

Controlling the Structural and Electrical Properties of Diacid Oligo(Phenylene Ethynylene) Langmuir–Blodgett Films

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Abstract: The preparation, characterization and electrical properties of Langmuir-Blodgett (LB) films composed of a symmetrically substituted oligomeric phenylene ethynylene deriv-4,4'-[1,4-phenyleneative, namely, bis(ethyne-2,1-diyl)]dibenzoic acid (OPE2A), are described. Analysis of the surface pressure versus area per molecule isotherms and Brewster angle microscopy reveal that good-quality Langmuir (L) films can be formed both on pure water and a basic subphase. Monolayer L films were transferred onto solid substrates with a transfer ratio of unity to obtain LB films. Both L and LB films prepared on or from a pure water subphase show a red shift in the UV/Vis spectrum of about 14 nm, in contrast to L and LB films

prepared from a basic subphase, which show a hypsochromic shift of 15 nm. This result, together with X-ray photoelectron spectroscopic and quartz crystal microbalance experiments, conclusively demonstrate formation of onelayer LB films in which OPE2A molecules are chemisorbed onto gold substrates and consequently -COO-Au junctions are formed. In LB films prepared on a basic subphase the other terminal acid group is also deprotonated and associates with an Na⁺ counter-

Keywords: carboxylic acids • conducting materials • Langmuir– Blodgett films • oligo(phenylene ethynylene)s • scanning probe microscopy ion. In contrast, LB films prepared from a pure water subphase preserve the protonated acid group, and lateral H-bonds with neighbouring molecules give rise to a supramolecular structure. STM-based conductance studies revealed that films prepared from a basic subphase are more conductive than the analogous films prepared from pure water, and the electrical conductance of the deprotonated films also coincides more closely with single-molecule conductance measurements. This result was interpreted not only in terms of better electron transmission in -COO-Au molecular junctions, but also in terms of the presence of lateral Hbonds in the films formed from pure water, which lead to reduced conductance of the molecular junctions.

Introduction

- The development of smaller and more efficient electronic devices has been a perennial concern for researchers and companies in the electronics industry. Since the seminal publication of Aviram and Ratner^[1] molecular electronics has been a much discussed future alternative to present-day silicon-based technologies. However, a confounding number of significant challenges need to be addressed before this technology reaches fruition, and practical molecular electronic devices still remain a concept rather than a nascent technology. However, the impact of molecular electronics on understanding charge transport in molecules has been more immediate. In particular, over the last decade it has become clear that the contact between metal and molecule plays a much more determining role in electronic transmission than was previously envisaged. In this regard, much attention has shifted in recent years to understanding and controlling metal-molecule contacts and developing new surface-contacting paradigms.^[2-26] For the development of new devices based on molecular electronics,^[27,28] it is of crucial
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importance to understand the chemical nature and structural properties of metal|molecule|metal junctions, since the nature of the metal molecule interface strongly influences the transport properties in molecular devices.^[29] A number of factors, including geometry of contacts,^[30-32] bonding,^[33-35] molecule-electrode distance^[36-38] and molecular orientation,^[39,40] have also been found to affect the transport process. Even more, it still remains a challenge to determine experimentally the role of the molecule metal interface in the transport process, and correlations between experimental observation and theoretical models remain challenging given the size of the computational problem and the variability of individual measurements.^[15,21,32,41-43] In addition, the electron-transfer process across the molecule/electrode junction is poorly understood,^[45,46] and problems related to this topic, such as the structure of the molecule-surface contact, dynamics of electron transfer and the transfer mechanism are topics of ongoing interest. In seeking to address some of these issues, the study of oligo(phenylene ethynylene) (OPE) derivatives, which have shown promising characteristics for use in molecular electronics, has been proven instructive.^[2,47-57] Thus, OPEs have been of particular interest in molecular electronics due to their effective π conjugation and rod-like structure.

Whilst many of these recent studies have been based on single-molecule measurements, more closely packed self-assembled monolayer (SAM) and Langmuir–Blodgett (LB) films have provided important data concerning the electrical properties of monomolecular films of active molecular components more likely to find application in device architectures. The two main advantages of the LB method over SAM films are 1) the compatibility of the LB technique with a wide variety of metal | organic interfaces through the large number of different polar functional groups that can be physically or chemically adsorbed onto an equally wide array of substrates, and 2) the fabrication of directionally oriented films containing two different groups that can be chemisorbed onto metal substrates.^[58]

This paper provides new data concerning the electrical properties of metal acid molecular junctions. For a better understanding of the role played by ionic interactions and the influence of the pH on the electrical properties of the films, 4,4'-[1,4-phenylenebis(ethyne-2,1-diyl)]dibenzoic acid (OPE2A, Figure 1) was synthesized and assembled in LB films, and the quality of the films was compared to that of SA films. In addition, the electrical properties of the films prepared under different experimental conditions were determined and compared with the single-molecule conductance.



Figure 1. Molecular structure of 4,4'-[1,4-phenylenebis(ethyne-2,1-diyl)]-dibenzoic acid (OPE2A).

