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Enantiomorphing chiral plasmonic nanostructures: a counter-intuitive sign reversal of the nonlinear circular dichroism

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Plasmonic nanostructures have demonstrated a remarkable ability to control light in ways never observed in nature, as the optical response is closely linked to their flexible geometric design. Due to lack of mirror symmetry, chiral nanostructures allow twisted electric field “hotspots” to form at the material surface. These hotspots depend strongly on the optical wavelength and nanostructure geometry. Understanding the properties of these chiral hotspots is crucial for their applications; for instance, in enhancing the optical interactions with chiral molecules. Here, we present the results of an elegant experiment: by designing 35

intermediate geometries, we “enantiomorph” the structure from one handedness to the other, passing through an achiral geometry. We use nonlinear multi-photon microscopy to demonstrate a new kind of double-bisignate circular dichroism due to enantiomorphing, rather than wavelength change. From group theory, we propose a fundamental origin of this plasmonic chiroptical response. Our analysis allows the optimization of plasmonic chiroptical materials.

Throughout the 19th and most of the 20th century, chirality has been associated with chemistry. However, whereas chirality can be crucial for understanding molecules, molecules are not best suited for understanding chirality. Indeed, there are various forms of chirality, such as helical chirality, propeller chirality, supramolecular chirality, extrinsic chirality, etc.^[1,2] These forms all depend on intrinsic chirality parameters. Ideally, we would like to be able to vary these parameters, i.e. to follow the parameter values as chiral systems transition from one chiral form into another. However, it is impossible to control the size of atoms, the length of chemical bonds and the orientation of orbitals. Modern nanofabrication techniques have lifted the limitations on tuning chiral parameters.

Using modern nanofabrication methods, it is possible to explore the evolution of chiral forms, by preparing numerous intermediate geometries. This is important because it opens the possibility to tune and optimize the chirality parameters, which enable interesting properties. For instance, by maximizing the *geometric chirality* parameter, it is possible to achieve negative refractive index materials.^[3] Such materials could lead to super-lenses^[4] and various applications that depend on the control of circularly polarized light. In turn, circularly polarized light could find applications in spintronics^[5] and quantum computing^[6,7]. Moreover, by optimizing a parameter called *optical chirality*^[8] it has been shown that “superchiral” light configurations can be achieved. In such configurations, the pitch of the electric field of light is shorter than that of circularly polarized light, thereby enabling stronger chiroptical effects.^[9–11] These effects are leading to more sensitive optical detection and characterization of chiral molecules – crucial for the pharmaceutical and chemical industries.^[11–13] Importantly, optical chirality is particularly enhanced at the surface of chiral plasmonic nanostructures,^[14,15] resulting in large enhancements in measurable circular dichroism (CD).^[16–19]

Despite the advantages of creating intermediate geometries, it is rare to find studies where these have been investigated in detail. Between two enantiomorphs, there can be several pathways for intermediate geometries and those might be quite different (**Figure 1a**).

Also, a priori, it is not clear what the best number of intermediate geometries should be. Indeed this is highly dependent on the geometric and material properties of the structures, as well as the wavelength ranges used. In the literature, examples can be found of studying both enantiomorphs of a structure, its achiral variant and a small number of intermediate steps only.^[20] Consequently, important interesting behavior can go unnoticed.

Here, we report an elegant experiment, impossible to perform with chiral molecules: by designing 35 intermediate geometries, we “enantiomorph” plasmonic nanostructures from one handedness to the other, passing through an achiral geometry. We demonstrate a new kind of bisignate (of two signs) circular dichroism due to enantiomorphing, rather than wavelength change, in the nonlinear emission from near-field hotspots. Contrary to what would be expected from pure geometric considerations, the nonlinear chiroptical signal reverses sign twice, i.e. it is double-bisignate. In order to understand this result, we perform a full modal analysis of the structures in combination with irreducible representations (group theory). Interestingly, we find that, regardless of their handedness, chiral nanostructures contain modes that can be excited by both left and right circularly polarized light (LCP and RCP). Furthermore, which modes are dominant (i.e. couple strongest to light) depends on the wavelength or the shape/dimensions of the nanostructure. It is therefore perfectly possible to engineer chiral nanomaterials that, at a given wavelength, can only be excited with the “wrong” kind of circularly-polarized light (CPL). Our findings offer the possibility of tuning chiroptical response by selecting particular electromagnetic modes, or sets of modes, among hundreds available, which can enable much more sensitive chiroptical control than what is currently available.

We begin by presenting the purely geometric considerations. Starting with left-handed crosses, we morph their geometry in discrete steps, first into achiral squares and then into right-handed chiral crosses (**Figure 1b**). For the purposes of comparison, we use a measure of “chiral geometric difference” (not to be confused with the *geometric chirality* parameter).

This quantity describes the area of maximal overlap that can be achieved between left- and right-handed structures, by rotating and translating the two mirror-image shapes relative to each other form (for full details see **Supporting Discussion 1**). As Figure 1b shows, the chiral geometric difference diminishes until it reaches 0, in the achiral case. However, the chiroptical properties of nanostructures depend on more than geometry alone; without considering material effects, and the properties of the incident light, no direct connection can be made between chiral geometric difference, and chiroptical effects. This measure of chirality is in stark contrast to the double-bisignate response found in our nonlinear CD measurements.

For our experiments, we made use of multi-photon microscopy performed with CPL illumination at 800 nm and schematized in **Figure 1c**. The instrument was a standard commercial model (the same as in our previous works^[21]). The collected light consisted mostly of the second harmonic generation (SHG). Specifically, a bandpass filter allowing 390 nm to 465 nm light was used and, although this filter passes a small part of two-photon luminescence signal, the SHG signal is clearly dominant in this spectral range (see **Figure S1**). Since these nonlinear optical processes are enhanced in the regions of strong local field,^[22,23] they act as a sensitive far-field probe for local field effects.

