



# Langmuir and Langmuir–Blodgett films of a quinoline-fluorene based copolymer

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## ABSTRACT

The fabrication of Langmuir–Blodgett (LB) films of synthetic polymers allows the control of molecular architecture in order to optimize physical properties. In this paper, the surface chemistry of a quinoline-fluorene based copolymer spread on the air–water interface is investigated. Surface pressure–area isotherms as well as Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) were employed to characterize the films, which could be transferred to solid supports by the LB technique. Atomic force microscopy as well as UV–Vis and fluorescence spectroscopies have shown a regular deposition of the polymers, and the luminescence properties could be controlled with the number of layers deposited on the solid support. As a result, the photoluminescence of the LB films was considerably higher than that observed for the spin coated film, and the maximum emission peak was shifted to higher energies, which is attributed to the molecular-level interactions within the layer-ordered structure of the LB film. The luminescence response would possibly be tuned to approach the highest level, which allows the films to be employed in future applications in efficient optical devices such as organic light-emitting diodes (OLEDs).

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## 1. Introduction

The study of conducting material has been conducted for various lighting, flat-panel display and sensors applications [1]. Polyfluorenes and fluorene-based conjugated polymers have emerged as one very promising class of light emitting materials due to their thermal stability, good solubility in several solvents, and facile functionalization at the C-9 position of the fluorine group, offering the prospect of controlling physical properties [2]. Moreover, the remote substitution at the C-9 position does not induce to steric effects in the adjacent aromatic rings [3].

It is interesting that n-type materials in polymeric semiconductors are further developed because of the possibility of obtaining thin and flexible devices improving the mechanical and thermal stability, and because of the interest for use in low-priced, ultrathin, and flexible products such as energy conversion cells and displays.

Employing quinolines in polymers leads to the formation of intrinsic good n-type materials, with good thermal and oxidative stability. Although polyquinolines is not soluble in water, they have been demonstrated as ET layers in light-emitting diodes (LEDs) due to their high thermal and oxidative stability, outstanding mechani-

cal property, and good film-forming ability [4]. However, the optical and electrical properties of OLEDs having polyquinoline as active layer are reported to have poor electroluminescent performances, with broad bands in the electroluminescence spectra attributed to the formation of aggregates and excimers in solid films, even after incorporating long alkoxy or alkyl side groups [5].

The incorporation of a pendent quinoline group in the fluorene 9-position resulted in an increased electron affinity and increased conducting properties of the fluorene polymer, which favored a more balanced transport of charges, enhancing the recombination rate in the polymer emissive layer. The improved electron injection and transport in the copolymer was observed to take place without significant alteration of the electronic properties of the polyfluorene conjugated backbone [6].

The immobilization of luminescent polymers in solid supports as ultrathin films has been reported as an approach to control the molecular architecture and consequently the optical properties of the polymer [7]. Particularly, films produced through the Langmuir–Blodgett (LB) technique allow precise control of the thickness and molecular architecture [8]. For that, insoluble amphiphiles are spread on the air–water interface forming liquid monolayers that can be laterally compressed to reach 2-D condensed states. Then the condensed film, usually at a relatively low surface tension value is subsequently transferred to solid supports through a vertical deposition at a pre-determined constant surface pressure, providing a high organized film at the molecular level [9].

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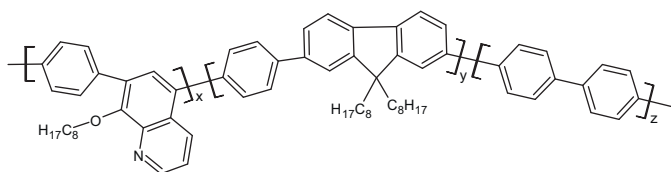


Fig. 1. Chemical structure of QFC.

The immobilization of synthetic polymers as LB films has been developed recently in the literature, and as such compounds are not classical amphiphiles, some strategies have been employed, such as alkylation of the core structure of the polymer [9], as well as the use of a lipid matrix to facilitate the spreading of the polymers on the air–water interface [10–12]. Immobilized polymers as LB films have been shown to enhance optical and electrical properties [11] and have been used to optical [13,14] and electronic devices [15,16], and also for electronic tongues [17,18]. The control of the structure of the film at the molecular level and the high lateral organization helps to control the film functional properties. The appealing attribute of LB films is the possibility to molecularly control the layer architecture based on the demands of the desired device, opening the possibility to process numerous materials with diverse functionalities. Particularly, for polyfluorenes, it has been shown an enhanced emission when they are co-immobilized with phospholipids as LB films [11].

