

Supporting information to:

**Dual stimuli-responsive coating designed through layer-by-layer assembly of
PAA-b-PNIPAM block copolymers for the control of protein adsorption**

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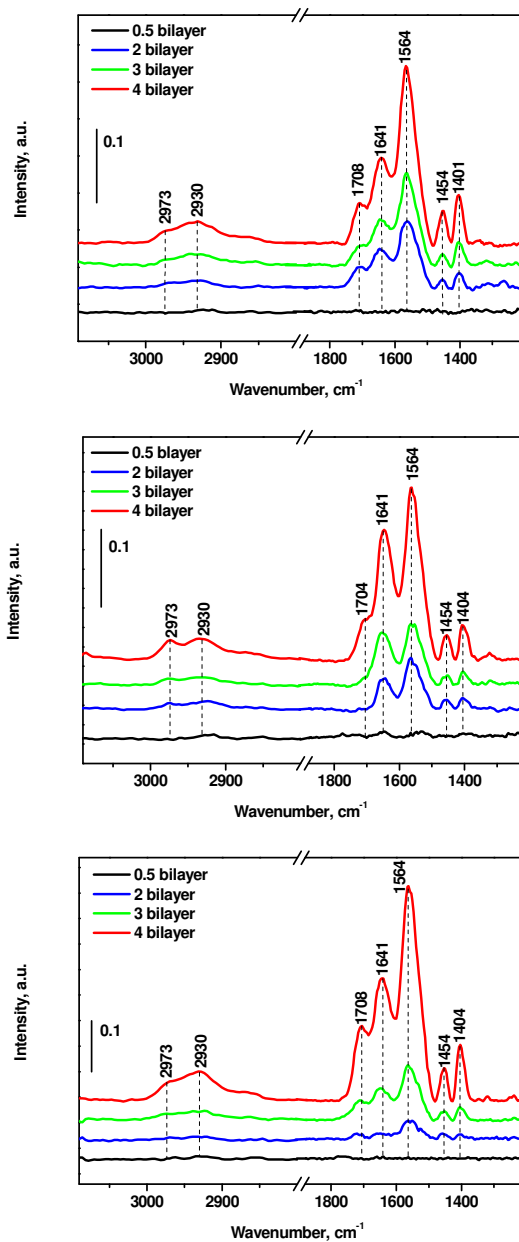


Figure S1. PM-IRRAS spectra recorded on PEMs made of PAH and (from top to bottom) F10, F11 and F22 copolymers.

The degree of ionization of carboxylic groups in PAA chains can be determined using the absorbance of the vibration bands associated with the symmetric and antisymmetric stretching modes of the COO^- moiety at about 1404 and 1546 cm^{-1} , $A_{\text{vs}}(\text{COO}^-)$ and $A_{\text{vas}}(\text{COO}^-)$, respectively, and the absorbance band at 1710 cm^{-1} attributed to $\nu(\text{C}=\text{O})$, as follows:

$$\alpha = \frac{A_{\text{vs}}(\text{COO}^-) + A_{\text{vas}}(\text{COO}^-)}{A_{\text{vs}}(\text{COO}^-) + A_{\text{vas}}(\text{COO}^-) + 1.74 \times A_{\text{v}}(\text{C}=\text{O})} \quad (\text{Eq. 1})$$

where 1.74 is a coefficient taking into account the difference in the absorbance of the three bands.¹

However, in the present study, the band due to antisymmetric stretching of COO^- moiety, $\nu_{\text{as}}(\text{COO}^-)$ is overlapping with amide II band, originating from PNIPAM, and vibrational features of $-\text{NH}_2$ groups from PAH. Thus it could not be exploited for the calculation of α . Moreover, PM-IRRAS bands can be affected by the degree of “disorder” of PEMs, as the configuration used for this technique is sensitive to the orientation of molecules on the plane surface.

For these reasons, only a rough estimation of the fraction of ionized PAA groups can be performed by using a simplified expression as follows:

$$f_{\text{COO}^-} = \frac{A_{\text{vs}}(\text{COO}^-)}{A_{\text{vs}}(\text{COO}^-) + 1.74 \times A_{\text{v}}(\text{C}=\text{O})} \quad (\text{Eq. 2})$$

Table S1. Rough estimation of the fraction of ionized PAA groups (f_{COO^-}) in different polyelectrolyte multilayers

(PEM) calculated using Eq. 2. Standard deviation is presented between brackets.

