

DNA-Enabled Self-Assembly of Plasmonic Nanoclusters

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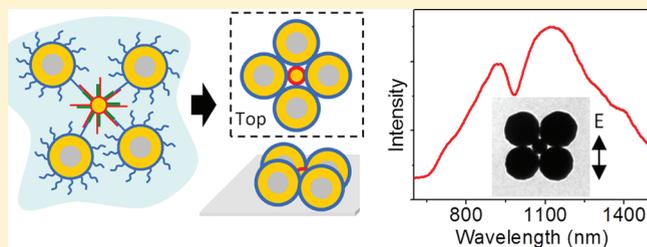
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S Supporting Information

ABSTRACT: DNA nanotechnology provides a versatile foundation for the chemical assembly of nanostructures. Plasmonic nanoparticle assemblies are of particular interest because they can be tailored to exhibit a broad range of electromagnetic phenomena. In this Letter, we report the assembly of DNA-functionalized nanoparticles into heteropentamer clusters, which consist of a smaller gold sphere surrounded by a ring of four larger spheres. Magnetic and Fano-like resonances are observed in individual clusters. The DNA plays a dual role: it selectively assembles the clusters in solution and functions as an insulating spacer between the conductive nanoparticles. These particle assemblies can be generalized to a new class of DNA-enabled plasmonic heterostructures that comprise various active and passive materials and other forms of DNA scaffolding.

KEYWORDS: Plasmonics, DNA, colloidal self-assembly, nanoshell, magnetic dipole, Fano resonance



Sub-wavelength-scale metallic particles are a basis for nanoscale light manipulation because they support localized surface plasmon resonances, which are oscillations of free electrons in metal that couple with electromagnetic waves.¹ By synthesizing particles into specific shapes and engineering their assembly, it is possible to construct nanoscale chemical sensors,² plasmonic rulers,³ optical nanocircuits,⁴ and metamaterials.^{5,6} DNA nanotechnology⁷ is a vehicle for the controllable assembly of nanoparticles⁸ because it enables the positioning of particles with nanoscale precision and the tailoring of their binding interactions. While simpler implementations of DNA particle assembly involve controlled nanoparticle aggregation,^{9,10} other efforts have focused on the construction of well-defined clusters and lattices. For example, micrometer-scale dielectric particles have been assembled into tetrahedral and octahedral clusters,¹¹ and in other schemes, trimer clusters,^{12,13} tetrahedral clusters,¹⁴ chiral helical assemblies,¹⁵ and two- and three-dimensional lattices^{16,17} of plasmonic nanoparticles have been constructed. It is tantalizing to envision these nanostructures as useful optical structures; however, these plasmonic assemblies have yielded little optical data in the literature because they typically utilize very small metallic particles (diameter <20 nm). With such small particles, optical measurements on individual nanostructures become

extremely difficult due to their small scattering cross sections. Larger optical signals can be obtained from ensemble measurements, but these suffer from sample heterogeneities that can weaken or completely eliminate the observation of certain optical resonances.¹⁸ Another issue with small particles is that, unlike large particles, they do not support many plasmonic modes; higher order resonances require retardation for their excitation, and Fano-like resonances, which will be discussed later, require strong linewidth broadening from radiative damping and retardation that exist only in large particle systems.

In this study, we use DNA to construct heteropentamer clusters consisting of a solid gold nanosphere surrounded by four larger nanoshells.¹⁹ The DNA route to particle assembly has distinct advantages over previous random capillary assembly methods:⁶ it introduces more specific and programmable interactions between metallic particles of different sizes and types and provides a potential route to more sophisticated three-dimensional particle assembly. The construction of the heteropentamer was partially motivated by prior calculations demonstrating

