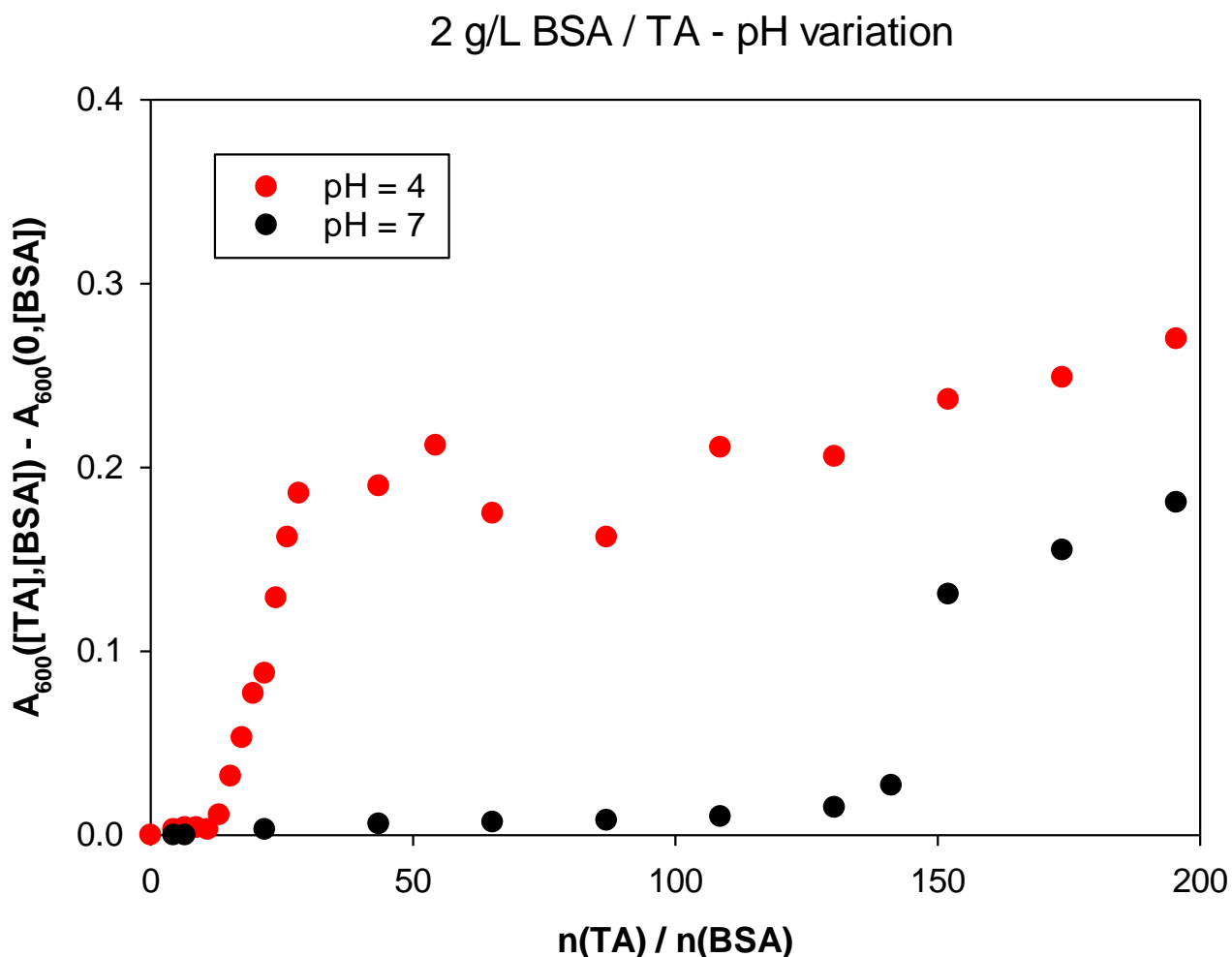


## SUPPLEMENTARY INFORMATION

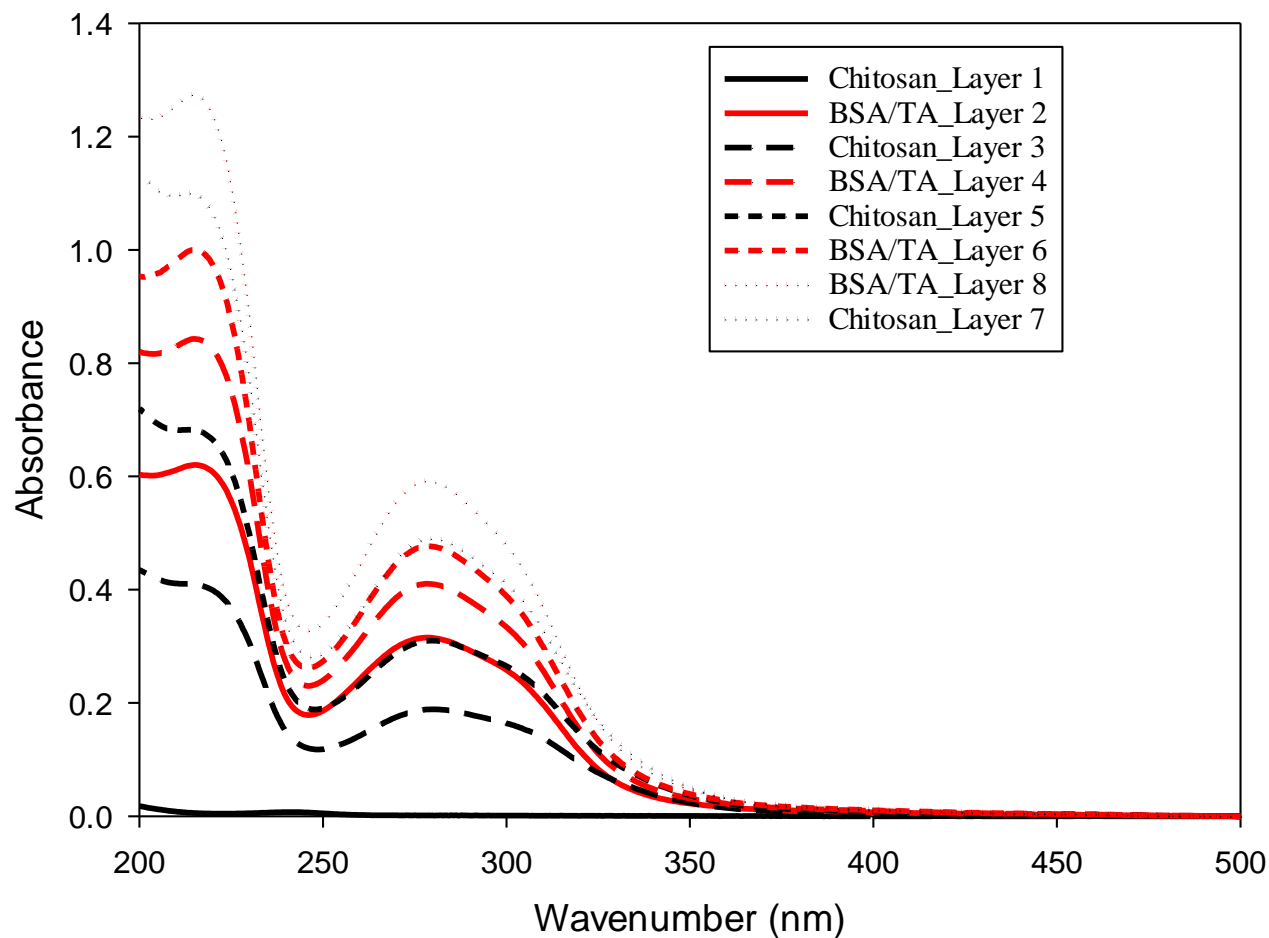
### Rational design of multilayer O/W emulsions using tannic acid as an interfacial antioxidant