Results and Discussion

The compound OPE2A is characterized by a rigid molecular structure with a highly conjugated π -electron system. In a manner entirely analogous to other amphiphilic molecules containing large polyaromatic moieties, OPE2A has a pronounced tendency to aggregate due to strong π - π interactions,^[12, 59, 60] as well as to the facility of acids to aggregate in organic solvents. Thus, the Lambert–Beer law is only followed at concentrations lower than 2.5×10⁻⁵ M (Figure 2) in



Figure 2. UV/Vis spectra of OPE2A in CHCl₃/EtOH (4/1) solution at the indicated concentrations. Molar absorptivity at 328 nm is $42700 \text{ L mol}^{-1} \text{ cm}^{-1}$.

chloroform/ethanol (4/1), with higher concentrations leading to deviations from linearity in the absorbance versus concentration plot. Consequently, highly dilute solutions are required to fabricate true monolayers at the air–water interface. The UV/Vis spectrum of OPE2A in solution features one peak at 328 nm with two shoulders at 359 and 380 nm attributable to π – π * electronic transitions.^[6,62]

A preliminary investigation of the formation of Langmuir films of OPE2A involving both the concentration and the volume of the spreading solution concluded that only solutions of concentration 1×10^{-5} M or lower yield reproducible isotherms. Figure 3 shows representative surface pressure versus area per molecule (π -A) isotherms of OPE2A on water (pH 5.9) and basic subphases (NaOH, pH 11.4). In contrast to other OPE acid derivatives, for which a basic



Figure 3. Surface pressure versus area per molecule isotherm of OPE2A on a water subphase and an aqueous NaOH subphase at 20 °C.

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Figure 4. BAM images recorded at the indicated surface pressures for a pure water subphase (pH 5.9) and a basic subphase (pH 11.4). The field of view along the x axes for the BAM images is 1650 µm.

subphase was necessary to avoid aggregation,^[19,26,63] Langmuir films of OPE2A were homogeneous (see BAM images in Figure 4) and did not show any evidence of 3D aggregates when a water subphase was used. The π -A isotherms of OPE2A on pure water are characterized by zero surface pressure, that is, gas phase, until an area of 0.8 nm²molecule⁻¹ is reached with a transition from gas to expanded liquid phase taking place for the monolayer fabricated on a water subphase. As the pH increases, the lift-off area per molecule⁻¹ for the monolayers obtained on a basic subphase. The lift-off in the isotherms is followed by a monotonous increase of the surface pressure upon compression.

Reflection spectroscopy is a useful method for in situ characterization of the monolayer at the air-water interface^[64,65] that provides relevant information about orientation of the molecules in the film, formation and types of aggregates, changes in the aggregation state during the compression process and so on. However, it is well-known that the normalized reflection spectra $\Delta R_{\text{norm}} = \Delta RA$ of the films provide more direct information about the orientation of the molecules in the compression process, since the influence of the surface density is eliminated.^[65,66] Normalized reflection UV/Vis spectra ΔR_{norm} recorded at different surface pressures for OPE2A Langmuir films are shown in Figure 5 a. In addition, quantitative analysis of the ΔR_{norm} spectra allowed us to calculate the tilt angle ϕ of the transition dipole moment of the molecule with respect to the liquid surface (Figure 5b). This angle was determined by comparing the reflection spectra at the air-water interface and the UV/Vis absorption spectrum of OPE2A in solution, as has been comprehensively detailed elsewhere.^[12,65] The tilt angle of the OPE moieties with respect to the water subphase is largely unchanged upon compression when the monolayers are prepared on a water subphase, and only a small variation in $\Delta R_{\rm norm}$ values is produced in the basic subphase. The tilt angle of the molecules is around 60° for films on pure



Figure 5. a) Normalized reflection spectra upon compression at the indicated surface pressures for OPE2A monolayers prepared on the indicated subphases. b) Tilt angle ϕ of OPE2A with respect to the liquid surface in the compression process for monolayers prepared on the indicated subphases.

water subphase and slightly higher (ca. 67°) in the condensed phase of a monolayer on the basic subphase, which is in agreement with the more expanded isotherm observed in pure water (Figure 5b).

Interestingly, the reflection band is shifted with respect to the solution depending on the subphase on which the monolayers were prepared. In the last few years a systematic study in which different polar terminal groups have been added to the OPE skeleton as well as alkyl chains of different length or other hydrophobic terminal groups has been carried out. In all previously studied cases, [12, 14, 19, 20, 26, 58, 63, 67-70] hypsochromic shifts of the main absorption band with respect to the solution were observed both in L and LB films, and this blue shift of the films was attributed to formation of H-aggregates. To our knowledge this is the first example of an OPE derivative which, when arranged in a Langmuir film, shows a bathochromic shift (monolayers on pure water) relative to the solution spectrum. However, the observation of a hypsochromic shift is maintained for monolayers on a basic subphase. It is also noteworthy that monosub-

stituted carboxyl OPE derivatives incorporated in L and LB films showed a significant hypsochromic shift (36–60 nm) compared to the solution spectrum,^[19,26,63] independent of the pH of the subphase, which leads to the conclusion that the effect observed in OPE2A is a unique feature of this dicarboxyl-substituted compound. The red shift of OPE2A in L films prepared on water could be due to several factors:

- Solvatochromic effect: To understand the influence of polarity on aggregation, OPE2A was dissolved in solvents ranging from CHCl₃ to EtOH/water (this compound is not soluble in apolar solvents). A significant hypsochromic shift was observed, from 325 (CHCl₃) to 315 (EtOH) and 302 nm (EtOH/H₂O 2/1). This indicates that the observed red shift is not attributable to an increase in the polarity of the environment, as might be expected at the air-water interface, especially at low surface pressures. However, due to the insolubility of this compound in apolar solvents it is not fully clear whether a less polar environment, which could be achieved in compact monolayers, might result in a red shift of the absorption profile.
- 2) Conjugation length:^[72] It has been experimentally observed that OPE derivatives exhibit a red shift when the number of phenylene ethynylene groups increases. As will be demonstrated later, the OPE2A compound generates a supramolecular structure in monolayers through lateral H-bonding interactions when monolayers are fabricated on a water subphase (see below). These H-bonds could constrain the phenylene rings to adopt more planarized orientations, resulting in more extended π -electron delocalization.^[73,74]
- 3) Formation of J-aggregates: For some compounds that tend to form mainly H-aggregates, for example, merocyanines^[75,76] and azo compounds,^[77,78] incorporation of certain functional groups capable of forming H-bonds leads to the formation of J-aggregates, which exhibit absorption spectrum which are red-shifted with respect to the solution spectrum. However, taking into account the angle of OPE2A monolayers with respect to the surface (ca. 60° for monolayers spread onto pure water) and the angle needed, according to the theoretical calculations,^[79] to exhibit a red shift (<54°), we believe that, although this effect could somehow contribute to the bathochromic shift, it may not be the main cause of the red shift observed for OPE2A Langmuir films.</p>

Transfer of these Langmuir films onto solid supports gives Langmuir–Blodgett films, which can be investigated by a wider range of spectroscopic, microscopic and electrochemical methods to provide further insight into the arrangement of OPE2A molecules in monolayers on different supports.