In this study, a quinoline-fluorene based copolymer (QFC), whose structure are shown in Fig. 1, was used to form Langmuir monolayers. The transfer of this material onto solid substrates as LB films could be carried out, exhibiting intense fluorescence emission, being therefore promising for the construction of optical devices such as energy conversion cells and displays. To the best of our knowledge, it is not reported the deposition of this kind of polymer as LB film in the literature. Although the polymer has been previously synthesized [19], it has never been immobilized before as an ultrathin film, such as a Langmuir–Blodgett one. The novelty of this work therefore lies in the possibility of producing LB films of quinoline-based copolymers with molecular control, and also in the possibility of understanding at the molecular level the interactions of the polymer with the interfaces involved in this work by employing tensiometry and vibrational spectroscopy.

## 2. Materials and methods

### 2.1. Synthesis

The fluorene quinoline copolymer was synthesized using a palladium catalyst. The material was prepared according to procedures described in the literature [19].

### 2.2. Spreading at the air–water interface

Ultrapure water (resistivity  $\approx 18.2 \text{ M}\Omega \text{ cm}$ ,  $\text{pH} \approx 5.5\text{--}6.0$ ), supplied by a Millipore® system, was used as subphase. QFC mentioned above were dissolved in chloroform to yield a  $0.5 \text{ mg mL}^{-1}$  solution. Aliquots of this solution were spread carefully drop by drop on the surface of the aqueous subphase. After spreading, an interval delay of 10–15 min for solvent evaporation was applied, just before starting the film compression with two movable barriers at a rate of  $3.0 \text{ Å}^2/(\text{molecule min}^{-1})$ . The surface pressure ( $\pi$ ) was measured during the monolayer compression using a Wilhelmy plate, with a KSV mini-trough (System 2, total volume of 220 mL). All monolayers were produced at a constant temperature of  $25 \pm 1^\circ \text{C}$ . The films thus prepared were characterized by Polarization-Modulation Infrared Reflection Absorption Spectroscopy using a KSV PMI 550 instrument (KSV Instrument Ltd, Helsinki, Finland). The Langmuir

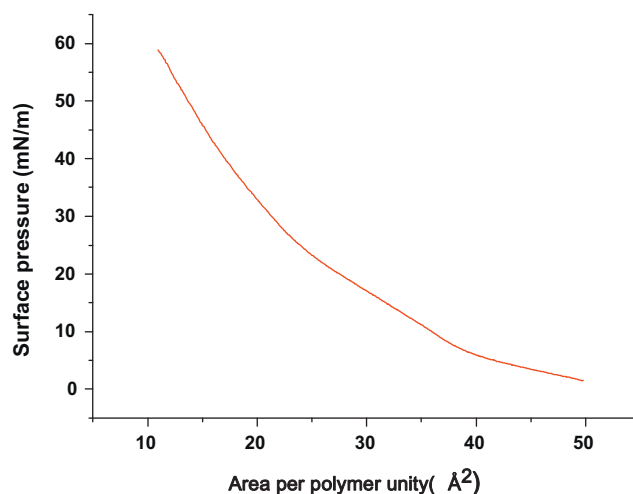


Fig. 2. Surface pressure–area isotherms for QFC spread on the air–water interface.

trough is set up so that the light beam reaches the monolayer at a fixed incidence angle of  $75^\circ$ .

In this angle, the signal-to-noise ratio is the best, and the reflectivity is the maximum. The incoming light was continuously modulated between *s*- and *p*-polarization at a high frequency, which allows the simultaneous measurement of the spectra of the film under both polarization conditions. The difference between the spectra provides surface-specific information, and the sum provides the reference spectrum. Using the technique of simultaneous measurements, the effect of the water vapor is largely reduced. The spectra of the films are subtracted background spectrum; the background spectrum is the spectrum of the water interface collected immediately before polymer spreading. For each spectrum, 6000 scans were used.

