Supporting Information: Analytic Optimization of Near-Field Optical Chirality Enhancement

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S.1 Calculation of Optical Chirality of Circularly Polarized Light (CPL) in Free Space

We calculate the optical chirality of CPL in free space, \( C_{\text{CPL}}^{\text{free}}(\omega) \), for a given frequency \( \omega \) and use the result as reference for the local optical chirality in the near fields of plasmonic nanostructures \( C(\mathbf{r}, \omega) \) in this work. Assuming that circularly polarized light propagates in free space along the positive \( z \) direction with time dependency \( \exp(-i\omega t) \) of its temporal electric and magnetic fields, the electric and magnetic fields in the frequency domain are given by

\[
\mathbf{E}_{\text{CPL}}^{\text{free}}(\omega) = \sqrt{\frac{I(\omega)}{4\epsilon_0 c}} \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix} \quad \text{and} \quad \mathbf{H}_{\text{CPL}}^{\text{free}}(\omega) = \sqrt{\frac{I(\omega)}{4\mu_0 c}} \begin{pmatrix} \mp i \\ 1 \\ 0 \end{pmatrix},
\]

(S.1)

with the total intensity \( I(\omega) \), the vacuum permittivity \( \epsilon_0 \), the vacuum permeability \( \mu_0 \), and the speed of light in free space \( c \). According to the definition of LCPL and RCPL from the
observer’s point of view, the light is left-circularly polarized, if the phase difference between
the x and y components of the fields is \((\varphi_y - \varphi_x) = +\pi/2\), and right-circularly polarized, if
the phase difference is \(-\pi/2\). Using Eq. (2) of the main text, we obtain

\[
C_{\text{CPL}}^{\text{free}}(\omega) = -\frac{\epsilon_0 \mu_0 \omega}{2} \text{Im}[E_{\text{CPL}}^{\text{free}}(\omega) \cdot H_{\text{CPL}}^{\text{free}}(\omega)] = \pm \frac{\epsilon_0 \mu_0 \omega I(\omega)}{4}
\]  

(S.2)

which coincides with Eq. (12) of the main text.

### S.2 Determination of Optimal Far-Field Polarizations

In this section we determine those far-field polarizations which lead to optimal local optical
chirality values. For this purpose, we differentiate Eq. (13) from the main text with respect
to \(\hat{I}_1(\omega)\) and \(\varphi(\omega)\), for any given frequency \(\omega\) independently, and set the derivatives

\[
\frac{\partial \hat{C}(r, \omega)}{\partial \hat{I}_1(\omega)} = -\left(C_{S_1}(r, \omega) - C_{S_2}(r, \omega) \right)
+ \frac{\left\{1 - 2\hat{I}_1(\omega)\right\}\left\{C_{S_p}(r, \omega) \cos[\varphi(\omega)] + C_{S_m}(r, \omega) \sin[\varphi(\omega)]\right\}}{2\sqrt{\hat{I}_1(\omega) - \hat{I}_1^2(\omega)}}
\]  

(S.3)

\[
\frac{\partial \hat{C}(r, \omega)}{\partial \varphi(\omega)} = -\left(\sqrt{\hat{I}_1(\omega) - \hat{I}_1^2(\omega)} \right)
\times \left\{-C_{S_p}(r, \omega) \sin[\varphi(\omega)] + C_{S_m}(r, \omega) \cos[\varphi(\omega)]\right\},
\]  

(S.4)

equal to zero. Solving for \(\hat{I}_1(\omega)\) and \(\varphi(\omega)\) leads to two critical points, i.e., two different
solutions for the far-field polarization. The first critical point \(P_1\) is at

\[
\hat{I}_{1P1}(r, \omega) = \frac{1}{2} - \frac{C_{S_1}(r, \omega) - C_{S_2}(r, \omega)}{2 \left\{C_{S_p}^2(r, \omega) + C_{S_m}^2(r, \omega) + \left[C_{S_1}(r, \omega) - C_{S_2}(r, \omega)\right]^2\right\}^{1/2}}
\]  

(S.5)

\[
\varphi_{P1}(r, \omega) = -2 \arctan \left[\frac{C_{S_p}(r, \omega) + \sqrt{C_{S_p}^2(r, \omega) + C_{S_m}^2(r, \omega)}}{C_{S_m}(r, \omega)}\right]
\]  

(S.6)
whereas the second critical point \( P_2 \) is at

\[
\hat{I}_1^{P2} (r, \omega) = \frac{1}{2} + \frac{C_{S_1} (r, \omega) - C_{S_2} (r, \omega)}{2 \left\{ C_{S_p}^2 (r, \omega) + C_{S_m}^2 (r, \omega) + [C_{S_1} (r, \omega) - C_{S_2} (r, \omega)]^2 \right\}^{\frac{1}{2}}}, \tag{S.7}
\]

\[
\varphi^{P2} (r, \omega) = 2 \arctan \left[ \frac{-C_{S_p} (r, \omega) + \sqrt{C_{S_p}^2 (r, \omega) + C_{S_m}^2 (r, \omega)}}{C_{S_m} (r, \omega)} \right]. \tag{S.8}
\]