**Figure S1:** Solution turbidity for mixtures of BSA and tannic acid at two different pH values.



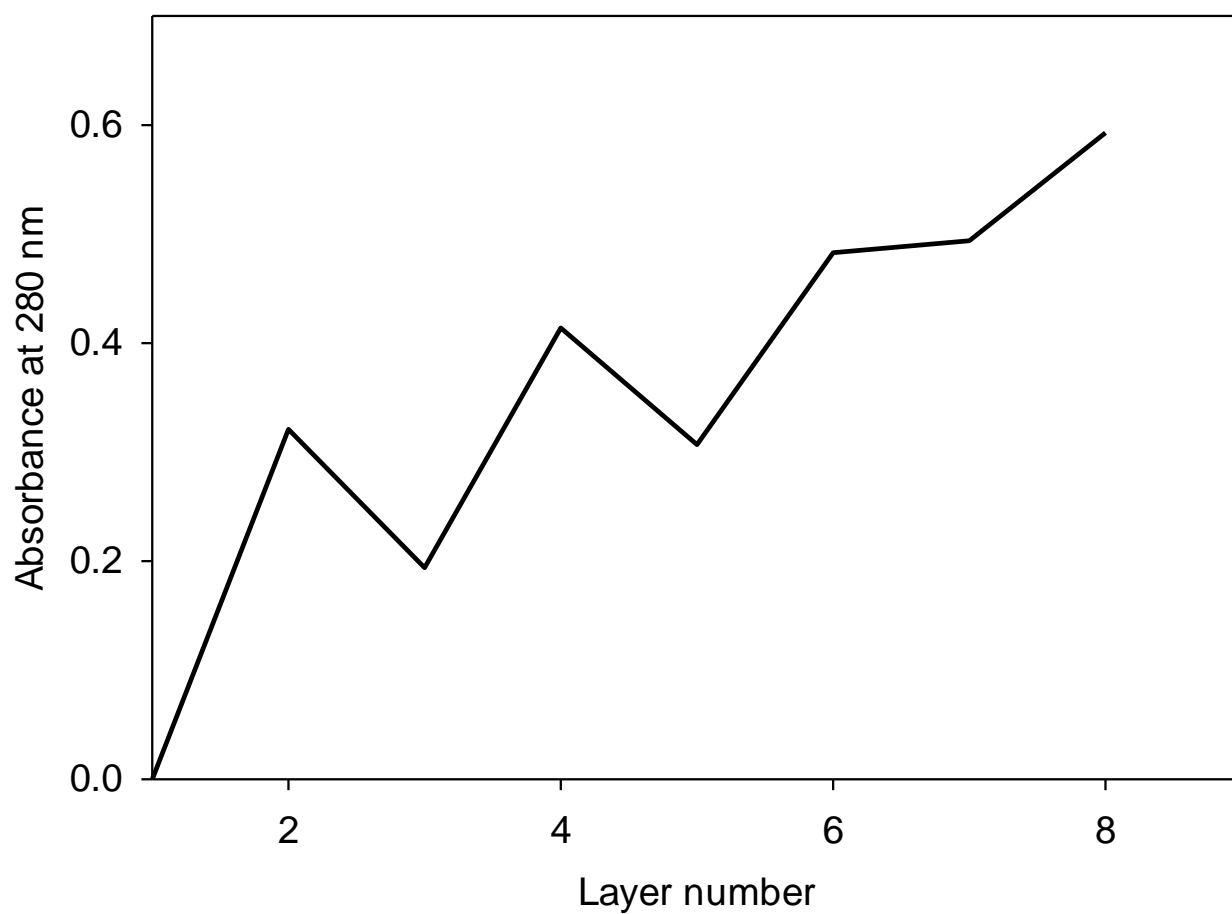
The interaction is much stronger at pH=4 as evidenced by the much lower critical ratio of tannic acid to BSA, for which the turbidity starts increasing abruptly. This is related to the pK<sub>a</sub> of TA (about 6) and the pI of BSA (about 4.6), which means that at pH=7 both molecules have a negative charge.