### 2.3. Deposition onto solid supports

All films were produced at a constant temperature of  $25 \pm 1^\circ \text{C}$ . Quartz slides were used as substrates for the transfer of the LB films. The quartz substrates were cleaned by treating with a 5% KOH ethanol solution in an ultrasonic bath for 5 min. The LB film transfer was performed with a dipping rate of  $1 \text{ mm min}^{-1}$  at a constant surface pressure ( $25.0 \pm 0.2 \text{ mN m}^{-1}$ ). The first layer was obtained by raising the substrate from the aqueous subphase

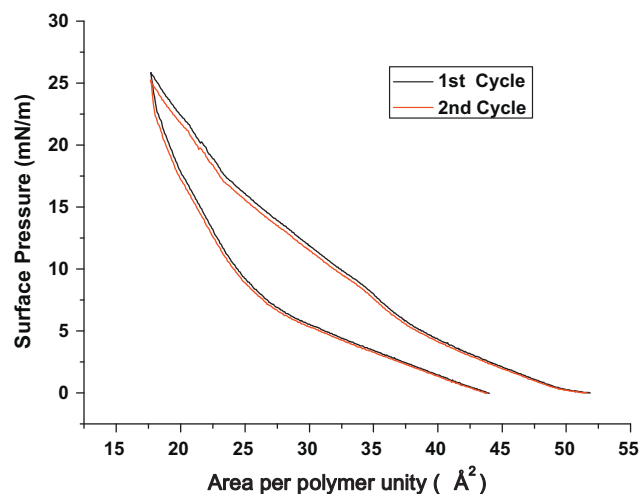
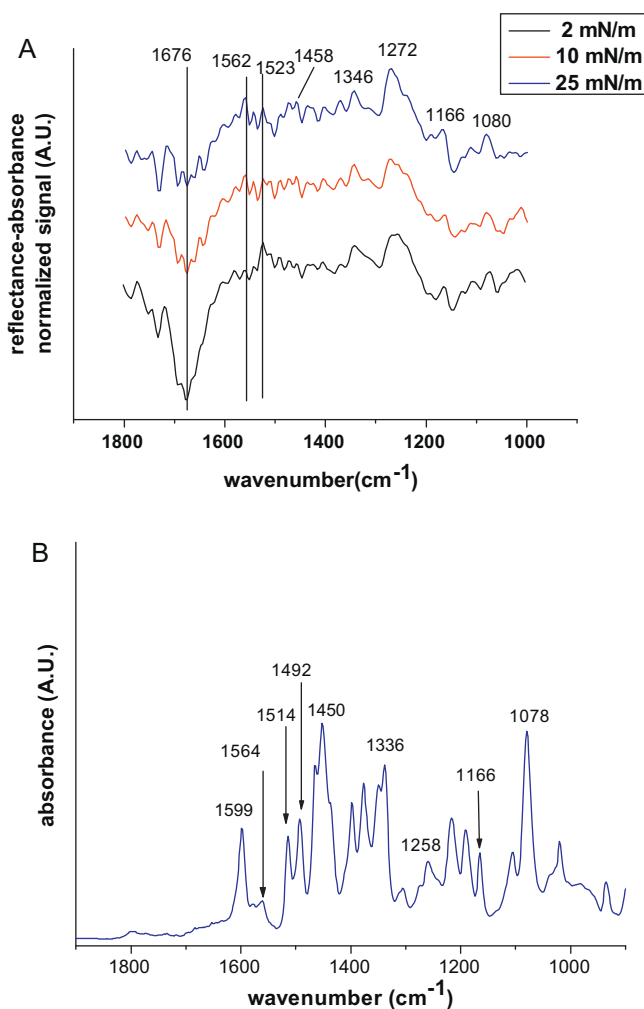
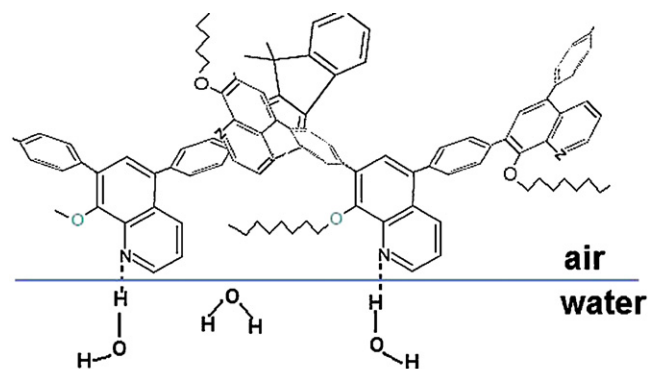


Fig. 3. Surface pressure–area isotherms for a cycle of compression–decompression of QFC spread on the air–water interface. Target pressure:  $25 \text{ mN m}^{-1}$ .