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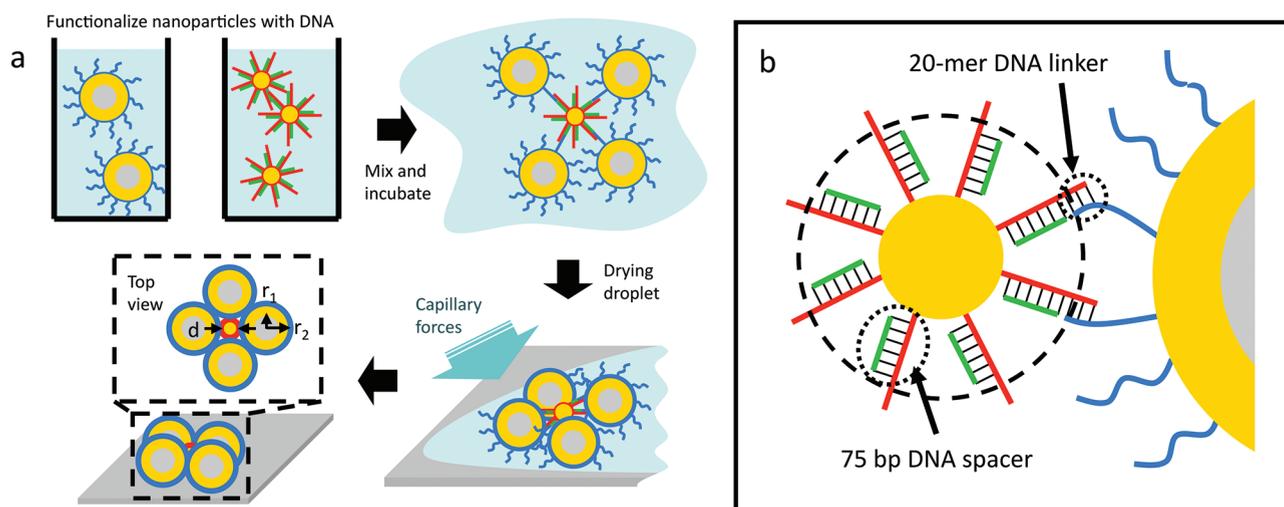


Figure 1. DNA-mediated assembly of plasmonic heteropentamers. (a) To assemble the clusters, gold nanospheres and nanoshells are functionalized separately with thiolated DNA strands, which form self-assembled monolayers on the particle surfaces. They are then mixed and incubated together at room temperature, where they assemble into “loosely” bound pentamers. Finally, the clusters are dried on a hydrophilic substrate, where capillary forces compress the pentamers into a close-packed two-dimensional configuration. (b) The nanospheres are functionalized with partially dsDNA molecules consisting of three regions: a gold attachment region comprising a thiol group and 5-mer polyT sequence, a 75bp ds “spacer” region, and a 20-mer “linker” region. Prior to nanosphere attachment, the thiolated 100-mer DNA (red) is mixed with complementary 75-mer strands (green) to form rigid dsDNA segments that effectively increase the nanosphere size in solution (dotted circle). The nanoshells are functionalized with ssDNA (blue) comprising a 50-mer polyT spacer sequence, followed by a 20-mer linker that complements the nanosphere linker.

Fano-like resonances for this cluster geometry;²⁰ sufficiently large nanoparticles are used here so that the Fano minima are clearly observable. The ratio of the nanoshell diameter to nanosphere diameter is set to approximately 2.4 to ensure a close packed geometry and strong coupling between all neighboring particles.

The self-assembly process is outlined in Figure 1a. First, the nanospheres and nanoshells are functionalized separately with different thiolated DNA molecules,²¹ which form self-assembled monolayers on the particle surfaces. The outermost 20-mers of DNA on the nanospheres and nanoshells are complementary, thus facilitating specific nanosphere–nanoshell binding while minimizing interactions between particles of the same type (Figure 1b). The particles are then cleaned and incubated together at high salt concentration and room temperature, where loosely packed pentamers are formed in three dimensions in aqueous suspension. The ratio of the number of nanoshells to nanospheres is set to 12:1 to enhance pentamer yield while limiting the assembly of large nanoshell–nanosphere aggregates, which were observed for particle mixtures with smaller ratios. Finally, the clusters are air-dried on a hydrophilic substrate at room temperature. During the drying process, capillary forces compress these loosely packed three-dimensional structures into two-dimensional pentamers. Both single-stranded DNA (ssDNA) and double-stranded DNA (dsDNA) collapse and pack to yield dense 2 nm thick dielectric spacers between all neighboring nanoparticles, ensuring their strong and controlled optical coupling. As a control experiment, nanoparticles were functionalized with non-complementary DNA sequences and mixed together, and no pentamers were observed. It is difficult to quantify the overall yield of these pentamer clusters (further discussed in the Supporting Information); nevertheless, it is easy to find many pentamers on a TEM grid, which is sufficient for single nanostructure experimentation. We also found other DNA-enabled clusters, ranging from dimers and trimers to small aggregates. Heteropentamer yields may be further enhanced by

increasing the number ratio of nanoshells to nanospheres and employing separation methods, such as density gradient centrifugation, to distill pentamers from single nanoshells and other cluster types, and this will be the subject of future study.

