

Supporting Information

Use of catechol-modified polymers in Layer-by-Layer assembly to enhance its stability and sustained release of biomolecules:

A bio-inspired approach

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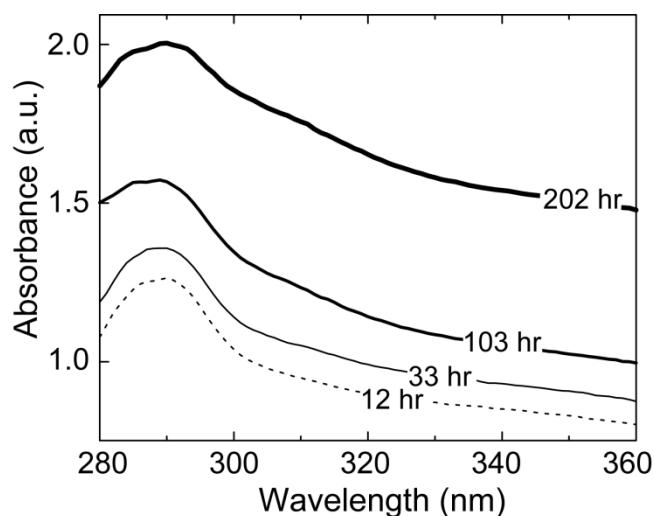


Figure S1. Compilation of UV-vis absorbance spectra of $(\text{LPEI}/\text{SPS})_{10}$ - $(\text{Poly}1/^{14}\text{C-DS})_{20}$ - $(\text{BPEIC}/\text{PAAC})_{25}$ films at different incubation times in PBS pH 7.4 at 37°C. The overall increase in UV-Vis intensity indicates a temporal increase in the degree of crosslinking¹ by the formation of various types of covalent bonds.²⁻⁵

