrate photoemission and inverse photoemission features are completely suppressed (Figure 2). A number of molecular orbitals combine to give rise to a single photoemission or inverse photoemission feature, but on the basis of our calculations all
to LUMO gap is far smaller for both the mono- and disiocyanoterminated molecular species than for the corresponding mono
thiol or dithiol species and, in almost all cases, smaller than
found from combined photoemission and inverse photoemission
studies. This suggests that the gap measured by molecular
conductance spectroscopy may be dominated by contributions
from the gold substrate, particularly for the occupied states
(negative sample bias), but in any case is not a good measure
of the HOMO–LUMO gap with this class of molecules. Also,
if the molecular film is not a single crystal, filamentary
conduction (through the film) could dominate.

The orientation of BPDI was investigated using the light
polarization dependent angle-resolved photoemission. As noted
above, different combinations of molecular conformation or
group geometry and orientation of the long molecular axis and benzene
ring plane orientation were considered. Each combination
yielded a molecular bonding configuration (molecular conformation
or geometry and orientation) whose expected light
polarization dependence, based on symmetry and selection rules
in photoemission, was compared with the experimentally
obtained dependence of almost all the photoemission features due to
light polarization. The correlation of irreducible symmetry representations, associated with
the D2h symmetry group (or lower). These high-
symmetry configurations for adsorbed biphenyldisocyanate are
(1) long molecular axis along surface normal, (2) long molecular
axis parallel to the surface with benzene plane also parallel to the surface, and (3) long molecular axis parallel to the surface with the benzene
plane perpendicular to the surface.

The correlation of irreducible representations, associated with
the reduction in symmetry from D2h to C2v, is given in Table 1.
The molecular coordinate system (placing the z-axis perpendicular
to the benzene plane, the x-axis parallel to the long molecular
axis, and the y-axis parallel to the benzene plane but perpendicular to the long molecular axis) is altered with the reduction of symmetry associated with adsorption so that the

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z-axis is along the surface normal. Strong enhancement of the photoemission features in p-polarized light with a molecular adsorption configuration (1), i.e., with the long molecular axis parallel with the surface normal, is a possible orientation consistent with our data. In view of the data, the configurations with both the molecular axis and the benzene planes parallel with the surface (2) is also a possible configuration.

Molecular orbitals of $a_2$ symmetry are forbidden in both photoemission and inverse photoemission. The clear observation of the highest occupied molecular orbital (HOMO) and the strong combined HOMO+2 and HOMO+3 photoemission feature in p-polarized light tend to exclude any possibility of a bonding configuration for 4,4′-biphenyldiisocyanide with the molecular axis parallel with the surface but with the benzene planes perpendicular (3) with the surface. The photoemission feature resulting from the combination occupied molecular orbitals HOMO+4 though HOMO+8, at 9.1 eV binding energy, is enhanced in p-polarized light, whereas the photoemission feature associated with HOMO+9, +10, +11, and +12 is not. From selection rules (eq 1) this slightly favors an orientation with the long molecular axis of 4,4′-biphenyldiisocyanide placed parallel with the surface normal.

Reflection absorption infrared spectroscopy (RAIR) of 4,4′-biphenyldiisocyanide on Au(111) was interpreted as providing evidence that the long molecular axis is parallel with the surface normal, i.e., configuration 1, in agreement with our photoemission results. Unfortunately, other BPDI bonding configurations might also lead to the same reflection absorption infrared spectroscopy results. These bonding configurations include placing the long axis of 4,4′-biphenyldiisocyanide nearly parallel with the surface, but with the C=N= group slightly bent so as to bond with the substrate. Thicker BPDI molecular films in which some (but not all) of the isocyno groups directly bond to the surface might also provide the observed RAIRS results. The precise orientation of the biphenyldiisocyanide molecular species at the gold interface, for our thicker (>3 nm) BPDI films deposited from solution, cannot be determined from the data presented here due to the limited photoelectron mean free path.

Because there is no evidence of photovoltaic charging (leading to large apparent increases in binding energy) for our BPDI films on gold, photoemission spectra of biphenyldiisocyanide on Au(111), adsorbed from vapor (Figure 3b) and deposited from solution (Figure 3c) can be compared. For the BPDI adsorbed on gold from the vapor, a few photoemission features attributable to the biphenyldiisocyanide molecular orbitals can be distinguished from the gold substrate photoemission features. It is difficult to assign the molecular orbitals to the photoemission features observed when the 4,4′-biphenyldiisocyanide is adsorbed on gold from the vapor, due the possibility that the highest occupied molecular orbital is obscured by the gold substrate 5d photoemission features. The most reasonable assignment (indicated in Figure 3) based upon the molecular orbital configuration suggests that there is a difference in binding energies, of approximately 3.5 eV, between the molecular orbital photoemission features observed for molecular adsorption from the vapor (Figure 3b) and deposition from solution (Figure 3c). The higher binding energies for the BPDI-induced photoemission features, resulting from adsorption on gold from the vapor, demonstrates that extramolecular bonding of BPDI to itself is much weaker than BPDI to the substrate. Unless the BPDI thin film samples, examined using RAIRS, are shown to be a single molecular monolayer, interpretation of the RAIRS spectra will be difficult.

We have shown that BPDI adsorbed from solution on Au(111) bonds with the long molecular axis parallel to the surface normal, although an orientation with the long molecular axis parallel with the surface and the benzene ring planes also parallel (2), cannot be conclusively eliminated. In this regard, the orientation appears to resemble the assignment derived from RAIRS, but with some limitations in the orientation assignment due to the multiple contributions to each photoemission feature.

We find that the calculated theoretical HOMO–LUMO gap for BPDI is very similar to the analogous dithiols. The experimental gap for BPDI, at 10.8 eV derived from combined photoemission and inverse photoemission results, is much larger than the experimental HOMO–LUMO gap obtained for the biphenylidimethylthiol at 7.8 eV. Furthermore, the Fermi level placement, within the HOMO–LUMO gap, suggests that adsorbed multilayers of biphenylidimethylthiol are more n-type than are multilayer films of biphenyldiisocyanide. BPDI exhibits a larger barrier to thermionic conduction due to the larger gap between the LUMO and the Fermi level ($E_{\text{LUMO}} - E_F$) and therefore should be a better dielectric than many oligobenzzenethiols. The experimental results here differ from previous measurements that suggest a smaller HOMO–LUMO gap for biphenyldiisocyanide than biphenylidimethylthiol. Previous measurements of the HOMO–LUMO gap may suffer from a number of experimental problems including, but not limited to, sample imperfections.

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References and Notes
