Supplementary Information

Chiral Plasmonic Fields Probe Structural Order of Biointerfaces

Christopher Kelly, Ryan Tullius,1 Adrian J. Lapthorn,1 Nikolaj Gadegaard,2 Graeme Cooke,1 Laurence D. Barron,1 Affar S. Karimullah*, 1,2 Vincent M. Rotello*,3 Malcolm Kadodwala*.1

1School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ, UK.

2School of Engineering, Rankine Building, University of Glasgow, Glasgow, G12 8LT, UK.

3Department of Chemistry, 710 Nt. Pleasant Street, University of Massachusetts Amherst, MA 01003, USA.

1.1 Asymmetry (ΔΔS) for salt solution

The asymmetry parameter, ΔΔS, Figure S1 is obtained for a series of salt solution with different refractive index is plotted. As expected for an achiral solution the ΔΔS values are all zero, within the precision of our measurements.

Figure S1. The ΔΔS values (relative to distilled water) for salt (NaCl) solutions of a range of refractive index.
1.2 Asymmetry (ΔΔλ) IgG

ORD spectra collected LH (red) and RH (blue) immersed in buffer (solid) and IgG (1.5×10^{-6} mgml^{-1}) (dashed) are shown in Figure S2.

![Figure S2](image)

**Figure S2.** ORD spectra collected from LH (red) and RH (Blue) TPS immersed in buffer (solid) and 1.5×10^{-5} mgml^{-1} of IgG (dashed)

Plots of ΔΔλ = Δλ_{RH} - Δλ_{LH} derived from peak 1 and 2 versus IgG concentration are plotted in Figure S3.

![Figure S3](image)

**Figure S3.** Plot of ΔΔλ versus IgG conc. Derived from peaks 1 and 2.
2.1 EM Simulations

The electromagnetic simulations were performed using the COMSOL Multiphysics software (v4.4) with the Wave Optics module. COMSOL uses the finite element method to solve Maxwell’s equations over a specified geometry for linearly polarized input light, with the reflection being measured at a surface above 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 [1]. The values for refractive index of polycarbonate were taken from Sultanova et al [2]. \( \mu_r = 1 \) for all the materials.

The chiral dielectric is realised using the constituent equations for a chiral dielectric medium [3]:

\[
D = \varepsilon_o \varepsilon_r E + i\xi B \tag{S1}
\]

\[
H = B/\mu_0\mu_r + i\xi^T E \tag{S2}
\]

Here, \( \varepsilon_o \) 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, \( E \) is the complex electric field, \( B \) is the complex magnetic flux density, \( H \) is the magnetic field, \( D \) 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. In addition, a refractive index of 1.4 is used in the chiral dielectric regions. To implement the constituent equations in COMSOL, a secondary set of electromagnetic equations was included and used solely in the chiral dielectric regions. Certain equations were altered in the equation view of the physics setup.

For the isotropic chiral dielectric, the electric displacement \( D \), magnetic field strength \( H \) and the time-varying derivative of the magnetic field \( dH/dt \) were changed to those given in equations S3-S5. Only the equations for the x components are shown. Similar changes have to be made for the y and z, using the corresponding \( \xi_{yy} \) and \( \xi_{zz} \) chirality tensor components.
\[\text{ewfd.} D_x = \epsilon_{\text{const}} * (\text{ewfd.} \epsilon_{\text{xx}} * \text{ewfd.} E_x) + i * (\xi_{xx} * \text{ewfd.} B_x)\] (S3)

\[\text{ewfd.} H_x = (1/\mu_{\text{const}}) * (\text{ewfd.} \mu_{\text{xx}} * \text{ewfd.} B_x) + i * (\xi_{xx} * \text{ewfd.} E_x)\] (S4)

\[\text{ewfd.} D_t + (\text{ewfd.} \mu_{\text{xx}} * \text{ewfd.} B_t + \text{ewfd.} \mu_{\text{yy}} * \text{ewfd.} B_t + \text{ewfd.} \mu_{\text{zz}} * \text{ewfd.} B_t)/\mu_{\text{const}}) - (\text{ewfd.} \omega_{x} * \xi_{xx} * \text{ewfd.} E_x)\] (S5)

