Single Gold Atom Containing Oligo(phenylene)ethynylene: Assembly into LB Films and Electrical Characterization

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Abstract

Monomolecular films of an Oligo(phenylene)ethynylene (OPE) derivative [2-isocyano-1,3-dimethylbenzene][4-(4'-amino-phenylethynyl)-phenylethynyl]-gold, **1**, containing a gold atom in the molecule backbone have been prepared by the Langmuir-Blodgett (LB) method in order to study how the electrical properties can be modulated in monolayers of OPEs by the incorporation of a gold center in their structures. UV-vis reflection spectra of Langmuir monolayers of **1** at the air-water interface reveal strong aurophilic interactions between neighbouring molecules that increase upon compression. Monolayer Langmuir-Blodgett (LB) films were readily fabricated by the transfer of Langmuir films of **1** onto solid substrates. Quartz crystal microbalance (QCM) experiments conclusively demonstrate the formation of monolayer LB films with a high surface coverage. The morphology of these films was analysed by atomic force microscopy (AFM), revealing the formation of homogeneous layers with an optimum surface pressure of transference of $6 \text{ mN}\cdot\text{m}^{-1}$. Film homogeneity and integrity was confirmed by cyclic voltammetry, with efficient blocking of gold electrodes by these well-formed monolayers of **1**. The electrical properties of LB films of **1** were investigated by scanning tunnelling microscopy (STM) using a 'tip-to-contact' method. Symmetrical, sigmoidal-shaped *I-V* curves were observed, with analysis of the pseudo-linear (Ohmic) region giving a conductance value $G = 3.9 \times 10^{-5} G_0$, which is relatively high for an OPE derivative and may indicate a beneficial role of metal atom incorporation within the wire-like -system.

Introduction

Oligo(phenylene)ethynylenes (OPEs) represent one of the most widely investigated class of molecules in the nascent field of molecular electronics.¹⁻⁹ The ethynyl phenylene (or more generally, ethynyl arylene)¹⁰ backbone offers a highly conjugated π -electron system, which can be tuned through conformational effects,¹¹⁻¹² although demonstration of such events must be carefully extracted from stochastic switching of the molecule-surface contact.¹³⁻¹⁴ The introduction of pendant moieties,¹⁵ or changes to the nature of the arylene fragment to modulate quantum interference pathways,¹⁶ permits the assembly of wire-like molecules of a wide range of lengths¹⁷⁻¹⁸ that are synthetically compatible with a diverse range of surface contacting groups.¹⁹⁻²¹ The conductance of the OPE scaffold can also be modulated through the introduction of metal centers²²⁻²⁹ or metallocene³⁰⁻³¹ fragments within this π -conjugated pathway, which augments a fast growing area of study concerning metal coordination complexes as components in molecular electronics.³²⁻⁴² To date, the vast majority of metal compounds and complexes studied within metal|molecule|metal junctions or related sandwich structures formed by contacting monolayer films have been based on the Group 8, 9 and 10 metals, for reasons of synthetic availability and redox activity, in an axially-substituted arrangement within the wire-like assembly. The presence of supporting equatorial co-ligands is a synthetic necessity and whilst these can be used to create structures that bear topological resemblance to 'insulated' wires,⁴³ the steric bulk of these equatorial ligands may also prevent close packing of the components.

With these parameters in mind, gold complexes LAuC $\equiv$ CR offer several appealing features. The linear Au(I) fragment can be supported by range of donor ligands, L such as phosphines and isocyanides, whilst the alkynyl moiety is readily incorporated into OPE-type structures,⁴⁴ and can be used to support surface binding groups. The generic linear structure LAuC $\equiv$ CR is also well suited to the formation of well-ordered molecular films, using either self-assembly or Langmuir-Blodgett methods, and further supported by intermolecular π - π and aurophilic interactions. Whilst the use of self-assembled monolayers (SAMs) in molecular electronics is well documented in the current literature⁴⁵⁻⁴⁶ the Langmuir-Blodgett (LB) technique is also an excellent tool with which to fabricate mono and multilayer structured films with a