The transfer ratio calculated by the trough software during deposition of the monolayer was approximately unity at a surface pressure of 20 mNm^{-1} for both pure water and aqueous NaOH subphases. This uniform transfer was also estimated by using a quartz crystal microbalance (QCM).

Thus, the frequency change Δf for a QCM quartz resonator before and after the deposition process was determined using the Sauerbrey equation (1),^[80]

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

where f_0 is the fundamental resonant frequency of 5 MHz, Δm the mass change [g], A the electrode area [cm²], ρ_q the density of quartz (2.65 g cm⁻³) and μ_q the shear modulus $(2.95 \times 10^{11} \text{ dyn cm}^{-2})$. Considering these values and the molecular weight of OPE2A (366 gmol⁻¹), the surface coverages Γ obtained from Equation (1) are 5.60×10^{-10} and $6.5 \times$ 10⁻¹⁰ mol cm⁻² for the water and basic subphases, respectively. These values correspond to transfer ratios of 0.96 for the monolayer on pure water and 0.98 for the monolayer onto a basic subphase. The slightly higher transfer ratio for monolayers prepared onto a basic subphase may indicate better interaction between the gold substrate and the carboxylate group in the monolayer as opposed to the carboxyl groups present in the pure water subphase. This suggestion is consistent with the presence of H-bonds between the carboxyl head groups in the L films prepared on the pure water subphase; transference of these films onto gold substrates requires rupture of this H-bond network prior to chemisorption of the monolayer onto the gold substrate (see below).

Electrochemical electron-transfer currents at electrodes under controlled potential provide an indirect measure of defect densities in thin films and can be conveniently studied by cyclic voltammetry for film-coated electrodes.[81,82] Cyclic voltammograms (CVs) obtained from aqueous solutions containing 1 mM [Ru(NH₃)₆]Cl₃ and 0.1 M KCl for a bare gold electrode (see details in the Experimental Section) and for a gold working electrode modified by a onelayer LB film deposited at 5, 10, 15 and 20 mNm⁻¹ from a monolayer prepared on a pure water subphase are shown in Figure 6a. (The same sort of sequence was obtained for monolayers prepared on a basic subphase, but not shown here for the sake of brevity.) The electrochemical response of a bare gold electrode exhibits a clear voltammetric wave characteristic of the ruthenium complex. There is a significant decrease in current density for the voltammograms recorded with gold electrodes covered by LB films, and this decrease in current density becomes more significant with increasing surface pressure of transference. When the surface pressure of transference was 20 mN m⁻¹, a drastic decrease of the reduction and oxidation peaks of the redox probe for the modified electrode indicates effective blocking of the electrode surface and therefore a low density of holes or defects in the monolayer. In addition, LB films fabricated from a basic solution block the electrode slightly better than those prepared in pure water (see Figure 6b), in agreement with the results obtained by other techniques (e.g., a less expanded isotherm, higher surface coverage, higher tilt angles).



Figure 6. Cyclic voltammograms (CVs) of a) a one-layer LB film of OPE2A (water subphase) deposited on a gold electrode at the indicated transference surface pressures. b) Comparison of the blocking effect on the gold electrode of an LB film transferred at a surface pressure of 20 mNm^{-1} and a self-assembled film prepared by incubation of a gold substrate in a 10^{-5} M solution for 48 h. CVs were recorded by immersing the gold substrate in a $1 \text{ mm} [\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ and 0.1 M KCl aqueous solution at a scan rate of 0.1 V s^{-1} at 20° C. An AglAgCl saturated reference electrode was employed and the counterelectrode was a Pt sheet.

Self-assembly is a commonly used method to fabricate films incorporating functionalized OPEs. It is well-known that the LB method is not the most appropriate to assemble doubly polar functionalized molecules in which strong competition of the polar groups to be anchored at the air-water interface could take place. However, in this particular case, the LB technique proved to be a good method to incorporate OPE2A molecules into well-ordered monolayers. This behaviour is probably due to the presence of a very rigid OPE backbone that prevents bending of the molecule and thus contact of both polar groups with the water surface. In addition, the very hydrophobic OPE core tends to be situated away from the water surface, and this leads to surface behaviour similar to that of amphiphilic materials containing just one polar group. To compare the efficiency of the LB method with that of self-assembly in the arrangement of OPE2A molecules in terms of surface coverage, self-assembled monolayer (SAM) films of OPE2A were fabricated. Gold substrates were immersed for 48 h in a 10^{-5} M solution of OPE2A in ethanol. Poor blocking of the gold electrode (Figure 6b) and a low coverage of OPE2A on gold surfaces was determined by QCM experiments (surface coverage of $3.8 \times 10^{-10} \text{ mol cm}^{-2}$ for SAMs versus $5.53 \times 10^{-10} \text{ mol cm}^{-2}$ for LB films prepared on a water subphase). The use of more concentrated solutions of OPE2A (up to 10^{-3} M) to produce SA films also did not result in better surface coverage.