The samples are chiral crosses made of Au, deposited by electron beam lithography (EBL) on a Si substrate with a thermal oxide layer, and whose dimensions and depth profile are given in **Figure 1d**. Each cross is composed of four separate nanostripes, with varying width w and length l . The separation distance between nanostripes, at the centre of the crosses, is constant at 200 nm. The crosses are arranged in a $40 \times 40 \mu\text{m}^2$ square array, with the distance between cross centres also kept constant at 3.2 μm .

Figure 2a shows scanning electron microscopy (SEM) images of sample arrays. In these arrays, the length of the nanostripes is fixed (1000 nm) and the width changes from 200 nm to 1000 nm in steps of 200 nm. Underneath each SEM are two corresponding multi-

photon micrographs, obtained with LCP and RCP. The multi-photon microscopy images are color-coded for intensity and they show bright hotspots at the center of the chiral crosses (indicated with dashed-line squares for clarity). Similar hotspots have previously been observed at the center of G-shaped^[24] and S-shaped^[25] nanostructured arrays. The hotspots correspond to a chiral coupling at the center of the unit cells that depends on the chirality of the nanostructures and the direction of CPL^[25–27]. This dependence is expressed as a directly observable nonlinear CD effect (brightness of the hotspots, depending on the direction of CPL). Interestingly though, in this set of samples, the nonlinear CD changes sign between the chiral crosses with nanostripe width 200 nm and 600 nm, even though the structures have the same handedness.

The nonlinear CD reversal can be seen more quantitatively in **Figure 2b**. Here, the nonlinear CD is obtained from the detected light upon LCR or RCP illumination according to $(I_{RCP}^{MP} - I_{LCP}^{MP}) / (I_{RCP}^{MP} + I_{LCP}^{MP})$. The individual multi-photon intensity terms I_{LCP}^{MP} and I_{RCP}^{MP} were obtained from the pixel intensity at the center of the chiral crosses, where the chiral coupling is maximum and the characteristic response is most pronounced. For each chiral cross, the central hotspot intensity was averaged over 25 pixels (5×5 pixel array at 0.09 μm per pixel). To account for individual variation between crosses, I_{LCP}^{MP} and I_{RCP}^{MP} were each obtained from further averaging the hotspots of 25 individual crosses. The error bars in **Figure 2b** correspond to the standard deviation from this averaging. It should also be noted that the SEM pictures in **Figure 2a** are only a subset of the entire range of samples we studied. The full set started from $w=100$ nm and progressed to $w=1000$ nm, in steps of 50 nm. Upon considering the nonlinear CD from all these samples, it is obvious that between $w=200$ nm and $w=800$ nm, the chiroptical response is unambiguously reversed, i.e. with clearly separated error bars. The nonlinear CD that we measured is collected in the far-field and it is very different from the linear CD in far-field.

In the far-field, the linear CD response is demonstrated by FDTD simulations data that are displayed in **Figure 3a** (further supporting data are provided in **Figure S2** and **Figure S3**). Clearly, the data in Figure 3a do not match those in Figure 2b. One reason for this difference is that the nonlinear CD originates in the near-field, which is very different from the far-field in this kind of structures. To understand the observed reversal of the nonlinear CD, we need to rigorously examine the electromagnetic behaviour at the surface of the nanostructures.

Here, we formulate the linear optical light interaction with the structures in the framework of the electric field - volume integral equations (EF-VIEs).^[28–33] For the sake of conciseness, we summarize the electric field volume integral equation in an operator form (for full forms see **Supporting Discussion 2**),

$$\mathbf{Z}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{J}(\mathbf{r}', \omega) = \mathbf{E}_{inc}(\mathbf{r}, \omega), \quad (1)$$

where $\mathbf{J}(\mathbf{r}', \omega)$ represents the full solution, i.e. the induced current (and charge) flowing in a nanostructure due to an incident field $\mathbf{E}_{inc}(\mathbf{r}, \omega)$, while the impedance operator $\mathbf{Z}(\mathbf{r}, \mathbf{r}'; \omega)$ is related with the Green's function that describes how a part of the nanostructure (at a source point \mathbf{r}') electromagnetically interacts with another part (at an observation point \mathbf{r}). The full solution is characterized by a set of modes that originate from the eigenvalue problem for equation (1):^[34]

$$\mathbf{Z}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{J}_n(\mathbf{r}', \omega) = \lambda_n(\omega) \cdot \mathbf{J}_n(\mathbf{r}', \omega), \quad (2)$$

where each mode $\mathbf{J}_n(\mathbf{r}', \omega)$ is a complex spatial distribution that is independent of the incident field, at a frequency ω and with a corresponding eigenvalue λ_n .

The EF-VIEs approach is well established but here we take the theoretical analysis a significant step further by making use of group theory. From the discussion detailed in **Supporting Discussion 3 and 4**,^[35] each available mode associated with a given structure geometry can be placed in one of four orthogonal irreducible representations $\Gamma_{j=1,2,3,4}$. These representations correspond to exclusive excitation with either the two orthogonal linear

polarizations (Γ_1 for horizontal and Γ_2 for vertical) or the two circular polarizations (Γ_3 for LCP and Γ_4 for RCP). Importantly, each mode in the 3rd irreducible representation has a “correlated” mode in the 4th irreducible representation, with identical eigenvalues forming an “accidentally degenerate pair”. Crucially, the LCP coupling coefficient of a given Γ_3 mode may be different from the RCP coupling coefficient of the correlated Γ_4 mode. This difference in a mode pair’s ability to couple to LCP and RCP incident light can be seen as a type of “modal circular-dichroism”, and is shown in **Figure 3b,c**.

Figure 3b shows pairs of correlated modes in the structures with width 200 nm. In blue, the Γ_3 modes are ranked according to their coupling coefficient to LCP. The correlated Γ_4 modes are shown in red, please note these only couple to RCP. In an achiral structure, both the blue and red sets would have identical values and ranking. Not surprisingly, the presence of chirality in the structure breaks the symmetry and, overall, the blue modes have higher coupling coefficients. But very counter-intuitively, we also find that, in some pairs, the red modes have higher coupling coefficients. This means that, for such modes, light of the “wrong chirality” couples more efficiently to the chirality of the nanostructure. An example of this behaviour is indicated with an arrow on the figure. As we will see next, the exception can become the rule as we continue changing the cross width towards an achiral structure.