The nature of each critical point is determined separately via the Hessian matrix of the local optical chirality,

\[
\begin{align*}
H_{\hat{C}} &= \left[ \frac{\partial^2 \hat{C}(r, \omega)}{\partial \hat{I}_1 (\omega) \partial \varphi (\omega)} \right], \tag{S.9}
\end{align*}
\]

where the frequency \( \omega \) is just a parameter. Hence, the dependency on \( \omega \) can be neglected for the following derivations. Calculating the eigenvalues \( \lambda^{P1} \) of Eq. (S.9) for the first critical point,

\[
\det \left[ H_{\hat{C}} \left( \hat{I}_1^{P1}, \varphi^{P1} \right) - \lambda^{P1} \mathbb{I} \right] = 0, \tag{S.10}
\]

with the identity matrix \( \mathbb{I} \), leads to

\[
\begin{align*}
\lambda_1^{P1} \left[ \hat{I}_1^{P1} (r, \omega), \varphi^{P1} (r, \omega) \right] &= -2 \left\{ [C_{S_1} (r, \omega) - C_{S_2} (r, \omega)]^2 + C_{S_p}^2 (r, \omega) + C_{S_m}^2 (r, \omega) \right\}^{\frac{1}{2}} \leq 0, \tag{S.11}
\end{align*}
\]

\[
\begin{align*}
\lambda_2^{P1} \left[ \hat{I}_1^{P1} (r, \omega), \varphi^{P1} (r, \omega) \right] &= - \frac{C_{S_p}^2 (r, \omega) + C_{S_m}^2 (r, \omega)}{2 \left\{ [C_{S_1} (r, \omega) - C_{S_2} (r, \omega)]^2 + C_{S_p}^2 (r, \omega) + C_{S_m}^2 (r, \omega) \right\}^{\frac{1}{2}}} \leq 0. \tag{S.12}
\end{align*}
\]

Since both eigenvalues \( \lambda_1^{P1} \) and \( \lambda_2^{P1} \) are negative, the Hessian matrix is negative definite and thus, the critical point \( P_1 \) is a local maximum. Due to the constraints \( 0 \leq \hat{I}_1 (\omega) \leq 1 \) and \( -\pi \leq \varphi (\omega) < \pi \) the critical point is even a global maximum.
The eigenvalues of the critical point \( P_2 \) are

\[
\lambda_1^{P2}\left[I_1^{P2}(\mathbf{r},\omega), \varphi^{P2}(\mathbf{r},\omega)\right] = 2 \left\{ \left[ C_{S_1}(\mathbf{r},\omega) - C_{S_2}(\mathbf{r},\omega) \right]^2 + C_{Sp}^2(\mathbf{r},\omega) + C_{Sm}^2(\mathbf{r},\omega) \right\}^{\frac{1}{2}} \geq 0, \tag{S.13}
\]

\[
\lambda_2^{P2}\left[I_1^{P2}(\mathbf{r},\omega), \varphi^{P2}(\mathbf{r},\omega)\right] = \frac{C_{Sp}^2(\mathbf{r},\omega) + C_{Sm}^2(\mathbf{r},\omega)}{2 \left\{ \left[ C_{S_1}(\mathbf{r},\omega) - C_{S_2}(\mathbf{r},\omega) \right]^2 + C_{Sp}^2(\mathbf{r},\omega) + C_{Sm}^2(\mathbf{r},\omega) \right\}^{\frac{1}{2}}} \geq 0. \tag{S.14}
\]

In this case, both eigenvalues are positive and therefore the definiteness of the Hessian matrix is positive, as well. Thus, the corresponding critical point represents a local minimum and, due to the above-mentioned constraints, even a global minimum.

Taking all results together leads to the assignment of maximum and minimum in Eqs. (14), (15) and (18) of the main text. Since both extrema are global within the range of the far-field polarization parameters \( I_1(\omega) \) and \( \varphi(\omega) \), there is one unambiguous far-field polarization for which the local optical chirality is maximal and one for which it is minimal (for every frequency).

### S.3 Relation between Far-Field Polarizations for Maximum and Minimum Local Optical Chirality

The far-field polarizations for the optimal local optical chirality are defined by the parameters \( \hat{I}_{1,\text{max}} \) and \( \varphi_{\text{max}} \) for \( \hat{C}_{\text{max}} \) as well as \( \hat{I}_{1,\text{min}} \) and \( \varphi_{\text{min}} \) for \( \hat{C}_{\text{min}} \). In order to derive a relation between both optimal far-field polarizations, we will now show how \( \hat{I}_{1,\text{max}} \) and \( \hat{I}_{1,\text{min}} \), as well as \( \varphi_{\text{max}} \) and \( \varphi_{\text{min}} \) are related to each other.

#### S.3.1 Relation between \( \hat{I}_{1,\text{max}} \) and \( \hat{I}_{1,\text{min}} \)

From the definitions of \( \hat{I}_{1,\text{max}} \) and \( \hat{I}_{1,\text{min}} \) in Eq. (14) in the main text one directly sees that they sum up to 1. This corresponds to Eq. (16) of the main text.
S.3.2 Relation between $\varphi_{\text{max}}$ and $\varphi_{\text{min}}$

According to Eq. (15) the relative phases of the far-field polarizations for maximum and minimum optical chirality are given by

$$\varphi_{\text{max}}(r, \omega) = -2 \arctan \left[ \frac{C_{Sp}(r, \omega) + \sqrt{C_{Sp}^2(r, \omega) + C_{Sm}^2(r, \omega)}}{C_{Sm}(r, \omega)} \right] \in [-\pi, \pi], \quad (S.15)$$

$$\varphi_{\text{min}}(r, \omega) = 2 \arctan \left[ \frac{-C_{Sp}(r, \omega) + \sqrt{C_{Sp}^2(r, \omega) + C_{Sm}^2(r, \omega)}}{C_{Sm}(r, \omega)} \right] \in [-\pi, \pi]. \quad (S.16)$$

We now derive their general relation by dividing both sides of Eqs. (S.15) and (S.16) by 2, applying the tangent, and using

$$\tan [\varphi] = \frac{2 \tan \left[ \frac{\varphi}{2} \right]}{1 - \tan^2 \left[ \frac{\varphi}{2} \right]} \quad (S.17)$$

to obtain

$$\tan [\varphi_{\text{max}}(r, \omega)] = \frac{-2C_{Sp}(r, \omega) + 2 \sqrt{C_{Sp}^2(r, \omega) + C_{Sm}^2(r, \omega)}}{1 - 2C_{Sp}(r, \omega) + C_{Sm}(r, \omega) + 2C_{Sp}(r, \omega) \sqrt{C_{Sp}^2(r, \omega) + C_{Sm}^2(r, \omega)}} = \frac{C_{Sm}(r, \omega)}{C_{Sp}(r, \omega)}, \quad (S.18)$$

$$\tan [\varphi_{\text{min}}(r, \omega)] = \frac{-2C_{Sp}(r, \omega) + 2 \sqrt{C_{Sp}^2(r, \omega) + C_{Sm}^2(r, \omega)}}{1 - 2C_{Sp}(r, \omega) + C_{Sm}(r, \omega) - 2C_{Sp}(r, \omega) \sqrt{C_{Sp}^2(r, \omega) + C_{Sm}^2(r, \omega)}} = \frac{C_{Sm}(r, \omega)}{C_{Sp}(r, \omega)}. \quad (S.19)$$

