Nanostructure LB Films of Novel OPV Compounds

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ABSTRACT

We studied the formation of Langmuir monolayers of two series of amphiphilic monodendrons π-conjugated from first to third generation number with different length of terminal chains C_3H_7 and $C_{12}H_{25}$, the characterization of the monolayer was made through isotherms and images obtained by Brewster Angle Microscopy (BAM) to confirm the phase transition, the six compounds formed Langmuir monolayers stable and reproducible, the stability and homogeneity of the monolayers increases with the increment in the generation number. In addition, we observed that when the length of terminal chains is increases from C_3H_7 to $C_{12}H_{25}$ the stability has a notable increment for the second and third generation number. We had showed that the monodendron the second generation with terminal chains $C_{12}H_{25}$ has the best stability and reproducibility.

Keywords: Langmuir, monolayer, monodendrons, OPV, Brewster microscopy.

1. INTRODUCTION

Langmuir films, composed of amphiphilic molecules adsorbed at the air-water interface, continue to attract widespread attention due to their importance as models for two dimensional structures and phase transitions, as model biological membranes, and as precursors for technologically important Langmuir-Blodgett films [1-4].

There are various modern applications requiring highly ordered coatings of nanoscale thickness with smart behavior and electronic properties, microelectronic systems, microfluidic devices, micro- and nanopatterning, and optical data storage devices [5]. The search for new materials with a suitable combination of properties, microstructure and intermolecular interactions attracts attention to dendrimers. Dendrimers are materials with cascade, tree-like architectures, generation-dependent sizes in the nanometer range and capability of self-assembling into superstructures [6]. Dendritic macromolecules with well-defined geometrical sizes and surface functionality can be suggested as promising candidates for functional coatings. Numerous examples of dendrimer synthesis with varying chemical nature have been published in the last decade [7].

However, there is limited information on dendrimeric microstructures in the bulk state, and few studies are devoted to their behavior at solid surfaces [8, 9].

One particular class of dendrimers, monodendrons, with a focal functional group and semi-spherical shape are interesting candidates for organized monolayer formation and surface functionalization because of the specific shape and dendritic nature of the shell. We believe that Π-conjugated dendrons are a promising class of organic materials for the fabrications of organic light emitting diode (OLED's). They can be thought of as consisting of a conjugated light-emitting core, conjugated branches, and surface groups. Such materials can be designed so that the core defines the color of light emission, the surface groups control the processing properties, and the branches allow transport of charge to the core. Chemi-or-physisorption may offer an important route to the fabrication of dendrimer assemblies at interfaces [10].

The general approach of this investigation is to form and study Langmuir monolayers formed on the air–water interface, organized through self-ensambled imposed by terminal chains and examination of the stability of these monolayers deposited on solid substrates. In this publication, we focus on Langmuir monolayers of amphiphilic monodendrons of the first three generations G1-C_3H_7, G2-C_3H_7, G3-C_3H_7, G1-$C_{12}H_{25}$, G2-$C_{12}H_{25}$ and G3-$C_{12}H_{25}$. (Fig.1). Compounds with an alcohol polar head group were used to estimate the effect of the number of generation and the length of terminal alkyl chains in the formation. Isotherm superficial pressure (Π) vs. Molecular Area (A) and Brewster Angle Microscopy were used to study the stability and the morphology of the Langmuir monolayers. We made a simulation of the monodendron configuration.
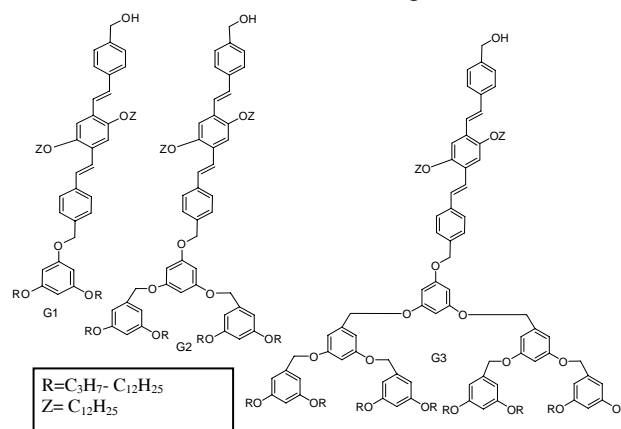

Figure 1: Dendrimeric compounds used for monolayer formation. GN corresponds to dendron of N generation; C_NH_N is the length of the alkyl terminal-chains.

