

Supporting Information

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Technical Details of the Simulation

Bond energy between cations and phenol in water is calculated by using computer simulation. Starting from various initial configurations of cations and phenol, depending on their angles and distance, we perform the configuration optimization. We consider about 1,440 different initial conditions, depending on the distance ($2 \text{ \AA} \sim 6 \text{ \AA}$) and the solid angle between cation and π residue. After the optimization, the total energy of the system is calculated. We distract the interaction energy by subtracting each energy of the single-molecule system from the total energy of the system. The energies of single-molecule systems are obtained from the separated simulations after the optimization process. All of the calculations were done by the DFT (Density Functional Theory) method with the 6-31+G** basis set, the M06-2X hybrid functional, and the SMD (Solvation Model based on Density) implicit water model, using the Gaussian09 program (43).

Macroscopic Like-Charged Polyelectrolyte Complexation Due to the Cation- π (or Short-Ranged) Bond

Our goal is to reveal the criterion that the short-ranged cation- π bond overcomes the longer-ranged electrostatic repulsion to lead the macroscopic phase separation. For this purpose, we construct the Ginzburg-Landau-like theory by using a relevant coarse-grained order parameter (46, 47). For systematic derivation, we start from the field theoretical representation. It is extremely difficult to consider the general polyelectrolyte in 3D. Instead we reduce the complexity of the work by assuming the polyelectrolytes are directed polymers and almost aligned along the z axis. Then, the contour of the polymer is $\mathbf{r}(z) = \mathbf{R} + \int_0^z d\mathbf{r}' \mathbf{u}(z')$, where \mathbf{R} is one end of the polymer and $\mathbf{u}(z) = d\mathbf{r}(z)/dz$ is the tangent vector along the polymer. The polymer segment density for N polymers of length L at a point \mathbf{x} is defined by $\hat{\rho}(\mathbf{x}) = \sum_{i=1}^N \int_0^L dz \mathbf{r}_i \delta(\mathbf{r}_i(z) - \mathbf{x})$. There are two competing interaction terms: the short-ranged cation- π bond and the longer-ranged electrostatic repulsion. The short-ranged bond is often well approximated by the Gaussian potential $U_A(x) = -\Gamma_A \exp(-(x^2/\lambda_A^2))$, whereas we use Debye-Huckel interaction for longer-ranged interaction, which becomes a modified Bessel function of the second kind of order zero after integrating out along the contour, $U_R(x) = \Gamma_R K_0(\kappa x)$, where $\kappa = \lambda_R^{-1}$. Because we model the short-ranged cation- π interactions in our model, we assume $\lambda_A < \lambda_R$. The total potential is then $U(x) = U_R(x) + U_A(x)$. The Hamiltonian of the system is then

$$H_N = \frac{\epsilon}{2} \sum_{i=1}^N \int_0^L dz \mathbf{u}^2(z) + \frac{N^2}{2} \int dx dx' \frac{1}{L} \int_0^L \hat{\rho}(\mathbf{x}, z) U(|\mathbf{r} - \mathbf{x}'|) \hat{\rho}(\mathbf{x}', z). \quad [\text{S1}]$$

The first term on the right-hand side is the mechanical energy of the directed polymers and ϵ is the line tension along the polymers. Here we assume $\epsilon = 3k_B T/2L$, similar to a Gaussian polymer. The Hamiltonian is rewritten in the Fourier,

$$H_N = \frac{\epsilon}{2} \sum_{i=1}^N \int_0^L dz \mathbf{u}^2(z) + \frac{N^2}{2} \int_0^L |\hat{\rho}(\mathbf{k}, z)|^2 U(\mathbf{k}), \quad [\text{S2}]$$

where ρ is the average areal density of the polymers, and $\hat{\rho}(\mathbf{k}, z) = (1/N) \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i(z))$. The partition function of the system is given by

$$Z = \int \prod_{i=1}^N d\mathbf{R}_i d\mathbf{u}_i \exp \left(-\mathcal{H}_0 - \frac{N\rho}{2L} \int_0^L dz \sum_{\mathbf{k}} \beta U(\mathbf{k}) |\hat{\rho}(\mathbf{k}, z)|^2 \right), \quad [\text{S3}]$$

where \mathcal{H}_0 is the noninteracting Hamiltonian of a Gaussian polymer in Eq. S1. Using the Hubbard-Stratonovich transformation

