Onset of Chirality in Plasmonic Meta-Molecules and Dielectric Coupling

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ABSTRACT: Chirality is a fundamental feature in all domains of nature, ranging from particle physics over electromagnetism to chemistry and biology. Chiral objects lack a mirror plane and inversion symmetry and therefore cannot be spatially aligned with their mirrored counterpart, their enantiomer. Both natural molecules and artificial chiral nanostructures can be characterized by their light–matter interaction, which is reflected in circular dichroism (CD). Using DNA origami, we assemble model meta-molecules from multiple plasmonic nanoparticles, representing meta-atoms accurately positioned in space. This allows us to reconstruct piece by piece the impact of varying macromolecular geometries on their surrounding optical near fields. Next to the emergence of CD signatures in the instance that we architect a third dimension, we design and implement sign-flipping signals through addition or removal of single particles in the artificial molecules. Our data and theoretical modeling reveal the hitherto unrecognized phenomenon of chiral plasmonic–dielectric coupling, explaining the intricate electromagnetic interactions within hybrid DNA-based plasmonic nanostructures.

KEYWORDS: chirality, plasmonics, nanoparticles, meta-molecules, circular dichroism, DNA origami, self-assembly

Most biomolecules are chiral, and this property plays a crucial role in molecular recognition and functionality, as these processes often depend on enantiomer-selective activity.1−4 CD spectroscopy thus has become a widespread method to analyze molecular compounds and proteins in science and industry.5−7 But despite much effort, however, we are not yet in the position to reliably predict the CD spectra of a macromolecule nor, the other way around, derive the molecular structure from a recorded CD spectrum.8 The resonances of the atomic bonds within a molecule determine its absorption spectrum, and it is the arrangement of the bonds relative to each other that defines chirality and thus the CD signal. Synthetic and biological molecules usually exhibit their optical responses in the UV range. Metallic nanostructures or DNA architectures with metallic nanoparticles, in contrast, can be designed to feature signals in the visible spectral range.9−18 In such structures, the plasmons—collective oscillations of electrons in metals—of the metallic surfaces couple to each other and create resonances that interact with the optical near field. Just as in their molecular counterparts, these resonances within the metallic nanostructure, or meta-molecules, lead to characteristic absorption and CD spectra. By tailoring the electromagnetic fields we can thus learn to understand the optical responses of nanostructures and molecules alike. Along this path, meta-materials with complex optical properties,19,20 sensing devices,21−24 and enantioselective catalysis applications25,26 have been studied. Chiral nanostructures can be built from silica,27 quantum dots,28−30 or metallic nanoparticles.14−18 Among those, plasmonic nanoparticles have proven to be well-suited candidates for artificial chiral nanostructures. While chirally shaped metal nanoparticles can already express strong CD responses,31,32 the assembly of achiral nanoparticles into chiral architectures offers significantly more freedom in design. Here, the plasmons of the individual particles couple to each other, leading to interactions with the surrounding optical fields that have been studied by many groups.33 For example, ligand-protected gold and silver particle clusters have shown chiral responses,34,35 and chiral assemblies have been achieved through several materials, including peptides,36 polyfluorenes,37 silica films,38 oxalamide fibers,39 proteins,40 or micelles.41 Chiral arrangements of individual entities have been achieved through various lithography methods;42−45

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however, DNA nanotechnology allows to design nanostructures with tailored optical responses on even smaller length scales and, importantly, of chiral objects being assembled and characterized in solution, where the chiral nanostructures are found in random orientations. This orientation averaging is of fundamental importance in measuring the intrinsic chiral property, as was demonstrated theoretically by Rosenfeld. Another kind of chiroptical effect, called extrinsic chirality, appears for oriented nanostructures, which can be either chiral or achiral. However, our study records intrinsic chirality of the DNA–gold nanoparticle complexes in the solution setting.

In particular, the DNA origami technique proved to be powerful to position nanoparticles with sub-nanometer accuracy. In DNA origami, a single-stranded scaffold is folded into any desired three-dimensional (3D) shape by a multitude of designed short DNA staple strands. The resulting objects are fully addressable using DNA handle strands that protrude from the structure and can capture any object that is functionalized with the complementary DNA sequence. DNA origami therefore provides a freely customizable molecular framework that has been employed to arrange left- and right-handed helices of spherical metal nanoparticles or chiral arrangements of metal nanorods.