**Fig. 4.** PM-IRRAS spectra for QFC spread on the air–water interface (A). Inset chart shows the value of surface pressure at which the spectra were obtained. FTIR spectrum of QFC in the range 1000–1700  $\text{cm}^{-1}$  is shown for comparison (B).

and the other layers were transferred alternating depositions by dipping and lifting up the substrate through the air–water interface. For multilayer Y-type LB films, an interval of 10 min was elapsed before the subsequent dipping with the plate at the most upward position for drying. The transfer ratio in each deposition, that is, the ratio between the trough area swept by the barriers to maintain the surface pressure constant and the substrate area in contact with the air–water interface when lifting or dipping the substrate, was employed as an indicative of the quality of the LB deposition, and only the regularly built up LB films were considered for further characterization. Polarized infrared spectroscopy (PM-IRRAS, KSV Instrument Ltd, Helsinki, Finland) allowed the study of the chain orientation within the LB films, while the fluorescence spectroscopy (Varian Eclipse fluorescence spectrophotometer), performed with an excitation at the wavelength of the maximum absorption according to the UV–Vis spectra, showed the behavior of the linked chromophore groups. The slit-widths were 5 nm for both excitation and emission light. To evaluate the morphology of the films, atomic force microscopy (AFM) images were obtained in the tapping mode, employing a resonance frequency of approximately 300 kHz, scan rate of 1.0 Hz, and scanned areas of  $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ . A Digital AFM–Nanoscope IIIA instrument was employed for these measurements using a silicon tip.



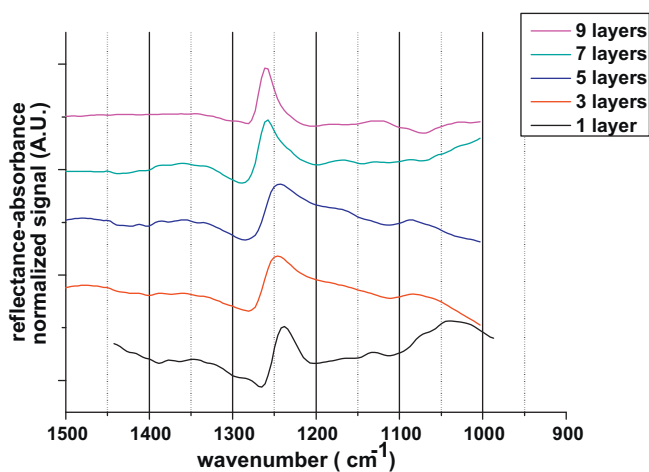
**Fig. 5.** Sketch of polymer orientation on the surface of the water.

### 3. Results and discussion

#### 3.1. Air–water interface

The surface pressure–area ( $\pi$ – $A$ ) isotherm illustrated in Fig. 2 shows that the polymer forms Langmuir films when spread on the air–water interface, reaching surface pressures as high as  $60 \text{ mN m}^{-1}$ . The surface compressional modulus ( $K$ ), defined as  $-(1/A) \cdot (\partial\pi/\partial A)_T$ , lies in the range of  $20$ – $60 \text{ mN m}^{-1}$ , characterizing liquid-expanded states. Two inflection points are observed in the isotherm, one at  $38 \text{ \AA}^2$  and the other one at  $24 \text{ \AA}^2$ , pointing to changes in the molecular orientations of the polymer at the air–water interface during compression. It is important to say that the range of area per polymer unity (from  $50$  to  $10 \text{ \AA}^2$ ) cannot be compared to the real area occupied by a QFC polymer unity. Since the polymer chain can be folded through a non-extended conformation, the same spot in the surface of the water might be filled, in average, by more than one polymer segment, increasing the thickness of the layer. Also, we can observe a change in the slope of the  $\pi$ – $A$  curve at about  $5$ – $10 \text{ mN m}^{-1}$ . This could be related to conformational changes in the polymer that may be caused by the surface compression. However, these changes did not alter the orientation of the main chemical groups in relation to the interface, as shown later in this manuscript by PM-IRRAS spectra.

