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# Analytic Optimization of Near-Field Optical Chirality Enhancement

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**Supporting Information** 

**ABSTRACT:** We present an analytic derivation for the enhancement of local optical chirality in the near field of plasmonic nanostructures by tuning the far-field polarization of external light. We illustrate the results by means of simulations with an achiral and a chiral nanostructure assembly and demonstrate that local optical chirality is significantly enhanced with respect to circular polarization in free space. The optimal external far-field polarizations are different from both circular and linear. Symmetry properties of the nanostructure can be exploited to determine whether the optimal far-field polarization is circular. Furthermore, the optimal far-field



polarization depends on the frequency, which results in complex-shaped laser pulses for broadband optimization. **KEYWORDS:** optical chirality, plasmonics, near-field response, analytic optimization, femtosecond polarization pulse shaping, chiroptical spectroscopy

hirality is a geometric property that is of relevance throughout a wide field of natural and artificial entities and materials. For example, many biomolecules such as amino acids or sugars are chiral, that is, they cannot be superimposed onto their mirror images. Such molecules interact differently with left- and right-handed circularly polarized light (LCPL and RCPL, respectively), leading to chiroptical effects, for example, optical rotatory dispersion (ORD) and circular dichroism (CD).<sup>1</sup> The latter is caused by the difference in absorption between LCPL and RCPL, and is exploited in CD spectroscopy. However, molecular CD signals are typically weak and thus difficult to measure with high fidelity, especially in variants where additional time resolution is  $desired^{2-8}$  or where concentrations are low, such as in sensing applications. Hence, for practical purposes, the question arises whether chiroptical signals can be enhanced with respect to the conventional measurement techniques. This also leads to a deeper fundamental question: Which electromagnetic field is actually most sensitive to chirality? Traditionally, circular polarization is employed. But can one do better? More specifically, we ask whether suitably "tailored" light fields can be used to enhance chiroptical effects, independent from the investigated specimen.

Formally, the absorption A of an electromagnetic field by a chiral molecule at frequency  $\omega$  can be expressed via<sup>9-11</sup>

$$A \propto \omega \left( \alpha'' U_{\rm e} + \frac{\chi''}{c^2} U_{\rm b} \right) - G'' C \tag{1}$$

wherein *c* is the speed of light in free space,  $U_{\rm e}$  and  $U_{\rm b}$  are the electric and magnetic energy density, respectively, and the imaginary parts of the electric and magnetic polarizability are

denoted by  $\alpha''$  and  $\chi''$ . The imaginary part of the so-called mixed electric-magnetic dipole polarizability, which arises for chiral molecules, is described by G'', and the optical chirality C introduced by Lipkin<sup>9</sup> quantifies the chiral nature of the electromagnetic field. A precise definition of C and its discussion are given in the following section. The sign of G''depends on the handedness of the chiral molecule,<sup>12</sup> whereas the sign of C depends on the handedness of the electromagnetic field. Considering eq 1, the difference in the absorption of light of opposite handedness results from the last term, which is proportional to the optical chirality. Hence, analogously to conventional CD spectroscopy, arbitrary pairs of electromagnetic field distributions with opposite optical chirality but identical  $U_e$  as well as  $U_h$  can be used for CDlike measurements. Thus, the difference in absorption of such enantiomorphic fields can, in principle, be enhanced by increasing the magnitude of C. For propagating plane waves, the largest optical chirality is achieved for CPL. Tang and Cohen have introduced an experimental scheme where they superimposed two counterpropagating circularly polarized beams of opposite handedness and slightly different amplitudes, leading to a standing wave pattern.<sup>13</sup> They observed an enhanced optical response of chiral molecules with respect to their relative differential absorption, that is, the difference in absorption of light with opposite handedness normalized to the absolute (chirality-independent) absorption, which is proportional to  $C/U_e$ . However, this relative signal was enhanced due to the reduction of  $U_e$  at the nodes of the standing waves and

Received: November 8, 2016 Published: January 25, 2017 not due to an increased optical chirality. An option for the enhancement of absolute instead of relative chiroptical signals is provided by the wide field of chiral plasmonics.<sup>14–22</sup> Geometrically chiral plasmonic nanostructures with large chiroptical far-field responses have been developed.<sup>23–33</sup>Furthermore, the interaction between chiral molecules and plasmonic nanostructures was investigated in theory<sup>34–39</sup> and experiments.<sup>40–46</sup> In recent years, it has been demonstrated that the near fields of plasmonic nanostructures can be utilized to locally enhance the optical chirality.<sup>47,48</sup> By means of specially tailored chiral nanostructures, local optical chirality values greater than that of CPL in free space were achieved.<sup>49–51</sup> Enhanced optical chirality was even found at distinct local positions near achiral nanostructures.<sup>52–54</sup> Additionally, an enhancement in a large volume region was demonstrated.<sup>55</sup>

In all approaches of optical chirality enhancement mentioned above, either linearly or circularly polarized excitation light has been used. However, besides the composition and geometry of the nanostructures, the modification of the far-field polarization of the exciting radiation offers another degree of freedom to increase local optical chirality. It has been shown previously, both theoretically and experimentally, that it is possible to coherently control the localization of near fields on a nm spatial and fs temporal scale using femtosecond polarization pulse shaping.<sup>56–62</sup> This is fundamentally different from arbitrary steady-state elliptical polarization due to the time dependence of the polarization.

In the present work we demonstrate local optical chirality enhancement by tuning the far-field polarization of the external light. In particular, we derive analytic expressions for the optimal external field. For an exemplary illustration, we then apply the principle to an achiral and a chiral nanostructure assembly. The numerical results confirm that local optical chirality is enhanced both with respect to free space as well as with respect to circular input polarization. Moreover, we compare the temporal electric and magnetic near-field evolution for optimal and circular far-field polarization to illustrate the control mechanism. We finally discuss the potential for enhancing the "local dissymmetry factor" before summarizing the theoretical findings and providing an outlook for future applications.

## ANALYTIC DERIVATION OF OPTIMAL LOCAL OPTICAL CHIRALITY

**One Given Position.** The basic idea of local optical chirality enhancement is illustrated in Figure 1. If a plasmonic nanostructure, for example, a gold sphere, is illuminated by external light, local electric and magnetic near fields in the vicinity of the nanostructure are generated. The local optical chirality  $C(\mathbf{r}, \omega)$  at position  $\mathbf{r}$  and frequency  $\omega$  can then be calculated via<sup>9,10</sup>

$$C(\mathbf{r},\,\omega) = -\frac{\epsilon_0 \mu_0 \omega}{2} \mathrm{Im}[\mathbf{E}^*_{\mathrm{loc}}(\mathbf{r},\,\omega) \cdot \mathbf{H}_{\mathrm{loc}}(\mathbf{r},\,\omega)]$$
(2)

wherein  $\epsilon_0$  is the vacuum permittivity,  $\mu_0$  is the vacuum permeability, and the complex-valued vectors  $\mathbf{E}_{loc}$  and  $\mathbf{H}_{loc}$  are the local electric and magnetic fields, respectively, with the asterisk (\*) denoting complex conjugation. Both fields depend on the local response of the nanostructure as well as on the farfield polarization of the external light. In Figure 1a, the far-field polarization is circular, leading to a certain value for  $C(\mathbf{r}, \omega)$ . However, there are possibly far-field polarizations for which the optical chirality value at this position is higher or lower. This



