Characterization and Conductivity of Langmuir–Blodgett Films Prepared from an Amine-Substituted Oligo(phenylene ethynylene)

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This paper reports the assembly of well-defined molecular films from 4-[4-(4-hexyloxyphenylethynyl)-phenylethynyl]-aniline (HBPEB amine), an oligomeric phenylene ethynylene (OPE) derivative, by means of the Langmuir–Blodgett technique. Initially, Langmuir films of HBPEB amine were prepared at the air–water interface and characterized with surface pressure vs area per molecule isotherms. Brewster Angle Microscopy was used to map the different phases of the monolayer at the air–water interface. UV–vis reflection spectroscopy showed a blue shift of 20 nm of the reflection spectrum of the Langmuir film with respect to the spectrum of a chloroform solution of HBPEB amine, which indicates that two-dimensional H-aggregates are formed at the air–water interface. The monolayers were transferred onto solid substrates with a Y-type deposition and a transfer ratio of 1. The excellent transfer characteristics permitted the construction of films comprising up to 150 layers, with a uniform architecture. The LB films fabricated from HBPEB amine show a blue shift of ca. 30 nm with respect to the chloroform solution of HBPEB amine, likely arising from a change in the orientation of the molecular transition dipole with respect to the surface normal in the solid-supported films in comparison with the Langmuir films at the air–water interface. The current–voltage ($I-V$) characteristics of LB monolayers are unexpectedly symmetrical, the asymmetric contacts not being apparent from the observed $I-V$ characteristics.

Introduction

There is a growing need for the miniaturization of mechanical and electronic components from the macroscopic to the nanoscopic world because of the social demand for smaller, quicker, and more efficient devices. However, the design of devices that work on the nanoscale requires more that the "simple" scaling down of a macroscopic cousin. Rather, the construction of devices that operate on the molecular level from molecular building blocks will require new design strategies, as quantum effects become important and possibly governing forces. In this context, a large effort is being made in the study of organic materials containing a highly conjugated skeleton that, under the appropriate assembling and ordering process, perform the function of molecular wires, single-electron transistors, electron turnstiles, molecular switches, chemical sensors, etc.[1] In turn, these efforts to develop a viable technology base from the ideas of molecular electronics lead back to more fundamental interests in the design, synthesis, and nature of the self-assembly processes that permit molecules to be used in the construction of new, functional materials.[2]

One of the most fascinating subsets of materials at the forefront of much of the chemistry related to the study of molecular electronic components and devices are the molecular, oligomeric, and polymeric compounds derived from the phenylene ethynylene motif.[3–6] Oligomeric phenylene ethynylenes (OPEs) exhibit a range of interesting photophysical properties including NLO response,[7,8] luminescence,[3,9,10] and electroluminescence.[11] Especially remarkable is the demonstration of OPEs as molecular wires, and other components for molecular electronics.[1,12–16] Although OPE

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derivatives are being widely studied by chemists, physicists, and molecular engineers, so far many have focused their attention on monolayer films of these materials formed by self-assembly (SA) of thiol-terminated derivatives on gold substrates. Although the gold-thiol monolayers are topologically very well formed, often free of defects, and show molecular conductivity,[17–21] three main limitations are noteworthy. First, thiols are prone to oxidative coupling to disulfides[22] and although the use of protected thiols can alleviate this problem, the incorporation of extraneous material within the system when in situ deprotection steps are employed[23] can add a degree of additional complexity to the process. Second, the use of SA methods rather limits the number of organic−metal interfaces. Third, studies based on gold-thiol self-assembled monolayers have shown that the gold−sulfur bond is rather fluxional, and changes in the gold−sulfur interaction are now thought to be largely responsible for the dynamic switching of conductivity observed in early studies of single molecule conductivity.[24–26] Taken together, these observations highlight the need for exploration of other organic−metal interfaces and the crucial role the metal−molecule interface plays in, for example, measurements of the conductivity of single molecules.[21,27–33]

Prompted by this picture of the current landscape, we have sought to employ alternative self-assembly methodologies for the preparation of oriented molecular films of OPE-type molecules. The Langmuir–Blodgett (LB) technique is well-suited to the task of fabricating molecular films, providing both a high internal order of the molecules in each layer and the possibility of transferring the desired number of ordered layers onto a large variety of solid substrates by making use of the wide variety of polar functional groups that can be physically or chemically adsorbed onto different substrates and hence create a large number of organic−metal interfaces.[34–38] The LB process is also well-suited to the production of mono- or multilayer structured films. However, in spite of the large body of published work on SA monolayers of OPE derivatives, and the general interest in films of these compounds, there are few data available in the literature reporting the fabrication of LB films of (OPE)-based compounds.[39–42]

