Chiral Plasmonic Nanostructures: Coupling of Biomolecules and Nanoparticles

Matthew Kottwitz Literature Seminar December 14, 2017

Extending the synthetic capabilities and understanding of chiral structures in molecular systems to nanomaterials holds many promising applications in areas such as chiral catalysis, separations, sensing, and optical devices.[1] While top-down fabrication processes for the incorporation of chiral structures into plasmonic materials is more established, the exploitation of biomolecules to direct the assembly of nanoparticles into chiral arrangements holds promise due to the range of accessible geometries and the ability to spontaneously generate 3D chiral nanostructures in bulk scale solution phase

Louis Pasteur, more widely known for his work as a microbiologist, had a profound impact on the field of chemistry early in his career through the discovery of molecular chirality. When he observed the crystal morphology of enantiomerically pure tartrate compounds, Pasteur hypothesized that the chiral structure of the crystals arose from the constituent molecules. After careful discrimination of racemic mixtures of sodium ammonium and sodium potassium tartrates, he discovered that half were right-handed while the remaining were left-handed, a consequence of those compounds crystallizing as racemic conglomerates rather than racemic compounds. In aqueous solution, the separated crystals had equal and opposite magnitudes of optical rotation of light, confirming Pasteur's hypothesis of molecular chirality.[3]

Modern studies of chiral structures are based on the use of circular dichroism spectroscopy (CD). In this method, linearly polarized light, which may be thought of as the superposition of left- and right-handed circularly polarized light (CPL) of equal magnitude, is filtered by a photoelastic modulator, generating CPL. By measuring the absorption of both left- and right-handed CPL, the ellipticity of the sample may be determined across a range of wavelengths.[4]

In the presence of an oscillating electric field, electrons in a metal NP will oscillate coherently in response, causing an oscillation of the electron cloud relative to the NP's nuclei.[5] When two NPs are in close proximity, there exists a hybridization of the individual NP plasmons that may be viewed as bonding and antibonding combinations analogous to the hybridization seen in atomic orbital. This results in a shift of the dimer plasmon dependent on the geometry and separation of the NP pair.[6] As the number of NPs and possible configurations is increased, predicting the plasmon energy of the system become more complex.[7]

Drawing on their previous work investigating the chirality of nanoparticle dimers formed through a polymerase chain reaction (PCR)[8], the Kotov Group demonstrated a method for the detection of attomolar DNA concentration. After anchoring primers to either the ends or sides of gold nanorods, PCR allowed for the controlled growth of NPs into assemblies of nanorods connected in either an end-to-end or side-by-side fashion (Figure 1a). CD spectra for the end-to-end morphology did not display evidence of chirality in the system. The strong bisignate CD wave was apparent in the side-by-side morphology arising from the DNA induced twist between adjacent nanorods throughout the structure. Beyond 20 cycles of PCR, the CD intensity quit increasing as the disorder and aggregation in the system grew. To demonstrate the ability to

detect attomolar DNA concentrations, the authors took the solution (M=0.156nM) used for the directed assembly demonstration and conducted stepwise 10x dilution. A faint bisignate peak appears shown for the 15.6 aM solution (Figure 1b), with a calculated limit of detection as low as 3.7 aM. Analysis of the same target DNA with the well-established reverse transcriptase PCR technique yielded a limit of detection of 156 aM.[9]

