Supplementary Information

Structure and dynamics of hagfish mucins in different saline environments

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The Supplementary Information contains information on

Section S1: Cryo-SEM of mucin vesicles

Compiled cryo-SEM images of mucin vesicles are shown in Figure S1. The scale bar in all images is 1 μm.

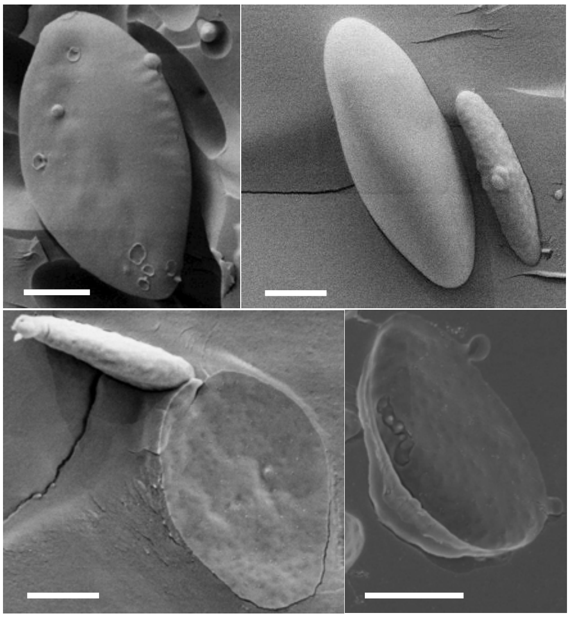

Figure S1. Compiles cryo-SEM images of mucin vesicles (scale bar in all image is 1 μm).

Section S2: Dynamic Light Scattering (DLS)

Compiled data on diffusion dynamics and total scattering intensity of mucin solutions as shown in Figure S2 and S3.

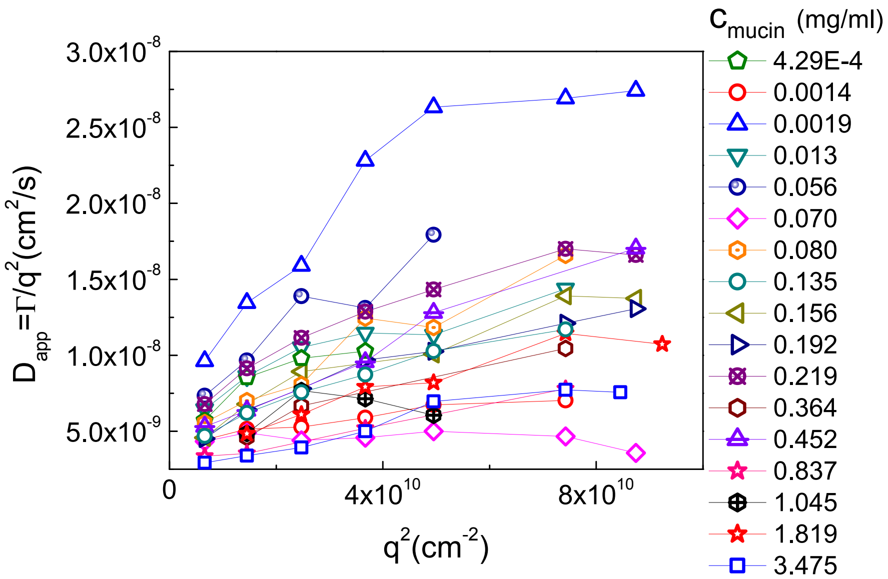

Figure S2. Apparent diffusion coefficient D_{app} as a function of q^2 for all measured mucin concentrations. All data exhibit a dependence of q^2, conforming to large sizes and possible aggregates.

