

SUPPORTING INFORMATION

Customized Metallodielectric Colloids and their Behavior in Dielectrophoretic Fields

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Experimental Section

General. 3-(Trimethoxysilyl)propyl methacrylate (TPM, 98%), 3-chloro-2-hydroxypropyl methacrylate (CHPMA), ammonium hydroxide solution (28% NH₃ in H₂O), 2,2'-azobis(2-methylpropionitrile) (AIBN), dichloromethane (DCM), Pluronic F127, ethylenediamine ($\geq 99.5\%$), Gold(III) chloride trihydrate ($\geq 99.9\%$ trace metals basis), formaldehyde solution (36.5-38% in H₂O), hexamethyldisilazane (HMDS, $\geq 99\%$), and poly(vinylpyrrolidone) (PVP, M_w = 40k) were purchased from Sigma-Aldrich. Gold pellets, chromium pellets, and tungsten baskets for metal thermal evaporation were acquired from Ted Pella, Inc. All chemicals were used as received. Bright-field optical micrographs were acquired using a Nikon TE300 microscope. Scanning electron microscope (SEM) images were acquired with a Merlin (Carl Zeiss) field-emission SEM. Particles sizes were measured from the SEM images.

Fabrication of TPM and TPM-Cl spheres. TPM spheres were synthesized via spontaneous emulsification.¹ In a 600 mL beaker, 1.8 mL ammonium hydroxide solution (28% in water) and 2.0 mL TPM monomer were added to 300 mL deionized (DI) water. The mixture was stirred for two hours at 400 rpm, followed by the addition of 3.0 mL of a F127 aqueous solution (1% w/v) and stirred for an additional twelve hours. The mixture was then transferred to a round bottom flask, placed in an oil bath, and 100 mg AIBN was added. Spherical TPM particles formed after twelve hours of polymerization at 70 °C while stirring mildly and were purified by repeated centrifugation and redispersion with DI water for three times. To incorporate the chloride (-Cl) groups onto the surface of the TPM spheres (TPM-Cl), 0.8 mL CHPMA was added to the mixture prior to the addition of an aqueous solution of F127 (1% w/v) during the above preparation process and kept stirring for three hours. All the other fabrication steps were the same as those described for the TPM particles.

Fabrication of two-component dimers. The above formed TPM and TPM-Cl spheres were used as seeds to fabricate dimers using sequential seeded growth.² In brief, the TPM monomer was added to a 10 mL aqueous suspension of TPM-Cl seed particles, followed by the addition of 25 mL ammonium hydroxide solution (28%). The mixture was then rotated (16 rpm) in a homemade rotating station (Figure S6) for three hours. Afterwards, 500 μ L DCM was added to the mixture and shaken mildly by hand for approximately five minutes. The reaction was placed in an oven at 60°C for three hours during which all DCM evaporated. To incorporate -Cl groups and/or adding F127 surfactants to the surface of the second lobe, CHPMA was added to the mixture and the reaction stirred at 200 rpm for one hour, followed by the addition of 1.0 wt. % F127 aqueous solution and additional stirring for 30 minutes. To the mixture, 5 mg of AIBN was added and the reaction placed in an oven at 60 °C for 12 hours for polymerization to occur. The resulting dimers were concentrated and collected by centrifugation. Table S1 lists the detailed recipe to fabricate the two-component dimers.

Fabrication of three-component particles. The above formed TPM and TPM-Cl spheres were used as seeds to fabricate dimers using the sequential seeded growth method. The as-fabricated dimers above were used as seeds to fabricate the three-component particles. Typically, a 500 μ L stock solution of dimers (2% w/v) was diluted with 10 mL DI water. Then 25 μ L ammonium hydroxide solution (28%) was added to the solution followed by the desired amount of TPM monomer. The mixture was rotated at 16 rpm in a homemade rotating station for three hours or for twelve hours (see Table S2). Afterwards, 500 μ L DCM was added and the mixture was shaken mildly by hand for approximately five minutes. The reaction was placed in an oven at 60°C for three hours during which all DCM evaporated. To incorporate -Cl groups and/or adding F127 surfactants to the surface of the second lobe, CHPMA was added to the mixture and the reaction stirred at 200 rpm for one hour, followed by the addition of 1.0 wt. % F127 aqueous solution and

