Induction of chirality in an achiral liquid crystal matrix

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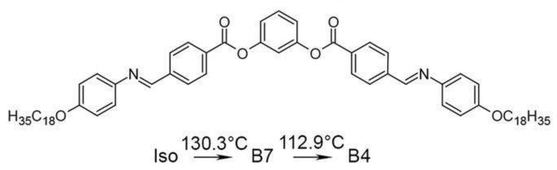
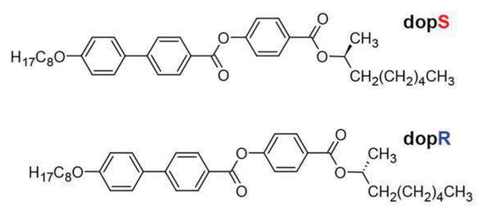
INTRODUCTION

Thin films sustaining plasmonic circular dichroism (PCD) have acquired high scientific relevance and a great potential for applications. While most efforts in PCD thin film structures focus on lithographically fabricated static metasurfaces, the bottom-up fabrication of active chiral plasmonic films constitutes an alternative approach. Herein, the preparation of PCD thin films by melting and freezing a mixture of liquid crystal, a chiral dopant, and gold nanoparticles (NPs), serving as a helical matrix, symmetry-breaking inducer, and plasmonic component respectively, is reported. UV–vis and circular dichroism spectroscopies are used to disclose the interactions among thin film components, toward maximizing the PCD dissymmetry factor (g-factor). Variation of substrate temperature affords reversible off/on switching of the chiroptical response.

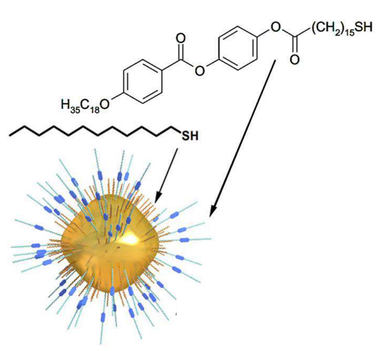
LC MATRIX



CHIRAL DOPANTS

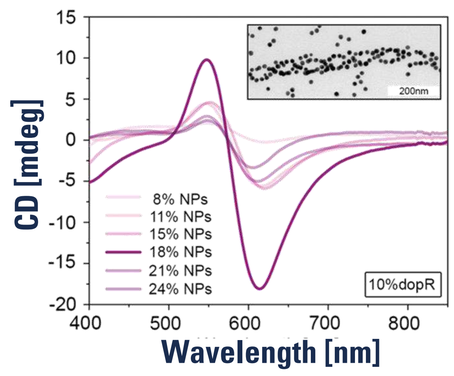


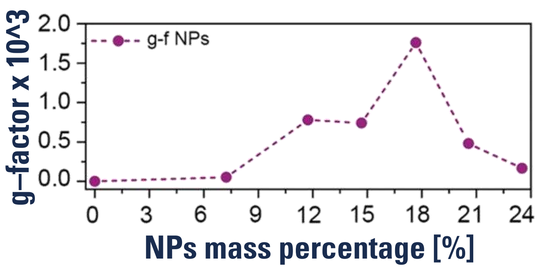
NANOPARTICLES



OPTIMIZATION OF NANOPARTICLE CONTENT

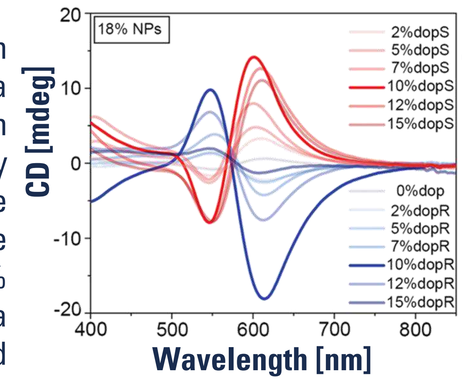
To prepare and optimize the content of chiral plasmonic composites, a series of THF solutions with judiciously chosen matrix/dopR ratio were prepared. Varying amounts of Au15 NPs (8–24 wt%) were then added to the solutions. Finally, the obtained samples were dropcasted onto glass slides, melted, and cooled in a controlled way. We concluded that 18 wt% was the optimal content of NPs, and, therefore, we used this doping rate in all further investigations.