Optical properties of the transferred films offer additional insight into the molecular arrangement and degree of order within the film. Langmuir films of OPE2A were transferred onto quartz substrates at 20 mN m⁻¹ and the UV/Vis absorption spectra were recorded. Figure 7 shows the electronic spectra of OPE2A LB films prepared from water and basic



Figure 7. Apparent molar absorptivity versus wavelength for a monomolecular LB film of OPE2A transferred at 20 mNm^{-1} from water and basic subphases and comparison with the molar absorptivity of a solution in CHCl₃/EtOH (4/1).

subphases together with the spectrum of OPE2A in solution and at the water–liquid interface for comparison. The molar (ε) and apparent molar absorptivities (ε_{app} , where apparent denotes the orientational effect of the molecules in the L or LB films) for solution and monolayer were obtained according to Equations (2) and (3) for the solution and the air– water interface^[83], respectively, and Equation (4) for LB films,

$$\varepsilon = \frac{A_{\rm b}}{Cl} \tag{2}$$

$$\varepsilon_{\rm app} = \frac{\Delta R}{2.303 \times 10^3 \Gamma \sqrt{R_w}} \tag{3}$$

$$\varepsilon_{\rm app} = \frac{A_{\rm b}}{1000\Gamma} \tag{4}$$

where Γ [mol cm⁻²] is the surface density, R_w the reflectivity of water (0.02), A_b the absorbance, C the solution concentration and l the cell width.

The spectra of LB films transferred from a water subphase are again red-shifted by about 17 nm compared to the solution spectra (see Figure 7), and they practically overlap with the spectra of the monolayers at the air-water interface (result not shown for clarity). In the case of films transferred from a basic substrate the spectrum is blue-shifted by 14 nm with respect to the solution, and again the LB film spectrum

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overlaps the reflection spectrum obtained on a basic subphase. These results indicate that the molecular arrangement at the air-liquid interface is retained when the films are transferred onto the solid support. Additionally, the difference in apparent molar absorptivity of the molecules in solution and in the films provides quantitative information on the orientation of the dipole moment of transition and the normal to the surface, as stated above. The results obtained here clearly indicate that OPE2A molecules are in a more vertical orientation with respect to the substrate when they are fabricated from a basic subphase compared to those fabricated from a water subphase. The LB films that were prepared by using a water subphase were incubated for 48 h in NaOH solution (pH 11.4) and then thoroughly rinsed with water and dried. The maximum wavelength was then shifted to 324 nm, that is, the initial red shift with respect to the solution disappears. This result is consistent with the red shift in films prepared on pure water being due to the presence of lateral H-bonds between neighbouring molecules that disappear after exposure of the film to a basic medium. The fact that, after incubation of these films in a water subphase, the peak is not shifted to 313 nm (position of the maximum wavelength for films prepared on a basic subphase) may be attributable to different orientations of the molecules in the two films.

Table 1 shows additional evidence for the formation of a supramolecular structure in the L and LB films. While the

Table 1. Position of the main absorption peak [nm] for the indicated solution and films.

| Solution | Cast | LB film | |
|----------------------|------|----------------------------------|----------------------------------|
| (CHCl ₃) | film | Basic subphase ^[a] | Water subphase ^[b] |
| 328 | 317 | 313 | 345 |

[a] pH 11.4. [b] pH 5.9.

absorption maxima of L and LB films formed on an aqueous subphase (pH 5.9), where the carboxyl groups are expected to be protonated, is red-shifted with respect to the solution spectrum in chloroform, the peaks of L and LB films prepared on a basic subphase (NaOH) are slightly blue-shifted. In basic subphases the carboxyl groups are deprotonated, and therefore no H-bonds between adjacent molecules are formed. In addition, the red shift observed for the LB films on the water subphase may be favoured by the spatial organization of the film, since the maximum absorption for cast

films of this compound prepared from a chloroform solution appears at 317 nm, that is, again blue-shifted with respect to the solution (328 nm). An LB film fabricated by using pure water as subphase was redissolved in chloroform. A significant blue shift (peak at 300 nm) of the solution of the redissolved film compared to the spectrum of the original solution was observed. After sonication of the solution of the redissolved film in chloroform for 10 min the original spectrum of this compound in a chloroform solution was obtained. This indicates that no chemical reaction has taken place but significant aggregation effects definitely occur in the monolayer. The initial blue shift of the spectrum after redissolving the film prepared from a water subphase might be due to the rupture of H-bonds between neighbouring molecules, and the preservation of lateral π - π interactions that may lead to H-aggregates. These interactions are lost after sonication. The electrical properties of the LB films also seem to point towards a different structure for films transferred from water and a basic subphase (see below).

Carboxylic acids readily form head-to-head dimers in solution and solid state through mutual H-bonding, which provides an avenue through which to explore the nature of the carboxyl groups in films of OPE2A, and to gather further support for the notion of a supramolecular network linking the exposed CO₂H moieties in LB films of this compound. Monolayers of OPE2A prepared on the two subphases were transferred onto QCM substrates by withdrawal of substrates that were initially immersed in the subphase. The modified substrates were introduced into a behenic acid solution (see Figure 8) and the frequency change Δf of the QCM quartz resonator before and after exposure of monomolecular OPE2A films to solution of behenic acid $(10^{-2} M)$ CH₃(CH₂)₂₀COOH in CHCl₃) was determined. No frequency change was observed after 24 h incubation of the films transferred from a water subphase in the behenic acid solu-



Figure 8. Schematic of monomolecular LB films deposited onto gold substrates and transferred from a water subphase a) and a basic subphase b) before and after incubation in a behenic acid solution according to the QCM experiments described in the text.

