

# Unexpected enhancement of pH-Stability in $\text{Au}^{3+}/\text{Ag}^+$ loaded H-bonded Layer-by-Layer thin films.

Nicolás Pomeraniec Altieri<sup>1</sup>, Lucy L. Coria-Oriundo<sup>1</sup>, Paula C. Angelomé<sup>2</sup>, Fernando Battaglini<sup>1</sup>, María Luz Martínez Ricci<sup>1\*</sup>, Lucila P. Méndez De Leo<sup>1\*</sup>

<sup>1</sup>Instituto de Química Física de los Materiales, Medio Ambiente y Energía (INQUIMAE – CONICET) Facultad de Ciencias Exactas y Naturales Universidad de Buenos Aires Intendente Guiraldes S/N – 1er piso, Buenos Aires, Argentina.

<sup>2</sup>Gerencia Química & Instituto de Nanociencia y Nanotecnología, Centro Atómico Constituyentes, CNEA, CONICET, Av. Gral. Paz 1499, 1650 San Martín, Buenos Aires, Argentina

E-mail: mricci@qi.fcen.uba.ar

lucilamdl@qi.fcen.uba.ar

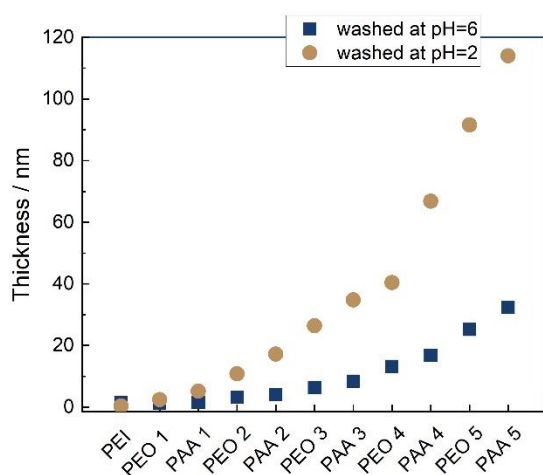


Figure S 1: Ellipsometric thickness as a function of the adsorbed layers for the deposition of a PAA/PEO film from pH 2 solutions. The substrate was a Au surface coated with a single PEI, poly(ethylene imine)adhesion layer. Blue squares: washed at pH=6, brown circles: washed at pH=2.

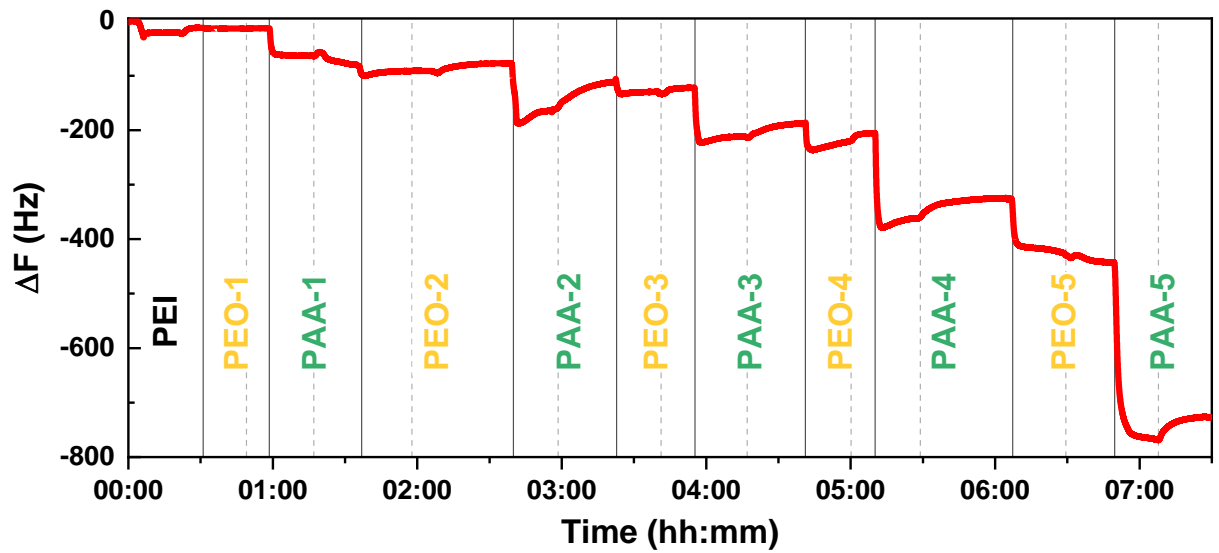


Figure S 2: Frequency change ( $\Delta F$ ) vs. time for each layer of the PEO/PAA assembly washing with water at pH 2.

