



## On the distinct molecular architectures of dipping- and spray-LbL films containing lipid vesicles



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### ABSTRACT

The introduction of spraying procedures to fabricate layer-by-layer (LbL) films has brought new possibilities for the control of molecular architectures and for making the LbL technique compliant with industrial processes. In this study we show that significantly distinct architectures are produced for dipping and spray-LbL films of the same components, which included DODAB/DPPG vesicles. The films differed notably in their thickness and stratified nature. The electrical response of the two types of films to aqueous solutions containing erythrosin was also different. With multidimensional projections we showed that the impedance for the DODAB/DPPG spray-LbL film is more sensitive to changes in concentration, being therefore more promising as sensing units. Furthermore, with surface-enhanced Raman scattering (SERS) we could ascribe the high sensitivity of the LbL films to adsorption of erythrosin.

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### 1. Introduction

The control of molecular architecture is crucial for many applications of organic films, particularly because synergy may be sought upon combining distinct materials in the same film [1,2], being also a key feature of the layer-by-layer (LbL) technique [3,4]. The synergy achieved in LbL films has been extensively exploited in various applications, including sensing and biosensing [1,5], as the mild conditions are required for film fabrication and the retention of entrapped water are essential for the successful immobilization of biomolecules [5,6]. For instance, judicious combinations of distinct materials for electronic tongues (e-tongues) [1,5,7,8] have allowed detection of analytes down to nanomolar concentrations or below [9,10], in addition to the diagnosis of diseases [11–14] and in food control [15]. In many such cases, altering the order at which the different materials are adsorbed or even the number of layers affects considerably the film response [5,9,16].

The recent variation of the LbL technique based on spraying [17–22] has brought new possibilities, since the fast procedure makes it probably compliant with industrial processes. With spraying one may obviate one practical limitation of dipping LbL films, which require long periods of time for complete layer adsorption and normally coat small areas.

Spraying is claimed to speed up the LbL process up to 500 times due to the immediate contact between the surface and the approaching sprayed material [18]. Spray-LbL films have been used for fabricating electrodes in high power and energy devices [23], solar cells [24], double-layer anti-reflection films [25], cotton fibers for flame retardancy [26], deposition of colloidal nanoparticles [27,28], polysaccharides [29] and conducting polymers [30,31].

An additional feature of the spray-LbL films is that the molecular architecture may differ from the corresponding dipping-LbL films [32], which calls for further research both in terms of film characterization as well as in the identification of novel applications. In this paper, we build upon a previous work [32] where dipped- and spray-LbL films containing phospholipid vesicles were compared, and investigate the molecular architectures of DODAB/DPPG LbL films. Using a combination of experimental methods, we shall show that the molecular architecture of spray-LbL films differs considerably from that of dipping LbL films. Because it is known that sensing units built with the same materials but different processing techniques may display different electrical responses, we correlate the type of LbL film with the ability to detect trace amounts of xanthene derivative erythrosin in water through impedance spectroscopy measurements. Our interest in the dye erythrosin arises from its versatile use, spanning from lasing action [33], photodynamic therapy (PDT) [34] to food industry [35,36], especially because in the latter its waste represents an environmental issue.

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## 2. Experimental section

### 2.1. Reagents and solutions

The anionic phospholipid DPPG [1,2-dipalmitoyl-*sn*-3-glycerophospho-*rac*-(1-glycerol)] was purchased from Genzyme Pharmaceuticals. The cationic lipid DODAB (dioctadecyldimethylammonium bromide), the anionic poly(sodium 4-styrenesulfonate) (PSS), the cationic poly(allylamine hydrochloride) (PAH) and xanthene erythrosin, were acquired from Sigma-Aldrich Co. All chemicals were used without further purification. The molecular weights of DPPG, DODAB, PAH, PSS and erythrosin are 744.95; 630.95; 15,000; 70,000; and 835.89 g/mol, respectively, and their molecular structures are shown in Fig. 1. The spray-LbL films were fabricated from DPPG and DODAB aqueous dispersion using ultrapure water (18.2 M $\Omega$ ·cm and pH 5.6) obtained from a Milli-Q system, model Simplicity. The DPPG dispersion at 0.74 mg/mL (1.0 mM) was prepared by adding ultrapure water at room temperature (22 °C) to the powder, under gentle stirring. The 0.63 mg/mL (1.0 mM) concentration of DODAB dispersion was prepared following the methodology by Feitosa et al. [37]: DODAB powder was added to ultrapure water and the mixture was heated under stirring to 60 °C (above DODAB fusion temperature,  $T_m \approx 45$  °C) for a few minutes. Then, the DODAB dispersion was cooled to room temperature (22 °C). The cast films reported here were prepared by dropping the desired solution (ca. 1 mL) onto the substrate, which was left to dry under room temperature.

### 2.2. Layer-by-layer film fabrication

#### 2.2.1. Dipping-LbL films

The DODAB/DPPG dipping-LbL films were grown upon adapting the experimental procedure reported in [38]. The substrate was immersed into distinct solutions according to the following sequence: DODAB dispersion (3 min)  $\rightarrow$  ultrapure water gently stirred to remove non-adsorbed DODAB (1 min)  $\rightarrow$  DPPG dispersion (3 min)  $\rightarrow$  ultrapure water to remove non-adsorbed DPPG (1 min). With this procedure the first DODAB/DPPG bilayer was formed, and multilayers were obtained by repeating this four-step sequence.

