Supporting Information

Detecting Antibody-Antigen Interactions with Chiral Plasmons: Factors Influencing Chiral Plasmonic Sensing.

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Smoothing of Gammadion Model Edges

Figure S1 displays a comparison of the CD spectra for two similar gammadia models. The smoothing (filleting) of the top edges of the gammadia, which can be seen to reduce the sharpness of the peak \(\sim 610\) nm in the simulated spectra of the main text. A comparison of the gammadia is also displayed with the upper version being that which was used in the main text.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figureS1.png}
\caption{Simulated CD spectra (left) for LH (solid) and RH (dashed) for two gammadia models: one in which the top face edges (bottom right) are not smoothed (black), and the other (top right) in which all outer edges are smoothed (red).}
\end{figure}
**Heterogeneous Broadening**

Smoothing of the simulated CD spectra using adjacent averaging within a 20 point window produces spectra which are in greater agreement with those obtained experimentally. The sharp peaks ca 610nm are less pronounced.

![Simulated CD Spectra](image)

**Figure S2**: Simulated CD spectra for the LH (red) and RH (blue) achiral gammapidae before smoothing (dashed) and when smoothed (solid) via the adjacent averaging method.
Periodic and Non-Periodic Simulations

The simulated transmissions of RCP and LCP light for LH and RH structures modelling a single gammadion and a periodic array of gammadia are shown in Figure S3. Figure S4 displays a comparison of the resultant CD spectra for the single and periodic simulations. The electric field and optical chirality plots for the single gammadion simulations are shown in Figures S5 and S6, respectively.

![Figure S3: Simulated RCP (red) and LCP (black) transmission for single (left column) and periodic (right column) gammadia.](image)

![Figure S4: Simulated CD spectra for LH (solid) and RH (dashed) single gammadia (black) and periodic gammadia (red)](image)
Figure S5: Electric field plots for all modes of the single gammadion simulation.

Figure S6: Optical chirality plots for all modes of the single gammadion simulation.
Irreducible Representation

The derivation of the irreducible representation for a gammadion structure is shown in Figure S7.

Figure S7: (A) A RH gammadion displayed as a basis set of vectors. (B) The resultant reducible and irreducible representations derived from the basis set of vectors.

|     | $C_4$ | $C_4$ | $(C_4)^3$ |
|-----|-------|-------|-----------|
| E   | 0     | 0     | 0         |

Reducible Representation

Irreducible Representation

$2A + 2B + 2E$
Asymmetries ($\Delta\Delta\lambda$) of Achiral Solutions

The asymmetries obtained from CD spectra of LH and RH gammadia in achiral solutions are displayed in figure S8. As expected for an achiral dielectric ($\xi = 0$) the $\Delta\Delta\lambda$ values are all 0 within experimental error. Acetate buffer (0.1M, pH 4.2) was prepared using sodium acetate ($C_2H_3NaO_2$) and acetic acid ($C_2H_4O_2$).

Figure S8: Asymmetry values obtained for gammadia placed in acetate buffer (top panel) and PBS buffer (bottom panel) with reference to water. Modes I (unseen), II (green) and III (blue), as described in the main text, are displayed.
Numerical Modelling of Chiral Dielectric (protein) Layers

The electromagnetic simulations were performed using the COMSOL Multiphysics software (v5.4) with the Wave Optics module. COMSOL uses the finite element method to solve Maxwell’s equations over a specified geometry for incident circularly polarised light, with the transmission being measured at a surface below the structure. Periodic boundary conditions at the vertical boundaries were used, creating an infinite array of structures to approximate the periodicity of the nanostructure array. We used values of Au permittivity from Johnson et al.

The chiral dielectric is realised using the constituent equations for a chiral dielectric medium:

\[ \mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E} + i \xi \mathbf{B} \]  \hspace{1cm} (S1)

\[ \mathbf{H} = \frac{\mathbf{B}}{\mu_0 \mu_r} + i \xi^T \mathbf{E} \]  \hspace{1cm} (S2)

Here, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) is the relative permittivity, \( \mu_0 \) is the permeability of free space, \( \mu_r \) is the relative permeability, \( \mathbf{E} \) is the complex electric field, \( \mathbf{B} \) is the complex magnetic flux density, \( \mathbf{H} \) is the magnetic field, \( \mathbf{D} \) is the electric displacement field and \( \xi \) is a second rank tensor describing the chiral property of a molecular layer. \( \xi \), the chirality tensor, is only non-zero for a chiral dielectric. The sign of tensor elements \( \xi_{ij} \) (\( i, j = x, y \) & \( z \)) is defined by the handedness of the chiral dielectric.