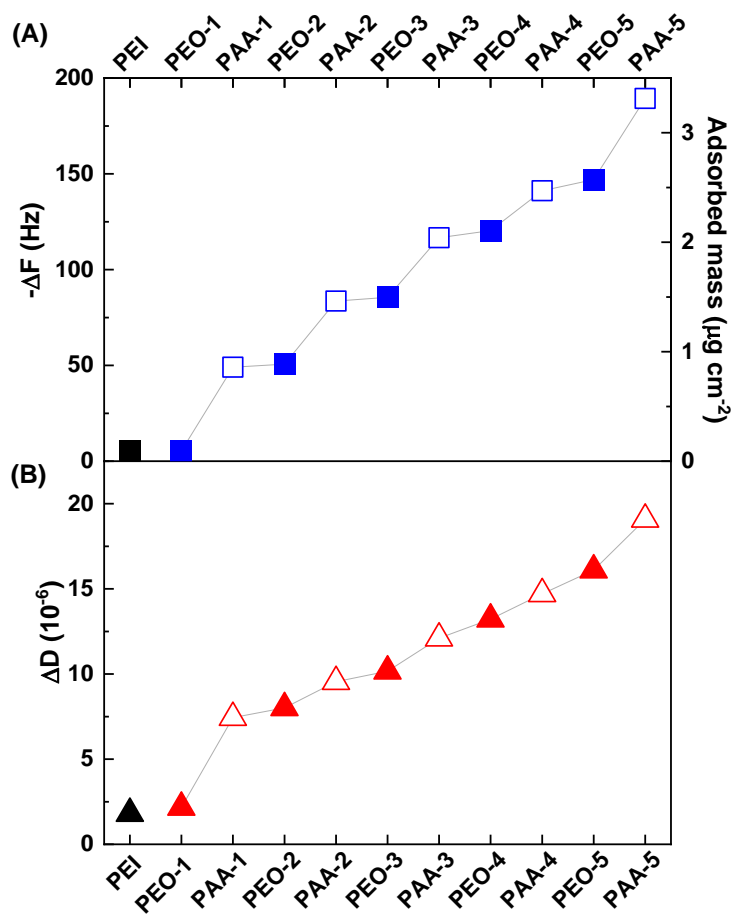


Figure S 3: (A) Frequency change ( $\Delta F$ ), adsorbed mass change ( $\Delta m$ ) and (B) dissipation change ( $\Delta D$ ) for each layer of the PEO/PAA assembly washing with water at pH 6.

