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Dynamic DNA Templates for Discrete Gold Nanoparticle Assemblies: Control of Geometry, Modularity, Write/Erase and Structural Switching

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Gold nanoparticle assemblies have recently emerged as a promising class of materials, with novel optical, electronic, catalytic, and sensing applications.[1] Many of their properties, such as electron transport and optical coupling, arise directly from the relative arrangement of the nanoparticles within the assembly.[1b,2] However, fundamental studies of these phenomena have been hampered by the lack of methods to systematically organize nanoparticles into well-defined discrete model structures.[3−5] As a result, these properties have been typically studied in a collective fashion using extended 2D and 3D assemblies.[3] Here we report a straightforward method to mediate the assembly of discrete structures of gold nanoparticles, using single-stranded and cyclic DNA templates with rigid organic vertices **1** and **2**. Hybridization of these cyclic templates with Au particles monofunctionalized with DNA allows for them to be directly positioned on the complementary arms of the templates (Figure 1). Control of geometry is demonstrated by the facile creation of triangles and squares of nanoparticles (Figure 1a). Modularity is shown by the ability to place different nanoparticles in precise locations on these cycles, thus assembling them into, for example, triangles of all possible combinations (Figure 1b). Structural switching is established by using the same square DNA template for the selective construction of square, trapezoidal, and rectangular assemblies (Figure 1c). Finally, write/erase function is shown by assembling triangles of three Au particles, selectively removing one particle, and "writing" of a different particle into the assembly (Figure 1d). Overall, this approach represents what is, to our knowledge, the highest level of control over the construction of discrete nanoparticle assemblies.[3,4] Unlike current methods of DNA-based construction,[6] which typically interweave many DNA units into a double-stranded and rigid scaffold, our approach relies on the creation of *dynamic* DNA templates that are fully functional in their single-stranded and cyclic form. The same template can give selective access to a large number of particle groupings, and these structures are addressable and switchable post-assembly.

Construction of DNA cyclic templates **1** and **2** is shown in Scheme 1a for **1**. Building blocks containing two DNA arms and a rigid organic vertex are first synthesized.[9] These are sequentially assembled into double-stranded triangle **3** (Scheme 1a-i). After its isolation, the cyclic nature of **3** is confirmed using Mung Bean nuclease assays.[4a] The "nicked" sides of **3** are ligated to yield fully cyclized construct **4** (Scheme 1a-ii). Finally, **1** is isolated using denaturing polyacrylamide gel electrophoresis (PAGE, Scheme 1a-iii).[9] Square template **2** is synthesized similarly.[9] For control experiments, single-stranded trimer **5** and tetramer **6**, linear analogues of **1** and **2**, are synthesized. **1**, **2**, **5**, and **6** are further characterized using PAGE titration experiments with complementary strands and MALDI-TOF MS.[9] Synthesis of monofunctionalized gold/DNA particles is carried out by incubation of Au particles with thiolated DNA and purification of the desired adducts from agarose gels.[4b,7] Adequate separation of the monoconjugates[7b] was achieved by noncovalent extension of the DNA strands with sequences constituted of two domains, a 15-base region that is