Fig. 3 shows that the film presents significant hysteresis, when the compression and the decompression of the monolayer are compared. This indicates that the polymer conformation states



**Fig. 6.** PM-IRRAS spectra for QFC LB films. Intensity of the bands are normalized to encompass the same maximum value in relation to minimum absorption at  $1100 \text{ cm}^{-1}$ .

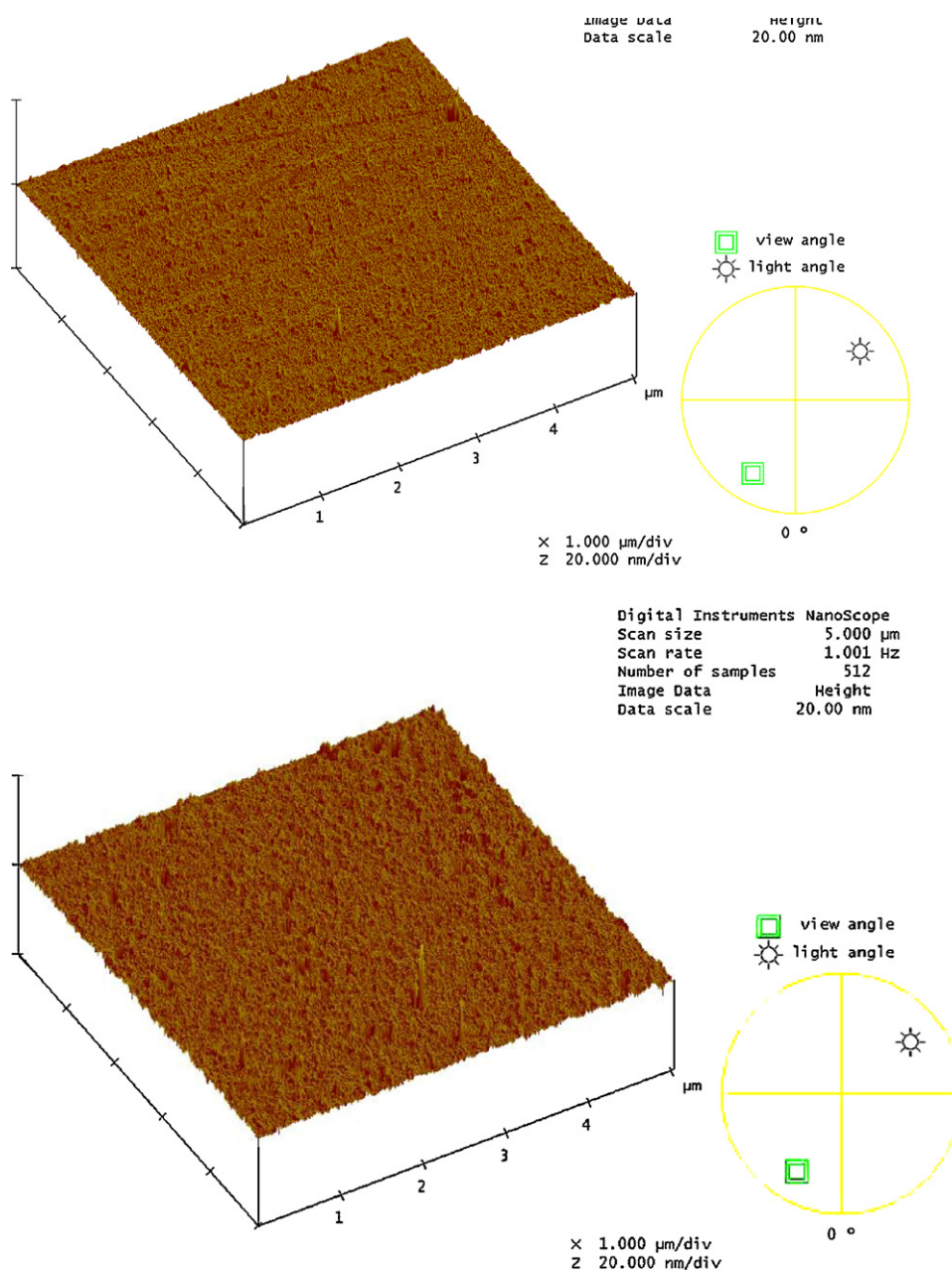


Fig. 7. AFM images for QFC LB films: 1 layer (A) and 9 layers (B).