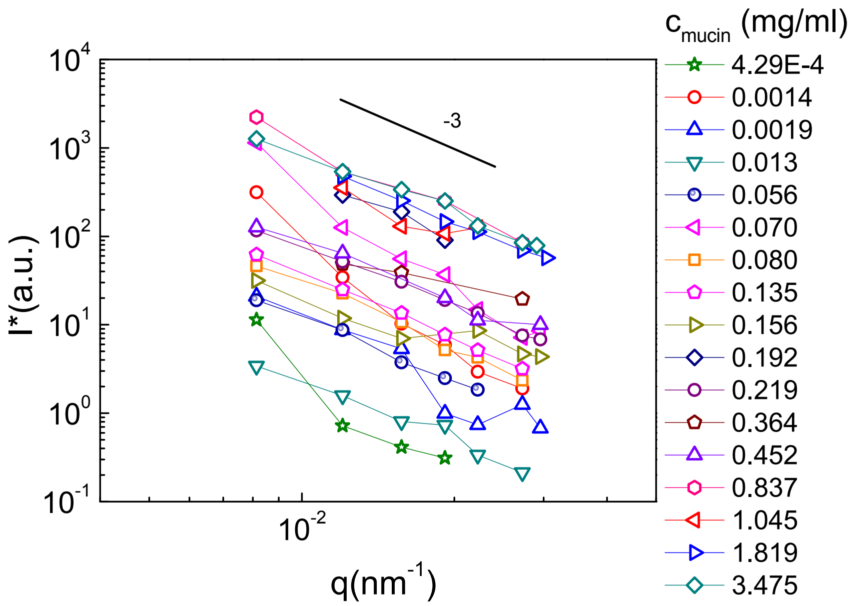

Figure S3. Dynamic total scattering intensities I as a function of the scattering wave vector q for all measured mucin concentrations. Whereas the limited range of q values does not allow extracting an unambiguous power-law, the line with slope of - 3 is added as an interesting observation.*

Section S3: Intensity at q→0

In order to estimate the value of the intensity at zero-q, we used the Debye plot [1], which is depicted in Figure S3. In particular, we plot $1/I^{0.5}$ against q^2 for concentration of c_{mucin} = 0.08 mg/ml as an example: The same procedure is performed for all the concentrations but not shown. The equation of $1/I^{0.5} = aq^2 + b$ provides information about I_o and correlation length ξ. More precisely, $\xi = (a/b)^{0.5}$ and $I_o = 1/b^2$, where a is the slope and b is the intercept (b = 0.2).

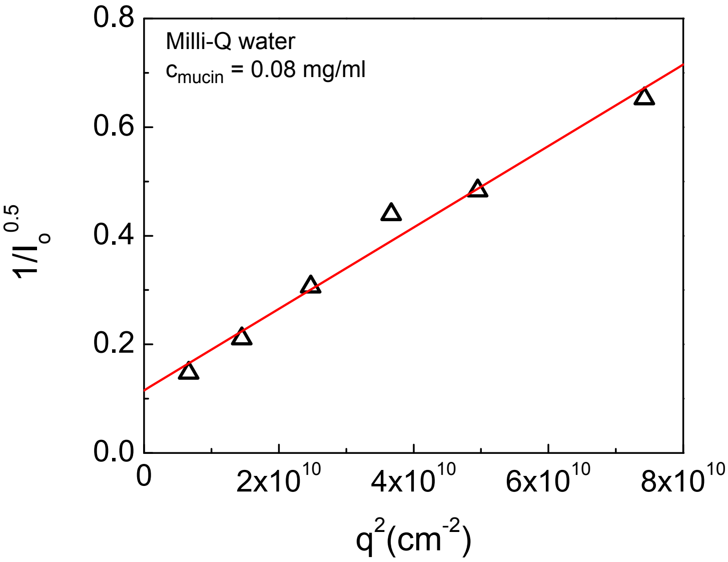

Figure S4. Debye plot, the inverse of the square root of the scattering intensity as a function of q^2 for mucin concentration of c_{mucin} = 0.08 mg/ml.

A clear concentration dependence was also followed by the intensity as shown in Figure S4. We plot the reduced intensity, i.e., the intensity when q → 0 over the concentration, against mucin concentration. At low and intermediate concentrations, the intensity is independent of concentration, but at c_e = 0.2 mg/ml it decreases. This cross-over concentration which corresponds to the entanglement concentration c_e is very well in agreement for both dynamic (diffusion coefficient D_{eff} in Figure 5) and static properties (intensity in Figure S4).

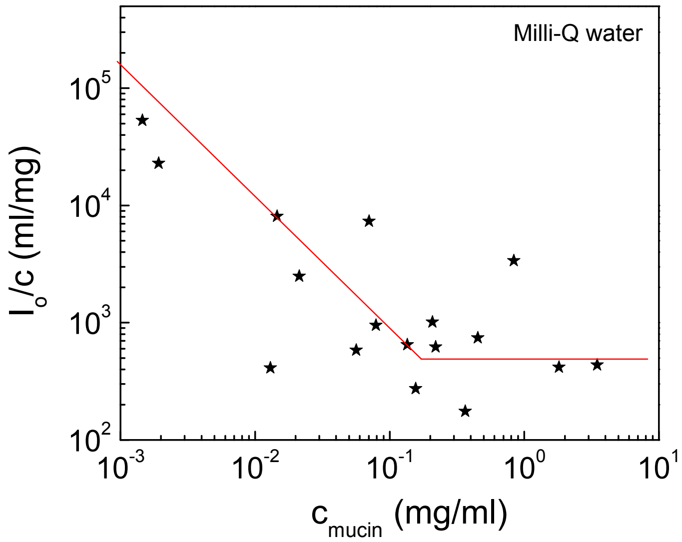

Figure S5. Reduced total intensity of mucin molecules at various concentrations.