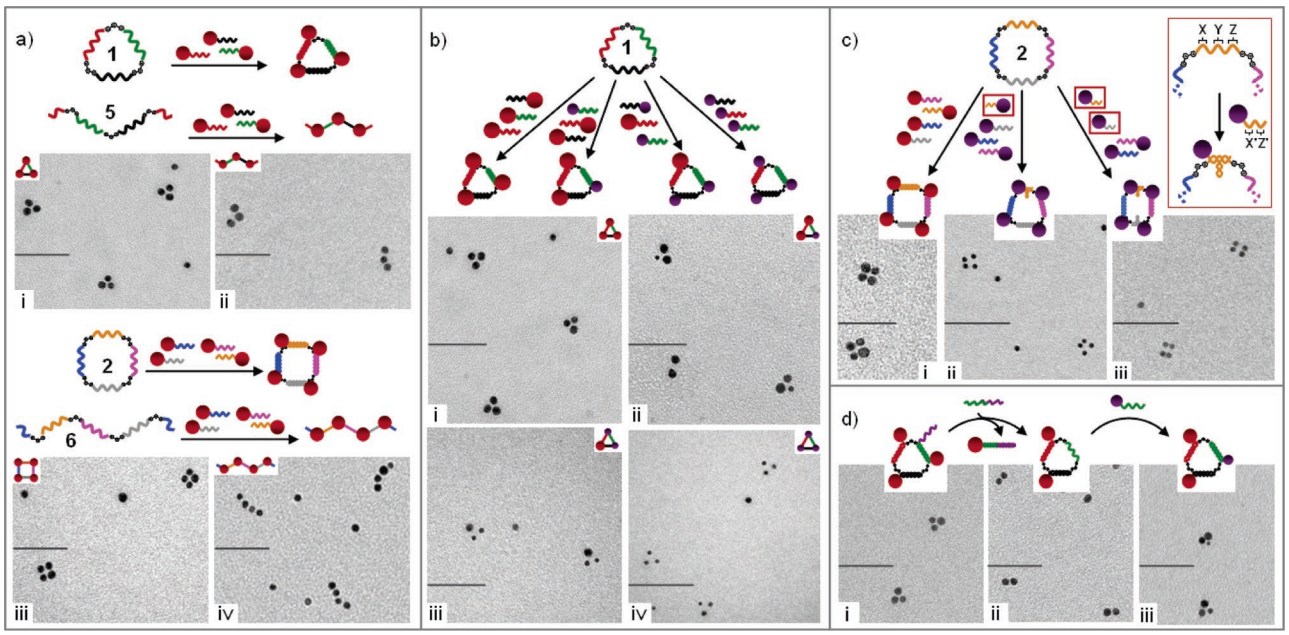

Figure 1. (a) **1** and **2** organize Au particles into triangles and squares; **5** and **6** result in open linear assemblies of three and four particles. (b) **1** generates triangles of (i) three large (15 nm, red), (ii) two large/one small (5 nm, purple), (iii) one large/two small, and (iv) three small particles. (c) **2** assembles four Au particles into (i) squares (15 nm particles), (ii) trapezoids, and (iii) rectangles (5 nm). Inset: use of a loop shortens the template's arm. (d) Write/erase function with **1** by (i) writing three Au particles (15 nm) into triangles, (ii) removal of a specific particle using an eraser strand, and (iii) rewriting with a 5 nm particle. Bar is 50 nm.

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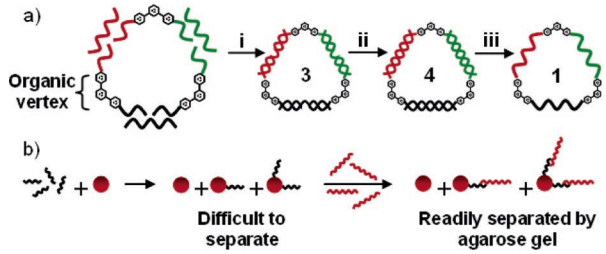
Scheme 1



complementary to the last 15 bases of the thiolated DNA strand and a 70-base run of thymines (Scheme 1b). This results in reversible lengthening of the 40-base DNA sequence into a 110mer.[9] Control experiments confirm that the extension strands can be readily displaced by either **1** and **2**.[9]