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high internal order. The LB method has been widely used to fabricate monolayer films with attractive features including the ability to assemble well-ordered molecular monolayers from molecules which cannot be prepared by conventional self-assembly and control of the monolayer film ordering and directionality through the conditions of LB film formation. As a result LB films have formed the basis of many studies in molecular electronics, including studies of rectifying molecular junctions,⁴⁷⁻⁴⁸ exciton migration control,⁴⁹ molecular switching behavior,⁵⁰⁻⁵¹ top-contact metallization,⁵²⁻⁵⁴ optical and opto-electronic applications,⁵⁵⁻⁵⁶ modulation of the electrical properties of the junction,⁵² and electrical measurements to the single molecule level.^{52, 57-58}

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This paper reports the synthesis of [2-isocyano-1,3-dimethylbenzene][4-(4'-amino-phenylethynyl)-phenylethynyl]-gold, **1**, the Langmuir and LB film forming behaviour of this compound, and electrical characterization of the resulting films. A number of methods are suited to the characterisation of electrical properties of LB films or SAMs forming 2D layers on flat substrates. This can be achieved by direct contact between a conducting Atomic Force Microscope (c-AFM) probe and the molecular monolayer, with the number of molecules being probed depending on the radius of curvature of the conducting tip, the contact force and the molecular packing density.⁵⁹⁻⁶⁰ In an alternative approach, which also uses the c-AFM, gold nanoparticles are adsorbed to chemical contacting groups on the upper periphery of the monolayer.⁶¹ The conducting AFM probes makes electrical contact with the gold nanoparticle (GNP) as it is pressed under controlled force onto the top of the GNP and the electrical properties of the ensuing GNP|molecule|metal junction are measured. By using mixed molecular monolayers and statistical analysis of the data from many nanoparticle contacts, the conductance of junctions containing just single molecules can be determined.⁶¹ A further approach uses an STM tip, which is lowered to just make contact with the molecular monolayer.^{57-58, 62} Under these conditions multiple *I-V* curves are recorded and statistically analyzed. It has been shown that if careful distance and monolayer thickness calibration is applied then predominantly single molecule junctions result.^{57-58, 62} It is this STM technique that is used in this present study for electrical characterization of molecules within the LB film. Since we wish to avoid pulling molecules out of the LB monolayer upon tip retraction a weakly (physi-) adsorbing aryl top contact group is used (Figure 1, left side of molecular structure), rather than a more “conventional” contacting group such as those based on, for example, thiol, pyridyl or

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amine functional groups, and which are widely used in single molecule electronics with gold electrodes. It has been previously shown that the phenyl moiety, $-\text{C}_6\text{H}_5$, can be used as a contacting group in the formation of molecular junctions.⁶³ The contact formation here was presumed to involve interaction of the π -electrons of the terminal phenyl ring with the gold contact.⁶³ We call this method for making conductance measurements on monolayer LB films the “STM touch-to-contact” method, since it involves bringing the STM tip precisely into contact with the molecular film, to distinguish from other STM-based methods of measuring electrical properties of molecules and molecular films.⁶⁴

Figure 1. The compound [2-isocyano-1,3-dimethylbenzene][4-(4'-amino-phenylethynyl)-phenylethynyl]-gold, **1**.

Experimental Section

Synthesis:

All reactions were carried out in oven-dried glassware under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Dichloromethane (CH_2Cl_2) and triethylamine (NEt_3) were dried and distilled under nitrogen prior to use. The compounds $\text{AuCl}(\text{tht})$,⁶⁵ $\text{Pd}(\text{PPh}_3)_4$,⁶⁶ $\text{HC}\equiv\text{CC}_6\text{H}_4\text{NH}_2$,²⁹ $\text{BrC}_6\text{H}_4\text{C}\equiv\text{CSiMe}_3$,²⁹ and $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{NH}_2$,^{7, 67} were prepared by literature methods, or minor variation as described below. Other reagents were purchased and used as received. NMR spectra were recorded in deuterated solvent solutions on Varian Mercury 400 or Bruker Avance 400 spectrometers and referenced against solvent resonances (^1H , ^{13}C). ESI mass spectra were recorded using a TQD mass spectrometer (Waters Ltd, UK). Samples were (1 mg/mL) in analytical grade methanol. Infrared spectra were recorded using a Nicolet Thermo FT6700 or a Nicolet Avatar spectrometers.

