Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information for:

The Effect of Nanoparticle Location and Shape on the Thermal Transitions Observed in Hydrated Layer-by-Layer Assemblies

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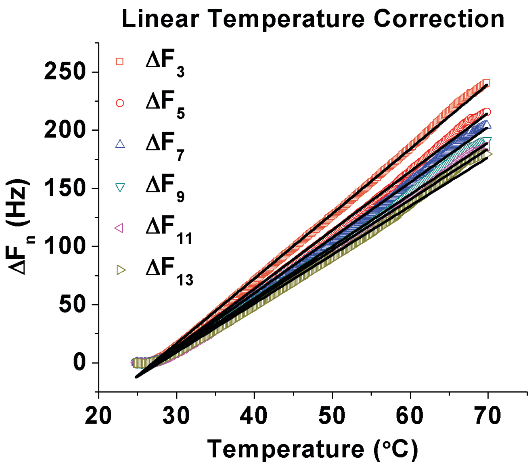

Figure S1. Linear temperature correction used for all frequency data. This correction was generated by fitting a linear trend line to the average of five separate bare crystal measurements. A bare crystal experiment consisted of flowing water with 0.5 M NaCl over a bare quartz QCM-D crystal while ramping from 25 to 70 °C. Colored points refer to data and the black line is the linear fit.

Table S1. Fitted Parameters for the Linear Temperature Correction of ΔF

	3rd	*5th*	*7th*	*9th*	*11th*	*13th*
m	5.57483	5.0355	4.7652	4.46392	4.34358	4.18887
b	-150.46108	-137.56887	-130.70455	-123.13058	-120.07559	-116.48175
R^2	0.99742	0.99617	0.99546	0.99467	0.99424	0.99345

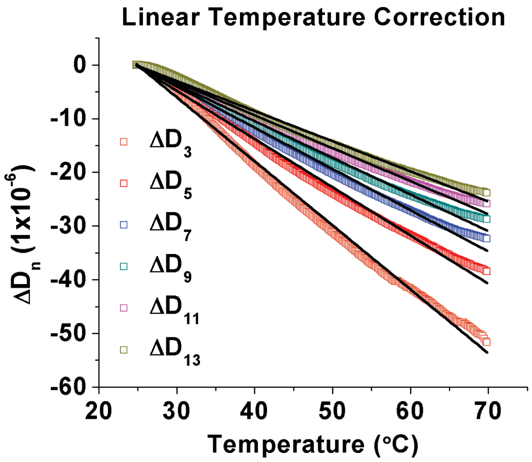

Figure S2. Linear temperature correction used for all dissipation data. This correction was generated by fitting a linear trend line to the average of five separate bare crystal measurements. A bare crystal experiment consisted of flowing water with 0.5 M NaCl over a bare quartz QCM-D crystal while ramping from 25 to 70 °C. Colored points refer to data and the black line is the linear fit.

Table S2. Fitted Parameters for the Linear Temperature Correction of ΔD

	3rd	*5th*	*7th*	*9th*	*11th*	*13th*
m	-1.19263	-0.89875	-0.76839	-0.68276	-0.61342	-0.5617
b	29.75383	22.16815	19.06106	16.85143	15.17946	13.88901
R^2	0.99519	0.9942	0.99413	0.99349	0.99399	0.99402

Table S3. Fitted Parameters Used for Extended Voigt Modeling

Parameters to Fit:	*Minimum*	*Maximum*	*Step (Iterations)*
L1 Viscosity (kg m^{-1} s^{-1})	0.0001	0.01	50
L1 Shear (Pa)	100	1E12	21
L1 Thickness (m)	9.5238E-11	1E-6	21
L1 Viscosity Frequency	-2	0	10
L1 Shear Frequency	0	2	10

Note: The fixed parameters utilized for these models were: fluid density (kg m^{-3}) of 1000, fluid viscosity (kg m^{-1} s^{-1}) of 0.001, and L1 density (kg m^{-3}) of 1100.