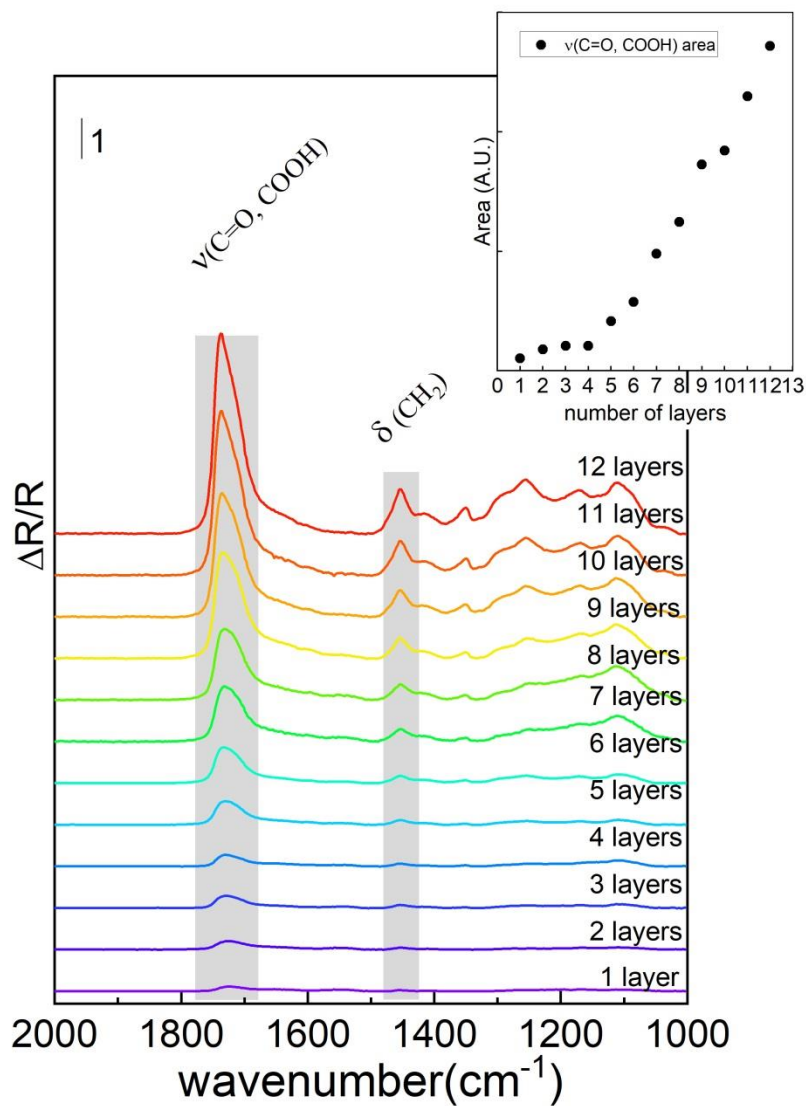


Figure S 4: (A) PMIRRAS spectra of films (prepared washing with water at pH=6) with increasing number of layers. Inset: Area of C=O stretching peak of -COOH

Table S 1: Thickness change for each bilayer for the PEO/PAA assembly washing with water at pH 2 or pH 6, according to what was measured by QCM-D

Layer	$\Delta \delta$ (nm)	
	pH 2	pH 6
PEO-1	0.1	0.1
PAA-1	9.5	6.1
PEO-2	-0.4	0.2
PAA-2	4.6	4.3
PEO-3	1.7	0.3
PAA-3	8.8	4.2

PEO-4	2.8	1.0
PAA-4	16.3	2.8
PEO-5	18.0	0.9
PAA-5	38.3	5.6
<b>Total</b>	<b>99.7</b>	<b>25.5</b>

Table S 2 Mass adsorbed change ( $\Delta F$ ), dissipation change ( $\Delta D$ ) and relative dissipation change ( $-\Delta D/\Delta F$ ) for each layer, and mass adsorbed ratio ( $\Delta m_{PAA}/\Delta m_{PEO}$ ) for bilayer for the PEO/PAA assembly washing with water at pH 6.

Layer	$\Delta m$ ( $\mu\text{g cm}^{-2}$ )	$\Delta D$ ( $10^{-6}$ )	$-\Delta D/\Delta F$ ( $10^{-6} \text{ Hz}^{-1}$ )	$\frac{\Delta m_{PAA}}{\Delta m_{PEO}}$
PEO-1	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
PAA-1	0.773	5.28	0.12	<i>nd</i>
PEO-2	0.028	0.57	0.36	20.8
PAA-2	0.583	1.54	0.05	
PEO-3	0.035	0.62	0.31	15.9
PAA-3	0.550	1.94	0.06	
PEO-4	0.066	1.12	0.30	5.6
PAA-4	0.369	1.48	0.07	
PEO-5	0.103	1.40	0.24	7.3
PAA-5	0.750	2.98	0.07	
Total PEO	0.233			
Total PAA	3.025			
Total	3.258			

