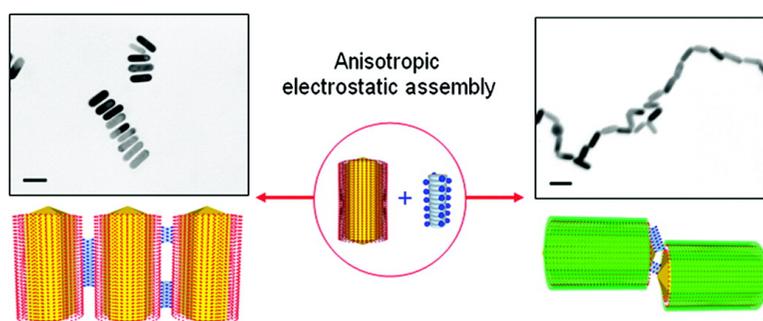


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Controllable Side-by-Side and End-to-End Assembly of Au Nanorods by Lyotropic Chromonic Materials

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We present a simple and universal technique for assembling gold nanorods (NRs) using self-assembled stacks of lyotropic chromonic materials, without covalent bonding between NRs and the linking agent. The anisotropic electrostatic interaction between the chromonic stacks and NRs allows one to achieve either side-by-side or end-to-end assembly, depending on the surface charge of NRs. The assembled superstructures are stable within an extended temperature range; the degree of NR aggregation can be controlled by a number of factors influencing the self-assembly of chromonic materials, such as the concentration and pH of the solution.

Introduction

Understanding and controlling the collective behavior of nanoparticles (NPs) is a challenging problem of fundamental and practical importance.^{1,2} This is particularly true for NRs because their anisotropy implies additional functionality on the scale of individual particles and their assemblies, enabling a variety of applications from cloaking devices³ to biological sensing⁴ and solar energy conversion.⁵ There are two basic approaches to NR assembly. The first one relies on the Onsager (excluded volume) mechanism, driving the parallel alignment of NRs when their volume fraction Φ and their aspect ratio are high enough.^{6,7} The second mechanism utilizes anisotropic attractive forces and thus allows one to produce assembled structures at practically any NR concentration. Examples include end-to-end assembly of NRs with covalently bound biotin connected into chains by streptavidin⁸ and side-by-side assembly of NRs with an oppositely charged B-DNA,⁹ as well as hydrophobic/hydrophilic interactions.^{10,11} Here we present a simple and universal technique of the second type that uses a new type of a noncovalent “linker” to assemble the nanorods through anisotropic attractive forces either side-to-side or end-to-end, depending on the surface charge of NRs. These universal linkers are electrically charged self-assembled aggregates of lyotropic chromonic molecules.

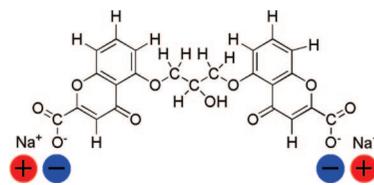


Figure 1. Molecular structure of DSCG.

We used chromonic material disodium chromoglycate (DSCG), also known as the antiasthmatic drug Intal. DSCG molecules (Figure 1) are disklike with a polyaromatic core and two ionizable groups at the periphery that make DSCG water soluble. DSCG molecules self-assemble into polydisperse stacks, being stacked face-to-face to avoid contact with water.^{12–16} At low concentrations up to 0.27 mol/kg (room temperature), the solution is isotropic, whereas at higher concentration, the stacks become sufficiently long to form a nematic phase.^{12–16} In the isotropic solution, the average length of a stack is expected to depend on the volume fraction ϕ of DSCG and the “sticking” energy E (i.e., the energy gain associated with the placement of the molecule within the stack)

$$\langle L \rangle \propto \sqrt{\phi} \exp \frac{E}{2k_B T} \quad (1)$$

as in the model of wormlike micelles.¹⁷ In the isotropic solution, $\langle L \rangle$ is on the order of a few nanometers¹⁶ whereas the diameter of the stack has been estimated to be ~ 1.5 nm.¹⁸ Because the repeat distance of stacking is 0.33 nm, the charge line density is high, in the range from ~ 6 e/nm (with one DSCG molecule in the cross-section) to ~ 24 e/nm (with four molecules in the cross-section), the same as in B-DNA (6 e/nm) or even higher. Although the chromonic stacks resemble the B-DNA duplexes

