

DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response

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INTRODUCTION

- ❖ Matter structured on a length scale comparable to or smaller than the wavelength of light can exhibit unusual optical properties.
- ❖ Metal nanostructures are promising components for such materials where structural alterations provide a straightforward means of tailoring their surface plasmon resonances and hence their interaction with light.
- ❖ Top-down fabrication of plasmonic materials with controlled optical responses in the visible spectral range remains challenging, because lithographic methods are limited in resolution and in their ability to generate genuinely three dimensional architectures.
- ❖ Molecular self-assembly provides an alternative bottom-up fabrication route not restricted by these limitations, and DNA- and peptide-directed assembly have proved to be viable methods for the controlled arrangement of metal nanoparticles in complex and also chiral geometries.
- ❖ Circular dichroism is measured as the difference in absorbance of left-hand-circularly polarized (LCP) and right-hand-circularly polarized (RCP) light as a function of wavelength
- ❖ Circular dichroism effects in the visible part of the spectrum have been achieved by exploiting the chiral morphology of organic molecules and the plasmonic properties of nanoparticles, or even without precise control over the spatial configuration of the nanoparticles.

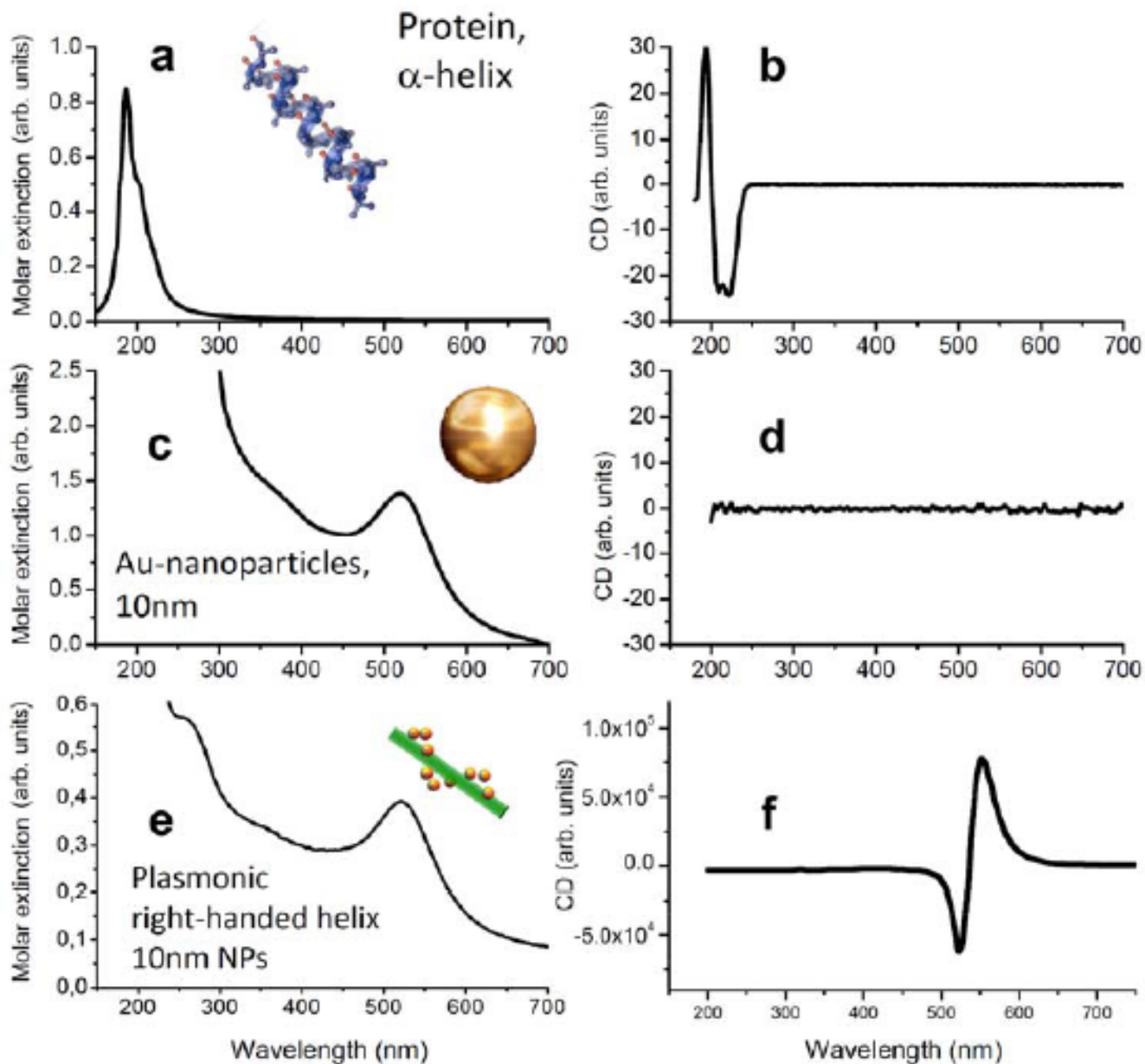
In this work.....

- ❖ DNA origami was used to achieve the high-yield production of plasmonic structures that contain nanoparticles arranged in nanometre-scale helices.
- ❖ In agreement with theoretical predictions that the structures in solution exhibit defined circular dichroism and optical rotatory dispersion effects at visible wavelengths that originate from the collective plasmon–plasmon interactions of the nanoparticles positioned with an accuracy better than two nanometres.