**Figure 1.** Basic idea of local optical chirality enhancement. (a) Farfield illumination of a gold sphere with left-handed circularly polarized light (LCPL, red circle) induces the local electric and magnetic fields  $\mathbf{E}_{loc}(\mathbf{r}, \omega)$  and  $\mathbf{H}_{loc}(\mathbf{r}, \omega)$ , respectively, at position  $\mathbf{r}$  and frequency  $\omega$ . Both fields determine the local optical chirality  $C(\mathbf{r}, \omega)$  according to eq 2. Since they depend not only on the local response of the nanostructure, but also on the far-field polarization of the external light,  $C(\mathbf{r}, \omega)$  can be optimized by tuning the far-field polarization. The propagation direction of the external light is indicated by the green arrow. (b) By means of optimization, far-field polarizations (blue/red ellipse) can be found that lead to maximum/minimum local optical chirality  $C_{max}(\mathbf{r}, \omega)/C_{min}(\mathbf{r}, \omega)$ .

can be understood because the response of the nanostructure crucially depends on the incident polarization. Additionally, interference between incident and scattered fields influences the local optical chirality. The goal is now to find the optimal far-field polarizations, that is, the far-field polarizations that lead to maximum (i.e., highest positive) local optical chirality  $C_{\text{max}}(\mathbf{r}, \omega)$  and minimum (i.e., highest negative) optical chirality  $C_{\min}(\mathbf{r}, \omega)$  (Figure 1b).

In the case of external plane-wave illumination, the electromagnetic field is transverse and, thus, the electric field consists of two orthogonal far-field polarization components,  $\alpha = \{1, 2\}$ , that can be expressed by

$$E_{\alpha}^{\text{ext}}(\omega) = \sqrt{\frac{I_{\alpha}(\omega)}{2\epsilon_{0}c}} e^{i\varphi_{\alpha}(\omega)}$$
(3)

with the intensity  $I_{\alpha}(\omega)$  and the phase  $\varphi_{\alpha}(\omega)$ . Assuming a linear response of the nanostructure, the local electric and magnetic fields can then be obtained via the linear superpositions

$$\mathbf{E}_{\rm loc}(\mathbf{r},\,\omega) = \sum_{\alpha=1,2} \, \mathbf{S}^{e}_{\alpha}(\mathbf{r},\,\omega) E^{\rm ext}_{\alpha}(\omega) \tag{4}$$

and

$$\mathbf{H}_{\rm loc}(\mathbf{r},\,\omega) = \sum_{\alpha=1,2} \,\mathbf{S}^{h}_{\alpha}(\mathbf{r},\,\omega) \frac{1}{\mu_{0}c} E^{\rm ext}_{\alpha}(\omega) \tag{5}$$

with the complex-valued local electric and magnetic response functions  $\mathbf{S}^{e}_{a}(\mathbf{r}, \omega)$  and  $\mathbf{S}^{h}_{a}(\mathbf{r}, \omega)$  of the corresponding far-field polarization components, respectively. The local response functions are dimensionless vectors and characteristics of the nanostructure. Furthermore, they depend on the illumination geometry, for example, the incidence angle and the focusing parameters of the external light, but they are independent from the far-field polarization state that is defined by the amplitudes  $\sqrt{I_{a}(\omega)}$  and the phases  $\varphi_{a}(\omega)$ .<sup>62</sup> Note that the electric field of the external light is sufficient to obtain both the local electric and local magnetic fields. Inserting eqs 4 and 5 into eq 2 leads to

$$C(\mathbf{r}, \omega) = -\frac{\epsilon_{\omega} u_{\omega} \omega}{4} \operatorname{Im} [\mathbf{S}_{1}^{e*}(\mathbf{r}, \omega) \cdot \mathbf{S}_{1}^{h}(\mathbf{r}, \omega) I_{I}(\omega) + \mathbf{S}_{1}^{e*}(\mathbf{r}, \omega) \cdot \mathbf{S}_{2}^{h}(\mathbf{r}, \omega) \sqrt{I_{I}(\omega)I_{2}(\omega)} e^{i[\varphi_{2}(\omega) - \varphi_{1}(\omega)]} + \mathbf{S}_{2}^{e*}(\mathbf{r}, \omega) \cdot \mathbf{S}_{1}^{h}(\mathbf{r}, \omega) \sqrt{I_{I}(\omega)I_{2}(\omega)} e^{i[\varphi_{1}(\omega) - \varphi_{2}(\omega)]} + \mathbf{S}_{2}^{e*}(\mathbf{r}, \omega) \cdot \mathbf{S}_{2}^{h}(\mathbf{r}, \omega) I_{2}(\omega)]$$
(6)

Since we are interested in optical chirality for a given incident spectrum, we rewrite this relation in terms of the total intensity  $I(\omega) = I_1(\omega) + I_2(\omega)$  and the relative phase between the two external electric-field components  $\varphi(\omega) = [\varphi_2(\omega) - \varphi_1(\omega)]$ ,

$$C(\mathbf{r}, \omega) = -\frac{\epsilon_{\omega} u_{\omega} \omega}{4} \Big( I_{I}(\omega) [C_{S_{1}}(\mathbf{r}, \omega) - C_{S_{2}}(\mathbf{r}, \omega)] \\ + I(\omega) C_{S_{2}}(\mathbf{r}, \omega) + \sqrt{I_{I}(\omega) [I(\omega) - I_{I}(\omega)]} \\ \times \{ C_{S_{p}}(\mathbf{r}, \omega) \cos[\varphi(\omega)] + C_{S_{m}}(\mathbf{r}, \omega) \sin[\varphi(\omega)] \} \Big)$$

$$(7)$$

with the abbreviations

$$C_{S_1}(\mathbf{r},\,\omega) = \operatorname{Im}[\mathbf{S}_1^{e*}(\mathbf{r},\,\omega)\cdot\mathbf{S}_1^h(\mathbf{r},\,\omega)]$$
(8)

$$C_{S_{p}}(\mathbf{r}, \omega) = \operatorname{Im}[\mathbf{S}_{1}^{e*}(\mathbf{r}, \omega) \cdot \mathbf{S}_{2}^{h}(\mathbf{r}, \omega) + \mathbf{S}_{2}^{e*}(\mathbf{r}, \omega) \cdot \mathbf{S}_{1}^{h}(\mathbf{r}, \omega)]$$
(9)

$$C_{S_{m}}(\mathbf{r},\,\omega) = \operatorname{Re}[\mathbf{S}_{1}^{e*}(\mathbf{r},\,\omega)\cdot\mathbf{S}_{2}^{h}(\mathbf{r},\,\omega) - \mathbf{S}_{2}^{e*}(\mathbf{r},\,\omega)\cdot\mathbf{S}_{1}^{h}(\mathbf{r},\,\omega)]$$
(10)

$$C_{S_2}(\mathbf{r},\,\omega) = \operatorname{Im}[\mathbf{S}_2^{e^*}(\mathbf{r},\,\omega)\cdot\mathbf{S}_2^h(\mathbf{r},\,\omega)]$$
(11)

Parameters  $C_{S_1}(\mathbf{r}, \omega)$  and  $C_{S_2}(\mathbf{r}, \omega)$  are proportional to the local optical chirality of the independent response functions, while  $C_{S_p}(\mathbf{r}, \omega)$  and  $C_{S_m}(\mathbf{r}, \omega)$  mix the electric and magnetic response of the two orthogonal far-field polarizations. It can be seen from eq 7 that the local optical chirality depends on the intensities of the two far-field components  $I_1(\omega)$  and  $I_2(\omega) =$  $[I(\omega) - I_1(\omega)]$  as well as on their relative phase  $\varphi(\omega)$ , that is, on the polarization state of the external light for a given total intensity  $I(\omega)$ . Hence, tuning of the external far-field polarization enables the control of local optical chirality.

