



Surface chemistry and structures of 1,4-phenylene diisocyanide on gold films from solution



Rasha Abuflaha, Dustin Olson, Dennis W. Bennett, Wilfred T. Tysoe *

Department of Chemistry and Biochemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

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ABSTRACT

The adsorption of 1,4-phenylene diisocyanide (PDI) is studied on gold films as a function of PDI exposure from benzene solution by a combination of attenuated total internal reflection infrared (ATR-IR) spectroscopy and conductivity measurements. The infrared spectrum found for low PDI doses exhibits a single isocyanide vibrational peak consistent with the formation of $-(\text{Au}-\text{PDI})-$ oligomer chains that have been identified previously on a Au(111) surface dosed in ultrahigh vacuum. Larger solution doses cause the isocyanide peaks to split into two, with the lower-frequency vibrations corresponding to a free isocyanide mode, indicating the formation of a perpendicular, vertically bonded PDI molecule. This observation also rationalizes the apparent disparity between studies of the chemistry of PDI on gold in ultrahigh vacuum and with solution dosing. Since it has been shown previously that the $-(\text{Au}-\text{PDI})-$ oligomer chains are capable of providing conductive linkages between gold nanoparticles on an insulating mica substrate, it was proposed that higher PDI doses from solution should cause a decrease in conductivity due to chain disruption. This effect was found experimentally, thereby providing corroborative evidence for the above conclusions.

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1. Introduction

Adsorbing 1,4-phenylene diisocyanide (PDI) on Au(111) single crystal surfaces in ultrahigh vacuum at room temperature results in the spontaneous formation of one-dimensional chains parallel to the surface which are observed when the surface is imaged using scanning tunneling microscopy (STM). The one-dimensional assemblies have been assigned to oligomeric species comprising alternating gold and PDI units [1–4] that form by extracting gold atoms from low-coordination sites on the gold substrate. The structure was confirmed by comparing the simulated images of oligomer structures predicted using density function theory (DFT) calculations with the experimental images, and from the reflection absorption infrared spectra of oligomer-covered surfaces [4]. Adatom structures formed on coinage metals are relatively common [5–8]. DFT calculations of the oligomer formation pathway reveal that a vertical Au–PDI adatom complex provides the propagating monomer that inserts into the isocyanide terminus of a tilted PDI molecule bound to a surface defect such as a step edge [9]. Since 1,4-PDI maintains its π -conjugation throughout the molecule and contains two linking isocyanide groups it has been proposed as a prototypical molecule for molecular electronic applications [10–15]. In contrast to these observations, the results of previous work to explore the chemistry of PDI adsorbed onto planar gold surfaces and powdered

gold from solution proposed structures in which the PDI adsorbed *via* one of the isocyanide groups, leaving a pendant, isolated isocyanide group [14–19]. Compelling evidence for this structure comes from the detection of a vibrational stretching mode due to an unbound isocyanide. There appears therefore to be a discrepancy between the results obtained under ultrahigh vacuum (UHV) conditions on Au(111) and those found when dosing from solution. However, it has recently been shown that adsorbing carbon monoxide on a Au(111) surface covered by $-(\text{Au}-\text{PDI})-$ oligomer chains results in the decoordination of one of the isocyanide groups in the oligomer chain to form a vertical PDI species adsorbed to a gold adatom, that exhibits two vibrational modes, one due to free and the other to bound isocyanide groups [20]. Similar isocyanide decoordination, induced by PDI adsorption rather than by CO, as in the above example, would rationalize the apparent discrepancy between the results for PDI on gold films and nanoparticles and the work on Au(111) single crystals in UHV. This proposal would involve the initial formation of $-(\text{Au}-\text{PDI})-$ oligomer chains oriented parallel to the surface that then decoordinate at higher PDI exposures to form vertically oriented species.

This postulate is tested here first by measuring the infrared spectra of PDI on gold films dosed from solution as a function of solution dose using attenuated total internal reflection infrared spectroscopy (ATR-IR) to determine the structure and orientation of adsorbed PDI. The molecular orientation can be determined using the surface selection rules [21–23], combined with comparison of the experimental vibrational frequencies with those from previous work.