Preparation of $\text{Me}_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{NH}_2$. To a 100 mL Schlenk flask charged with NEt_3 (40 mL), 4-ethynylaniline (1.25 g, 10.7 mmol), $\text{BrC}_6\text{H}_4\text{C}\equiv\text{CSiMe}_3$ (2.71 g, 10.7 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.610 g, 0.528 mmol) and CuI (0.118 g, 0.621 mmol) were added. The resulting suspension was heated at reflux overnight. The black mixture was taken to dryness under reduced pressure and the residue purified by silica gel column chromatography (hexane: CH_2Cl_2 / 1:1). Yield 2.5 g, 8.6 mmol, 80%. ^1H NMR (CDCl_3): δ 7.41 (s, 4H, *i/j*); 7.32 (d, $J = 9$ Hz, 2H, *d*); 6.63 (d, $J = 9$ Hz, 2H, *c*); 3.82 (br. s, 2H, NH_2); 0.26 (s, 9H, *n*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 147.0 (*b*); 133.2, 132.0, 131.2 (*d/i/j*); 124.2, 122.3 (*h/k*); 114.9 (*c*), 112.4 (*e*), 105.0, 96.0, 92.4, 87.3 (*f/g/l/m*), 0.1 (*n*). IR (nujol) / cm^{-1} : $\nu(\text{NH}_2)$ 3483, 3395m; $\nu(\text{C}\equiv\text{C})$ 2153, 2144w.

Preparation of $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{NH}_2$. A solution of $\text{Me}_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{NH}_2$ (2.41 g, 7.14 mmol) in 50 mL THF:MeOH (1:1) was treated with K_2CO_3 (3.00 g, 21.7

mmol) and the reaction stirred at r.t. overnight. The orange precipitate was collected by filtration and washed thoroughly with water and then acetone. The orange solid (1.4 g, 6.4 mmol, 90 %) was used in subsequent reactions without further purification. ^1H NMR (CDCl_3): δ 7.44 (s, 4H, *i/j*); 7.33 (d, $J = 9$ Hz, 2H, *d*); 6.64 (d, $J = 9$ Hz, 2H, *c*); 3.85 (br. s, 2H, NH_2), 3.15 (s, 1H, *n*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 147.0 (*b*); 133.2, 132.1, 131.3 (*d/i/j*); 124.6, 121.3 (*h/k*); 114.9 (*c*); 112.4 (*e*); 92.5, 87.1, 83.6, 78.7 (*f/g/l/m*). IR (nujol) / cm^{-1} : $\nu(\text{NH}_2)$ 3482w, 3389m; $\nu(\equiv\text{C-H})$ 3249m; $\nu(\text{C}\equiv\text{C})$ not observed.

Preparation of **1.** To a Schlenk flask charged with a solution of $\text{AuCl}(\text{tht})$ (0.20 g, 0.62 mmol) in CH_2Cl_2 (10 mL), 2,6-dimethylphenyl isocyanide (0.08 g, 0.62 mmol) was added. The clear solution was allowed to stir at room temperature overnight. To the reaction mixture, NEt_3 (0.5 mL) and $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{NH}_2$ (0.14 g, 0.64 mmol) were added and allowed to react overnight. The precipitate was removed by filtration and the filtrate taken to dryness under reduced pressure. The orange residue was purified by silica gel column chromatography using hexane: CH_2Cl_2 / 1:1 as the eluent. Removal of solvent from the main fraction yielded the pure product as an orange solid. Yield 0.20 g, 0.37 mmol, 60%. ^1H NMR (CDCl_3): δ 7.41, 7.36 (2 $\times$ d, $J = 9$ Hz, 2 $\times$ 2H, *i/j*); 7.34–7.31 (m, 3H, *d/s*); 7.16 (br. d, $J = 8$ Hz, 2H, *r*); 6.63 (d, $J = 9$ Hz, 2H, *c*); 3.82 (br. s, 2H, *a*); 2.44 (s, 6H, *q*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 160.1 (t, $J = 24$ Hz, *n*); 146.8 (*b*); 136.4 (*p*); 133.1, 132.5, 131.1 (*d/i/j*); 131.00 (*s*); 128.6 (*r*); 124.5 (t, $J = 13$ Hz, *m*); 124.3 (*o*); 124.0, 122.5 (*h/k*); 114.9 (*c*); 112.8 (*e*); 104.1, 91.6, 87.6 (*f/g/l*); 18.8 (*q*). MS (ESI) $^+$ m/z (%): 586.2 (100, $[\text{M}+\text{H}+\text{MeCN}]^+$). IR (CH_2Cl_2) / cm^{-1} : 3485, 3394 (br. w); 2208 $\nu(s)$ $\nu(\text{N}\equiv\text{C})$.