For reference, we use the optical chirality of CPL in free space that is given by (see Supporting Information, section S.1)

$$C_{\text{CPL}}^{\text{free}}(\omega) = \pm \frac{\epsilon_0 \mu_0 \omega I(\omega)}{4}$$
(12)

to normalize all later results on local optical chirality via

$$\hat{C}(\mathbf{r}, \omega) = \frac{C(\mathbf{r}, \omega)}{|C_{CPL}^{\text{free}}(\omega)|}$$

$$= -\left(\hat{I}_{1}(\omega)[C_{S_{1}}(\mathbf{r}, \omega) - C_{S_{2}}(\mathbf{r}, \omega)] + C_{S_{2}}(\mathbf{r}, \omega) + \sqrt{\hat{I}_{1}(\omega) - \hat{I}_{1}^{2}(\omega)} \{C_{S_{p}}(\mathbf{r}, \omega)\cos[\varphi(\omega)] + C_{S_{m}}(\mathbf{r}, \omega)\sin[\varphi(\omega)]\}\right)$$
(13)

with the normalized intensity  $\hat{I}_1(\omega) = I_1(\omega)/I(\omega)$ . The normalized optical chirality in free space is then  $\hat{C}_{CPL}^{free}(\omega) = \pm 1$ . The sign indicates the handedness of the chiral electromagnetic field.

By means of eq 13, it is possible to find the far-field polarization that leads to either the highest positive or negative values of local optical chirality, that is, maximum optical chirality with opposite handedness. In order to determine extremal values for  $\hat{C}(\mathbf{r}, \omega)$ , we differentiate eq 13 with respect to  $\hat{I}_1(\omega)$  and  $\varphi(\omega)$ , for any given frequency  $\omega$  independently, and set the resulting derivatives to zero. Solving for  $\hat{I}_1(\omega)$  and  $\varphi(\omega)$  leads to two different solutions that can be identified as global maximum and minimum (Supporting Information, section S.2). The corresponding far-field polarization parameters are expressed by

$$\begin{split} \hat{\mathbf{f}}_{l_{j_{\min}}}^{\max}(\mathbf{r},\,\omega) &= \\ \frac{1}{2} \mp \frac{C_{S_{1}}(\mathbf{r},\,\omega) - C_{S_{2}}(\mathbf{r},\,\omega)}{2\{C_{S_{p}}^{2}(\mathbf{r},\,\omega) + C_{S_{m}}^{2}(\mathbf{r},\,\omega) + [C_{S_{1}}(\mathbf{r},\,\omega) - C_{S_{2}}(\mathbf{r},\,\omega)]^{2}\}^{1/2}} \end{split}$$
(14)
$$\varphi_{\min}^{\max}(\mathbf{r},\,\omega) &= \mp 2\arctan\left[\frac{\pm C_{S_{p}}(\mathbf{r},\,\omega) + \sqrt{C_{S_{p}}^{2}(\mathbf{r},\,\omega) + C_{S_{m}}^{2}(\mathbf{r},\,\omega)}}{C_{S_{m}}(\mathbf{r},\,\omega)}\right]$$
(15)

with  $\varphi_{\max}(\mathbf{r}, \omega)$  and  $\varphi_{\min}(\mathbf{r}, \omega) \in [-\pi, \pi]$ . Equations 14 and 15 constitute a first major result of the present work, as they allow us to calculate analytically the external field for optimal local optical chirality.

Due to the linear response of the nanostructure, the optimal external polarizations for different frequencies are independent from each other. Therefore, the result is not restricted to a monochromatic wave as external light source. Laser pulses, that is, the superposition of monochromatic waves, can also be used to optimize the local optical chirality for a continuous frequency range simultaneously. Note that in general the optimal far-field polarization parameters  $\hat{I}_{1,\text{opt}}$  and  $\varphi_{\text{opt}}$  with opt = {max, min} can strongly vary for different locations near the nanostructure, so they depend on the local position r. It can be proven (Supporting Information, section S.3) that the normalized intensity  $\hat{I}_1$  and the relative phase  $\varphi$  for maximum and minimum optical chirality are related via:

$$\hat{I}_{1,\max}(\mathbf{r},\,\omega) + \hat{I}_{1,\min}(\mathbf{r},\,\omega) = 1$$
(16)

$$|\varphi_{\max}(\mathbf{r},\,\omega) - \varphi_{\min}(\mathbf{r},\,\omega)| = \pi \tag{17}$$

The relative phases  $\varphi_{\max}(\mathbf{r}, \omega)$  and  $\varphi_{\min}(\mathbf{r}, \omega)$  differ by a constant offset of  $\pm \pi$ . An analogous " $\pi$  rule" was derived previously for coherent control of energy localization<sup>60</sup> and experimentally confirmed in gold nanotriangles.<sup>61</sup> According to eq 17, an optimal optical chirality contrast, that is, maximally different local optical chirality, is achieved by applying a  $\pi$  shift to the far-field phase difference  $\varphi$ . Moreover, together with eq 16, it can be shown (Supporting Information, section S.4) that the ellipticities of the two optimal far-field polarizations differ only in their sign, that is, in their direction of rotation, and that the angle between their orientations, that is, between the principal axes of their ellipses, is  $\pm \pi/2$ . The relation between the two optimal far-field polarization states is illustrated by the Poincaré sphere in Figure 2. Each point on the surface of the sphere represents a polarization state determined by its ellipticity  $\epsilon$  and orientation angle  $\theta$ . Due to the relations  $\epsilon_{\rm max} = -\epsilon_{\rm min}$  and  $\theta_{\rm max} = \theta_{\rm min} \pm \pi/2$  the points of the far-field polarizations for minimum optical chirality are the antipodal points of the corresponding far-field polarizations for maximum optical chirality, that is, "maximally different external polar-ization states" lead to "maximally different local optical chirality". In the example of Figure 2, the green line through



**Figure 2.** Relation between exemplary optimal far-field polarizations on the surface of the Poincaré sphere. Each point of the surface represents a polarization state determined by the ellipticity  $\epsilon$  and the orientation angle  $\theta$ . The latitude and longitude of the surface have the values  $2\epsilon$  and  $2\theta$ , respectively. In the upper hemisphere, the polarization states are left elliptical ( $\epsilon > 0$ , red solid ellipses) with the pole representing LCPL, in the lower hemisphere right elliptical ( $\epsilon < 0$ , blue dashed ellipses) with the pole representing RCPL. The polarization states at the equator are linear ( $\epsilon = 0$ , black lines). The two points of optimal far-field polarization are connected by a green line through the origin. The point of the far-field polarization for minimum optical chirality is the antipodal point of the corresponding far-field polarization for maximum optical chirality.

the origin of the Poincaré sphere connects external polarization states leading to maximum and minimum local optical chirality.

