

Supplemental Information For:

Phase Separation of 2D Coulombic Crystals of Meso-scale Dipolar Particles from Meso-scale Polarizable “Solvent”

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Experimental Details

Materials. Teflon spheres ($d_T = 3.175$ mm), Nylon-6,6 spheres ($d_N = 3.175$ mm), and sheets of aluminum (0.8 and 1.0 mm) were purchased from McMaster-Carr (Princeton, NJ).

Construction of the Aluminum Frames. Circular frames were made by bending thin strips of aluminum (0.8 or 1.0 mm wide, 4–6 mm high, and 171–2 mm long) into circles of diameter 53.6 ± 0.2 mm.¹ We glued the frames to square (75 mm) aluminum plates with 5-minute epoxy (Devcon), and cured the epoxy at 50 °C overnight.

Staining the Nylon-6,6 Spheres. Nylon-6,6 spheres were immersed in an aqueous solution of disperse blue 14 and placed on a hot plate at a temperature of 100 °C for 30 min to stain the spheres blue. The blue Nylon-6,6 spheres were removed from the solution, washed with water, washed with ethanol, dried under a stream of nitrogen, and then placed in an oven at 60 °C for at least 2 h to remove any remaining water from the spheres.

Cleaning and Storing the Spheres and Surfaces. To remove dirt and oil, and to discharge the spheres and the gold-coated plate prior to use, we rinsed the plate and spheres (T, N, Au^N, and Au^T) with copious amounts of water (Milli-Q, 18 MΩ) and ethanol (95%, Pharmco), and dried them with a stream of N₂. The plate and spheres were stored in an oven at 60 °C for at least 2 h to remove water, and kept in a glove bag with low ($8 \pm 1\%$) relative humidity during use (Captair Pyramid, Erlab). We measured the humidity within the bag with a hygrometer (VWR, unit 35519-050). This bag also prevented the accumulation of dust on the spheres and plate.

Formation of TN and Au₂ Particles. We glued spheres made of Nylon-6,6 ($d_N = 3.175$ mm) to spheres made of Teflon ($d_T = 3.175$ mm) with 5-minute epoxy (Devcon) so that no epoxy was exposed (Figure S1). We placed a ~0.5 μL drop of epoxy on one sphere (e.g., T), placed a second sphere (e.g., N) on top of the epoxy, and placed the glued spheres on their side while the epoxy cured. The epoxy cured for at least 4 h at room temperature prior to agitation of the TN particle. To make Au^TAu^N particles, we used the same procedure to glue one sphere of T to one sphere of N, and then sputtered a thin film of gold onto the TN particles, as described below.

Sputter-Coating Surfaces with Gold. The aluminum plate, frames, and lid were coated with a ~220-nm film of gold by sputtering at 80 mA for 360 s using a sputter coater (Cressington, Model 208HR). In order to obtain a uniform coating of gold on Nylon-6,6 spheres to form Au^N,

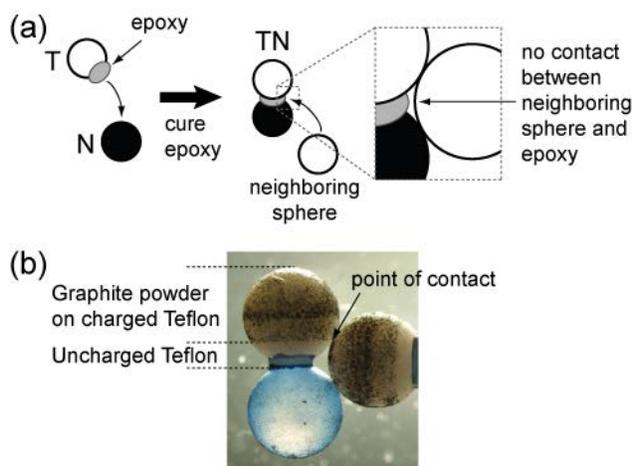


Figure S1. Attaching T and N spheres to make TN particles. (a) We attached pairs of spheres (e.g., T and N, which form a TN particle) with 5-minute epoxy. The epoxy cured overnight. We used an amount of epoxy that was small enough to ensure that neighboring spheres could not touch the cured epoxy. (b) A TN particle (T = white, N = blue) next to the Teflon sphere of a second TN powder. To visualize the distribution of charge developed on the surfaces of the spheres, we exposed them to particulates of fine (1–2 μm) graphite powder. Charge was everywhere on the spheres except for the region (marked as “uncharged Teflon”) nearest the epoxy, beyond the point of contact of hexagonally closed-packed spheres (spheres arranged as shown here).

on Teflon spheres to form Au^T, [REF: monomers paper] or on TN particles to form Au^TAu^N, we placed ~50 spheres (25 TN particles) in a 4-cm diameter poly(styrene) Petri dish (VWR) and set the dish at an ~30° incline on the rotating stage of the sputter coater. As the stage rotated, the spheres rolled inside the dish and were coated with a ~165-nm (330 nm total / 2 sides of each sphere) film of gold by sputtering at 80 mA for 540 s. We weighed Au^T, Au^N, and Au^TAu^N particles, and compared their weights to those of T, N, and TN particles to confirm that the layer of gold did not add significantly to the weight of the Au^T, Au^N, and Au^TAu^N (Table S1).

Agitation of Particles. We placed particles on the gold-coated plate, confined within the circular, gold-coated frame (Figure S2a). The plate and frame were clamped to a square (75 mm), aluminum platform that was fixed beneath its center to a linear magnetic actuator (LinMot). Computer software controlled the amplitude and frequency of oscillation of the linear actuator, which we programmed to vibrate at frequency $\omega = 15\text{--}80$ Hz, and amplitude $A = 0.1\text{--}1.5$ mm (Figure S2b). Prior to agitating a mixture of TN and Au₂ particles, we placed them on the plate in a way that completely mixed them (i.e., we placed Au₂ particles between pairs of TN particles) so that they were arranged as in Figure 1(c, left). This initial configuration of particles ensured that any observed separation of the particles occurred because of the interactions among the agitated particles, rather than because the particles began and remained in a separated configuration. Once we arranged the particles on the plate, we neutralized any electrostatic charge on them, and on the plate with a ZeroStat® 3 antistatic gun (Milty).

The circular frame enclosed a surface area equal to that of ~258 hexagonally close-packed spheres (~129 particles).¹ On top of this frame, we secured a lid (Figure S2c)—a gold-coated, square (75 mm, 0.8 mm thick), aluminum sheet—with c-clamps. The lid constrained the motion

Table S1.