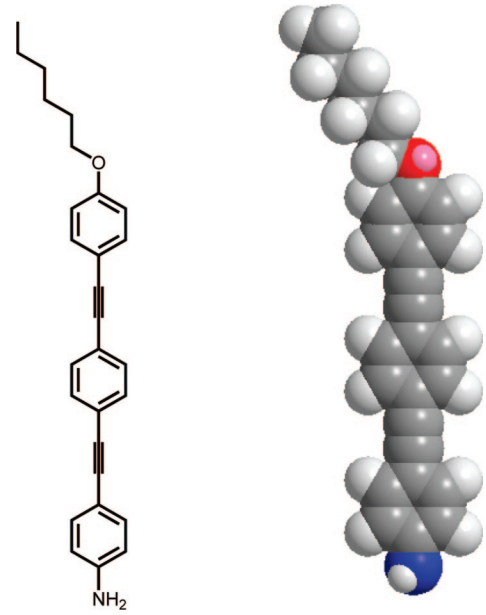

Figure 1. Molecular structure (left) and space-filling molecular model (right) of 4-[4-(4-hexyloxyphenylethynyl)-phenylethynyl]-aniline (HBPEB amine).

In this work, we have utilized the particular chemical and physical properties of 4-[4-(4-hexyloxyphenylethynyl)phenylethynyl]aniline (HBPEB amine) (Figure 1), containing a polar NH_2 headgroup that facilitates the spreading of the molecule on the aqueous subphase; its anchoring onto the water surface, together with having a hydrophobic phenylene ethynylene core and relatively long alkyl chain, both prevents the material from being dissolved in water and provides stability to the monolayer through both lateral $\pi-\pi$ and van der Waals interactions with neighboring molecules, in the preparation of well-structured LB films. The films have been characterized by a range of optical spectroscopic methods and microscopy, whereas $I-V$ curves are obtained from monolayers of HBPEB amine on gold-coated HOPG substrates.

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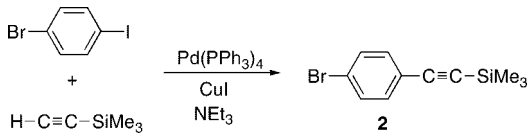
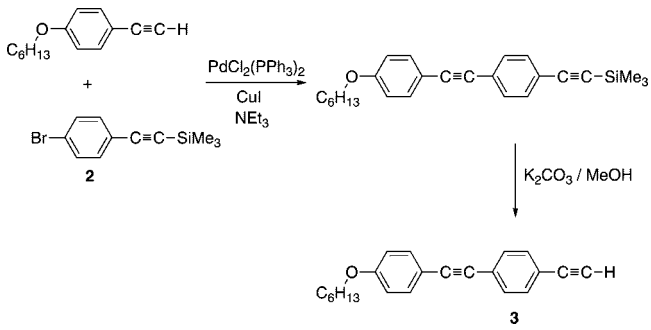
Scheme 1.



Scheme 2.



Experimental Section

Synthesis. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified and dried using an Innovative Technology SPS-400, or in the case of NEt_3, by distillation from KOH, and degassed before use. No special precautions were taken to exclude air or moisture during workup. The compounds $Pd(PPh_3)_4$,[43] $PdCl_2(PPh_3)_2$,[44] and 4-hexyloxylphenylacetylene[45] were prepared by the literature methods. Other reagents were purchased and used as received. NMR spectra were recorded on a Bruker Avance (^1H 400.13 MHz, ^{13}C 100.61 MHz) spectrometers from $CDCl_3$ solutions and referenced against solvent resonances.

Preparation of (2). The compound 1-bromo-4-iodobenzene (10.0 g, 3.54 x10^{-2} mol), CuI (0.135 g, 7.08 × 10^{-4} mol) and $Pd(PPh_3)_4$ (0.409 g, 3.54 × 10^{-4} mol) was added to a solution of toluene (40 mL) and NEt_3 (40 mL) (Scheme 1). The reaction flask was cooled in an ice bath; trimethylsilylacetylene (5.5 mL, 3.28 g, 3.89 × 10^{-2} mol) was added, and the reaction mixture was allowed to warm slowly to room temperature while stirring. When the reaction was complete (24 h), the precipitate formed was removed by filtration and washed with toluene. The organic fractions were combined and evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane) to yield the product as a white solid. Yield: 7.44 g, 2.94 × 10^{-2} mol, 83%. ^1H NMR: δ 7.43 (AA′XX′, 2H, Ar*H*); 7.35 (AA′XX′, 2H, Ar*H*); 0.26 [s, 9H, −-Si(CH_3)$_3$]. ^{13}C NMR: δ 133.7, 131.8, 123.1, 122.5 (Ar); 104.2, 95.9, (−*C*≡*C*−); 0.28 (−Si(*C*H$_3$)$_3$). EI-MS 254.0 (68), 252 (66) $[M]^+$, 237 (100) $[M - CH_3]^+$, 239 (98) [M-CH_3]. IR (KBr): ν(C≡C) 2158 cm^{-1}. Found: C, 52.18; H, 5.24. Requires: C, 52.18; H, 5.17.