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tion. In contrast, after 4 h of incubation of OPE2A films transferred from a basic subphase, a frequency change of -27 Hz was recorded, which indicates, through application of the Sauerbrey equation, that one molecule of behenic acid was deposited per molecule of OPE2A in the film. This result suggests that when OPE2A molecules are transferred from a water subphase the carboxylic acid remains protonated and lateral H-bonds are formed, which renders the CO₂H group insensitive to further H-bonding interactions. These H-bonds are strong enough to prevent surface binding of behenic acid to the OPE2A monolayer through Hbonded carboxylic acid dimers. However, when OPE2A molecules are transferred from a basic subphase the carboxyl groups are deprotonated, and consequently they are free to form face-to-face H-bonds with behenic acid molecules (see Figure 8). Although this QCM experiment clearly shows different states of the terminal carboxyl groups depending on the subphase used, it does not provide information about the dissociation state of the carboxyl groups directly attached to the gold substrate.

Figure 9 shows XPS spectra in the C 1s spectral region of OPE2A powder and OPE2A LB films transferred onto gold substrates from the two different subphases. The powder



Figure 9. C 1s XPS spectra of OPE2A in powder and in LB films deposited onto gold substrates from water and a basic aqueous subphase.

spectrum shows a peak at 288.8 eV corresponding to the carbon atom in the carboxyl moiety.^[84–90] Films of OPE2A molecules on gold substrates prepared from a basic subphase show a peak attributable to the carboxylate carbon atom at 287.1 eV.^[91,92] This clearly indicates that OPE2A is entirely deprotonated when transferred from a basic subphase. In contrast, the peak at 288.8 eV is preserved in LB films transferred from a water subphase, and a peak at 287.1 eV is also observed. This indicates that OPE2A contains both carboxylate and carboxyl groups when transferred from a water subphase, which, in combination with the data provided by the QCM experiments described above, suggests that the group attached to the gold substrate is deprotonated and chemisorbed as carboxylate, independent of the

subphase used. In contrast, the other terminal carboxyl group remains protonated when the Langmuir film is prepared on a pure water subphase and is deprotonated when a basic subphase is used. Further confirmation of these conclusions was provided by angle-resolved (AR) XPS. Representative C 1s XPS spectra measured at take-off angles of 90 and 60° with respect to the surface are shown in Figure 10 for an OPE2A LB film prepared from pure water.



Figure 10. Angle-resolved XPS spectra of a monomolecular LB film deposited onto a gold substrate from a pure water subphase at take-off angles of 90 and 60°.

From the AR-XPS spectra, it is clear that the intensity of the peak corresponding to the protonated carboxyl group (C_{COOH}) is larger, while a decrease in the take-off angle results in a more prominent C_{COO^-} peak. This result is consistent with the model presented in Figure 8, in which the adsorbate group contacting the gold surface is likely to be the deprotonated carboxyl group, while the terminal carboxylic acid remains protonated.

The LB films of OPE2A transferred from a pure water subphase and a basic subphase showed very significant differences in electrical behaviour that may also be explained by the different protonation states of their carboxyl groups. To determine the electrical characteristics of a monomolecular LB film transferred onto gold substrates at 20 mN m⁻¹ by using pure water as subphase, I-V curves were recorded by STM and averaged from multiple (ca. 420) scans at different locations on the substrate and by using different samples to ensure the reproducibility and reliability of the measurements. Moreover, before recording the I-V curves, both the thickness of the monolayer and the tip-to-substrate distance (s) should be estimated in order to position the STM tip just above the LB film and thus avoid penetration of the STM tip into the film or the existence of a substantial gap between the STM tip and the monolayer. By using the attenuation of the Au 4f signal of the substrate (see Experimental Section), the thickness of the LB films on the gold electrode was estimated to be (1.81 ± 0.05) nm, in good agreement with the determination of the tilt angle obtained from the UV/Vis reflection spectra at the air-water interface. Once the thickness of the LB film is known, the tip-substrate distance must be calibrated so that the STM tip can be placed at a known distance above the LB film. This is achieved by converting the set-point parameters of the STM ($I_0 \equiv$ "setpoint current" and $U_t \equiv$ "tip bias") to an absolute gap separation, as has been reported previously and is described below.^[93-95] Depending on these parameters, the STM tip can be located above the monolayer, in contact with the top of the monolayer or embedded within the monolayer film. In order to most accurately measure the trans-film conductance, it is necessary to first determine the set-point conditions under which the tip is just touching the top of the LB film. A quantitative estimation of the current decay $d \ln I/ds$ in the LB film is required to evaluate this separation at which the tip just touches the top of the film. Firstly, current-distance scans were recorded with the tip fully embedded in the film at sufficiently high set-point currents ($I_0 =$ 20 nA and $U_t = 0.6$ V) to ensure that the tip was embedded within the film, and only current-distance traces which displayed a monotonic exponential decrease of the tunnelling current were selected for this quantification of $d \ln I/ds$. These $d \ln I/ds$ data were recorded at different substrate locations and at regular intervals during the measurements. Any curves showing current plateaux synonymous with molecular-wire formation were rejected, since they are unsuited for quantification of $d \ln I/ds$. The monotonic exponential decay curves were then plotted as $\ln I$ versus s. Averaging the slope of the collected $d \ln I/ds$ plots gave $d \ln I/ds$ values typically in the range of (6.91 ± 1.37) nm⁻¹. This value is in good agreement with those reported for similar highly conjugated compounds incorporated in molecular films^[20,26,58] and for single molecules.^[21,93] With $U_t = 0.6 \text{ V}$ and $I_0 =$ 0.15 nA as the set-point parameters, the initial tip-to-substrate distance is estimated as 1.82 nm according to Equation (5), in which I_0 and U_t are the set-point parameters of the STM, in good agreement with the thickness of the monolayer.