Type of Sphere or Particle	Weight (mg)	Combination of Spheres or Particles	Weight (mg)
N	18.8 ± 0.2	T + N	55.7 ± 0.3
Au ^N	18.9 ± 0.2	TN - (T+N) ^a	0.3 ± 0.5
T	36.9 ± 0.1	Au ^T + Au ^N	55.4 ± 0.3
Au ^T	36.5 ± 0.2	Au ^T Au ^N - (T+N) ^b	0.6 ± 0.9
TN	56.0 ± 0.4	Au ^T Au ^N - TN ^c	0.3 ± 0.9
Au ^T Au ^N	56.3 ± 0.8		

^a Approximate weight of the epoxy of TN particles. ^b Approximate weight of the epoxy and the gold on the epoxy and spheres of Au₂ particles. ^c Approximate weight of the gold on Au₂ particles.

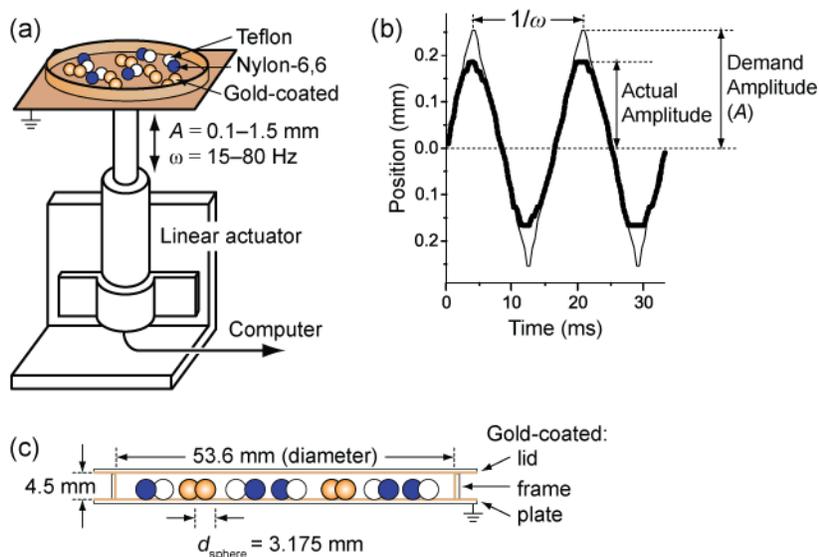


Figure S2. (a) TN and Au₂ particles on the planar, horizontal, electrically grounded plate, within a circular frame. A magnetic linear actuator connected to the plate and frame, and oscillated vertically at an amplitude (A) and linear frequency (ω) that we determined using a computer program. The apparatus was in a glove bag (not shown). (b) Position of the plate as a function of time for agitation of the system (particles, plate, and lid) at $\omega = 60$ Hz, $A = 0.26$ mm. We programmed the linear magnetic motor to oscillate in a triangular wave, in which the amplitude (A) was half the difference between the maximal and minimal heights of the plate, and the frequency (ω) was the inverse of the time between maxima of the wave. The amplitude of the motor (“Actual” amplitude) deviated from the programmed (“Demand”) position at the maxima and minima, where the acceleration of the system would have had to exceed the maximum possible acceleration of the motor in order to achieve the programmed wave function. The maximal speed of the system (>57.4 mm s⁻¹) was, however, within ~5–10% of the programmed maximal speed (62.4 mm/s). (c) Schematic of the particles, plate, square (47.8 ± 0.1 mm) or circular ($d = 53.6 \pm 0.2$ mm) frame, and lid.

of the particles to two dimensions (i.e., to prevent the particles from aggregating in 3D), and prevented them from being expelled from the agitated plate. With the particles constrained to remain in 2D, they covered a controlled, constant amount of the plate. If particles layered in 3D, then the surface density (ρ , proportional to the number of particles per mm^2 ; see next section) decreased during agitation. The height of the frame ($4.5 \text{ mm} = 1.4 d$, Figure S2(c)) determined the distance between the plate and lid. This distance allowed the spheres to maintain as much mobility as possible, while keeping them confined to 2D.¹

Shaking the system vertically (i.e., its motion was perpendicular to the plane of the plate) caused the spheres to collide with the plate, each other, and the frame with random trajectories, and allowed the spheres to visit the entire area of the surface within the frame. Agitation was performed in a glove bag (Captair Pyramid; Erlab, Inc.). We kept the relative humidity of the air in the glove bag at $8 \pm 1\%$ at room temperature ($21 \pm 2 \text{ }^\circ\text{C}$); previous work had indicated that the separation of spheres did not depend on RH in the range of 8–30%.¹ We measured the humidity and temperature with a traceable hygrometer (VWR, unit 35519-050). After agitation of the system, we removed the lid to photograph the particles and to measure their charge.

Calculation of the Density of Particles, ρ . We defined ρ (spheres/ cm^2) as the total number of spheres (n_S) divided by the area of the plate within the frame, $Area_{\text{plate}} = 22.60 \pm 0.20 \text{ cm}^2$ (Equation (S1a)).

$$\rho = \frac{n_S}{Area_{\text{plate}}} \quad (\text{S1a})$$

$$n_S = 2n_{\text{TN}} + 2n_{\text{Au}_2} \quad (\text{S1b})$$

In Equation (S1b), n_{TN} is the number of TN particles, and n_{Au_2} is the number of Au_2 particles on

the plate. To calculate the maximal value of ρ , we assumed that the density of particles was maximal when the spheres of the particles were hexagonally close-packed. Since $Area_{\text{sphere}} = 0.087 \text{ cm}^2/\text{sphere}$ is the area of a hexagon that circumscribes a circle with $d = 3.175 \text{ mm}$, there can be as many as $22.6/0.087 = 258$ spheres on the plate, or $11.5 \text{ spheres/cm}^2$.

Measurement of the Charge on Particles. As in our previous study,¹ we measured the charge on TN or Au₂ particles by removing a particle from the horizontal surface with poly(butylene terephthalate) (PBTP), needle-nose tweezers, and dropping the particle into a Faraday cup (Table S2). We used PBTP tweezers, rather than stainless steel tweezers,² so that we did not discharge the spheres by touching them. An electrometer measured the charge inside the Faraday cup, and a homemade program in LabView recorded this charge as a function of time. The charge on a particle corresponded to the difference in charge inside the cup before and after the particle entered the cup (Figure S3).