that are reached upon compression are not immediately unformed upon decompression, which indicates the presence of metastable states during decompression. However, successive cycles presented similar behaviors for the surface pressure–area isotherms when compared to the first compression–decompression cycle, indicating reversibility of the structure of the polymer film at the air–water interface, and monolayer stability when performing successive cycles.

It is important to emphasize that the reversibility and hysteresis depends on the maximum surface-pressure during compression. In other words, it depends on different molecular architectures at different surface pressures. As we transferred the film at the surface pressure of  $25 \text{ mN m}^{-1}$ , we obtained the compression–decompression curves with this target value. Also, it has to be stressed that this behavior is specific for such specific condition employed in this work.

Fig. 4 shows the PM-IRRAS spectra for the QFC monolayer under different degrees of compression. A strong negative band to the baseline at  $1676 \text{ cm}^{-1}$  due to the water O–H bending appears and tends to disappear with compression. Bands at  $1458$ ,  $1523$  and  $1562 \text{ cm}^{-1}$  appears due to  $\text{CH}_2$ ,  $\text{C}=\text{C}$  and  $\text{C}-\text{N}$  stretches, respectively; the band at  $1346 \text{ cm}^{-1}$  may be attributed to  $\text{CH}_3$  deformation; the one at  $1272 \text{ cm}^{-1}$  to alkyl aryl ether  $\text{C}-\text{O}-\text{C}$  stretches, and the one at  $1080$  and  $1166 \text{ cm}^{-1}$ , owing to the symmetric  $\text{C}-\text{O}-\text{C}$  vibrations. A Fourier Transform Infrared Spectrum (FTIR) spectrum of QFC in the range  $1000\text{--}1700 \text{ cm}^{-1}$  is shown for comparison (Fig. 4b). A strong absorption appears at  $1078 \text{ cm}^{-1}$ , and it is positioned close to the value encountered for QFC as a Langmuir monolayer. Comparing the major bands for QFC at the air–water interface and in solution, the bands for the Langmuir monolayers are shifted to higher energies, except for that at  $1562 \text{ cm}^{-1}$ . This implies a higher freedom for the vibration dipoles,



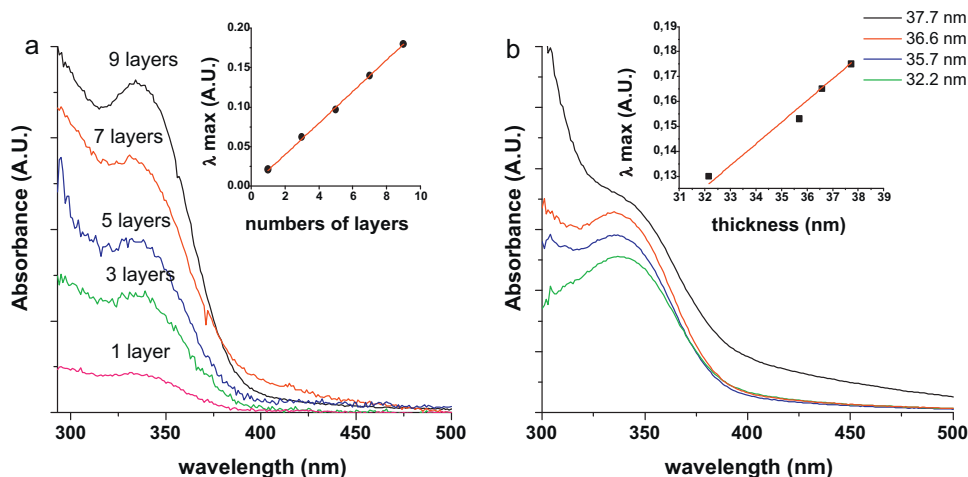


Fig. 8. (a) UV-Vis spectra for QFC LB film; (b) UV-Vis spectra for QFC films deposited by the spin coater technique.

suggesting a significant change in the conformation of the polymer when it goes from an organic solution, in which it is dissolved, to a condition in which it is disposed interacting with water molecules at the air–water interface.