To model the specific and non-specific binding of proteins in experiment, the gammadia geometries in COMSOL had additional 20nm layers added to their outer surfaces in the \( x, y \) and \( z \) axes. Each of these extended domains could be assigned their own refractive index. These domains were made chiral by altering the constitutive equations, with \( \xi = 5 \times 10^{-4} \). Non-specific binding was modelled with an isotropic refractive index of 1.4 for the chiral dielectric regions. For specific binding, the chiral dielectric was given a birefringence of 1.3/1.6. The axial component of the refractive index tensor in the direction of the surface normal of the protein domain was given the larger value of 1.6:

\[ n_{x \text{domain}} = \begin{bmatrix} 1.6 & 0 & 0 \\ 0 & 1.3 & 0 \\ 0 & 0 & 1.3 \end{bmatrix} \]  \hspace{1cm} (S3)

\[ n_{y \text{domain}} = \begin{bmatrix} 1.3 & 0 & 0 \\ 0 & 1.6 & 0 \\ 0 & 0 & 1.3 \end{bmatrix} \]  \hspace{1cm} (S4)

\[ n_{z \text{domain}} = \begin{bmatrix} 1.3 & 0 & 0 \\ 0 & 1.3 & 0 \\ 0 & 0 & 1.6 \end{bmatrix} \]  \hspace{1cm} (S5)
CD Spectra

Figures S9-S11 compares CD spectra of individual modes (I, II and III respectively) of the specific binding of streptavidin (biotin-streptavidin) in experiment and the isotropic and birefringent simulations.

**Figure S9:** A comparison of experimental (top panel), isotropic (middle panel) and birefringent (bottom panel) LH (solid) and RH (dashed) CD spectra for mode I. Biotin/achiral reference spectra (blue) are shown against the streptavidin/chiral spectra (black). Modes are labelled with LH (solid) and RH(dashed) lines to aid the eye.
Figure S10: A comparison of experimental (top panel), isotropic (middle panel) and birefringent (bottom panel) LH (solid) and RH (dashed) CD spectra for mode I. Biotin/achiral reference spectra (blue) are shown against the streptavidin/chiral spectra (black). Modes are labelled with LH (solid) and RH (dashed) lines to aid the eye.
Figure S11: A comparison of experimental (top panel), isotropic (middle panel) and birefringent (bottom panel) LH (solid) and RH (dashed) CD spectra for mode I. Biotin/achiral reference spectra (blue) are shown against the streptavidin/chiral spectra (black). Modes are labelled with LH (solid) and RH(dashed) lines to aid the eye.
Average Spectral Shifts from Experiment

Figure S12 displays the averaged shifts measured for each mode at subsequent additions of biomolecule.

Figure S12: A comparison of the average shifts from LH and RH CD spectra for the isotropic and birefringent experiments. Mode I (red), mode II (green) and mode III (blue).
Electromagnetic Field and Optical Chirality Plots

Field plots were taken in the xy plane from the middle point (z=50nm) of the gammadia. Figures S13 and S14 display the electric field and optical chirality plots for modes I, II and III for both isotropic and birefringent simulations, respectively.

Figure S13 Electric field and optical chirality plots of all modes for the isotropic simulations.
The field values quoted in Table 1 of the main text were calculated directly from the plots of mode II. Four equivalent regions between each of the arms had their field and \( C \) intensities averaged (as shown in the main text).
Influence of Structural irregularities of modes

We investigated the influence of surface irregularities, which would be possessed by a real nanostructure, on the simulated behaviour of modes I, II and III, figure S15. The field maps derived from these simulations demonstrate that the presence of irregularities has a much more significant effect on mode II and the other modes. This supports the hypothesis that the presence of irregularities could be the origin of why experimentally asymmetries for mode II are larger than are predicted by the perfect model.

Figure S15: Z-component of the electric field for modes I, II and III in a plane 50 nm above the quartz substrate