Supporting Information

DNA-Guided Plasmonic Helix with Switchable Chirality

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Note S1. Experimental methods

Basically, we followed our previously-published protocols¹ for self-assembly of DNA origami, conjugation of gold nanorods to DNA origami, self-assembly of gold nanorod superstructures and CD measurements. Table S1 presents the detailed annealing procedures for different experiment steps in this work.

Table S1. Annealing conditions for different steps of experiment.

Reconfiguration 1 is for the conversion of AuNR superstructure between the folded state and the extended state.

Reconfiguration 2 is for the chirality inversion of the AuNR superstructure.

Table S2. Plasmon treatments for different hydrophilicities of the TEM grid surface.

Table S3. Condition for obtaining a negative or positive staining of the DNA structures.

Aqueous layer means that a thin layer of 2% uranyl formate solution was left on the TEM grid surface after staining for 30 s.

Note S2. Simulation techniques

Extinction and CD spectra were obtained by utilizing a commercial software package (FDTD solutions, Lumerical Inc.). Using a perfectly matched layer (PML) as the boundary conditions, the CD spectra were respectively calculated and averaged in the $\pm x$, $\pm y$, and $\pm z$ directions. Balancing the need for accuracy in the calculations with computational time and memory requirements, the mesh sizes were specified as 1 nm in the *x*, *y*, and *z* directions. To better address the curved surface of the AuNR, the mesh sizes were further refined with the Yu-Mittra method². Additionally, due to the inhomogeneous broadening effect that originated from the polydispersity in the superstructures, the dielectric function of the Au was modified and followed the methods used in our previous approach³:

$$
\mathcal{E}_{\text{Au}}(\omega) = \mathcal{E}_{\text{bulk-Au}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_{\text{bulk-Au}}} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_{\text{bulk Broadened}}}
$$

(1)

where $\varepsilon_{bulk\text{ Aul}}(\omega)$ denotes the frequency-dependent complex permittivity of bulk gold and the values were taken from the tabulated data⁴. $\Gamma_{bulk\ \text{Au}} = 0.076 \text{ eV}$ and $\omega_p = 8.9 \text{ eV}$ were fitting parameters in the Drude model⁵. $\Gamma_{bulk\ Broadened} = 5 \Gamma_{bulk\ Au}$ was a broadened damping parameter that was obtained by fitting the results with the experimental extinction spectra of the individual AuNR.

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Note S3. Additional TEM images of self-assembled AuNR chiral superstructures

Figure S1. Wide field TEM images of left-handed AuNR superstructures. DNA origami in the folded state that are used for the assembly process.

Figure S2. Zoomed-in TEM images of individual AuNR superstructures and the corresponding 3D models that have a similar spatial orientation. DNA origami in the folded state was used during the assembly process.

Note S4. TEM characterization of monomeric and polymeric DNA origami

Figure S3. These TEM images show the liquid movement while the sample deposited on the surface of a weakly-charged TEM grid was drying. The weak wettability of the surface was due to the low hydrophilicity. The DNA origami prefer to stand up with the ends of the helices in contact with the TEM grid surface.

In this work, the DNA origami (both V-shape and H-shape) has 3 layers of parallel DNA double helix in each arm. The helical ends that have single-stranded scaffold loops are relatively more hydrophobic than the helical sides because of the exposure of the DNA bases. The hydrophobic interactions between DNA blunt ends have been demonstrated in high ion concentrations or at low temperatures.⁶

In our case, although the DNA origami have weak hydrophobic interactions between each other because of the relatively low ion concentrations (~ 6 mM Mg²⁺), the hydrophobicity differences between the helical ends and sides of DNA origami still greatly influence the attachments of the DNA origami on TEM grid surfaces with different treatments, such as glow discharging of the formvar or carbon film (Table S2). The helical sides of the DNA origami with more hydrophilicity were preferentially attached to the strongly charged surfaces (formvar), while the helical ends of the DNA origami with more hydrophobicity were more likely attached to the weakly charged surfaces (carbon). Overall, it is the hydrophilicity variations between the helical sides and helical ends that dominates the different preference of DNA origami attachments on TEM grid surfaces.

