Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Bacterial Lipopolysaccharides Form Physically Cross-Linked, Two-Dimensional Gels in the Presence of Divalent Cations

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1.) Viscous behavior of LPS Re monolayers on Ca^{2+}-free subphase

The Newtonian behavior of the LPS Re monolayer on a Ca^{2+}-free subphase even in a highly compressed state was confirmed by measuring G" at 133 Å^2 over a wide frequency regime (19 – 82 rad/s). As seen in Fig. S1, G'' exhibits a linear frequency dependence corresponding to a frequency-independent value of the surface shear viscosity η =G''/ω.

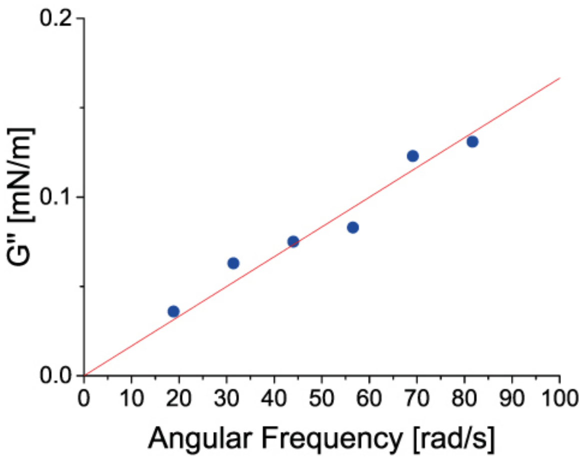

Fig S1: Viscous modulus G'' of LPS Re monolayer compressed to 133 Å^2 per molecule on **Ca^{2+}-free subphase**

2.) Amplitude-dependence of G' for viscoelastic monolayers of LPS Re and LPS Ra

The dependence of G' on the shear amplitude was measured for all conditions exhibiting viscoelastic behavior, namely for compressed monolayers of LPS Re on Ca^{2+}-loaded subphase (Fig. S2), LPS Ra on Ca^{2+}-free subphase (Fig. S3), and LPS Ra on Ca^{2+}-loaded subphase (Fig. S4). The area per molecule was 127 Å^2, 172 Å^2, and 132 Å^2, respectively. It is seen that, in all cases, G' is only mildly dependent on the shear amplitude up to the largest amplitude applied (10 mRad), which is ten times larger than the one applied in the measurements described in the main text (1 mRad). This result confirms that an amplitude of 1 mRad is well covered by the linear response regime.

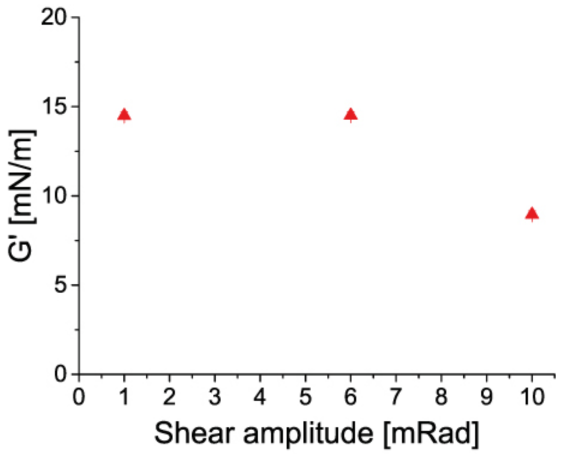

Fig S2: Elastic modulus G′ of **LPS Re** monolayer compressed to 127 Å^2 per molecule on **Ca^{2+}-loaded** subphase

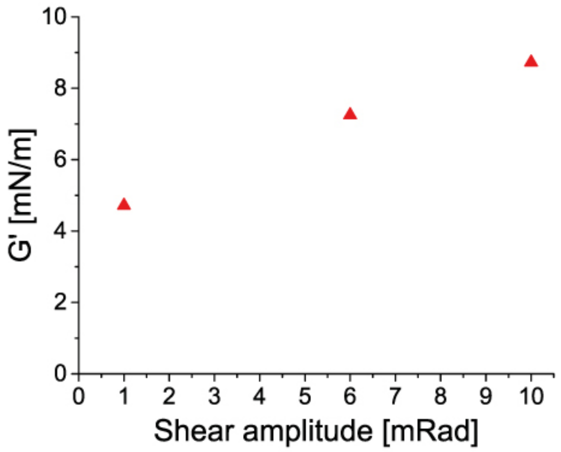

Fig S3: Elastic modulus G′ of **LPS Ra** monolayer compressed to 172 Å^2 per molecule on **Ca^{2+}-free** subphase

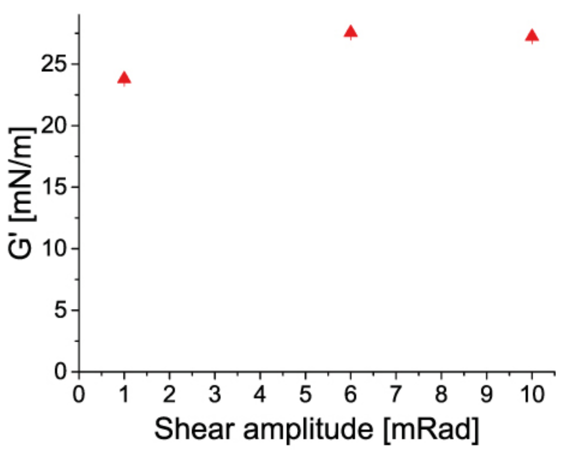

Fig S4: Elastic modulus G′ of **LPS Ra** monolayer compressed to 132 Å^2 per molecule on **Ca^{2+}-loaded** subphase

3.) Physical explanation for the occurrence of slightly negative measurement values of G'

The Camtel rheometer CIR 100 employs the technique of normalized resonance, which can lead to the occurrence of unphysical negative values for G'. The rheometer is a DuNouy ring attached to a galvanometer, which rotates around an axis perpendicular to the water surface. Hence the system can be described as a driven damped harmonic torsional oscillation with the common differential equation:

$$T(t) = T_0 e^{i\omega t} = I\ddot{\omega} + D\dot{\omega} + K\omega,$$

where *I* is the inertia, *D* is the damping constant and *K* the torsion wire constant of the system. As explained also in the instrument manual of the CIR 100, inertia is in phase with the elastic constant of the system and contributes with a negative sign. The electronic controller of the rheometer regulates the damping and elastic constants in a manner that the system is in resonance conditions at any measured frequency. Since the damping and elastic contributions from the system are known, one can calculate G' and G'' under the assumption that all system parameters including inertia are constant. In the case a purely viscous film adsorbs to the DuNouy ring, it increases the system's inertia, resulting in the calculation of a negative contribution to the elastic modulus G'.