To measure the charge on the individual T and N spheres of intact TN particles, we constructed a miniature Faraday cup (Figure S3c) that had an opening of 5 mm, which was large enough to allow a single sphere (and nothing else) into the interior of the miniature cup. We measured the charge each sphere of a TN particle by holding one sphere (e.g., N) and inserting the other (e.g., T) into the hole of the miniature Faraday cup. The charge reached a plateau as we held the sphere inside the hole, and the charge returned to a baseline value when we removed the sphere from the hole. The charge on the sphere was the difference in charge between that of the plateau and that of the baseline. We repeated this procedure to measure the other sphere (e.g., N) of the TN particle. The charge on the T and N spheres of TN particles after 3 min of agitation (Table S2) remained constant for at least 60 min of continuous agitation. The charge on T

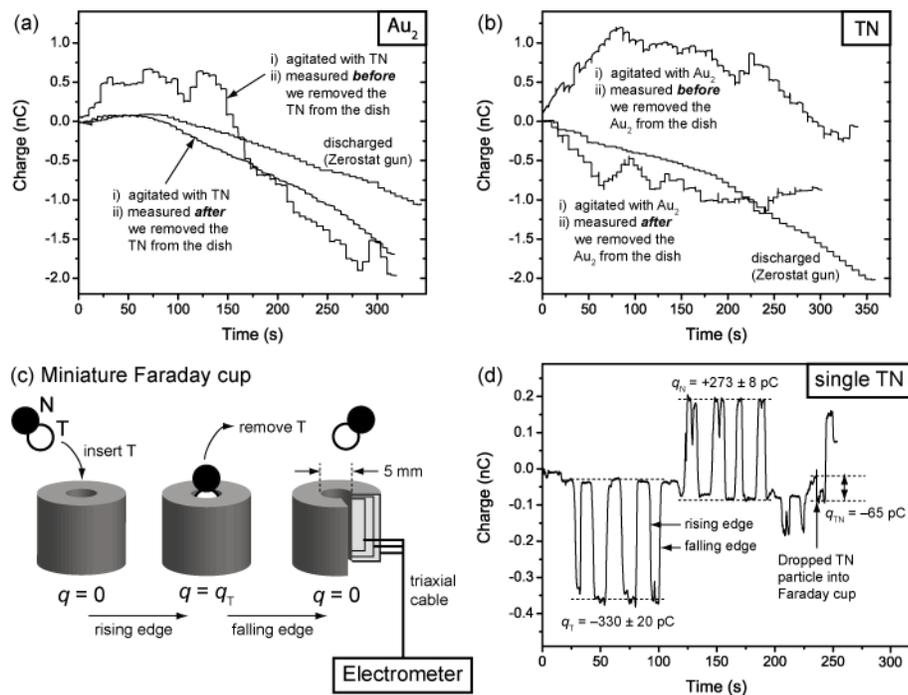
Table S2.

Type of Sphere or Particle	Charge prior to agitation (pC) ^b	Charge after agitation, measured first (pC) ^{c,d}	Charge after agitation, measured last (pC) ^{c,e}
T ^f	-16 ± 11	-800 ± 70	-720 ± 80
N ^f	-2 ± 13	610 ± 60	550 ± 50
TN	-39 ± 22	-23 ± 87	-18 ± 74
<u>TN</u> ^a	-2 ± 6	-370 ± 40	-350 ± 70
<u>TN</u> ^a	10 ± 12	250 ± 40	250 ± 80
Au ^{Nf}	8 ± 10	120 ± 130	17 ± 17
Au ^T Au ^N	-21 ± 17	-45 ± 120	-17 ± 25

^a Underline indicates the portion of the particle on which we measured the charge. ^b To determine the charge on particles and spheres prior to charging by contact electrification, we placed a mixture of particles or spheres (50 TN and 50 Au₂, or 50 T, 50N and 100 Au) on the plate, discharged the spheres with a Zerostat gun, and measured the charge on the particles or spheres as described in the supplemental information. ^c We agitated the particles or spheres within the gold-coated container at frequency $\omega = 60$ Hz, and amplitude $A = 0.26$ mm for 3 min. ^d We measured the charge on these particles and spheres *before* measuring the charge on (i.e., removing from the plate) the other particles. ^e We measured the charge on these particles and spheres *after* measuring the charge on (i.e., removing from the plate) the other particles. ^f These values are from ref 1.

Figure S3. Charge on (a) 50 Au₂ particles (q_{Au_2}) and (b) 50 TN particles (q_{TN}); see Figure 2 for histograms. We agitated ($\omega = 60$ Hz, $A = 0.26$ mm) Au₂ with TN particles for 3 min on a gold-coated plate, and then measured the charge on each particle, one at a time, by removing it from the plate with poly(butylene terephthalate) (PBTP) tweezers, and dropping it into a Faraday cup. The integration time on the electrometer was set to 16.7 ms, and the electrometer recorded the value of the charge at 57-ms intervals. (a) The average charges on Au₂ particles were -21 ± 17 pC (discharged), -45 ± 120 pC (*before* we measured q_{TN} —while TN particles remained on the plate), and -17 ± 25 pC (*after* we measured q_{TN}). (b) The average charges on TN particles were -39 ± 22 pC (discharged), -23 ± 87 pC (*before* we measured q_{Au_2}), and -18 ± 74 pC (*after* we measured q_{Au_2}). (c) To measure the charges on the T and N spheres of a TN particle, we inserted and removed each sphere, one at a time, into a miniature Faraday cup that had a cavity large enough to fit only a single sphere. Insertion of the sphere resulted in the rising edge of a peak of charge, and removal of the sphere resulted in the falling edge of the same peak. (d) The charges on the T sphere ($q_{\text{T}} = -330 \pm 20$ pC; the error is the standard deviation of eight measurements—the rising and falling edges of the four peaks) and the N sphere ($q_{\text{N}} = 273 \pm 8$ pC) of a single TN particle added up to -57 ± 21 pC, whereas $q_{\text{TN}} = -65$ pC when measured by dropping the entire TN particle into a Faraday cup.

Figure S3.



remained constant for at least 96 hours after agitation had stopped; whereas the charge on N decreased ~45% (250 ± 40 pC to 140 ± 60 pC) over the same 96 hours.

Charge per Sphere of Au₂ Particles. In our experimental design, we assumed that the charge *per sphere* that TN particles induced on Au₂ would be smaller than the charge that T and N spheres induced on Au spheres. To test this assumption, we compared the maximal magnitude of the charge on Au₂ (q_{\max, Au_2}) in the presence of TN particles to that on Au spheres ($q_{\max, \text{Au}}$) in the presence of T and N spheres. We used Equation (S2) to estimate q_{\max} (in this equation, q_{ave} is the average charge, and q_{sd} is the standard deviation of charge). The charge on Au₂ in the presence of TN was -45 ± 120 pC (Table S2), so $q_{\max, \text{Au}_2} = 165$ pC; that on Au in the presence of T and N was 120 ± 130 pC, so $q_{\max, \text{Au}} = 250$ pC. The maximal charges on Au and Au₂ were similar, but the charge on Au₂ was spread over *two* spheres, whereas that for Au was spread over one sphere. Therefore, the maximal charge *per sphere* (i.e., the charge density) on Au₂, in the presence of TN, was smaller than (~one-third) that on Au spheres in the presence of T and N spheres. This decrease in the maximal charge per sphere of Au₂ is consistent with the factor-of-two decrease in the charge per sphere on the T and N spheres of the TN particles, relative to that on isolated T and N spheres (Table S2).¹

$$q_{\max} = \max(|q_{\text{ave}} + q_{\text{sd}}|, |q_{\text{ave}} - q_{\text{sd}}|) \quad (\text{S2})$$

Distribution of Charge on TN Particles. To verify the distribution of charge on the surfaces of the T and N spheres of TN particles, we exposed charged TN particles to particulates of fine (1–2 μm) graphite powder (Figure S1(b)).² The graphite (and therefore charge) covered the entire surface of these spheres, except for that portion—nearest the epoxy adhesive—that

adjacent spheres could not contact.