Films Fabrication and Characterization

The films were prepared on a Nima Teflon trough with dimensions (720 $\times$ 100) mm^2 , which was housed in a constant temperature (20 ± 1 $^\circ\text{C}$) clean room. A Wilhelmy paper plate pressure sensor was used to measure the surface pressure (π) of the monolayers. The sub-phase was Millipore Milli-Q water, resistivity 18.2 $\text{M}\Omega\cdot\text{cm}$. A solution of **1** in chloroform (purchased from LabScan HPLC grade 99.8%) was

delivered from a Hamilton syringe held very close to the surface, allowing the surface pressure to return to a value as close as possible to zero between each addition. The spreading solvent was allowed to completely evaporate from the surface of the subphase over a period of at least 20 min before compression of the monolayer commenced at a constant sweeping speed of $0.015 \text{ nm}^2 \cdot \text{molecule}^{-1} \cdot \text{min}^{-1}$. Each compression isotherm was recorded at least three times to ensure the reproducibility of the results so obtained. Under the described experimental conditions the isotherms were highly reproducible. The ΔV -A measurements were carried out using a Kelvin Probe provided by Nanofilm Technologie GmbH, Göttingen, Germany. A commercial mini-Brewster angle microscope (mini-BAM) also from Nanofilm Technologie GmbH, Göttingen, Germany, was employed for the direct visualization of the monolayers at the air/water interface and a commercial UV-vis reflection spectrophotometer, details described elsewhere,⁶⁸ was used to obtain the reflection spectra of the Langmuir films during the compression process.

The solid substrates used for the transferences were cleaned carefully as described elsewhere.⁶⁹⁻⁷⁰ The monolayers were deposited onto glass, freshly cleaved mica, and gold substrates at a constant surface pressure by the vertical dipping method (dipping speed $3 \text{ mm} \cdot \text{min}^{-1}$). Quartz Crystal Microbalance (QCM) measurements were carried out using a Stanford Research System instrument and employing AT-cut, α -quartz crystals with a resonant frequency of 5 MHz having circular gold electrodes patterned on both sides. Atomic Force Microscopy (AFM) experiments to study the topography of the monolayers were performed by means of a Multimode 8 AFM system from Veeco using the tapping mode. The data were collected in air conditions with a silicon cantilever provided by Bruker, with a force constant of $40 \text{ N} \cdot \text{m}^{-1}$ and operating at a resonant frequency of 300 kHz.

Cyclic voltammetry (CV) experiments were carried out in an electrochemical cell containing three electrodes as described before.⁷¹ The working electrode was a gold electrode with the deposited LB film. Gold substrates were purchased from Arrandee®, Schroeer, Germany.

An Agilent STM running Picoscan 4.19 Software was used for characterization of the electrical properties of the LB films, by recording current, I , as a function of tip potential, U_t . STM tips were freshly prepared for each experiment by etching of a 0.25 mm Au wire (99.99%) in a mixture of HCl (50%) and ethanol (50%) at +2.4 V. Gold

films were flame-annealed at approximately 800–1000 °C with a Bunsen burner immediately prior to use. This procedure is known to result in atomically flat Au(111) terraces.⁷²