Helical shapes not only play a fundamental role in biology—most notably the right-handed form of double-stranded DNA and the α-helical protein units—but also offer a step-by-step path to understand space and the exact mechanisms behind chiral optical activity. Theoretical models have shown that geometrical features of pitch length, number of particles, or particles per turn can have significant influences on the CD response. In this study we present two types of model meta-molecules for simulating and predicting the CD responses of gold nanoparticle helices that are assembled particle by particle on a DNA origami scaffold. In total we assembled 18 different species with an accuracy that allowed us to comprehend the onset of the emerging CD signals as well as spectral signatures arising from the helical pitch length. Our findings contribute to a detailed understanding about the origins of molecular and plasmonic CD, and we elucidate in this context the role of dielectric materials in the vicinity of plasmonic arrangements.

Approaching the concept of chirality through an arrangement of spherical particles in space, one may consider how the given number of particles determines the highest possible dimension of any attainable geometrical configuration. While any single sphere \(S_1\) is coercedly a zero-dimensional assembly (Figure 1a), two spheres, \(S_2\) and \(S_3\), always define a line \(L\) connecting them. Such a one-dimensional assembly has an infinite number of mirror planes through \(L\) as well as one mirror plane perpendicular to \(L\) halfway between the particles (Figure 1b). When adding a third sphere, \(S_3\), two possibilities arise. Either \(S_3\) will be located on \(L\), leaving the geometry one-dimensional, or it will be located at any other arbitrary position in space, expanding the structure to the second dimension. In the latter case, \(S_3\), \(S_4\), and \(S_5\) will form a plane \(P\), which will automatically function as the structure’s imperative mirror plane (Figure 1c). An additional mirror plane that is perpendicular to \(P\) may arise if the three particles form an isosceles triangle. Finally, when the fourth particle, \(S_4\) is added (and not placed on \(P\)), the structure becomes three-dimensional (Figure 1d). If this particle is positioned such that no mirror plane exists anymore, the structure is chiral, as is our example in Figure 1d. Note that by adding further particles, a previously chiral structure can become achiral or, vice versa, an achiral structure can become chiral.

**RESULTS AND DISCUSSION**

Here we explore the onset of chirality by assembling unit-by-unit two types of nanoparticle helices around a DNA origami trunk. One helix type contains up to seven 40 nm gold particles with an offset of 29 nm and a rotation around the helical axis of \(90^\circ\) per particle (design details are given in Supporting Information Note 1). We term this helix “large pitch helix”, LPH, as the pitch will be crucial to understand the various CD responses of helices assembled from four, five, and six particles. The second helix is termed “small pitch helix”, SPH, and can host up to six 30 nm spherical gold nanoparticles with an offset of 11 nm. This geometry leads to the particular feature that the fifth particle is located right above the first one at a distance very similar to the distances between the first and the second particle, or second and third, etc. All gold particles are functionalized with thiol-modified DNA sequences, the “anchors”, which are complementary to DNA sequences, the “handles”, protruding from the surface of a multihelix DNA origami bundle, a 24-helix bundle in the case of the LPH, and a 48-helix bundle for the SPH. We prepared samples containing varying numbers of particles, always starting with a single particle at one end of the trunk (assembly and purification are described in Supporting Information Note 3). Figure 2 displays schematic drawings and TEM images of all samples. Note that the presented images can only provide a 2D representation of our samples. The reliability of DNA origami to sculpt 3D geometries as designed, however, has been demonstrated previously.

We achieved satisfactory yields for correctly assembled LPH-ii to LPH-ixi architectures of 76%, 65%, 68%, 70%, 77%, 56%, and 56%, respectively (Figure 2a,b and Supporting Information Note 3). Most misassemblies are the result of nanoparticles binding nonspecifically to the ends of the multihelix DNA bundles, leading to fractions of \(7\%−18\%\) of the structures carrying one or more extra particles. We therefore added a design feature to the 48-helix bundle of the SPH, where the otherwise accessible ends of the DNA helices are protected by short DNA duplexes crossing the top and bottom of the
origami trunk (details on design and synthesis are given in Supporting Information Notes 1−3). With this modification we eliminated the unintended binding events resulting in lower fractions of structures carrying more particles than intended (<3%) for the SPH. This way, we achieved yields for assembled SPH-i to SPH-vi architectures of 97%, 96%, 87%, 74%, 70%, and 53%, respectively (Figure 2c,d).

