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Adsorption and Oligomerization of 1,3-Phenylene Diisocyanide on Au(111)

by

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Abstract

The adsorption and self-assembly of 1,3-phenylene diisocyanide (1,3-PDI) is studied on Au(111) using reflection-adsorption infrared spectroscopy (RAIRS), scanning tunneling microscopy (STM) and temperature-programmed desorption (TPD) supplemented by density functional theory (DFT) calculations and the results compared with the structures formed from 1,4-PDI where it assembled to form $-(\text{Au-PDI})-$ oligomer chains that incorporate gold adatoms. The infrared spectra display a single isocyanide feature consistent with the isocyanide binding to gold adatoms while DFT calculations confirm that isocyanide binding to gold adatoms is more energetically favorable than binding to the surface. STM images show that 1,3-PDI forms zig-zag chains containing hairpin bends that cause the chains to double back on each other, consistent with the 120° angle between the isocyanide groups. Hexagonal structural motifs are also observed that are proposed to be due to the self-assembly of three isocyanides as well as small structures that are assigned to 1,3-PDI dimers. The results suggest that the formation of gold-containing oligomers from isocyanide-containing molecules is a general phenomenon.

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Introduction

It has been shown that 1,4-phenylene diisocyanobenzene (1,4-PDI) self-assembles on the Au(111) surface to form one-dimensional, oligomeric chains comprising alternating gold and 1,4-PDI units.¹⁻³ Since 1,4-PDI maintains its π -conjugation throughout the molecule and contains two linking groups it has been proposed as a prototypical molecule for nanoelectronic applications.⁴⁻⁹ It has also been recently demonstrated that it is possible to link between gold nanoparticles using a similar chemistry in which the 1,4-PDI extracts gold atoms from the gold nanoparticles to form oligomeric bridges between them.¹⁰ The propagating monomer for oligomer growth consists of a vertical, mobile Au–PDI adatom complex that oligomerizes by the gold adatom attaching to the isocyanide terminus of a growing chain.¹¹ In this case, the *para* geometry of PDI ensures that the free isocyanide group of the Au–PDI adatom complex is sterically hindered from accessing the surface, thereby allowing it to oligomerize. This raises the issue of whether other PDI isomers can also form stable propagating adatom complexes and this question is explored in the following.

It has recently been shown that 1,4-benzenedithiol (1,4-BDT) can oligomerize in a manner similar to that exhibited by 1,4-PDI – by incorporating gold adatoms in the chain.¹²⁻¹⁵ Because the Au–S–C bond is non-linear, the chains create a zig-zag pattern.¹⁶ In contrast, oligomers were not found for 1,6-hexanedithiol and biphenyl-4,4'-dimethanethiol suggesting that longer-chain dithiols cannot form mobile, gold-containing intermediates that allow oligomerization to occur.¹⁷ Nevertheless, 4,4'-biphenyl diisocyanide does form oligomeric assemblies on Au(111), implying that rigid, longer-chain diisocyanides can self-assemble to form conducting oligomers.¹⁸

Thus, by analogy to 1,4-BDT, 1,3-PDI should be capable of forming oligomers that incorporate gold adatoms when adsorbed on Au(111), and should show a zig-zag pattern as a

consequence of the non-linear isocyanide dihedral angle. The experimental results described below demonstrate that this is the case. This indicates that the oligomerization of bifunctional molecules with ligands that bind stably to gold adatoms, such as thiols or isocyanides, is a generally applicable self-assembly strategy, as long as the molecules' stereochemistry and the rigidity of the interconnecting backbone allow a mobile propagating adatom complex to form.

Experimental Methods

Experiments were carried out in ultrahigh vacuum (UHV) using a Au(111) single crystal (Princeton Scientific) that was cleaned with cycles of ion bombardment using 1 keV argon ions for 30 minutes ($1 \mu\text{A}/\text{cm}^2$), annealing to 900 K for 5 minutes and then to 600 K for 30 minutes. Scanning tunneling microscopy (STM), temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) measurements were made in separate ultrahigh vacuum (UHV) chambers operating at base pressures of $\sim 2 \times 10^{-10}$ Torr after bakeout. STM experiments were carried out using an RHK UHV 350 dual AFM/STM as described elsewhere,² along with the methods used to prepare the tungsten tip. RAIRS experiments were carried out in a Bruker Equinox spectrometer, typically for 1000 scans at a resolution of 4 cm^{-1} as described elsewhere.¹⁹ The sample could be cooled to ~ 80 K in both chambers by thermal contact to a liquid-nitrogen-filled reservoir and resistively heated to ~ 1200 K.