Results and Discussion

The formation of aggregates of large π -conjugated organic materials due to the attractive π - π interactions between the conjugated skeletons of neighbouring molecules, even in highly dilute solutions, is well-known,⁷³ and this phenomenon has been recognised as one of the main difficulties in the preparation of true monomolecular films of such compounds at the air-water interface.⁷⁴⁻⁷⁵ In the case of **1** aggregation phenomena are potentially augmented by additional aurophilic interactions.⁷⁶⁻⁷⁸ Thus, the Beer-Lambert law is only followed at concentrations of **1** lower than $7.5 \cdot 10^{-5}$ M (Figure 2) in chloroform, with higher concentrations leading to deviations from linearity in the absorbance vs. concentration plot. Consequently, highly diluted solutions are required to fabricate true monolayers of **1** at the air-water interface. The UV-vis spectrum of **1** in solution features an absorption band at 332 nm (molar absorptivity $30900 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) arising from intramolecular charge transfer between the amino tolan-based HOMO and isocyanide π^* -based LUMO, and a vibronically-structured π - π^* band in the 240-270 nm region (molar absorptivity $23300 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) characteristic of the amino-tolan fragment.⁷⁹⁻⁸⁴ These assignments are consistent with TDDFT calculations on **1** (B3LYP, LANL2DZ on Au, 6-31G** on all other atoms, CHCl_3 continuum solvent model).

Figure 2. UV-vis spectra of **1** in chloroform for the indicated concentrations. Molar absorptivities at 332 and 248 nm are 30900 and 23300 L·mol⁻¹·cm⁻¹, respectively.

A preliminary investigation of the formation of Langmuir films of **1** involving both the concentration and the volume of the spreading solution concluded that only solutions of concentration $5 \cdot 10^{-5}$ M or lower and initial surface densities lower than $9.2 \cdot 10^{-11}$ mol·cm⁻² yield reproducible isotherms. Under these experimental conditions a reproducible surface pressure vs. area per molecule (π -A) isotherm is shown in Figure 3. The π -A isotherm of **1** is characterized by a zero surface pressure in the 1.60-0.45 nm²·molecule⁻¹ range, featuring a lift-off at ca. 0.44 nm²·molecule⁻¹ followed by a monotonous increase of the surface pressure upon compression. Figure 3 also shows the normalized surface potential (surface potential multiplied by the area per molecule), ΔV_n , vs. area per molecule isotherm. The surface potential isotherm can often provide useful information relating to the molecular order within the monolayer. Compression of **1** monolayer results in a region, at areas per molecule higher than 0.5 nm², characterized by fluctuations in the surface potential. This might be due to the presence of domains in the gas phase. After the coalescence of these domains a region, without fluctuations, in the 0.5-0.4 nm² exhibits a practically linear increase of the normalized surface potential. This observation may be explained in terms of the appearance of significant intermolecular attractive forces between **1** molecules upon compression even in the gas phase (π - π interactions between the aromatic units as well as aurophilic interactions), leading to an increase in the hydrophobic environment of the molecules. This in turn leads to a decrease in the local dielectric constant of the head group region,⁸⁵ which is consistent with an increase in the normalized surface potential. At ca. 0.4 nm² a change in the slope of the normalized surface potential isotherm occurs, in agreement with a phase change in the monolayer that transforms to the liquid phase. An almost linear decrease in the normalized surface potential values with decreasing area per molecule in the 0.4-0.3 nm² range is observed, and attributed primarily to the reorientation of the amine group and the water molecules at the interface. Finally, the sudden decrease in ΔV_n at areas per molecule lower than 0.3 nm² (7 mN·m⁻¹) is consistent with the appearance of local collapses of the monolayer with dipole moments randomly distributed in three dimensional arrangements of **1** molecules.

Figure 3. Surface pressure vs. area per molecule (π - A) and normalized surface potential vs. area per molecule (ΔV_n - A) for **1** isotherms recorded at 20 °C.

Reflection spectroscopy is a useful method for the *in situ* characterization of the monolayer at the air-water interface.^{68, 86-87} Aggregation phenomena associated with **1** at the air-water interface were investigated by *in situ* UV-vis reflection spectroscopy through reflection of unpolarized light under normal incidence. The reflection spectra, ΔR , at different values of the area per molecule upon compression were recorded and are shown in Figure 4.a. As can be seen in Figure 4.a, there is a red shift of the reflection spectra recorded at the air-water interface relative to the solution spectrum, which is more significant at high surface pressures. The red-shift of **1** in the Langmuir films could be due to several factors:

