学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Chiroptical Activity of Nanorod-DNA Polyion-Complexes
（ナノロッド-DNA ポリイオン複合体のカイロプティック活性）

Chirality, the lack of mirror symmetry, exists from individual molecules to supramolecular systems and is characterized by circular dichroism (CD) — the difference in absorption of left- and right-handed circularly polarized light. While the conformational changes in chiral molecules can be directly detected using CD spectrometer, the technique suffers from low detection sensitivity. Plasmonic CD, arising from complexes of molecules and nanoparticles complex, has attracted great attention due to its tunable wide-spectrum range and enhanced CD intensity, offering promising applications in biochemical sensing, disease diagnostics and optical devices. However, the relationship between molecule structure and plasmonic CD remains unclear. Notably, deoxyribonucleic acid (DNA) can be utilized as an ideal molecule for investigating the relationship between molecule structure and plasmonic CD, owing to its clearer structural information. Examples include the G-quartet of guanine-rich DNA, the i-motif of cytosine-rich DNA, and the single-stranded helical structure of adenine-rich DNA. Recently, our research group demonstrated the uniform structures formed by AuNR-DNA polyion complexes in solution. These advances underscore the potential of constructing nanoparticle-DNA polyion complexes to induce plasmonic CD. However, up to these dates, there have been no report on the plasmonic CD in AuNR-DNA polyion complexes in solution.

In this study, I aim to investigate the relationship between molecule structures and plasmonic CD using AuNR-DNA polyion complexes. I first prepared cationic AuNRs (size: ~40 nm × ~10 nm) by the surface exchange of cetyltrimethylammonium bromide (CTAB)-covered AuNRs with primary amine-terminated hexaethylene glycol thiol ligands, to make them both more stable and avoid the combination between CTAB

and DNA in solution. The cationic AuNRs were then mixed with DNA in Tris-HCl buffer (pH=7.6) solutions to form AuNR-DNA polyion complexes.

Chapter 2, I investigated the plasmonic CD of AuNR–DNA polyion complexes. In particular, I investigated the effects of AuNR–DNA mixing ratio, base sequence, the presence or absence of duplex formation and mixture of noncomplementary DNA on the plasmonic CD and discussed the structural features of the adsorbate required to induce the plasmonic CD. In addition, I also showed by cryo-TEM that AuNRs are assembled into twisted ribbons via DNA.

Chapter 3, I explored the potential of AuNR–DNA polyion complexes in enhancing the chirality of metal-mediated DNA. Specifically, in the absence of metal ions (Hg^{2+}/Ag^{+}), the polyion complexes formed between ssDNA (dT_{22}/dC_{22}) and AuNR did not exhibit any plasmonic CD response. However, in the presence of metal ions (Hg^{2+}/Ag^{+}), the interactions between T-Hg^{2+}-T or C-Ag^{+}-C base pairs mediate the conversion of ssDNA (dT_{22}/dC_{22}) into dsDNA. This transformation results in significant plasmonic CD when forming polyion complexes with AuNR. Specially, polyion complexes formed by AuNRs and Ag^{+}-mediated DNA exhibited plasmonic circular dichroism (CD) that are up to ~400 times stronger than the molecular CD signal of DNA.

Chapter 4, I summarized the thesis and discussed the prospective use of this chiroptical AuNR–DNA polyion complexes.

Through this study, we not only successfully elucidated the relationship between DNA structures and plasmonic CD in AuNR-DNA polyion, but also demonstrated their ability in mental ion detection. This research advances the detailed understanding of molecule structure-plasmonic CD relationship in nanoparticle-molecule complexes, paving the way for deeper explorations into the origin of plasmonic CD and expanding the potential applications of such complexes, especially in chiral sensing.