The assembly of pentamers in solution involves the sequential attachment of nanoshells onto a nanosphere (Figure 2a). The first association between a single nanoshell and nanosphere is straightforward: Brownian motion brings the two particles into close proximity and their surface-attached DNA hybridizes. However, the association of additional nanoshells onto a nanosphere becomes more difficult kinetically for two principal reasons (Figure 2b). The first involves steric hindrance: already associated nanoshells will physically block other nanoshells from getting close to and associating with the nanosphere. The second is due to the lack of hybridizable DNA on the nanosphere surface. Single-stranded DNA is a polymer with $\sim 1\text{--}2$ nm persistence length in solutions containing high salt concentration (ref 22), such that multiple DNA strands from a single nanoshell can attach to multiple nanosphere DNA strands in a polyvalent interaction. In our system where the length of DNA is on the order of the nanosphere diameter, the DNA from two or three nanoshells can associate with most of the nanosphere strands, leaving very few free nanosphere strands for additional association events. In order to overcome these problems, we design the 75 base double-stranded spacer on the nanosphere. Since the persistence length of dsDNA is 50 nm, this rigid spacer effectively increases the size of the nanosphere in solution by 50 nm²³ (Figure 1b), alleviating the steric hindrance problem. Also, the rigidity of the dsDNA and relatively short length of the ssDNA linker reduce the polyvalent association between the nanoshells and nanospheres.

Individual heteropentamers are identified using transmission electron microscopy (TEM), and scattering spectra from individual clusters are measured in the near-infrared frequency range using dark-field microscopy. (See Supporting Information for setup.) Here, the incident light is s-polarized (i.e., the electric

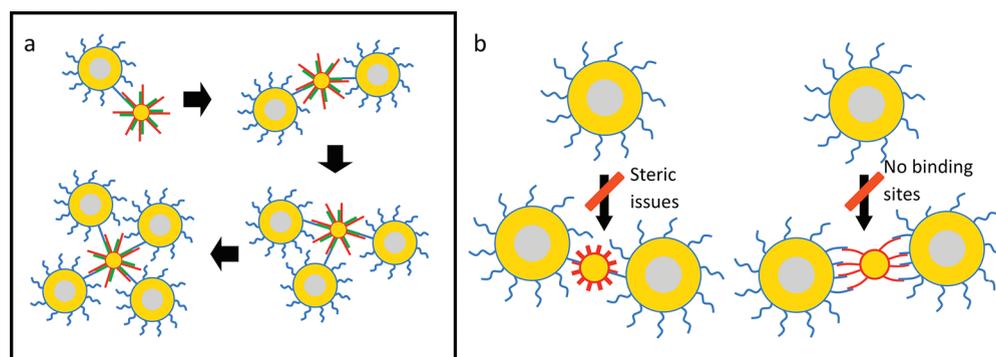


Figure 2. Detailed view of plasmonic cluster formation in solution. (a) The pentamer assembles in solution by the sequential attachment of nanoshells onto a nanosphere. Successful pentamer assembly requires each of these intermediate steps to be stable (i.e., the nanoshells remain attached) and kinetically accommodating to additional nanoshell association events. (b) There exist at least two issues that can impede the attachment of additional nanoshells to a cluster. One is that already associated nanoshells can sterically hinder other single nanoshells from getting close to and attaching to the nanosphere (left). This is especially a problem if the nanosphere DNA strands are too short. Another is that if the nanosphere DNA is too long and floppy, DNA from just two or three nanoshells can associate with most of the nanosphere DNA, reducing the total number of available linker DNA on the nanosphere and suppressing additional nanoshell association events (right). Both of these issues are addressed by utilizing the long dsDNA spacer on the nanosphere.