With single-stranded cyclic DNA templates **1** and **2** and monofunctional gold/DNA in hand, we proceeded to test the ability of these templates to yield nanoparticle groupings with geometrical control. When **1** is incubated with three 15 nm gold particle−DNA monoconjugates that are complementary to each of the three arms, well-defined triangles of gold nanoparticles are observed using transmission electron microscopy (Figure 1a-i). However, incubation of **5**, the linear analogue of **1**, with complementary gold monoconjugates yields gold trimers with many more degrees of freedom than the triangles constructed from **1** (Figure 1a-ii). Similarly, hybridization of **2** with four complementary gold monoconjugates yields well-defined Au particle squares, in contrast to the more conformationally mobile groupings assembled on linear template **6** (Figure 1a-iii,iv). Cyclic templates **1** and **2** thus result in the selective assembly of Au particle triangles and squares with high degree of spatial control.[9]

The modular nature of this method was then examined by testing whether different nanoparticles can be instructed to assemble on their correct locations within the template. Using triangle **1**, we introduced two nanoparticles of different sizes, a larger 15 nm and a smaller 5 nm particle, monofunctionalized with DNA strands of appropriate sequences. This results in the specific organization of triangles of these different particles into all possible combinations (Figure 1b). Triangles with three larger gold particles (Figure 1b-i), two larger/one smaller (Figure 1b-ii), one larger/two smaller (Figure 1b-iii), and three smaller particles (Figure 1b-iv) were all created selectively, using the same DNA template **1**. Statistical analysis of the mixed particle assemblies shows that the expected groupings (e.g., one large/two small) are formed in >90% yield of all triangles observed.[9]

The capacity of our Au particle assemblies to undergo structural switching was then tested. If the length of each arm could be selectively modified, a single template could result in many assemblies of different geometries. This can be achieved by the incorporation of internal loops that shorten the arms of the templates (Figure 1c inset). Gold particles were monofunctionalized with a short 20-base DNA strand that is only complementary to the two outer 10-base regions of the arms of template **2**. When one such shorter gold conjugate is placed on one of the arms of **2**, and three fully complementary gold conjugates are placed on the other three arms, the square of Au particles turns into a trapezoid (Figure 1c-ii). When two such shorter Au conjugates are selectively placed on two parallel arms of **2**, and two fully complementary Au conjugates are positioned on the other arms, the square turns into a rectangle of Au particles (Figure 1c-iii). Analysis shows that the expected trapezoid and rectangle geometries are observed in >90% of the Au particle tetramers.[9] Thus, **2** results in Au squares, trapezoids, and rectangles.

The ability to write and erase information into nanoparticle assemblies could give rise to *dynamic* circuitry, whose properties may be switched in real time and in response to external stimuli.[8] The particle to be erased is labeled with a 60-base strand of DNA, of which only 40 bases are complementary to the template arm, leaving a 20-base overhang. This allows for its specific removal upon hybridization to a fully complementary 60-base "eraser" DNA strand. The newly produced empty position can then be rewritten with a different nanoparticle (Figure 1d). In the present case, three larger sized gold particles are assembled into a triangle (Figure 1d-i), and the particle containing the 20-base overhang is removed using a fully complementary eraser strand (Figure 1d-ii) and replaced with a smaller sized gold particle (Figure 1d-iii).[7] Statistical analysis shows the formation of the expected assembly with near quantitative selectivity in all steps.[9] Control experiments show that the removal of the larger gold particle can only be achieved with the eraser DNA strand.[9]

In summary, we created DNA templates for the dynamic and modular assembly of discrete gold nanoparticle groupings. This approach not only provides the ability to finely control the geometry of the assembly and the precise position of each nanoparticle but also allows the modification and tuning of these structural features post-assembly. In principle, any DNA-labeled nanocomponents can be assembled with these templates, and thus, this represents a highly economical method to organize materials using DNA.[6] Access to libraries of precisely positioned particle groupings will allow for the systematic examination of their optical, electronic, and catalytic properties as a function of structure and will lead to advances in the use of these particles as components of nanoelectronic/nanophotonic circuitry, as plasmonic tools, and as surface-enhanced Raman scattering substrates.

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Supporting Information Available: Synthesis of **1**, **2**, and gold/DNA conjugates. Statistical analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See Supporting Information; additional TEM images of Au assemblies.

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