- (i) *Solvatochromic effect.* In order to understand the influence of polarity in aggregation, **1** was dissolved in solvents such as hexane, chloroform, ethanol and acetonitrile. A red-shift was observed, from 330 nm (hexane) to 332 nm (chloroform), 339 (ethanol), and 343 nm (acetonitrile). This result indicates that the gradual red-shift observed upon compression is not attributable to changes in the environment polarity since the polarity of the film decreases with increasing surface pressure.
- (ii) *Formation of J-aggregates.* Aggregate formation may result in a significant change in the electronic absorption spectra. In H-aggregates molecules align face-to-face yielding a sandwich-type arrangement which results in blue-shifted absorption bands.⁸⁸ In contrast to H-aggregates, J-aggregates give rise to red-shifted absorption bands. J-aggregates are composed of molecules staggered in an edge-to-edge

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configuration,⁸⁹ OPE derivatives arranged in L and LB films tend to form H-aggregates.^{62, 75, 90-91} It has been noted that, for some compounds that tend to form H-aggregates, e.g. merocyanines⁹²⁻⁹³ and azo compounds,⁹⁴⁻⁹⁵ the incorporation of certain functional groups capable of forming hydrogen bonds leads to the formation of J-aggregates exhibiting a red-shift in the absorption spectrum with respect to the solution spectrum. However, other similar highly conjugated OPE derivatives also containing $-NH_2$ groups lead to the formation of H-aggregates,^{57, 90-91} which rules out that the presence of the amine group could induce the formation of J-aggregates and therefore be the cause of the red shift observed for **1** Langmuir films.

(iii) *Conjugation length.* It has been experimentally observed that OPE derivatives exhibit a red-shift when the conjugation increases.⁹⁶ Compound **1** is characterized by the presence of strong aurophilic interactions between neighbour molecules which could constrain the phenylene rings to adopt more planar orientations, resulting in a more extended π -electron delocalization.⁹⁷⁻⁹⁸ This phenomenon has been previously observed in highly conjugated OPE derivatives capable of forming lateral hydrogen bonds with neighbour molecules.⁵² In contrast, other OPE derivatives of similar length lacking such aurophilic interactions do not exhibit any red shift in the absorption band of the LB films with respect to the solution.⁹⁰ Therefore, aurophilic interactions may be the main cause of the red-shift observed in Langmuir films with this effect being more significant upon the compression effect since these interactions increase.

Figure 4. (a) Absorption spectrum of **1** in chloroform (dark blue curve and left axis) and reflection spectra of Langmuir films upon compression (remaining curves and right axis). (b) Normalized reflection spectra upon compression at the indicated areas per molecule.

The normalized reflection, ΔR_n , defined as $\Delta R_n = \Delta R \cdot A$, where A is the area per molecule, more clearly demonstrates changes of orientation, aggregation, multilayer formation or loss of material into the subphase, than the directly measured spectra, ΔR . Figure 4.b. shows the normalized reflection spectra upon compression. No significant changes in the ΔR_n values are observed in the region between 0.85 and 0.31 nm² indicating that no changes in the orientation of the dipole transition moment occur during the compression process. However, at surface areas below 0.31 nm² a decrease in the ΔR_n values is observed. This is consistent with the material being expelled from the monolayer into the subphase probably due to the collapse of the film leading to micelle formation and loss of material into the subphase.⁹⁹

Langmuir monolayers were transferred onto solid substrates by the vertical dipping method onto cleaved mica at several surface pressures of transference. AFM was used to provide topographic images of the LB films and, thus, to check the homogeneity and quality of the films transferred onto mica substrates at different surface pressures. Representative images of **1** monomolecular LB films transferred at 4, 6, 10 and 14 mN·m⁻¹ are shown in Figure 5. The films transferred at 4 mN·m⁻¹ show large uncovered areas and a high root mean square (RMS) roughness of 0.42 nm. The films transferred at 6 mN·m⁻¹ are homogenous with no evidences of holes and a low RMS roughness of 0.10 nm. The higher spots observed in this image could be due to a few local collapses. In films transferred at 10 and 14 mN·m⁻¹ the RMS roughness increases again up to 0.48 and 0.54 nm, respectively, with the images clearly indicating multi-layered films. From these results it was concluded that 6 mN·m⁻¹ is an optimum surface pressure of transference.

Figure 5. AFM images and profile section of one-layer LB films of **1** transferred at the indicated surface pressures.