additional stirring for 30 minutes. To the mixture, 5 mg of AIBN was added and the reaction placed in an oven at 60 °C for 12 hours for polymerization to occur. The resulting particles were concentrated and collected by centrifugation. Table S2 lists the detailed recipe to fabricate the three-component particles.

Site-specific gold-coating. To coat a thin layer of gold onto a specific area of a particle surface, the -Cl groups on the particle surface have to be converted to amine groups. Briefly, 2 mL of the particle stock solution (0.5% w/w) was diluted with 4 mL of 0.5% F127 aqueous solution, followed by the addition of 300 μ L of ethylenediamine and a trace amount of potassium iodide (KI). The mixture was heated at 70°C in an oil bath for four hours converting the chlorine groups into primary amines.³ The as-obtained particles were then washed with DI water for three times and redispersed into 1 mL of DI water. The gold coating was done in two steps. First, 120 μ L of an aqueous chloroauric acid (HAuCl₄) solution (4 mg/mL) was added to the particle solution and the mixture was vortexed for three minutes. After washing with DI water for three times, a trace amount of sodium borohydride (NaBH₄) was added to the mixture and the reaction vortexed for an additional five minutes, during which Au³⁺ salt adhered on the particle surface was reduced to Au(0) and formed gold nuclei. The resulting particles were then redispersed in 0.5 ml of a 3 % PVP aqueous solution, followed by the addition of 600 μ L of freshly-made gold hydroxide (Au(OH)₃ (made by dissolving 20 mg of K₂CO₃ in 2 mL of 4 mg/mL HAuCl₃ aqueous solution and stirring overnight) and formaldehyde (HCHO, 67.5 μ L). The mixture was gently rotated (6 rpm) in the homemade rotating station for twelve hours allowing for the continuous growth of gold onto the particle surface to form a thin layer of gold.

Density gradient centrifugation. Particles for the assembly experiments were purified by density gradient centrifugation. A 20-40% w/w linear gradient of glycerol-water mixture was prepared by a gradient maker (Gradient Master 108, BioComp Instruments), and 0.5 mL of a particle solution was added to the upper surface of 12 mL of gradient solution for the following centrifugation at room temperature. For Au-TPM dimers, the centrifugation was set at 1500 rpm for 15 minutes. For three-component particles, the centrifugation was set at 800 rpm for twelve minutes. The separated layers were collected by syringe with pipetting needles, washed three times with DI water, and re-dispersed in DI water for the assembly experiments. Table 3 summaries the size distribution of purified particles after density gradient centrifugation.

Assembly in DEP device. The DEP device was assembled according to a previously reported method.⁴ The schematic representation of the DEP device is illustrated in Figure S2. In a typical setup, a 10 nm thick chromium layer and a 30 nm thick gold layer were deposited successively via thermal evaporation onto a glass slide (variable 130 to 160 μ m thick, Ted Pella, Inc.) with a rectangular glass tube (400 μ m wide, Vitrocom) in the middle as a mask, creating two parallel electrodes in a coplanar arrangement. After thermal evaporation, the glass tube was removed, and the glass slide was pre-treated with oxygen plasma for three minutes and exposed to HMDS vapor to render it hydrophobic. The pre-treated glass side was rinsed with 1.0 wt.% Pluronic F127 solution prior usage to prevent particles from sticking to the glass channel. A channel was constructed by affixing two pieces of adhesive tape (ca. 120 μ m thick) along the edges of the electrodes as spacers and attaching a glass coverslip onto the top surfaces of the two spacers with UV curable, thiolene-based adhesive (NOA 81, Norland Products). Copper wire (500 μ m diameter) was attached to each electrode with copper tape and connected to an AC power source (BK Precision 4007B). The DEP device then was mounted on the microscope stage to provide real-time observation of the crystallization process. The purified particles were suspended in DI water and injected into the channel of DEP device. During preparation, the dimers were negatively charged due to the hydrolysis of TPM molecules and trapped with Pluronic surfactant molecules on the surface, which together contributed to the high stabilization ability in the DI water medium.