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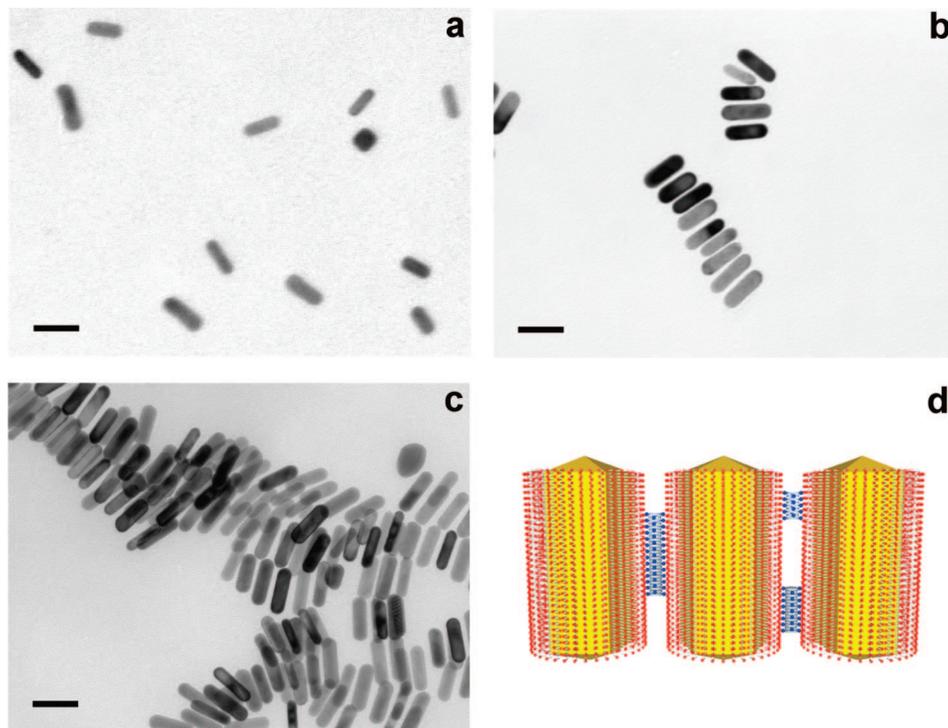


Figure 2. Side-by-side self-assembly of Au NRs induced by 0.8 mM DSCG solution mixed with 2 nM Au NR solution in water in a 1:1 ratio. (a) TEM image of the control sample, no DSCG, isolated NRs; (b) rafts of NRs formed approximately 5 min after the addition of DSCG; (c) assemblies of NR formed about 15 min after the addition of DSCG; (d) schematic representation of the side-by-side assembly of positively charged Au NRs mediated by negatively charged stacks of DSCG serving as self-assembled multivalent counter ions. The scale bars are 50 nm.

geometrically and electrostatically, there is an important difference: in the chromonic stacks, there are no covalent bonds along the lateral surface to link the molecules and thus to fix the size of the stack; the latter can be controlled by the temperature, ionic content of the solution, etc.¹⁹ The stacks thus represent self-assembled macroions with the ability to interact with other charged species, such as gold NRs. The resulting NR architecture has two levels of assembly: first, the chromonic linkers are anisotropically self-assembled into stacks, and second, the NRs assemble into different oriented states through anisotropic electrostatic interactions with the chromonic linkers.

The assembly process is very simple. When the NRs are positively charged, DSCG assembles them side-by-side. When the NRs are coated with poly(acrylic acid) to render negative surface charge, DSCG assembles them end-to-end.