Figure 3c shows pairs of correlated modes in the structures with width 800 nm. Here, there are more red-dominant pairs of correlated modes than in **Figure 3b**, to the point that the overall calculated near-field CD is reversed, as in the experimental observation. Therefore, in these plasmonic nanostructures, the chiroptical response originates from the superposition of all the individual modal responses. The modes themselves represent complex spatial distributions of the charge density; as an illustration, the first and second modes from **Figure 3b** and **3c** are shown in **Figure 3d** and **3e**, respectively. Since the near-field intensity is directly related to the total charge density, regions of high charge density will result in SHG

hotspots (via local fields) on the structure surface. Therefore, differences in the coupling of charge density modes to LCP and RCP light are directly responsible for the observed SHG-CD.

Mathematically, the overall near-field CD originates from the full solution obtained by linearly superposing the contributions from all eigenmodes \mathbf{J}_n ,

$$\mathbf{J}(\mathbf{r}', \omega) = \sum c_n(\omega) \mathbf{J}_n(\mathbf{r}', \omega), \quad (3)$$

where, for a given incident field, the coupling coefficients c_n are given by

$$c_n(\omega) = \frac{\int_V \mathbf{J}_n(\mathbf{r}', \omega) \cdot \mathbf{E}_{\text{inc}}(\mathbf{r}', \omega) d\mathbf{r}'}{\lambda_n(\omega)} \quad (4)$$

and the volume integration is carried out over the whole nanostructure. Full solutions are shown in **Figure S4**. To calculate an overall near-field CD, we make use of the inner product of the coupling coefficients given by

$$\|c_n(\omega)\|^2 = \langle c_n(\omega), c_n(\omega) \rangle = \sum_n c_n(\omega) c_n^*(\omega). \quad (5)$$

Here, $c_n^*(\omega)$ denotes the complex conjugate of $c_n(\omega)$. Since the local field intensity is dependent on the square of all coupling coefficients, the local field circular-dichroism can be expressed as:

$$\text{CD}^{(Local)} \propto \frac{\|c_n^R(\omega)\|^2 - \|c_n^L(\omega)\|^2}{\|c_n^R(\omega)\|^2 + \|c_n^L(\omega)\|^2}. \quad (6)$$

The L and R superscripts refer to the solutions for LCP and RCP (the achiral case of $w=1000$ nm is treated separately, see **Supporting Discussion 5**). The results from equation (6) can be found in **Figure 3f**; where the calculated near-field CD is plotted as a function of the nanostripe width (w), for the left-handed and right-handed crosses. These numerical results show a bisignate near-field CD response corresponding well to the experimental nonlinear CD curves in **Figure 2b**. While **Figure 2a** reveals slight deformation towards the center of the measured crosses, for large (> 400 nm) cross widths, the effect of this deformation on the

SHG-CD is minor (see reference ^[25]). Indeed, the bisignate trend seen in **Figure 3f** is in good agreement with the experimental data found in **Figure 2b**.

We further verify this agreement with a second set of intermediate structures (**Figure S5**) in which the nanostripe length is varied, for a constant width of 200 nm. We observe in both the experiments (originating from near-field) and the near-field simulations that the CD emerges away from the achiral structure, and subsequently plateaus. Although longer nanostripes support more electromagnetic modes than shorter ones, these additional modes spread across the whole structure, and do not influence dramatically the key central region. The nonlinear CD measurements probe the the *center* of the crosses and, consequently, it plateaus as nanostripe length increases.

This study has focussed on the bisignate CD response as a function of varying structure geometry. With respect to wavelength, both linear and nonlinear chiroptical spectra often exhibit complex bisignate (of two signs) features.^[36-40] This behavior can be linked to Kuhn's sum-rule,^[41] which states that the chiroptical response must be zero over all wavelengths. This dependence on wavelength has been analyzed in terms of exciton coupling,^[42] nanoparticle-nanoparticle Coulomb coupling,^[43] and energy level hybridization.^[44] In particular, in the linear optical case it was shown that the energetic ordering of the hybridized modes can be changed, resulting in a reversal of the linear CD, upon making small relative position shifts between L-shaped nanoparticles.^[45] In the context of our group-theory discussion, the coupling coefficients of each mode pair are highly dependent on the wavelength of light. Changing the wavelength will change which mode pairs are dominant within the set, for a particular structure geometry. In principle, this can also be used to optimize the CD for a fixed structure and variable wavelength. However, it is often desirable, or even necessary, to operate at a particular wavelength, for example if probing molecules attached to the nanostructure surface. In these cases, tuning the structure geometry allows the near-field CD to be optimized around the available wavelength.

In this work, we made use of nonlinear chiroptical methods. There are several techniques for mapping near-fields that are based on, for instance, using a superlens,^[46,47] a nanorod array,^[48] or hotspot decorations.^[49] Yet the most popular method of sub-wavelength imaging remains scanning near-field optical microscopy (SNOM),^[50] which can be performed with circularly polarized light for studies of chirality.^[51–56] For all its advantages, SNOM necessitates long scanning times, which renders impractical the imaging of large areas and large sample arrays. Moreover, SNOM is limited to samples where the near-field is accessible to the tip of the microscope and the presence of the tip itself leads to an increase in complexity.^[57] An interesting alternative can therefore be found in nonlinear microscopy. In particular, second harmonic generation (SHG) microscopy is highly sensitive to the near-field intensity, it can probe buried interfaces and, for samples that do not require very high mapping resolution (such as ours), it is fast and practical. Owing to the lack of background, SHG chiroptical techniques are usually three orders of magnitude more sensitive to chirality than their linear optical counterparts,^[25–27] which justifies their use.