Preparation of (3). A Schlenk flask was charged with **2**, (3.00 g, 1.19 × 10^{-2} mol) and a solution of 4-hexyloxyphenylacetylene (2.43 g, 1.20 × 10^{-2} mol) in NEt_3 (40 mL) was added, followed by CuI (0.045 g, 2.38 × 10^{-4} mol) and $PdCl_2(PPh_3)_2$ (0.167 g, 2.38 × 10^{-4} mol) (Scheme 2). The reaction was heated under reflux for 16 h. The reaction was then allowed to cool and the solvent was removed under reduced pressure. The reaction mixture was extracted into chloroform and washed with water (2 × 50 mL) and aqueous NaCl solution (1 × 50 mL). The chloroform was removed under reduced pressure and the crude product purified on a pad of silica, eluting with hexane. This product was treated with a suspension potassium carbonate in methanol (100 mL) and stirred (6 h). The product was extracted into ether, the solvent evaporated and the residue taken up in dichloromethane. The organic phase was separated from the aqueous residue and evaporated under reduced pressure to yield the product as an off-white waxy solid. Yield: 2.00 g, 7.18 mmol, 60%. ^1H NMR: δ 8.02 (m, 6H, Ar*H*); 6.87 (AA′XX′, 2H, Ar*H*); 3.97 [t, ^3J(H,H) = 6.4 Hz, 2H, OCH_2R]; 3.17 (s, 1H, −C≡C*H*); 1.76 (m, 2H, −CH_2−aliphatic); 1.45 (m, 2H, −CH_2-aliphatic); 1.33 (m, 4H, −CH_2−aliphatic); 0.89 [t ^3J(HH) = 6.8 Hz 3H, −CH_3]. ^{13}C NMR: δ 159.8, 133.4, 132.4, 131.6, 124.6, 121.8, 115.1, 114.9 (Ar); 91.9, 87.9, 83.7, 79.0 (−*C*≡*C*−); 68.5 (O*C*H$_2$-R); 31.9, 29.5, 26.0, 22.9 (−*C*H$_2$− aliphatic); 14.4 (−*C*H$_3$). EI-MS 302.1 (26) $[M]^+$, 218.1 (100) $[M - C_6H_{12}]$. IR (KBr): ν(−C≡C−H) 3298, 3271 cm^{-1}; ν(C≡C) 2214 cm^{-1}. Found: C, 86.90; H, 7.30. Requires: C, 87.38; H, 7.33.

Preparation of (4). To 1-bromo-4-nitrobenzene (0.441 g, 2.18 mmol) in NEt_3 (30 mL) were added compound **3** (0.660 g, 2.18 mmol), CuI (2.18 × 10^{-5}mol), and $PdCl_2(PPh_3)_2$ (0.015 g, 2.18 × 10^{-5} mol), and the reaction was stirred overnight at room temperature (Scheme 3). The solvent was then removed and the crude product was extracted into chloroform and washed with water (2 × 40 mL) and NaCl solution (20 mL). The solvent was removed and the crude product purified by chromatography on silica gel using Hexane/DCM (1:1) as eluent. Yield: 0.710 g, 1.68 mmol, 77%. ^1H NMR δ 8.23 (AA′XX′2H, Ar*H*); 7.67 (AA′XX′, 2H, Ar*H*); 7.48 (s, 4H, Ar*H*); 7.46 (AA′XX′, 2H, Ar*H*); 6.89 (AA′XX′, 2H, Ar*H*); 3.98 [t, ^3J(H,H) = 6.4 Hz, 2H, OCH_2R]; 1.79 (m, 2H, aliphatic); 1.45 (m, 2H, aliphatic); 1.30 (m, 4H, aliphatic); 0.88 [t ^3J(HH) = 6.8 Hz 3H, −CH_3]. ^{13}C NMR δ 159.93, 133.49, 132.61, 132.10, 131.82, 130.82, 130.43, 125.11, 124.03, 121.68, 114.99, (Ar); 100.35, 92.61, 89.43, 87.94 (−*C*≡*C*−); 68.49 (−OCH_2R); 31.91, 29.5, 26.04, 22.94 (aliphatic); 14.35 (−CH_3).