Dipolar TN Particles Rotate in an Electric Field. We also verified qualitatively that TN particles comprised charged T and N spheres by placing a charged TN particle in a strong, uniform electric field (20 kV across parallel plates, separated by 2 cm). The TN particle rotated in the field with the positively charged N closest to the negatively charged plate and negatively charged T closest to the positively charged plate (see Figure S4). We repeated this experiment with a discharged TN particle and with a TN particle for which only one sphere (T) was charged. These TN particles did not rotate in the electric field.

Imaging and Analysis: Calculation of Φ . We took photographs of the of TN and Au₂ particles with a Nikon D40 camera that was attached to a ring stand. In order to illuminate each particle evenly (for easier image analysis), we attached a macro ring flash (SmartFlash RF46N, Phoenix) to the lens of the camera. We set the aperture to f/25, set the shutter speed to 1/500 s, and collected the pictures with Camera Control Pro software.

A homemade program, written in MATLAB, analyzed each photograph, and calculated the extent of separation (Φ) or mixing of the TN and Au₂ particles in that photograph according to the following procedure. Each photograph contained n_{Au} gold-coated (Au) spheres and n_{P} polymeric (P) spheres; we treated Au^T and Au^N as indistinguishable, and we treated T and N as indistinguishable (P) spheres. We measured the x- and y-coordinates of each sphere, and calculated the distances between each pair of spheres on the surface. For each Au sphere, we determined how many of the six spheres closest to that Au sphere were Au. This number gave $n_{\text{Au-Au}}$ for that Au sphere. We then determined how many of the 6 spheres closest to that Au

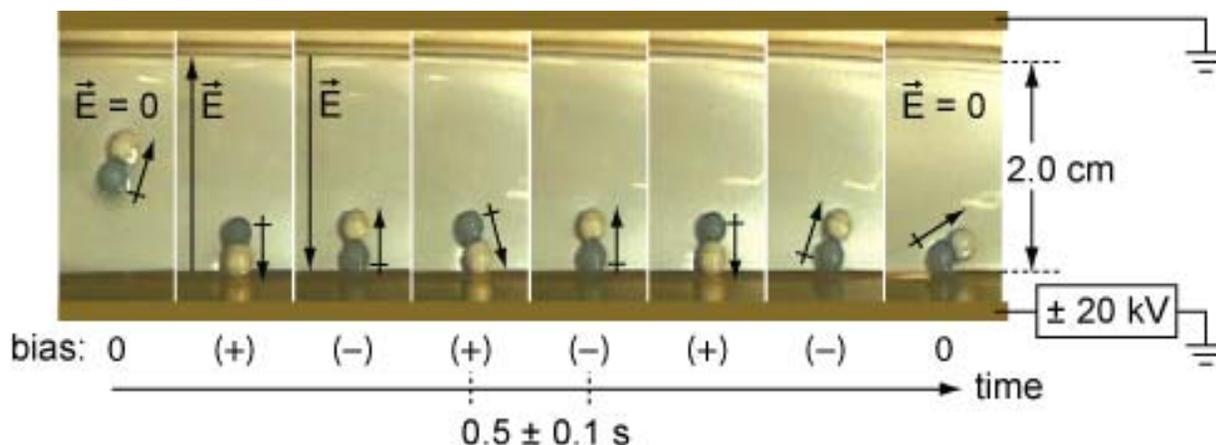


Figure S4. Top-down view of the orientation of a TN particle in an electric field, $E = \pm 1 \times 10^6$ V m^{-1} . We tribocharged this TN particle for 3 min at $\omega = 60$ Hz, $A = 0.26$ mm, and placed it into a bath of perfluoro(methyl decalin) (PFMD) in a poly(styrene) (PS) Petri dish between two copper plate electrodes. The PFMD increased the buoyancy and decreased friction between the TN particle and the dish, so that it could move more freely on the dish than without the PFMD. An arrow next to the TN particle in each image shows the dipole that points from the Nylon-6,6 sphere (N, blue, positive) to the Teflon sphere (T, white, negative). We recorded a video as we applied a voltage of 0 V or ± 20 kV (as indicated below each frame) to the bottom plate and kept the top plate at ground. The TN particle rotated in the electric field (within 0.5 ± 0.1 s of switching the direction of the electric field), with the positively charged N attracted to the negatively charged plate, and the negatively charged T attracted to the positively charged plate.

sphere were polymeric spheres, P. This number gave $n_{\text{Au-P}}$ for that Au sphere. We define a “neighbor” of a sphere to be one of these six closest spheres: $n_{\text{Au-Au}} + n_{\text{Au-P}} = n_{\text{tot}} = 6$. We calculated the average of $n_{\text{Au-Au}}$ and $n_{\text{Au-P}}$ over all the gold-coated spheres to obtain the average number of Au spheres that neighbored each Au sphere, $\langle n_{\text{Au-Au}} \rangle$, and the average number of polymer (again, P = T or N) spheres that neighbored each Au sphere, $\langle n_{\text{Au-P}} \rangle$. Other values of n_{tot} yielded quantitatively different, but qualitatively similar values and trends for Φ , and so we used only $n_{\text{tot}} = 6$ for all our calculations. We repeated this procedure for each P sphere (again, we treated T and N as indistinguishable) to calculate the average number of P spheres that neighbored each P sphere, $\langle n_{\text{P-P}} \rangle$, and the average number of Au spheres that neighbored each P sphere, $\langle n_{\text{P-Au}} \rangle$. The values for $\langle n_{\text{Au-Au}} \rangle$, $\langle n_{\text{Au-P}} \rangle$, $\langle n_{\text{P-P}} \rangle$, and $\langle n_{\text{P-Au}} \rangle$ each ranged from 0 (no neighbors of that type of sphere) to N_{tot} , and by definition obeyed Equation (S3).

$$N_{\text{tot}} = \langle n_{\text{Au-Au}} \rangle + \langle n_{\text{Au-P}} \rangle = \langle n_{\text{P-P}} \rangle + \langle n_{\text{P-Au}} \rangle \quad (\text{S3})$$

To calculate the extent of separation or mixing of TN and Au₂ spheres, we calculated how many neighbors there were, on average, among spheres of the *same* phase (like neighbors), and divided this average number of like neighbors by the total number of neighbors for each sphere, according to Equations (S4a) and (S4b).