Electrochemical electron transfer currents at electrodes under controlled potential provide an indirect measure of defect densities in thin films¹⁰⁰⁻¹⁰¹ where electron transport by tunneling directly through the film is significantly blocked. This can be conveniently studied by cyclic voltammetry for the film coated electrodes. Cyclic voltammograms (CV) obtained from aqueous solutions containing 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl for a bare gold and for a gold working electrode modified by a one-layer LB film deposited at 6, 10 and 14 $\text{mN}\cdot\text{m}^{-1}$ surface pressures of transference are shown in Figure 6. The electrochemical response of a bare gold electrode exhibits a clear voltammetric wave for the ferrocyanide redox probe. The Faradaic current, on the other hand, is blocked for the electrode modified by the LB film transferred at 6 $\text{mN}\cdot\text{m}^{-1}$. This result is consistent with a low density of holes or defects in the monolayer in agreement with the AFM observations. Higher surface transference pressures give rise to much more significant voltammetric waves, indicating that they offer a substantially lower current blockage due to the local collapse of the monolayer and higher number of defects in the monolayer. These electrochemical results confirm that 6 $\text{mN}\cdot\text{m}^{-1}$ is an optimum surface pressure of transference for the formation of well-ordered monolayer films of **1**.

Figure 6. Cyclic voltammograms of **1** monolayers deposited on gold electrodes at the indicated surface pressures of transference and a bare gold electrode for comparison. A electrochemical potential was applied to the LB films deposited on a working gold electrode immersed in aqueous solutions containing 1 mM K₃[Fe(CN)₆] and 0.1 M KCl. The scan rate was 0.05 V·s⁻¹ and the initial scan direction was negative. The reference electrode was Ag|AgCl|sat'd KCl and the counter electrode was a Pt sheet.

During the upstroke of the film transfer process, the deposition ratio (defined as the decrease in monolayer area during the deposition divided by the area of the substrate) determined by the software of the Langmuir trough is close to unity for a transference surface pressure of 6 mN·m⁻¹. This transfer ratio was also assessed using a quartz crystal microbalance (QCM). Thus, the frequency change (Δf) for a QCM quartz resonator before and after the deposition process was determined and results interpreted through the relationships found in the Sauerbrey equation:¹⁰²

$$\Delta f = -\frac{2 \cdot f_0^2 \cdot \Delta m}{A \cdot \rho_q^{1/2} \cdot \mu_q^{1/2}} \quad (1)$$

where f_0 is the fundamental resonant frequency of 5 MHz, $\Delta m(g)$ is the mass change, A is the electrode area, ρ_q is the density of the quartz (2.65 g·cm⁻³), and μ_q is the shear modulus (2.95·10¹¹ dyn·cm⁻²). The molecular weight of **1** (544 g·mol⁻¹) gives a surface coverage (Γ) of 5.4·10⁻¹⁰ mol·cm⁻² through application of the Sauerbrey equation. This is in good agreement with the estimated value for the saturated surface coverage, 5.3·10⁻¹⁰ mol·cm⁻², determined from the molecular area of **1** at the air-water interface at 6 mN·m⁻¹. The UV-vis spectrum of monolayer LB films of **1** transferred at a surface pressure of 6 mN·m⁻¹ shows an absorption band at 352 nm with a similar profile to the reflection spectra obtained from the Langmuir films at the air-water interface (band at 358 nm at a surface pressure of 6 mN·m⁻¹).

To determine the electrical characteristics of the LB films the “STM touch-to-contact” method mentioned in the introduction and described in detail elsewhere^{57-58, 62} has been used.^{57-58, 62} In brief this involves bringing the STM tip just into contact with the top of the LB film and hence requires calibration of the tip-substrate separation and film thickness. With this knowledge of the tip-substrate distance and monolayer thickness the STM tip is positioned just above the LB film avoiding either penetration of the STM tip into the film or allowing a gap between the STM tip and the monolayer.

I-V curves were then recorded using a scanning tunneling microscope (STM) and averaged from multiple (ca. 450) scans at different locations on each substrate and across a number of different samples to ensure the reproducibility and reliability of the measurements.