1,3-phenylene diisocyanide was synthesized by the phase-transfer method²⁰⁻²¹ and purified by vacuum sublimation at 80°C and introduced into vacuum *via* a home-built source as described previously.² 1,3-PDI doses are indicated as exposure times from the source.

Density functional theory (DFT) calculations were performed with the projector augmented wave (PAW) method²²⁻²³ as implemented in the Vienna *ab initio* simulation package, VASP.²⁴⁻²⁶ The exchange-correlation potential was described using the generalized gradient

approximation (GGA) of Perdew, Burke and Ernzerhof.²⁷ A cutoff of 400 eV was used for the planewave basis set, and the wavefunctions and electron density were converged to within 1×10^{-5} eV. The first Brillouin zone was sampled with a $4 \times 4 \times 1$ Γ -centered k-point mesh. Geometric relaxations were considered to be converged when the force was less than 0.02 eV/Å on all unrestricted atoms.

Results

The adsorption of 1,3-PDI on Au(111) at 300 K, monitored from the C KLL Auger peak, is shown in Figure 1(a) and is mirrored by the growth of a much less intense N KLL Auger feature at ~380 eV (data not shown). This shows a smooth uptake of 1,3-PDI with increasing exposure. However, C KLL and N KLL signals show very little variation in intensity as the sample is heated to ~900 K (data not shown) demonstrating that the majority of the 1,3-PDI is very stably adsorbed on the surface and hydrogen is the only desorption product detected after dosing at ~300 K (data not shown). This indicates that 1,3-PDI thermally decomposes at ~900 K by desorbing hydrogen with the carbon and nitrogen remaining on the surface. Figure 1(b) shows the 76 amu desorption profiles of 1,3-PDI adsorbed on Au(111) at ~90 K and the signals collected at 26, 50 and 64 amu show identical shapes, with relative intensities that agree well with the mass spectrometer ionizer fragmentation pattern of 1,3-PDI measured using the same mass spectrometer as used to collect the TPD data. The desorption profiles consist of a sharp feature centered at ~225 K at low exposures, that shifts slightly to higher temperatures (~230 K) as the 1,3-PDI exposure increases and this desorption temperature is close to that found for 1,4-PDI on Au(111) of ~245 K,³ due to the desorption of second-layer PDI. This sharp feature is accompanied by a broad tail to higher temperatures.

RAIRS of 1,3-PDI dosed onto Au(111) at 300 K for various times are displayed in Figure

2 as a function of dosing time, and also after heating the sample to 373 K (Top Spectrum). Note that the dosing geometries in the chambers used to collect the desorption data (Figure 1) and infrared spectra (Figure 2) were different, leading to different dosing times. The most intense features are detected after an initial dose (of 15 s) at room temperature, exhibiting a sharp peak at $\sim 2153\text{ cm}^{-1}$, with weaker features at 849 and 772 cm^{-1} . While these assignments will be discussed in greater detail below, the $\sim 2153\text{ cm}^{-1}$ peak is assigned to a stretching mode of a gold-coordinated isocyanide and confirms the adsorption of molecular 1,3-PDI on the surface.²⁸ As the exposure increases, the peak intensities of all of these features decrease, but the peaks also broaden significantly. Heating the sample to $\sim 373\text{ K}$, a temperature at which any second-layer 1,3-PDI has completely desorbed (Figure 1(b)), has essentially no effect on the spectrum thereby confirming that the spectra shown in Figure 2 are for 1,3-PDI strongly bound to the surface.