$$s = \frac{\ln(G_0 U_t / I_0)}{\mathrm{d} \ln(I) / \mathrm{d} s} \tag{5}$$

Therefore, these set-point parameters were used to position the tip just above the monolayer. For higher set-point currents (e.g., 0.6 nA, s = 1.63 nm) the tip would be embedded within the monolayer, and for lower set-point currents, the tip would not be in contact with the monolayer and, in this case, the tunnelling current measured represents tunnelling through both the monolayer and the gap between the top of the monolayer and the tip. Figure 11 a shows a representative I-V curve obtained for a one-layer LB film from water as subphase at $U_t=0.6$ V and $I_0=0.15$ nA. The profile of the I-V curve is clearly symmetrical and exhibits an approximately sigmoidal profile over the full voltage region. Nevertheless, the I-V curve becomes linear in the low-voltage region (from -0.6 to +0.6 V), that is, the ohmic region, where the conductance is $0.26 \times 10^{-5} G_0$. This conductance is



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Figure 11. a) I-V curve of a one-layer LB film of OPE2A transferred onto Au(111) at 20 mN m⁻¹ from water as subphase (solid line) and fitting according to the Simmons equation (Φ =1.1 eV, α =0.41; dashed line). Note that the experimental data and Simmons model nearly overlap, and this may interfere in visualization of the experimental curve. The inset shows a magnification of the y axis to observe in more detail the sigmoidal shape of the I-V plot. A representative STM image of the monolayer is also shown in the inset. b) I-V curve of a one-layer LB film of OPE2A transferred onto Au(111) at 20 mNm⁻¹ by using a basic subphase (solid line), from single-molecule conductance values obtained by using the I(s) method (circles) and fitting according to the Simmons equation (Φ =0.73 eV, α =0.34; dashed line). The error bars represent the standard deviation. U_i =0.6 V.

significantly lower than that exhibited by other OPE derivatives assembled by the LB technique, even when these OPE derivatives have different end groups.^[20,26] This low conductance for the OPE2A monolayer fabricated on a water subphase could be attributed to the "supramolecular structure" promoted by the carboxyl group that is used as linker to make contact with the STM tip. This supramolecular structure is formed through the lateral H-bonding interactions between the carboxyl groups, which may also be synergistic with lateral π - π stacking. The lower conductivity of OPE2A monolayers fabricated on a pure water subphase would then arise from the less effective contact of this H-bonded carboxylate group to the gold STM tip compared with the chemisorption bond formed between the carboxylate group and gold contacts.

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A basic subphase (pH 11.4) was used to retain the lower contacting group in its deprotonated carboxylate state. The thickness of the monolayer determined by using the attenuation of the Au 4f signal from the substrate was $(1.95\pm$ 0.05) nm. Taking into account that the average slope of the corresponding $d \ln I/ds$ curves used to calculate the tip-tosubstrate distance was (5.48 ± 0.89) nm⁻¹ when the set-point parameters $U_t = 0.6 \text{ V}$ and $I_0 = 1 \text{ nA}$ were used, the initial tip-to-substrate distance was 1.95 nm, which is in agreement with the thickness of the monolayer and indicates that the tip is positioned just above the monolayer when these setpoint parameters are used. Figure 11b shows a representative I-V curve obtained for a one-layer LB film from a basic subphase at $U_t = 0.6$ V and $I_0 = 1$ nA. The profile of the I-Vcurve is clearly symmetrical and exhibits an approximately sigmoidal profile over the full voltage region, although the I-V curve becomes linear in the low-voltage region (from -0.6 to +0.6 V), the ohmic region, where the conductance is 1.75×10^{-5} G₀. This conductance is similar to, or even larger than, that obtained for other OPE derivatives assembled by using the LB technique^[20,58] or for single molecules.^[21,93] In addition, Figure 11b also shows an *I-V* curve constructed from single-molecule conductance (SMC) values for OPE2A obtained by using the I(s) method at eight different bias voltages. This I(s) method, developed by Haiss et al.,^[15,21,96] has been used to determine the SMC of molecular junctions. The SMC curve coincides with the I-Vcurve obtained for the LB film at 1 nA and 0.6 V, and this indicates that with these parameters the STM tip is located directly above the LB film and electronically coupled to a single molecule. The two I-V curves show similarity, despite the different molecular surroundings in the two cases: in the LB film the molecules are packed together with neighbouring OPE2A molecules, whereas no such neighbours exist for the SMC determinations. The higher conductance for the COO-Au molecular junctions than COOH-Au junctions supports the notion that the former are more effective in both their surface binding ability and in promoting electrical transmission of the junctions, which is in agreement with previous work.[38]

The sigmoidal shape of both I-V curves (for water or basic subphase) is indicative of a non-resonant tunnelling mechanism of transport through these metal-molecule-metal junctions. The Simmons model^[97] is one of the simplest tunnelling barrier models which has been widely used for describing charge transport through metal |SAM or metal |LB film junctions.^[20,56,58,98] In this model, the current I is defined as Equation (6),