Method

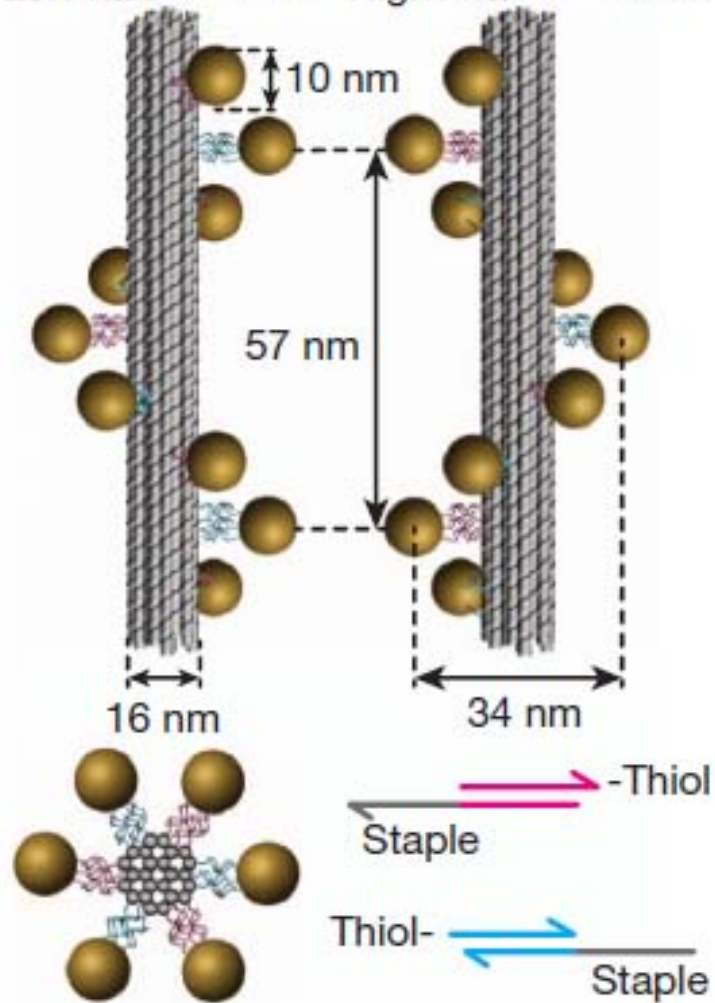
- ❖ Citrate-capped Au NPs were stirred with BSPP (Bis(*p*-sulfonatophenyl)phenylphosphine dihydrate dipotassium) salt.
- ❖ This Au NPs were conjugated with thiolated ssDNA.
- ❖ For the left-handed and the right-handed design of the 24 helix bundle we used 10 nM of P7560 scaffold and a staple mix containing 100 nM of each staple. Thermal annealing and cooling produced the helices.

Chiro-optical properties of α -helix protein, gold nanoparticle and gold nanohelix