Preparation of 4-[4-(4-hexyloxyphenylethynyl)-phenylethynyl]-aniline (1). Compound **4** (0.260 g, 6.14 × 10^{-4} mol) was dissolved in ethanol/THF (1:1) to which sodium sulfide nonahydrarate (0.608 g, 2.53 × 10^{-3} mol) in water (30 mL) was added and refluxed (48 h) (Scheme 3). The solvent was then removed and the product purified by recrystallization in ethanol/water. Yield: (0.130 g, 3.30 × 10^{-4} mol), 48%. ^1H NMR δ 7.45 (AA′XX′, 6H, Ar*H*); 7.34 (AA′XX′, 2H, Ar*H*); 6.87 (AA′XX′, 2H, Ar*H*); 6.64 (AA′XX′, 2H, Ar*H*); 3.97 [t, ^3J(H,H) = 6.8 Hz, 2H, OCH_2R]; 3.83 (s, br. 2H ArNH_2); 1.79 (m, 2H, aliphatic); 1.46 (m, 2H, aliphatic); 1.35 (m, 4H, aliphatic); 0.91 [t ^3J(HH) = 6.8 Hz 3H, −CH_3]. ES(+)-MS 393.2, $[M]^+$. Found: C, 85.32; H, 6.83. Requires: C, 85.46; H, 6.92.

Film Fabrication and Characterization. The films were prepared on a Nima Teflon trough with dimensions 720 × 100 mm^2, which was housed in a constant-temperature (20 ± 1 °C) clean room. The surface pressure (π) of the monolayers was measured by a Wilhelmy paper plate pressure sensor. The subphase was water (Millipore Milli-Q, resistivity 18.2 MΩ cm). To construct the Langmuir films, we delivered 0.5 mL of a 1 × 10^{-4} M solution of 4-[4-(4-hexyloxyphenylethynyl)-phenylethynyl]-aniline (HBPEB amine) in chloroform (HPLC grade, 99.9%, purchased from Aldrich and used as received) from a 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 solvent was allowed to completely evaporate over

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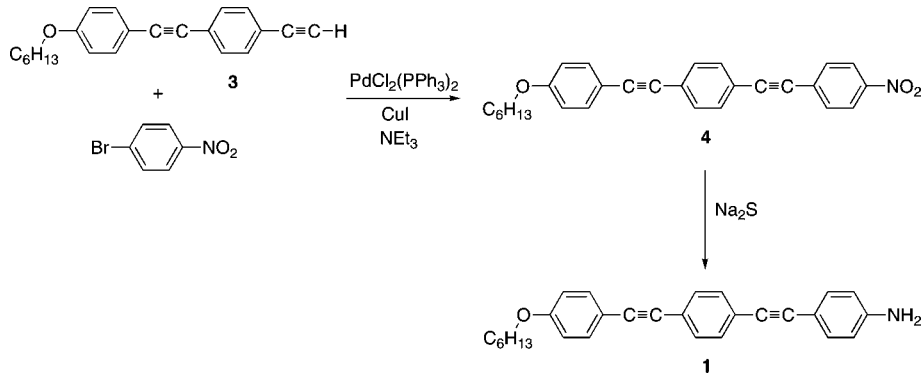
Scheme 3.



a period of at least 15 min before compression of the monolayer commenced at a constant sweeping speed of 0.02 nm^2 molecule^{-1} min^{-1}. Under these experimental conditions, the isotherms were highly reproducible. A commercial mini-Brewster angle microscope (mini-BAM), also from Nanofilm Technologie, was employed for the direct visualization of the monolayers at the air/water interface and a commercial UV–vis reflection spectrophotometer, details described elsewhere,[46] was used to obtain the reflection spectra of the Langmuir films during the compression process.

The quartz substrates used for the transferences were cleaned carefully as described elsewhere.[47] The monolayers were deposited at a constant surface pressure by the vertical dipping method and the dipping speed was 6 mm/min. Quartz crystal microbalance (QCM) measurements were carried out using a Stanford Research System instrument and employing AT-cut, α-quartz crystals with a resonance frequency of 5 MHz having circular gold electrodes patterned on both sides. UV–vis spectra of the LB films were acquired on a Varian Cary 50 spectrophotometer and recorded using a normal incident angle with respect to the film plane. Cyclic voltammetry (CV) experiments were carried out in an electrochemical cell containing three electrodes as described before.[48] The working electrode was a gold electrode with the deposited LB film, the counter electrode was a platinum sheet, and the reference electrode was Ag|AgCl sat'd KCl. Highly oriented pyrolytic graphite (HOPG) substrates were freshly coated with gold overlays using a BOC Edwards evaporator and LB films deposited on these. Ambient temperature current–voltage ($I-V$) studies were performed using a Digital Instruments STM (Nanoscope IV), the probe being a gold tip that was plasma cleaned to remove organic contamination prior to investigation.