The ends of the channel were sealed with wax. The particle suspension was allowed to settle for 20 minutes before applying a square wave AC electric field across the electrodes.

COMSOL modeling of AC electric field profiles. The 2D electrostatics modeling package (COMSOL Multiphysics 5.3a) was used to simulate the local electric field intensity distribution around the particles within chain structures. The dielectrophoretic field was created by an arrangement of two parallel gold electrodes with a gap of 400 μm . The dielectric permittivity (ϵ) of DI water medium, gold lobe and the TPM lobe was set at 78, 10^9 and 2.8, respectively.⁵ The effective field strength was assigned at 200 V/cm and the simulation was computed in the frequency domain (10 kHz).

Statistical image processing. Analysis was performed on each individual image using a custom script written in MATLAB (version 2021a). Each image was filtered and converted into binary (particle and background) by a series of image analysis processes, including image inversion, blurring using a Gaussian filter, intensity adjustment, watershed transform, and filtering out particle aggregates based on size. The centroid of each particle was determined using the MATLAB function `regionprops`. Neighboring particles were then located using a distance threshold between centroids, which created an adjacency matrix. This matrix was converted into the counts of the particle chains by the function `digraph` and `conncomp`. The image was then labeled, and the quantitative data of chain counts collected.

Table S1. Summary of spherical seeds, detailed volume of TPM monomer, CHPMA and F127 used to fabricate the two-component dimers.

Dimer particles	Seeds	TPM monomer/ μL	CHPMA/ μL	1.0 wt.% F127/ μL
2a-1	CI-TPM spheres	25	0	0
2a-2	CI-TPM spheres	30	0	35
2b	CI-TPM spheres	30	20	25
2c	TPM spheres	30	0	50

Table S2. Summary of dimer seeds, detailed volume of TPM monomer, CHPMA and F127 used to fabricate the three-component particles.

Dimer Particles	Seeds	TPM monomer/ μL	Rotation time (hours)	CHPMA/ μL	1.0 wt.% F127/ μL
3a	2a-2	25	3	0	10
3b	2b	20	12	0	10
3c-1	2c	20	3	8	25
3c-2	2c	30	3	20	25

Table S3. Size summary of Au-T particles, Au-T-T particles purified by density gradient centrifugation.

	Au-T	Au-T-T	T-Au-T	T-Au-T
Particle length	$1.95 \pm 0.06 \mu\text{m}$	$2.53 \pm 0.08 \mu\text{m}$	$2.46 \pm 0.06 \mu\text{m}$	$2.42 \pm 0.05 \mu\text{m}$
Gold lobe	$1.30 \pm 0.06 \mu\text{m}$ (diameter)	$1.37 \pm 0.02 \mu\text{m}$ (diameter)	1.11 ± 0.04 (aspect ratio w_c/h_c)	1.53 ± 0.03 (aspect ratio w_c/h_c)