Side-by-Side Assembly. The experiments were performed with Au NRs coated with CTAB that provides a positive charge to the rods. In control samples with no DSCG, we observe no self-assembly because the gold NRs repel each other (Figure 2a). The side-by-side attraction of NRs and their assembly starts immediately when a proper amount of DSCG is added, as suggested by both TEM (Figure 2b) and light absorption data (Figure 3a). We used 0.5 mL of NR solution (concentration ~ 2 nM²⁰), to which we added 0.5 mL of DSCG solution in water. Assembly was especially efficient for DSCG concentration in the range of 0.4–0.8 mM. (The aggregation rate increased with the concentration.) The assembly was not detected for DSCG concentration lower than ~ 0.1 mM; at concentration higher than 20 mM, the NRs formed large clusters and precipitated.

At the given concentration of the solutions, the size of the assembled structures increases with time (Figure 2). The NRs

in the superstructures are parallel to and in registry with each other so that their ends are aligned fairly well along a common line. The superstructures resemble wooden rafts, with the width approximately equal to the length of an NR and the thickness equal to the diameter of the NR. We do not observe “island” assembly in which the NR would be surrounded by more than two neighbors. However, as time progresses and the number of NR rafts increases, separate rafts might eventually overlap. In some instances, TEM of highly concentrated regions shows that the individual rafts run parallel to each other so that the individual NRs from different rafts are associated in an end-to-end fashion (Figure 2c).

In the TEM, the assembly might be an artifact of solvent evaporation. Further evidence of the side-to-side assembly is obtained by UV–vis spectroscopy (Figure 3). An isotropic solution of isolated gold NRs shows two absorption peaks associated with the oscillations of free electrons, a longitudinal and a transverse plasmon. The peaks’ characteristics change when the NRs assemble. After the DSCG addition (Figure 3a), the longitudinal peak experiences a strong blue shift (toward the shorter wavelengths) and decreases in amplitude. The transverse peak becomes red-shifted and increases in amplitude. These distinct changes qualitatively agree with the numerical simulations of model systems.^{21–23}

The observed side-by-side assembly cannot be caused by the Onsager mechanism because the concentration of NRs is much lower than needed to satisfy the Onsager criterion,²⁴ $\Phi L/d \geq 4$. In our case, the length-to-diameter ratio is $L/d \approx 3–5$ for the used NRs, and Φ is on the order of 10^{-5} . We explain the assembly

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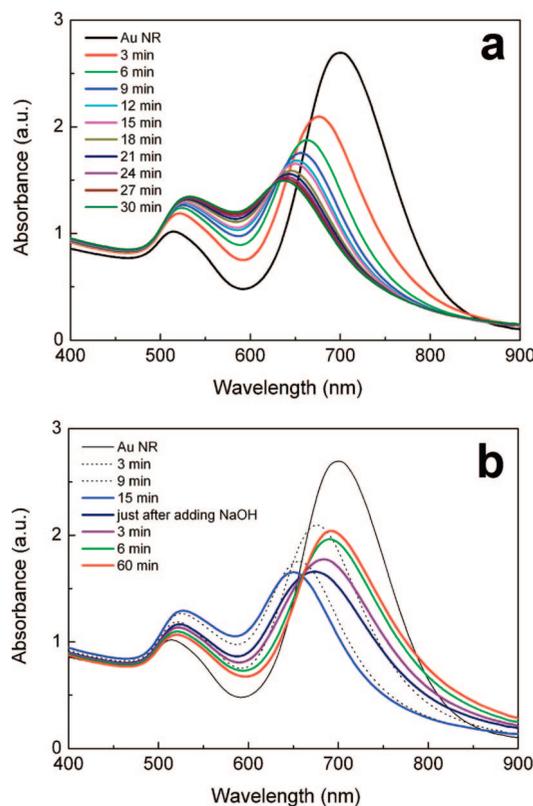