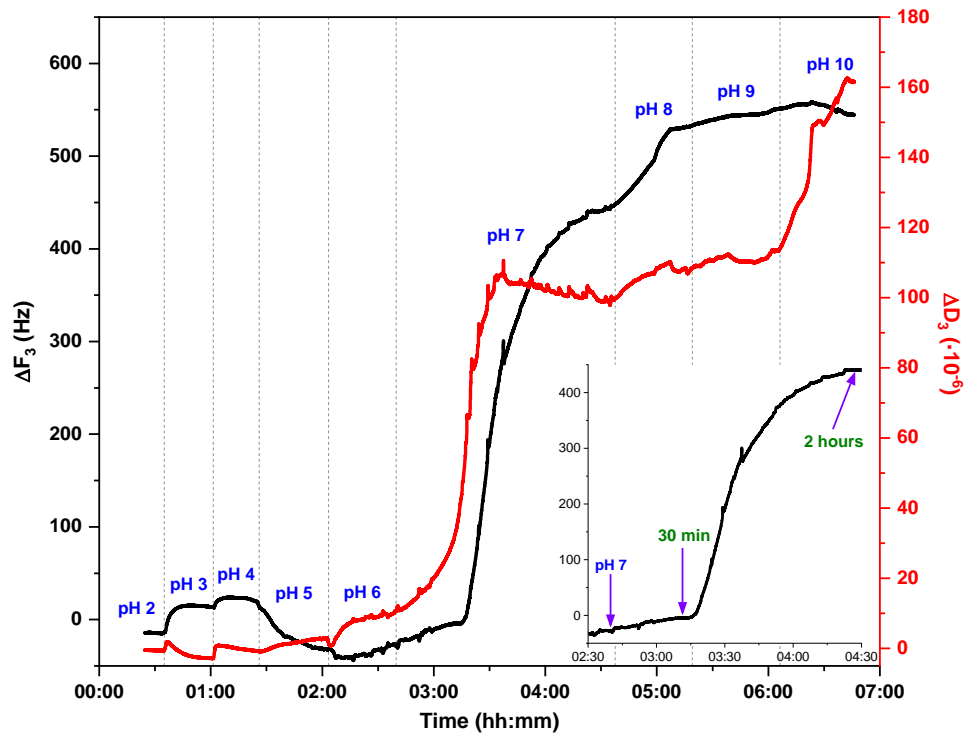


Figure S 5: Frequency and Dissipation versus time for the exposition at different pHs for the assembly built rinsed with water at pH 2. Inset graph shows the frequency change after 30 minutes or 2 hours (up to signal stabilization) of exposition to pH 7.