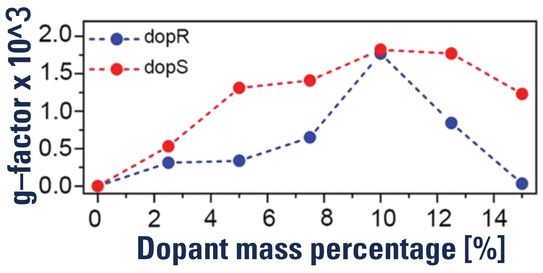


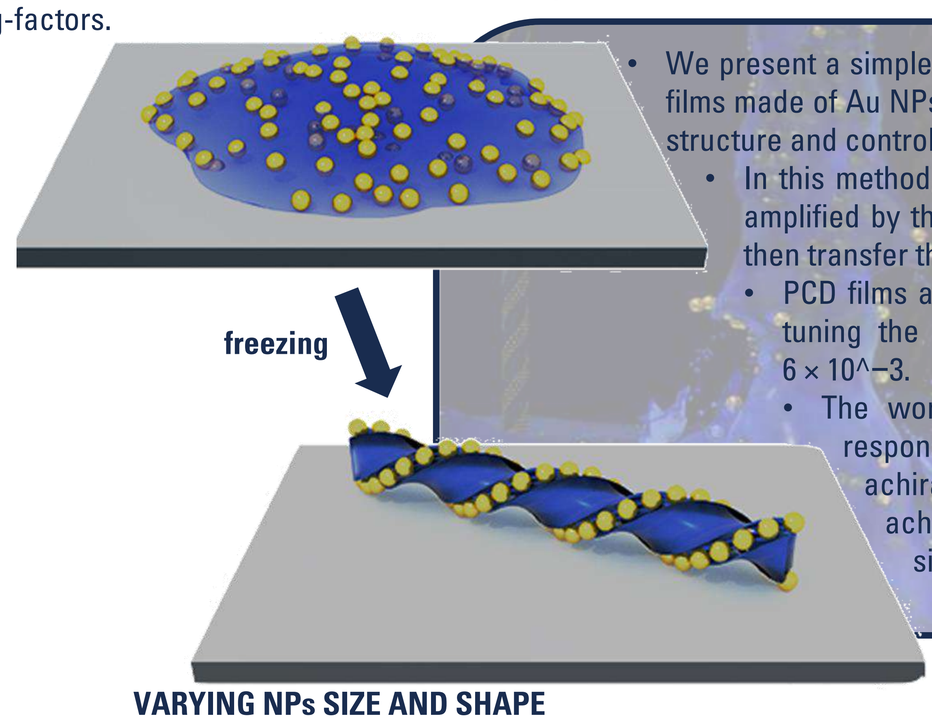


OPTIMIZATION OF DOPANTS CONTENT

Next, we optimized the amount of the chiral dopant in the mixture (2–15 wt%). The acquired CD spectra from the resulting film nanocomposites, doped with either dopR or dopS, were mirror images. By increasing the mass percentage of either of the dopants, we observed a gradual enhancement in the measured CD signals and g-factors, up to 10 wt% dopant. In contrast, for 12 and 15 wt%, we observed a significant decrease in the measured CD signals and g-factors.