$$\frac{\text{Number of neighbors of the same phase (Au)}}{\text{Number of neighbors of any phase (Au or P)}} = \frac{\langle n_{\text{Au-Au}} \rangle - x}{\langle n_{\text{Au-P}} \rangle + \langle n_{\text{Au-Au}} \rangle - x} \quad (\text{S4a})$$

$$\frac{\text{Number of neighbors of the same phase (P)}}{\text{Number of neighbors of any phase (Au or P)}} = \frac{\langle n_{\text{P-P}} \rangle - y}{\langle n_{\text{P-Au}} \rangle + \langle n_{\text{P-P}} \rangle - y} \quad (\text{S4b})$$

In these equations, x and y are the number of permanently attached spheres. We added Equations

(S4a) and (S4b), and subtracted 1 to obtain Equation (S5a). We subtracted 1 so that for a random mixture Φ would equal 0 (see below). Combining Equations (S3) and (S5a) yielded Equation (S5b). For TN, $y = 1$, and for Au₂, $x = 1$ (Equation (1) in the text). For separate spheres (T, N, Au^T, and Au^N), $x = y = 0$, and Eq. (1) reduces to the one we used previously.³

$$\Phi = \frac{\langle n_{\text{Au-Au}} \rangle - x}{\langle n_{\text{Au-P}} \rangle + \langle n_{\text{Au-Au}} \rangle - x} + \frac{\langle n_{\text{P-P}} \rangle - y}{\langle n_{\text{P-Au}} \rangle + \langle n_{\text{P-P}} \rangle - y} - 1 \quad (\text{S5a})$$

$$\Phi = \frac{\langle n_{\text{Au-Au}} \rangle - x}{n_{\text{tot}} - x} + \frac{\langle n_{\text{P-P}} \rangle - y}{n_{\text{tot}} - y} - 1 \quad (\text{S5b})$$

Limiting Behavior of Φ . Equation (S5b) has the limiting behavior that $\Phi = 0$ for a random mixture of particles, or for an infinite dilution of one phase in the other. For example, if n_{Au} is the number of Au spheres and n_{P} is the number of polymer spheres on the surface, then as we include more and more spheres as neighbors of each sphere (i.e., n_{tot} approaches the number of spheres on the surface), we obtain Equation (S6a).

$$\Phi \xrightarrow{n_{\text{tot}} = n_{\text{P}} + n_{\text{Au}}} \frac{n_{\text{Au}} - x}{n_{\text{tot}} - x} + \frac{n_{\text{P}} - y}{n_{\text{tot}} - y} - 1 \quad (\text{S6a})$$

If we consider enough spheres (>50 P and >50 Au, or >25 TN and >25 Au₂) such that both x and y are much less than n_{Au} , n_{P} , and n_{tot} , then Equation (S6a) simplifies to Equation (S6b).

$$\Phi \approx \frac{n_{\text{Au}} + n_{\text{P}}}{n_{\text{tot}}} - 1 = \frac{n_{\text{tot}}}{n_{\text{tot}}} - 1 = 1 - 1 = 0 \quad (\text{S6b})$$

That is, $\Phi = 0$ for a mixture (e.g., a random mixture) in which the relative populations of P and Au *entirely* determine the number of like neighbors ($\langle n_{\text{Au-Au}} \rangle$ and $\langle n_{\text{P-P}} \rangle$) for each sphere. For an infinite dilution of one phase (e.g., Au) in the other (TN), $\langle n_{\text{Au-Au}} \rangle \rightarrow 0$, $\langle n_{\text{P-Au}} \rangle \rightarrow 0$, and

$\langle n_{P-P} \rangle \rightarrow n_{\text{tot}}$. The value of Φ is also 0 in this limit (Equation (S7)).

$$\Phi \xrightarrow{\text{infinite dilution}} \frac{0}{n_{\text{tot}}} + \frac{n_{\text{tot}}}{n_{\text{tot}}} - 1 = \frac{n_{\text{tot}}}{n_{\text{tot}}} - 1 = 1 - 1 = 0 \quad (\text{S7})$$

Equation (S5b) also has the limit that $\Phi = 1$ for completely separated (non-touching) phases. In this limit, $\langle n_{\text{Au-P}} \rangle = \langle n_{\text{P-Au}} \rangle = 0$, and by Equation (S3), $\langle n_{\text{Au-Au}} \rangle = \langle n_{\text{P-P}} \rangle = n_{\text{tot}}$ (Equation (S8)).

$$\Phi \xrightarrow{\text{completely separated}} \frac{n_{\text{tot}}}{n_{\text{tot}}} + \frac{n_{\text{tot}}}{n_{\text{tot}}} - 1 = 1 + 1 - 1 = 1 \quad (\text{S8})$$

As mentioned in the text, $\Phi < 0$ (typically, about -0.30) for mixtures of particles in which we intentionally placed Au_2 particles between pairs of TN particles, as in Figure 1c (left).

Calculation of Scaled Separation, Φ^* . To generate center-surround (core-shell) configurations of spheres, we drew blue circles (to represent Nylon spheres), light blue circles (to represent Teflon spheres), and red circles (to represent gold-coated spheres). We positioned these circles in the configurations shown in Figure S5b using Adobe Illustrator CS2, and then calculated Φ for each configuration (as described above) to obtain values of $\Phi_{\text{max}}^{\text{C-S}}$. Dividing Φ , calculated for our experimentally obtained configurations of spheres, by the appropriate value of $\Phi_{\text{max}}^{\text{C-S}}$ (same number of TN, and Au_2 particles) gave the values of Φ^* reported in the text.

Separation was Independent of the relative numbers of TN and Au_2 particles. To investigate how Φ depended on the relative numbers of TN and Au_2 particles ($\chi_{\text{TN}} = 2n_{\text{TN}} / n_{\text{S}}$), we prepared mixtures of TN and Au_2 in which χ_{TN} varied from 0 to 1. We agitated the particles for 5 min at $\omega = 60$ Hz and $A = 0.25$ mm. Figure S6(a) shows the values of Φ and $\Phi_{\text{max}}^{\text{C-S}}$ as a function of χ_{TN} , for $\rho = 0.54$ and 0.77 . For both values of ρ , the value of $\Phi^*(\chi_{\text{TN}})$ did not change