To summarize, we have shown that the origin of the chiroptical response in plasmonic nanostructures is due to the selective excitation of available modes, therefore any physical property that affects the modes will allow tuning of the chiroptical response. This mechanism could also be used to explain previous experimental observations of bisignate CD spectra, where different sets of modes can be coupled differently depending on the wavelength of light. Furthermore, we can predict that variation of temperature of the nanostructures (e.g. by laser heating) will change the sets of available modes, due to thermal expansion or a change in permittivity,^[58] and can lead to tuning the chiroptical response. Further physical processes that involve excitation of specific plasmonic modes (Fano resonance, spasers, electromagnetically induced transparency, etc.) can also be used to tune that response for desired applications (through achieving large chirality parameter). In practice, maximizing the chiroptical response in any plasmonic nanostructure is allowed by suppression of the modes that couple to light

“with the wrong chirality”. Equally important, by locally enhancing a particularly strong mode (e.g. via coupling to an auxiliary structure) it is possible to enhance the chiroptical interaction with molecules. In many cases, these molecular interactions will occur at specific wavelength ranges. We show that the chiroptical response at a specific wavelength can be enhanced, and even reversed, by tuning structure geometry alone. This tuneability will lead to improved enantioselectivity for molecular sensing, separation and synthesis.

Experimental Section

Sample preparation

Samples were fabricated using an off-the-shelf Silicon wafer with a 100nm thermal oxide layer. A dicing saw was used to slice the wafer into 7.5x7.5 mm² samples, followed by a solvent clean and an O₂ plasma ashing step. The samples were spin coated with a 100 nm thick polymethyl methacrylate (PMMA) supplied by MicroChem and formulated with a 950k molecular weight. A sputter coater was used to deposit a 5 nm gold layer on top of the PMMA, which helped minimize charging effects during electron beam exposure. A Raith150 Two electron beam lithography (EBL) system was used to expose the nanostructures into the PMMA. Each plasmonic array was patterned within a 40x40 μm² area. The main process parameters were 10 kV acceleration voltage, 20 μm aperture and 110μC/cm² beam dosage. Before development of the PMMA resist, the samples were immersed for 10 s in a gold etchant solution from Sigma-Aldrich, rinsed with deionized water and dried with a nitrogen gun. Development of the resist was achieved by immersing the samples for 60 s in a 1:3 methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) solution, followed by a 60 s immersion in IPA and dried using a flow of nitrogen gas. A 5 nm titanium and 30 nm gold layers were deposited using an Edwards Auto 500 electron beam evaporator at a base pressure below 10⁻⁶ mbar, and using respectively the evaporation rates 0.085 nm/s and 0.22 nm/s. The final process step involved a lift-off of the metallic film around the exposed areas of PMMA. This was achieved by leaving the samples immersed in acetone overnight, followed the application of a 15 s ultrasonic bath, immersion in IPA for another 60 s and dried with a flow of nitrogen gas.

SHG Microscope

SHG microscopy techniques are also the same as seen in Valev, V. K. et al., 2014^[25]. Images are collected with a confocal laser scanning microscope, Zeiss LSM 510 META (Jena,

Germany). The sample is illuminated by a femtosecond pulsed Ti:Sapphire laser, directed to the sample by a dichroic mirror (HFT KP650) and through a Zeiss 100x Alpha Plan-APOCHROMAT oil objective of numerical aperture 1.46. The fundamental excitation wavelength is 800 nm. After passing through a dichroic mirror (NFT545) and a band-pass filter (BP 390-465), the nonlinear signals are collected by a photomultiplier tube. The image is formed with a scanning speed of 12.8 μ s for the pixel dwell time; and each frame is scanned 8 times and averaged.

Analysis

The nonlinear microscopy images obtained contain roughly 60 crosses of each type (normal and mirror), with separate images for LCP and RCP illumination. A Python script was used to specify the central regions of 25 crosses, with clearly damaged structures avoided. For each cross, a 5-pixel by 5-pixel square at the defined central region was intensity-averaged. This result was itself then averaged over the 25 selected crosses to obtain a final intensity and statistical uncertainty for a particular orientation of cross (normal or mirror) and input polarization (LCP or RCP). This was done for each of the considered geometries. These intensities and their corresponding uncertainties are used to obtain the results shown in **Figure 2b**.

Near-field simulations

The optical response of chiral nanostructures is obtained by solving Maxwell's equations with the aid of an in-house developed solver: MAGMAS. In MAGMAS, a Volume Integral Equation (VIE) based approach is pursued to model the light interaction with nanostructures of arbitrary geometries (see the underlying mathematics in **Supporting Discussion 1**). The VIE is then solved by a Method of Moments algorithm. The details on the implementation of this algorithm can be found in.^[28–33] Lastly, based on the group theoretical

approach ^[35] (also see **Supporting Discussion 2 – 4**), an eigenmode mode analysis ^[34] is performed to study the near field behavior of the chiral nanostructures.

FDTD simulations

Full-field electromagnetic wave simulations were performed by using the Finite-Difference Time-Domain Method solver (FDTD solutions, Lumerical) and the Finite Element Method solver (COMSOL Multiphysics). The simulation domain included a unit cell of the investigated structures with periodic boundary conditions along the x and y axes and perfectly matched layers along the propagation direction of electromagnetic waves (z axis). Plane wave light sources with LCP and RCP were used to illuminate the structure along the $-z$ direction. Reflection CD spectra were calculated by extracting the difference of reflection spectra between LCP and RCP. In the simulations, we used Johnson and Christy data and Palik data for the Au and Si complex refractive indices, respectively. The refractive index of SiO₂ was taken as 1.45.

Supporting Information Supporting Information is available from the Wiley Online Library or from the author.

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All data supporting this study are openly available from the University of Bath data archive at <https://doi.org/10.15125/BATH-00483>.