Section S4: DLS in the presence of $CaCl_2$

In Figure S5 we depict the intermediate scattering function obtained at the reference concentration of c_{mucin} = 0.08 mg/ml in the presence of 0.01 M of $CaCl_2$. Under these conditions, mucin vesicles swell and consequently open-up. The slow mode at long times reflects the structural collapse of the network.

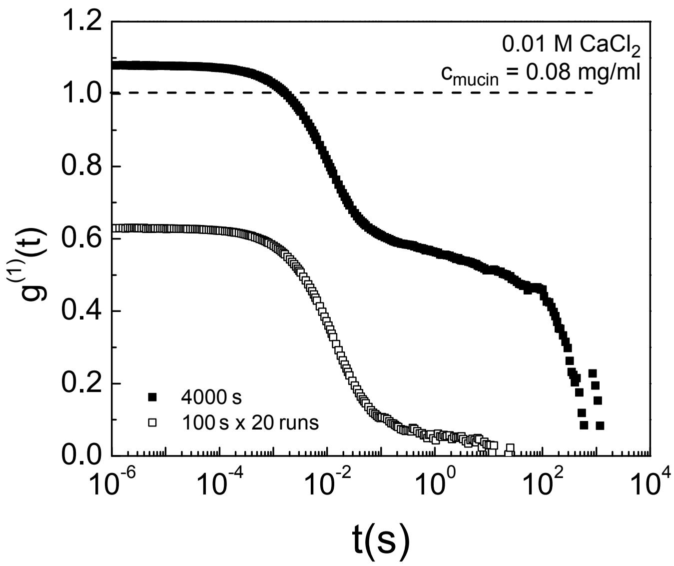

Figure S6. Intermediate scattering function of mucins at c_{mucin} = 0.08 mg/ml and 0.01 M $CaCl_2$.

In Figure S6, we show the corresponding total scattering intensity over roughly 4500 s whereas in Figure S7 we illustrate the total scattering intensity over 20 runs for 100 s. In order to determine the diffusion dynamics of mucin macromolecules in $CaCl_2$ saline environment we performed long time light scattering test (e.g. roughly 4500 s) as shown in Figure S6. The electric field correlation function overcomes the value of 1 and this is the signature of very large aggregated structures which provide slow modes. The corresponding trend of intensity appears in Figure S7 and verifies their presence. The cartoon illustrated in Figure 9 supports that behavior due to Ca^{2+} bridges. For the diffusion coefficient estimation, a second test performed within 20 runs for 100 s each and via this way we subtracted the effect of slow modes. The related intensity profile is shown in Figure S7 over 100 s run.

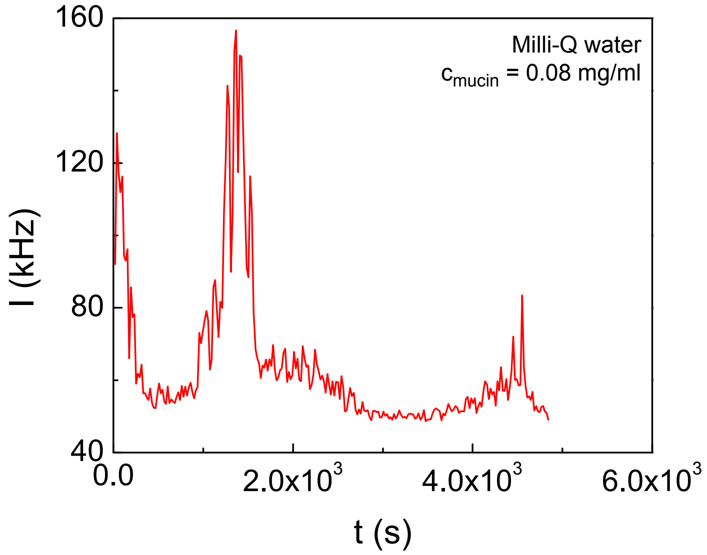

Figure S7. Total scattering intensity fluctuations at mucin concentration c_{mucin} = 0.08 mg/ml in salt free environment at a duration of roughly 4500 s at θ = 45^o (q = 0.01204 nm^{-1}).