Results and Discussion

The reproducible surface pressure vs area per molecule ($\pi-A$) isotherm of HBPEB amine is illustrated in Figure 2. The liftoff in the isotherm takes place at ca. 0.42 nm^2/molecule, after which the surface pressure increases upon compression reaching very high values for the Young modulus, K_s, as shown in the inset of Figure 2:[49]

$$K_s = -A\left(\frac{\partial \pi}{\partial A}\right)_T \quad (1)$$

The large values of K_s for monolayers of HBPEB amine are indicative of strong intermolecular interactions within the Langmuir film and the formation of a rigid monolayer.[50]

Brewster angle microscopy (BAM) investigations were made during the compression of the Langmuir film and gave further insight about the formation of the monolayer (Figure 2). It is important to note that in spite of the tendency for molecules containing polyaromatic moieties to aggregate because of strong $\pi-\pi$ interactions,[51] no three-dimensional aggregates[52] are observed in BAM images under the experimental conditions used, probably because of the low surface coverage of the water surface before compression (7.2×10^{-11} mol/cm^2, equivalent to 2.3 nm^2/molecule). At a surface pressure of 3 mN/m, the monolayer covers practically the whole water surface. At higher surface pressures, BAM images show a similar aspect but are even more brilliant, suggesting a progressive tilt of the molecules to a more vertical position, i.e., a thicker monolayer.

Molecular orientation and aggregation phenomena associated with HBPEB amine 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 the compression process were recorded. Figure 3 shows the normalized spectra, $\Delta R_n = \Delta R \cdot A$, with A being the area per molecule of HBPEB amine at the air–water interface at several surface pressures and the absorption spectrum of HBPEB amine as a solution in chloroform.

As can be seen in Figure 3, there is a significant blue shift of the reflection spectra recorded at the air–water interface by ca. 20 nm relative to the solution spectrum, consistent with the formation of H-aggregates as reported before for other LB films formed from compounds in which the chromophore has the main transition dipole arranged more

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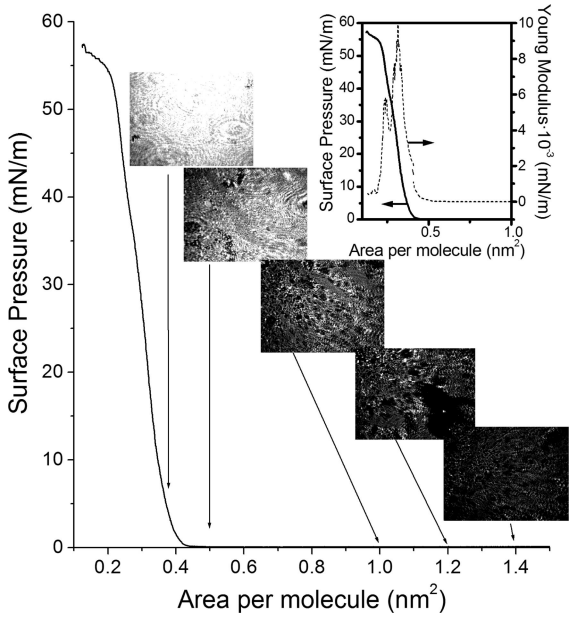

Figure 2. $\pi-A$ isotherm and BAM images of the Langmuir films at the indicated areas per molecule for HBPEB amine. The field of view along the x axis for the BAM images is 3000 μm. The inset graph shows the Young modulus values upon compression (right) together with the $\pi-A$ isotherm (left).

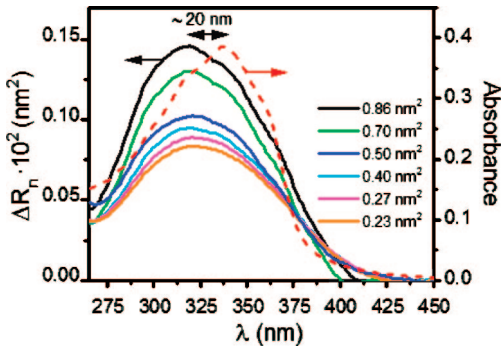

Figure 3. Normalized reflection spectra upon compression and (dotted line) absorption spectra of a 1×10^{-4} M solution of HBPEB amine in chloroform.

