Supporting Information

Quartz Crystal Microbalance (QCM)

The build up process of the multilayered films was monitored *in situ* by quartz crystal microbalance-dissipation using the axial flow chamber QAFC 302 (QCM-D, D300, Q-Sense,Götenborg, Sweden). The QCM technique consists of measuring the resonance frequency (*f*) and the dissipation (D) of a quartz crystal induced by polyelectrolyte adsorption on the crystal, in comparison with the crystal in contact with the rinsing solution. The crystal used here is coated with a 50 nm thick SiO_2 film deposited by active sputter-coating. The quartz crystal is excited at its fundamental frequency (5 MHz), and the measurements are performed at the first, third, fifth and seventh overtones (denoted as ν) corresponding to 5, 15, 25 and 35 MHz, respectively. Changes in the resonance frequency, Δf, and in the dissipation factor, ΔD, during each adsorption step are measured. A shift in Δf can be associated, in first approximation, with a variation of the mass adsorbed to the crystal. To characterize the film at a given step, only the frequencies and dissipations at the end of the rinsing steps following the exposure to either polycation or polyanion were taken into consideration. The measurement methodology has been addressed in detail elsewhere and is applied in the present work.[1]

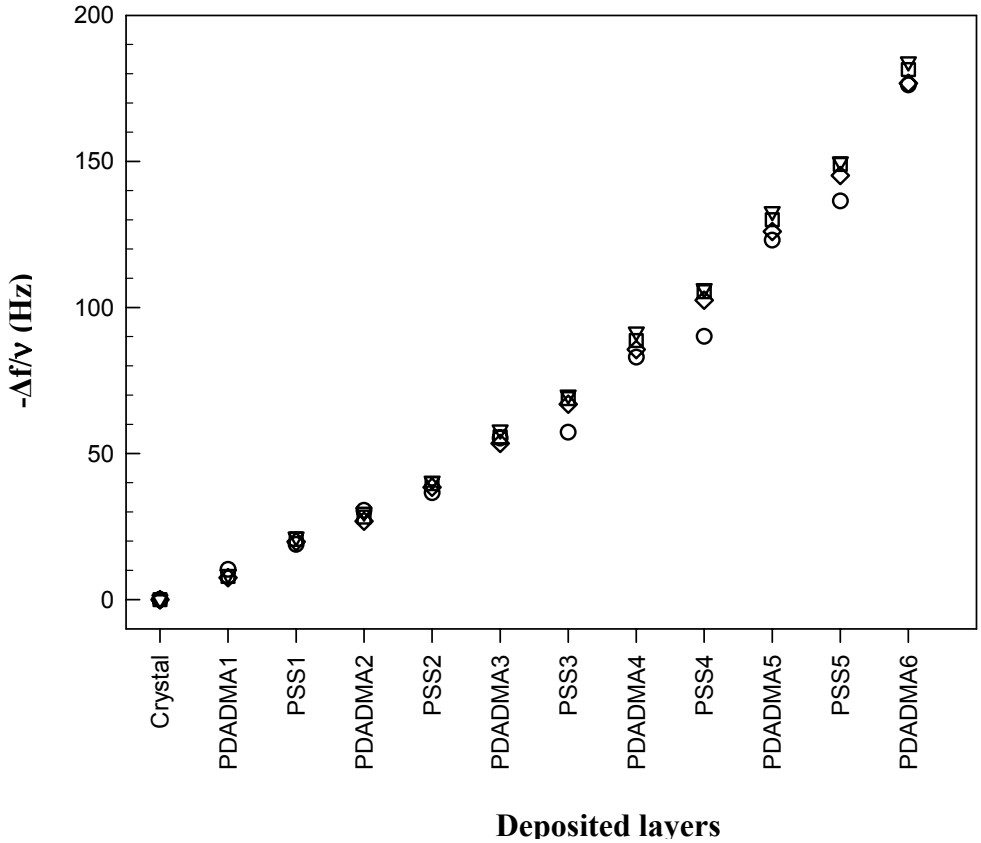
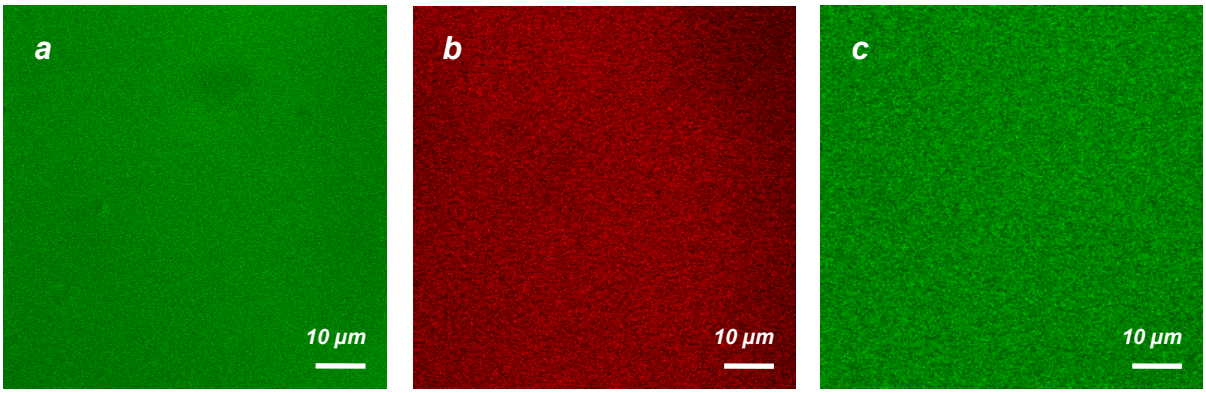