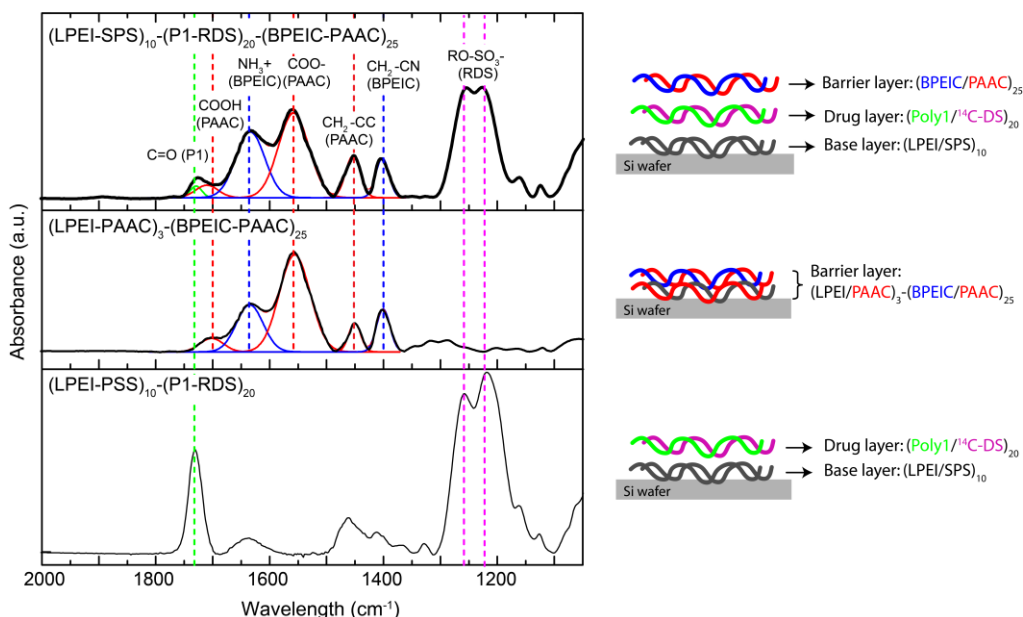


Figure S2. FTIR spectra of $(\text{LPEI/SPS})_{10}$ - $(\text{Poly}1/^{14}\text{C-DS})_{20}$ - $(\text{BPEIC/PAAC})_{25}$ in the top panel; $(\text{LPEI/PAAC})_3$ - $(\text{BPEIC/PAAC})_{25}$ in the middle panel; and $(\text{LPEI/SPS})_{10}$ - $(\text{Poly}1/^{14}\text{C-DS})_{20}$ in the bottom panel. The spectra in the bottom panel show two significant peaks such as C=O stretching bonds from Poly 1 at $\nu=1740\text{ cm}^{-1}$ ⁶ and the asymmetric stretching of the S=O from dextran sulfate between $\nu=1250$ and 1200 cm^{-1} ⁷. The middle panel shows the FTIR spectra of the barrier layer, consisting of BPEIC and PAAC. For this barrier layer, three distinct peaks such as two types of carboxylates and CH_2 deformation at $\nu=1450\text{ cm}^{-1}$ ⁸ are observed, indicative of the presence of PAAC. In addition, the peaks from the amine functional groups and CH_2 groups in BPEIC clearly appear at $\nu=1640\text{ cm}^{-1}$ and $\nu=1400\text{ cm}^{-1}$ respectively. As shown in the top panel, the spectra of LbL films consisting of these three layers clearly suggest that the individual components from base, drug, and barrier layers are successfully embedded into the films during entire buildup process and therefore must be internal parts.

To determine the effect of the catechol modification on the overall interactions between polymer layers, we compared the relative magnitudes of hydrogen bond interactions, π - π stacking, and Coulomb interactions. Typically, hydrogen bond and π - π stacking interactions have similar strengths of several $k_B T$.⁹ In salt-containing aqueous medium, the screened Coulomb interaction potential, $U_{+/-}$, for one pair of two oppositely charged ions is given by:¹⁰⁻¹²

$$U_{+/-} = \frac{e^2}{4\pi\epsilon_0\epsilon_w} \frac{\exp(-\kappa d_{+/-})}{d_{+/-}}, \quad d_{+/-} \geq R_+ + R_-, \quad (\text{S1})$$

where R_+ and R_- denote the radii of positively or negatively charged points respectively, ϵ_0 is the permittivity of vacuum, ϵ_w is the relative permittivity of interfacial or trapped water (≈ 40)¹³, and $d_{+/-}$ is the distance between the centers of two oppositely charged points. The overall interaction potential is destined to be screened out in the presence of salts as described by the definition of κ , denoting the inverse Debye screening length given by:⁹

$$\kappa = \sqrt{\frac{\sum_i \rho_i e^2 z_i}{\epsilon_0 \epsilon_w k_B T}} \quad (\text{S2})$$

where z_i denotes the valence of the ions of type i (either positive or negative) carrying an electronic charge e , ρ_i is the number density of the ions, k_B is Boltzmann's constant, and T is the temperature. The magnitude of the Debye screening length depends solely on the properties of the liquid and not on any surface properties of the polyelectrolyte layers, such as their charges or potentials. At the molecular level, within LbL films, the Coulomb interaction potential arises and depends on the center-to-center distance between two oppositely charged points, which falls off as $d_{+/-}$ increases. For example, as shown in Figure S3, the $U_{+/-}$ is calculated as less than $1.5 k_B T$ even at molecular level of contact ($d_{+/-} = 0.5 \text{ nm}$)¹² when $\sim 0.8 \text{ nm}$ of the Debye screening length

is used in the presence of 0.138 M NaCl. In essence, when any of Coulomb pairs are replaced by hydrogen bond and/or π - π stacking interactions via the catechol modification, the overall attraction increases, thereby resulting in improving the film stability in solution (See Figure 3-5).

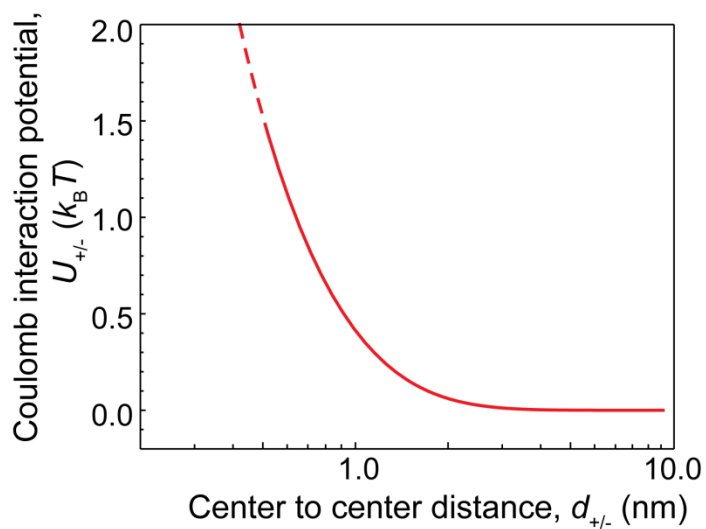


Figure S3. Calculated Coulomb interaction potential for one pair of two oppositely charged ions as a function of center to center separation.

References

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