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References

- [1] J. T. Collins, C. Kuppe, D. C. Hooper, C. Sibia, M. Centini, V. K. Valev, *Adv. Opt. Mater.* **2017**, 1700182, 1700182.
- [2] V. K. Valev, J. J. Baumberg, C. Sibia, T. Verbiest, *Adv. Mater.* **2013**, 25, 2517.
- [3] J. B. B. Pendry, *Science* **2004**, 306, 1353.
- [4] M. Khorasaninejad, W. T. Chen, A. Y. Zhu, J. Oh, R. C. Devlin, D. Rousso, F. Capasso, *Nano Lett.* **2016**, 16, 4595.
- [5] R. Farshchi, M. Ramsteiner, J. Herfort, A. Tahraoui, H. T. Grahn, *Appl. Phys. Lett.* **2011**, 98, 162508.
- [6] C. Wagenknecht, C.-M. Li, A. Reingruber, X.-H. Bao, A. Goebel, Y.-A. Chen, Q. Zhang, K. Chen, J.-W. Pan, *Nat. Photonics* **2010**, 4, 549.
- [7] J. F. Sherson, H. Krauter, R. K. Olsson, B. Julsgaard, K. Hammerer, I. Cirac, E. S. Polzik, *Nature* **2006**, 443, 557.
- [8] Y. Tang, A. E. Cohen, *Science* **2011**, 332, 333.
- [9] E. Hendry, T. Carpy, J. Johnston, M. Popland, R. V. Mikhaylovskiy, J. Laphorn, S. M. Kelly, L. D. Barron, N. Gadegaard, M. Kadodwala, *Nat. Nanotechnol.* **2010**, 5, 783.
- [10] E. Hendry, R. V. Mikhaylovskiy, L. D. Barron, M. Kadodwala, T. J. Davis, *Nano Lett.* **2012**, 12, 3640.
- [11] R. Tullius, A. S. S. Karimullah, M. Rodier, B. Fitzpatrick, N. Gadegaard, L. D. D. Barron, V. M. M. Rotello, G. Cooke, A. Laphorn, M. Kadodwala, *J. Am. Chem. Soc.* **2015**, 137, 8380.
- [12] Y. Zhao, A. N. Askarpour, L. Sun, J. Shi, X. Li, A. Alù, *Nat. Commun.* **2017**, 8, 14180.
- [13] Z. Wu, Y. Zheng, *Adv. Opt. Mater.* **2017**, 1700034.
- [14] M. Schäferling, D. Dregely, M. Hentschel, H. Giessen, *Phys. Rev. X* **2012**, 2, 31010.
- [15] A. S. Karimullah, C. Jack, R. Tullius, V. M. Rotello, G. Cooke, N. Gadegaard, L. D. Barron, M. Kadodwala, *Adv. Mater.* **2015**, 27, 5610.

- [16] B. M. Maoz, Y. Chaikin, A. B. Tesler, O. Bar Elli, Z. Fan, A. O. Govorov, G. Markovich, *Nano Lett.* **2013**, *13*, 1203.
- [17] R.-Y. R. Y. Wang, P. Wang, Y. Liu, W. Zhao, D. Zhai, X. Hong, Y. Ji, X. Wu, F. Wang, D. Zhang, W. Zhang, R. Liu, X. Zhang, *J. Phys. Chem. C* **2014**, *118*, 9690.
- [18] W. Ma, H. Kuang, L. Xu, L. Ding, C. Xu, L. Wang, N. A. Kotov, *Nat. Commun.* **2013**, *4*, 2689.
- [19] H. Zhang, A. O. Govorov, *Phys. Rev. B* **2013**, *87*, 75410.
- [20] S. Zu, Y. Bao, Z. Fang, *Nanoscale* **2016**, *8*, 3900.
- [21] V. K. Valev, *Langmuir* **2012**, *28*, 15454.
- [22] T. Wang, D. Halaney, D. Ho, M. D. Feldman, T. E. Milner, *Biomed. Opt. Express* **2013**, *4*, 584.
- [23] C. K. Chen, T. F. Heinz, D. Ricard, Y. R. Shen, *Phys. Rev. B* **1983**, *27*, 1965.
- [24] V. K. Valev, N. Smisdom, A. V. Silhanek, B. De Clercq, W. Gillijns, M. Ameloot, V. V. Moshchalkov, T. Verbiest, *Nano Lett.* **2009**, *9*, 3945.
- [25] V. K. Valev, J. J. Baumberg, B. De Clercq, N. Braz, X. Zheng, E. J. Osley, S. Vandendriessche, M. Hojeij, C. Blejean, J. Mertens, C. G. Biris, V. Volskiy, M. Ameloot, Y. Ekinici, G. a E. Vandenbosch, P. a. Warburton, V. V Moshchalkov, N. C. Panoiu, T. Verbiest, *Adv. Mater.* **2014**, *26*, 4074.
- [26] T. Petralli-Mallow, T. M. Wong, J. D. Byers, H. I. Yee, J. M. Hicks, *J. Phys. Chem.* **1993**, *97*, 1383.
- [27] J. D. Byers, H. I. Yee, J. M. Hicks, *J. Chem. Phys.* **1994**, *101*, 6233.
- [28] G. A. E. Vandenbosch, A. R. Van de Capelle, *IEEE Trans. Antennas Propag.* **1992**, *40*, 806.
- [29] F. J. Demuyneck, G. A. E. Vandenbosch, A. R. Van De Capelle, *IEEE Trans. Antennas Propag.* **1998**, *46*, 397.
- [30] M. Vrancken, G. A. E. Vandenbosch, *IEEE Trans. Microw. Theory Tech.* **2003**, *51*,

216.