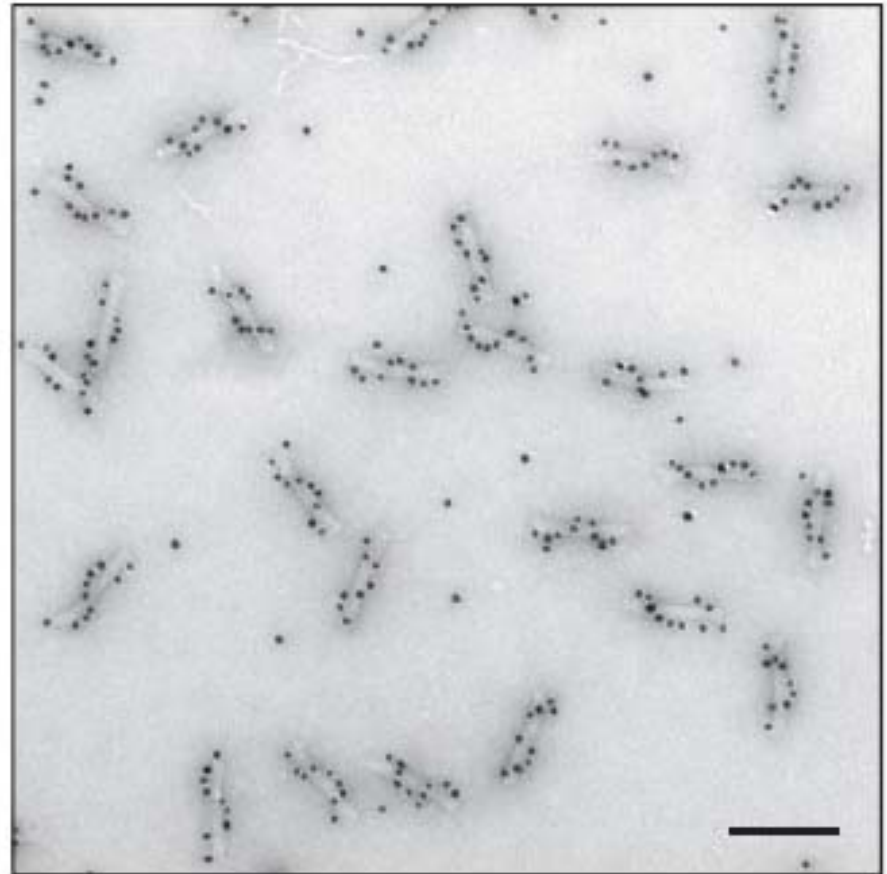


Assembly of DNA origami gold nanoparticle helices

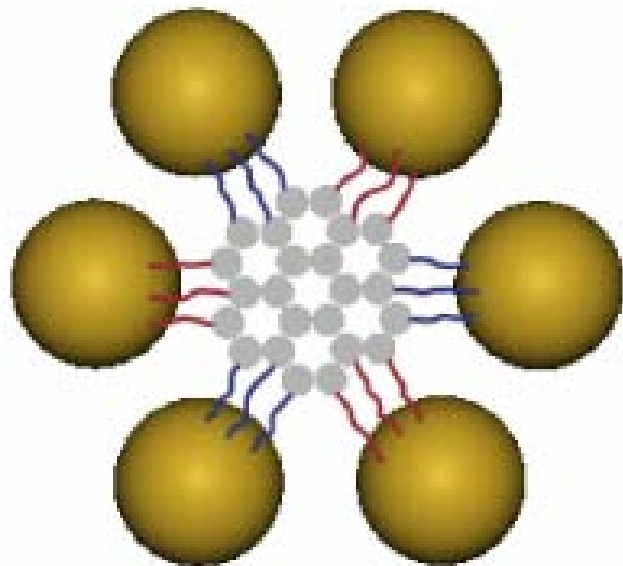
a Left-handed helix Right-handed helix



b

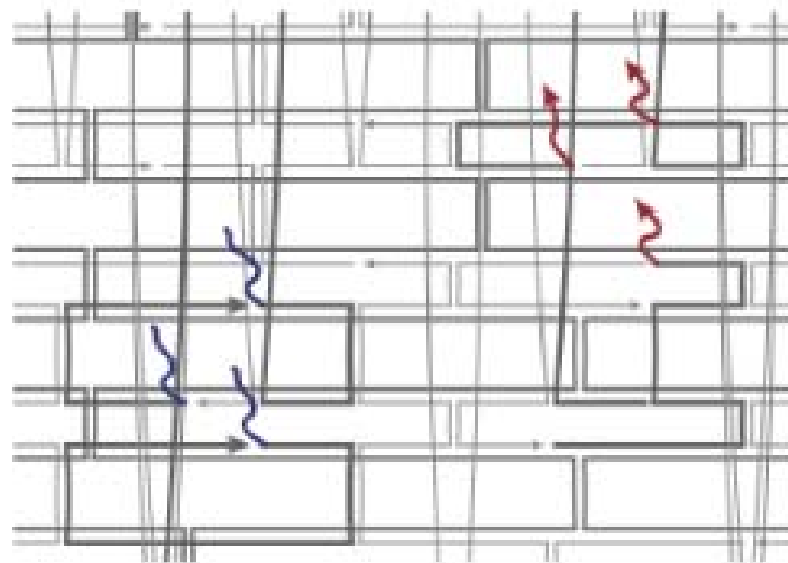
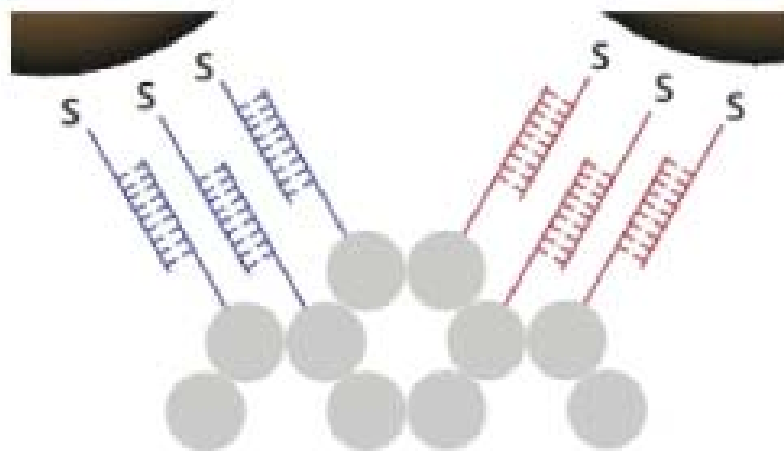


Scale bar: 100 nm

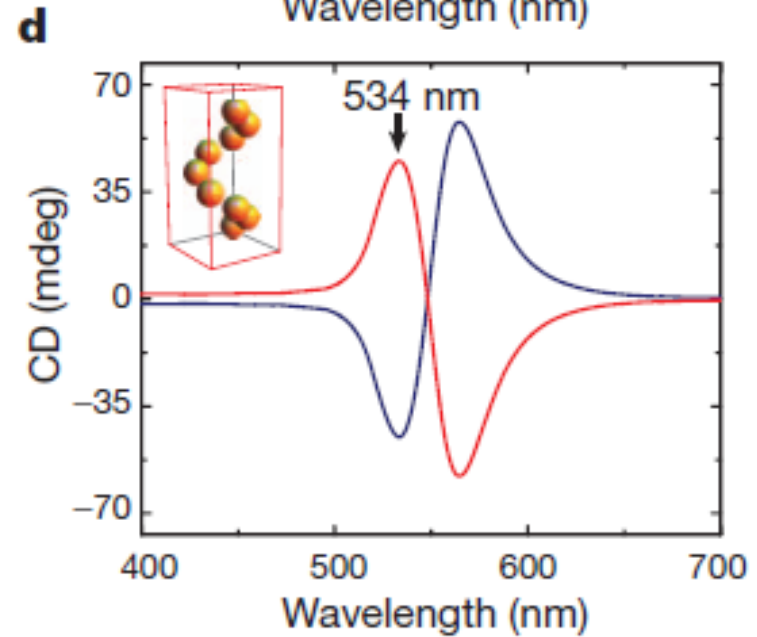
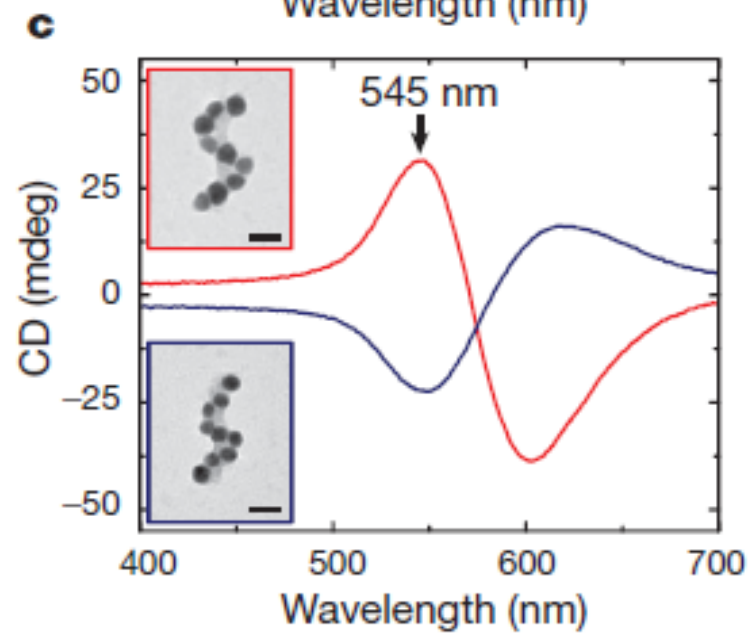
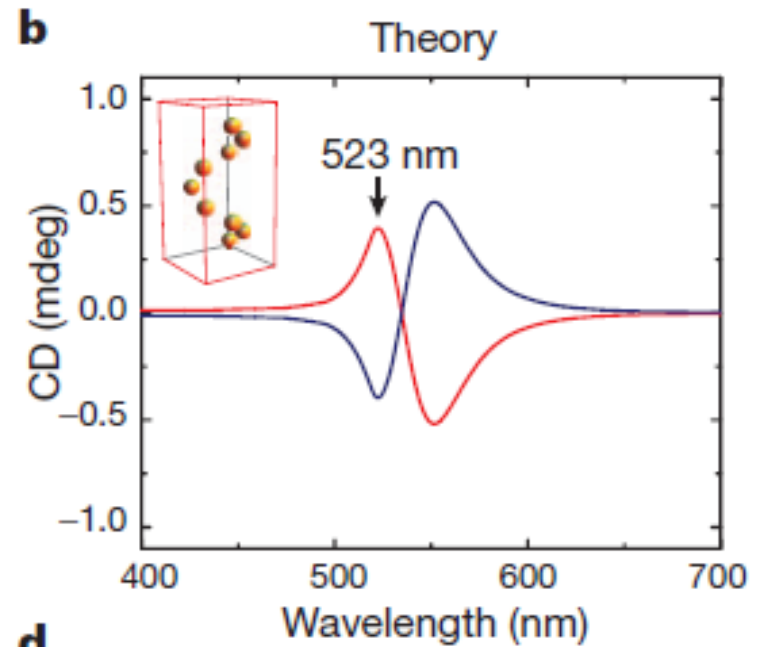
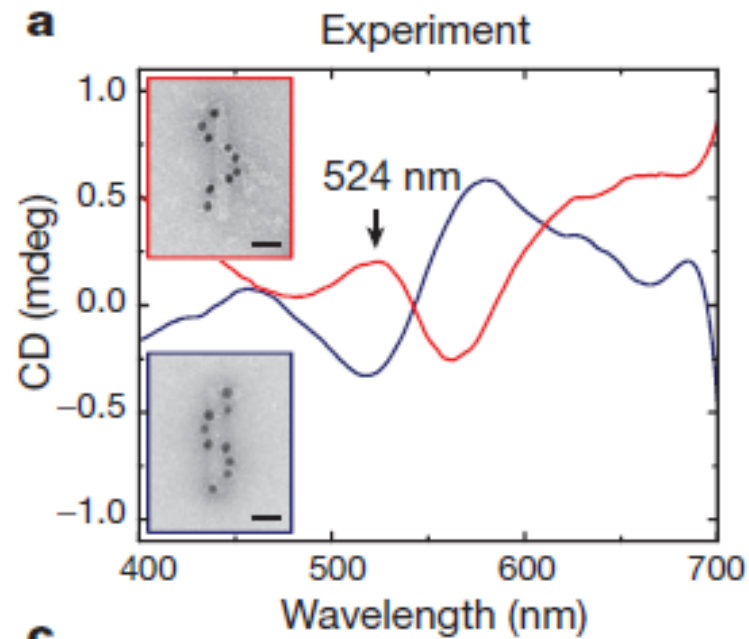
a**c**