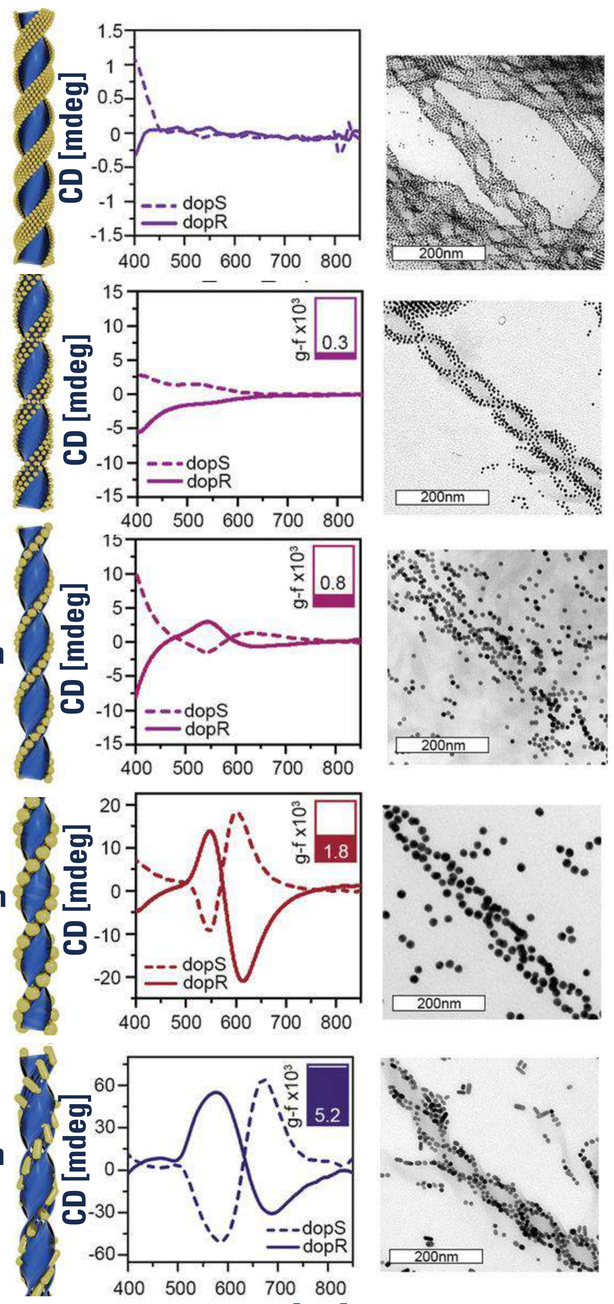




- We present a simple strategy for fabricating centimeter-scale chiral plasmonic films made of Au NPs and liquid crystals, exhibiting a reversibly reconfigurable structure and controllable chiroptical properties.
  - In this method, the chirality of a minute amount of an organic dopant is amplified by the LC molecules assembling into helical nanofibers, which then transfer the chirality onto achiral Au NPs, by guiding their assembly.
    - PCD films are easily realized with different sizes of Au NPs, enabling tuning the PCD wavelengths with high dissymmetry factors up to 6 × 10^−3.
      - The work presented here reveals a way to combine thermal responsiveness of LC materials and plasmonic coupling of achiral plasmonic NPs, resulting in a useful methodology to achieve tunable and moldable PCD thin films which may hold significant potential in future active, flexible chiroptical materials.