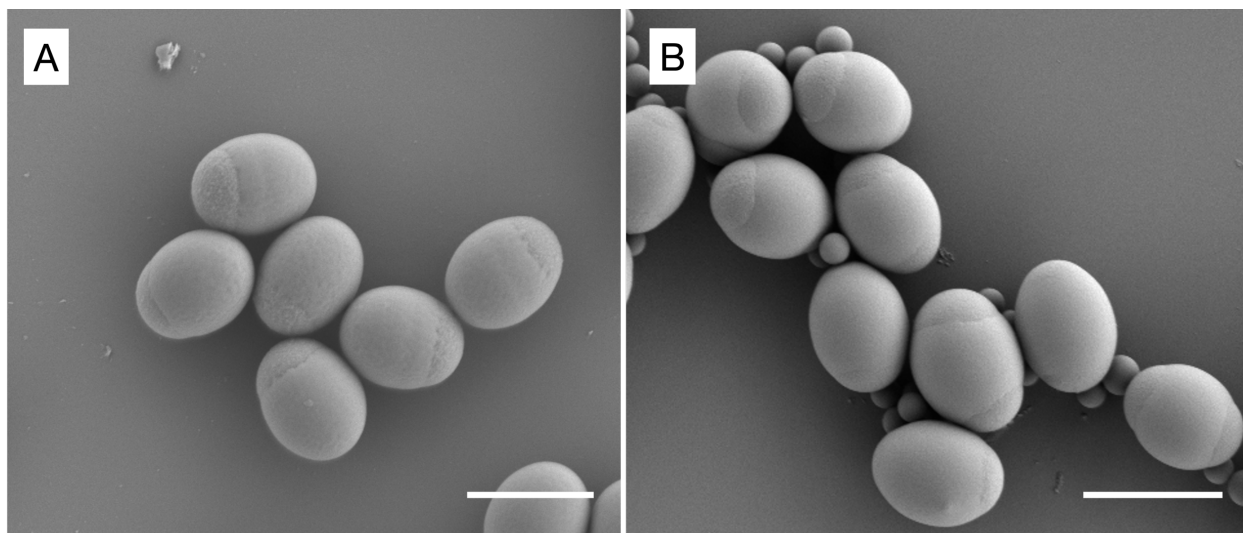


Figure S1. SEM images of three-component TPM particles formed from dimer seeds: (A) particles without the addition of F127 surfactant during the synthesis and (B) particles with the addition of 50 μL 1.0 wt. % F127 during the synthesis of the second lobe. Scale bars = 2 μm .

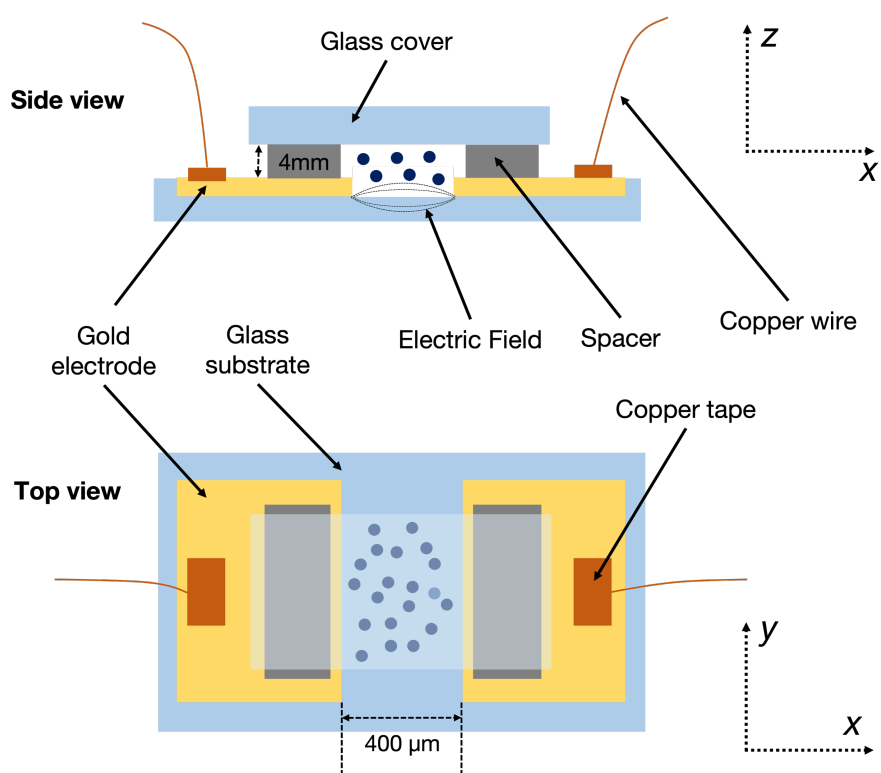


Figure S2. Schematic illustration of the DEP device: from side and top view, respectively.

