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Formation of Colloidal Molecules Induced by Alternating-Current Electric Fields

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Supporting Information

ABSTRACT: We report a versatile method for building colloidal molecules from particles that are isotropic in geometry and interfacial properties. When an external alternating-current electric field is applied, the particles experience anisotropic interactions that lead to the formation of colloidal oligomers via different assembly pathways that strikingly resemble chemical reactions of real molecules. We propose a mechanism for the formation of colloidal molecules that agrees well with the experiments. Our method can be used to build colloidal analogues of molecules using spherical particles with isotropic properties, which offers considerable advantages over existing methods. Moreover, our approach does not rely on material-specific properties and thus could have potential applications to a broad range of particles with different chemical properties.

Nature assembles relatively simple building blocks (such as atoms and molecules) into well-defined structures of exquisite complexity and functionality. The acquisition of comparable skill by scientists is an extremely challenging yet highly desirable goal for the efficient production of next-generation functional materials. However, the difficulty of directly observing the assembly mechanisms for molecules limits our current understanding of and ability to control matter at the molecular level. Therefore, colloidal molecules (i.e., clusters of colloids with predefined configurations and constituents)[1] could be valuable model systems that allow us to visualize and probe complex phenomena such as crystal nucleation and glass transitions at experimentally accessible length and time scales. Beyond their role as molecular analogues, colloidal molecules can interact with a broad range of electromagnetic waves in unique ways and can exhibit collective plasmonic[2] and photonic[3] properties that are not manifested at the level of single particles. Therefore, they are important buildings blocks for metamaterials[4] and photonic crystals.[3a]

Creating colloidal molecules with well-controlled configurations is challenging, however. Current methods often involve the self-assembly of particles that are anisotropic in geometry or interfacial properties. For example, particles with and without dimples can form lock-and-key colloids via the geometry-dependent depletion force.[5] Janus particles can form monovalent[6] or multivalent "bonds"[7,8] that lead to well-defined colloidal clusters. However, those anisotropic building blocks are difficult to make, typically suffering from low throughput, limitation to certain types of materials, or polydispersity. Ideally, one would prefer to fabricate colloidal molecules using spherical particles with uniform surface properties, since a rich library of such particles have been developed and are being produced on an industrial scale. Here we report a versatile method for creating colloidal molecules based on isotropic particles by applying external alternating-current (AC) electric fields. The anisotropic interactions between particles resulting from the external field lead to the formation of colloidal oligomers via different assembly pathways. Because of its physical nature, our method potentially provides an efficient route for making colloidal molecules based on spherical particles with a wide range of chemical properties.

Figure 1a shows the formation of colloidal oligomers under AC electric fields when the particles are suspended dilutely in deionized water. The experimental setup is shown in Figure S1a in the Supporting Information (SI). In brief, the AC field is

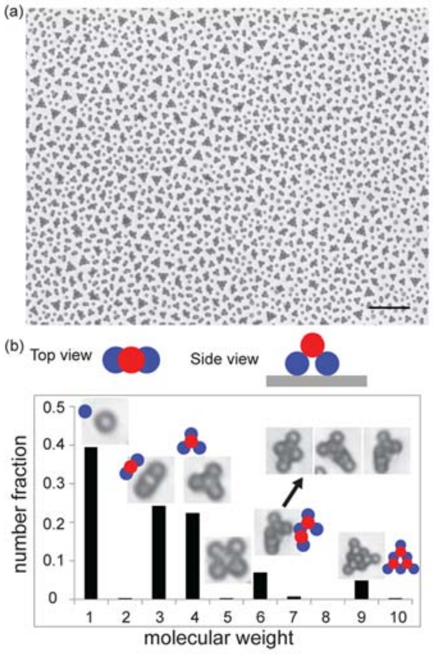

Figure 1. (a) Optical image of colloidal oligomers formed at low frequency (ω = 645 Hz) with a peak-to-peak voltage (V_{pp}) of 6 V in deionized (DI) water. Scale bar: 20 μm. (b) Number densities of oligomers with different "molecular weights".