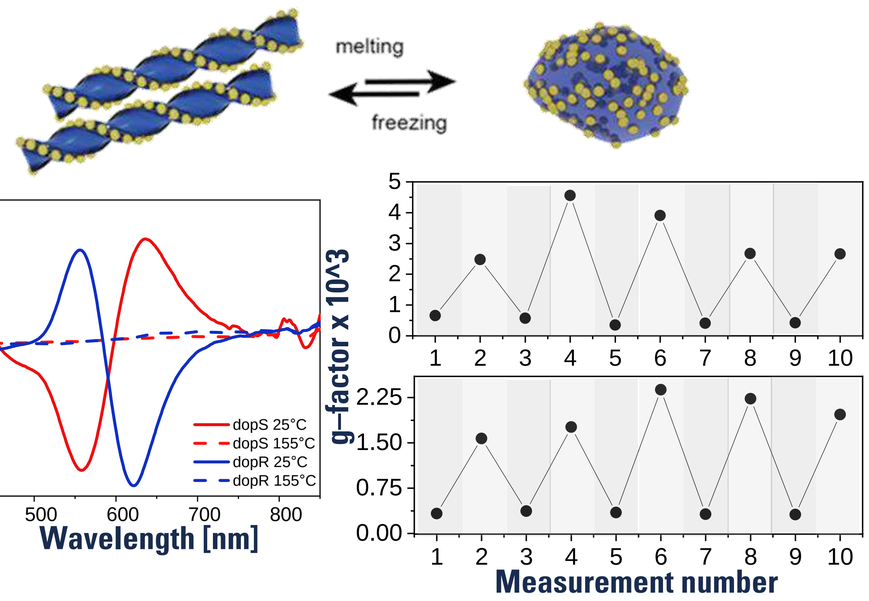
VARYING NPs SIZE AND SHAPE

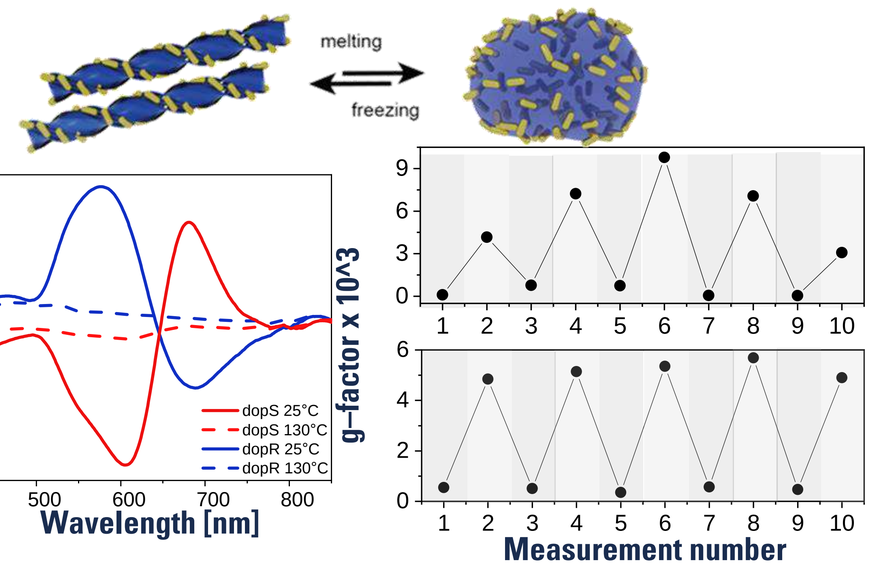
To test if the organic matrix can host different NPs, we prepared ≈4 (Au4), ≈6 (Au6), and ≈10 (Au10) nm diameter spherical Au NPs, as well as 8 × 20 nm (Au20) gold nanorods (NRs). Nanocomposites comprising 18 wt% NPs were then prepared and heat annealed. TEM images of the resulting thin films again revealed double-helical assemblies of Au nanocrystals. Interestingly, Au10 and Au15 NPs formed helically twisted 1D chains, while Au4 NPs formed helically twisted 2D ribbons since several NPs could fit across the HNF edge. CD spectra of films comprising Au4 NPs did not exhibit PCD. For larger NPs, a positive correlation between NP size and PCD intensity was observed, as expected, with similar characteristics of the signals. In the case of Au20, plasmonic Cotton bands were evidenced, centered at 590 and 690 nm. The signs of the lower and higher wavelength bands were analogous to those in films comprising spherical NPs.



SWITCHABLE OPTICAL PROPERTIES

We have also tested whether the soft, responsive character of the LC matrix, can translate into responsiveness toward external stimuli of the chiral, composite thin films. We measured CD spectra of thin films comprising Au15 and Au20 at 25 and 155 °C, corresponding to HNF and Iso phases of the matrix, respectively. At the molten state, no CD signals were recorded between ≈400 and 900 nm The lack of CD signals in the plasmonic range suggests that NPs do not form chiral assemblies without the guidance of HNFs. After cooling the mixtures down to 25 °C, CD signatures from HNFs and helically arranged NPs were visible. To test the reversibility of CD switching, we performed 5 consecutive heating/cooling cycles.





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Detailed measurement results with theoretical models.

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