This leads to the condition that

$$\tan [\varphi_{\text{max}}(r, \omega)] = \tan [\varphi_{\text{min}}(r, \omega)] \quad (S.20)$$

which is fulfilled for

$$\varphi_{\text{max}}(r, \omega) = \varphi_{\text{min}}(r, \omega) + n\pi \quad (S.21)$$

with $n \in \mathbb{Z}$, and thus, considering $\varphi_{\text{max}}(r, \omega) \neq \varphi_{\text{min}}(r, \omega)$ and that values for $\varphi_{\text{max}}(r, \omega)$ as well as $\varphi_{\text{min}}(r, \omega)$ are between $-\pi$ and $\pi$, to Eq. (17) of the main text.
S.4 Relation between Optimal Far-Field Polarizations with respect to Ellipticity and Orientation

We use Eqs. (16) and (17) from the main text to investigate the relation between the optimal far-field polarizations with respect to their ellipticity and orientation. For this purpose, we transform the polarization parameters $I_1(\omega), I_2(\omega), \varphi_1(\omega)$ and $\varphi_2(\omega)$ into elliptical parameters. This representation allows a direct and more intuitive interpretation. An arbitrary ellipse perpendicular to the propagation direction of the external light $e_k$ is described via its amplitudes $eA_1(\omega)$ and $eA_2(\omega)$ along its principal axes $T_1$ and $T_2$, respectively (see Figure S1). In general, these amplitudes are different from the amplitudes $A_1(\omega)$ and $A_2(\omega)$ that are oriented along the axes $T_1$ and $T_2$, respectively, and are given according to Eq. (3) from the main text as

$$A_\alpha(\omega) = \sqrt{\frac{I_\alpha(\omega)}{2\epsilon_0 c}} \quad (S.22)$$

with $\alpha = \{1, 2\}$. The ellipticity of the polarization state is defined by the angle of ellipticity $\epsilon(\omega)$ and its orientation by the orientation angle $\theta(\omega)$, which is the angle between $\tilde{T}_1$ and $T_1$. It was shown previously that these two elliptical parameters can be expressed via

$$\epsilon(\omega) = \frac{1}{2} \arcsin \left\{ \sin[2\chi(\omega)] \sin[\varphi(\omega)] \right\} \quad \in [-\pi/4, \pi/4] \quad (S.23)$$

and

$$\theta(\omega) = \begin{cases} \tilde{\theta}(\omega) & \in [-\pi/4, \pi/4] \quad \text{if } \chi(\omega) \leq \pi/4, \\ \tilde{\theta}(\omega) + \pi/2 & \in [\pi/4, \pi/2] \quad \text{if } \chi(\omega) > \pi/4 \land \tilde{\theta}(\omega) < 0, \\ \tilde{\theta}(\omega) - \pi/2 & \in [-\pi/2, -\pi/4] \quad \text{if } \chi(\omega) > \pi/4 \land \tilde{\theta}(\omega) \geq 0, \end{cases} \quad (S.24)$$

wherein

$$\tilde{\theta}(\omega) = \frac{1}{2} \arctan \left\{ \tan[2\chi(\omega)] \cos[\varphi(\omega)] \right\} \quad \in [-\pi/4, \pi/4], \quad (S.25)$$

and

$$\chi(\omega) = \arctan \left[ \frac{A_2(\omega)}{A_1(\omega)} \right] \quad \in [0, \pi/2]. \quad (S.26)$$
The relative phase is defined as

$$\varphi (\omega) = \varphi_2 (\omega) - \varphi_1 (\omega) \quad \in [-\pi, \pi].$$

With these relations, both $\epsilon (\omega)$ and $\theta (\omega)$ can be calculated from the polarization parameters $A_1 (\omega)$, $A_2 (\omega)$ and $\varphi (\omega)$.

Using the definitions $\hat{I}_2 (\omega) = [I (\omega) - I_1 (\omega)] / I (\omega)$ and $\hat{I}_1 (\omega) = I_1 (\omega) / I (\omega)$ as well as Eq. (S.22) the angle $\chi$ of the far-field polarization for maximum local optical chirality is then given by

$$\chi_{\text{max}} (r, \omega) = \arctan \left[ \sqrt{\frac{1 - \hat{I}_{1,\text{max}} (r, \omega)}{\hat{I}_{1,\text{max}} (r, \omega)}} \right],$$

and that for minimum local optical chirality by

$$\chi_{\text{min}} (r, \omega) = \arctan \left[ \sqrt{\frac{\hat{I}_{1,\min} (r, \omega)}{1 - \hat{I}_{1,\text{max}} (r, \omega)}} \right] = \arctan \left[ \sqrt{\frac{\hat{I}_{1,\text{max}} (r, \omega)}{1 - \hat{I}_{1,\text{max}} (r, \omega)}} \right].$$