Combining eqs 14 and 15 with eq 13 leads to the local maximum and minimum normalized optical chirality

$$\hat{C}_{\min}^{\max}(\mathbf{r}, \omega) = -\frac{1}{2} \Big( C_{S_1}(\mathbf{r}, \omega) + C_{S_2}(\mathbf{r}, \omega) \\ \mp \{ C_{S_p}^2(\mathbf{r}, \omega) + C_{S_m}^2(\mathbf{r}, \omega) + [C_{S_1}(\mathbf{r}, \omega) - C_{S_2}(\mathbf{r}, \omega)]^2 \}^{1/2} \Big)$$
(18)

As a next step, we compare these optimal chirality values with those obtained by CPL as external input. In that case, using  $\hat{I}_1(\omega) = 1/2$  and  $\varphi(\omega) = \pi/2$  for LCPL and  $\varphi(\omega) = -\pi/2$  for RCPL the normalized local optical chirality is

$$\hat{C}_{\text{RCPL}}^{\text{LCPL}}(\mathbf{r},\,\omega) = -\frac{1}{2} [C_{S_1}(\mathbf{r},\,\omega) + C_{S_2}(\mathbf{r},\,\omega) \pm C_{S_m}(\mathbf{r},\,\omega)]$$
(19)

Comparing eqs 18 and 19, CPL is the optimal far-field polarization only if either

$$C_{S_1}(\mathbf{r},\,\omega) = C_{S_2}(\mathbf{r},\,\omega) = C_{S_p}(\mathbf{r},\,\omega) = 0$$
<sup>(20)</sup>

or if

$$C_{S_1}(\mathbf{r}, \omega) = C_{S_2}(\mathbf{r}, \omega) \text{ and } C_{S_p}(\mathbf{r}, \omega) = 0$$
 (21)

In all other cases, circular input polarization is not optimal, and eqs 14 and 15 provide room for enhancement.

**Region of Interest (ROI).** For practical purposes, one is often interested in enhanced optical chirality over a finite volume of space, rather than just at an isolated point. In particular, this is relevant for potential experiments in chiral sensing or chiral spectroscopy where, for example, chiral interactions between molecules and light play a key role for the measured signal. In CD-like measurements with pairs of electromagnetic field distributions with opposite handedness, an enhanced local optical chirality throughout the sample volume of the investigated molecules would lead to an enhanced difference in absorption. Therefore, we also define and investigate the averaged normalized optical chirality  $\overline{C}(\omega)$ of a certain region of interest (ROI) by integrating the normalized local optical chirality over the complete ROI and normalizing the result to the volume *V*:

$$\overline{C}(\omega) = \frac{1}{V} \int_{V} \hat{C}(\mathbf{r}, \, \omega) \mathrm{d}\mathbf{r}$$
(22)

Using the result for the normalized local optical chirality, we obtain

$$\overline{C}(\omega) = -\left(\widehat{I}_{1}(\omega)[\overline{C}_{S_{1}}(\omega) - \overline{C}_{S_{2}}(\omega)] + \overline{C}_{S_{2}}(\omega) + \sqrt{\widehat{I}_{1}(\omega) - \widehat{I}_{1}^{2}(\omega)} \{\overline{C}_{S_{p}}(\omega)\cos[\varphi(\omega)] + \overline{C}_{S_{m}}(\omega)\sin[\varphi(\omega)]\}\right)$$
(23)

by replacing in eq 13 the local parameters  $C_{S_j}(\mathbf{r}, \omega)$  with  $j = \{1, 2, p, m\}$  from eqs 8–11 with their ROI averages

$$\overline{C}_{S_j}(\omega) = \frac{1}{V} \int_V C_{S_j}(\mathbf{r}, \, \omega) \mathrm{d}\mathbf{r}$$
(24)

As a consequence, we obtain the optimal optical chirality within the ROI,  $\overline{C}_{opt}(\omega)$ , and the required far-field polarizations defined by  $\hat{I}_{1,opt}(\omega)$  and  $\varphi_{opt}(\omega)$  via eqs 14, 15, and 18 as well, using the averaged parameters  $\overline{C}_{S_j}(\omega)$  instead of the local ones  $C_{S_j}(\mathbf{r}, \omega)$ . Note that the optimal results do not depend explicitly on  $\mathbf{r}$  any more because of the volume integration, but an implicit dependence on the spatial location is retained via the choice of the ROI.

## NUMERICAL ILLUSTRATION

Calculation Technique. Now we illustrate the fundamental result from the previous section numerically using two specific nanostructure assemblies. We will optimize the local optical chirality by tuning the far-field polarization of the external light that propagates in positive z direction along its normalized wave vector  $\mathbf{e}_k$  either as a monochromatic plane wave with frequency  $\omega$  or as a superposition of monochromatic plane waves, that is, a laser pulse with a defined spectral bandwidth. In the latter case the following optimization procedure is carried out for each frequency component separately. The two orthogonal far-field polarization components 1 and 2 of the external light are parallel to the x axis along the unit vector  $\mathbf{e}_1$ and parallel to the y axis along  $\mathbf{e}_{2}$ , respectively. The corresponding far-field polarization state for a given total intensity  $I(\omega)$  is then defined by the normalized intensity  $\hat{I}_1(\omega)$ and the relative phase between the two components  $\varphi(\omega)$ . In the first step, the local response functions  $S^{e}_{\alpha}(\mathbf{r}, \omega)$  and  $S^{h}_{\alpha}(\mathbf{r}, \omega)$ , with  $\alpha = \{1, 2\}$ , are determined for both far-field polarization components. This is done for each component separately by means of multiple elastic scattering of multipole expansions (MESME), introduced by García de Abajo.<sup>63</sup> First, the local electric and magnetic fields  $\mathbf{E}_{loc}(\mathbf{r}, \omega)$  and  $\mathbf{H}_{loc}(\mathbf{r}, \omega)$ are simulated for external light with a linear polarization along the x axis and field amplitude of unity, that is,  $E_1^{\text{ext}}(\omega) =$  $E_x^{\text{ext}}(\omega) = 1$  and  $E_2^{\text{ext}}(\omega) = E_y^{\text{ext}}(\omega) = 0$ . The resulting local electric field is then identified as response function  $S_1^e(\mathbf{r}, \omega)$  and the local magnetic field as  $\frac{1}{\mu_{o^c}}\mathbf{S}_1^h(\mathbf{r},\omega)$ . After that, the simulations are repeated for external light under the same