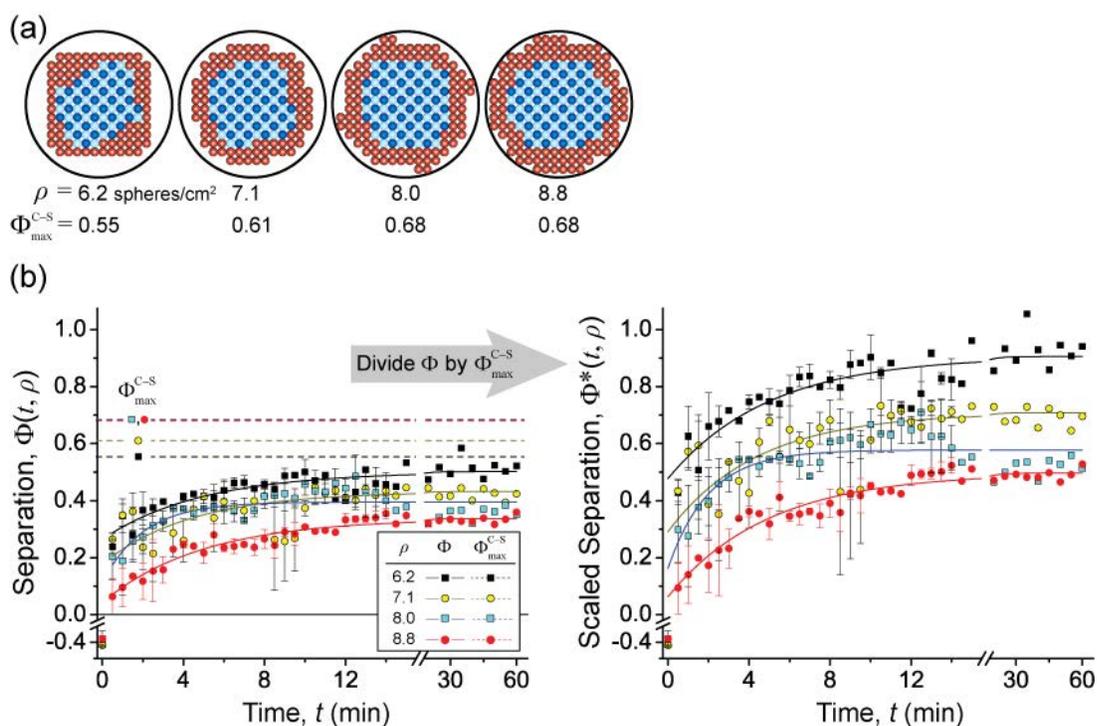


Figure S5. (a) Center-surround configurations (TN center with Au surround in a circular dish (black circle), drawn to scale) from which we calculated $\Phi_{\max}^{\text{C-S}}(\rho)$. (b) Separation (Φ , left) and scaled separation (Φ^*) as a function of density (ρ) and time (t). We agitated mixtures of TN and Au₂ ($\chi_{\text{TN}} = 0.50$) at $\omega = 60$ Hz, $A = 0.25$ mm. The data in Figure 4 (scaled separation, $\Phi^*(\rho, t)$) are these values of $\Phi(\rho, t)$ divided by $\Phi_{\max}^{\text{C-S}}(\rho)$.

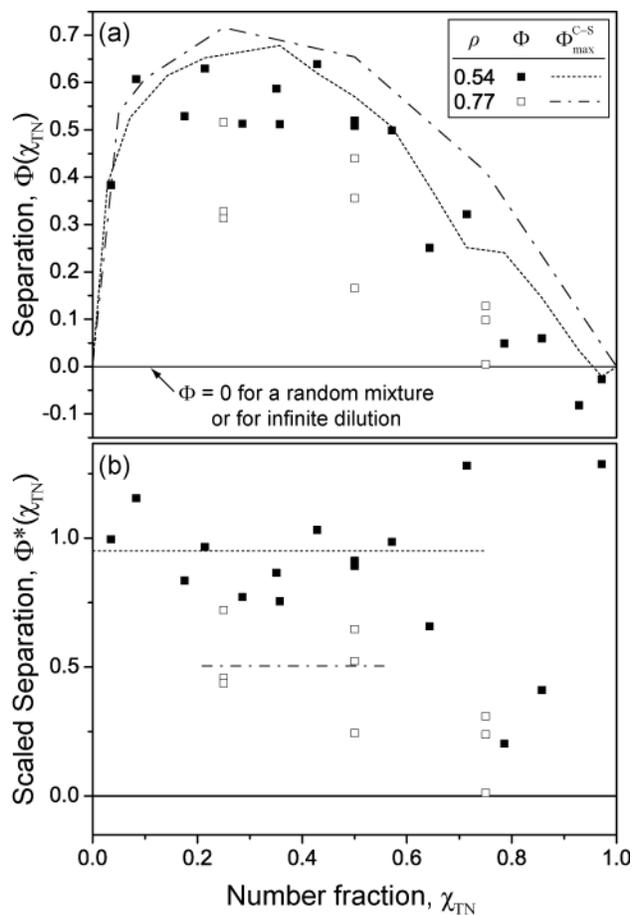


Figure S6. (a) Separation of TN from Au₂ ($\omega = 60$ Hz, $A = 0.25$ mm, 5 min) as a function of the number fraction of TN (χ_{TN}) for two densities. The solid line at $\Phi = 0$ is the value for either a random mixture or infinite dilution of either phase in the other (see text). The dotted ($\rho = 0.54$) and dash-dotted ($\rho = 0.77$) lines correspond to calculated values of $\Phi_{\max}^{C-S}(\chi_{TN})$. (b) Scaled separation, $\Phi^*(\chi_{TN}) = \Phi(\chi_{TN}) / \Phi_{\max}^{C-S}(\chi_{TN})$.

significantly as we varied χ_{TN} (Figure S6(b)). The values of $\Phi^*(\chi_{\text{TN}})$ were similar to those in Figure 4, regardless of χ_{TN} . Therefore, changing χ_{TN} did not significantly change the behavior of the system with regard to the extent of separation or mixing of TN and Au₂. For all experiments described in the text, we prepared mixtures with $\chi_{\text{TN}} = 0.5$ (i.e., $n_{\text{TN}} = n_{\text{Au}_2}$).

Separation as Decreased with Increasing Angle between the Directions of Agitation and Gravity. We prepared a mixture of TN and Au₂ particles ($\chi_{\text{TN}} = 0.75$; $\rho = 0.77$), and agitated the particles at $\omega = 60$ Hz, and $A = 0.19$ mm and 0.25 mm. To adjust the angle (α) between the normal of the plate and the direction of gravity, either we tilted the motor, or we had a vertical motor and tilted the plate (Figure S7, inset). We used a 4-mm-high circular frame ($d = 53.6$ mm) for these experiments to minimize 3D aggregation of the particles. For $\alpha > 0^\circ$, gravity pulled the particles into a close-packed configuration, and the particles were less able to move relative to each other than at $\alpha = 0^\circ$. The value of Φ therefore decreased with increasing α because the agitated particles more closely resembled the mixed starting configuration than they did after agitation at $\alpha = 0^\circ$.