In the last step in Eq. (S.29) the relation from Eq. (16) in the main text was applied. Using the relation

$$\arctan \frac{1}{x} = \frac{\pi}{2} \text{sign} x - \arctan x,$$

and Eqs. (S.28) and (S.29) leads to

$$\chi_{\text{max}} (r, \omega) + \chi_{\text{min}} (r, \omega) = \pi / 2.$$
Equation (S.31) and Eq. (17) from the main text can be exploited to compare the ellipticities of the optimal far-field polarizations:

\[ \epsilon_{\text{max}}(r, \omega) = \frac{1}{2} \arcsin \left\{ \sin[2\chi_{\text{max}}(r, \omega)] \sin[\varphi_{\text{max}}(r, \omega)] \right\} \]

\[ = \frac{1}{2} \arcsin \left\{ \sin[\pi - 2\chi_{\text{min}}(r, \omega)] \sin[\varphi_{\text{min}}(r, \omega) \pm \pi] \right\} \]

\[ = -\frac{1}{2} \arcsin \left\{ \sin[2\chi_{\text{min}}(r, \omega)] \sin[\varphi_{\text{min}}(r, \omega)] \right\} \]

\[ = -\epsilon_{\text{min}}(r, \omega). \quad \text{(S.32)} \]

Analogously, a relation between the angles \( \tilde{\theta} \) of the optimal far-field polarizations can be found via

\[ \tilde{\theta}_{\text{max}}(r, \omega) = \frac{1}{2} \arctan \left\{ \tan[2\chi_{\text{max}}(r, \omega)] \cos[\varphi_{\text{max}}(r, \omega)] \right\} \]

\[ = \frac{1}{2} \arctan \left\{ \tan[\pi - 2\chi_{\text{min}}(r, \omega)] \cos[\varphi_{\text{min}}(r, \omega) \pm \pi] \right\} \]

\[ = \frac{1}{2} \arctan \left\{ \tan[2\chi_{\text{min}}(r, \omega)] \cos[\varphi_{\text{min}}(r, \omega)] \right\} \]

\[ = \tilde{\theta}_{\text{min}}(r, \omega). \quad \text{(S.33)} \]

Considering Eq. (S.31), there are three cases for \( \chi_{\text{max}}(r, \omega) \) and \( \chi_{\text{min}}(r, \omega) \):

\[ \chi_{\text{max}}(r, \omega) > \pi/4 \quad \land \quad \chi_{\text{min}}(r, \omega) < \pi/4, \quad \text{(S.34)} \]

\[ \chi_{\text{max}}(r, \omega) < \pi/4 \quad \land \quad \chi_{\text{min}}(r, \omega) > \pi/4 \quad \text{(S.35)} \]

and

\[ \chi_{\text{max}}(r, \omega) = \chi_{\text{min}}(r, \omega) = \pi/4. \quad \text{(S.36)} \]
According to Eqs. (S.24) and (S.34) the orientation angles of the optimal far-field polarizations are in the first case

$$\theta_{\text{max}} (r, \omega) = \tilde{\theta}_{\text{max}} (r, \omega) \pm \pi/2 \quad \text{and} \quad \theta_{\text{min}} (r, \omega) = \tilde{\theta}_{\text{min}} (r, \omega)$$  \hspace{1cm} (S.37)

and according to Eqs. (S.24) and (S.35) in the second case

$$\theta_{\text{max}} (r, \omega) = \tilde{\theta}_{\text{max}} (r, \omega) \quad \text{and} \quad \theta_{\text{min}} (r, \omega) = \tilde{\theta}_{\text{min}} (r, \omega) \pm \pi/2.$$  \hspace{1cm} (S.38)

In the third case, Eq. (S.33) is not valid because the tangents of $2\chi_{\text{max}} (r, \omega) = \pi/2$ and $2\chi_{\text{min}} (r, \omega) = \pi/2$ are not defined due to a pole of the function for this value. Nevertheless, the relation between $\tilde{\theta}_{\text{max}} (r, \omega)$ and $\tilde{\theta}_{\text{min}} (r, \omega)$ can be obtained in this case by the limits

$$\lim_{\chi_{\text{max}} \to \frac{\pi}{4} +} \tilde{\theta}_{\text{max}} (r, \omega) = \lim_{\chi_{\text{max}} \to \frac{\pi}{4} +} \frac{1}{2} \arctan \{ \tan[2\chi_{\text{max}} (r, \omega)] \cos[\varphi_{\text{max}} (r, \omega)] \}$$

$$= \pm \frac{\pi}{4} \text{sign} \{ \cos[\varphi_{\text{max}} (r, \omega)] \}$$

$$= \pm \frac{\pi}{4} \text{sign} \{ \cos[\varphi_{\text{min}} (r, \omega) \pm \pi] \}$$

$$= \pm \frac{\pi}{4} \text{sign} \{ \cos[\varphi_{\text{min}} (r, \omega)] \}$$

$$= \lim_{\chi_{\text{min}} \to \frac{\pi}{4} +} \tilde{\theta}_{\text{min}} (r, \omega).$$  \hspace{1cm} (S.39)

The corresponding orientation angles of the optimal far-field polarizations are then received by means of Eqs. (S.24) and (S.39):

$$\lim_{\chi_{\text{max}} \to \frac{\pi}{4} +} \theta_{\text{max}} (r, \omega) = \lim_{\chi_{\text{max}} \to \frac{\pi}{4} +} \tilde{\theta}_{\text{max}} (r, \omega) \pm \pi/2,$$

$$\lim_{\chi_{\text{min}} \to \frac{\pi}{4} -} \theta_{\text{min}} (r, \omega) = \lim_{\chi_{\text{min}} \to \frac{\pi}{4} -} \tilde{\theta}_{\text{min}} (r, \omega),$$  \hspace{1cm} (S.40)

as well as

$$\lim_{\chi_{\text{max}} \to \frac{\pi}{4} -} \theta_{\text{max}} (r, \omega) = \lim_{\chi_{\text{max}} \to \frac{\pi}{4} -} \tilde{\theta}_{\text{max}} (r, \omega),$$

$$\lim_{\chi_{\text{min}} \to \frac{\pi}{4} +} \theta_{\text{min}} (r, \omega) = \lim_{\chi_{\text{min}} \to \frac{\pi}{4} +} \tilde{\theta}_{\text{min}} (r, \omega) \pm \pi/2.$$  \hspace{1cm} (S.41)
Applying Eq. (S.33) to Eqs. (S.37) and (S.38), and Eq. (S.39) to Eqs. (S.40) and (S.41) leads to the relation

\[ \theta_{\text{max}}(r, \omega) = \theta_{\text{min}}(r, \omega) \pm \pi/2. \]  

(S.42)

The results from Eqs. (S.32) and (S.42) determine the relation between the optimal far-field polarizations. The ellipticity of the far-field polarization for \( C_{\text{max}}(r, \omega) \) is the same as that for \( C_{\text{min}}(r, \omega) \), but with opposite sign, i.e., the shape of the ellipse is the same, but in one case the field is left elliptically polarized, and in the other case it is right elliptically polarized. Furthermore, its orientation is rotated by \( \pm \pi/2 \) with respect to \( e_k \) compared to the orientation of the far-field polarization for \( C_{\text{min}}(r, \omega) \).