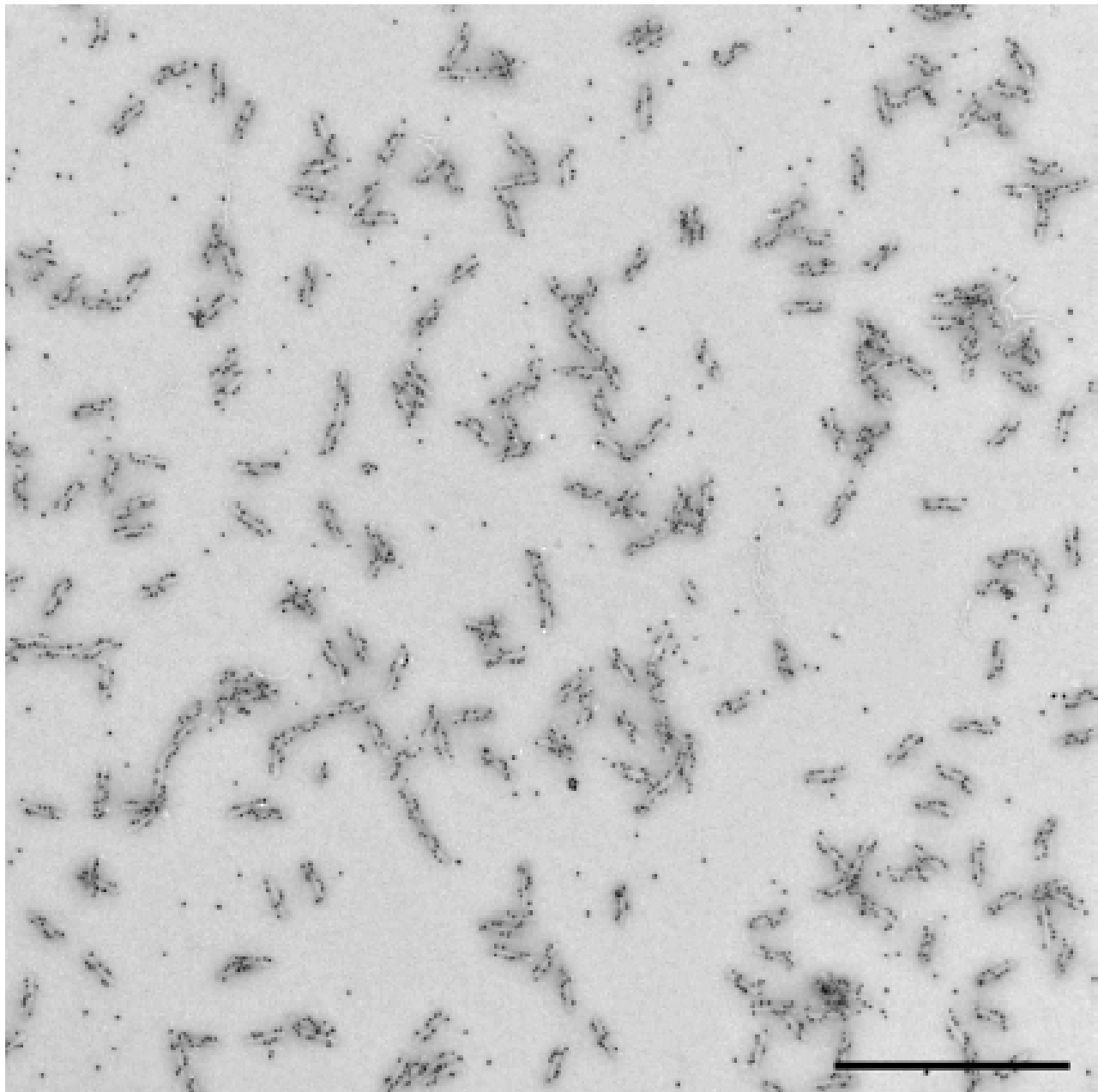
5'ATTATTATTATTATTTTTT3'-thiol
 3'stapleTAATAATAATAATA5'

thiol-5'TTTTTTTTTTTTTTTTTT3'
 3'AAAAAAAAAAAAA staple5'