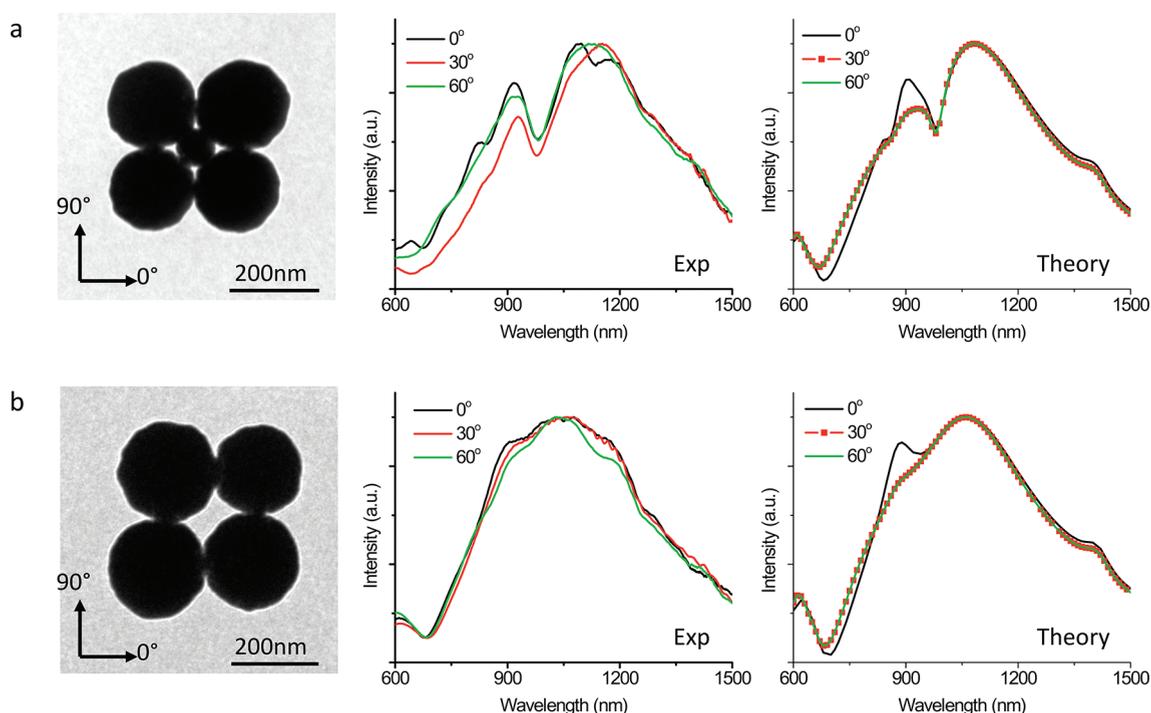


Figure 3. TEM images and scattering spectra of individual heteropentamer and quadramer clusters. (a) s-polarized spectra of a pentamer for different electric field polarization angles. Both the experimental and theoretical spectra are characterized by a broad electric dipole peak and a narrow Fano dip near 1000 nm. The in-plane isotropy of these spectra is consistent with the symmetry of these clusters. The simulated geometry is based on the TEM image and uses a nanosphere diameter $d = 74$ nm, nanoshell $[r_1, r_2] = [62.5, 92.5]$ nm, and interparticle gaps of 2 nm that are filled with dielectric. (b) TEM image and s-polarized spectra of a symmetric quadramer. These spectra exhibit a broad electric dipole peak but no clear Fano dip, indicating that the nanosphere is necessary for this cluster system to exhibit a strong Fano-like resonance. The experimental spectra generally match those simulated using the same nanoshell geometry and gap dielectric as in (a).

field is in the plane of the cluster) and the polarization angle of the electric field relative to the nanostructure is controlled. Scattered light from an individual structure is selected with a confocal-type technique, by placing a pinhole at a reimaged focal plane and allowing light from only the structure of interest to enter the spectrometer. Spectra of a single pentamer for three different polarization angles are shown in Figure 3a and are

characterized by a broad electric dipole resonance spanning the entire range of the plot. There exists a narrow and asymmetric dip near 1000 nm, which is a Fano resonance. These resonances arise from interference between a superradiant “bright” mode and a subradiant “dark” mode and have been studied extensively in plasmonic systems.^{5,24} These experimental spectra match those calculated using the finite element simulation software