It is worth noting that the calculations performed in this section were done in the frequency domain. For pulses in the time domain, the temporal polarization states defined by \( \epsilon(t) \) and \( \theta(t) \) result from the superposition of the monochromatic waves with the corresponding polarization states in the frequency domain, i.e., after performing a Fourier transformation. Thus, the relations (S.32) and (S.42) are not directly seen in the three-dimensional temporal pulse representations of Fig. 4 in the main text and Fig. S3 in Supporting Information Section S.6.

S.5 Consequences of Symmetry

In order to analyze consequences of symmetry of the chosen geometry for the optimal external field, we consider the following situation. A plasmonic nanostructure is illuminated by external light that propagates along the direction of its normalized wave vector \( e_k \) either as a plane wave or as a Gaussian beam whose center axis goes through the center of the nanostructure. The far-field polarization components 1 and 2 of the external light are parallel to the unit vectors \( e_1 \) and \( e_2 \), respectively.

**Proposition:** If the nanostructure has at least \( C_{4v} \) symmetry with the principal axis parallel to \( e_k \), then for any ROI that is also \( C_{4v} \) symmetric with identical principal axis and mirror planes, circularly polarized light is the optimal external polarization to achieve either the highest positive (\( C_{\text{max}} \)) or highest negative (\( C_{\text{min}} \)) optical chirality within the ROI.
Proof: We start from Eqs. (20) and (21) of the main text stating that \( \mathcal{C}_{\text{CPL}} = \mathcal{C}_{\text{opt}} \) if

\[
\mathcal{C}_{S_1}(\omega) = \mathcal{C}_{S_2}(\omega) = \mathcal{C}_{S_p}(\omega) = 0 \quad (S.43)
\]
or if

\[
\mathcal{C}_{S_1}(\omega) = \mathcal{C}_{S_2}(\omega) \quad \text{and} \quad \mathcal{C}_{S_p}(\omega) = 0. \quad (S.44)
\]

Now we analyze these conditions with respect to the symmetry by using the definitions (8)–(11) and (24) of the main text in terms of the response functions \( S_{\alpha}^e(r, \omega) \) and \( S_{\alpha}^h(r, \omega) \) with \( \alpha = \{1, 2\} \). In the following, the local position \( r \) is expressed by the coordinates \( (x, y, z) \) and the dependency on \( \omega \) is omitted for brevity, i.e., \( S_{\alpha}^{e,h}(r, \omega) \equiv S_{\alpha}^{e,h}(x, y, z) \).

Throughout the proof, we exemplarily use a golden truncated square pyramid for illustration purposes (see Fig. S2a). It is centered around the \( z \) axis of a Cartesian coordinate system with the two parallel planes perpendicular to this axis. The normalized wave vector \( e_k \) propagates along the \( z \) axis, and the unit vectors \( e_1 \) and \( e_2 \) are parallel to the \( x \) and \( y \) axis, respectively. In this geometry, the nanostructure has four mirror planes with the principle axis parallel to \( e_k \) and thus is \( C_{4v} \) symmetric with respect to the propagation direction of the external light. Due to the symmetry of the nanostructure, the response-function components \( S_{\alpha q}^{e,h}(x, y, z) \) with \( q = \{x, y, z\} \) can be classified as either even or odd functions with respect to the \( xz \) or \( yz \) plane. For example, component \( S_{1z}^e(x, y, z) \) is odd with respect to the \( x \) and even with respect to the \( y \) axis:

\[
S_{1z}^e(x, y, z) = -S_{1z}^e(-x, y, z) = +S_{1z}^e(x, -y, z). \quad (S.45)
\]

Analogously, the symmetry properties of all response-function components can be derived and are shown in Table S1. Note that in general, under the same illumination conditions, these properties would be also valid for plasmonic nanostructures that are only \( C_{2v} \)-symmetric with respect to the \( xz \) and the \( yz \) plane as mirror planes. The stronger \( C_{4v} \) symmetry, however, enables that the response functions of far-field polarization component 2 can be expressed by those of far-field polarization component 1 because they only differ from each other in a rotation by \( \pi/2 \) with respect to the \( z \) axis. This leads to the following relations:

\[
S_1^{e,h}(x, y, z) = \mathbb{R}_z(-\pi/2) S_2^{e,h}(-y, x, z), \quad (S.46)
\]

\[
S_2^{e,h}(x, y, z) = \mathbb{R}_z(+\pi/2) S_1^{e,h}(y, -x, z). \quad (S.47)
\]
Figure S2: Golden truncated square pyramid illuminated by external light with the normalized wave vector $\mathbf{e}_k$ (green arrows) and the far-field polarization components 1 and 2 along the unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$, respectively (red arrows). (a) The truncated square pyramid has mirror symmetry to the $xz$ and $yz$ plane (orange cuts) as well as to the $x = y$ and $x = -y$ plane (yellow cuts). (b) The blue-colored ROI has mirror symmetry with respect to the $yz$ plane and the pink-colored ROI with respect to the $xz$ plane. For both ROIs the parameters $\overline{C}_{S_1}$ and $\overline{C}_{S_2}$ are zero. (c) The blue-colored ROI has mirror symmetry with respect to the plane $x = y$ and the pink-colored ROI with respect to the plane $x = -y$. For both ROIs $\overline{C}_{S_p}$ is zero. (d) The blue-colored ROI has mirror symmetry to all four planes. Due to the vanishing parameters $\overline{C}_{S_1}$, $\overline{C}_{S_2}$, and $\overline{C}_{S_p}$ the optimal external polarization for maximum and minimum optical chirality within this ROI is CPL.
respectively. Then, we conclude that if a ROI lacks this mirror symmetry, but can be decomposed into ROIs that are mirror-symmetric with respect to the $xz$ plane, we can express the symmetry properties a ROI must have in order to fulfill Eqs. (S.43) and (S.44).