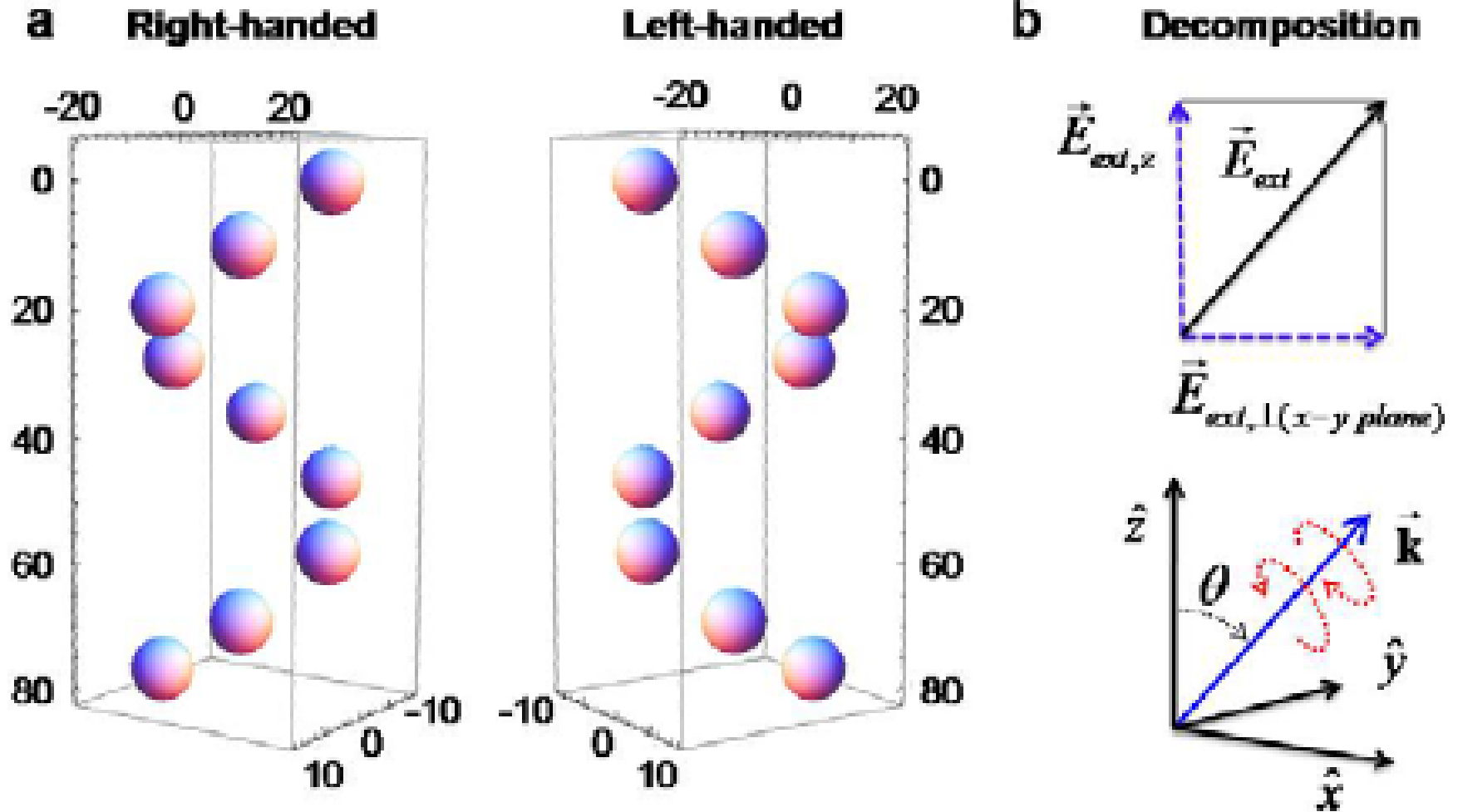
b**d**

Circular dichroism of self-assembled gold nanohelices



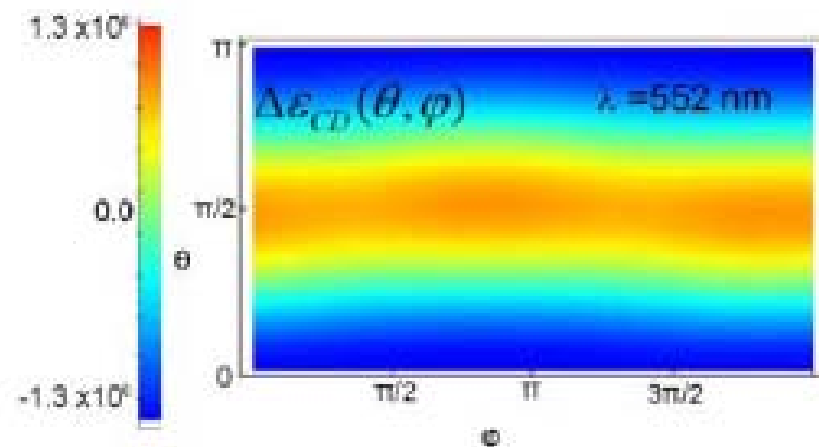
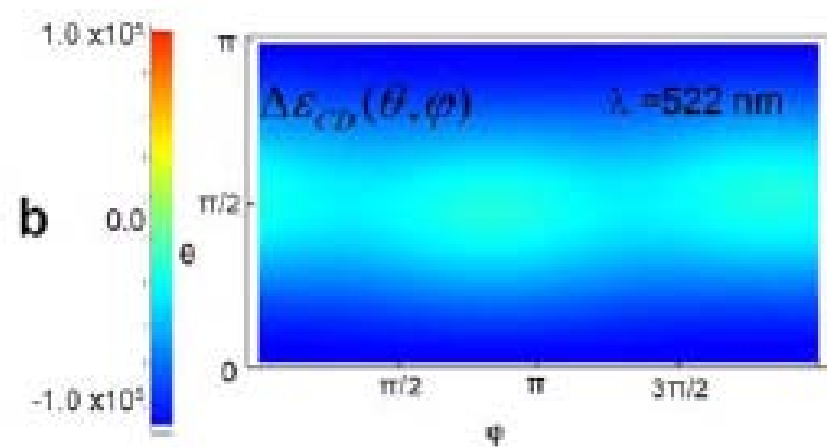
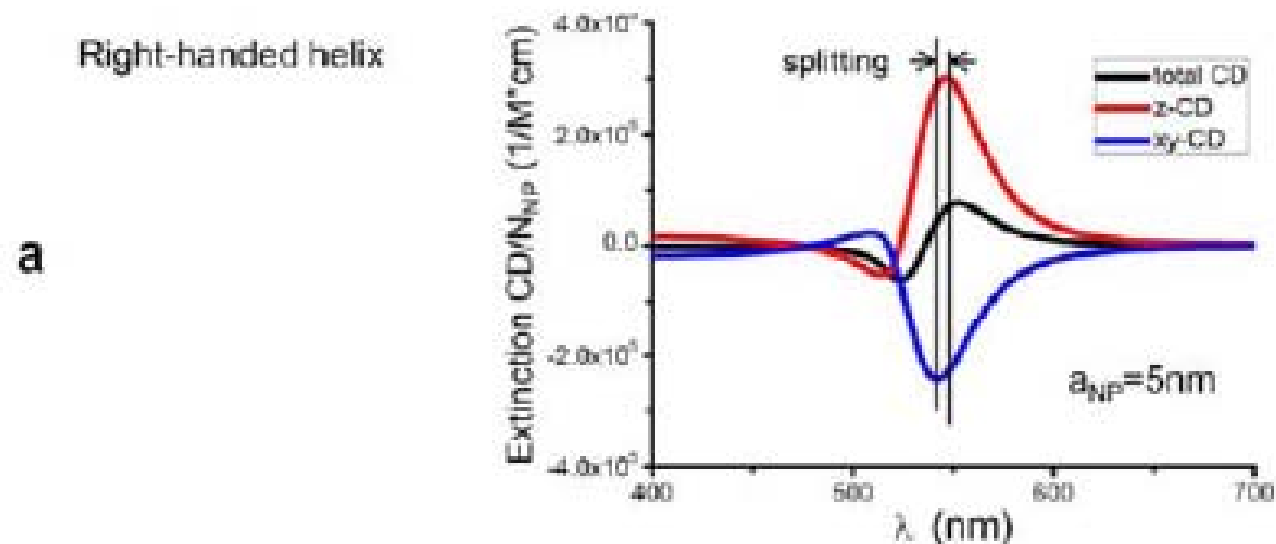


Models of the helices and the coordinate system.