$$\exp(c|w|^2) = \frac{c}{\pi} \int dy \exp(-c|y|^2 + 2c\Re(yw^*)),$$

$$\exp(-c|w|^2) = \frac{c}{\pi} \int dy \exp(-c|y|^2 + 2ic\Re(yw^*)),$$

we obtain

$$Z = \int \prod_{i=1}^N d\mathbf{R}_i d\mathbf{u}_i \exp(-\mathcal{H}_0) \prod_{\mathbf{k}, U(\mathbf{k}) < 0} \int \mathcal{D}n(\mathbf{k}, z) \frac{\beta U(\mathbf{k})}{2}$$

$$\times \exp \left(-\frac{N\rho}{2L} \int_0^L dz \beta U(\mathbf{k}) |n(\mathbf{k}, z)|^2 + \beta U(\mathbf{k}) \frac{N}{L} \int_0^L dz \Re(n(\mathbf{k}, z) \rho^*(\mathbf{k}, z)) \right)$$

$$\times \prod_{\mathbf{k}, U(\mathbf{k}) > 0} \int \mathcal{D}n(\mathbf{k}, z) \frac{\beta U(\mathbf{k})}{2} \exp \left(-\frac{N\rho}{2L} \int_0^L dz \beta U(\mathbf{k}) |n(\mathbf{k}, z)|^2 \right.$$

$$\left. + i\beta U(\mathbf{k}) \frac{N}{L} \int_0^L dz \Re(n(\mathbf{k}, z) \rho^*(\mathbf{k}, z)) \right)$$

$$= \int \mathcal{D} \left(\frac{\beta U(\mathbf{k}) n(\mathbf{k}, z)}{2} \right) \exp(-Nf[n]). \quad [\text{S4}]$$

In the derivation above, we introduce a new field $n(\mathbf{k}, z)$ that turns out to be an order parameter in the mean field limit later on. $f[n]$ is an Landau-Wilson-type free energy and given by

$$f[n] = \sum_{\mathbf{k}} \frac{1}{2L} \int_0^L dz |\beta U(\mathbf{k})| |n(\mathbf{k}, z)|^2 - \ln \mathfrak{z}. \quad [\text{S5}]$$

\mathfrak{z} is a single polymer partition function, which is defined by

$$\mathfrak{z} = \int \prod_{i=1}^N d\mathbf{R}_i d\mathbf{u}_i$$

$$\times \exp \left[-\mathcal{H}_0 + \frac{1}{L} \int_0^L \sum_{\mathbf{k}} |\beta U(\mathbf{k})| \{ \Theta(U(\mathbf{k}) < 0) \right.$$

$$\left. + i\Theta(U(\mathbf{k}) > 0) \} n(\mathbf{k}, z) \rho^*(\mathbf{k}, z) \right]. \quad [\text{S6}]$$

In the mean field the free energy minimization yields,

$$n^{\text{sp}}(\mathbf{k}, z) = \langle \hat{\rho} * (\mathbf{k}, z) \rangle \Theta(U(\mathbf{k}) < 0) + i \langle \hat{\rho} * (\mathbf{k}, z) \rangle \Theta(U(\mathbf{k}) > 0). \quad [\text{S7}]$$

From Eq. S7, we see that $n^{\text{sp}}(k)$ can be a parameter to distinguish the liquid stated and the densely ordered structure. In other words, $n^{\text{sp}}(k)$ can be an order parameter for macroscopic phase transition of dense packing. $\langle \cdots \rangle$ is an average with respect to a single Gaussian polymer Hamiltonian.

The Ginzburg–Landau type of equation is obtained for the Hamiltonian around the saddle point:

$$\begin{aligned} f^{\text{sp}}[n^{\text{sp}}] &= \frac{\rho L}{2} \sum_{\mathbf{k}} |\beta U(\mathbf{k})| |n^{\text{sp}}(\mathbf{k})|^2 \\ &\times \left[1 - \frac{\rho \epsilon^2}{L^2 k^4} |\beta U(\mathbf{k})| b(\mathbf{k}) \right] \Theta(U(\mathbf{k}) < 0) + \frac{\rho L}{2} \sum_{\mathbf{k}} |\beta U(\mathbf{k})| |n^{\text{sp}}(\mathbf{k})|^2 \\ &\times \left[1 + \frac{\rho \epsilon^2}{L^2 k^4} |\beta U(\mathbf{k})| b(\mathbf{k}) \right] \Theta(U(\mathbf{k}) > 0). \end{aligned} \quad [\text{S8}]$$

Here

$$b(\mathbf{k}) = \left[-8 + 8 \exp \left\{ -\frac{1}{2} \left(\frac{Lk^2}{\beta \epsilon} \right)^2 \right\} + 4 \left(\frac{Lk^2}{\beta \epsilon} \right)^2 \right] / \left(\frac{Lk^2}{\beta \epsilon} \right)^4.$$

The system becomes unstable when $U(k^*) < 0$ and the coefficient of the second-order term of [S8] is negative; i.e.,

$$\rho^* |U^*(k^*)| b(k^*) > 1. \quad [\text{S9}]$$

Here, k^* , ρ^* are dimensionless quantities scaled by $\sqrt{(\beta \epsilon / L)}$ and $(\beta \epsilon / L)^{3/2}$, and the energies are scaled by $k_B T$.