Now we exploit the symmetry properties of the response functions to determine which symmetry properties a ROI must have in order to fulfill Eqs. (S.43) and (S.44).

Parameter $\overline{C}_{S_1}$ of a ROI with volume $V$ is obtained via Eqs. (8) and (24) from the main text as

$$\overline{C}_{S_1} = \frac{1}{V} \iiint_V \text{Im} \left[ S_{1x}^e (x, y, z) S_{1y}^h (x, y, z) + S_{1y}^e (x, y, z) S_{1y}^h (x, y, z) + S_{1z}^e (x, y, z) S_{1z}^h (x, y, z) \right] \, dx \, dy \, dz .$$  \hspace{1cm} (S.49)

Since, according to Table S1, each term of the sum in Eq. (S.49) is a product of an odd and an even function with respect to $x$ and $y$, all three terms are odd functions with respect to both $x$ and $y$. Analogously, the three terms of parameter $\overline{C}_{S_2}$ are odd functions with respect to $x$ and $y$ as well. Thus, if a ROI has mirror symmetry with respect to the $xz$ and/or $yz$ plane, i.e., the plane that is spanned by $e_k$ and $e_1$ and/or the plane that is spanned by $e_k$ and $e_2$, respectively, then $\overline{C}_{S_1} = \overline{C}_{S_2} = 0$. In Fig. S2b, two exemplary box-shaped ROIs are shown that are mirror-symmetric with respect to the $xz$ (pink-colored) and $yz$ plane (blue-colored), respectively. Note that a fusion of both ROIs would also lead to vanishing parameters $\overline{C}_{S_1}$ and $\overline{C}_{S_2}$, although the fused ROI does not fulfill the mirror-symmetry condition. Therefore, we conclude that if a ROI lacks this mirror symmetry, but can be decomposed into ROIs which are mirror-symmetric separately from each other, then $\overline{C}_{S_1}$ and $\overline{C}_{S_2}$ are zero, as well.

As opposed to the parameters $\overline{C}_{S_1}$ and $\overline{C}_{S_2}$, parameter $\overline{C}_{S_0}$ contains response functions...
Table S1: Symmetry properties of response functions for plasmonic nanostructures that have mirror symmetry with respect to the $xz$ and the $yz$ plane. The external light propagates along the $z$ axis, and the far-field polarization components 1 and 2 are parallel to the $x$ and $y$ axis, respectively.

| Response-function component $S_{\alpha q}^{e,h} \in \mathbb{C}$ | Symmetry with respect to $x$ ($x \rightarrow -x$) | Symmetry with respect to $y$ ($y \rightarrow -y$) |
|---------------------------------------------------------------|---------------------------------|---------------------------------|
| $S_{1x}^e (x, y, z)$                                          | even                            | even                            |
| $S_{1y}^e (x, y, z)$                                          | odd                             | odd                             |
| $S_{1z}^e (x, y, z)$                                          | odd                             | even                            |
| $S_{1x}^h (x, y, z)$                                          | odd                             | odd                             |
| $S_{1y}^h (x, y, z)$                                          | even                            | even                            |
| $S_{1z}^h (x, y, z)$                                          | even                            | odd                             |
| $S_{2x}^e (x, y, z)$                                          | odd                             | odd                             |
| $S_{2y}^e (x, y, z)$                                          | even                            | even                            |
| $S_{2z}^e (x, y, z)$                                          | even                            | odd                             |
| $S_{2x}^h (x, y, z)$                                          | even                            | even                            |
| $S_{2y}^h (x, y, z)$                                          | odd                             | odd                             |
| $S_{2z}^h (x, y, z)$                                          | odd                             | even                            |

of both far-field polarization components. It is defined by Eqs. (9) and (24) from the main text as

$$
\mathcal{C}_{S_p} = \frac{1}{V} \iiint_V \text{Im} \left[ S_{1x}^e (x, y, z) \cdot S_{2y}^h (x, y, z) \right] \, dx \, dy \, dz
\underbrace{+ \frac{1}{V} \iiint_V \text{Im} \left[ S_{2x}^e (x, y, z) \cdot S_{1y}^h (x, y, z) \right] \, dx \, dy \, dz}_{\mathcal{C}_{S_{p1}}}
$$

$$
+ \frac{1}{V} \iiint_V \text{Im} \left[ S_{2x}^e (x, y, z) \cdot S_{1y}^h (x, y, z) \right] \, dx \, dy \, dz
\underbrace{+ \frac{1}{V} \iiint_V \text{Im} \left[ S_{2x}^e (x, y, z) \cdot S_{1y}^h (x, y, z) \right] \, dx \, dy \, dz}_{\mathcal{C}_{S_{p2}}}
$$

(S.50)
Since all terms of both scalar products in Eq. (S.50) are even functions with respect to $x$ and $y$, they would not vanish for a ROI with mirror symmetry with respect to the $xz$ and/or $xy$ plane. Nevertheless, $C_{S_{p1}}$ and $C_{S_{p2}}$ can cancel out each other so that $C_{S_p}$ becomes zero. Applying Eqs. (S.46) and (S.47) to $C_{S_{p1}}$ leads to

\[
C_{S_{p1}} = \frac{1}{V} \iiint_V \text{Im} \left[ R_z (-\pi/2) S_2^{e*} (-y, x, z) \cdot R_z (\pi/2) S_1^h (y, -x, z) \right] dx \, dy \, dz
\]

\[
= \frac{1}{V} \iiint_V \text{Im} \left[ -S_2^{e*} (-y, x, z) S_1^{h*} (y, -x, z) - S_2^{e*} (-y, x, z) S_1^{h*} (y, -x, z) - S_2^{e*} (-y, x, z) S_1^{h*} (y, -x, z) \right] dx \, dy \, dz
\]