- [31] Y. Schols, G. A. E. Vandenbosch, *IEEE Trans. Antennas Propag.* **2007**, *55*, 1086.
- [32] G. A. E. Vandenbosch, V. Volski, F. P. G. de Arquer, N. Verellen, V. Moshchalkov, in *2010 URSI Int. Symp. Electromagn. Theory*, IEEE, **2010**, pp. 257–260.
- [33] X. Zheng, V. K. Valev, N. Verellen, Y. Jeyaram, A. V. Silhanek, V. Metlushko, M. Ameloot, G. A. E. Vandenbosch, V. V. Moshchalkov, *IEEE Photonics J.* **2012**, *4*, 267.
- [34] X. Zheng, N. Verellen, V. Volskiy, V. K. Valev, J. J. Baumberg, G. a E. Vandenbosch, V. V Moshchalkov, *Opt. Express* **2013**, *21*, 31105.
- [35] X. Zheng, N. Verellen, D. Vercruysse, V. Volskiy, P. Van Dorpe, G. A. E. Vandenbosch, V. Moshchalkov, *IEEE Trans. Antennas Propag.* **2015**, *63*, 1589.
- [36] W. Li, Z. J. Coppens, L. V. Besteiro, W. Wang, A. O. Govorov, J. Valentine, *Nat. Commun.* **2015**, *6*, 8379.
- [37] S. Lee, Z. Wang, C. Feng, J. Jiao, A. Khan, L. Li, *Opt. Commun.* **2013**, *309*, 201.
- [38] M. Decker, M. W. Klein, M. Wegener, S. Linden, *Opt. Lett.* **2007**, *32*, 856.
- [39] S. Droulias, V. Yannopapas, *J. Phys. Chem. C* **2013**, *117*, 1130.
- [40] E. Plum, V. a Fedotov, N. I. Zheludev, *J. Opt. A Pure Appl. Opt.* **2009**, *11*, 74009.
- [41] W. Kuhn, *Trans. Faraday Soc.* **1930**, *26*, 293.
- [42] A. Guerrero-Martínez, B. Auguie, J. L. Alonso-Gómez, Z. Džolić, S. Gómez-Graña, M. Žinić, M. M. Cid, L. M. Liz-Marzán, *Angew. Chemie Int. Ed.* **2011**, *50*, 5499.
- [43] Z. Fan, A. O. Govorov, *Nano Lett.* **2010**, *10*, 2580.
- [44] B. Auguie, J. L. Alonso-Gómez, A. Guerrero-Martínez, L. M. Liz-Marzán, *J. Phys. Chem. Lett.* **2011**, *2*, 846.
- [45] M. Hentschel, V. E. Ferry, A. P. Alivisatos, *ACS Photonics* **2015**, *2*, 1253.
- [46] J. B. Pendry, *Phys. Rev. Lett.* **2000**, *85*, 3966.
- [47] N. Fang, *Science* **2005**, *308*, 534.
- [48] A. Ono, J. Kato, S. Kawata, *Phys. Rev. Lett.* **2005**, *95*, 267407.

- [49] V. K. Valev, A. V. Silhanek, Y. Jeyaram, D. Denkova, B. De Clercq, V. Petkov, X. Zheng, V. Volskiy, W. Gillijns, G. A. E. Vandenbosch, O. A. Aktsipetrov, M. Ameloot, V. V. Moshchalkov, T. Verbiest, *Phys. Rev. Lett.* **2011**, *106*, 226803.
- [50] E. H. Synge, *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **1928**, *6*, 356.
- [51] T. Narushima, H. Okamoto, *Phys. Chem. Chem. Phys.* **2013**, *15*, 13805.
- [52] T. Narushima, H. Okamoto, *J. Phys. Chem. C* **2013**, *117*, 23964.
- [53] T. Narushima, S. Hashiyada, H. Okamoto, *ACS Photonics* **2014**, *1*, 732.
- [54] H. Okamoto, T. Narushima, Y. Nishiyama, K. Imura, *Phys. Chem. Chem. Phys.* **2015**, *17*, 6192.
- [55] T. Narushima, S. Hashiyada, H. Okamoto, *Chirality* **2016**, *28*, 540.
- [56] S. Hashiyada, T. Narushima, H. Okamoto, *J. Phys. Chem. C* **2014**, *118*, 22229.
- [57] D. Denkova, N. Verellen, A. V. Silhanek, V. K. Valev, P. Van Dorpe, V. V. Moshchalkov, *ACS Nano* **2013**, *7*, 3168.
- [58] L. N. Aksyutov, *J. Appl. Spectrosc.* **1977**, *26*, 656.