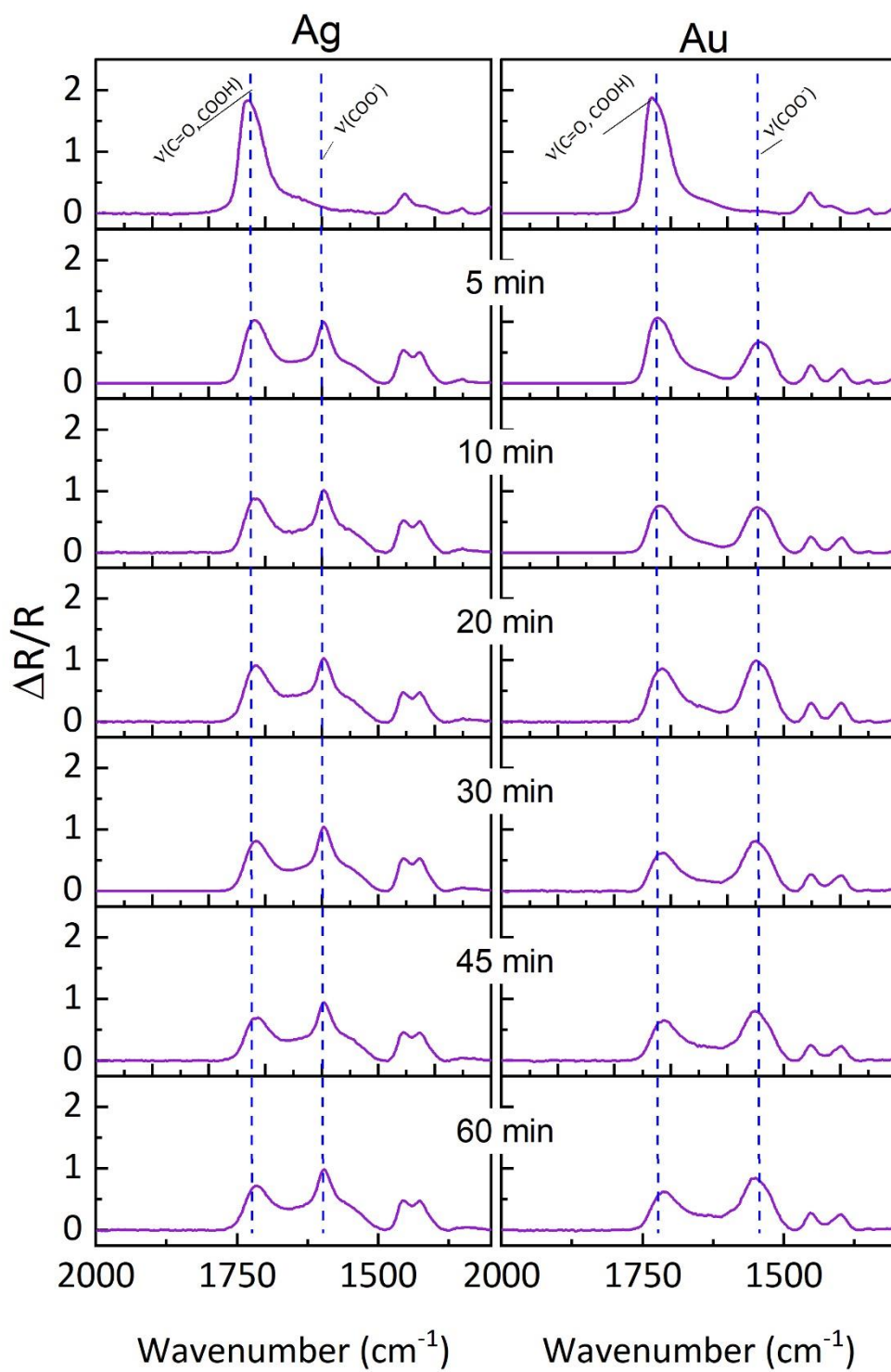


Figure S 6: PMIRRA Spectra of films after increasing times immersed in 0.5 mM metal solution. Left panel: Ag, Right panel: Au

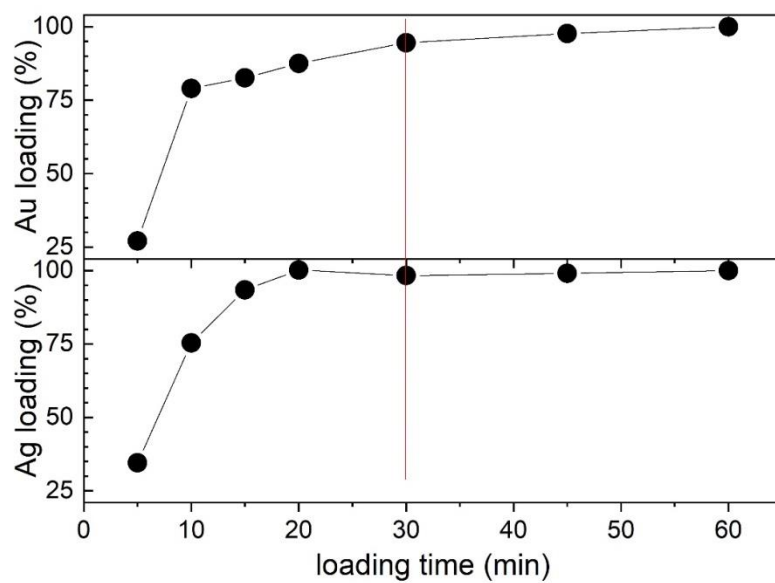


Figure S 7: Percentage of the area of the carboxylate peak / maximum area of the carboxylate peak vs time. Upper panel: film immersed in Au solution, Lower panel: Film immersed in Ag solution