For the anisotropic chiral dielectric, the x and y component equations gain dependencies on other B-field and E-field components, as a result of the addition of the \(\xi_{xy}\) and \(\xi_{yx}\) terms. All of these equations are written out here (note that \(\xi_{xy} = \xi_{yx}\), hence only \(\xi_{xy}\) is shown for simplicity). The z equations are the same as in the isotropic case:

\[\text{ewfd.} D_x = \epsilon_{\text{const}} * (\text{ewfd.} \epsilon_{\text{xx}} * \text{ewfd.} E_x) + i * (\xi_{xx} * \text{ewfd.} B_x + \xi_{xy} * \text{ewfd.} B_y)\] (S6)

\[\text{ewfd.} D_y = \epsilon_{\text{const}} * (\text{ewfd.} \epsilon_{\text{yy}} * \text{ewfd.} E_y) + i * (\xi_{yy} * \text{ewfd.} B_y - \xi_{xy} * \text{ewfd.} B_x)\] (S7)

\[\text{ewfd.} H_x = (1/\mu_{\text{const}}) * (\text{ewfd.} \mu_{\text{xx}} * \text{ewfd.} B_x) + i * (\xi_{xx} * \text{ewfd.} E_x - \xi_{xy} * \text{ewfd.} E_y)\] (S8)

\[\text{ewfd.} H_y = (1/\mu_{\text{const}}) * (\text{ewfd.} \mu_{\text{yy}} * \text{ewfd.} B_y) + i * (\xi_{yy} * \text{ewfd.} E_y + \xi_{xy} * \text{ewfd.} E_x)\] (S9)

\[\text{ewfd.} dH/dt_x = ((\text{ewfd.} \mu_{\text{xx}} * \text{ewfd.} B_t + \text{ewfd.} \mu_{\text{yy}} * \text{ewfd.} B_t + \text{ewfd.} \mu_{\text{zz}} * \text{ewfd.} B_t)/\mu_{\text{const}}) - (\text{ewfd.} \omega_{x} * \xi_{xx} * \text{ewfd.} E_x) + (\text{ewfd.} \omega_{x} * \xi_{xy} * \text{ewfd.} E_y)\] (S10)

\[\text{ewfd.} dH/dt_y = ((\text{ewfd.} \mu_{\text{yy}} * \text{ewfd.} B_t + \text{ewfd.} \mu_{\text{yy}} * \text{ewfd.} B_t + \text{ewfd.} \mu_{\text{zz}} * \text{ewfd.} B_t)/\mu_{\text{const}}) - (\text{ewfd.} \omega_{x} * \xi_{yy} * \text{ewfd.} E_x) + (\text{ewfd.} \omega_{x} * \xi_{xy} * \text{ewfd.} E_y)\] (S11)
2.2 Chirality Plots from Simulation

The spatial distribution of optical chirality of the LH and RH structures for the isotropic and anisotropic chiral layers is shown in figure S4. Qualitatively the isotropic and anisotropic cases seem very similar, but the difference can be discerned by calculating the optical chirality at the maximum points (seen as the darkest areas on the chirality maps) which are noted in the figure.

![Figure S4](image)

**Figure S4.** Optical chirality maps for the matched and linear combinations at the left peak (~693nm), dip (~703nm) and right peak (~711nm).

2.3 Chirality Calculation of $\xi$

$\xi$ is a local parameter describing the chirality of a chiral dielectric, the sign of which defines the handedness of the chiral dielectric.[6] The value for molecular chiral dielectrics can be estimated using the general form given by:

$$\xi = \beta_c \left( \frac{1}{\hbar \omega + \hbar \omega_0 + i \Gamma_{12}} + \frac{1}{\hbar \omega - \hbar \omega_0 + i \Gamma_{12}} \right)$$ (S12)