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applied perpendicular to the substrate, and the gap between the two electrodes (H) is much larger than the particle diameter (D). The oligomer distribution (Figure 1b) reveals several peaks, corresponding to monomers (i.e., spherical particles), trimers, tetramers, hexamers, and nonamers; for hexamers, three isomeric configurations were observed. All of the colloidal oligomers are three-dimensional and have similar characteristics in geometry. For example, the central particle (red in Figure 1b) sits on top of the bottom particles (blue), although all of the particles are identical with respect to both interfacial and geometrical properties. The bottom particles are typically separated from each other with the same characteristic center-to-center spacing (L), while the top particle is nearly in contact with the bottom ones. This geometry was confirmed by using a confocal microscope to image fluorescent oligomers in different z planes (Figure S2a). For a trimer built with 2 μm spheres, the distance between the central planes of the top and bottom particles (h_{exp}) was measured to be between 1.2 and 1.5 μm. This is close to the theoretical value of 1.54 μm obtained by assuming that the top particle is in close contact with the bottom particles (Figure S2c).

To understand why certain types of oligomers are formed with high number fractions, we examined the dynamics of oligomer formation. As shown in supplementary movie 1 in the SI and in Figure 2a, trimers and tetramers are the fundamental building blocks for other oligomers. This fact is also reflected by their high number densities in Figure 1b. They can coexist and transform from one to the other in response to changes in frequency, with tetramers being more stable at lower frequencies ($\omega < 1000$ Hz) and trimers being more stable at higher frequencies ($\omega > 3000$ Hz). For $\omega > 10^4$ Hz, square pentamers were found to be more stable. At low particle concentrations, a trimer typically possesses a 180° bond angle, presumably to minimize the repulsive force between the bottom particles. However, this bond angle is flexible. When other oligomers approach, the trimer can change its bond angle to 120° (tetramer) or even 90° (pentamer) to accommodate additional particles. For example, a trimer can associate with another trimer to form one of the three isomeric hexamers. It can also associate with monomers to form linear chains, with one tetramer to form a heptamer, or with two trimers to form a nonamer. Because of the high "reactivity" and abundant reaction pathways of trimers, their second- and third-order reaction products (hexamers and nonamers) are also present with relatively high concentrations in the mixture of oligomers shown in Figure 1b. As an illustrative example, Figure 2b shows three common pathways that lead to the formation of nonamers. First, one trimer can join with a hexamer (which is often formed by two trimers); the combination is transformed into a nonamer by both reorientation of existing bonds and creation of new bonds. Second, a decamer (three tetramers sharing two corners) can also transform into a more stable nonamer by liberation of a monomer. Third, a tetramer can combine with a linear pentamer to produce a nonamer. Optical images showing reaction pathways for other oligomers are presented in Figure S3.

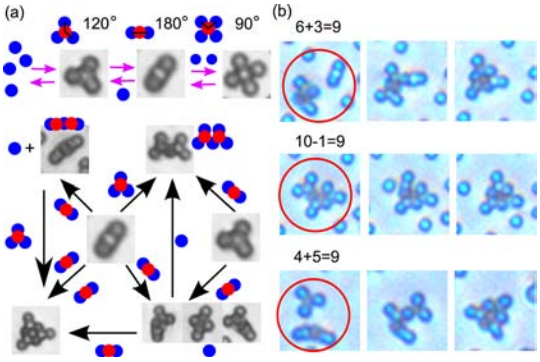

Figure 2. (a) Schematic illustration of transformations between different colloidal oligomers. Pink arrows indicate frequency changes. (b) Representative dynamic pathways for the formation of nonamers. The time interval between two consecutive frames is 1 s.

We note that flexibility is one of the key features in this colloidal assembly: bond angles can be changed, old bonds can be broken, and new bonds can be created. Because of this flexibility, we observed that those low-molecular-weight oligomers can further assemble into higher-order structures, depending on the particle concentration. As shown in Figure 3, a group of trimers can form hierarchical rings with increasing pore sizes. Similarly, closed loops can be formed by a group of nonamers or a combination of trimers and nonamers.