**Figure S2:** UV-vis absorbance of LbL films of chitosan (odd layers) and BSA/TA mixtures (even layers)



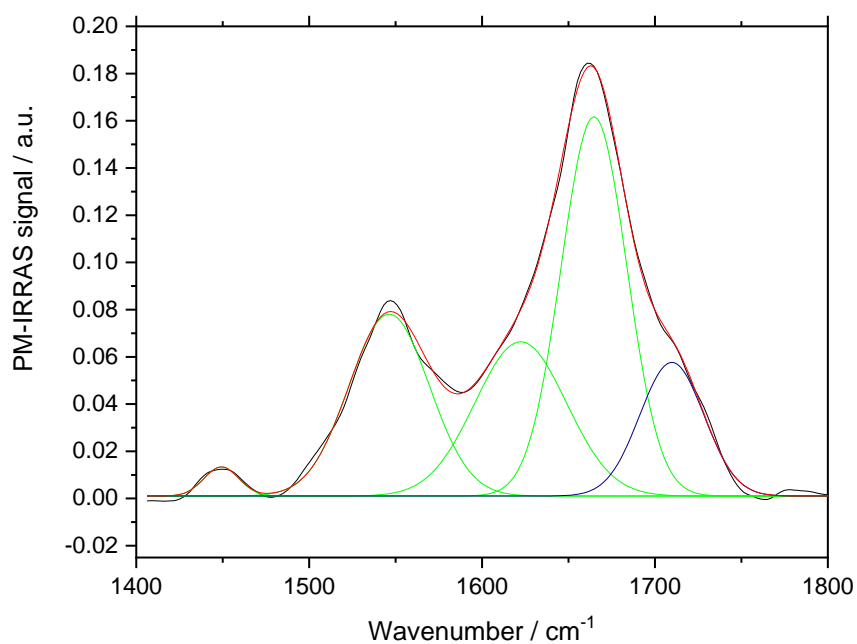
After the addition of each BSA/TA layer, which increases the absorbance, the next layer of chitosan appears to decrease the absorbance. This can be understood as some level of desorption, as discussed in the text, since there is no significant change in the spectra.

**Figure S3:** Zig-zag increase of the absorbance at the wavelength of maximum absorbance for the LbL films of Figure S2.