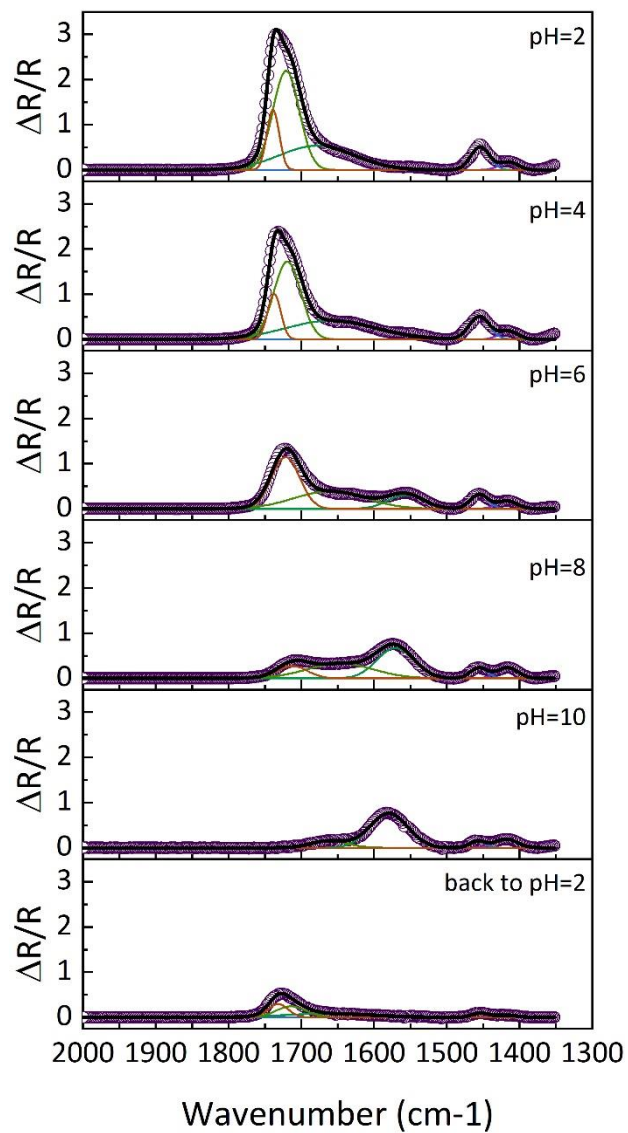


Figure S 8: PMIRRA spectra of LBL films at different pH fitted by 5 gaussians



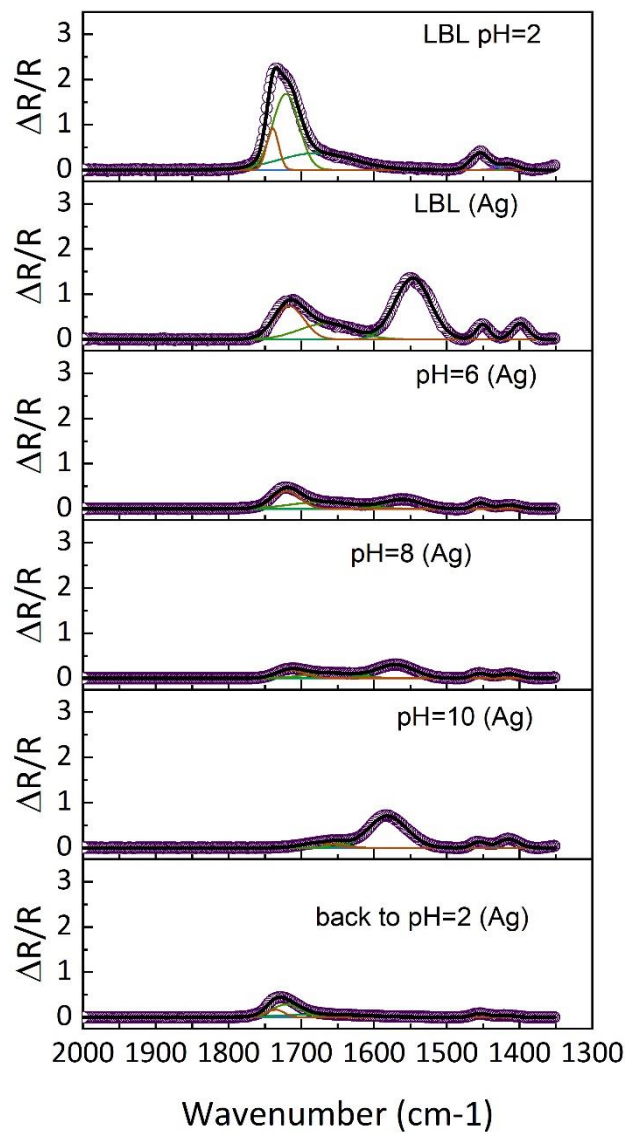


Figure S 9: PMIRRAS spectra of LBL films immersed for 30 minutes in Ag solution at different pH fitted by 5 gaussians