Figure 3 displays a wide-scan area STM image of a saturated overlayer of 1,3-PDI dosed onto Au(111) at 300 K and imaged at 120 K to minimize thermal effects. The direction of an underlying close-packed $\langle 1\bar{1}0 \rangle$ direction on the Au(111) surface is indicated. The structures formed on the surface are less well ordered than those found either from 1,4-PDI^{1, 28} or 1,4-BDT,¹⁶ but zig-zag chains are clearly evident originating from the *meta* location of the isocyanide groups of 1,3-PDI. Rather than oligomers propagating over long distances on the surface, there are numerous loops in which the chains double back on each other, where examples are highlighted by red and green circles. The parallel zig-zag chains can either be in-phase (Highlighted in red) or out-of-phase (Highlighted in green) with each other. The zig-zags are preferentially oriented at approximately 30, 90 and 150° with respect to the close-packed directions, although there is some variability in this value. In addition, there are some brighter regions on the surface which may be due to some second-layer 1,3-PDI remaining on the surface after dosing at $\sim 300\text{ K}$ (Figure 1(b)).

In addition, 1,3-PDI forms a number of local, hexagonal structures, where a cluster of typical structures are indicated by a blue circle, although there are a number of variants of this structure. It appears that the formation of such local structures, as well as the formation of hairpin bends, inhibits the chains propagating over larger distances.

Higher-resolution images of the local structures of 1,3-PDI on Au(111), imaged at ~120 K are shown in Figure 4. In particular, Figures 4A and B show sequential images, taken 330 seconds apart, which are essentially identical, indicating that the structures are not mobile at ~120 K. Here the local, hexagonal structures clearly comprise three identifiable subunits along each of the linear portions of the edges of the hexagon, where the length of the edge is ~0.95 nm and is similar to the spacing in the zig-zags. In some cases, additional, smaller local structures are seen as shown in Figure 4C. Here, the image shows two parallel lines of protrusions that form a rectangular image. The distance between the brightest areas along the center of the long axis of the rectangle is ~1.42 nm, while the corresponding distance along the short axis of the rectangle is ~0.85 nm.

Discussion

1,3-PDI adsorbs strongly on Au(111) at 300 K and thermally decomposes above ~800 K. Adsorption at ~90 K (Figure 1(a)) results in second-layer 1,3-PDI desorption at ~230 K, close to the desorption temperature of 1,4-PDI.³ This indicates that the self-assembly chemistry of 1,3-PDI on Au(111) is similar to that found for 1,4-PDI,¹⁻³ which forms one-dimensional oligomer chains on the surface comprising repeat $-(\text{Au-PDI})-$ units, by extracting gold atoms from low-coordination sites on the Au(111) substrate.²⁸ In order to investigate the structural motifs that result in oligomer formation, and to explore the most-stable adsorption sites, the formation of stable species following 1,3-PDI adsorption is investigated using DFT calculations. Note that

the calculations did not include van der Waals interactions which have been shown to influence the geometry of 1,4-PDI.¹¹ In order to establish the nature of the structural unit that assembles to form extended surface structures, calculations were first performed for 1,3-PDI adsorbed directly on Au(111) (without a gold adatom), giving a binding energy of ~54 kJ/mol for the most stable structure, where binding energies are calculated from the energy difference between the most stable adsorbate structure and the sum of the energies of a clean Au(111) surface and gas-phase 1,3-PDI. Next, based on the geometry found for 1,4-PDI on Au(111),^{10-11, 28} a structure was generated with gold adatoms on the Au(111) surface, with the gold adatom located at a three-fold hollow site. The initial structures were constructed with the plane of 1,3-PDI fixed at various angles (0, 30, 60 and 90°) with respect to the surface and the geometries allowed to relax. The most stable structure is depicted in Fig. 5, where the 1,3-PDI plane is shown perpendicular to the surface with a binding energy of ~250 kJ/mol and is much larger than the energies of 1,3-PDI bonded directly to the gold surface, in accord with previous results for 1,4-PDI on gold. This confirms that diisocyanides bind strongly to gold adatoms on Au(111). The results in Figure 5 are shown for the plane of the molecule aligned along the close-packed $\langle 1\bar{1}0 \rangle$ surface crystallographic directions. Similar calculations were carried out for 1,3-PDI gold adatom structures with the molecular plane aligned along the $\langle \bar{1}\bar{1}2 \rangle$ directions and yielded an essentially identical binding energy of ~249 kJ/mol. The binding energy of the structure shown in Figure 5 was calculated as a function of the tilt angle of the molecular plane, and the results are shown in Figure 5D, indicating that only a relatively modest energy of ~15 kJ/mol is needed to tilt the molecular plane. Similar tilt energies are calculated for the species aligned along the $\langle \bar{1}\bar{1}2 \rangle$ directions. The large binding energy of this species (~250 kJ/mol binding energy) is in accord with its stability found on heating. Previous calculations for 1,4-PDI show that van der Waals interactions result in the aryl ring moving closer to the surface,¹¹ implying that including