If this criterion holds only for some finite k_c , the system is unstable and the polyelectrolytes aggregate to form a finite-sized bundle of size $2\pi/k_c$. On increasing the bonding energy (or increasing bonding distance) or reducing the repulsion (reducing the screening length), k_c becomes smaller (i.e., the size of the bundle becomes larger) and it eventually becomes zero, which implies the system undergoes macroscopic phase separation. In Fig. 6, we find that the phase separation due to the stronger cation– π bond between MADQUAT and tyrosine agrees with our theoretical analysis.

Pore Size Estimate from the Self-Energy of the Spherically Charged Shell

Here we show that the few 10-nm-sized pores can be formed from the interplay of the adhesive cation– π bond and repulsive electrostatic interaction. We find the optimal pore size that minimizes the free energy of the system within the low salt concentration approximation, similarly to refs. 48 and 49. For simplicity, we ignore the interaction between pores, which allows us to approximate each pore as a single charged sphere of radius R , which carries its charge Q on its shell. Under the Debye–Huckel approximation, the potential satisfies the relation

$$\nabla^2 \phi(\vec{r}) \simeq \kappa_D^2 \phi(\vec{r}), \quad [\text{S10}]$$

where, κ_D^{-1} is Debye screening length.

The boundary condition is

$$\nabla \phi(\vec{r})|_{r=R} \simeq -\frac{4\pi e \sigma}{\epsilon}, \quad [\text{S11}]$$

where R is the radius of the pore, σ is a number density of surface charge, e is a unit charge, and ϵ is a dielectric constant of water.

Then, the solution of the outer surface is given by

$$\phi(\vec{r}) = \frac{Q \exp\{-\kappa_D(r-R)\}}{2\kappa_D R \epsilon r}, \quad [\text{S12}]$$

when $\kappa_D R \gg 1$.

The self-energy W_{el} of the spherically charge shell is expressed as

$$W_{\text{el}} = \frac{\epsilon}{2} \iint \int_{r>R} d^3r |\nabla \phi(\vec{r})|^2. \quad [\text{S13}]$$

By substituting [S12],

$$W_{\text{el}} = \frac{4\pi^2 e^2 \sigma^2 R^2}{\kappa_D \epsilon}. \quad [\text{S14}]$$

On the other hand, the adhesive attraction due to the cation– π bond is given by

$$W_{\text{adh}} = \frac{4\pi R^3}{3} \rho_{\pi} E_{+\pi}. \quad [\text{S15}]$$

Here ρ_{π} is a volume density of π residues and $E_{+\pi}$ is a bond energy of cation– π . Then, the optimal radius is determined by

$$R = \frac{2\pi l_B \sigma^2}{\kappa_D \rho_{\pi} (E_{+\pi} / k_B T)}. \quad [\text{S16}]$$

Although the acetic acid concentration is only about 1 mM, additional chloride ions exist that are produced during the dissolution of MADQUAT. It is difficult to determine the surface charge density, because we do not know the thickness of the shell and how strongly they are neutralized inside the shell due to the strong electrostatics. Because we want to consider a very thin shell, we consider the phase boundary of coacervation that gives the minimum concentration of MADQUAT and chloride ions, about 200 mM. Then, $\kappa_D^{-1} \simeq 0.96$ nm, $\sigma \simeq 2$ nm⁻². Further, $l_B \simeq 0.7$ nm. $E_{+\pi}$ is the value estimated by quantum simulation, and ρ_{π} in the coacervate phase is approximated as 0.65 M, which translates to 0.39 nm⁻³. Then, $R \simeq 4.8$ nm, and hence pore size is about 9.6 nm. This is a little bit smaller than the experimental results because we assume the infinitely thin shell. If we consider the polyelectrolytes in the shell, σ can be larger, which results in larger pore size.