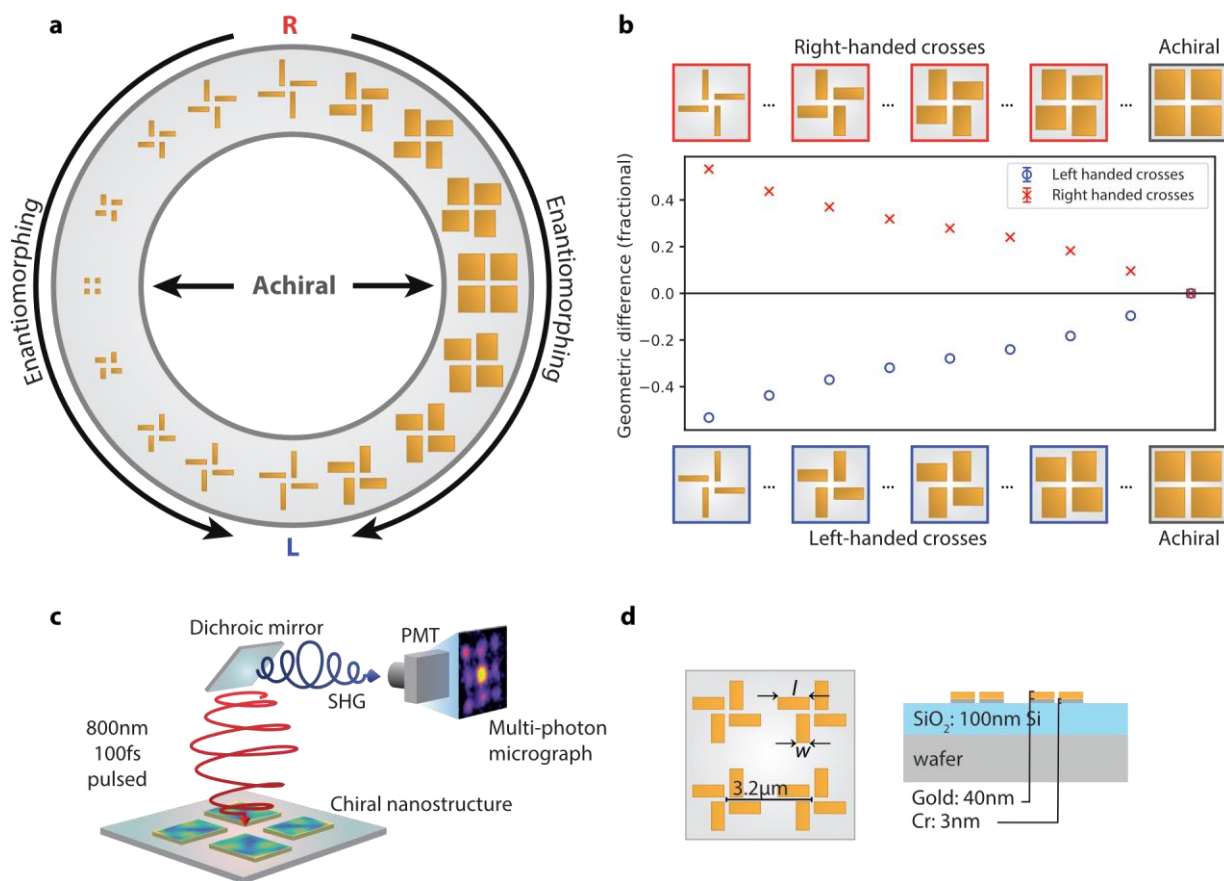


Figure 1. **a.** Representation of two possible pathways to enantiomorph a right-handed structure (R) into a left-handed structure (L), through an achiral geometry. Here we examine the pathway on the right side of the circle. **b.** As the left handed chiral crosses change into achiral square structures and into right handed chiral crosses, the chiral geometric difference diminishes until it reaches 0 in the achiral case and then reverse its value. **c.** Schematic diagram of the multiphoton microscopy experiments. **d.** Geometry and depth profile of the chiral crosses samples.

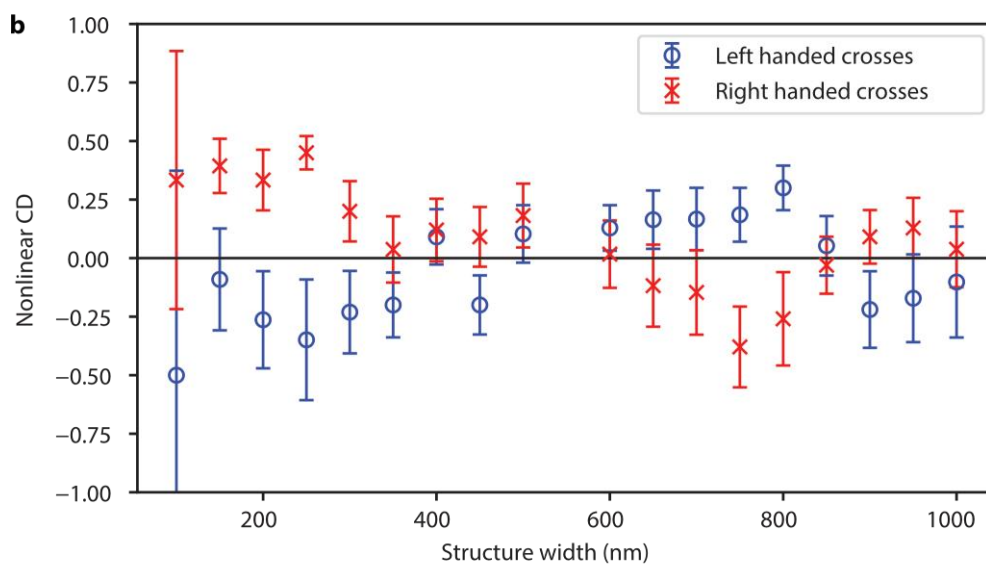
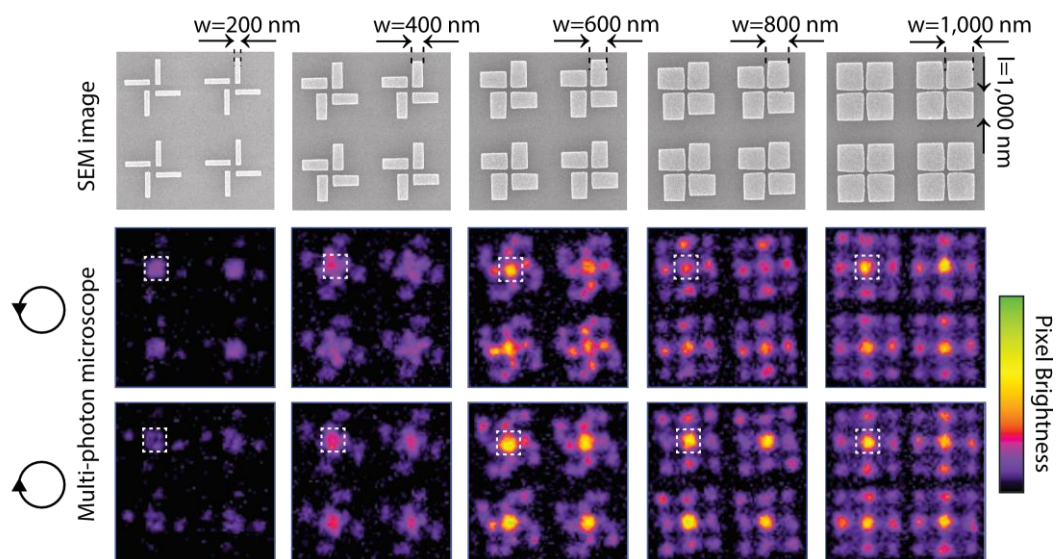
a Left-handed crosses with $l=1,000$ nm, $\lambda=800$ nm