van der Waals interaction in the calculations would result in the structures shown in Figure 5 tilting towards the surface, given the relatively low tilt energy (Figure 5D). This stable structure is used as a basis for constructing larger assemblies to assign the observed STM images shown in Figs. 3 and 4.

The structure of 1,3-PDI in the oligomers can be obtained from the infrared data (Fig. 2) using the surface infrared selection rules.²⁹⁻³⁰ While no work has been carried out previously on 1,3-PDI on metal surfaces, a significant amount of work has been carried out using 1,4-PDI. Early work on self-assembled monolayers (SAMs) of 1,4-PDI on gold films³¹ suggested that it adsorbs perpendicularly to the surface with the free isocyanide group having a vibrational frequency of 2120 cm^{-1} and the surface-bound group shifted to 2181 cm^{-1} . More recent work³² showed similar frequencies of 2121 (free) and 2172 (surface-bound) cm^{-1} . Sum-frequency generation (SFG) results⁴ found corresponding vibrational frequencies of 2122 and 2195 cm^{-1} . An average of the vibrational frequencies of isocyanide SAM's on gold (summarized in reference⁴) results in values of $2123 \pm 1 \text{ cm}^{-1}$ for a free isocyanide group and $2181 \pm 4 \text{ cm}^{-1}$ for the surface-bound species.

The vibrational spectrum of 1,4-PDI alone, with D_{2h} symmetry, has been assigned with the aid of quantum calculations³³ and the most intense vibrations are at 850 (B_{1g} symmetry), 1505 (B_{1u}), 2127 (A_g) and 2132 cm^{-1} (B_{1u}). The first two modes are aryl ring modes while the last two are the symmetric and asymmetric $\text{N}\equiv\text{C}$ stretching vibrations respectively. This confirms that the 2153 cm^{-1} feature is due to a bonded isocyanide stretching mode and the presence of a single $\text{N}\equiv\text{C}$ vibrational mode suggests that the isocyanides are symmetrically equivalent. The $\sim 849 \text{ cm}^{-1}$ and 772 cm^{-1} features are due to in- and out-of-plane C-H wagging modes. The frequencies of out-of-plane modes in aryl rings depend strongly on the number and location of substitutional groups on the ring which affect the coupling between the C-H groups.³⁴

Thus, the three adjacent hydrogen atoms in a 1,3-disubstituted molecule have in-phase, out-of-plane vibrations between 770 and 795 cm^{-1} , so that the vibration at 772 cm^{-1} is assigned to this mode. An isolated hydrogen atom has an out-of-plane mode between 835 and 890 cm^{-1} , allowing the 849 cm^{-1} mode to be assigned to this frequency.

Adsorbed 1,3-PDI, bonded to a gold atom with the molecular plane perpendicular to the surface (Figure 5), has C_{2v} symmetry. According to the surface selection rules,²⁹⁻³⁰ the isocyanide stretching vibration (at 2153 cm^{-1}) is infrared allowed for this geometry, but the C–H bending modes are forbidden. However, if the aryl plane tilts to closer to parallel to the surface, the symmetry is reduced to have a C_s point group with a σ_{xy} mirror symmetry plane. Now the $\text{N}\equiv\text{C}$ stretches and C–H modes are both infrared allowed. However, planar 1,3-PDI with the aryl ring parallel to the surface would result in the isocyanide modes being infrared forbidden. This suggests that adsorbed 1,3-PDI at low coverages is either somewhat bent or slightly tilted with respect to the surface, due to van der Waals interactions with the surface, consistent with the small energies required to tilt that plane of the molecule with respect to the surface (Figure 5D). Note that the isocyanide mode in the oligomer chains formed from 1,4-PDI on Au(111), which is tilted only by $\sim 13^\circ$ away from the surface, exhibits a reasonably intense $\text{N}\equiv\text{C}$ infrared peak.