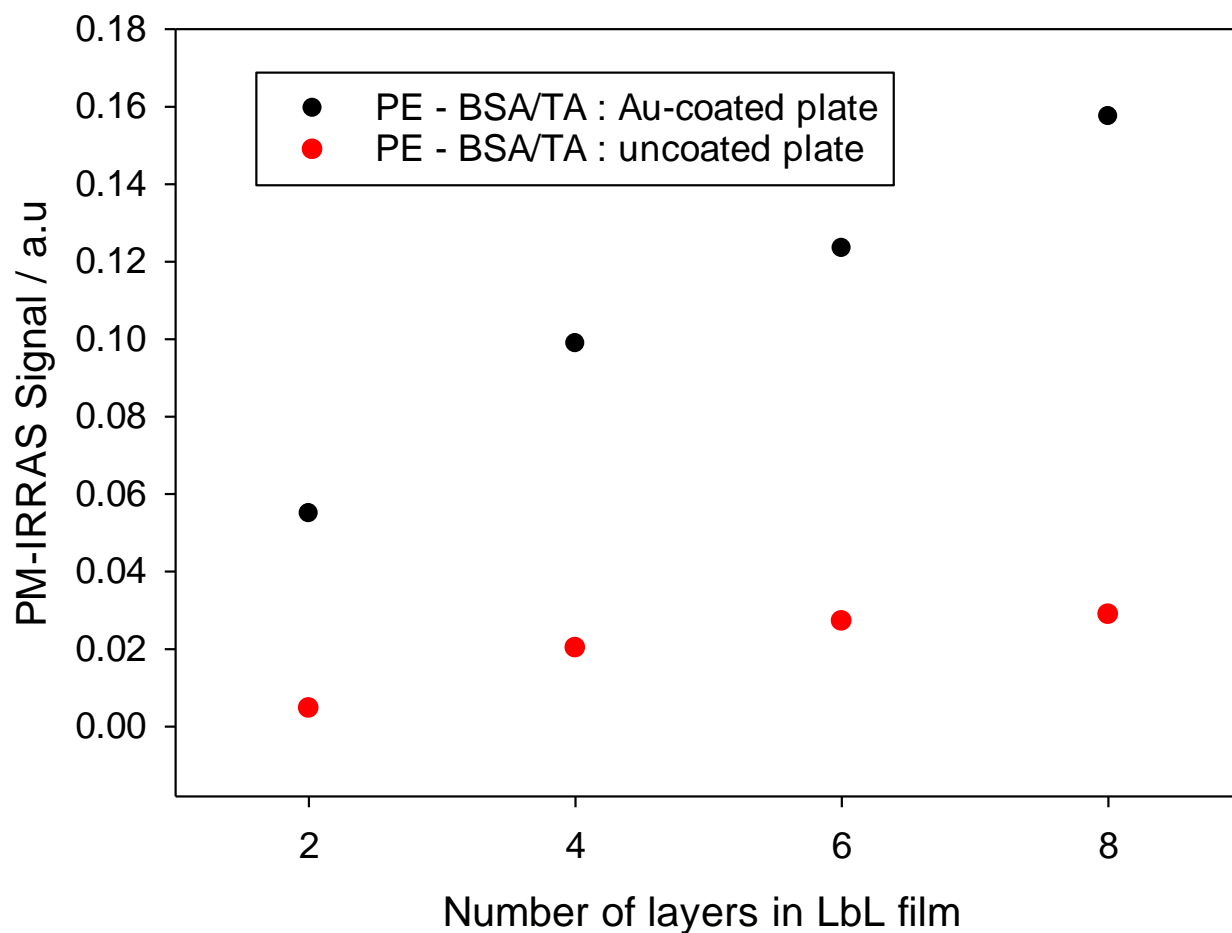


This is a demonstration that some quantity of the active material (BSA/TA) is desorbed when the next layer of chitosan is added. This zig-zag increase may have an impact on the PM-IRRAS spectra reported in the main body of the paper.

**Figure S4:** Procedure to isolate the tannic acid peak from the PM-IRRAS spectrum of a film in the range 1400-1800  $\text{cm}^{-1}$ . This is a film containing six layers: chitosan is used in the odd layers and BSA/TA at a molar ratio  $n(\text{TA})/n(\text{BSA}) = 15$  in the even layers.