Figure 3. (a) Absorption spectra of ~ 0.2 nM Au NRs with CTAB coatings modified by the addition of 0.5 mM DSCG as a function of time; the longitudinal plasmon peak is blue-shifted, and the transverse plasmon peak is red-shifted. (b) The same as for plot a, but 15 min after the addition of 0.5 mM DSCG, we add 8 μL of 0.5 M NaOH; the longitudinal plasmon peak reverses its shift back to the longer wavelength, and the transverse plasmon peak shifts back to the shorter wavelength.

by electrostatic attraction between negatively charged DSCG stacks and positively charged CTAB-stabilized NRs (Figure 2d). The affinity of CTAB for the lateral surfaces of NRs (corresponding to $\{110\}$ and $\{100\}$ facets) is higher than for the end facets $\{111\}$ of the rod.^{8,25,26} As a result, the lateral surface is charged by CTAB more strongly than are the end facets.^{25,26} Thus, the DSCG stacks should be attracted to the lateral sides of NRs (and less so to their ends). This binding of DSCG is the ultimate reason for the mutual side-by-side attraction of Au NRs.

In the absence of DSCG, the NRs experience Coulomb repulsion, which promotes their mutually perpendicular arrangements. In the presence of “linkers” such as multivalent counterions, the behavior changes dramatically, as evidenced by the bulk of research on stiff polyelectrolytes such as DNA and F-actin.^{27–29} The competition between the long-range electrostatic repulsion and short-range attraction mediated by linkers often results in parallel assemblies and the condensation of rods. For example, as predicted by Borukhov et al.,²⁹ linkers that absorb at the surface of the rods drive the formation of bundles in which the rods are parallel to each other, connected by linkers, as in Figure 2d. The effect is predicted for a concentration of rods that is much lower than the Onsager limit needed for the formation

of the liquid-crystalline phases of rods. The absence of side-by-side assembly at low concentrations of DSCG linkers is also in qualitative agreement with the model.²⁹ Note that in our experiments the rafts have a pronounced shape anisotropy, being only one NR diameter thick, at least in the early stages of association. This shape might be simply an experimental artifact associated with TEM sample preparation. However, we point out a physical mechanism favoring rafts over islands of larger thickness. Because the DSCG stacks bound to the same rod should strongly repel each other, they might prefer to bind at the antipodal sides of the NR, thus triggering an assembly in which each NR has only two neighbors.

The observation of end-to-end arrangements in some highly concentrated samples observed in TEM (Figure 2c) is consistent with the idea that the affinity of CTAB to the ends of NRs is low; the bare ends might experience attraction through van der Waals forces when they find themselves in close proximity to each other. Alternatively, the arrangement might be promoted by the entrapment of DSCG stacks between the NR ends covered with a small but finite amount of CTAB or by an attraction of polyaromatic cores of DSCG molecules to the bare Au end facets $\{111\}$. Finally, capillary attractions of the rafts in TEM samples prepared through solvent evaporation might also contribute to the observed arrangements in Figure 2c.

An important feature of side-by-side assembly is that it can be controlled by a number of factors influencing the self-assembly of DSCG itself, such as pH. Orendorff et al.³⁰ reported that by adding an adipic acid whose charge depends on the pH and evaporating the solvent to facilitate the Onsager type of alignment one can assemble NRs into raft structures similar to those shown in Figure 2. For our system, increased pH causes a different effect, a disassembly of the NRs (Figure 3b). In the experiment, we first mixed a 2 nM solution of NRs and a 0.5 mM solution of DSCG in a 1:1 proportion. One milliliter of the mixture was left for 15 min to allow the NRs to assemble, after which time an 8 μL of a 0.5 M solution of NaOH in water was added. Whereas the NR–DSCG mixture demonstrated the shift of the longitudinal and transverse plasmon peaks toward each other, the addition of NaOH reversed this trend (Figure 3b). A tentative explanation is that higher pH increases the negative charge of the DSCG molecules, which decreases the energy E (because of the increased electrostatic repulsion of the DSCG molecules within the stacks) in eq 1. The DSCG stacks become shorter or disintegrate and are less capable of binding the NRs.