In the case of 1,4-PDI on Au(111), the intensities of the vibrational modes increase with increasing 1,4-PDI coverage,¹ while for 1,3-PDI on Au(111), both the $\text{N}\equiv\text{C}$ stretching and C–H wagging modes decrease in peak intensity (Figure 2), and the infrared features broaden significantly. This could be due to a change in orientation of the plane of the 1,3-PDI molecule. However, if the molecular plane were perpendicular to the surface (as in Figure 5), the $\text{N}\equiv\text{C}$ vibration would become more intense and the C–H modes disappear, while, if the plane moved closer to parallel to the surface, the opposite would occur.

The broadening of the infrared features is consistent with the presence of rather

heterogeneous surface structures (Figure 3), resulting in an array of different environments around each adsorbed 1,3-PDI unit. One possible explanation for the lack of significant growth in the intensity of the infrared features with increasing exposure is the existence of a number of different local structures with a variety of tilt geometries with respect to the surface. This observation is consistent with the increasing width of the infrared features as a function of exposure (Figure 2) and the lower degree of surface order found for 1,3-PDI (Figure 3) than the highly symmetric linear chains observed for 1,4-PDI. An alternative possibility is that, as 1,3-PDI assembles into higher-symmetry units, fewer modes become infrared allowed. Thus, each 1,3-PDI molecule in the tilted version for the structure shown in Figure 5, discussed above, has one allowed isocyanide-derived normal mode (comprising in-phase $\text{N}\equiv\text{C}$ vibrations). However, the proposed hexagonal structure (Figure 6B, which will be discussed in greater detail below), which is quite abundant on the surface (Figure 3) has C_{6v} symmetry, and 12 isocyanide groups. However, in this case, only two normal modes have A_1 symmetry and are therefore infrared allowed on the surface.

We now examine the possible structural motifs formed following the adsorption of 1,3-PDI on Au(111) assuming that there are assembled from the monomeric units shown in Figure 5. Calculations for 1,4-PDI bonding to gold suggest that there is a strong preference for the formation of linear $\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{N}$ geometries² suggesting that oligomer chains formed from 1,3-PDI should have a tendency to form zig-zag structures due to a similar binding of the isocyanides to gold adatoms. This conjecture is borne out by the STM images of 1,3-PDI on Au(111) (Figure 3) where a number of such structures are identified. However, there are clearly also regions in which this zig-zag structure is not maintained and, in several cases, hexagonal structures can be discerned.

Based on the DFT calculations (Figure 5) and the infrared spectra (Figure 2), which

indicate the presence of 1,3-PDI coordination to gold where the plane is tilted with respect to the surface, the structural building block is shown in Figure 6A. The gold adatoms are shown bound to three-fold sites for convenience, although direct experimental evidence for this site is not available from the STM images. However, this does not affect the proposed structural assignments. The gold adatoms are shown aligned along the close-packed $\langle 1\bar{1}0 \rangle$ surface crystallographic directions, but alignment along the $\langle \bar{1}\bar{1}2 \rangle$ directions occurs with essentially the same energy.

The resulting zig-zag chains are shown in Figures 6C and E, where, as discussed above, they are proposed to form because of the preference for the isocyanide groups bonding to the gold atoms at 180° to each other. The periodicity of the model structures along the chain is 1.7 nm, in good agreement with the measured repeat distance of 1.65 ± 0.05 nm. The proposed structures are also in accord with the higher-resolution STM images (Figure 4A and B) where three identifiable units can be discerned for the linear portions that connect the 120° turns, ascribed to the aryl rings and the linking gold adatom. The proposed structures of both the in-phase and out-of-phase zig-zag structures are depicted in Figures 6C and E, which requires the presence of non-linear $\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{N}$ structures to accommodate the turns. An identical growth motif can also be used to construct the hexagonal structures, as shown in Figure 6B. The proposed structure has a calculated distance of 1.95 nm between opposite apices of the hexagon, in good agreement with a measured value of 2.1 ± 0.1 nm.