Extended Voigt Model Equations:

The application of the extended Voigt model is described very well by Sun *et al.* (*Macromolecules* 2014, *ASAP,* http://dx.doi.org/10.1021/la500716d). The standard Voigt model assumes a frequency-independent shear elastic modulus and viscosity. The extended Voigt model allows for the shear elastic modulus and viscosity to vary with thickness according to Eqns. 1 and 2. f_o Is the fundamental frequency (5 MHz), G_n' is the shear modulus for overtone *n*, and similarly for shear viscosity η.

$$G_n' = G_0' \left(\frac{f_n}{f_0}\right)^{\alpha'} \tag{1}$$

where G_0’ equals L1 Shear, f_n/f_0 is approximately equal to the nth overtone, and α’ equals the L1 Shear Frequency.

$$\eta_n = \eta_0 \left(\frac{f_n}{f_0}\right)^{\alpha^{\eta}} \tag{2}$$

where η_0’ equals L1 Viscosity, f_n/f_0 is approximately equal to the nth overtone, and $\alpha^{\eta'}$ equals the L1 Viscosity Frequency.

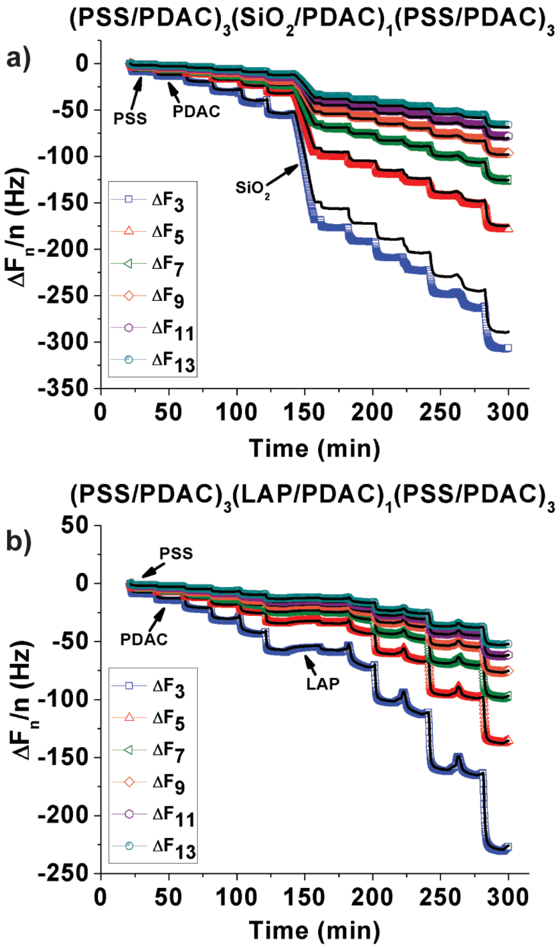

Figure S3. Raw (ΔF_3 = blue, ΔF_5= red, ΔF_7 = green, ΔF_9 = orange, ΔF_{11} = purple, and ΔF_{13} = turquoise) and fitted (black lines) frequency data for PDAC/PSS films incorporating a) SiO_2 and b) LAP. This figure serves to illustrate the abrupt change in film properties following the adsorption of the nanoparticle layer.

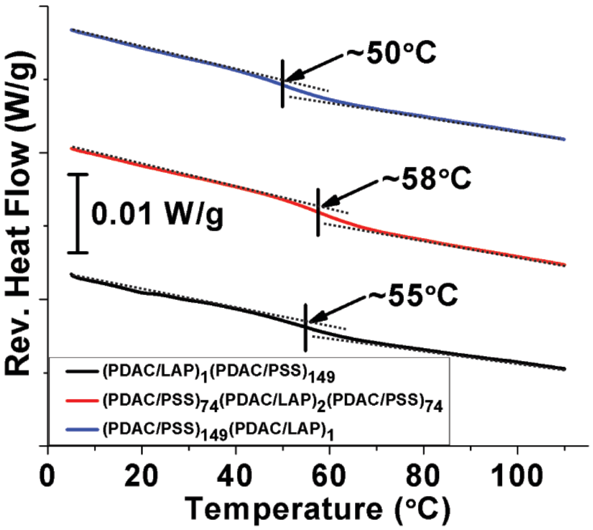

Figure S4. Reversing heat flow for $(PDAC/LAP)_1(PDAC/PSS)_{149}$ (black line), $(PDAC/PSS)_{74}(PDAC/LAP)_2(PDAC/PSS)_{74}$ (red line), and $(PDAC/PSS)_{149}(PDAC/LAP)_1$ (blue line) films obtained via MDSC.