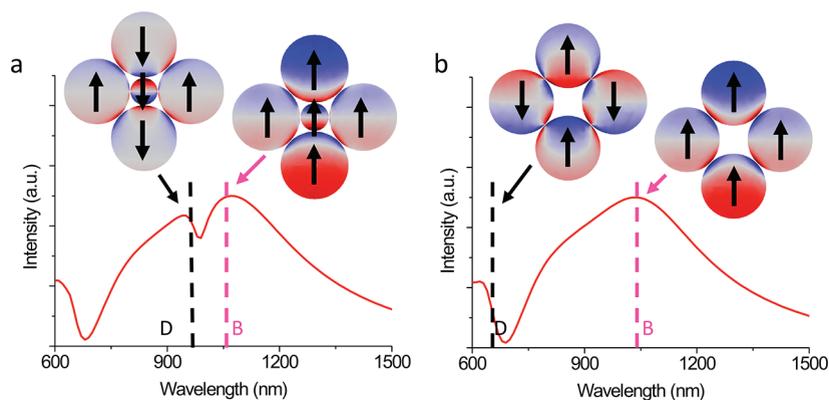


Figure 4. Theoretical analysis of the bright and dark modes involved with Fano-like resonances. (a) Extinction spectrum and surface charge plots of the heteropentamer excited at normal incidence with a 45° polarization angle. The charge density of the bright mode, which is peaked at 1050 nm (pink dashed line), shows the charge oscillations on each nanoparticle oriented in the same direction, yielding a large cluster dipole moment. The dark mode at 980 nm (black dashed line) shows the charge oscillations on each nanoparticle oriented in different directions, yielding a small cluster dipole moment and suppressed radiative losses. There is clear capacitive coupling between the nanosphere and the two nanoshells above and below the nanosphere, which redshifts the mode close to the bright mode peak. (b) Extinction spectrum and surface charge plots of the quadramer excited with the same conditions as in (a). The bright mode peak is near 1040 nm (pink dashed line) and the charge distribution shows a large cluster dipole moment. The dark mode peaked at 650 nm (black dashed line) shows the total cluster dipole moment is small. The absence of capacitive coupling between the nanoparticles prevents strong overlap in frequency between the dark and bright modes.

COMSOL (Figure 2a) and are nearly independent of incident polarization angle due to the D_{4h} group symmetry of the cluster, which supports isotropic in-plane resonances in the quasistatic limit.

To further probe the interaction of the nanosphere with the nanoshells in the pentamer, we identified and optically characterized symmetric nanoshell quadramers. These nanostructures assembled by entirely different means from the pentamer: here, four single nanoshells trapped in a drying droplet clustered together by capillary forces, in similar fashion to clusters assembled previously.⁶ The strong electrostatic repulsion between the nanoshells, provided by the negatively charged DNA, helps them arrange in a non-close packed configuration; it is noted that in previous experiments utilizing uncharged PEG-functionalized nanoshells, symmetric quadramers were not found.⁶ The spectra from an individual quadramer display a broad electric dipole resonance but no strong Fano dips, indicating that the nanosphere in the pentamer is required for strong Fano-like resonances to be observed (Figure 3b). As with the pentamer, this cluster possesses isotropic in-plane resonances due to its group symmetry.

The Fano-like resonances in these clusters are further analyzed by examining the surface charge distributions of their bright and dark modes (Figure 4). In both the quadramer and pentamer, the bright modes are characterized by nanoparticle polarizations oriented in the same direction. As such, the cluster dipole moments are large and the mode strongly redshifts due to strong capacitive coupling between neighboring nanoparticles. Physically, this coupling arises from the attractive quasi-static interaction between surface charges on these nearly touching particles.²⁵ The dark modes of each cluster, however, have very different spectral positions. The pentamer dark mode charge distribution shows that the small nanosphere capacitively couples with two of the nanoshells, which strongly redshifts the mode. The total dipole moment of this cluster is small but non-negligible, which limits the magnitude of the Fano dip. The quadramer dark mode, which has been studied elsewhere,²⁶ exhibits little capacitive coupling between adjacent nanoshells. As a result, the mode is