2. EXPERIMENTAL

The six compounds were synthesized as described elsewhere [11]. Solutions at $\approx$ 1 mg/mL concentration were prepared, using HPLC chloroform (Aldrich, 99.9% pure). The dendrimer solution was spread over ultrapure water ρ=18.2 MΩ•cm used for the subphase was obtained from a Milli-DIPAK/ Milli-Q185 ultrapurification system from Millipore and allowed to stay for 15 min for residual solvent evaporation. The monolayer was then compressed at 10mm min^{-1} until the desired surface pressure was reached and deposited onto a hydrophilic surface of glass slide at a lift speed of 5 mm•min^{-1} at room temperature. Successive layers were deposited onto glass substrates (type Z). We typically spread 80–180 µL of solution on the water surface for isotherm, BAM images or Langmuir-Blodgett films.

The monitoring the monolayer formation was made by Π-A isotherms and Brewster angle microscopy (BAM) that are used to characterize the behavior of a monolayer film at the air-water interface. The trough employed for the formation and deposition of the Langmuir monolayers is a KSV 5000 system 3. The trough was set in a flexiglas enclosure soas to be protected from drafts and dust, the temperature was controlled to ± 0.1˚C. All the isotherms presented here were taken at 20˚C. The BAM images were gotten with a miniBAM plus of Nanofilm Technology Gmbh and the Langmuir films were formatted on a NIMA trough. Π-A isotherms were collected and *in situ* during acquisition of BAM images, surface pressure was measured by means of a platinum Wilhelmy plate.

Molecular semiempirical models of all compounds were built considering one molecule in the vacuum and taking into account just the hydrophilic and hydrophobic character of dendrimeric molecules and finding favorable energy were searched using Spartan 4.0 program. The simulation of a possible orientation of the monodendrons in the water-air interface in base to the Π-A isotherms and the calculated area thought the software Spartan.

3. RESULTS AND DISCUSSION

All compounds studied here were spread on an air–water interface to form a Langmuir monolayer. The lateral compression of the monolayers resulted in a gradual increase of the surface pressure that resembled classic amphiphilic behavior [12]. We got Π–A isotherms, BAM images of monodendrons of first to third generation with C_3H_7 chains (fig. 2).

An increase in the generation number caused significant shift in the Π–*A* isotherm to a higher cross-sectional area per molecule *(A)* and higher superficial pressure of phase transitions [13]. The BAM images show that with an increase in the generation number the homogeneity is higher and that the monolayers collapse forming multilayers. In addition, the BAM images show that the monolayers are formed for the self-assembled of molecules because we can watch the same images when we spread and when we decompress the monolayer, when the generation number is increase the self-assembled monolayers are more stable and homogeneous. At higher surface pressure (14 mN•m^{-1}), the initial stages of monolayer collapse become visible, manifesting itself as multiple islands of second layer formed on top of the primary monolayer [14].

The Π-A isotherms together with the BAM images provide the area per molecule of the liquid-condensed and the superficial pressure ideal for the deposit on a solid substrate of the Langmuir monolayers.

The Hysteresis curves (fig. 3b) show that the second generation monodendron with C_3H_7 terminal chains form the monolayers more reproducible and stable of the three monodendrons with C_3H_7 terminal-chains, it is understood like the effect of the C_3H_7 terminal chains is stronger than the sterics effects in the case of the second generation monodendron and weaker than the sterics effects of the rigid part of the third generation monodendron, It can be explain because even when the third generation monodendron has a bigger number of C_3H_7 chains, it has a bigger rigid structure too and the C_3H_7 chains are too short to have enough effect over the rigid part like in the second generation monodendron. The Π–A isotherms and the modeling show the area per molecule occupied for every monodendron in the liquid-condensed phase.
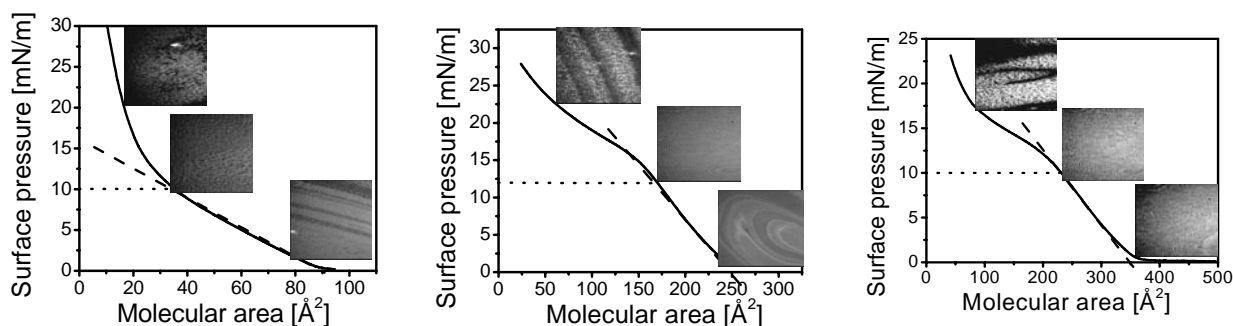