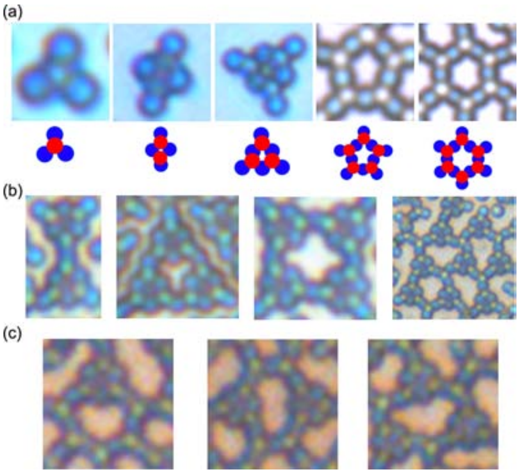

Figure 3. Hierarchical ring structures formed by different numbers of (a) trimers or (b) nonamers or (c) a mixture of trimers and nonamers. Particle size: 1.2 μm.

As we have shown so far, the breaking, creation, and reconfiguration of bonds are all induced by physical means: the externally applied electric field. Therefore, it is important to understand the colloidal interactions that lead to the formation of oligomers, especially for trimers and tetramers. We observed that colloidal oligomers can form only at both low salt concentrations and low frequencies, an experimental regime that has not been probed before. As shown in Figure S4 and supplementary movie 2, colloidal spheres aggregate into 2D hexagonal arrays (instead of oligomers) at relatively high salt concentrations[9] (e.g., 10^{-3} M). This is due to an electro-osmotic flow[10] that acts on the excess surface charges near the conducting substrate, attracting particles into 2D close-packed arrays. However, this flow is inversely proportional to the Debye length.[11] Thus, at low salt concentrations, the electro-hydrodynamic attraction between colloids is weak, preventing the formation of 2D crystals. At high ω (e.g., ~1 MHz), colloidal chains form perpendicular to the substrate (parallel to the field) as a result of dipolar attractions.[12]

Here we hypothesize that the dipolar interaction, electric double layer (EDL) repulsion, and dielectrophoretic attraction between the particle and substrate are the key forces that control the architecture of colloidal oligomers, as shown schematically in Figure 4a. The particles in our experiments are negatively

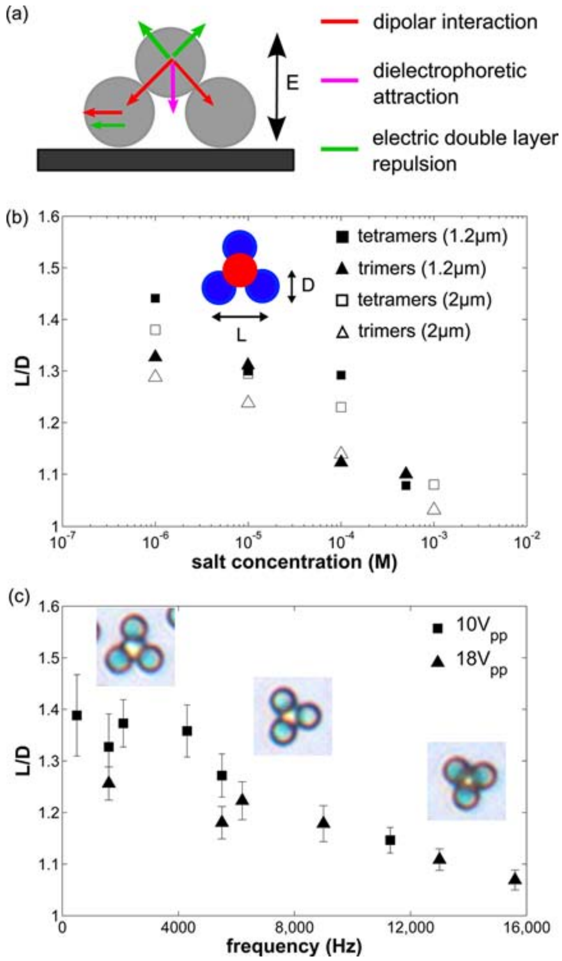

Figure 4. (a) Schematic showing the key forces involved in the formation of colloidal oligomers. (b) Effect of the salt (NaCl) concentration on the geometries of both trimers and tetramers for two different sizes of particles (D = 1.2 or 2 mm) at V_{pp} = 10 V and ω = 500 Hz. (c) Effect of frequency on the geometry of tetramers. The insets show representative optical images of the tetramers. The particles (D = 2 μm) were suspended in DI water.

charged at neutral pH (Figure S1b). At low salt concentrations, the relatively long-ranged EDL repulsion keeps the bottom particles in an oligomer separated. As shown in Figure 4b, we can tune this separation (L) by varying the salt concentration. With increasing salt concentration, the EDL repulsion becomes screened and short-ranged. Therefore, the separation between bottom particles decreases.