Table 1. Surface Pressure (π), Area per Molecule (A), and Calculated Tilt Angle (φ) for HBPEB Amine at the Air–Water Interface

π (mN/m)	0.0	0.0	0.0	0.1	1.5	14.0	36.8	49.0
A (nm^2/molecule)	1.10	0.86	0.70	0.50	0.40	0.33	0.27	0.23
φ (deg)	13	45	49	53	54	55	56	57

or less along the amphiphile backbone, e.g., amphiphilic *trans*-stilbenes,[51] *trans*-azobenzenes,[53] hemicyanine derivatives,[54] squaraines,[55] and tolan derivatives,[41] that can be considered as the first members of the OPE family. The hypsochromic shift of the floating layer is persistent and practically independent of the applied surface pressure, which indicates that the arrangement observed in the Langmuir film must represent a minimum-free-energy conformation for the system and suggests that the formation of the aggregate or assembly responsible for the blue-shifted spectroscopic

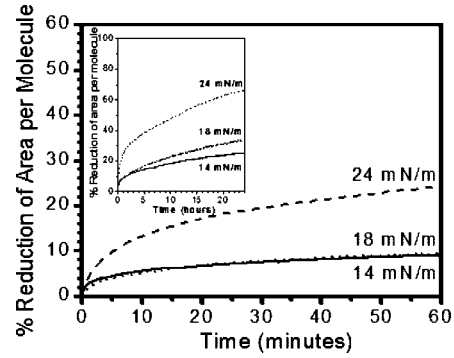

Figure 4. Percentage of reduction of area per molecule vs time for the indicated surface pressures. The inset graph shows the evolution after 24 h.

profile aggregate does not depend for its formation upon the orientation imposed by the LB technique.

A quantitative analysis of the reflection spectra of HBPEB amine and a comparison of the reflection spectra with the UV–vis spectrum obtained in dilute solution has allowed us to calculate the tilt angle of the transition dipole moment of the molecule with respect to the water surface, φ (Table 1). The method and relationships used to arrive at these results have been comprehensively detailed elsewhere.[41,46] From the data summarized in Table 1, it can be concluded that molecules of HBPEB amine undergo a transition from an orientation nearly parallel to the air–water interface at large areas per molecule to a more vertical position by the beginning of the isotherm liftoff, with a tilt angle close to 60° just before the collapse.

The monolayer stability at the air–water interface strongly depends on the surface pressure. Thus, the maximum stability of the monolayer is obtained at relatively low surface pressures (in the 12–15 mN/m range) and higher surface pressures lead to a larger decrease in the area per molecule at a constant surface pressure (Figure 4). This is probably related to the high K_s values (π > 15mN/m → K_s > 5000 mN/m), indicative of a very rigid monolayer at high surface pressures. Moreover, BAM images show that practically the whole surface is covered, even at low surface pressures (Figure 2).

Langmuir films were transferred onto hydrophilic quartz and gold substrates initially immersed in the water subphase. The deposition was Y-type. The transfer ratio was close to 1 at 14 mN/m, although this value decreases with increasing transference surface pressure. Langmuir films were deposited onto gold electrodes to obtain further information relating to the quality of the LB films as a function of the transference surface pressure. The ion current at the electrode under controlled applied bias is an indirect measure of defect densities in thin films.[56] Figure 5 shows the cyclic voltammograms (CV) obtained from aqueous solutions containing 1 mM $K_3[Fe(CN)_6]$ and 0.1 M in KCl, using gold working electrodes modified by monolayer LB films deposited at several different surface pressures of transference. Deposition of a monolayer film at a transference surface pressure of 10 mN/m significantly passivates the electrode. Thus, the current

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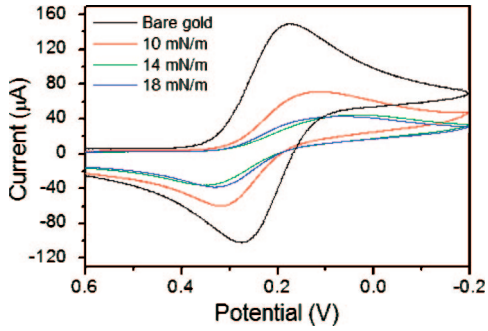

Figure 5. Cyclic voltammograms of one-layer-thick LB films of HBPEB amine deposited on gold electrodes at different surface pressures of transference. A bias voltage was applied to the LB films deposited on a working gold electrode immersed in aqueous solutions with 1 mM $K_3[Fe(CN)_6]$ and 0.1 M in KCl. The scan rate was 0.05 V/s at 20 °C and the initial scan direction was negative. The working electrode surface was 1 cm^2 in all cases. The reference electrode was Ag AgCl sat'd KCl and the counter electrode was a Pt sheet.