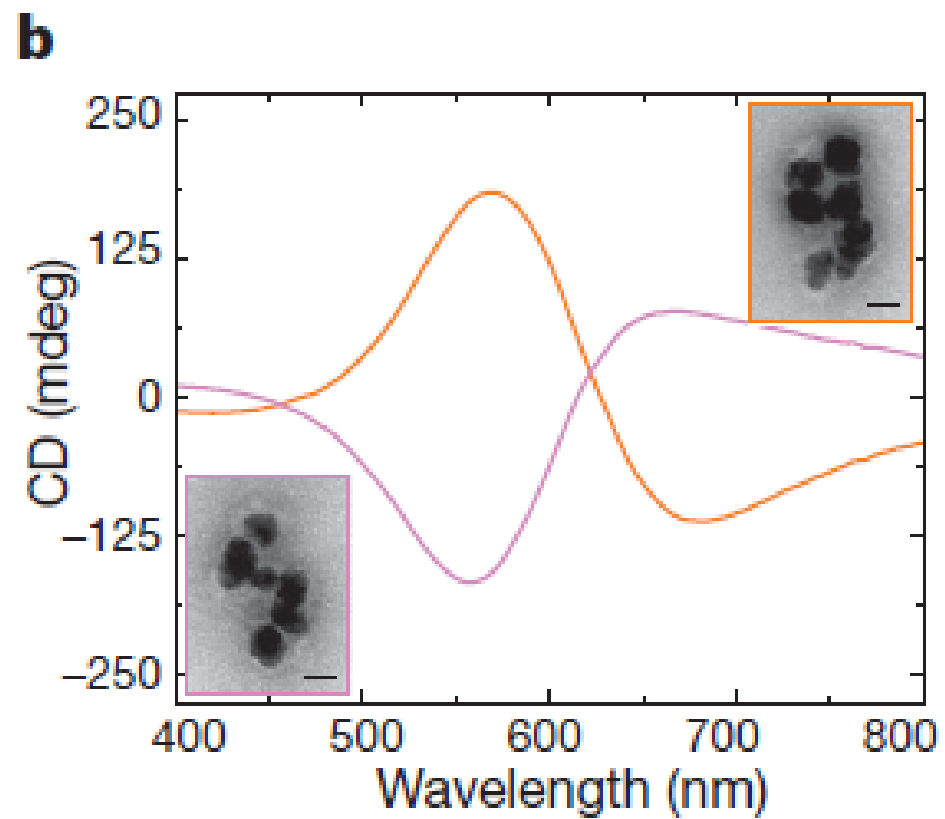
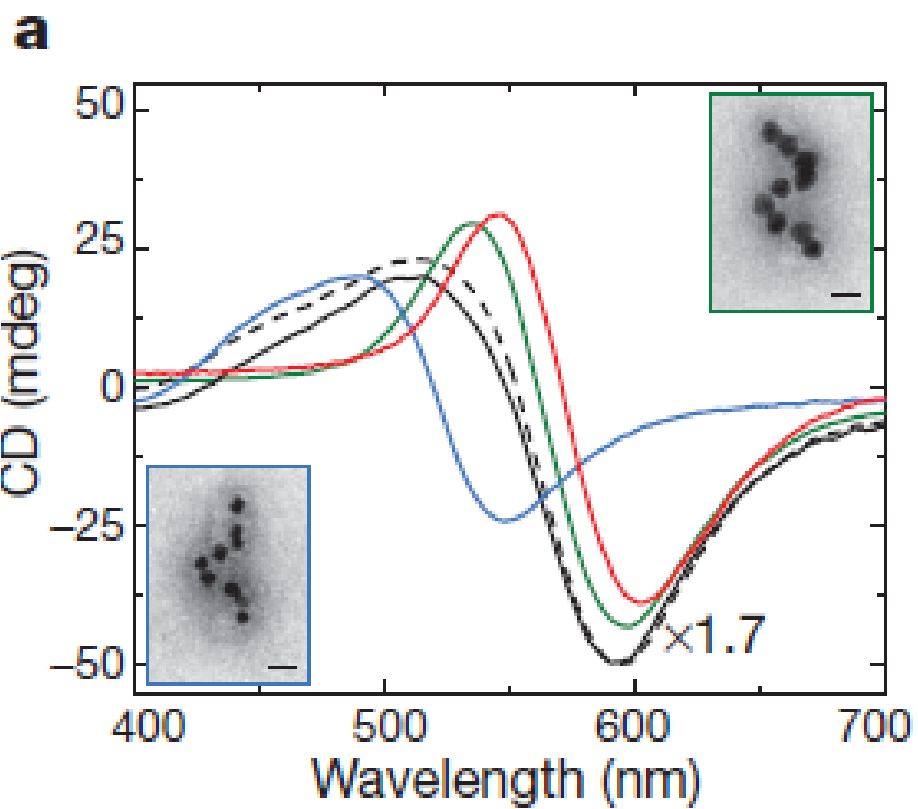