Metallic nanoparticle-based meta-molecules are optically most active near their plasmonic resonance frequency, resulting in the highest absorbance as well as CD responses around this frequency. For left-handed objects, as used primarily in this study, typically bisignate peak−dip signals are observed, and we obtain exactly such signals with peaks around 524 nm and dips around 558 nm for both our minimal chiral meta-molecules, i.e., the helices containing exactly four particles (Figure 3a,b; details on the optical characterization can be found in the Supporting Information Note 4). Also, just as expected, we observe no or only negligible CD responses for LPH and even negligible for SPH. Approximately 250 individual assemblies per sample were studied.

Figure 2. Gold nanohelix synthesis. (a) Large pitch helices (LPH) with different numbers of 40 nm particles attached (LPH-i to LPH-vii) and (b) small pitch helices (SPH) with different numbers of 30 nm particles attached (SPH-i to SPH-vi), displayed in electron micrographs and 3D models. Scale bar: 200 nm. (c) Distribution of assemblies in the samples LPH-i to LPH-vii and (d) distribution of assemblies in the samples SPH-i to SPH-vi. Structures assembled as designed pose the majority for all samples. Structures with one particle less attached are increasingly common in samples with higher particle numbers, whereas structures with more particles than intended are less common for LPH and even negligible for SPH. Approximately 250 individual assemblies per sample were studied.

Figure 3. Emergence of CD in experiment and theory. (a) CD spectra of samples LPH-i through LPH-vii and (b) samples SPH-i through SPH-vi, all normalized by the maximum extinction value for each sample. (c) Simulated CD signal of structures LPH-i through LPH-vii and (d) structures SPH-i through SPH-vi. The scale is matched to the strength of the experimental CD. (e) Differences between the maximum and minimum CD response and (f) wavelength of the peak extinction for LPH-i through LPH-vii (red) as well as SPH-i through SPH-vi (blue) in experiment (squares) and theory (circles).

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samples carrying one or two particles, i.e., for SPH-i, SPH-ii, LPH-i, and LPH-ii. Surprisingly, the three-particle meta-molecules show a CD response around 535 nm, and the signal of the large pitch sample (LPH-iii) even shows a dip—peak-shaped spectrum. Numerical simulations for gold “helices” with only three particles—obviously three particles only form a plane and not a helix—do not show any CD signal in empty space or if the refractive index of the background matches that of the supporting structure (Supporting Information Note 5). If, however, the simulations account for the DNA origami, which here is approximated as a dielectric cylinder penetrating the plane formed by three spheres in an oblique angle, a CD response emerges (Figure 3c,d). These augmented simulations yield CD signals not only for the LPH-iii and SPH-iii samples but also noticeable resonances for the LPH-ii and SPH-ii assemblies, where the symmetry is equally broken. Importantly, the five-particle helices show distinct behavior depending on their pitch. In the case of the LPH, every added particle augments the chiral shape of the meta-molecule, leading to a noticeable increase of the signal (Figure 3a). Our simulations corroborate this observation (Figure 3c).

For the short-pitch helix the situation is different. Here the fifth particle is very close to the first particle. So instead of increasing the CD signal, the plasmon—plasmon interactions between particle $S_1$ and $S_5$, which are located right on top of each other, induce a right-handed geometry within the structure, which effectively leads to annihilation of the original left-handed signal. This effect leads to SPH-v showing close to no CD response (Figure 3b), which is accurately reflected in the simulated spectra (Figure 3d). The addition of a sixth particle rescues the signal in our experiments, while this effect is less pronounced in the simulations. Figure 3e displays the peak CD intensities for all experimental samples and the corresponding simulation results showing overall very good agreement. Also the absorbance peak intensities of the experiments match those of our simulations (Figure 3f).

Typical for assemblies that exhibit plasmonic coupling, the spectra shift into the red with increasing numbers of particles.