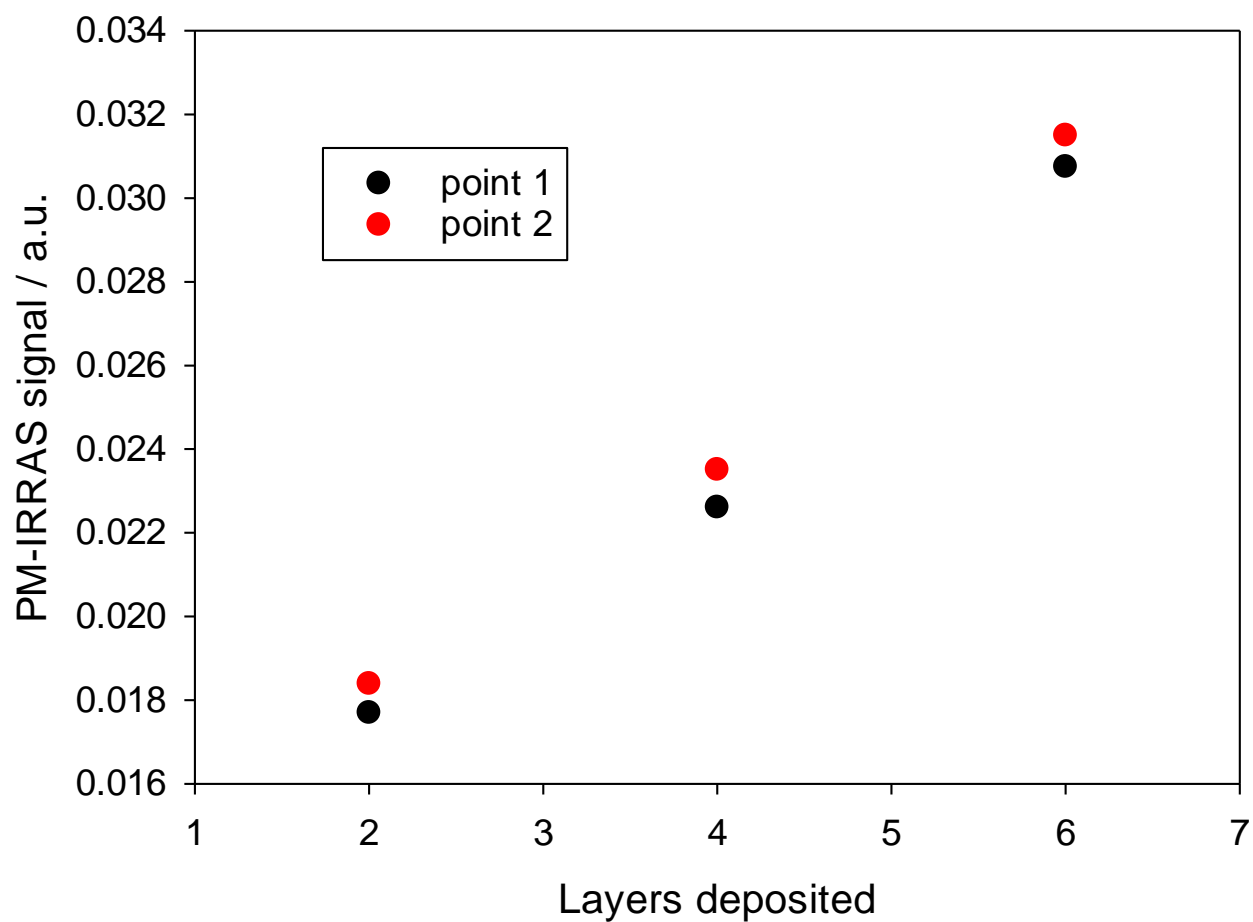


**Figure S5:** Demonstration of the effect of the material of the plate, on which the LbL film of pectin – BSA/TA is deposited, on the PM-IRRAS signal.



