Supporting Information

for

Three-dimensional Chiral Plasmonic Oligomers

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Methods

Structure fabrication

First, the quartz glass substrate (Suprasil, Heraeus) is covered with a 70 nm thick spacer layer by spin-coating. A solidifiable photopolymer, PC403 (JCR, Japan), is used. A prebaking process is first carried out to remove the solvent from the polymer (increase of the baking temperature from 90 °C to 130 °C). A sufficiently long bake at a higher temperature (30 min at 180 °C) further hardens the layer. Next the three particle L-shape layer (dot diameter 200 nm, surface-to-surface distance 20 nm) and alignment markers are defined in resist (double layer PMMA, Allresist) using electron-beam lithography (Raith e_Line). The substrate is then covered with a 2 nm Cr adhesion layer and a 40 nm gold film using thermal evaporation followed by a lift-off procedure. Subsequently, a 70 nm thick spacer layer of PC403 is applied. Afterwards the substrate is coated once more with PMMA resist. Computer-controlled alignment at the sub-10 nm level using the gold alignment markers is applied to ensure the accurate positioning of the upper dot layer. Metal evaporation, lift off, and final planarization are repeated. All samples have a total area of 30 μm $\times$ 30 μm .

All scanning electron microscope (SEM) images are taken with a Hitachi S-4800 scanning electron microscope.

Optical characterisation

The spectra are measured using a Fourier-transform infrared spectrometer (Bruker Vertex 80, tungsten lamp), equipped with an infrared microscope (Bruker Hyperion). The incident light is focused with a Cassegrain objective with numerical aperture $N = 0.4$, and the transmitted intensities are detected with Si and InGaAs diodes. The incident polarization is set with an infrared polarizer and a broadband (700 nm – 2500 nm) infrared quarterwaveplate (B. Halle Nachfl., Berlin). The measured spectra are normalized with respect to the substrate.

Figure S1: Comparison of the ΔT spectra (dark blue and red) and the difference spectra of the absorbance (light blue and light red). Due to limitations of the used spectrometer, reflectance spectra for circularly polarized light are only measurable in the depicted wavelength regime. The spectra show that indeed all signals are caused by circular dichroism and the $\Delta T_{RCP-LCP}$ spectra yield the same information as the absorbance spectra. The scale bar is 200 nm.

Figure S2: T_{RCP} and T_{LCP} spectra as well as the difference spectrum for the depicted enantiomer of the structures shown in Figure 3 in the main text. The cluster shows a strong optical response and well modulated transmittance spectra.

Figure S3: T_{RCP} and T_{LCP} spectra as well as the difference spectrum for the depicted enantiomer of the structures shown in Figure 4 in the main text. Despite the very different particle sizes we observe a strong plasmonic response of the structure which manifests itself in well modulated spectra, yet, only minor differences can be observed in the response of the structures to left- and right-hand polarized illumination.

Figure S4: *Compositional* optical chirality only leads to vanishing optical chirality in a plasmonic system. The constituting dots in the structures are of different size (200 nm, 150 nm, 90 nm, and 60 nm, respectively) and consequently do not couple via their plasmonic near-fields to one another. The clusters hence comprise of four nearly uncoupled and thus individual particles and therefore do not show a chiral optical response. The scale bar for the insets is 200 nm, for the overview images 500 nm.

Figure S5: T_{RCP} and T_{LCP} spectra as well as the difference spectra for the depicted enantiomers. All spectra show signatures of strong plasmonic modes. Under decreasing upper particle diameter, the coupling between the two layers vanishes, rendering the clusters two-dimensional in a plasmonic sense. Consequently, the chiral optical response vanishes and the T_{RCP} and T_{LCP} spectra become almost identical.

Figure S6: Demonstration of the three-dimensional chiral plasmon ruler. The upper dot is successively displaced in nominal steps of 10 nm. Despite the rather small relative displacements one can observe clear and pronounced changes in the spectral shape as well as in the magnitude. The spectra are shifted upwards for clarity. The scale bar is 200 nm

Figure S7: Demonstration of the three-dimensional chiral plasmon ruler for displacements which are not along the arms of the lower layer L-shape. It is still possible to observe strong and well modulated $\Delta T_{\text{RCP-LCP}}$ spectra. The scale bar is 200 nm.

Figure S8: Exemplary tilted view SEM images of chiral quadrumer clusters arranged in a regular square lattice. All scale bars are 500 nm.

Figure S9: Chiral optical response of the clusters arranged in a regular square lattice (with no C_4 superstructure symmetry). All scale bars are 200 nm.

a) ΔT spectra for forward and backward illumination of only the first layer. A strong signal is present which is nearly perfectly mirrored at the zero line for change of the illumination direction. This signal stems from the fact that the superstructure consisting of the individual clusters is biaxial. Hence, there is a strong signal due to polarisation conversion. This contribution indeed flips sign under illumination direction change.

b) ΔT spectra for forward and backward illumination of the structure shown in the inset. For a true chiral signal the spectra should be identical. Contrary to this, the spectra change significantly. Again, this behavior is caused by polarization conversion. As it changes sign under illumination direction change it is added in the one case and subtracted in the other. In a first approximation one can take this into account by assuming the following to hold true

$$\begin{aligned}\Delta T_{\text{measured}}^{\text{up}} &= \Delta T + \Delta T_{\text{planar}}^{\text{up}} \\ \Delta T_{\text{measured}}^{\text{down}} &= \Delta T + \Delta T_{\text{planar}}^{\text{down}} \\ \text{and } \Delta T_{\text{planar}} &= \Delta T_{\text{planar}}^{\text{up}} = -\Delta T_{\text{planar}}^{\text{down}} \\ \text{then } \Delta T_{\text{planar}} &= \frac{1}{2} (\Delta T_{\text{measured}}^{\text{up}} - \Delta T_{\text{measured}}^{\text{down}}),\end{aligned}$$

where up and down denotes the two illumination directions, ΔT the “true” chiral signal which does not change upon illumination direction change, and ΔT_{planar} the contribution from polarization conversion. This allows calculating the ΔT spectra from the two measurements.^{S1} It is important to note that this technique might not be entirely correct as it assumes the chiral signal to stay perfectly the same upon change of direction. Additionally, we assume that the

chiral signal and the polarization conversion are purely additive and can be disentangled which is not necessarily true for strong signals.^{S2,S3}

c) Calculated ΔT spectra using the above relation. Overall, we find a good agreement with the expected behavior.

Supporting Information References

- S1. Kuroda, R., Harada, T. & Shindo, Y. A solid-state dedicated circular dichroism spectrophotometer: Development and application. *Review of Scientific Instruments* **2001**, 72, 3802-3810.
- S2. Kuball H.-G., Höfer, T. Chiroptical Spectroscopy. *Oriented Molecules and Anisotropic Systems in Encyclopedia of Spectroscopy and Spectrometry* (Academic Press: London) **1999**, 267-281.
- S3. Kuball, H.-G. CD and ACD Spectroscopy on Anisotropic Samples - Chirality of Oriented Molecules in Anisotropic Phases, *Enantiomer* **2002**, 7, 197-205.