**Figure 3.** (a) Schematic of first structure for optical chirality control, where different cubic regions of interest (ROIs, blue boxes, 20 nm edge length) are investigated in the vicinity of a gold sphere with a radius of 50 nm. The external light propagates in positive *z* direction along its normalized wave vector  $\mathbf{e}_k$  (green arrow). Its two orthogonal far-field polarization components 1 and 2 are parallel to the *x* axis along unit vector  $\mathbf{e}_1$  and to the *y* axis along  $\mathbf{e}_2$ , respectively (red arrows). The ROI positions are scanned in steps of 10 nm along the *y* axis (pathway I) as well as along the *z* axis (pathway II). (b) Normalized optical chirality values  $C_{max}$  (blue circles),  $\overline{C}_{min}$  (red squares),  $\overline{C}_{LCPL}$  (pink crosses), and  $C_{RCPL}$  (green triangles) as a function of the ROI center position at the resonance frequency  $\omega_R = 3.65$  rad/fs of the sphere. (c) Far-field polarization for maximum (blue) and minimum optical chirality (red) defined by the normalized intensities  $\hat{I}_{1,max}$  and  $\hat{I}_{1,min}$  (dashed lines) as well as the relative phases  $\varphi_{max}$  and  $\varphi_{min}$  (solid lines with circles, squares) as a function of the ROI center position. For all ROIs, both  $\hat{I}_{1,max}$  and  $\hat{I}_{1,min}$  remain constant at 1/2.

illumination conditions, but with linear polarization along the *y* axis, that is,  $E_1^{\text{ext}}(\omega) = 0$  and  $E_2^{\text{ext}}(\omega) = 1$ , to obtain the response functions  $\mathbf{S}_2^e(\mathbf{r}, \omega)$  and  $\mathbf{S}_2^h(\mathbf{r}, \omega)$ . For any given ROI, we then calculate parameters  $\overline{C}_{S_1}(\omega)$ ,  $\overline{C}_{S_p}(\omega)$ ,  $\overline{C}_{S_m}(\omega)$ , and  $\overline{C}_{S_2}(\omega)$  from eqs 8–11 and 24 in order to finally obtain  $\overline{C}_{\text{opt}}(\omega)$  via eq 18 as well as  $\hat{I}_{1,\text{opt}}(\omega)$  and  $\varphi_{\text{opt}}(\omega)$  via eqs 14 and 15, respectively. Considering the averaged quantities also reduces the risk of artifacts resulting from numerical inaccuracies at singular points in the local fields for single positions  $\mathbf{r}$ .

Single Gold Sphere. The first investigated nanostructure is a single gold sphere in vacuum with a radius of 50 nm located at the origin of the coordinate system (Figure 3a). The electric and magnetic response functions of far-field polarization components 1 and 2 are calculated for the resonance frequency of the sphere,  $\omega_{\rm R}$  = 3.65 rad/fs, as described above. The optimization of optical chirality is performed for several cubic ROIs (edge length of 20 nm) that differ only in their positions with respect to the gold sphere. The center of the first ROI is located at (0, 0, 70) nm. From there, the positions of subsequent ROIs are obtained by shifting the cube in steps of 10 nm in positive y direction, until its center is at (0, 70, 70) nm. This scan of the ROI position is called pathway I in the following and indicated by the symbol "I" in Figure 3a. After that, the scan is continued by shifting the cube from (0, 70, 70) nm in steps of 10 nm in negative z direction to the position at (0, 70, 0) nm (pathway II indicated by "II" in Figure 3a). The results for  $\overline{C}_{opt}$  as well as  $\overline{C}_{LCPL}$  and  $\overline{C}_{RCPL}$  are shown in Figure 3b as a function of the ROI center position and the optimal far-field polarization parameters  $I_{1,\mathrm{opt}}$  and  $\varphi_{\mathrm{opt}}$ are depicted in Figure 3c. For the first ROI with its center at (0, 0, 70) nm, the far-field polarizations for  $\overline{C}_{max}$  and  $\overline{C}_{min}$  are equal to LCPL and RCPL, respectively, with  $\hat{I}_{1,\max}(\omega) = 1/2$ and  $\varphi_{\max}(\omega) = \pi/2$  as well as  $\hat{I}_{1,\min}(\omega) = 1/2$  and  $\varphi_{\min}(\omega) =$  $-\pi/2$ . This can be explained by the symmetry of the nanostructure with respect to  $\mathbf{e}_k$  as well as by the position and the symmetry properties of the ROI. We show in section S.5 of Supporting Information that, in general, for a  $C_{4\nu}$ 

symmetric nanostructure with the principal axis parallel to  $\mathbf{e}_k$ the parameters  $\overline{C}_{S,i}$ ,  $\overline{C}_{S,i}$ , and  $\overline{C}_{S_n}$  of a ROI are simultaneously zero if the shape of the ROI is also  $C_{4\nu}$  symmetric with identical principal axis and mirror-symmetry planes. Thus, the condition for CPL as optimal far-field polarization defined in eq 20 is fulfilled at this ROI position. In contrast to the first ROI, the subsequent ROIs along pathways I and II do not share their principle axis with the nanostructure. Nevertheless, they still have mirror symmetry with the yz plane, that is, the mirrorsymmetry plane of the nanostructure parallel to  $\mathbf{e}_2$  and  $\mathbf{e}_k$ . This also leads to vanishing parameters  $\overline{C}_{S_1}$  and  $\overline{C}_{S_2}$ , but parameter  $\overline{C}_{S_n}$  is nonzero and thus the optimal far-field polarizations for these ROIs are different from CPL (see Supporting Information, section S.5). Note that  $\overline{C}_{S_1}$  and  $\overline{C}_{S_2}$  would also vanish if the ROIs had mirror symmetry with respect to the xzplane, that is, the mirror-symmetry plane of the nanostructure parallel to  $\mathbf{e}_1$  and  $\mathbf{e}_k$ . In the case of  $\overline{C}_{S_1} = \overline{C}_{S_2} = 0$ ,  $\overline{C}_{max}$  and  $\overline{C}_{min}$ as well as  $\overline{C}_{LCPL}$  and  $\overline{C}_{RCPL}$  differ only in their sign according to eqs 18 and 19. Therefore, it is sufficient to discuss the relation between  $\overline{C}_{max}$  and  $\overline{C}_{LCPL}$  for all ROIs along both pathways.

We observe that, for the first ROI,  $\overline{C}_{max}$  is lower than +1, the normalized optical chirality value for LCPL in free space  $\hat{C}_{\underline{LCPL}}^{\text{free}}.$ For the subsequent ROIs along pathway I, the values for  $\overline{C}_{max}$ rise up from 0.32 to 0.94, but the difference  $(\overline{C}_{max} - \overline{C}_{LCPL})$ increases only up to about  $10^{-3}$  and the optimal far-field polarization is only slightly different from LCPL. For the ROIs along pathway II, however, a further rise of  $\overline{C}_{max}$  up to 1.5 is observed, significantly larger than  $\hat{C}_{LCPL}^{free}$ . Simultaneously, this value also exceeds  $\overline{C}_{LCPL}$  by 0.3, indicating that optical chirality can be increased significantly with respect to circular input polarization. Along pathways I and II, the optimal far-field polarization changes from LCPL to more and more elliptically polarized light. This is achieved by a variation of the relative phase  $\varphi_{\text{max}}$ , whereas the intensity  $\hat{I}_{1,\text{max}}$  remains constant at 1/2. This can be explained by considering eq 14: Due to the vanishing parameters  $\overline{C}_{S_1}$  and  $\overline{C}_{S_2}$ , the intensity  $\hat{I}_{1,\max}$  has to be