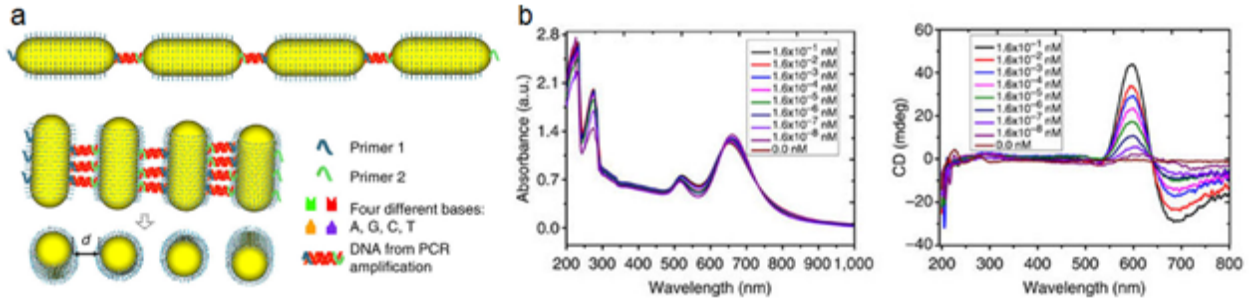

Figure 1. (a) Controlling the orientation of NPs assembled via PCR is possible by controlling the location of the anchored primers. (b) Comparison of UV-Vis with CD for the detection of DNA shows a remarkably enhanced sensitivity for CD.

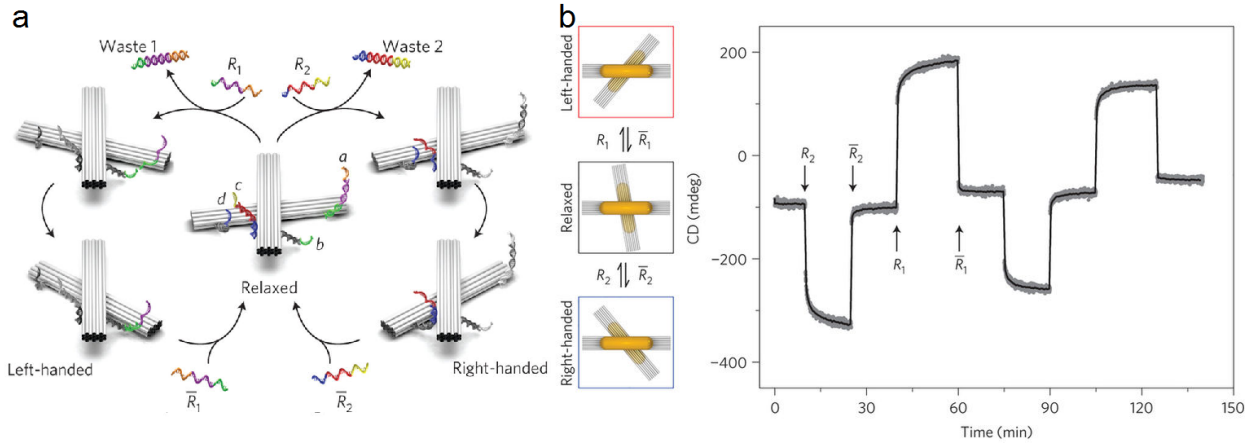

Figure 2. (a) Illustration of the cycling process of gold nanorods (not shown) by input of "fuel" DNA strands. (b) CD spectra of the cycling of the structure

In another study involving the coupling of NPs and DNA to form chiral plasmonic nanostructures, the Liu Group demonstrated a reconfigurable 3D plasmonic metamaterial. The system developed consists of two gold nanorods anchored to a reconfigurable DNA origami template (Figure 2a). Adjacent arms of the crossed DNA origami template are functionalized with complementary DNA strands the will bind or unbind resulting in a conformational change when the appropriate "fuel" strand is added to the system. In this manner, the system may be alternated between relaxed, right-handed, and left-handed conformational states (Figure 2b).[10]

In a subsequent report, the binding strands of DNA are modified to respond to a change in pH of their solution. Adjacent arms of the crossed DNA origami template are functionalized with either a single or double strand of complimentary DNA. Under the right pH conditions dependent upon the ratio of CGC to TAT triplets, a DNA triplex will form, locking the pair of gold nanorods in a chiral orientation. A quasi-racemic mixture of DNA origami templates where

both enantiomers are functionalized with DNA strands of different ratios of CGC to TAT base pairs will show a CD dependence on the pH of the solution due to the different pKa values of the DNA strands.[11]

In conclusion, the coupling of NPs with biomolecules, particularly DNA, holds promise as a method for the fabrication of metamaterials with particular strong CD signature due to the plasmonic resonance arising from the NPs and the chirality imparted by the biomolecules. Applications for the enhanced sensing of biomolecules and the formation of reversibly chiral structures are amongst the numerous possibilities present as the field continues to develop.

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