Enlarged photos of figures from the text. Figure S8 contains enlarged photographs of each photo in the text: Figures 1(a), 1(c), 3(b), and 4(a).

¹ G. K. Kaufman, S. W. Thomas, III, M. Reches, B. F. Shaw, J. Feng, and G. M. Whitesides, "Phase Separation of 2D Meso-scale Coulombic Crystals from Meso-scale Polarizable 'Solvent'", *Soft Matter* (submitted).

² B. A. Grzybowski, A. Winkleman, J. A. Wiles, Y. Brumer, and G. M. Whitesides, *Nat. Mater.* **2**, 241 (2003).

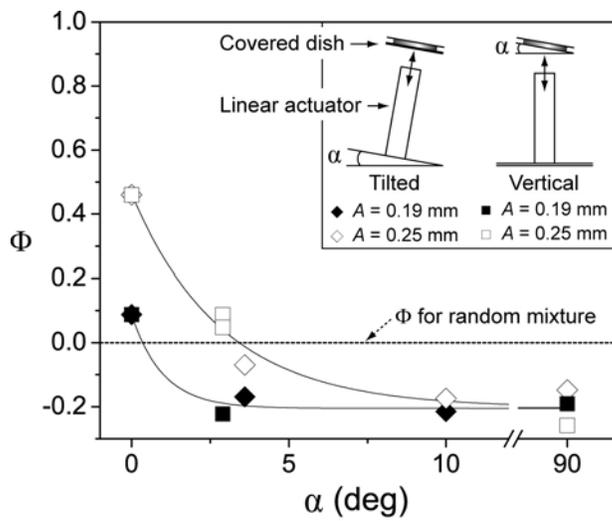


Figure S7. The value of Φ for the separation of TN and Au_2 , for $\omega = 60$ Hz, $A = 0.19$ mm and 0.25 mm, $\chi_{\text{TN}} = 0.75$, and $\rho = 0.77$, as a function of the angle (α) between the normal of the plate and the direction of gravity. Inset: Illustration of α for a tilted motor (“Tilted”) and for a vertical motor and tilted plate (“Vertical”).

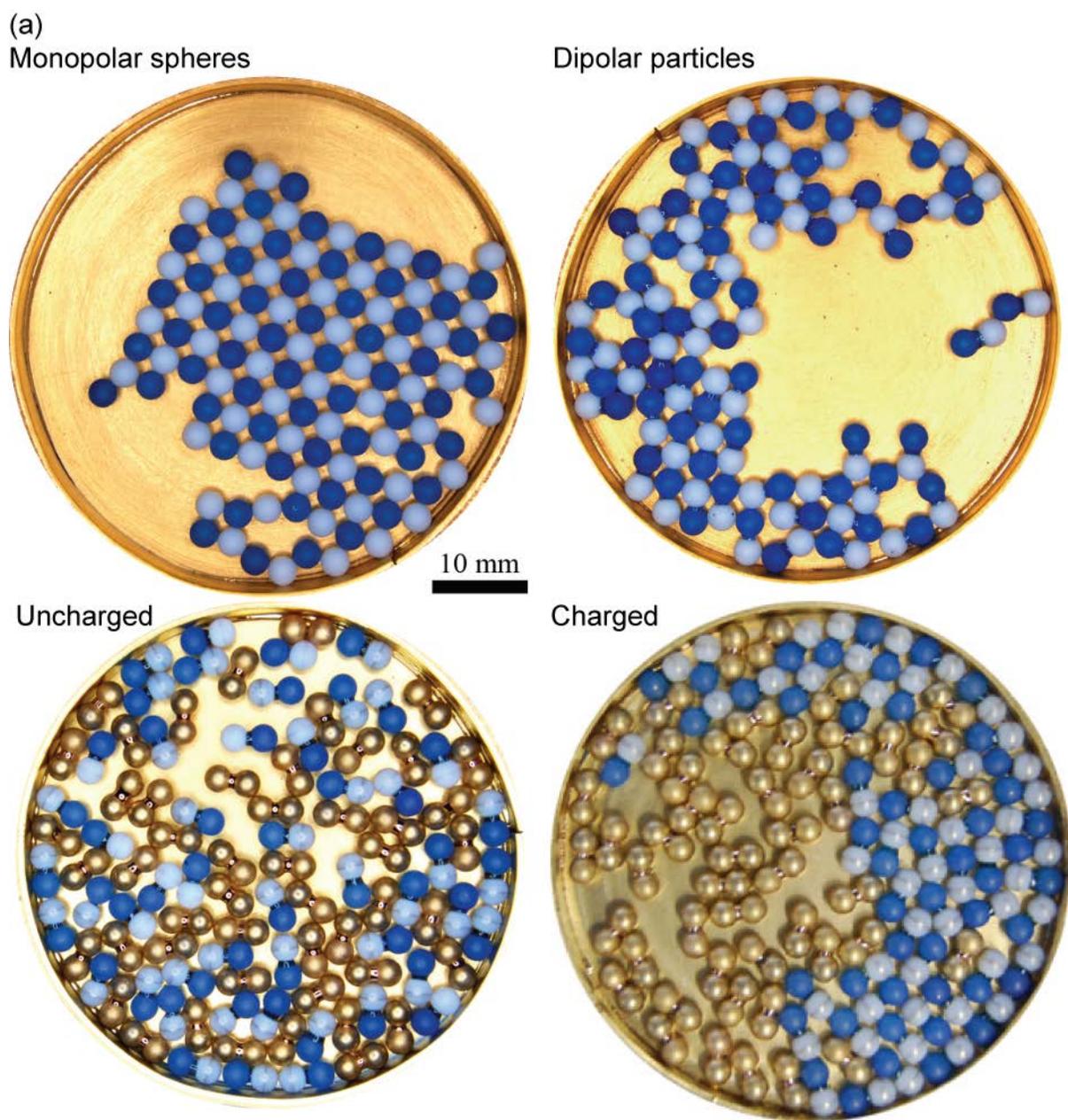


Figure S8. Full-size photographs of the images in the text: (a) Figure 1(a) and 1(c); (b) Figure 3(b); and (c) Figure 4(a). (This figure continues on the next two pages.)