Figure 4. (a) Schematic of second structure for optical chirality control: 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 the 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) is a cube with an edge length of 48 nm and located between two spheres of the lower L shape. (b) Normalized optical chirality values  $\overline{C}_{max}$  (blue circles),  $\overline{C}_{min}$  (red squares),  $\overline{C}_{LCPL}$  (pink crosses), and  $\overline{C}_{RCPL}$  (green triangles) as a function of the angular frequency  $\omega$ . The black dashed lines show the values for  $\widehat{C}_{CPL}^{free} = \pm 1$ . (c) Far-field polarization for maximum (blue) and minimum (red) optical chirality defined by the normalized intensities  $\widehat{I}_{1,max}$  and  $\widehat{I}_{1,min}$  (dashed lines) as well as the relative phases  $\varphi_{max}$  and  $\varphi_{min}$  (solid lines with circles, squares) as a function of  $\omega$ . (d, e) Examples for polarization-shaped laser pulses in the time domain leading to  $C_{max}$  (d) and  $\overline{C}_{min}$  (e) within the ROI. The temporal polarization states are shown in quasi-three-dimensional representations as cylinders with corresponding orientations and ellipticities. 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.

1/2 for each ROI. Note that the intensity  $\hat{I}_{1,\min}$  is constant at 1/2 for the same reason. In contrast to the parameters  $\overline{C}_{S_1}$  and  $\overline{C}_{S_2}$  parameters  $\overline{C}_{S_p}$  and  $\overline{C}_{S_m}$  vary along pathways I and II such that the relative phase  $\varphi_{\max}$  decreases from  $\pi/2$  to about  $0.3\pi$ . According to eq 17, the relative phase  $\varphi_{\min}$  shows the same behavior as  $\varphi_{\max}$  with a constant phase offset of  $\pi$ .

Chiral Nanostructure Assembly. In the preceding section, we have demonstrated the optical chirality enhancement for a single frequency. In general, the far-field polarizations required for optimum local optical chirality can vary for different frequencies. This variation is especially strong in more complex nanostructure assemblies with several resonance frequencies and reduced symmetry. We illustrate this effect on a nanostructure consisting of six single gold spheres with a radius of 70 nm each, arranged in the configuration shown in Figure 4a. The structure is composed of two L shapes, each of which contains three gold spheres within the same xy plane at z = +80 nm for the upper and z =-80 nm for the lower L shape, respectively. The gap between the neighboring spheres is 20 nm in x, y, and z direction such that the near fields of the single spheres are coupled. The upper L shape is directly above the lower L shape and rotated by  $\pi/2$ with respect to the z axis. Thus, the nanostructure is lefthanded with respect to  $\mathbf{e}_{i}$ . Note that, from a geometrical point of view, the structure is achiral itself, but it can be classified as chiral under the given illumination geometry. The response functions of the nanostructure are determined in the same way as for the single sphere, but now calculated for 16 equidistant frequencies  $\omega$  in a range of 2.28 to 3.80 rad/fs. We choose a cubic ROI (edge length 48 nm) whose center is located at (x =-80, y = 0, z = -80) nm, that is, exactly between the centers of two spheres of the lower L shape (blue box in Figure 4a). Points of the ROI that are positioned within the spheres or on

their surfaces are omitted in the calculations of the averaged optical chirality.

The resulting chirality values  $\overline{C}_{max}$  and  $\overline{C}_{min}$  as well as  $\overline{C}_{LCPL}$ and  $\overline{C}_{\text{RCPL}}$  are shown in Figure 4b. The maximum optical chirality  $\overline{C}_{max}$  rises up to more than a factor of 4 for low frequencies, then drops down at about 2.8 rad/fs and increases again, followed by a decay at higher frequencies. Compared to the chirality values obtained for CPL, the values for  $C_{\text{max}}$  are slightly higher in the low-frequency range and significantly enhanced in the high-frequency range. Moreover,  $\overline{C}_{max}$  exceeds +1, the chirality value of  $\hat{C}_{LCPL}^{free}$  for every frequency component. In contrast to this,  $\overline{C}_{LCPL}$  as well as  $\overline{C}_{RCPL}$  are well below +1 in the high-frequency range. Hence, for this spectral range the optical chirality in the chosen ROI is enhanced with respect to free space by using the optimal far-field polarization, whereas for CPL, it would be considerably reduced to values < +1. It is noteworthy that both  $\overline{C}_{LCPL}$  and  $\overline{C}_{RCPL}$  change their sign for higher frequencies. If chiral molecules were located in the ROI, chiroptical effects arising from the light-matter interaction, for example, handedness-dependent absorption, would also have opposite sign for high and low frequencies. As opposed to this, the optimal chirality values lead to either positive or negative C values throughout all frequencies and, thus, a mutually opposite behavior of the chiroptical effects would be prevented. Compared to  $\overline{C}_{max}$  the values for  $\overline{C}_{min}$  are similar, but have the opposite sign. However, since  $\overline{C}_{S_1} \neq 0$  and  $\overline{C}_{S_2} \neq 0$ , as well as  $\overline{C}_{S_1} \neq -\overline{C}_{S_2}$ , the magnitudes of  $\overline{C}_{max}$  and  $\overline{C}_{min}$  are slightly different according to eq 18. For the same reason,  $|\overline{C}_{LCPL}| \neq$  $\overline{|C_{\text{RCPL}}|}$  according to eq 19. This results from the reduced symmetry of the nanostructure. Since there is no plane of mirror symmetry parallel to  $\mathbf{e}_{k}$ , the response functions of farfield polarization components 1 and 2 cannot be expressed by



Figure 5. Snapshots of the movies from Supporting Information showing the temporal evolution of electric (blue) and magnetic (red) fields obtained for different far-field polarizations. The little spheres indicate the tips of the momentary field vectors and the solid lines their temporal traces. (a) Electric and magnetic field of LCPL in free space without a nanostructure at position (0, 0, 0) nm and  $\omega = 2.89$  rad/fs (see SI, movie "Free LCPL"). (b) Temporal near fields at position (6, 78, 66) nm in the vicinity of the chiral nanostructure assembly for  $\omega = 2.89$  rad/fs and LCPL as input polarization. The electric and magnetic field components parallel to the *x* axis oscillate nearly in phase (see SI, movie "LCPL"). (c) Temporal near fields at the same position and frequency as in (b) obtained for the optimal far-field polarization leading to  $\hat{C}_{max}$ . The phases of the electric and magnetic field to the *x* axis are shifted by roughly  $\pi/2$  (see SI, movie "C max"). (d) Temporal near fields at the same position with the optimal far-field pulse leading to  $\hat{C}_{max}$  for the frequency range from 2.28 to 3.80 rad/fs (see SI, movie "Pulse C max").

each other and, thus, the parameters  $\overline{C}_{S_1}$  and  $\overline{C}_{S_2}$  are not related as they were for the single sphere.