Figure S1. Quartz Crystal Microbalance (QCM) measurements monitoring the changes in the normalized frequency shifts $-\Delta f/\nu$ at 5 MHz (o), 15 MHz (◊), 25 MHz ( ) and 35 MHz (∇) during the build-up of $(PDADMA/PSS)_5/PDADMA$ multilayer films on a SiO_2 crystal.



Figures S2. Confocal laser scanning microscopy (CLSM) (*x*,*y*) images of three different polyelectrolyte multilayers deposited on bare silicone sheets and observed at the non-stretched state: $(PLL/HA)_{30}/PLL^{FITC}$ film (a), $(PDADMA/PSS)_{30}/(PDADMA/PSS^{Rho})$ film (b), $(PAH^{FITC}/PSS)_{30}$ film (c). Image sizes are $77\times77\mu m^2$.

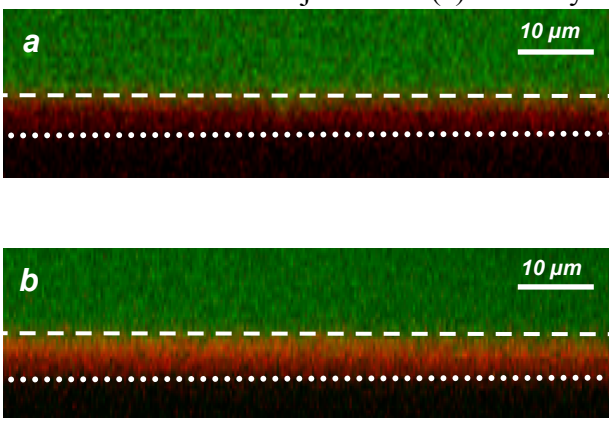


Figure S3. Confocal laser scanning microscopy (CLSM) section *(x,z)* image of a) $(PLL/HA)_{30}/PLL^{Rho}/(HA/PLL)/(PSS/PAH)_5$ multilayer film and b) $(PLL/HA)_{30}/PLL^{Rho}/(HA/PLL)/(PSS/PDADMA)_5$ multilayer film deposited on a silicone sheet and brought in contact with a PLL^{FITC} solution. Observations are performed in both the green and the red channels at the non-stretched state. The dotted line indicates the interface between the silicone sheet and the multilayer film, whereas the dashed line locates the barrier on top of the PLL/HA compartment. Image sizes are 115×32 μm^2.

Reference

1. C. Picart, P. Lavalle, P. Hubert, F. J. G. Cuisinier, G. Decher, P. Schaaf and J.-C. Voegel, *Langmuir*, 2001, **17**, 7414-7424.