Two features, however, diverge in our simulations: for one, the shape of the CD spectra of SPH-iii does not exactly match the experimental result. Second, the drop in intensity as well as the increase of the signal upon addition of the sixth particle is less pronounced in the simulations compared to the experiments. One reason for these discrepancies could be found in the fact that already nanometer-scale changes of the helical pitch result in strikingly different behavior in our simulations: If, for example, the $z$-distance between two particles is reduced by only 1 nm, the weak peak—dip signal switches to a dip—peak shape (Supporting Information Note 5). In contrast, when increasing the $z$-distance by 1 nm, the coupling between the first and fifth particle vanishes almost entirely. Despite our initial claim of nanometer accuracy, we acknowledge the fact that individual particles may differ slightly in size and shape. Additionally, the calculated overall shape of a DNA origami structure can vary by a few percent in response to electrostatic interactions, leading to minute discrepancies in the designed particle positions and hence distorted signals.

As a control experiment we assembled right-handed short pitch helices and consistently observed mirrored behavior compared to their left-handed counterparts (Supporting Information Note 6). Notably, the dip—peak signal for the three-particle case is already rather pronounced. Potentially, the dielectric DNA cylinder. Neighboring particles exhibit plasmonic coupling, which manifests itself as increased energy densities, or hot spots, wherever their surfaces come close to each other. Notably, where the nanoparticles are close to the dielectric surface, we also observe the formation of weak hot spots. Hence, a discernible CD signal emerges already for the cases of three nanoparticles (LPH: Figure 4a, SPH: Figure 4b) owing to the dielectric cylinder protruding through the nanoparticle plane in an oblique angle, leading to an overall chiral assembly. The shape of this CD signal differs from the bisignate spectra that are usually observed for helical assemblies but describes a single dip that is rather typical for right-handed assemblies. Four particles define a full helical turn, and thus clear, bisignate CD signals of left-handed helices appear for both the four-particle LPH and the four-particle SPH. In the five-particle case no coupling between the first and fifth particle arises in the long pitch helix (Figure 4a); thus the structure gains chiral features and the signal increases further for every added particle. We speculate that this effect would not continue ad infinitum, but new modes could arise due to the transfer of the UV CD signature of right-handed dsDNA into the plasmonic regime is contributing to this signal. The four-particle species exhibits the expected, strongest dip—peak signal, and, strikingly, we observe sign-flipping for the five-particle sample. For simplicity and clarity we have excluded the CD transfer effect from our simulations and have focused this work on left-handed helices.

Figure 4 shows the energy densities of the electric field $u$ color-coded on the surfaces of the metallic nanoparticles and...
coupling of the electromagnetic far field with the helix’s periodicity.\(^\text{44}\) Strikingly, in the case of the short pitch helix, a new hot spot between the first and the fifth particle becomes apparent (Figure 3b), which drastically changes the near field of the incoming light and results in an almost complete breakdown of the CD signal.

CONCLUSIONS
Using DNA origami and plasmonic particles we are able to design plasmonic meta-atoms and sculpt light–matter interactions through carefully considering the geometrical features of two self-assembled model systems with nanometer precision. Our simulated CD responses in multangle illumination settings, reflecting the situation of meta-molecules tumbling in solution, explain the experimentally observed spectral details, in accordance with the computed near field illumination settings, reflecting the situation of meta-molecules. This model, incorporating the dielectric response of the DNA scaffold, adds an additional layer of understanding to the complex analysis of CD spectra of both artificial chiral assemblies and natural molecules.

METHODS
DNA scaffold strands (p8064) were prepared following previously described procedures.\(^\text{10,16}\) Unmodified staple strands (purification: desalting) were purchased from Eurofins MWG. Thiol-modified strands (purification: HPLC) were purchased from Biomers. Uranyl formate for negative TEM staining was purchased from Polysciences, Inc. Spherical gold nanoparticles were purchased from BBI Solutions. Other chemicals were purchased from CarlRoth and Sigma-Aldrich.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsnano.2c04729.

DNA origami designs, synthesis and purification details, supporting data including agarose gels, TEM images, CD and extinction spectra, numerical simulation methods and experimental data on right-handed helices (PDF)

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