Using the relations from Table S1 on these terms we obtain

\[
C_{S_{p1}} = \frac{1}{V} \iiint_V \text{Im} \left[ -S_2^{e*} (y, x, z) S_1^{h*} (y, x, z) - S_2^{e*} (y, x, z) S_1^{h*} (y, x, z) \right. \\
\left. - S_2^{e*} (y, x, z) S_1^{h*} (y, x, z) \right] dx \, dy \, dz
\]

\[
= -\frac{1}{V} \iiint_V \text{Im} \left[ S_2^{e*} (y, x, z) \cdot S_1^{h*} (y, x, z) \right] dx \, dy \, dz
\]  

(S.52)

It is seen that for a ROI with mirror symmetry to the plane $x = y$, $C_{S_{p1}}$ is equal to $C_{S_{p2}}$ with opposite sign, and thus, $C_{S_p} = 0$. In addition, it can be shown by means of the relations from Table S1 and Eq. (S.52) that for a ROI with mirror symmetry to the plane $x = -y$, $C_{S_p}$ is zero as well. Hence, we conclude that if a ROI has mirror symmetry with respect to the plane $x = y$ and/or with respect to the plane $x = -y$, i.e., the plane that is spanned by $\mathbf{e}_k$ and $1/\sqrt{2}(\mathbf{e}_1 + \mathbf{e}_2)$ and/or the plane that is spanned by $\mathbf{e}_k$ and $1/\sqrt{2}(\mathbf{e}_1 - \mathbf{e}_2)$, respectively, then $C_{S_p} = 0$ (compare blue- and pink-colored ROIs in Fig. S2c). In addition, if a ROI lacks this mirror symmetry, but can be decomposed into single ROIs which have the required mirror symmetry separately from each other, then $C_{S_p}$ becomes zero as well.

According to Eqs. (S.43) and (S.44) the optimal external polarization is circular not only for the condition $C_{S_1} = C_{S_2} = C_{S_p} = 0$, but also for the condition $C_{S_1} = C_{S_2}$ and $C_{S_p} = 0$. Therefore, we now analyze the relation between $C_{S_1}$ and $C_{S_2}$ and try to find the case for which both parameters are equal. The parameter $C_{S_1}$ can be expressed via Eqs. (8) and (24)
from the main text and Eq. (S.46) as

\[ C_{S_1} = \frac{1}{V} \iint \iint_V \text{Im} \left[ R_z(-\pi/2) S_{2x}^{*}(-y, x, z) \cdot R_z(-\pi/2) S_{2z}^{h}(-y, x, z) \right] \, dx \, dy \, dz \]

\[ = \frac{1}{V} \iint \iint_V \text{Im} \left[ S_{2y}^{*}(-y, x, z) S_{2y}^{h}(-y, x, z) + S_{2x}^{*}(-y, x, z) S_{2x}^{h}(-y, x, z) ight. \right. \\

\left. \left. + S_{2z}^{*}(-y, x, z) S_{2z}^{h}(-y, x, z) \right] \, dx \, dy \, dz \right. \]  \quad (S.53)

Using the symmetry properties from Table S1 leads to

\[ C_{S_1} = \frac{1}{V} \iint \iint_V \text{Im} \left[ -S_{2y}^{*}(y, x, z) S_{2y}^{h}(y, x, z) - S_{2x}^{*}(y, x, z) S_{2x}^{h}(y, x, z) \right. \right. \\

\left. \left. - S_{2z}^{*}(y, x, z) S_{2z}^{h}(y, x, z) \right] \, dx \, dy \, dz \right. \]  \quad (S.54)

It is obvious by comparing Eq. (S.54) with the definition of \( C_{S_2} \),

\[ C_{S_2} = \frac{1}{V} \iint \iint_V \text{Im} \left[ S_{2x}^{*}(x, y, z) S_{2x}^{h}(x, y, z) + S_{2y}^{*}(x, y, z) S_{2y}^{h}(x, y, z) \right. \right. \\

\left. \left. + S_{2z}^{*}(x, y, z) S_{2z}^{h}(x, y, z) \right] \, dx \, dy \, dz \right. \]  \quad (S.55)

that \( C_{S_1} = -C_{S_2} \) for a ROI with mirror symmetry to the plane \( x = y \). Furthermore, it can be demonstrated by means of the symmetry properties from Table S1 and Eq. (S.54) that this is the case for a ROI with mirror symmetry to the plane \( x = -y \) as well. These results coincide with the result obtained for \( C_{S_p} = 0 \). Thus, if a ROI has mirror symmetry with respect to the plane \( x = y \) and/or with respect to \( x = -y \), then not only \( C_{S_p} = 0 \), but also \( C_{S_1} = C_{S_2} \). With the condition \( C_{S_1} = C_{S_2} \), this results in \( C_{S_1} = C_{S_2} = 0 \).

Combining all results the parameters \( C_{S_1}, C_{S_2} \) and \( C_{S_p} \) are zero if the ROI has mirror symmetry with respect to the four mirror planes of the nanostructure. As a consequence, a ROI with these symmetry properties is centered around the principle axis of the nanostructure (compare blue-colored ROI in Fig. S2d). According to Eq. (20) from the main text this proves the proposition.

Note that there are ROIs possible which do not have these symmetry properties, but nevertheless fulfill the condition \( C_{S_1} = C_{S_p} = C_{S_2} = 0 \) and thus, \( C_{CPL} = C_{opt} \). For instance, the fusion of the blue- and pink-colored ROI in Fig. S2c would also lead to vanishing
parameters $C_s^1$, $C_s^2$, and $C_s^2$, since the fused ROI is mirror-symmetric with respect to the $xz$ plane and can be decomposed into two ROIs with mirror symmetry with respect to the planes $x = y$ and $x = -y$, respectively.