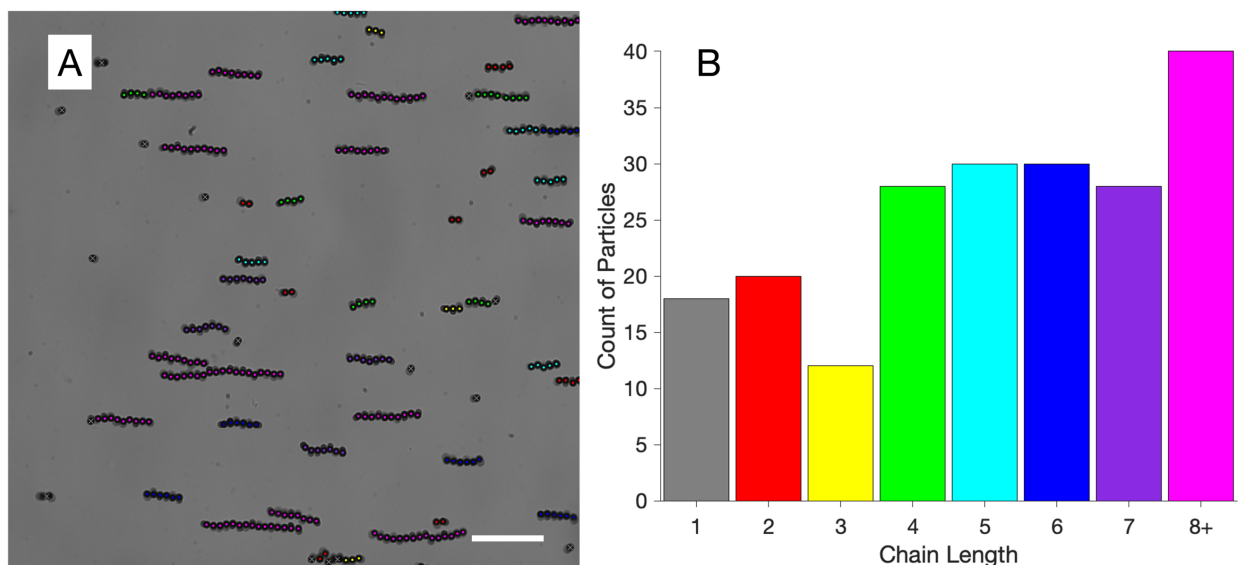


Figure S3. Representative and color labeled optical micrographs (A), and statistical data summary (B) of assembled chain structures from Au-TPM dimers using the developed image analysis algorithm. Scale bar = 20 μm .