End-to-End Assembly. The mode of NR assembly can be controlled by the surface charge, which changes the interaction with DSCG. We used Au NRs coated first with CTAB and then with poly(acrylic acid) (PAA) to make them negatively charged. A 0.2 M DSCG solution (0.5 mL) was added to 0.5 mL of an NR solution, which triggered end-to-end assembly (Figure 4). TEM shows that the NRs are connected end-to-end, with a small lateral shift apparently caused by the prismatic geometry of the ends with tilted $\{111\}$ triangular facets.

Spectroscopic data show that after DSCG is added the amplitude of the longitudinal peak, centered at 706 nm for isolated NRs, gradually decreases with time and concomitantly a new peak located at a longer wavelength emerges and increases in amplitude (Figure 5). The spectra show a behavior with a characteristic isosbestic point at 770 nm. For chains of NRs, one expects that the longitudinal peak is located at longer wavelengths (as compared to the peak at 706 nm for isolated

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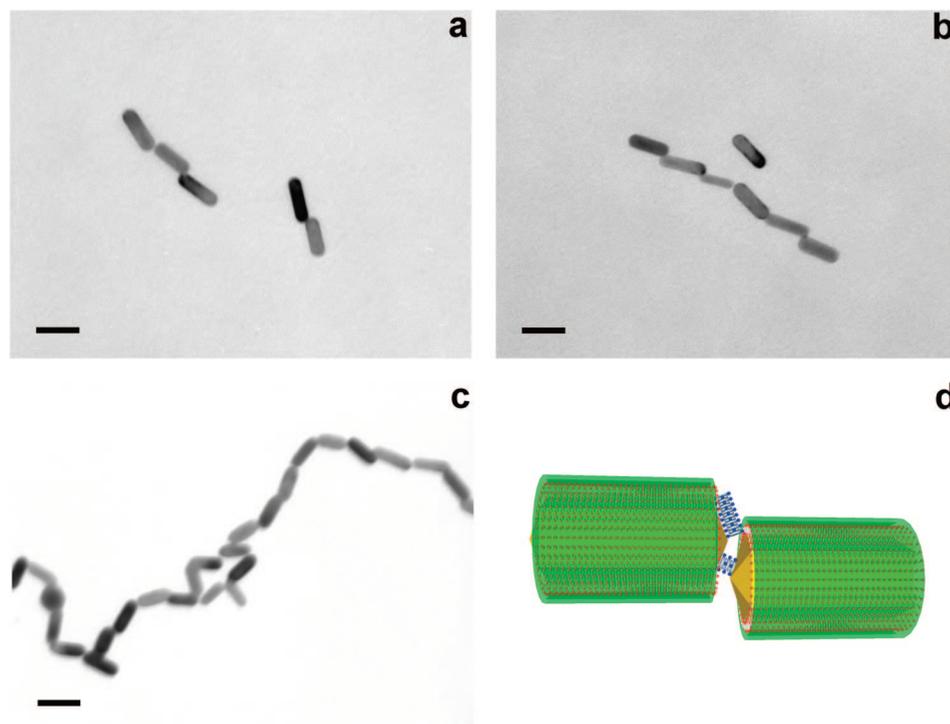


Figure 4. End-to-end self-assembly of Au NRs with CTAB and PAA coatings, induced by 0.1 M DSCG added to an ~ 2 nM Au NR solution in water in a 1:1 proportion. TEM images of the end-to-end chains are taken (a, b) about 6 h and (c) 24 h after mixture preparation. (d) Schematic representation of the end-to-end assembly. The scale bars are 50 nm.