Figure S4. The differential attachments of DNA origami on strongly-charged (A) and weakly-charged (B) TEM grid surfaces, respectively. DNA origami in the extended state that were transformed from the folded state are presented here. On the strongly charged grid surface, the DNA origami prefer to lie down with the flat surface of the DNA helical bundle in contact with the surface, while on the weakly charged grid surface, they prefer to stand up with the ends of the DNA helices in contact with the surface.

Figure S5. A full cycle of structural reconfiguration. The DNA origami's structure was cycled from the folded state to the extended state and back to the folded state.

Figure S6. Histograms of the inter-arm angle of the DNA origami for a full cycle of conversion between the folded state and the extended state. The yield of the structural conversion was not 100% and some intermediate states were present. 300 and 1000 particles were counted for the folded state and the extended state, respectively.

Figure S7. These TEM images show a full cycle of DNA origami supramolecular polymer structural reconfiguration. This conversion allowed the DNA origami to change from the folded state to the extended state and back to the folded state. A, B, E, F) the folded state; C, D) the extended state.

Figure S8. The structural reconfiguration from H-shaped origami (B) to two mirror-image V-shaped structures in (A) and (C). A) The monomeric DNA origami that were used for the self-assembly procedures for the left-handed superstructures; C) The monomeric DNA origami that were used for the self-assembly of the right-handed superstructures.

Figure S9. Histograms of the inter-arm angle of two V-shaped structures that were transformed from the H-shaped DNA origami. VL and VR denote the monomeric DNA origami for the corresponding lefthanded and right-handed superstructures, respectively. 300 particles were counted for both VL and VR.

Figure S10. A collection of DNA superstructures that were assembled from H-shaped DNA origami monomers. The scale bar in the bottom-right image is 50 nm.

Note S5. Experimental absorption spectra of AuNR superstructures

Figure S11. The experimental absorption spectra change after a single step reconfiguration of the AuNR superstructures from the folded state to the extended state. A spectral red shift is observed because the dominant plasmon modes was changed from that of an anti-bonding to a bonding mode after the structural reconfiguration. No apparent aggregation was observed from the absorption spectra.

Figure S12. The experimental absorption spectra change after a single step reconfiguration of the AuNR superstructures from the relaxed state to the left-handed and right-handed state. No apparent aggregation was observed from the absorption spectra.

Note S6. Theoretical discussions

Figure S13. Power absorption maps (unit: $W/m³$) of the $4#$ AuNR (inset on the top-left) within a chiral supra-structure at $\lambda_0 = 670$ nm (a, b) and $\lambda_0 = 768$ nm (c, d) under LCP (a, c) and RCP (b, d), respectively. The handedness of the polarization is labelled with a rotated arrow. The *x*-*y* cut plane passes halfway through the nanorod.

Figure S13 clearly shows the difference between the power absorption at the CD_{max} wavelength λ_0 = 670 nm (a, b) and CD_{min} wavelength λ_0 = 768 nm (c, d). CD spectra can be understood by the absorption differences between the LCP and RCP, with negligible contributions from scattering. In Figure S13, absorption per unit volume can be defined by the following equation⁷:

$$
P_{abs}(\omega) = \frac{1}{2}\omega |E|^2 \, \text{imag}[\varepsilon_{Au}(\omega)] \qquad \qquad ,
$$

(2)

where ω , $|E|$, and imag[$\varepsilon_{Au}(\omega)$] denote angular frequency, amplitude of electric field, and an imaginary part of permittivity of gold. Note that the absorption difference of the individual nanorods in the x - y plane (e.g. a, b) only takes up a small percentage of the overall extinction difference, therefore the strong CD spectra are obtained due to the volume integral within the entire superstructures. Additionally, the induced surface current mostly flows along the *x*-axis, which enables the absorption to be dominant along the *x*-axis.