Figure 2: Pressure-area (Π-A) isotherms and BAM images of dendrimers at 25°C. (a) G1-C3H7 1.75mg/mL, 80µL. (b) G2-C3H7 1.18mg/mL, 100µL (c) G3-C3H7 0.93mg/mL, 100µL.
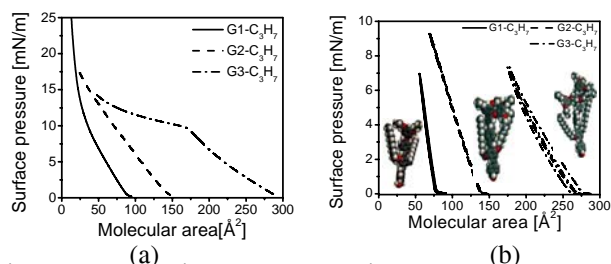
Figure 3: Comparison between the isotherms and hysteresis curves of the monodendrons with C_3H_7 terminal chains from first to third generation number.

For the monodendrons G1, G2 and G3 with C_3H_7 terminal-chains, we can observe that when increases the generation number (fig. 3a) the phase transitions are more marked and there for the monolayer is more stable. We can se the increment of molecular area with the generation number because the rigid part is increasing with the generation number and the increment in the slope of the phase transition can be understand like an increase in the self-assembled but to the third generation monodendron the hysteresis curve is wider than the second generation.

For the monodendrons with $C_{12}H_{25}$ terminal-chains we can observe an increase in the generation number caused significant shift in the Π-A isotherm (fig. 6) to a higher cross-sectional molecular area and higher superficial pressure of phase transitions [15]. The BAM images show phase images (Fig. 6) witch ones are extremely homogeneous with minor phase contrast over several micrometers across illustrating uniform composition of these monolayers that with an increase in the generation numbers the homogeneity is higher and that the monolayers collapse forming multilayers. In addition, the BAM images show that the monolayers are formed for the self-assembled of molecules because we can see the same images when we spread and when we decompress the monolayer, when the generation number is increased the self-assembled monolayers are more stable and homogeneous [16]. At higher surface pressure (20 mN•m^{-1}), the initial stages of monolayer collapse become visible, manifesting itself as multiple crest of second layer formed on top of the primary monolayer. The Π-A isotherms together with the BAM images provide the area per molecule of the liquid-condensed and the superficial pressure ideal for the deposit on a solid substrate of the Langmuir monolayers. The Π-A isotherms and the modeling show the area per molecule occupied for every monodendron in the phase of liquid-condensed.

Through the hysteresis curves (fig. 4b) we can get important information about the stability and reproducibility, there for, like is show in the hysteresis curves the reproducibility is good to the three monodendrons with terminal chains $C_{12}H_{25}$ and we can say that the monodendron of second generation number shows the best stability and reproducibility. The molecular semiempirical models show the most probable configuration of the moieties witch have a good congruence between the molecular area calculated for the

molecular semiempirical model and the area obtained from the isotherm.

For the monodendrons G1, G2 and G3 with $C_{12}H_{25}$ terminal-chains (fig. 4a), we can observe that when increases the generation number the change of phase transitions are more visible and there for the monolayer is more stable. We can se the increment of molecular area with the generation number because the rigid part is increasing with the generation number and the increment in the slope of the phase transition can be understand like an increase in the self-assembled.
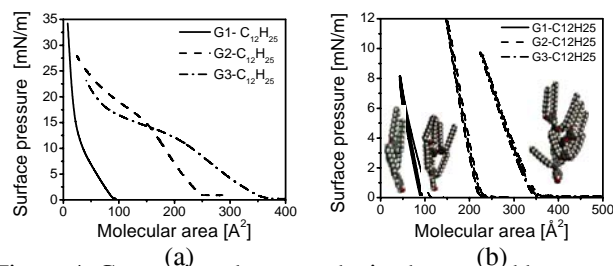

Figure 4: Comparison between the isotherms and hysteresis curves of monodendrons with $C_{12}H_{25}$ terminal chains.