Under external fields, particles can be polarized through both bulk dielectric response and mobile ions in the diffuse layer. Therefore, the dipolar interaction between particles is also important. This interaction depends on the angle between the line connecting the centers of the two particles and the direction of the external field (θ).[13] It is repulsive (attractive) when the particles are aligned perpendicular (parallel) to the applied field. Therefore, in addition to the EDL repulsion, the dipolar repulsion between bottom particles in oligomers also keeps them separated from each other. However, the dipolar interaction between top and bottom particles can be attractive depending on θ or, equivalently, the geometric ratio L/D. From simple geometric relationships it can be shown that $L/D = [4(1 - \cos^2 \theta)]^{1/2}$ for trimers and $L/D = [3(1 - \cos^2 \theta)]^{1/2}$ for tetramers (Figure S2c). If we assume that all of the particles behave like point dipoles, the critical angle at which the dipolar interaction is neither attractive nor repulsive is $\theta_c \approx 54.7°$. This translates to critical L/D values of ~1.63 for trimers and ~1.41 for tetramers. We found that all of the experimental L/D values for both trimers and tetramers were close to or smaller than the corresponding critical values (Figure 4b,c). This suggests that the dipolar attraction between top and bottom particles contributes to the strong bonding in oligomers. Nonetheless, this dipolar attraction itself favors the chaining of particles along the field direction at high frequencies and cannot be solely responsible for the zigzag architecture observed in the oligomers.

We hypothesize that a dielectrophoretic force between the particles and the substrate facilitates the formation of colloidal oligomers instead of vertical chains. This force arises from a nonuniform electric field near the substrate due to the electrode polarization effect,[14] which is significant at low frequencies. The calculated[14a] electric field in an electrolyte between two conductive substrates is shown in Figure S5. Although the applied field is uniform across the two electrodes at high frequencies, two salient features can be recognized for low frequencies. First, the electric field is nonuniform at low ω. Mobile ions form a dynamic EDL near the substrate when an oscillating voltage difference $\Delta\phi e^{i\omega t}$ is applied. The excess ions in the EDL lead to an enhanced field that is locally much stronger than the apparent field $\Delta\phi/H$. Second, the capacitive nature of the EDL also inhibits the penetration of the electric field into bulk electrolytes. Therefore, the field far away from the substrate can be much weaker than the apparent field. This anisotropic nature of the electric field near electrodes can strongly affect the assembly of colloids on a conducting substrate. First, particles with positive polarizability (e.g., dielectric particles in low-salt aqueous solutions) can experience a dielectrophoretic attraction toward the substrate. This force favors the formation of oligomers rather than vertical chains. In fact, it is strong enough to overcome gravity, causing similar oligomers to form on the top electrode also (Figure S6). Second, the transition regime where the field strength is nonuniform typically extends to several (5–10) Debye lengths from the electrode, especially at low salt concentrations and low frequencies.[15] Therefore, this electrode polarization effect is particularly important for submicrometer-sized[16] and micrometer-sized particles.[15] At much larger particle sizes (D = 4 and 5 μm), few oligomers were observed (Figure S7). Third, the field beyond this transition regime is weaker than the apparent field $\Delta\phi/H$. This weak field in the bulk could make vertical chains unfavorable. At high ω, however, the field is uniform and equal to the apparent field, and linear colloidal chains that are parallel to the field direction are energetically stable.[12] Such chains are also stable when the dipolar attraction is strong, as in the case of large particles. For example, we observed both oligomers and vertical chains of dimers for 3 μm particles (Figure S7d). Last, this nonuniform electric field near the electrode is sensitive to the frequency. As ω increases, both the field gradient and field strength become smaller. The top particle thus experiences a weaker dielectrophoretic attraction to the substrate. Simultaneously, the bottom particles experience weaker dipolar repulsion. Therefore, the colloidal oligomers would be expected to become more close-packed. This effect was observed in our experiments (Figure 4c): as ω increased, L/D for tetramers decreased. Thus, both the salt concentration and the frequency provide convenient means to tune the geometries of colloidal oligomers. We also found that the stability of the central particle in oligomers strongly depends on the applied voltage but is less sensitive to frequency (Figure S8).