Figure S14. $|E_y|$ field maps of the 4# AuNR (inset on the top-left in Figure S13) at $\lambda_0 = 670$ nm (a, b) and λ_0 = 768 nm (c, d) under LCP (a, c) and RCP (b, d), respectively. The map scale bar is normalized with the source intensity. The handedness of the incident polarizations are labelled with a rotated arrow. The *xy* cross-section passes halfway through the nanorod. The '+' and '-' signs denote the positive and negative values of the real (E_v) .

In order to analyze the electromagnetic mode that was oscillating in the individual AuNR, $|E_v|$ field profiles were calculated as shown in Figure S14. $|E_v|$ fields were the main components of the E-fields, which were the signature of the evanescent wave (along the *x*-axis) and the oscillating plasmonic modes. The direction of the fields was evaluated with the real (E_v) (denoted by the sign '+' or '-' in Figure S14). When comparing Figure S14 a&b at the wavelength of 670 nm (CD_{max}), it is evident that chiral field patterns had been generated. The stronger source-induced net dipole moment was along the *x*-axis in Figure S14a by evaluating areas with E_v fields that had oppositely paired signs. Likewise, when a comparison was made between Figure S14 c&d at the wavelength of 768 nm (CD_{min}), the stronger net dipole moment was confirmed in Figure S14d. For dipole-light interactions, only the net dipole moment along the *x*axis in the 4# AuNR was responsible for the coupling of the *x*-polarized component of the incident LCP or RCP. This coupling gave rise to the different absorption (CD effect). The stronger power absorption maps as shown in Figure S13 a&d, as compared to those in Figure S13 b&c, respectively, could be explained due to the coupling as well.

Note S7. DNA design and sequences

Figure S15. A strand diagram of the folded-state DNA origami. Inset at the bottom-right is the end view of the numbered DNA helices. The purple colored strands are the hinge strands that bridge the arm and the spacer. The green colored strands are the handle strands for the AuNR attachment. The brown colored strands are the helper strands for the 8 helix-bundle spacer. The red colored strands are the connector strands that were used for the hierarchical self-assembly.

Figure S16. Strand diagram of the extended-state DNA origami. Inset at the bottom-right is the end view of the numbered DNA helices. The purple colored strands are the hinge strands bridging the arm and the spacer. The green colored strands are the handle strands for AuNR attachment. The brown colored strands are the helper strands for the 4 helix-bundle spacer. The red colored strands are the connector strands for the hierarchical self-assembly.

Figure S17. A strand diagram of the H-shaped DNA origami. Inset at the bottom-right is the end view of the numbered DNA helices. The red and green colored strands are the touching strands at the two ends, respectively. The purple colored strands are the hinge strands that bridge the arm and the spacer. The orange colored strands are the handle strands for AuNR attachment. The brown colored strands are the connector strands for hierarchical self-assembly.

DNA sequence for the capping strands that were modified on the surface of AuNRs:

5'- GTG AGT ATC TGG ACT GC/Thiol/-3'

Scaffold strand: home-made M13mp18

DNA sequences for the helper strands used in forming the V-shaped DNA origami (Figure 1B in the main text) and those of the lock and key strands used in the reconfiguration.

- K1 CTC CCT CAT TTC CGT CTG ATA ATT TAA TGC TGA CTG
- K1 ATG AAT TTG TCT TTG GTG CTA CTG CAA GTC GGC GAA CAT GTA AC
- K1 CAC CTT TAG GGG GCT ATA ATT CCC AAT GAA TTA CTT TAC CCC TCA GGT AGG A
- K1 GCT GGC TCT GAC GTT TTT GCA GGC GCG TTC TGT CTG AAA GTA CT
- K1 TCG ATG GTT TCA TTG GCT TGA TTC CGT CGT GAG GTA GAA AC
- K1 AAG GCA AAT GAC CGA ATT ACT AGA CGG ATG TTA
- K1 TTT TGT CGT TCT CTT AAA TGC CGA ATT AGA CCT ATC
- K1 GGC TCG AAT AAA TGA ATA AAT CGG TTG AAA TGG CTG TGA TTT TAT CCG CCA AAG A

DNA sequences of the helper strands used in forming the H-shaped DNA origami (Figure 5 in the main text) and those of the touch strands, block and release strands used in the reconfiguration.

References

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