The proposed structure of the smaller assembly, shown in the high-resolution image on Figure 4C, is depicted in Figure 6D, showing a similar rectangular structure as found in the image, with a distance along the long axis of the rectangle of 1.41 nm and across the short axis of 0.85 nm, in good agreement with the measured values. In this case, the $\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{N}$ bond formed along the shorter edge of the rectangle is bent from the most stable linear structure and

the hexagonal units (Figure 6B).

Conclusions

1,3-PDI is proposed to bind to Au(111) at 300 K in an analogous manner to that found previously for 1,4-PDI on Au(111), with the isocyanide group coordinating to a gold adatom to form oligomeric species on the surface. However, the 120° dihedral angle in 1,3-PDI results in different surface structural motifs from the linear structures found with 1,4-PDI. In particular, 1,3-PDI forms predominantly zig-zag chains on the surface. The chains propagate over relatively short distances and have frequent hairpin turns to form parallel lines of both in-phase and out-of-phase zig-zags. Other local structures form on the surface, presumably inhibiting the formation of longer chains. The most abundant of these is a hexagonal unit which facilitates the formation of the most-stable linear $\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{N}$ geometry, although strained tetramers are occasionally observed. The chains are extremely thermally stable on the surface and decompose only on heating above ~800 K. A low-temperature (~230 K) desorption state is detected when 1,3-PDI is adsorbed at ~90 K, due either to 1,3-PDI bonded to the gold surface via a single isocyanide group or bonded to gold atoms in the oligomer chain.

These results suggest that the self-assembly of oligomeric species from bifunctional molecules that contain two groups that bind to gold via a gold adatom is quite general and has been seen for diisocyanides and dithiols. The nature of the resulting chains, whether they are linear or have a zig-zag structure is dictated either by the location of the functional groups (whether they are *meta* or *para* to each other, as in PDI) or the hybridization of the bond to gold (as in dithiols, which form zig-zag structures).

It has been suggested that oligomerization of 1,4-PDI occurs via a gold adatom structure in which one of the isocyanide groups binds to a gold adatom to provide a mobile monomeric

species, implying that similar mobile intermediates also occur for 1,3-PDI and 1,4-BDT. Similar self-assembly chemistry found for 4,4'-biphenyl diisocyanide suggests that longer-chain diisocyanides with a rigid backbone can also form stable propagating intermediates, while dithiols with more flexible backbones such as 1,6-hexanedithiol and biphenyl-4,4'-dimethanethiol cannot.

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Figure Captions

Figure 1: (a) Uptake of 1,3-PDI on Au(111) at 300 K from the peak-to-peak intensity of the carbon KLL Auger features. (b) TPD profiles for 1,3-PDI on Au(111) at 90 K as a function of exposure monitoring the 76 amu signal for 1,3-PDI adsorbed at 300 K.

Figure 2: Reflection-adsorption infrared spectra of 1,3-PDI adsorbed on Au(111) at 300 K as a function of exposure time. The top spectrum shows the effect of heating the sample to 373 K.

Figure 3: An STM image of a saturated overlayer of 1,3-PDI adsorbed on Au(111) at 300 K ($I_t = 229$ pA, $V_b = -1.1$ V, Scale bar = 12 nm).

Figure 4: A and B, Sequential high-resolution STM images of a saturated overlayer of 1,3-PDI adsorbed on Au(111) at 300 K ($I_t = 191$ pA, $V_b = -1.0$ V, Scale bar = 3 nm), taken 330 seconds apart, highlighting the atomic structure of the hexagonal units and chains. C, High-resolution STM image of the 1,3-PDI tetramers ($I_t = 178$ pA, $V_b = -0.95$ V, Scale bar = 2.1 nm) (see text).

Figure 5: Depiction of the A, top, B, side and C, end views of 1,3-PDI adsorbed on gold adatoms on a Au(111) substrate calculated using density functional theory. D, Change in energy as a function of tilt angle from the most-stable structure shown in Figures 5A-C.

Figure 6: Postulated structures for the observed STM images for 1,3-PDI on Au(111).

(a)

(b)

Kestell *et al*, Fig. 1

Kestell *et al*, Fig. 2

Kestell *et al*, Fig. 3

Kestell *et al*, Fig. 4

Kestell *et al*, Fig.5

Kestell *et al*, Fig.6

Graphical Abstract