The negative band to the baseline for water hydroxyl bending can be explained by the difference of reflectivity between the water surface covered and uncovered by the polymer layer, which is associated to a probable re-orientation of the interfacial water molecules upon polymer spreading. The spectra did not vary significantly in terms of wavenumbers of the main bands when we compare the spectra for the three values of surface pressures selected, showing in a first moment that there was no significant variation in the orientation of the chemical groups in relation to the interface during compression. However, the relative intensities of the absorption maximums for the bands for the polymer chemical groups changed with surface pressure, indicating in fact a certain re-orientation of the polymer chains during compression. This fact points to water–polymer interactions at the interface and to the progressive polymer chain folding process when subject to lateral compression. The intensity of the negative bands to the baseline indicates a preferential alignment of the correspondent dipole perpendicular to the water surface, at the same time a positive band to the baseline indicates a parallel orientation. Following this reasoning, one can assume that upon film compression, the

hydrogen bonds associated to the polymer chain keeps a perpendicular alignment toward the water surface, suggesting that the quinoline ring is also upright, with the hydrogen bond linked to the nitrogen atom. The PM-IRRAS spectra also indicated that the aromatic rings presented no preferential orientation, while the ether bonds remained preferentially parallel. Increasing the surface pressure did not change the overall orientation of the polymer chains, which means that the chains are not able to adopt an upright extended conformation. However, under compression, the aromatic rings might be laterally packed to form piled structures as roughly illustrated in Fig. 5.

### 3.2. Langmuir–Blodgett films

Before the transfer of the monolayer from the liquid interface to solid supports, the film was compressed up to  $25 \text{ mN m}^{-1}$ , and this pressure was kept constant by moving the barriers. The area variation rate was not higher than  $2 \text{ mm}^2 \text{ min}^{-1}$  after 10 min, indicating monolayer stability. Then, the solid substrate, which was previously dipped into the aqueous subphase, could be lifted. This is a first guarantee of the monolayer stability in order to better evaluate its deposition as an LB film. The polymer could be transferred as Y-type LB films with transfer ratio close to 1.0 until 9 layers. Although the film can be transferred

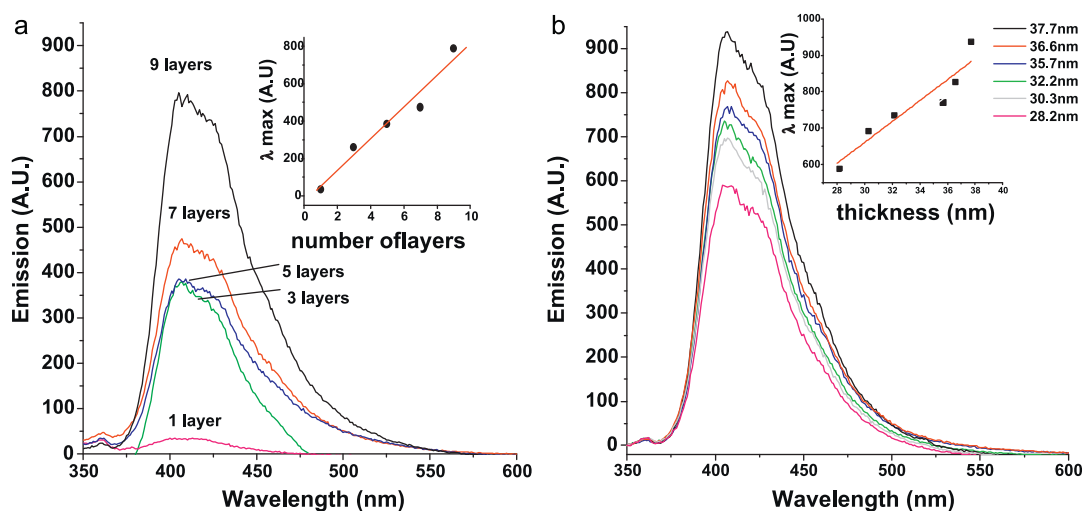


Fig. 9. (a) Fluorescence spectra for QFC LB films. (b) Fluorescence spectra for QFC films deposited by the spin coater technique.

even in surface pressures as low as  $10 \text{ mNm}^{-1}$ , the value of  $25 \text{ mNm}^{-1}$  has been chosen because it is enough high to allow the monolayer transfer, conferring to the film a highly packed structure. This value of surface pressure is also enough low to be far from the monolayer collapse. The substrates were chosen according to the corresponding characterization technique. For AFM, mica plates were used; for fluorescence and UV–Vis measurements, quartz; and for PM-IRRAS, gold. The nature of the substrate did not caused significant changes in the transfer ratios obtained.