Figure S8 (continued)

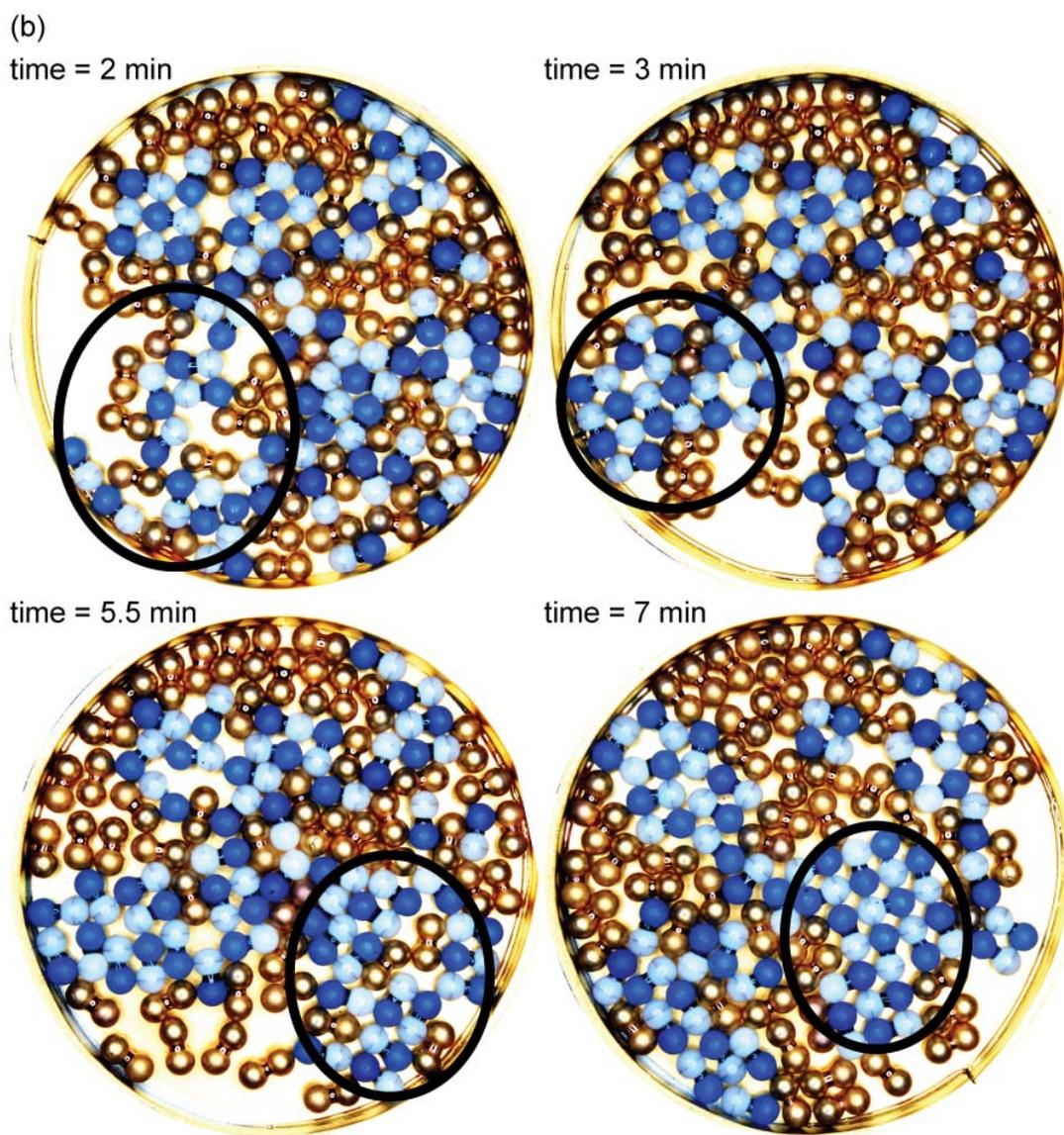
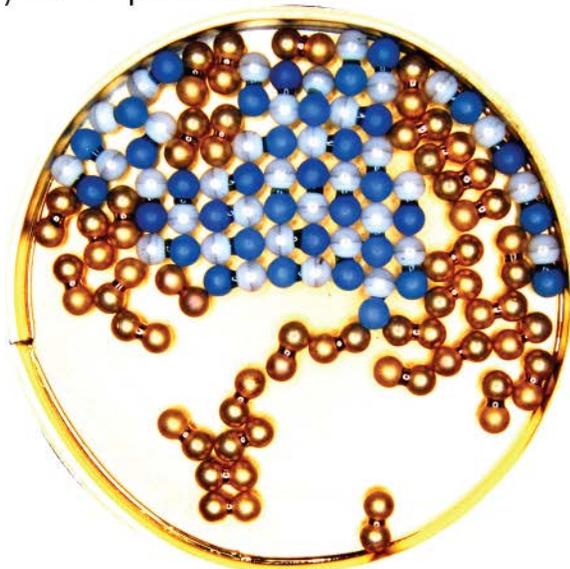


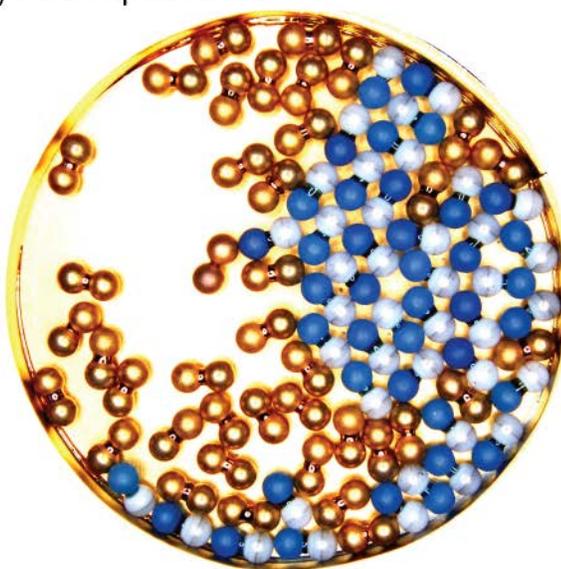
Figure S8 (continued)

(c)

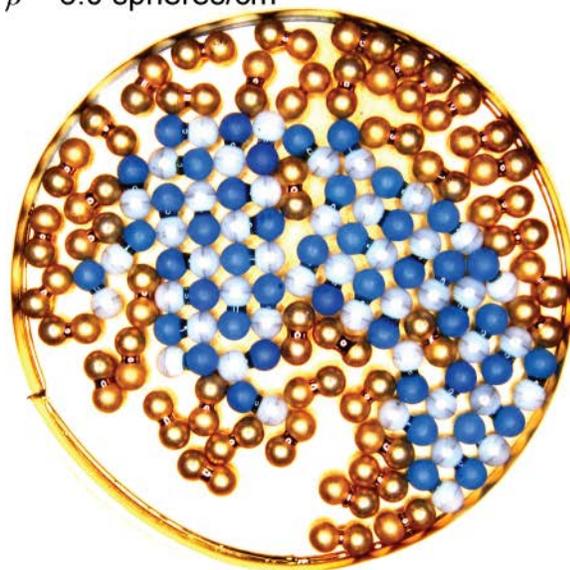
$\rho = 6.2$ spheres/cm²



$\rho = 7.1$ spheres/cm²



$\rho = 8.0$ spheres/cm²



$\rho = 8.8$ spheres/cm²