PEM	f_{COO^-}	
After build-up		
(PAH/F10) ₄	0.30	
(PAH/F11) ₄	0.34 (0.03)	
(PAH/F22) ₄	0.38 (0.02)	
(PAH/PAA) ₄	0.37 (0.06)	
After incubation		
pH ~ 3.9		
	20 °C	50 °C
(PAH/F22) ₄	0.19	0.27
(PAH/PAA) ₄	0.25	0.25
pH ~ 5.7		
	20 °C	50 °C
(PAH/F22) ₄	0.40	0.37
(PAH/PAA) ₄	0.34	0.37
pH ~ 8.1		
	20 °C	50 °C
(PAH/F22) ₄	0.67	0.56
(PAH/PAA) ₄	0.57	0.63

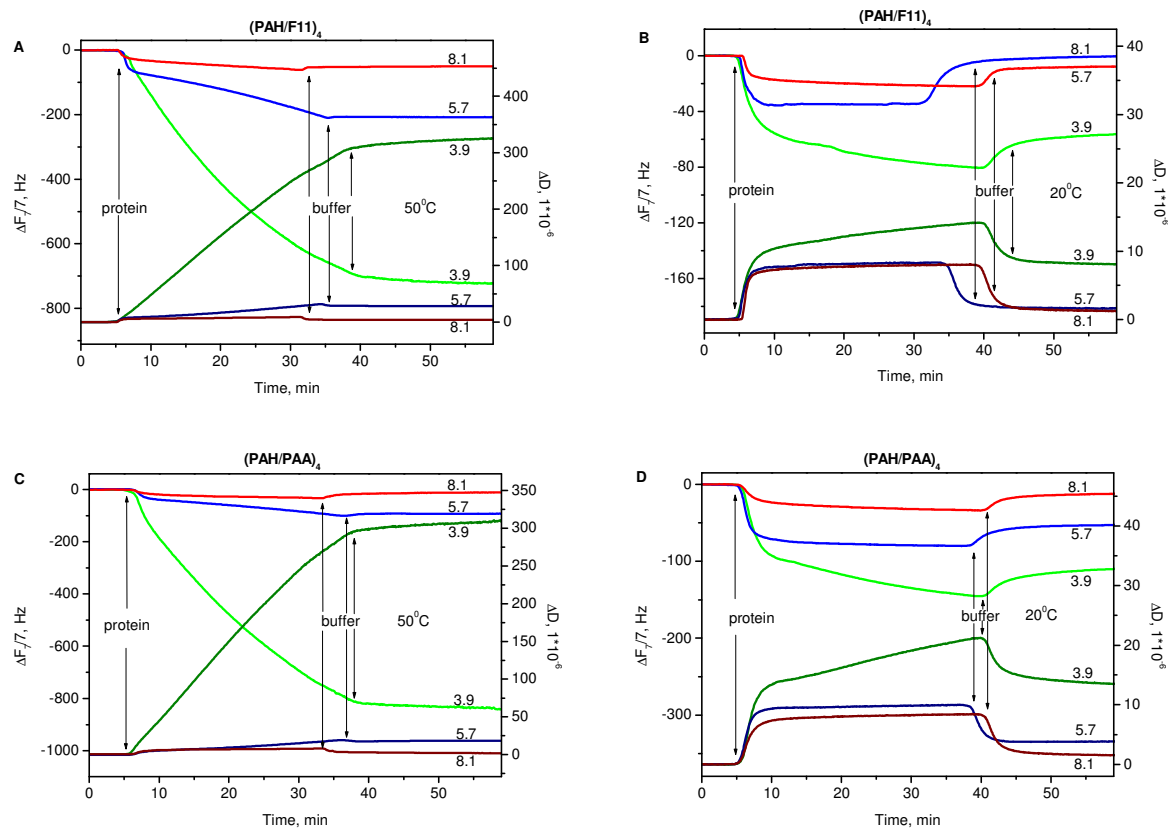


Figure S2. Representative QCM-D measurements showing frequency changes in the 7th overtone and the corresponding dissipation vs time during the adsorption of ovalbumin (25 mg ml⁻¹) on (PAH-F11)₄ (A and B) and (PAH-PAA)₄ (C and D). Protein adsorption was performed in acetate buffer adjusted at acidic (pH~3.9) or basic (pH~8.1) conditions, either at 20 or 50^oC, as indicated.

Reference

1. M. Muller, M. Brissova, T. Rieser, A. C. Powers and K. Lunkwitz, *Mater. Sci. Eng., C* 1999, **8-9**, 163.