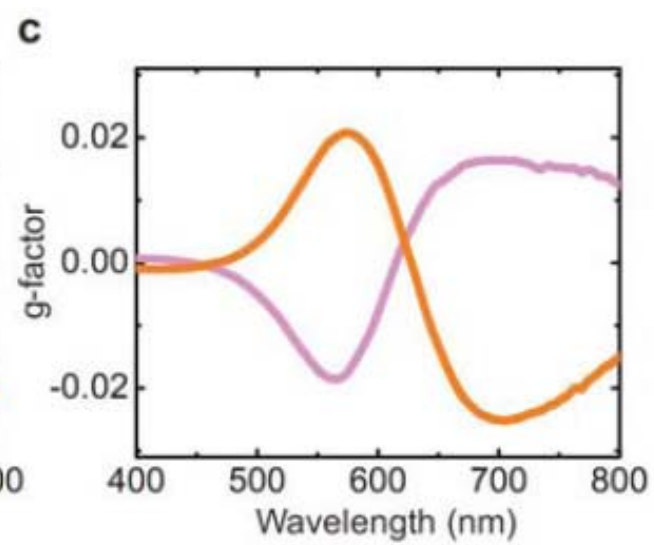
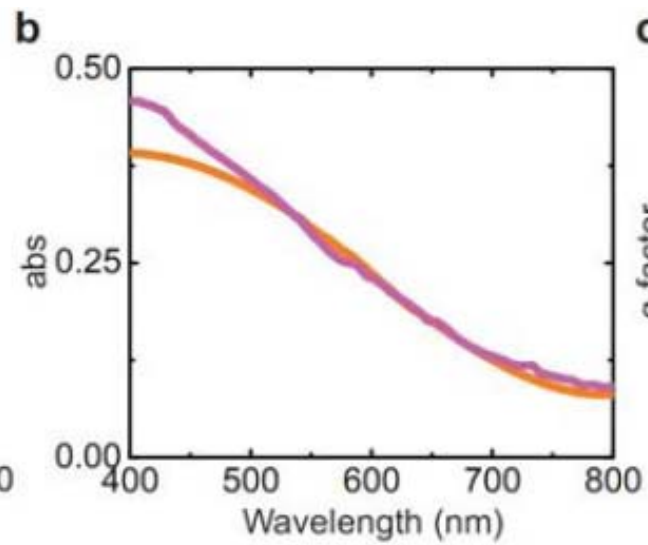
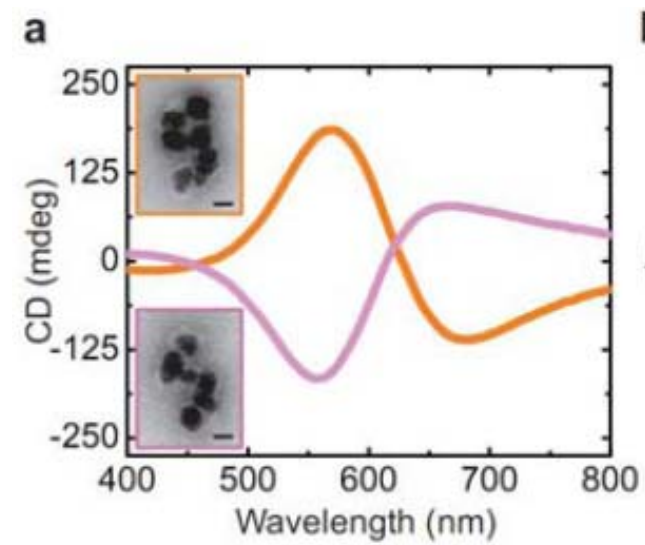
(a). Models of right- and left-handed helices (numbers in nm). (b). The graph also shows the decomposition of the electric field and the coordinate system

Calculated CD properties of the right-handed helix composed of 9 nanoparticles

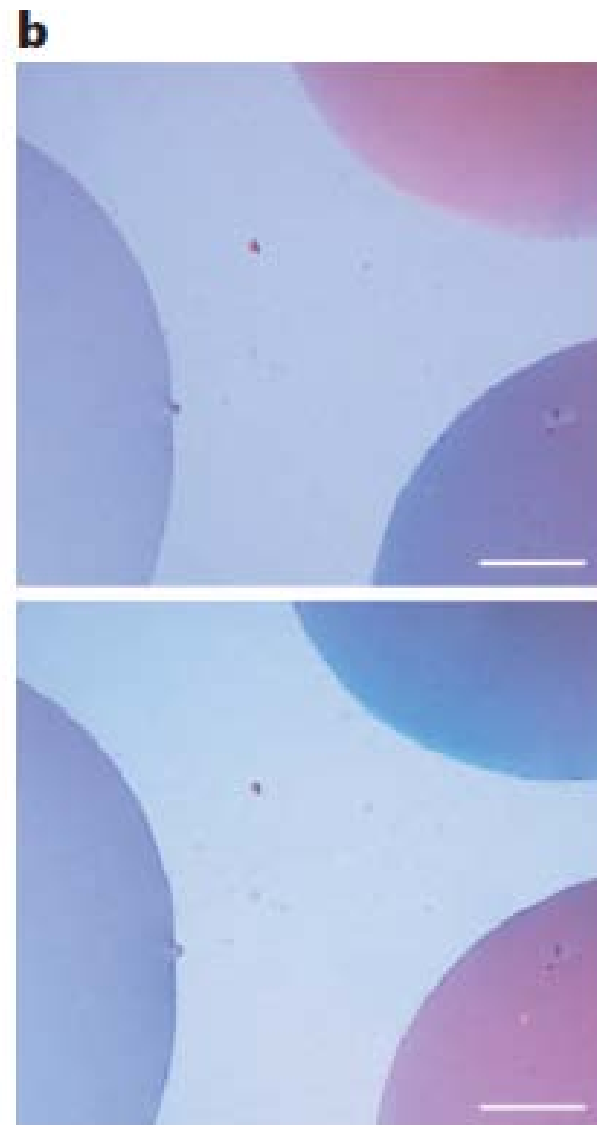
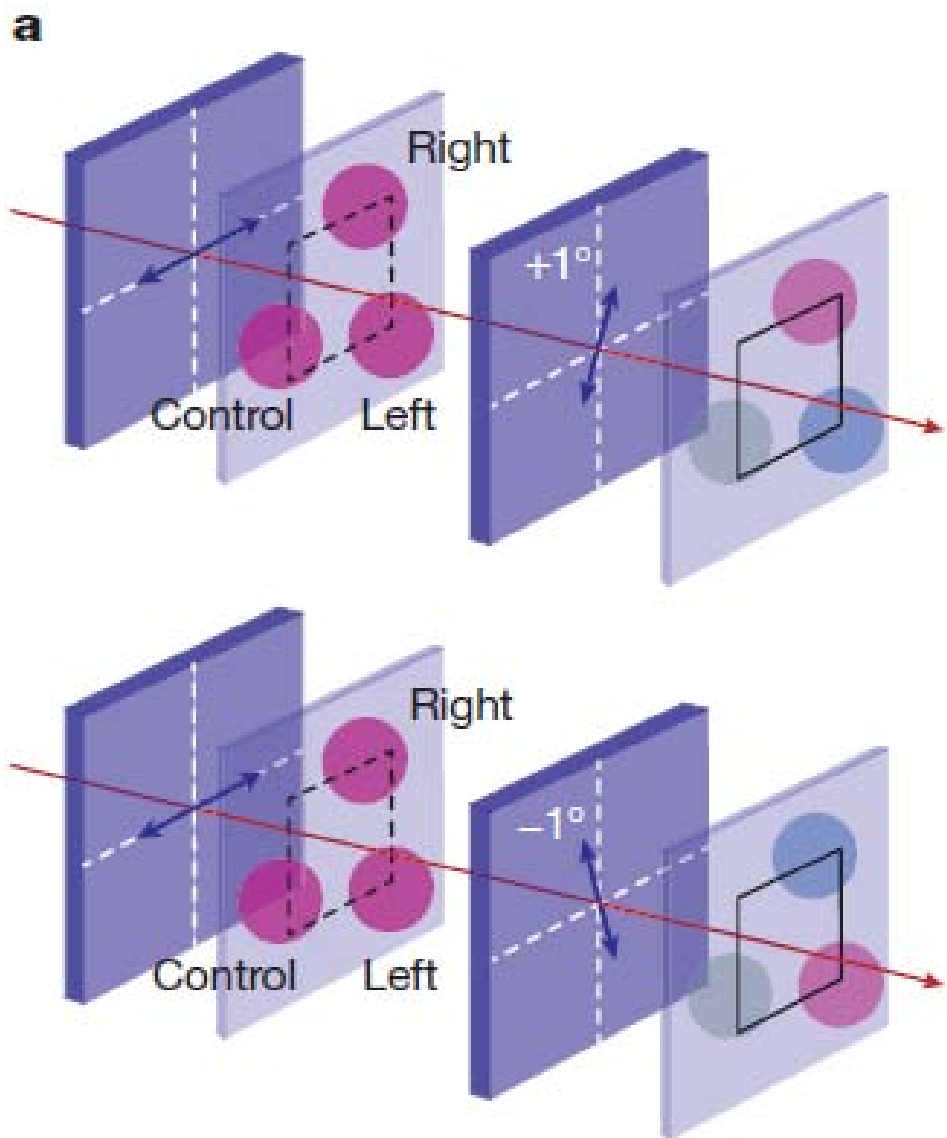