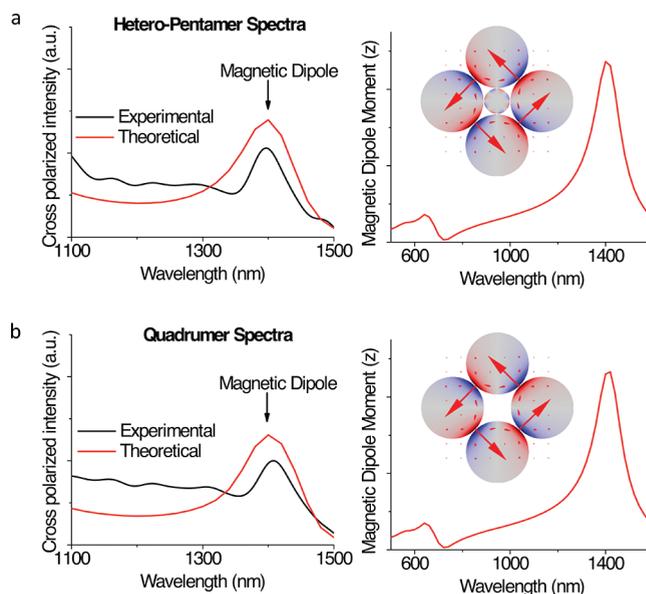


Figure 5. Magnetic dipole resonances in nanoparticle clusters. (a) Experimental and theoretical cross-polarized spectra of the pentamer at 0° polarization angle (left) reveal a narrow peak near 1400 nm, which matches the peak position of the calculated out-of-plane magnetic dipole moment of the cluster (right). The inset is a quasistatic mode plot of the surface charges (color) and displacement current (arrows) of the magnetic dipole mode. (b) Experimental and theoretical cross-polarized spectra of the quadramer with the same electric field polarization angle (left) also reveal a narrow magnetic dipole peak near 1400 nm that matches the peak position of the calculated magnetic dipole moment (right) of the cluster. The inset is a quasi-static mode plot of the magnetic dipole mode and shows a circulating current around the ring of nanoshells similar to that in (a). These plots and calculated magnetic dipole moments show that the magnetic dipole mode in the pentamer and quadramer is due to near-field interactions between the nanoshells and that the mode in the pentamer is effectively decoupled from the nanosphere.

blueshifted beyond the bright mode and there is no clearly visible Fano minimum. As observed with other nanocluster structures previously studied,⁷ the key to engineering a strong Fano dip is to design bright and dark modes that exhibit similar levels of capacitive coupling between particles, thereby enforcing strong spectral overlap between the two modes.

We also analyze magnetic dipole modes in these clusters. These resonances are excited by the magnetic component of the incident electromagnetic field and were previously measured in nanoshell trimers.⁶ They are predicted to be supported here by the outer ring of nanoshells, which form a closed loop of metallic nanoinductors and dielectric nanocapacitors²⁷ in similar fashion to the trimer. These modes are not clearly visible in the scattering spectra in Figure 5 because they weakly scatter compared to the electric dipole; a cross-polarizer oriented 90° relative to the incident light polarization can be placed after the collection objective to filter out elastically scattered electric dipole radiation.⁶ The cross-polarized spectra of the quadramer and pentamer are shown in Figure 5 and they both exhibit clear, narrow peaks near 1400 nm. The positions of these peaks match those of the calculated magnetic dipole moments, confirming that they are magnetic resonances. There is less background in these spectra compared to those of the trimer previously studied because unlike the trimer, these clusters have inversion symmetry and, based on the criteria outlined in ref 28, do not support extensive optical activity. The simulated electric field profile and displacement current of this mode in both cluster types show a circulating current around the quadramer ring, which is a hallmark of a classical magnetic dipole. The matching magnetic dipole moments from both clusters indicate that the presence of the nanosphere in the pentamer does not affect the magnetic resonance from the nanoshell ring. This can be further understood by group theory, in which the irreducible representation of the pentamer can be expressed as $\Gamma_{\text{Pent}} = \Gamma_{\text{Nanosphere}} + \Gamma_{\text{Quad}}$. The magnetic mode in the quadramer has an irreducible representation of A_{2g} while the nanosphere has an irreducible representation of E_{1u} ; as modes with different representations do not couple with each other, the nanosphere does not affect the magnetic mode.

The DNA-enabled assembly of nanoparticles can be generalized to a broad range of two- and three-dimensional heteroclusters. These are not limited to passive plasmonic particles and can include other types of dielectric, nonlinear, active, and organic materials to create new functional nanostructures such as active antennas,²⁹ surface plasmon lasers,³⁰ clusters with tailorable hot spots,³¹ and metamaterial fluids.³² Other forms of DNA nanotechnology, such as DNA origami,³³ have great potential as rigid scaffolds with high spatial resolution for particle assembly. In this study, the pentamers were assembled in two steps, first by DNA to “loosely” assemble the clusters in suspension and then by capillary forces to “compact” the clusters in two dimensions; loosely assembled clusters can be compacted or manipulated in three dimensions in suspension via depletion³⁴ or optical forces³⁵ or by tailoring new chemical interactions between particles,³⁶ and new regimes of capillary assembly can be employed using patterned substrates,³⁷ surfactants, or other additives to further control cluster assembly on substrates. The merging of biomaterials like DNA with plasmonic nanostructures is suggestive of new forms of plasmon-enhanced biomolecular detection schemes, dynamically reconfigurable nanostructure geometries, and even direct integration and assembly of nanoclusters within biological systems.

■ ASSOCIATED CONTENT

S Supporting Information. Materials and methods details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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