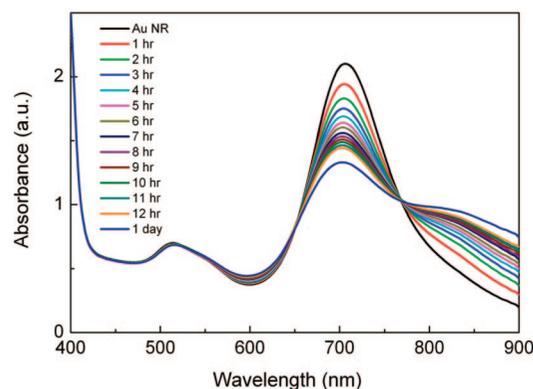


Figure 5. Time evolution of the absorption spectrum of the Au NR solution after 0.1 M DSCG was added to start the end-to-end assembly.

NRs); the transverse peak centered at 514 nm should remain unaffected, in agreement with other experiments and calculations.^{21,23,31–33}

A plausible mechanism of end-to-end assembly is the difference in charge characteristics of the lateral surface and the end facets of the NRs. The negatively charged PAA binds easily to the CTAB bilayer on the lateral side of the NRs but not to the end facets deprived of CTAB. These end facets are likely to attract the DSCG molecules through electrostatic or van der Waals forces (Figure 4d). Comparing the time evolution of side-by-side (Figure 3) and end-to-end (Figure 5) assembly, one notices that the latter is a much slower process. This feature is natural

because the interaction cross section for NR particles in the end-to-end assembly is much lower than that in the side-by-side assembly.

Note that heating the samples to 70 °C does not produce any changes in the absorption spectra, demonstrating the excellent thermostability of the linking agent as compared to that of currently available protein-based and DNA-based agents.

To conclude, we described a new concept of NR self-organization using lyotropic chromonic material DSCG that self-assembles into charged stacks. These stacks serve as noncovalent universal linkers capable of side-by-side and end-to-end assembly of NRs. The advantages of the proposed technique are both practical and conceptual. First, no covalent functionalization of the NRs is required as in previous methods. This simplifies the process and makes it more flexible. Second, both side-by-side and end-to-end geometries of assembly can be achieved with the same agent. Third, chromonic materials such as DSCG can withstand temperatures much higher than the temperatures allowable for DNA and proteins, which is significant for many potential applications; these materials are relatively cheap, as evidenced by the fact that many of them are used in the food industry as colorants.³⁴ Fourth, the organization in the NR superstructures is based on a fundamentally distinct approach in which the anisotropic electrostatic interactions are combined with the self-assembly nature of the linking elements. Finally, the described method allows the researchers fine control over the degree of NR assembly by controlling the chromonic self-assembly, for example, by controlling the concentration of DSCG or the pH of the solution.¹⁹

Experimental Section

Materials. Hexadecyltrimethylammonium bromide (CTAB), silver nitrate, ascorbic acid, sodium borohydride, gold(III) chloride, L-cystine, thioglycolic acid (TGA), and poly(acrylic acid) (PAA) (mol. wt. 400 000) were purchased from Aldrich and used without

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further purification. We used deionized water (Barnstead, E-pure system) to prepare solutions.

Synthesis. Gold NRs with an average aspect ratio of 2.8 (length ~ 50 nm and diameter ~ 18 nm) were synthesized by using a seed-mediated growth method. A 20 mL solution of gold NRs is centrifuged twice and redispersed into a final volume of 1 mL of deionized water to remove excess CTAB stabilizer in the solution. The purified gold NRs have a bilayer of surfactant on the surface and have a net positive charge (zeta potential +30 mV). To make the gold NRs negatively charged, 100 μL of a 1% PAA solution in water is slowly added to 1 mL of the purified gold nanorod solution under vigorous stirring. The negatively charged PAA is adsorbed onto the positively charged gold NRs by electrostatic attraction, and the excess COOH groups provide a net negative charge to the rods (zeta potential -25 mV).

TEM Imaging. TEM images were obtained using a JEOL JEM-100S electron microscope. TEM samples were prepared by dropping the mixture onto a 300 mesh carbon-coated copper grid and allowing the solvent to evaporate.

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