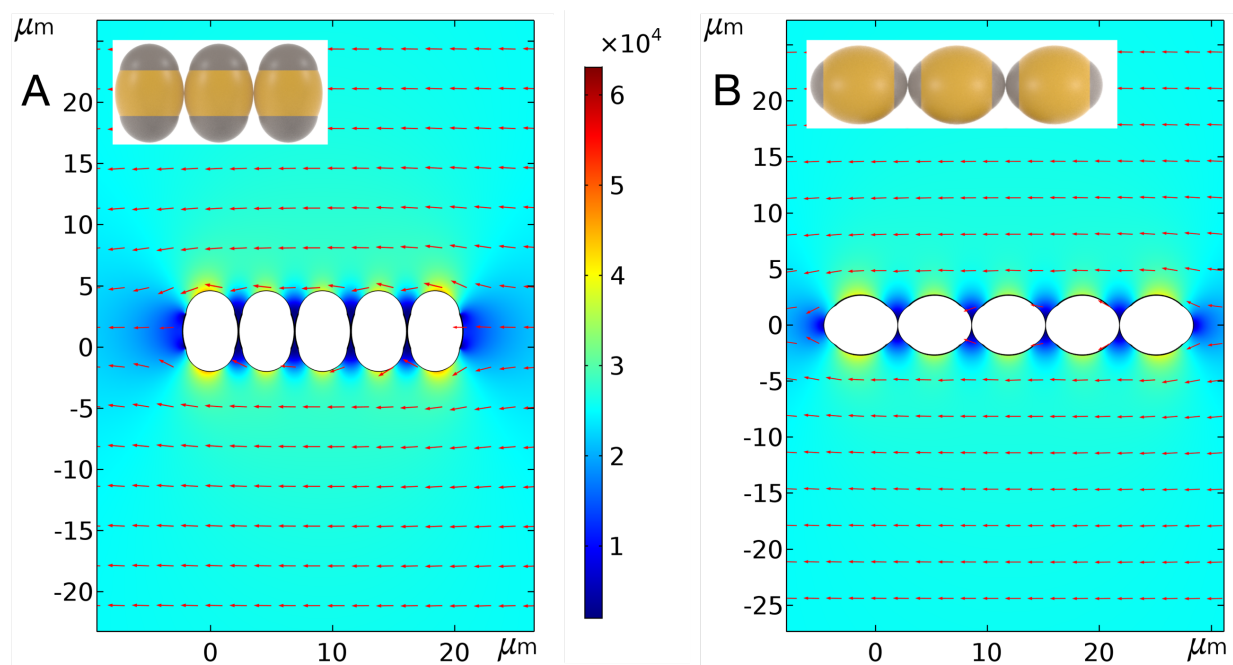


Figure S4. The nonuniform electric field locally distributed around a chain of T-Au-T particles ($w_0/h_c = 1.5$, A) and a chain of T-Au-T particles ($w_0/h_c = 1.1$, B) at AC frequency of 10 kHz, respectively. Red arrows represent the direction of electric field lines. Color bar: Electric field strength. Black arrows indicate the direction of the electric field.