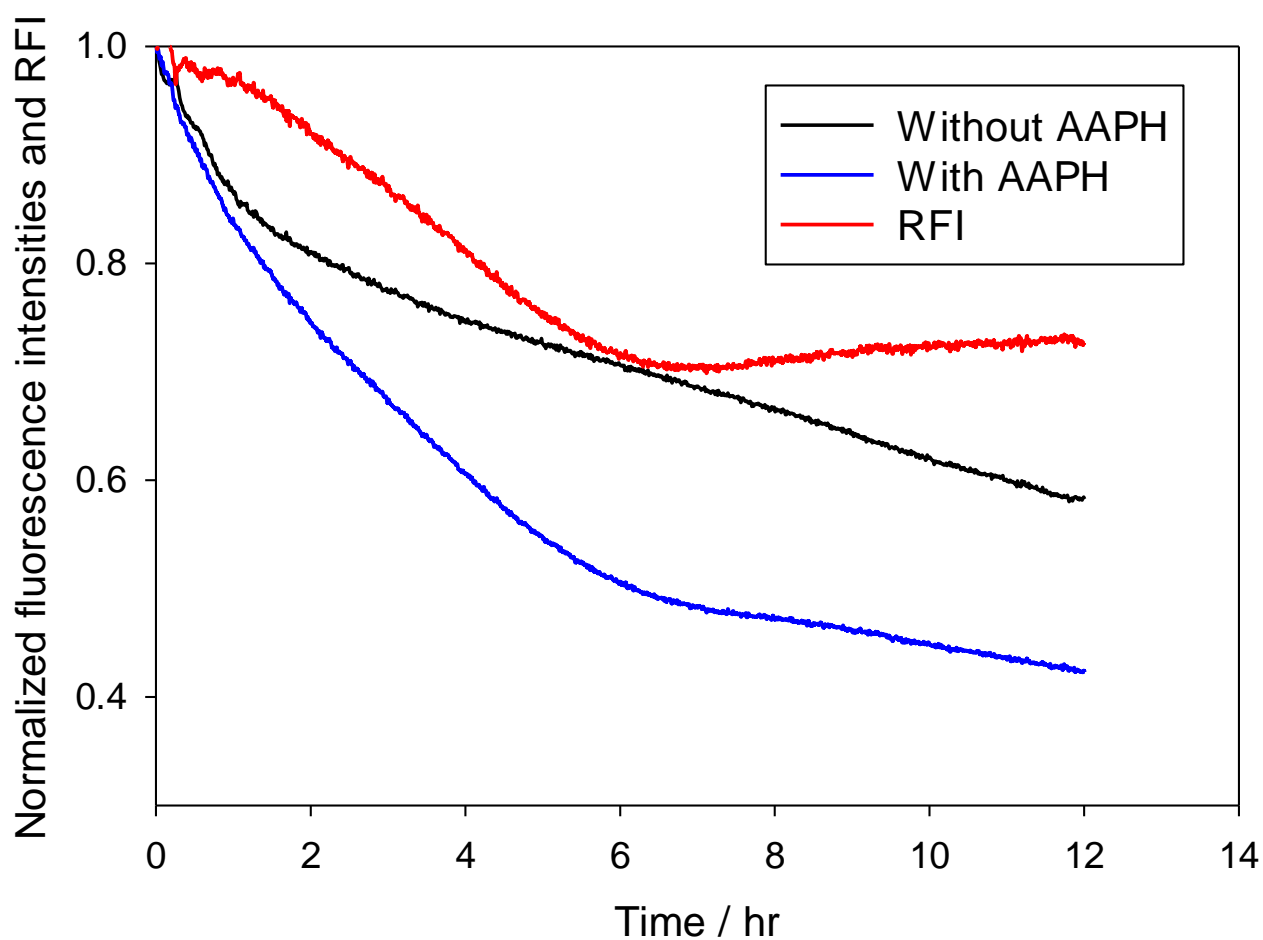
This figure demonstrates that the gold coating on the original steel plate is necessary to render the plate reflective enough, so that a good PM-IRRAS signal is achieved with satisfactory sensitivity.

**Figure S6:** Examination of the homogeneity of deposited LbL films of chitosan – BSA/TA by measuring at two different positions of the plate.



These and related results show that the homogeneity of the LbL films deposited on gold-coated plates is satisfactory.

**Figure S7:** Examination of the temporal fluorescence decay of Nile red solubilized in the linseed-oil cores, in the presence and the absence of the radical generator AAPH. The RFI is the ratio of the two other curves.



The results are from a linseed oil in water emulsion stabilized with a single layer containing BSA and TA such that  $n(\text{TA})/n(\text{BSA}) = 9$ .