* Corresponding author. Tel.: +1 (414) 229 5222; fax: +1 (414) 229 5036.
E-mail address: wtt@uwm.edu (W.T. Tysoe).

In addition, it has been found that gold-containing $-(\text{Au-PDI})-$ oligomers can form conductive bridges between a random array of isolated gold nanoparticles deposited onto a mica substrate by gold evaporation [24]. This is proposed to occur by PDI molecules binding to gold atoms from the nanoparticles to form conductive $-(\text{Au-PDI})-$ oligomeric bridges between them. Since the π -orbitals extend throughout the PDI molecule, and the PDI in the $-(\text{Au-PDI})-$ oligomers is coordinated to gold atoms, this provides a conductive pathway between the gold nanoparticles, and the connection of initially isolated gold nanoparticles by $-(\text{Au-PDI})-$ oligomers is therefore expected to cause the conductivity to increase. This conjecture is confirmed experimentally. Furthermore, it is found that the resistance R of an oligomer-linked gold nanoparticle array on mica varies as $\ln(R) \propto 1/\sqrt{T}$, where T is the absolute temperature. This temperature variation is in accord with the Abeles model for the temperature dependence of conductivity between a random array of linked nanoparticles [25,26].

Thus, it is expected that, if the additional exposure of the $-(\text{Au-PDI})-$ oligomers to PDI does induce decoordination as suggested above, this will interrupt the conductive pathway of the linking oligomers and should therefore result in a conductivity decrease. Note that, CO exposure to a gold nanoparticle array linked by $-(\text{Au-PDI})-$ oligomers to induce PDI decoordination did result in a decrease in conductivity, in accord with this postulate [20]. Accordingly, the conductivity of a gold-nanoparticle array grown on an insulating mica support was measured after exposing it to increasing PDI doses from solution. It is thus anticipated that, if the PDI restructures at the higher exposures available by solution dosing to induce PDI decoordination to form an η^1 -Au-PDI configuration via one isocyanide group, the conductive path should also be interrupted, thereby lowering the conductivity. This will provide an additional *in situ* probe of any change in molecular configuration. The results of these experiments are reported here, where it is found that, at low PDI doses from solution, the infrared spectra show a single isocyanide peak at a similar frequency to that found for PDI on Au(111), due to the formation of $-(\text{Au-PDI})-$ oligomer chains, where the conductivity of a PDI-dosed nanoparticle array increases over the same range of PDI doses. At higher doses, the free isocyanide mode appears in the infrared spectrum, accompanied by a conductivity decrease, in accord with PDI deCOORDINATING to form an η^1 species.

2. Experimental methods

The conductivity of PDI on nanoparticle-covered mica was measured as described in detail elsewhere [24]. First, gold electrodes used for subsequent conductivity measurements were fabricated by masking the central portion of a cleaved mica substrate (highest grade, Ted Pella), and then evaporating gold pads ~ 200 nm in thickness onto the mica substrate in vacuum to leave an area of ~ 1.4 cm² between the electrodes. Gold nanoparticles were then deposited by controlled evaporation, also in vacuum, onto this substrate to deposit gold particles that are ~ 8 nm in diameter between the gold electrodes. The amount of deposited gold was controlled to ensure that the gold nanoparticle coverage remains below the percolation limit by continually monitoring the resistance between the electrodes during evaporation. This ensures that the gold nanoparticle remains isolated from each other. The samples were then allowed to age until there was no further change in the sheet resistance, a process that was complete after 2 h depending on the initial gold coverage. An STM image of a typical nanoparticle array on the mica surface showing the isolated gold nanoparticles that are deposited between the gold pad electrodes is displayed as an inset to Fig. 2. The sample was then removed to air and dosed with PDI from solution. 10 μl aliquots of serially diluted PDI solutions (with a 5 mM initial solution concentration) in benzene were deposited onto the surface of the nanoparticle-covered sample using an Eppendorf pipette and then waited until all of the solvent had evaporated. The sample was then rinsed with benzene to remove any remaining weakly bound PDI and again allowed to dry in air.