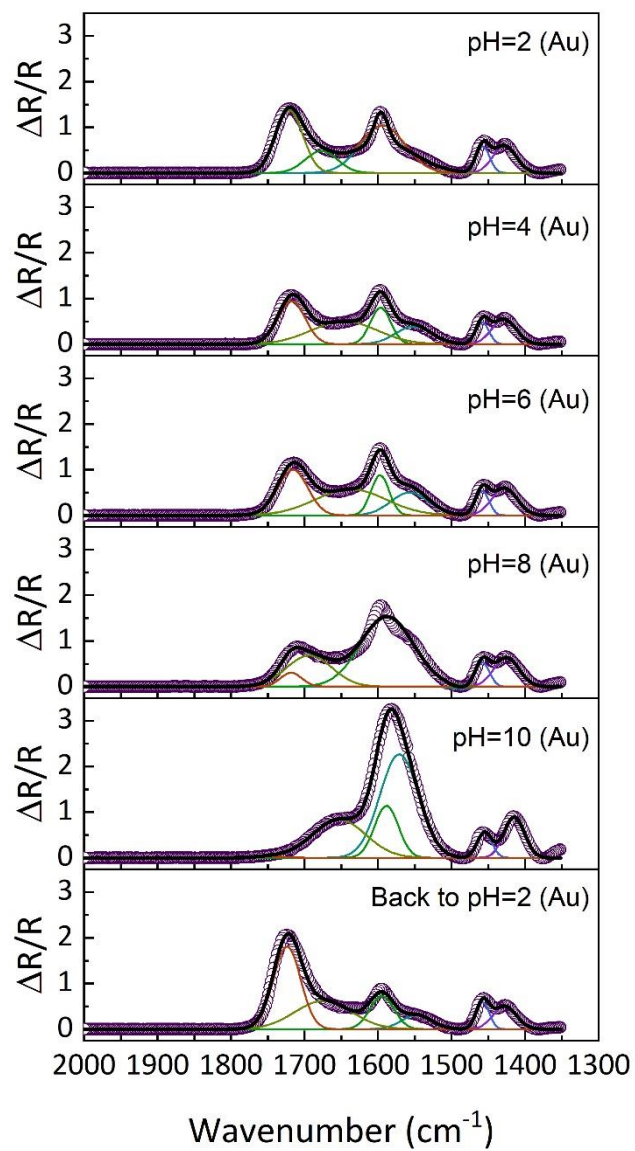


Figure S 10: PMIRRAS spectra of LBL films immersed for 30 minutes in Au solution at different pH fitted by 5 gaussians

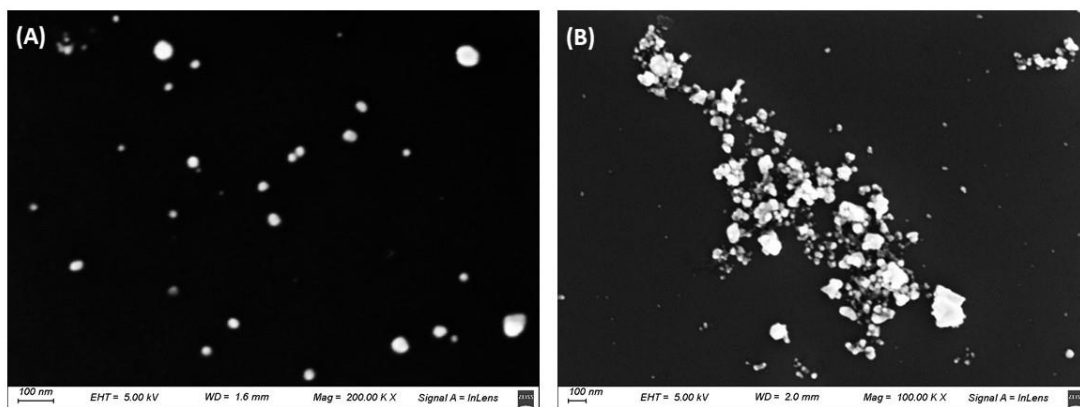


Figure S 11: SEM images of 5 LBL samples loaded with ions and treated with  $\text{NaBH}_4$  (10 M) (A)  $(\text{PEO-PAA})_5$  – 5 cycles Au samples, (B)  $(\text{PEO-PAA})_5$  – 5 cycles Ag sample.