For calibration of the “STM touch-to-contact” method the thickness of the LB films on a gold electrode was estimated by AFM tip lithography, in which the tip was used to scratch and determine the thickness of the monolayer (2.02 ± 0.05 nm). The tip-substrate distance was next calibrated by converting the set-point parameters of the STM ($I_0 \equiv$ “set-point current” and $U_t \equiv$ “tip bias”) to an absolute tip-to-substrate separation.¹⁰³⁻¹⁰⁵ To achieve this calibration, current–distance scans were recorded at a sufficiently high set-point current ($I_0 = 60$ nA and $U_t = 0.6$ V) to ensure that the tip was embedded within the film before retracting it, and only current–distance traces which displayed a monotonic exponential decrease of the tunneling current were selected for quantitative estimate the current decay $d \ln I / ds$ within the LB film. These $d \ln I / ds$ data were recorded at different substrate locations and at regular intervals during the measurements and any curves showing current plateaux synonymous with molecular-wire formation were rejected since they are unsuited for quantification of $d \ln I / ds$ within the film. Then, these monotonic exponential decay curves were plotted as $\ln I$ versus s . Averaging the slope of these collected $\ln I$ versus s plots gave $d \ln I / ds$ values typically in the range of (5.7 ± 0.6) nm⁻¹ which is in good agreement with those reported for similar highly conjugated compounds incorporated in molecular films.^{52, 57-58, 63, 90, 103, 106} Using the $d \ln I / ds$ value for the LB film and assuming that the conductance at the point where metal-tip contact occurs is G_0 ($G_0 = 2e^2/h = 77.4 \mu S$), provides the basis for an absolute calibration of the gap separation according to the following equation:

$$s = \frac{\ln G_0 \times U_t / I_0}{d \ln I / ds} \quad (2)$$

where I_0 and U_t are the set-point parameters of the STM ($I_0 \equiv$ “set-point-current” and $U_t \equiv$ “tip bias”).

Using this calibration method and knowledge of the thickness of 1 LB films (2.02 nm), the *I-V* curves can be measured with the tip directly in contact with the monolayer at $I_0 = 0.5$ nA and $U_t = 0.6$ V as the set-point parameters ($s = 2.02$ nm). Figure 7 shows a representative *I-V* curve obtained for a one layer LB film transferred onto Au(111) at 6 mN·m⁻¹ using these derived set-point parameters. The profile of the *I-V* curve is nearly

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symmetrical and exhibits an approximately sigmoidal profile over the full voltage region in spite of the inherent asymmetry of the molecule. Nevertheless, the I - V curve becomes approximately linear in the low-voltage region (from -0.6 to +0.6 V), that is, the Ohmic region, where the conductance is $3.9 \times 10^{-5} G_0$. This conductance is significantly higher than that exhibited by other three-ring OPE derivatives assembled by the LB technique^{52, 57-58, 90} (in the $0.26 \times 10^{-5} G_0$ to $1.48 \times 10^{-5} G_0$ range), although the comparison is tentative since other contacting groups have been used.^{52, 57-58, 90} This increase in the conductance value may arise from a better alignment of the molecular states of the organometallic molecule with the Fermi levels of the gold contacts.²³⁻²⁴

Figure 7. Averaged I - V curve over 450 curves of a one layer LB film of **1** transferred onto Au(111) at $6 \text{ mN}\cdot\text{m}^{-1}$.

Conclusions

An organometallic gold complex, **1**, has been synthesized and assembled into Langmuir and Langmuir-Blodgett films. Langmuir films were prepared at the air-water interface and characterized by surface pressure and surface potential vs. area per molecule isotherms and reflection spectroscopy, which revealed that **1** can form true monomolecular films at the air-water interface. These monomolecular films were transferred undisturbed onto solid substrates with a transfer ratio close to unity.

Electrical characteristics of the LB films on gold substrates were obtained by recording I - V curves with a gold STM tip positioned just above the monolayer. These I - V curves reveal that the presence of the gold atom in the backbone of the **1** increases considerably the conductance value of the junctions with respect to other OPE derivatives without a metal in the backbone. Whilst the mechanism of conductance in through compound **1** remains to be fully elucidated, the observations here add further momentum to the study of metal complexes and organometallic compounds as components within molecular junctions and ultimately in a molecular electronics technology. Further studies to more precisely define the role of the gold atom in **1** and related compounds are now underway.

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