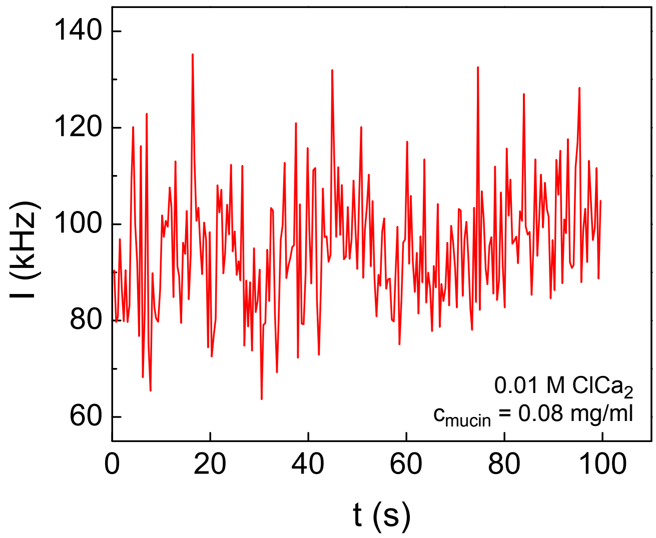

Figure S8. Total scattering intensity fluctuations at mucin concentration c_{mucin} = 0.08 mg/ml in environment of 0.01M $CaCl_2$. Measurements represent averages of 20 runs, each with duration of 100 s at $\theta = 45^o$ ($q = 0.01204$ nm^{-1}).

Section S5: Correlation length and hydrodynamic correlation length

The (static) correlation length ξ was extracted and its values at different mucin concentrations are presented in Figure S8, along with the hydrodynamic correlation length ξ_H. Both ξ and ξ_H are concentration-independent up to a threshold value of about c_{mucin} = 0.2 mg/ml (same mucin concentration as observed for the diffusion coefficient D_{eff} in Figure 5) beyond which they exhibit a change with concentration. Figure S9 depicts ξ and ξ_H for different salt concentrations and salt mixtures revealing only small differences.

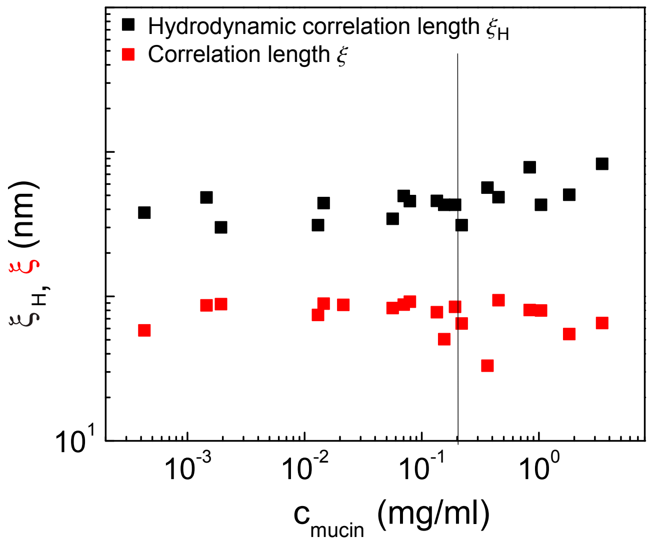

Figure S9. Dynamic and static apparent sizes of mucin molecules plotted against mucin concentration. The vertical line represents the entanglement concentration of c_{mucin} = 0.2 mg/ml.

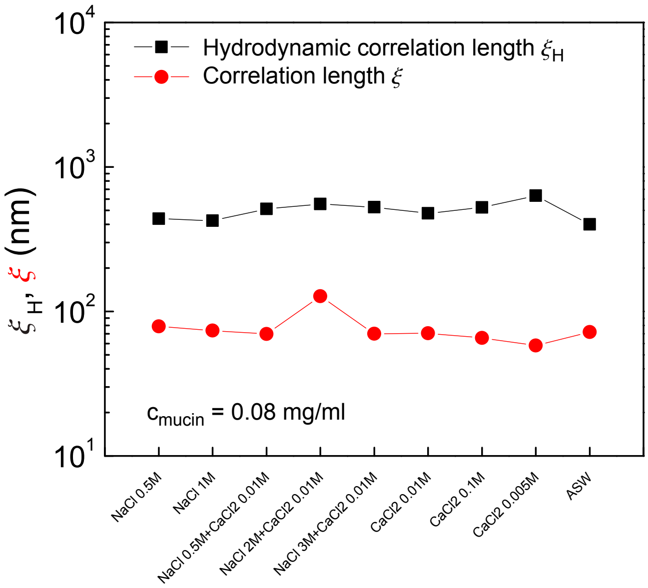

Figure S10. Dynamic and static apparent sizes of mucin molecules plotted for various salt concentrations at mucin concentration of c_{mucin} = 0.08 mg/ml. We note that the variability of salts and their ionic strength do not affect the present sizes.

Reference:

[1] P. Debye, H. R. Anderson, and H. Brumberger, "Scattering by an Inhomogeneous Solid. II. The Correlation Function and Its Application," *Journal of Applied Physics*, vol. 28, no. 6, pp. 679–683, Jun. 1957.