Fig. 6 shows the PM-IRRAS spectra for such films. Water bands are absent in these spectra showing the successful drying of the films. The band for Ar–O ether alkyl aril stretches is negative to the baseline with 1 layer deposited, but tends to change its orientation as long as thicker films are deposited. This is indicated not only by the fact that, with 9 layers, the band is completely orientated upwards, but also because the maximum goes from  $1224 \text{ cm}^{-1}$  (1 layer) to  $1258 \text{ cm}^{-1}$  (9 layers). Successive depositions of polymers in several layers probably alter the relative orientation of this vibration dipole. The negative band disappears with 9 layers, indicating that the thickest film possesses, in average, alkyl-aryl ether dipoles mainly in the parallel position in relation to the solid interface. This implies that the molecular orientation of the polymer is dependent on the process of layering QFC when it is transferred from the liquid interface to the solid support.

The AFM images in Fig. 7 show that the films are relatively homogenous in the scale obtained in the micrographs, with maximum thickness of  $0.7 \text{ nm}$  by layer approximately. The control image for mica was obtained and presents a uniform image without significant interferences (not shown). The images for QFC visually present a higher roughness confirming the covering of the solid substrate by the polymer, and suggesting the regularity of the deposition of the polymer onto the solid support by using the LB technique.

From absorption and emission spectra, the properties of the films were then investigated. In Fig. 8, the absorption spectra of QFC deposited as LB films (Fig. 8a) and deposited by the spin coater technique (Fig. 8b) are presented. In both cases, QFC showed the maximum absorption spectra in  $330 \text{ nm}$ . Also, increasing the number of layers (and consequently the film thickness) led to the increase of the maximum absorption, but with no displacement observed ( $333 \text{ nm}$ ). The spectra for the LB films show that there is no change in the shape and position of the band with the number of deposited layer, proving no significant alteration of the polymer optical properties due to interlayers interactions. The insert chart shows that the maximum values vary approximately linearly with number of layers. Also, for all the cases, the optical band gap calculated from the onset of thin film absorption spectrum was the same (around  $2.25 \text{ eV}$ ). The insertion of quinoline in the copolymer caused a red shift with respect to the copolymer without quinoline [11].

In Fig. 9, the emission spectra of QFC as LB films (Fig. 9a) and deposited by the spin coater technique (Fig. 9b) are presented. Concerning the emission spectra, it is also possible to observe an increase in the emissions with number of layers (insert chart). The peak observed at  $405 \text{ nm}$ , attributed to the fluorescence of benzyl and pyridyl groups presented in the molecules for the films deposited by both techniques, is also red shifted with regard to the copolymer without quinoline, whose maximum emission was  $380 \text{ nm}$  [11]. Such film emission can be affected by intermolecular species (aggregates and excimers), much stronger than in solution and can generate the shoulder at about  $425 \text{ nm}$ . Similar results were observed in the work presented by Mikroyannidis et al. [5].

## 4. Conclusions

The results presented here show a new way to immobilize quinoline-based copolymers in solid matrices as ultrathin films by using the Langmuir–Blodgett technique. The copolymers could be spread on the air–water interface, and stable Langmuir monolayers could be formed. Transfer to solid supports as LB films was successful, forming homogenous films with optical properties that could be controlled by the number of layers.

The analyses of the results obtained from emission and absorption spectra, comparing the films produced with the LB technique with those deposited by conventional techniques (spin coater) showed great similarities, which bring us a new possibility for thin films deposition via LB-techniques for assembly of new PLEDs devices, which should be very appealing because this technique allows the high control of the architecture and the directionality of the film. Therefore, these results are remarkable because the emission properties can be tuned by varying the number of layers, which results in a film produced with high control of the architecture at the molecular level.

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