Electrical measurements were made by mounting the sample in a stainless-steel vacuum chamber that was pumped by means of an ion pump to a base pressure of $\sim 2 \times 10^{-8}$ Torr without baking to avoid thermally altering the sample. The I/V characteristics were measured by applying a voltage via a D/A converter and the resulting current measured by means of a picoammeter that was monitored by an A/D converter to yield I/V curves directly.

Infrared spectra of PDI adsorbed on gold films were also collected by evaporating gold onto a zinc selenide ATR plate with an ~ 8 cm² area, and the infrared spectra collected using a Bruker Vertex infrared spectrometer operating at a resolution of 4 cm⁻¹, typically for 2000 scans, using a DTGS detector. The gold film thickness was selected to allow reasonable infrared transmission through the sample to be obtained and spectra were collected after dosing with 200 μl aliquots of a 0.5 mM PDI solution in benzene. The sample was allowed to dry in air and again rinsed with benzene to remove any residual, weakly bound PDI. Both PDI and benzene were obtained from Aldrich Chemicals and were 99.9% pure.

3. Results

Fig. 1 shows a series of ATR-IR spectra of a gold film dosed sequentially with solutions of PDI in benzene displayed as a function of PDI solution dose, where the PDI doses are indicated adjacent to the corresponding spectrum. Low PDI exposures give rise to a single, relatively broad feature centered at ~ 2166 cm⁻¹ in the C \equiv N stretching region. The peak frequency remains constant at this value up to a dose of ~ 40 nmol/cm². The detection of a single isocyanide stretching mode is consistent with the presence of a single type of isocyanide group expected for the formation of a $-(\text{Au-PDI})-$ oligomer chain. When formed on Au(111), the oligomers exhibit a single C \equiv N mode at ~ 2154 cm⁻¹ at low coverage, shifting to lower frequencies (~ 2139 cm⁻¹) at higher exposures, likely due to coupling between the isocyanide groups as the chains grow, so that the isocyanide mode frequencies found by solution dosing are within the range expected for oligomer chains [4,9,27].

After dosing with 50 nmol/cm² of PDI solution, the ~ 2166 cm⁻¹ mode shifts to a slightly lower frequency, with a sharper peak appearing at ~ 2120 cm⁻¹. Adding further PDI shifts the broad feature slightly to ~ 2158 cm⁻¹ and is accompanied by the growth in intensity of the ~ 2120 cm⁻¹ peak. These spectra are in reasonable agreement with the results from previous work on 1,4-PDI on gold films [16] that suggested that the molecules are oriented perpendicular to the surface with the free isocyanide group exhibiting a vibrational frequency of

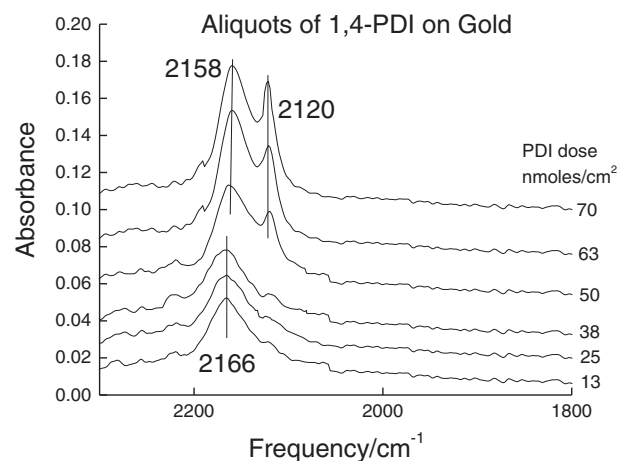


Fig. 1. A series of ATR infrared spectra of PDI adsorbed on a thin gold film using aliquots of 200 μl of solution of 0.5 mM PDI. The resulting PDI doses, in nmol/cm², are indicated adjacent to the corresponding spectrum.

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