Spectral tuning of circular dichroism by metal composition



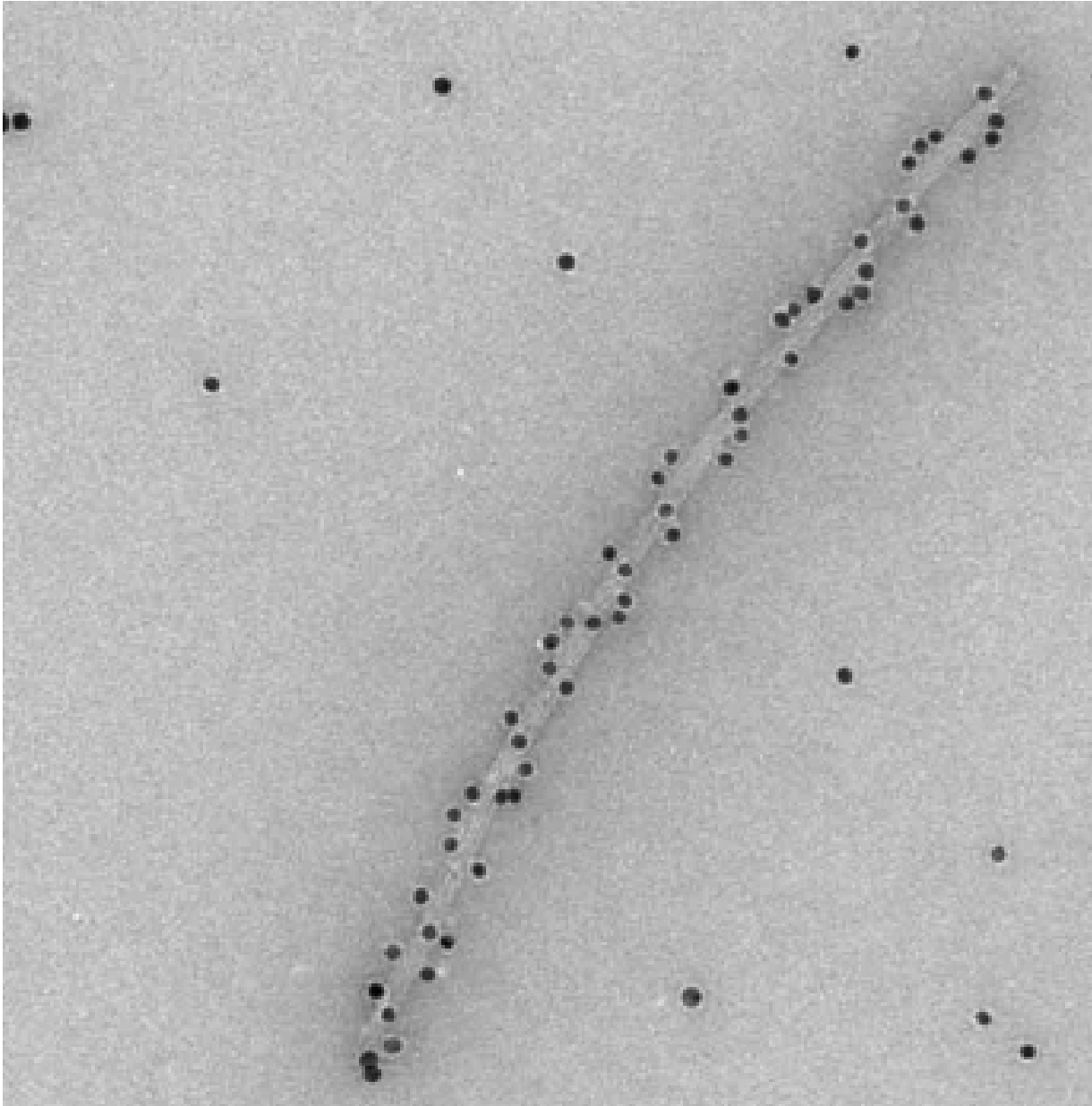


Optical rotatory dispersion of self-assembled gold nanohelices



Scale bar: 1 mm

TEM image of a left-handed nanohelix polymer consisting of six monomers



CONCLUSIONS

- ❖ DNA origami was used to precisely arrange plasmonic nanoparticle in helical structures.
- ❖ Such structures exhibits expected CD and ORD features due to the interactions of plasmons of individual nanoparticles.
- ❖ The nanohelices showed high stability over time.
- ❖ Anisotropy factors (0.025) was obtained which is comparable with protein complexes and polyaromatic compounds.
- ❖ Present findings clearly establish DNAorigami as a valuable addition to the existing tools at the material engineer's disposal for precisely arranging nanoparticles into assemblies with desired electric or magnetic properties.

Future prospects

- ❖ SWCNT enantiomers can be tested as scaffolds for plasmonic CD.**
- ❖ Chiral quantum clusters in chiral organogels/peptide nanotubes without additional ligands.**
- ❖ Quantum clusters protected by achiral ligand in above mentioned chiral scaffold in order to check induction of chirality.**

THANKS