The optimal far-field polarizations are depicted in Figure 4c as a function of frequency. It is obvious that the far-field polarization for  $\overline{C}_{max}$  depends on  $\omega$  and is different from circularly polarized light. Both, the normalized intensity  $\hat{I}_{1,\max}$ and the relative phase  $\varphi_{\max}$  vary for different frequencies. In the low-frequency range, the external polarization is elliptical with intensities slightly larger than 1/2 and relative phases near  $\pi/2$ , that is, close to LCPL. On the other hand, due to a strong decrease of the relative phase by roughly  $\pi/2$  within the frequency region at about 2.8 rad/fs, the values of  $\varphi_{\rm max}$  are near zero in the high-frequency range and, therefore, close to the relative phase of linear polarization. The behavior of  $\hat{I}_{1,\min}$  is symmetric to  $\hat{I}_{1,\text{max}}$  with respect to  $\hat{I}_1 = 1/2$  (compare eq 16) and the behavior of  $arphi_{\min}$  connected to that of  $arphi_{\max}$  by a phase offset of  $\pi$  (compare eq 17). Thus, the present example illustrates that for optimum local optical chirality far-field polarizations different from circular and linear are required.

If we want to fulfill the optimal chirality condition simultaneously for all frequencies, this requires tuning of the external polarization state independently throughout the optical spectrum. Such a technique is available via femtosecond laser polarization pulse shaping that we developed first for two independent degrees of freedom (the spectral phases of the two transverse polarization components).<sup>64–67</sup> Recently, it has become possible to manipulate all four external degrees of freedom (amplitude and phase for both polarization components separately).<sup>68–73<sup>1</sup></sup> The latter technique is also called vector-field pulse shaping. The temporal electric fields of the two pulses that lead to maximum and minimum optical chirality are shown in Figure 4d and e, respectively. Here we assumed a Gaussian spectrum with center frequency  $\omega_0$  = 2.99 rad/fs and a bandwidth-limited pulse duration of 10 fs. Since the absolute phases  $\varphi_1$  and  $\varphi_2$  of the far-field polarization components are not determined by eqs 14 and 15, one of these can be chosen arbitrarily. This means that for the polarizationshaping only three degrees of freedom,  $I_1(\omega)$ ,  $I_2(\omega)$ , and either  $\varphi_1(\omega)$  or  $\varphi_2(\omega)$ , are necessary to optimize the local optical chirality. The additional fourth degree of freedom,  $\varphi_1(\omega)$  or  $\varphi_2(\omega)$ , can be used, for example, for the manipulation of the temporal evolution of the local near fields, for the generation of spectroscopic pulse sequences or for pulse compression.<sup>62</sup> For

the depicted pulses  $\varphi_1(\omega)$  is set to zero and, thus,  $\varphi(\omega) = \varphi_2(\omega)$ . Both the pulse for  $\overline{C}_{max}$  and the one for  $\overline{C}_{min}$  are clearly different from circular and linear polarization and vary with time.

We repeated the calculation of optical chirality enhancement for a second ROI of identical size located directly between the centers of two spheres of the upper L shape (Supporting Information, section S.6). At this ROI position, a similarly successful optimization with increased values for the local optical chirality compared to  $\overline{C}_{CPL}$  and  $\widehat{C}_{CPL}^{free}$  was observed. Since the properties of the response functions within the ROI were different from those within the first ROI, the frequencydependent optimal far-field polarizations and, thus, the optimal polarization-shaped laser pulses differed significantly as well.

## ELECTRIC AND MAGNETIC NEAR-FIELD EVOLUTION

In the previous sections, we demonstrated that the local optical chirality in the vicinity of plasmonic nanostructures can be enhanced by far-field polarizations different from CPL. Now we illustrate the control mechanism. In general, considering eq 2, the local optical chirality is maximal (minimal) if the scalar product of  $\mathbf{E}_{loc}^*$  and  $\mathbf{H}_{loc'}$  respectively, contains a minimal (maximal) imaginary part. This is the case if the amplitudes of the components  $\mathbf{E}_{loc,q}$  and  $\mathbf{H}_{loc,q}$  with  $q = \{x, y, z\}$  are maximal and the corresponding phases between the components are shifted by  $\pm \pi/2$ , due to the complex conjugation of the electric near field in eq 2. We now exemplify this general finding on the exemplary temporal field evolutions shown in Figure 5 (associated movies are found in Supporting Information).

For light in free space, circular polarization leads to extremal optical chirality. Figure 5a (see SI, Movie "Free LCPL") shows the temporal evolution of the electric (blue) and magnetic (red) field vectors at position (0, 0, 0) nm without any nanostructure for LCPL propagating along the *z* axis with  $\omega = 2.89$  rad/fs. The blue and the red little spheres denote the momentary tips of the field vectors with respect to the chosen position, and the blue and red solid lines illustrate the temporal traces. In addition, the projections onto the *xy*, *xz*, and *yz* planes facilitate the investigation of individual polarization components. The vectors of both fields are always perpendicular to each other as expected for a transverse wave and rotate around (0, 0, 0) nm on a circle in the *xy* plane. Since the

oscillations of the components  $\mathbf{E}_x$  and  $\mathbf{H}_x$ , as well as  $\mathbf{E}_y$  and  $\mathbf{H}_y$ , have a phase shift of  $\pi/2$  with respect to each other, maximal optical chirality is achieved. For any given intensity, circular polarization is thus optimal.

In the vicinity of plasmonic nanostructures, the situation is more complex, because the associated light modes do not constitute propagating transverse waves, and thus all three polarization components are available.<sup>74</sup> Increased optical chirality is possible via near-field enhancement of the amplitudes. For optimum chirality, however, one also has to fulfill the phase requirement. If circular far-field polarization is employed, near-field enhancement occurs, but the phases do not necessarily fulfill the optimal criterion. This is seen in Figure 5b (SI, movie "LCPL"), which shows the temporal nearfield evolution of the chiral nanostructure assembly at position (6, 78, 66) nm and  $\omega$  = 2.89 rad/fs obtained for LCPL as input polarization. The illumination geometry is identical to that in Figure 4a. The chosen position is located within the second ROI (Supporting Information, section S.6), that is, between two spheres of the upper L-shape. Let us focus on the field projection in the xy plane. The snapshot indicates a momentary maximal electric field (blue) along the x direction. At this instant, the magnetic field (red) also reaches its (albeit smaller) maximum amplitude along x. Thus, the two fields are in phase and the  $\pi/2$  optimality condition is not fulfilled. On the other hand, for optimal far-field excitation, the corresponding local fields shown in Figure 5c (see SI, movie "C max") behave differently. Now the snapshot reveals that while the electric field is maximal, the magnetic field passes through zero (along the *x* direction), indicating a  $\pi/2$  phase shift. Analogous analysis can be carried out for the other polarization directions, but it has to be kept in mind that the optimization reaches the global optimum as resulting from a sum (due to the scalar product) of three field-component multiplications. For the chosen position, the contributions to the local optical chirality of the local field components along the y and z directions are negligible for both LCPL and the optimal far-field polarization, because the amplitude of  $\mathbf{E}_{loc,y}$  is very small and the phase between  $\mathbf{E}_{loc,z}$  and  $H_{loc,z}$  is shifted by  $\pi$ . Thus, it may be most important to fulfill the phase condition for that component with the highest amplitude product.