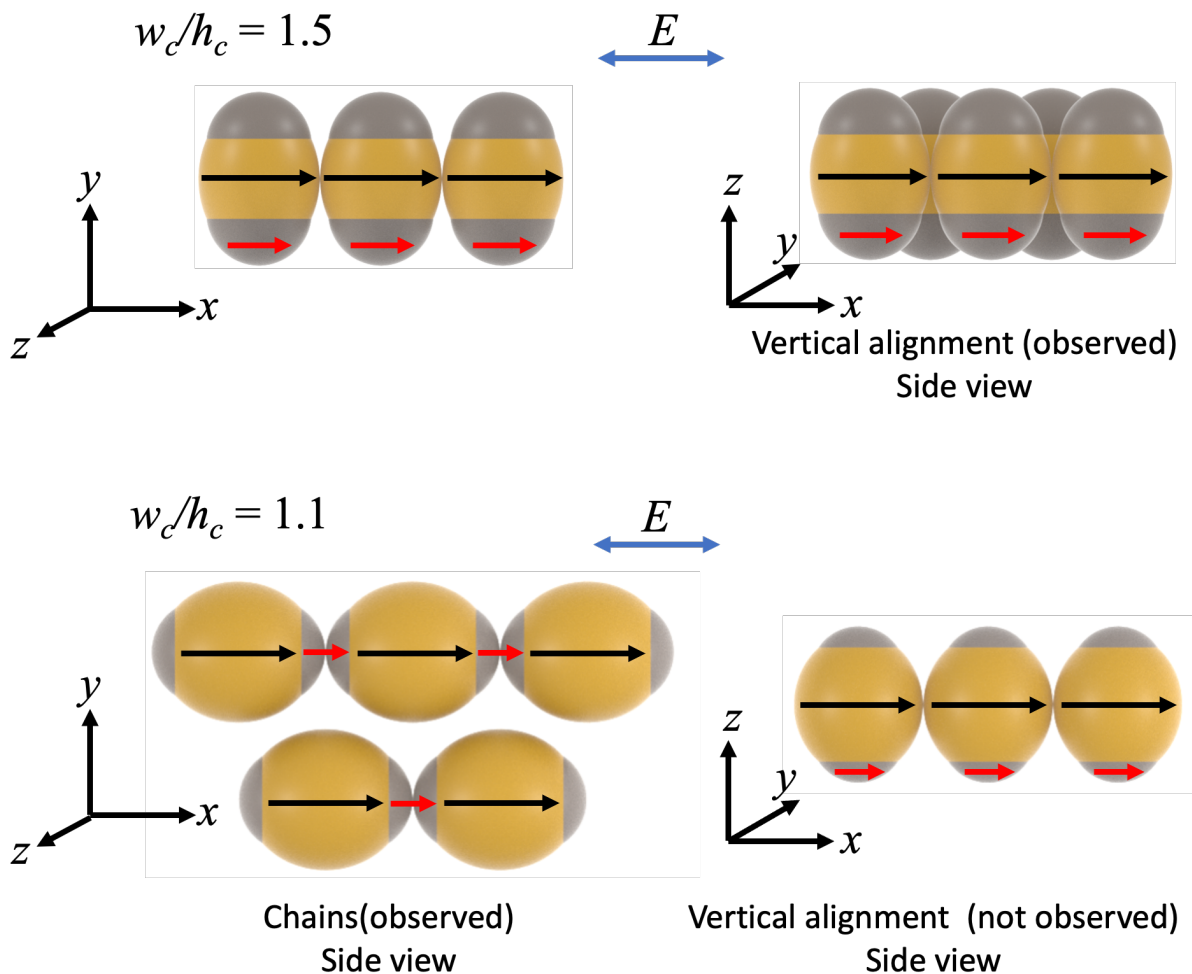


Figure S5. Schematic representation of $w_c/h_c = 1.5$ and $w_c/h_c = 1.1$ T-Au-T particles. The $w_c/h_c = 1.5$ particles are initially aligned with their long axes parallel to the x-y plane and perpendicular to the electric field. A 90° rotation about the axis coincident with the field direction results in the long axes aligned along the z direction. This permits the formation of hexagonal 2D domains as a consequence of favorable head-to-tail interactions between dipoles. In the case of the $w_c/h_c = 1.1$ particles, the long axis is aligned parallel to the electric field direction, such that the particles may exist in a “dipole trap” that frustrates a 90° rotation about an axis perpendicular to the electric field direction required for a vertical arrangement of the particles.