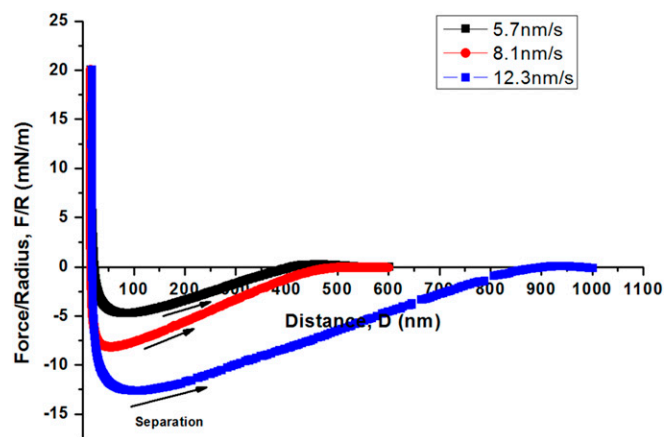


Fig. S4. Dependence of capillary bridging force on separation velocity of complex coacervate phase confined between two mica surfaces.

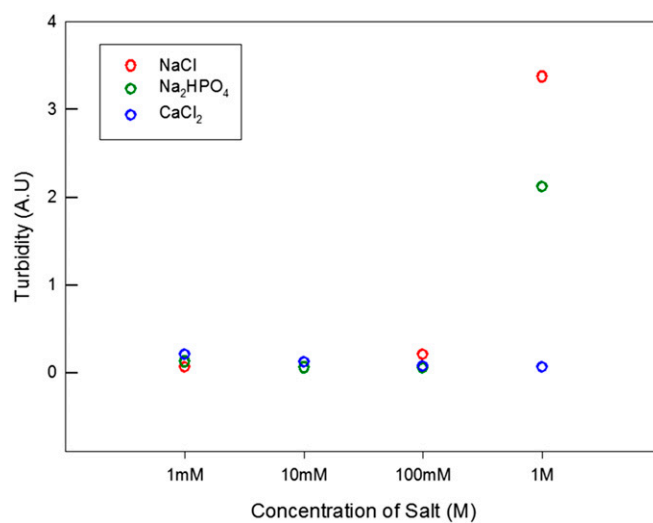


Fig. S5. Relative turbidity of like-charged complex coacervates of Rmfp-1 and MADQUAT, depending on salt concentration.

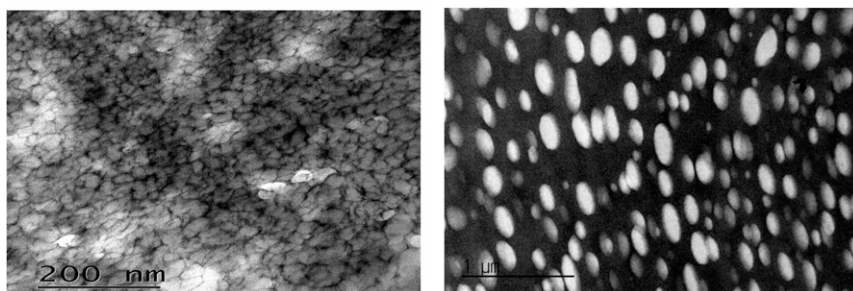


Fig. S6. Cryo-TEM images of Rmfp-1/MADQUAT coacervate (*Left*, no salt; *Right*, with 0.5 M NaCl).

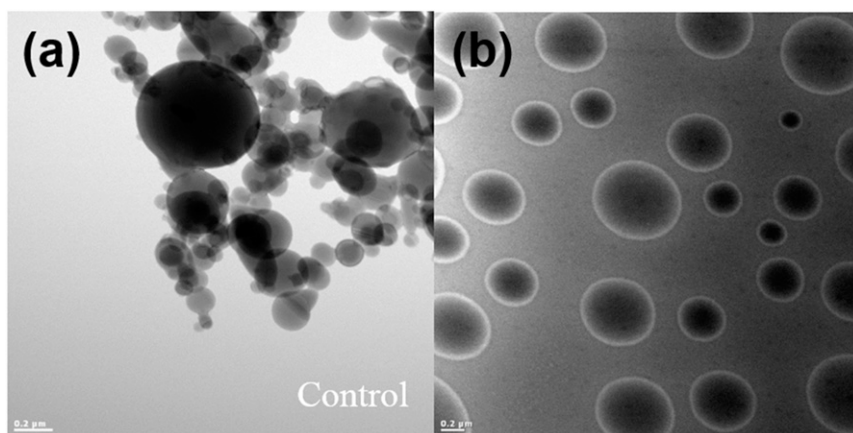


Fig. S7. TEM images of (A) pure silica nanoparticles and (B) silica nanoparticles suspended in the like-charged coacervate (Rmfp-1/MADQUAT).