cordance with the isotherms shown in Figure 3 at a surface pressure of 20 mNm^{-1}), s the width of the tunnelling barrier, which was assumed to be the geometric distance between the end groups in the OPE molecular wire as calculated with a molecular modelling program (2.07 nm), Φ the effective barrier height of the tunnelling junction (relative to the Fermi level of Au), α is related to the effective mass of the tunnelling electron and m and e represent the mass and the charge of an electron. The Φ and α parameters are then used to best fit the I-V data in Figure 11. Good agreement between the data and the model were obtained for $\Phi =$ 1.1 eV and $\alpha = 0.41$ when water is used as subphase, and for $\Phi = 0.73 \text{ eV}$ and $\alpha = 0.34$ when a basic subphase is used. Firstly, we emphasize that Equation (6), which is based on a very simple model of non-resonant tunnelling, gives a reasonable description of our experimental I-V data, and it is therefore reasonable to assume that the mechanism of transport through these metal molecule metal junctions is nonresonant tunnelling. Secondly, the Φ value depends on the subphase used. Thus, for a basic subphase, $\Phi = 0.73 \text{ eV}$, which is in good agreement with those obtained for similar OPE derivatives assembled by self-assembly^[44, 56] or by the LB technique.^[14,19,20,26,58] Meanwhile, when the subphase is water, the effective barrier height is $\Phi = 1.1 \text{ eV}$, which is higher than those obtained for a basic subphase and for other OPE derivatives.^[15, 20, 56,58] Therefore, these results seem to indicate that the presence of protonated surface groups (COOH) and consequent lateral H-bonds within the monolayer decreases the conductance. This is attributed to a more compromised electrical contact between the STM tip and the carboxyl-terminated surface.

Conclusion

A symmetrical acid-terminated OPE derivative has been synthesized and assembled into well-packed monolayer films by means of the Langmuir–Blodgett technique, which has proved to be a suitable method for obtaining homogeneous films with high surface coverage, superior to those achieved by self-assembly techniques for this material. Langmuir films were prepared at the air–water interface by using a pure water subphase and a basic subphase and characterized by surface pressure versus area per molecule isotherms and Brewster angle microscopy, which revealed that OPE2A can form true monomolecular films at the air–water interface on both subphases, in contrast to singly acid substituted OPEs, which only form three-dimensional defect-free

$$I = \frac{Ae}{4\pi^2\hbar s^2} \left\{ \left(\Phi - \frac{eV}{2} \right) \exp\left[-\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi - \frac{eV}{2} \right)^{1/2} s \right] - \left(\Phi + \frac{eV}{2} \right) \exp\left[-\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi + \frac{eV}{2} \right)^{1/2} s \right] \right\}$$

$$\tag{6}$$

monolayers on basic subphases. These monomolecular films were transferred undisturbed onto solid

in which V is the applied potential, A the contact area of the molecule with the gold surface $(0.31 \text{ nm}^2 \text{ and } 0.25 \text{ nm}^2 \text{ for a water subphase or basic subphase, respectively in con-$

substrates with a transfer ratio close to unity. Both L and LB films of OPE2A fabricated on a pure water subphase show a red shift of the main absorption band with respect to

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the solution, whilst films prepared on a basic subphase exhibit a blue shift. A combination of QCM, XPS and UV/Vis spectra experiments demonstrated that OPE2A was linked through a deprotonated carboxyl group to the gold substrate when the LB films were prepared from either a pure water or a basic subphase. Monolayers fabricated on a pure water subphase feature a supramolecular structure due to lateral

H-bonding interactions through the terminal carboxyl groups. In contrast, these lateral H-bonds are not present in monolayers fabricated on basic subphases.

Electrical characteristics of the LB films on gold substrates were obtained by recording I-Vcurves with a gold STM tip

positioned just above the monolayer (as determined from calibration of the tip-to-substrate distance and knowledge of the thickness of the LB film determined from XPS measurements). These I-V curves and good fits to the Simmons model indicate that charge flow through the metal molecule metal junction occurs by a non-resonant tunnelling mechanism. Importantly, the conductance in films prepared on basic subphases is quite similar to the SMC values. However, LB films fabricated on a pure water subphase exhibit conductances around seven times lower. This result has been attributed to the more effective electrical junctions

formed between carboxylate groups and gold surfaces, as opposed to carboxyl groups, which also form lateral H-bonding interactions that decrease the conductance. Thus, modulation of conductance by pH and molecular structure control is achieved.

Experimental Section

General synthetic conditions: Syntheses were carried out under an oxygen free nitrogen atmosphere by using standard Schlenk techniques. All reaction vessels were flame-dried before use. Triethylamine was purified by distillation over CaSO₄. Other reagents were purchased commercially and used as received. Hexyl 4-ethynylbenzoate was prepared according to literature procedures.^[26] NMR spectra were recorded on solutions in deuterated solvents on Bruker DRX-400 and Varian 500 spectrometers and referenced against solvent resonances (¹H, ¹³C). ESI mass spectra were recorded on a TQD mass spectrometer (Waters Ltd, UK). Samples were 0.1 mgmL⁻¹ soloutions in analytical-grade methanol. Thermal analyses were performed with a PerkinElmer Pyris thermogravimetric analyser (heating rate 10°C min⁻¹).

Preparation of dihexyl 4,4'-[1,4-phenylenebis(ethyne-2,1-diyl)]dibenzoate: Hexyl-4-(ethynyl)benzoate (0.34 g, 1.5 mmol), 1,4-diiodobenzene (0.25 g, 0.76 mmol), $[Pd(PPh_3)_4]$ (0.045 g, 0.040 mmol) and CuI (0.007 g, 0.037 mmol) were added to NEt₃ (15 mL), and the resulting white suspension stirred at room temperature overnight. The precipitate was collected by filtration and washed thoroughly with hexane. The solids were dissolved in CH₂Cl₂ and the solution filtered through silica gel. Solvent removal from the yellowish filtrate yielded the pure product as an off-



534.28 [M]+ (53).