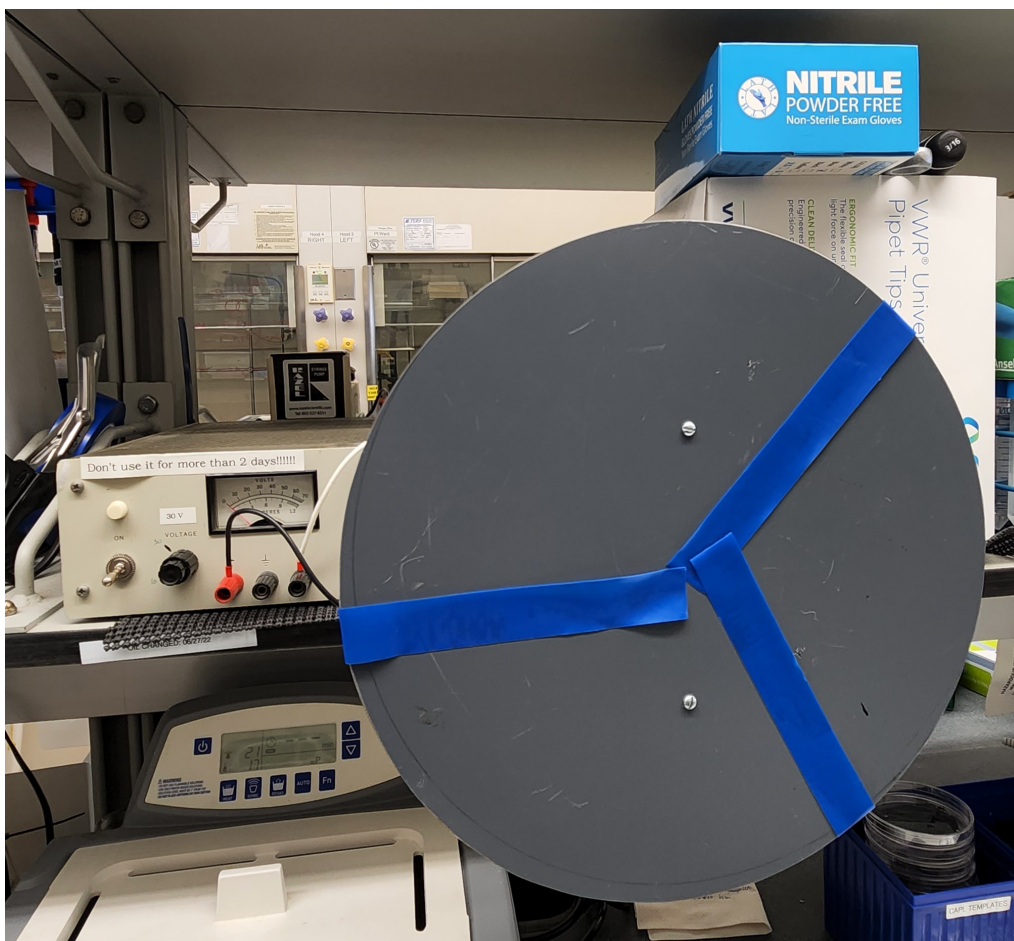


Figure S6. Photo of the homemade rotating station.

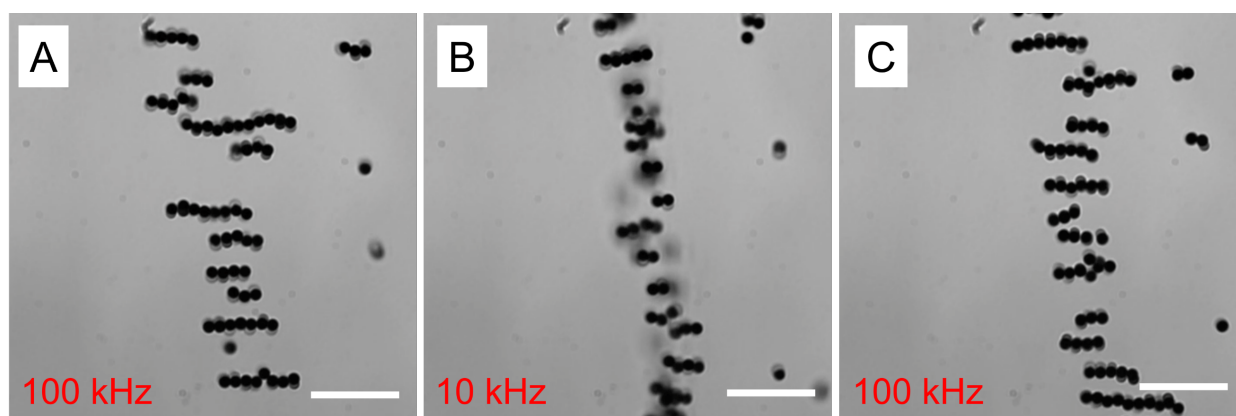


Figure S7. Video snaps of formed structures in the same region after turning on the electric field (200 V/cm) for (A) 30 seconds, (B) 50 seconds, and (C) 80 seconds, respectively. Scale bars = 10 μ m.

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