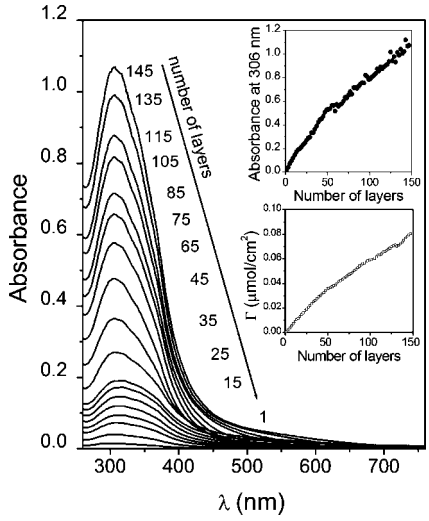

Figure 6. Absorption spectra for LB films of HBPEB amine transferred at 14 mN/m. The inset graphs exhibit the dependence of the film absorbance at 306 nm with the number of layers as well as the surface coverage, Γ, with the number of layers.

is decreased by slightly more than half, and the difference between the reduction and oxidation peak potentials is increased compared to that of the bare gold electrode. If the LB film is transferred at 14 mN/m, the redox current is largely decreased. However, films transferred at higher surface pressures, e.g., 18 (Figure 5) or 30 mN/m, do not show any further significant decrease in the current. This result indicates that the effective monolayer surface coverage achievable with the LB method practically reaches its highest value at 14 mN/m. However, the current on the voltammograms does not completely disappear even at high surface pressures of transference, which is indicative of a certain number of holes or defects in the monolayers. These holes have been mapped with STM imaging (discussed later).

To assess the reproducibility of the deposition process, the UV–vis absorption spectra of LB films with increasing number of layers have been measured (Figure 6). Films containing up to 150 layers were deposited onto quartz substrates leading to yellowish-colored multilayers. The inset of Figure 6 illustrates the absorbance of the film at a constant wavelength of 306 nm versus the number of layers. The nearly linear relationship implies that the transference is reproducible, i.e., a constant amount of HBPEB amine is transferred and the molecular environment of the molecules in each layer is practically constant upon deposition. Similar conclusions can be made from the data summarized in the other inset Figure 6, where the surface coverage (Γ) determined with a quartz crystal microbalance, QCM,[41,57] versus the number of layers is represented.

It is noteworthy that the absorption maximum of the LB films (306 nm, Figure 6) is blue-shifted with respect to not only the solution, 337 nm, but also with respect to the Langmuir films at the air–water interface, 318 nm. These results indicate that the environment of the molecules significantly changes after the transference process, either because of the less-polar environment in the LB films compared with the Langmuir films on an aqueous subphase, or because of a reorganization of the molecules that results in a different angle between neighboring molecules forming the H-aggregates. We have verified that there is a certain influence of the polar environment on the position of the maximum absorption peak in solution, which is slightly blue-shifted with decreasing solvent polarity. For instance, the wavelength of maximum absorption of HBPEB amine is 339 nm in acetonitrile and 337 nm in chloroform, and when hexane drops are added to the chloroform solution (HBPEB amine is not soluble in hexane), the peak is progressively blue-shifted to 333 nm. However, it seems that the environment polarity shifts the peak position only a few nanometers versus the more significant blue shift from 318 nm at the air–water interface to 306 nm in LB films. These data point out the formation of two-dimensional aggregates at the air–water interface that might have a different tilt angle when they are transferred to the solid substrates.

Cursory studies of the LB film surface of HBPEB amine on gold-coated HOPG were performed using a Nanoscope IV MultiMode scanning tunnelling microscope and $I-V$ characteristics obtained by landing the gold probe on targeted features distant from grain boundaries. The operating conditions were varied to ensure that the set point current and voltage have minimal effect on the shapes of the curves and, in each case, the $I-V$ data were collected by averaging multiple scans on the same spot. Specific sites across LB monolayers deposited at 14 and 30 mN/m were investigated and each exhibited either symmetrical or very nearly symmetrical $I-V$ characteristics (Figure 7). Such behavior was anticipated as, unlike the donor−(electron bridge)−-acceptor sequence that acts as a molecular diode,[58] the molecule in this case is simply an amphiphilic electron-donating wire. We note, however, that the oligomeric moiety is attached at one electrode through the amine moiety and is separated from the other by the hexyloxy tail but the effect of asymmetric coupling is not apparent from the observed $I-V$ characteristics. Furthermore, bilayer LB structures, which are assumed to be Y-type and therefore symmetrical, exhibit almost identical curves to those obtained from monolayer LB films.