Preparation of 4,4'-(1,4-phenylenebis(ethyne-2,1-diyl))dibenzoic acid (OPE2A): NBu₄OH·30H₂O (0.30 g, 0.38 mmol) dissolved in THF (3 mL) was added to a solution of dihexyl 4,4'-[1,4-phenylenebis(ethyne-2,1-diyl)]dibenzoate (0.05 g, 0.09 mmol) in THF (3 mL). The resulting brown solution was stirred at room temperature for 30 min, taken to dryness and redissolved in CHCl₃ (2 mL). White solids precipitated upon addition of concentrated HCl and sonication of the two phases. The precipitate was collected by filtration and washed with water (2×5 mL), acetone (2 mL) and Et₂O (5 mL) and dried in air. Yield: 0.03 g, 0.08 mmol, 89 %. ¹H NMR (500 MHz, [D₆]DMSO): δ =13.21 (brs, 2H, j), 7.97 (d, *J* = 8 Hz, 4H, f), 7.64 ppm (s, 4H, a); ¹³C NMR [¹H] (126 MHz, [D₆]DMSO, 50°C): δ =166.4 (i), 131.6, 131.4 (f/g), 130.8 (h), 129.3 (a), 126.0, 122.2 (b/e), 91.1, 90.6 ppm (c/d); ESI-MS(-): *m/z* (%): 183.3 [*M*-2H]² (100), 365.5 [*M*-H]⁻ (34); TGA: incomplete combustion (91 %) at 1000°C.

white solid. Yield: 0.30 g, 0.56 mmol, 75 %. ¹H NMR (400 MHz, CDCl₃):

 $\delta = 8.04$ (d, J = 9 Hz, 4H, g), 7.59 (d, J = 9 Hz, 4H, f), 7.54 (s, 4H, a), 4.33

(t, J=7 Hz, 2H, j), 1.82-1.72 (m, 4H, k), 1.49-1.40 (m, 4H, l), 1.39-1.29

(m, 8H, m/n), 0.92 ppm (t, J=7 Hz, 6H, o); ${}^{13}C{}^{1}H$ NMR (101 MHz,

CDCl₃): $\delta = 166.2$ (i), 131.9, 131.6 (f/g), 130.3 (h), 129.7 (a), 127.6, 123.2

(b/e), 91.9, 90.9 (c/d), 65.5 (j), 31.6 (k), 28.8 (l), 25.8 (m), 22.7 (n),

14.1 ppm (o); ASAP-MS(+): m/z (%): 451.19 $[M+H-C_6H_{13}]^+$ (100),



Film fabrication and characterization: The films were prepared on a Nima Teflon trough with dimensions 720×100 mm, which was housed in a constant temperature (20±1°C) clean room. A Wilhelmy paper-plate pressure sensor was used to measure the surface pressure π of the monolayers. The subphase was either pure water (Millipore Milli-Q purification system, resistivity 18.2 MQ cm) or a solution of NaOH or HCl prepared with Milli-Q water as solvent and with pH as indicated in the paper. To fabricate the Langmuir films a 1×10^{-5} M solution of OPE2A in chloroform/ethanol (4/1, HPLC grade purchased from LabScan (99.8%) and Panreac (99.5%), respectively) was spread by using a Hamilton syringe held very close to the surface and allowing the surface pressure to return to a value close to zero between each addition. The use of ethanol in the spreading solvent limits the formation of hydrogen-bonded carboxylic acid dimers and aggregates in solution prior to deposition.^[63] After waiting about 15 min to allow the solvent to evaporate, slow compression of the film began at a speed of 0.022 nm²molecule⁻¹ min⁻¹. Under these experimental conditions the isotherms were highly reproducible. Direct visualization of monolayer formation at the air-water interface was studied with a commercial micro-Brewster angle microscope (micro-BAM) from KSV-NIMA having a lateral resolution better than 12 µm. A UV/ Vis reflection spectrophotometer with FiberLight DTM 6/50 light source. an absolute wavelength accuracy of <0.3 nm and a resolution (Rayleigh criterion) of >3 nm was used to obtain the reflection spectra of the Langmuir films during the compression process.[65]

The monolayers at the air-water interface were transferred onto solid supports at a constant surface pressure by the vertical dipping method

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(dipping speed 3 mmmin⁻¹) onto gold or quartz substrates, which were carefully cleaned as described previously.^[61,71] QCM measurements were carried out by using a Stanford Research Systems instrument with AT-cut α -quartz crystals with a resonant frequency of 5 MHz and circular gold electrodes patterned on both sides. UV/Vis spectra of the LB films were acquired on a Varian Cary 50 spectrophotometer and recorded at a normal incident angle with respect to the film plane.

Cyclic voltammetry (CV) experiments were carried out in an electrochemical cell containing three electrodes. The working electrode was made of either a gold substrate or a gold substrate modified by the deposited LB film. Gold substrates were purchased from Arrandee, Germany. These 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. The counterelectrode was a platinum sheet, and the reference electrode was Ag|AgCl|saturated KCl.

X-ray photoelectron spectra were acquired on a Kratos AXIS ultra DLD spectrometer with a monochromatic Al_{Ka} X-ray source (1486.6 eV) by using a pass energy of 20 eV. To provide precise energy calibration, the XPS binding energies were referenced to the C 1s peak at 284.6 eV. The thickness of LB films on gold substrates was estimated using the attenuation of the Au 4f signal from the substrate according to $I_{\rm LB film} = I_{\rm substrate} \exp(-d/\lambda \sin \theta)$, where *d* is the film thickness, $I_{\rm LB film}$ and $I_{\rm substrate}$ are the average of the intensities of the Au 4f_{5/2} and Au 4f_{7/2} peaks attenuated by the LB film and bare gold, respectively, θ is the photoelectron take-off angle and λ is the effective attenuation length of the photoelectron ((4.2 ± 0.1) nm).^[44]

An Agilent STM running Picoscan 4.19 Software was used for characterization of the electrical properties of the LB films with tip potential U_{l} . 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 treated as described above to obtain atomically flat Au(111) terraces.

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