Figure 2. Varying arm width of the nanostructure features at fixed $l=1000$ nm. SEM images of 4 structure cells for each geometry (**a**, top), and SHG microscopy images (**a**, lower) under illumination from left and right circularly polarized light, at 800 nm wavelength. Scale (right) corresponds to image pixel brightness. **b.** Measured total nonlinear CD under 800 nm wavelength light is then calculated for each geometry. Our experiments reveal a counter-intuitive behavior for the second-harmonic generation circular dichroism (SHG-CD) – both the 0 value and the reversal occur before reaching the achiral geometry

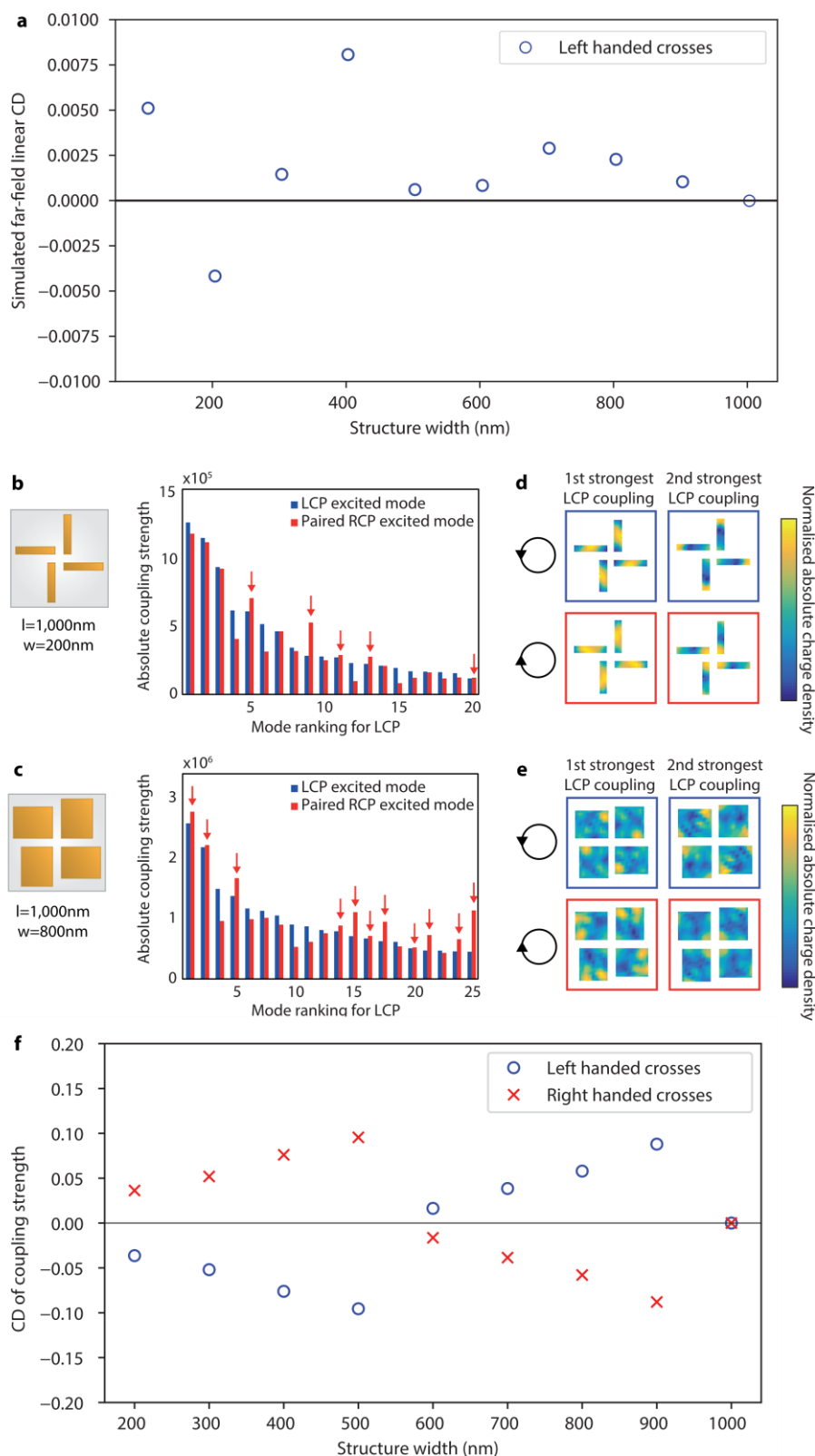


Figure 3. a. Numerically-obtained far-field linear reflection CD for left-handed chiral cross structures. The lineshape of the linear CD response is significantly different to that obtained from nonlinear CD measurements. **b-f.** Simulation results showing modal composition of

chiroptical response. Modal analysis of structures with arm length 1000nm, width 200nm (**b**) and 800nm (**c**). The most LCP-dominant modes for each structure are plotted showing both LCP coupling strength (blue) and the correlated-mode RCP coupling strength (red). Modes coupling stronger to RCP than LCP are marked with arrows. Examples of individual modes (normalized absolute charge density) are shown for width 200nm (**d**) and 800nm (**e**). The total coupling strength CD as defined in equation (6) is plotted for varying arm width, at fixed $l=1000\text{nm}$ under 800nm wavelength light (**f**).

Contrary to what is possible with molecules, modern nanofabrication techniques allow the dimensions of chiral nanostructures to be finely tuned, morphing from one handedness to another (*enantiomorphing*). Additionally, multiple enantiomorphing paths are possible, by varying different structure dimensions. Upon exploring such paths, counter-intuitive chiral optical behavior can be revealed.

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Enantiomorphing chiral plasmonic nanostructures: a counter-intuitive sign reversal of the nonlinear circular dichroism