S.6 Second ROI in the Vicinity of Chiral Nanostructure Assembly

In this section we consider an additional example for a second ROI (ROI2) in the vicinity of the chiral nanostructure assembly introduced in the main text. The ROI has the same size as the ROI from the main paper (ROI1) but is located at $(x = 0, y = +80, z = +80)$ nm, i.e., directly between the centers of the two spheres of the upper L shape (blue box in Fig. S3a). We calculate the optimal optical chirality values and the corresponding external far-field polarizations as well as the chirality values obtained for CPL for the same frequency range as the one that has been investigated for ROI1. The resulting chirality values $C_{\text{max}}$, $C_{\text{min}}$, $C_{\text{LCPL}}$, and $C_{\text{RCPL}}$ are shown in Fig. S3b as a function of $\omega$. Similarly to ROI1, the optimal chirality values are significantly enhanced in the complete frequency range compared to the values obtained for CPL as input polarization. Moreover, for $\omega < 3.39$ rad/fs, the magnitudes of $C_{\text{max}}$ and $C_{\text{min}}$ are up to two times higher than those obtained for ROI1 and therefore a stronger enhancement with respect to the optical chirality for CPL in free space $(|C_{\text{free}}^{\text{CPL}}| = 1)$ is achieved. Only for $\omega > 3.39$ rad/fs, the magnitudes are lower than those of ROI1 and decrease below 1. As already mentioned in the main text, the slightly lower magnitudes of $C_{\text{min}}$ compared to $C_{\text{max}}$ can be explained by the reduced symmetry of the nanostructure.

The optimal far-field polarizations are depicted in Fig. S3c and reveal a clearly different behavior compared to those of ROI1 in the investigated frequency range. This is explained by the different properties of the response functions at both ROI positions. In contrast to ROI1, the normalized intensity $\hat{I}_{1,\text{max}}$ of ROI2 is closer to $1/2$ and for low as well as for high frequencies $< 1/2$. The relative phase $\varphi_{\text{max}}$ continuously increases from about $0.6\pi$ in the low-frequency range to values near $\pi$ for high frequencies, whereas for $\varphi_{\text{max}}$ of ROI1 a strong decrease of roughly $\pi/2$ was observed within the frequency range at about 2.8 rad/fs. According to Eqs. (16) and (17) from the main text, the behavior of $\hat{I}_{1,\text{min}}$ is symmetric to $\hat{I}_{1,\text{max}}$ with respect to $\hat{I}_1 = 1/2$ and the behavior of $\varphi_{\text{min}}$ is identical to that of $\varphi_{\text{max}}$ with the phase offset of $\pi$.

The temporal electric fields of two pulses that lead to maximum and minimum optical chirality are shown in Figures S3d and S3e, respectively. We use the same Gaussian spectrum
Figure S3: Example of optical chirality control for a second ROI in the vicinity of the chiral nanostructure assembly introduced in the main text. (a) Nanostructure composed of two twisted L shapes, each of which contains three gold spheres within the same xy planes. The radius of the spheres is 70 nm and the gap between neighboring spheres in x, y, and z direction is 20 nm. The external light propagates in positive z direction along its normalized wave vector $\mathbf{e}_k$ (green arrow). Its far-field polarization components 1 and 2 are parallel to the x axis along unit vector $\mathbf{e}_1$ and parallel to the y axis along $\mathbf{e}_2$, respectively (red arrows). The ROI (blue box, ROI2) is a cube with an edge length of 48 nm and located between two spheres of the upper L shape. (b) Normalized optical chirality values $\overline{C}_{\text{max}}$ (blue circles), $\overline{C}_{\text{min}}$ (red squares), $\overline{C}_{\text{LCPL}}$ (pink crosses) and $\overline{C}_{\text{RCPL}}$ (green triangles) as a function of the angular frequency $\omega$. The black dashed lines show the values for $\overline{C}_{\text{CPL}}^{\text{free}} = \pm 1$. (c) Far-field polarization for maximum (blue) and minimum optical chirality (red) defined by the normalized intensities $\hat{I}_{1,\text{max}}$ and $\hat{I}_{1,\text{min}}$ (lines) as well as the relative phases $\varphi_{\text{max}}$ and $\varphi_{\text{min}}$ (dashed lines with circles, squares) as a function of $\omega$. (d, e) Examples for polarization-shaped laser pulses in the time domain leading to $\overline{C}_{\text{max}}$ (d) and $\overline{C}_{\text{min}}$ (e) within the ROI. The temporal polarization states are shown in quasi-three-dimensional representations as cylinders with corresponding orientations and ellipticities, and the amplitudes of the electric far-field components 1 and 2 are indicated by shadows. The momentary frequency $\omega(t)$ is made visible by means of the color. Zero padding in the frequency domain is used to obtain a smoother behavior in the time domain.
as the one that has been used for the two polarization-shaped pulses of ROI1 with center frequency $\omega_0 = 2.99$ rad/fs and a bandwidth-limited pulse duration of 10 fs. The absolute phase of far-field polarization component 1, $\varphi_1(\omega)$, is set to zero and thus, $\varphi(\omega) = \varphi_2(\omega)$. In contrast to the pulses of ROI1, the two pulses of ROI2 are nearly linearly polarized in the time domain and thus, differ significantly from the temporal polarization of the pulses of ROI1. This is explained by the behavior of the optimal external polarization parameters within the spectral overlap with the Gaussian laser spectrum. Since for the highest intensities of the Gaussian spectrum around the center frequency the optimal external polarization is close to linear, the temporal polarization of the pulses in the time domain is nearly linear as well. As opposed to this, the optimal far-field polarizations for ROI1 are partially linear and, in addition, elliptical within the high-intensity range of the Gaussian spectrum. Thus, the corresponding pulses in the time domain reveal a more complex behavior.

References

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