Derivation and detailed description is available in work by Govorov et al.[3] Here $\beta_c$ is an intrinsic coefficient that determines the magnitude of chiral properties. Also $\hbar \omega_0$ (where $\hbar$ is the reduced Planck’s constant, $\hbar/2\pi$, and $\omega_0$ is the absorption frequency) and $\Gamma$ are the energy and intrinsic width of the
resonant chiral excitation of the dielectric. Consequently, the value of $\xi$ is wavelength dependent. This equation can also be written as:

$$\xi = \beta \varepsilon \left( \frac{1}{hc/\lambda + hc/\lambda_0 + i\Gamma_{12}} + \frac{1}{hc/\lambda - hc/\lambda_0 + i\Gamma_{12}} \right)$$  \hspace{1cm} (S13)

Using the following parameters:

- $hc = 1.23984193$ eV.$\mu$m
- $\lambda_0 = 0.28$ $\mu$m.
- $\Gamma = 0.4$ eV
- $\beta \varepsilon = 4.5 \times 10^{-4}$ eV

Proteins absorb in the UV region, so we use an estimate of $\lambda_0 = 280$ nm (IgG absorption). Figure S5 shows the plot of $\xi$ for $\lambda_0 = 280$ nm. As our resonance lies at ~700nm, we make the approximation that the $\xi$ value over the entire plasmonics resonance region is equal to the value at 700nm; we calculate that $\sim 1 \times 10^{-4}$. The magnitude is used as the imaginary part is negligible here. This value is approximate based on generic biomolecules absorbing in the UV region for an isotropic layer. The value used in the manuscript for an isotropic dielectric ($\xi = 1.7 \times 10^{-4}$) has been identified as the optimum value to match the $\Delta\Delta S$ values of the experimental results. We expect these differences between the above model and a real system occur due to the thickness of a real layer that influences the effective $\xi$ value.
3.1 Templated Plasmonic Substrates: Fabrication and Properties

The TPSs are made using an injection moulding machine (ENGEL), following the technique explained by Gadegaard et al [4]. The master shim for this is made using e-beam lithography. To create the master, 100 nm of PMMA is spin coated onto a Si wafer and baked for an hour at 180 °C. The resist is patterned using a VB6 UHR EWF lithography tool (Vistec). The exposed resist is developed in IPA and Methyl Isobutyl Ketone, MIBK (3:1 ratio) for 60 secs. Ni is electroplated onto the surface and removed from the wafer to provide the Nickel shim that is then used as the master in a tool placed in the injection moulder. Polycarbonate pellets are thermally heated and pushed into the tool to create small plastic slides with the nanostructures indented on the surface. These slides are then coated with 100 nm of Au in an e-beam evaporator at a rate of ≈0.3 nm s⁻¹.

The nano patterns are indentations in the surface and have a depth of ~80 nm, are 500 nm in length from arm to arm, and have a pitch of 700 nm. When gold is evaporated onto the surface, it takes the shape of the indentation and forms a hybrid plasmonic structure constituting an inverse structure at the

Figure S5: ξ magnitudes for the resonances corresponding to a generic protein. The dotted black line is the position where the values for the simulations were taken from.
top and a solid one at the bottom – see Figure 2 in the main text. For more information on the
plasmonic behaviour of the TPS refer to Karimullah et al [5].

References

[1] Johnson, P; Christy, R. Optical Constants of the Noble Metals. Phys. Rev. B, 1972, 6, 4370–4379.
[2] Sultanova, N; Kasarova, S; Nikolov, I. Dispersion properties of optical polymers. Acta Phys. Pol. A., 2009, 116, 585–587
[3] Govorov, A O; Fan, Z. Theory of chiral plasmonic nanostructures comprising metal nanocrystals and chiral molecular media. Chemphyschem., 2012, 13, 2551–60
[4] Gadegaard, N; Mosler, S; Larsen, N B. Biomimetic Polymer Nanostructures by Injection Molding. Macromol. Mater. Eng., 2003, 288, 76–83
[5] Karimullah, A S; Jack, C; Tullius, R; Rotello, V M; Cooke, G; Gadegaard, N; Barron, L D; Kadodwala, M. Disposable Plasmonics: Plastic Templated Plasmonic Metamaterials with Tunable Chirality. Adv. Mater., 2015, 27, 5610–5616
[6] Bassiri, S; Papas, C H; Engheta, N. Electromagnetic Wave Propagation through a Dielectric-Chiral Interface and through a Chiral Slab. J. Opt. Soc. Am. A, 1988, 5, 1450.