Figure 5d shows the temporal electric and magnetic fields that are obtained for an optimal polarization-shaped laser pulse as input and lead to maximum local optical chirality values in the frequency range from 2.28 to 3.80 rad/fs at this position (see SI, movie "Pulse C max"). Since the optimal far-field polarizations differ with frequency and therefore consist of different elliptical polarization states in the frequency domain, the behavior in the time domain is much more complex after Fourier transformation. In particular, the orientation of the temporal ellipses strongly changes over time.

## OPTIMIZATION OF THE LOCAL DISSYMMETRY FACTOR

We have hitherto focused on the optimization of the local optical chirality  $C(\mathbf{r}, \omega)$  that is proportional to the absolute chirality-induced signal in a spectroscopy experiment, that is, *C* is responsible for the absolute signal difference between measurements of systems with opposite chirality according to eq 1. In some cases, one may be interested in the relative, rather than the absolute, signal difference, in which case one has to normalize the obtained signal difference with respect to the absolute (chirality-independent) absorption signal. The result-

ing quantity, often called dissymmetry factor g, is responsible for the signal contrast. Using CPL for excitation, the dissymmetry factor is given by<sup>10</sup>

$$g_{\rm CPL} = \frac{A_{\rm LCPL} - A_{\rm RCPL}}{\frac{1}{2}(A_{\rm LCPL} + A_{\rm RCPL})}$$
(25)

with the absorption of LCPL  $A_{\rm LCPL}$  and that of RCPL  $A_{\rm RCPL}$ . Tang and Cohen defined a generalized dissymmetry factor  $g_{\rm TC}$ , including pairs of arbitrary enantiomorphic electromagnetic fields, that is expressed via<sup>10,13</sup>

$$g_{\rm TC} = g_{\rm CPL} \frac{cC}{2U_{\ell}\omega} \tag{26}$$

wherein  $g_{CPL}$  is the dissymmetry factor from eq 25, that is, the dissymmetry factor obtained for CPL in free space. Considering eq 26, it is obvious that for an optimization of  $g_{TC}$ , the fraction  $C/U_e$  is important instead of the optimization of *C* alone such that  $|g_{TC}/g_{CPL}| > 1$ . Since an enhanced local optical chirality  $C(\mathbf{r}, \omega)$  is often accompanied by an increased electric field amplitude  $|\mathbf{E}_{loc}(\mathbf{r}, \omega)|$ , the corresponding local electric energy density

$$U_{e}(\mathbf{r},\,\omega) = \frac{\epsilon_{0}}{4} \left| \mathbf{E}_{\rm loc}(\mathbf{r},\,\omega) \right|^{2}$$
(27)

is enhanced mostly as well. Thus, the optimal far-field polarization for  $C(\mathbf{r}, \omega)$  does usually not coincide with that for  $g_{TC}(\mathbf{r}, \omega)$ . Nevertheless, analogously to the optimization of  $C(\mathbf{r}, \omega)$ , it should be possible to optimize the local normalized dissymmetry factor  $\hat{g}_{TC}(\mathbf{r}, \omega) = g_{TC}(\mathbf{r}, \omega)/g_{CPL}$  by means of the far-field polarization. One has to consider in this case, however, that increasing  $\hat{g}_{TC}$  can be carried out by significantly decreasing  $U_{\rm e}$  such that in effect the overall absorption is strongly reduced and small signals result. For practical reasons, therefore, one has to decide carefully whether the absolute or the relative signal is the relevant quantity. Hence, for applications of molecular chiral sensing or spectroscopy, one should analyze in addition signal-to-noise ratios to find "optimal" external driving fields, and very likely one should be interested in the right balance between absolute chiral signal strength, that is, optimization of C, and contrast, that is, optimization of  $\hat{g}_{TC}$ .

It has to be mentioned that in eq 26 the magnetic energy density  $U_b$  is neglected. A more precise equation was introduced by Choi and Cho via<sup>11</sup>

$$g_{\rm CC} = g_{\rm CPL} \frac{cC}{2\omega(U_e + \gamma U_b)}$$
(28)

wherein the parameter  $\gamma \propto \chi''/\alpha''$  depends on the investigated specimen and is typically in the range  $\approx 10^{-6}$  to  $10^{-4}$ .<sup>11</sup> Hence, eq 26 is only valid in the case that  $U_e \gg \gamma U_b$  or, independently from the specimen,  $U_e \gg 10^{-2}U_b$ . This leads to a limitation of the maximal/minimal value of the generalized dissymmetry factor and should be taken into account in an analytic derivation for the optimization of  $\hat{g}_{\rm TC}$ .

In this section, the definitions of the dissymmetry factor consider only the electric and magnetic dipole response of the chiral medium. However, if the electromagnetic fields vary strongly across chiral molecules located in the vicinity of a nanostructure, it might be necessary to include higher multipoles for the calculation of g.<sup>75</sup> Nevertheless, an optimization of the chiral response in the near field of

nanostructures via tuning the far-field polarization should be possible.

## SUMMARY AND OUTLOOK

In this work, we investigated theoretically the control of local optical chirality enhancement in the near field of plasmonic nanostructures by tuning the far-field polarization of the external light field. We derived an analytic expression for the optimal far-field polarization and demonstrated on the basis of numerical simulations for two specific nanostructure assemblies that the local optical chirality can be improved significantly in comparison with the optical chirality of circularly polarized light in free space. Optimal enhancement is achieved by using farfield polarizations different from linear or circular. The handedness of local optical chirality can be switched by switching the optimal far-field polarization, and local optical chirality can be coherently controlled over a continuous frequency range by means of femtosecond polarization pulse shaping. We showed that the symmetry properties of nanostructures can be exploited to determine the optimal farfield polarization. For a nanostructure that is at least  $C_{4\nu}$ symmetric with respect to the propagation direction of the external light, circularly polarized light is the optimal far-field polarization to enhance optical chirality in near-field regions whose shapes are  $C_{4\nu}$  symmetric, as well, with the same principle axis and mirror-symmetry planes like those of the nanostructure.

In conclusion, tuning the far-field polarization can be used to control local optical chirality for any given nanostructure geometry. This should enable enhanced chirally specific interactions of light with molecular and other quantum systems in the vicinity of specially designed nanostructures. Applications are envisioned in chiral sensing of adsorbed molecules, timeresolved chirality-sensitive spectroscopy, and chiral quantum control. For the latter two cases it is of relevance that the time structure of the optimal field can still be varied by means of the spectral phase of one polarization component, while nevertheless retaining the optimality conditions derived above that depend on the relative phase only.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.6b00887.

Calculation of optical chirality of circularly polarized light (CPL) in free space; Determination of optimal far-field polarizations; Relation between far-field polarizations for maximum and minimum local optical chirality; Relation between optimal far-field polarizations with respect to ellipticity and orientation; Consequences of symmetry; Second ROI in the vicinity of chiral nanostructure assembly (PDF).

Movie "Free LCPL" (AVI). Movie "LCPL" (AVI). Movie "C max" (AVI). Movie "Pulse C max" (AVI).

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## Notes

The authors declare no competing financial interest.

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