The molecular area presents a different value with the increment in the chains length from C_3H_7 to $C_{12}H_{25}$ for the same generation (fig. 5), this can be understood like exits a number of changes witch begins to have an effect over the stability and the homogeneity of the monolayer, the chart of the first generation monodendrons show a little change, it can be explain like the two $C_{12}H_{25}$ chains have a little effect in the orientation of the monodendrons that the C_3H_7 chains do not have [17]. The figure 8b shows a big difference between the molecular areas of the second generation monodendrons ~100 Å^2 respect to the monodendron with C_3H_7 chains [18]. The difference of the surface pressure of the phase transition between the monodendrons of second generation number with C_3H_7 and $C_{12}H_{25}$ terminal chains, show that in this case the effect of the long chains is bigger than in the firs case, for this reason we get a monolayer more stable and homogenious, so we can expect that if we duplicate the number of chains again, we are going to get increment the stability and homogeneity, but if we see the figura 5c, we can observe that it does not happen, the reason why it did not happen, is because we increase the number of chains, but we increase the number of generation and the rigid part of the monodendrons is bigger, and the effect of the chains is not enough to get one monolayer as stable and homogenious as the monolayer of the second generation monodendron with $C_{12}H_{25}$ chains [19].
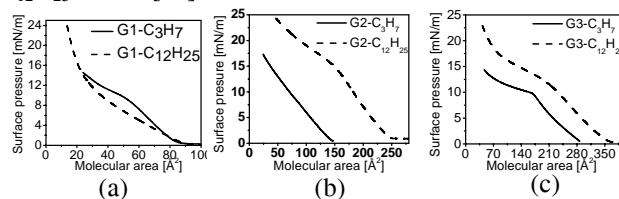

Figure 5: Comparison between the same generation number monodendrons with different length of terminal chains.
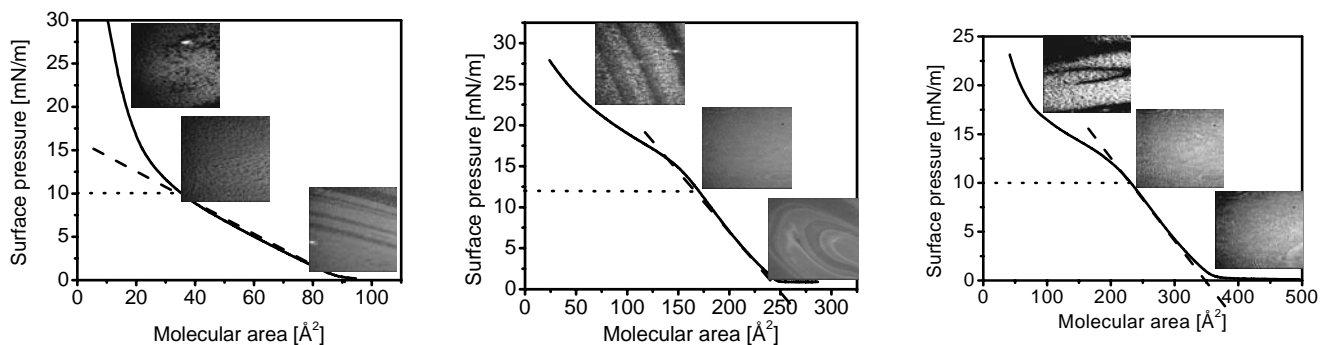
Figure 6: Pressure-area (Π-A) isotherms and BAM images of dendrimers at 25°C. (a) G1-C12H25 1.15mg/mL, 150μL. (b) G2-C12H25 0.5mg/mL, 171μL and (c) G3-C12H25 0.55mg/mL, 150μL.

4. CONCLUSIONS AND PERSPECTIVES.

We have form Langmuir monolayers of six new monodendrons with π-conjugated units. The isotherms and the BAM images confirmed the formation of the monolayer, the phase transitions and show that the length and number of terminal chains has a important effect in the stability. We had showed that the monodendron the second generation with terminal chains $C_{12}H_{25}$ has the best stability and reproducibility. There for, we can say that the generation number of the monodendrons is important factor to take into a count in the formation of Langmuir monolayers, but is too important to consider the length and number of terminal chains to get monolayers with the best stability and reproducibility too. The molecular semiempirical models showed a very good congruence with the molecular area obtained from the isotherms less than 10 $Å^2$.

We are working in the transference of the monolayers onto a glass substrate to form Langmuir-Blodgett films and will be able to study the electronics proprieties and fabrication of devices.

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