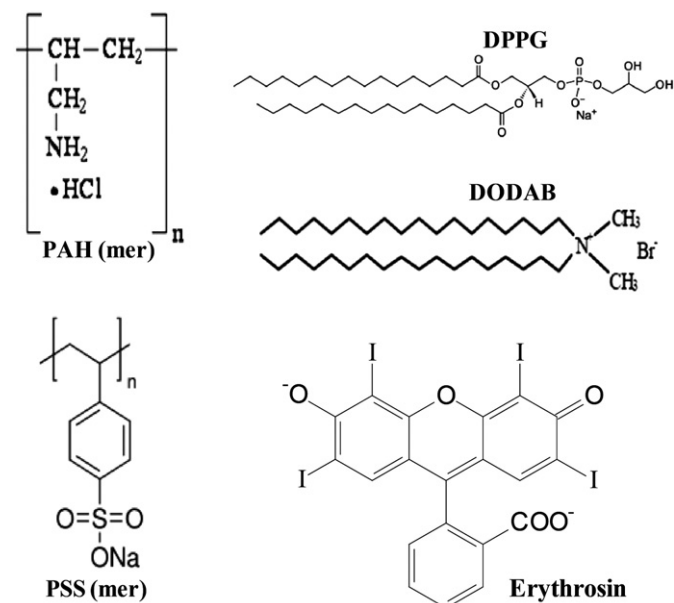


Fig. 1. Molecular structures of PAH (mer), PSS (mer), DPPG, DODAB and erythrosin.

#### 2.2.2. Spray-LbL films

The deposition of (DODAB/DPPG) $_n$  spray-LbL films was performed by spraying DODAB and DPPG dispersions alternately using the experimental setup described in ref. [32], which consisted of an airbrush spray, model BD-123A from LEEpro tools with a nozzle of 0.3 mm diameter and 7 mL of fluid cup capacity. For spraying deposition, a perpendicular orientation was adopted between the spray axis and the coating surface, being 30 cm apart from each other. The airbrush sprays were filled with DODAB and DPPG dispersions alternately using a constant pressure of 10 psi during 2 s. A valve regulator was used to control the spraying pressure from the compressor. These parameters were chosen after testing different combinations involving spraying pressures, spraying times, with and without rinsing steps [32]. The final setup allows for spraying solutions to form a thin layer on the desired surface, which dries within a few seconds.

The number of spraying (or dipping) bilayers and the type of substrate were chosen according to the characterization technique. For instance, films were grown onto quartz plates for UV–Vis extinction spectroscopy, onto AT-cut quartz crystal coated with Au plates for quartz crystal microbalance (QCM) measurements, onto Ge for Fourier transform infrared spectroscopy (FTIR), onto glass thermally treated (600 °C for 2 h) for atomic force microscopy (AFM), and onto interdigitated Pt electrodes for impedance spectroscopy. The substrates were previously cleaned using neutral detergent, being sequentially and extensively washed in distilled water, acetone (5 min sonication), chloroform (5 min sonication), and ultrapure water. This procedure was sufficient to prepare substrate surfaces without drastic treatments such as with the use of piranha solution.

### 2.3. Characterization techniques

The growth of LbL films (spray and dipping) was monitored via UV–Vis extinction spectroscopy using a Varian spectrophotometer; model Cary 50, from 190 to 1100 nm, and via mass adsorption using a quartz crystal microbalance Stanford Research Systems Inc., model QCM 200. Shifts in frequency were continuously monitored with time and the mass gain ( $\Delta m$ , in grams) was obtained using the Sauerbrey equation [39]:  $\Delta F = (-2.3 \times 10^6 F_0^2 \Delta m) / A$ , where  $\Delta F$  is the frequency shift (in Hz),  $F_0$  is the resonance frequency (without coating, in MHz), and  $A$  is the electrode area (0.4 cm $^2$ ). The FTIR spectra were taken using a Bruker spectrometer, model Vector 22, equipped with a DTGS detector. The morphology was characterized through AFM using a Nanosurf Instrument model easyScan 2, with a tip of silicon nitride and using the tapping mode. All images were collected with high resolution (512 lines per scan) at a scan rate of 0.5 Hz. The images were processed with the software Gwyddion 2.19. The micro-Raman scattering experiments were conducted with a micro-Raman Renishaw spectrograph, model inVia, with laser excitation at 633 nm. The system is equipped with a Leica microscope, whose 50 $\times$  (NA 0.75) objective lens allows for collecting the spectra with ca. 1  $\mu\text{m}^2$  spatial resolution. Single-point spectra were recorded with 4 cm $^{-1}$  resolution and 10 s accumulation time, whereas two dimensional (2D) mapping results were collected through the rastering mode by using a computer-controlled motorized stage (XY).

Impedance spectroscopy measurements were carried out with a Solartron 1260A impedance analyzer. The sensing array comprised 6 sensing units: a bare Pt interdigitated electrode and Pt interdigitated electrodes coated with 5 bilayers of the following LbL films: dipping PAH/PSS, spray PAH/DPPG, dipping PAH/DPPG, spray DODAB/DPPG and dipping DODAB/DPPG. The bare Pt electrode was used to monitor any change in the electrical response caused by ultrathin films. The details of fabrication of dipping and spray-LbL films of PAH/DPPG can be found in ref. [32]. Impedance spectra were acquired from 1 Hz to 1 MHz using 50 mV of amplitude, with the data analyzed in terms of real capacitance. Three consecutive measurements were performed with sensing units immersed into ultrapure water (18.2 M $\Omega$ ·cm)

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