Although the building blocks used in this work were isotropic in terms of both geometry and interfacial properties, the applied electric field induced anisotropic interactions that led to surprisingly complex patterns. One example is shown in Figure 5a and supplementary movie 3. At low frequencies (e.g., $\omega = 1.5$ kHz), colloidal oligomers formed. When ω was increased, the array of separated oligomers was transformed into a honeycomb-like non-close-packed network by rearrangements between oligomers. Within one hexagonal ring, each vertex is formed by a tetramer, and each edge is occupied by one spherical particle that is shared between two tetramers. As shown in the movie, this open structure seems to be more stable than the separated array of oligomers both mechanically and thermodynamically. This non-close-packed structure could be formed by the competition between short-range attraction and long-range repulsion. The semiquantitative phase diagrams are summarized in Figure S9.

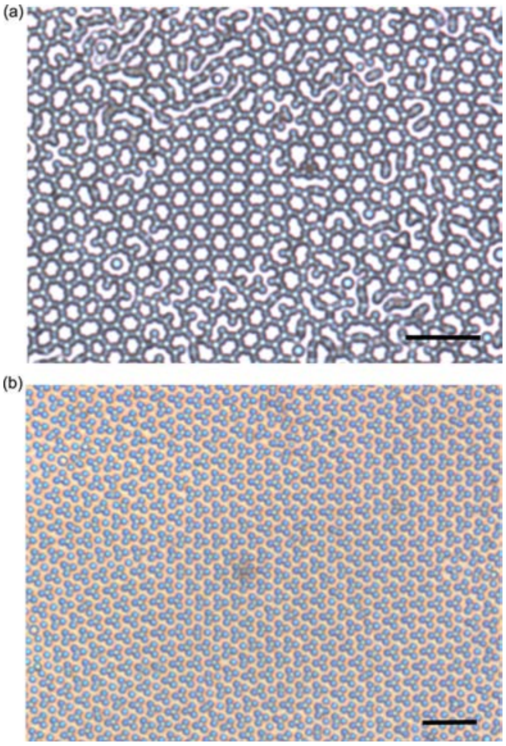

Figure 5. (a) "Honeycomb-like" open structure. (b) Large array of colloidal tetramers with high monodispersity. Scale bars: 10 μm.

The experimental simplicity demonstrated in this work provides a convenient method to fabricate new building blocks. For example, colloidal tetramers are of special interest because they could potentially form diamondlike lattices for photonic crystals.[3a] However, making monodisperse colloidal tetramers is challenging. Figure 5b shows a large array of colloidal tetramers with high monodispersity. These tetramers could potentially be fixed using several reported methods.[17,18] Moreover, our method is based on physical principles that can be applied to a variety of particles with different chemical properties. In fact, the phenomenon we report here is universal: we have successfully made colloidal oligomers with organic or inorganic particles, positively or negatively charged particles, and spherical or nonspherical particles (Figure S10).

In summary, we have demonstrated a versatile method for creating colloidal molecules using particles that are isotropic with respect to geometric and interfacial properties. When a low-frequency AC electric field is applied, the particles experience anisotropic dipolar and dielectrophoretic interactions that lead to the formation of colloidal oligomers and hierarchically non-close-packed structures. The assembly dynamics involves the breaking of old bonds, the generation of new bonds, and reversible transformations between different oligomers. Our findings could potentially open a new realm of building colloidal molecules based on isotropic particles.

ASSOCIATED CONTENT

Supporting Information

Procedures, supplementary figures, and movies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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