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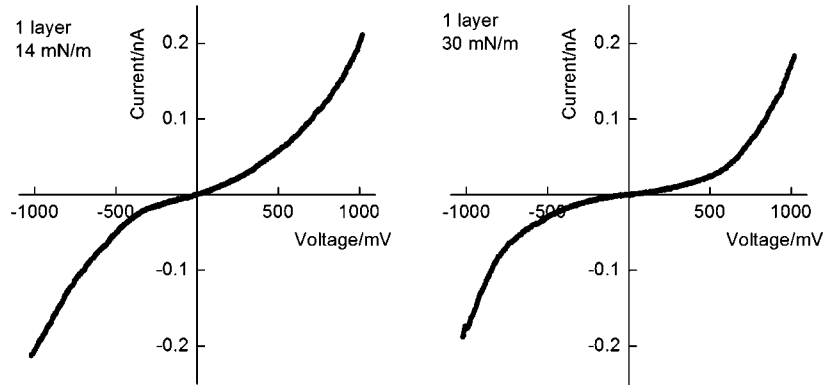

Figure 7. *I*−*V* characteristics of LB monolayers of HBPEB amine transferred onto gold-coated HOPG substrates at the indicated surface pressures of 14 and 30 mN/m and obtained for a set point current of 500 pA at a sample bias of 850 mV.

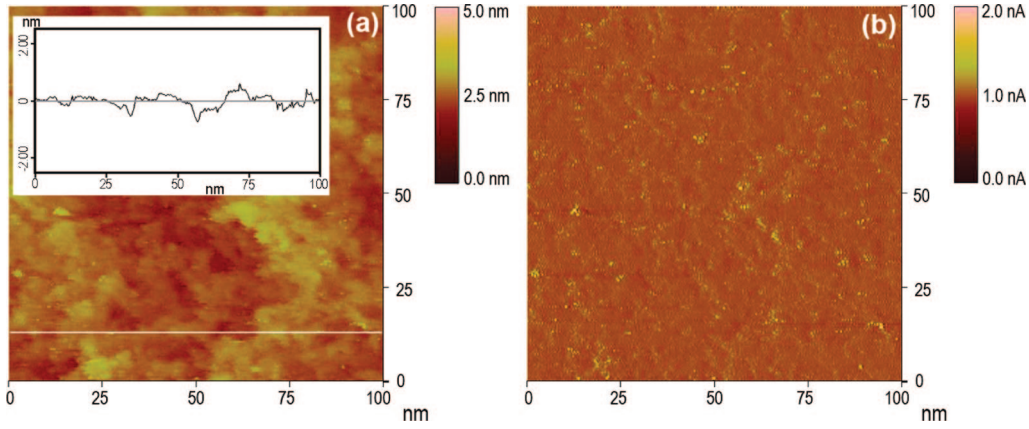

Figure 8. (a) STM image of an HBPEB amine monolayer transferred at a surface pressure of 14 mN/m on Au (111) single crystal. Inset: profile along the white line. (b) Current image of the area shown in the left image (bias voltage $V_b = 1$ V and tunnelling current $I_t = 250$ pA).

Figure 8 shows a representative STM image where, as mentioned above, a certain number of holes or defects can be observed in the monolayer.

Conclusions

In this contribution we have presented the formation of Langmuir and Langmuir–Blodgett films from an amine-terminated OPE derivative. Langmuir films have been characterized by means of π−A isotherms, Brewster angle microscopy, and reflection spectroscopy concluding that homogeneous well-ordered monolayers of HBPEB amine can be fabricated at the air–water interface. A significant degree of order is progressively achieved upon the compression process, accompanied by a gradual tilt of the molecules reaching a value close to 60° before the collapse of the monolayer. A hypsochromic shift of the absorption spectrum of the Langmuir film of ca. 20 nm with respect to the spectrum of a chloroform solution of HBPEB amine indicates that two-dimensional H-aggregates are formed. The observation that the blue shift is more pronounced in the LB multilayers than in the Langmuir film is remarkable, suggesting a reorientation and an increase of association upon the transference. UV absorption spectroscopy and QCM measurements show that the Langmuir monolayers can be transferred up to 150 layers with a constant architecture. These wirelike molecules deposited as LB films exhibit symmetrical *I*−*V* characteristics.

OPE derivatives have so far been investigated to a small extent when assembled by the LB technique despite the wealth of opportunities offered by this method for convenient ordering this family of compounds in thin solid films. Notably, the amine functional group provides a significantly strong anchor to a variety of common substrates to permit stable, well ordered films to be prepared. The prospect for using such simple molecular structures in the construction of robust molecule-surface interfaces is intriguing, and hints at a wider role for such interactions in molecular electronics.

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