Induced chirality through electromagnetic coupling between chiral molecular layers and plasmonic nanostructures


Supporting Information
Supplementary data

1. Theory.

Figure 1S: Model of the chiral plasmonic system incorporating a metal (Au) sphere and a chiral molecular shell.

1.1. General formalism.

The exact solution for the chiral spherical core-shell objects [S1] can be found in the spirit of the Mie theory [S2] by solving Maxwell’s equations,

\[
\nabla \times \mathbf{E} = -\frac{1}{c_0} \frac{\partial \mathbf{B}}{\partial t} \\
\nabla \times \mathbf{H} = \frac{1}{c_0} \frac{\partial \mathbf{D}}{\partial t} \\
\n\nabla \cdot \mathbf{D} = 0 \\
\n\nabla \cdot \mathbf{B} = 0
\]

(S1)

that should be combined with the important equations for the fields (1) in chiral and absorbing media. The model to solve is given above, in Fig. 1S. The Mie functions for the electromagnetic fields should be written for the three special regions: The
outside space, the shell, and the plasmonic sphere. Then, the standard procedure is applied: The fields should be matched at the two interfaces via the standard electromagnetic boundary conditions [S2-S4]. The extinction of the chiral plasmonic system is then found using the known expressions for the electromagnetic fields [S3-S5].

The responses of a single molecule (absorption and CD strength) are derived from the microscopic quantum-mechanical equations [S6, S7]. Then, the medium parameters are constructed according to Eqs. 2 in the main text. In these equations, the parameter $n_c$ is an effective density of chiral molecules, taken as $8 \cdot 10^{21} \text{cm}^{-3}$. For such density, one molecular dipole is related to a box of 0.5nm-size. The molecular resonance broadening is estimated as $\Gamma_{12} = h \omega_0 \frac{\text{FWHM}_{\text{mol}}}{2 \cdot \lambda_{\text{mol}}}$. The resulting parameter $\xi_c$ is small, $|\xi_c| \sim 10^{-3}$, as expected. Realistic molecular materials show only weak optical chirality. Then a realistic estimate for the molecular dipole is taken as $\mu_{12} / e = 1.5 \text{Å}$, that corresponds to the single-molecule extinction of $\bar{\varepsilon}_{\text{mol}} = 10^4 / M \cdot \text{cm}$. The corresponding equation for the dielectric constant (2) again gives realistic numbers, $|\varepsilon_c| \sim 1 \div 2$.

In the parameter $\xi_c$ given by Eq. 3 include the key combination $\mu_{12} \cdot \mathbf{m}_{21}$. Molecules and a molecular medium are chiral only if a molecule has optically active transition with non-zero magnetic dipole $\mathbf{m}_{21}$. This assumes that the molecule is chiral. The magnitude of $\text{Im}[\mu_{12} \cdot \mathbf{m}_{21}]$ gives the strength of molecular CD (the parameter $(\varepsilon_{\text{CD,mol}})$ and also determines the related ORD effect.

1.2. Some applications.

We now give a few additional plots for the chiro-optical spectra within the model. First we show the properties of a small shell structure, $a = 10\text{nm}$ and $b = 20\text{nm}$ (Figs. 2S and 3S). Figure 3S points out to an important property of chiral plasmonic nano-shells – the plasmonic CD peak in the geometry of Fig. 1S is very weak for small structures with weak retardation effects [S5]. This property can be demonstrated analytically using the Mie theory and taking the limit of small sizes [S5]. For large
structures \((a \sim b \sim \lambda)\), the plasmonic CD peak is strong and, importantly, the scattering effects start to dominate the extinction (Fig. 4S).

Finally, we show CD plots (Fig. 5S) for a large chiral plasmonic structure with a strong electromagnetic chirality at the plasmon peak for a variable chiral parameter \(\xi_c\). For simplicity we take \(\xi_c\) real and frequency-independent. Then we see in Fig. 9S that the plasmonic CD \(\sim \xi_c\). Since the molecular ORD effect \(\sim \text{Re} \xi_c\), the plasmonic CD is \(\sim\) the molecular ORD signal. This shows the origin of the plasmonic chirality.

**Figure 2S**: Optical and chiral properties of the components assuming small sizes. Electromagnetic effects for these dimensions are weak. The upper panels show the absorption and CD for a small Au sphere. The lower papers show the same for the chiral shell.
Figure 3S: Optical and chiral properties of a small core-shell structure. Plasmonic structure in the CD is very weak.
Figure 4S: Optical and chiral properties of a large core-shell structure. Plasmonic structure in the CD is well expressed.
Figure 5S: CD for a large chiral plasmonic structure with a strong electromagnetic chirality at the plasmon peak. For simplicity, we take $\xi_c$ real and frequency-independent.
2. Fabrication

The crosses were designed using CAD software with a line width of 80 nm and a periodicity of 800 nm, figure 6S. They were arrayed to cover a total area of $5 \times 5 \text{ mm}^2$. The PCMs were fabricated on borosilicate glass slides $25 \times 25 \times 1 \text{ mm}^3$. The slides were cleaned for 5 min in acetone and 5 min in isopropanol both under ultrasonic agitation before being blown dry in a stream of nitrogen. A bilayer of poly(methyl methacrylate) (PMMA) was spun to a thickness of about 200 nm and baked at 180°C for 1 hour. A 10 nm NiCr layer was evaporated as a charge conduction layer during the electron beam lithography. The pattern was exposed in a Vistec VB6 UHR EWF lithography tool. After exposing the samples, the NiCr layer was removed in a chromium etch, rinsed in water and dried in a stream of nitrogen before development in isopropyl alcohol (IPA): methyl isobutyl ketone (MIBK) (2.5:1). Prior to metal deposition, the samples were exposed for 1 minute at 60W to an oxygen plasma. 5 nm of titanium was used as an adhesion layer and followed by 100 nm of gold. The final patterns were achieved in a lift-off process by leaving the samples in acetone for about 3 hours.
Figure 6S A) A schematic drawing of the Au nanostructures is given. B) A Electron micrograph of an individual Au cross nanostructure. C) The molecular structure of FMN
Figure 7S. Extinction spectra showing the effects of increasing FMN surface densities on the position of the plasmonic resonance. The green spectrum is for a $0.1 \mu g cm^{-2}$ film of FMN on a plain glass substrate. The magenta spectrum is collected from a plain cross, while blue, red and black spectra are taken from crosses with FMN films of surface densities (thickness) of 0.7 (--8nm), 7 (--80nm) and 70 mgcm$^{-2}$ (--800nm).
Figure 8S. The CD data from which g-factor spectra shown in figure 2A are derived from are shown. Spectra show the effects of FMN film surface densities on the induced chiral plasmonic resonances (black 35, red 70, green 105 and blue 140 µg cm⁻²).
Fig 9S. g-factor spectra (black filled) shown in figure 2A, showing the evolution of the plasmonic resonance with FMN film thickness, are re-plotted here, with the equivalent spectra taken from FMN films deposited on plain glass (red filled).
β-lactoglobulin   Trytophan
Figure 10S CD spectra collected from crosses which had β-lactoglobulin and tryptophan films with surface densities of 70µgcm$^{-2}$ deposited upon them.
Figure 11S In the upper panels are CD spectra collected from crosses which had crystal violet and rhodamine 6G achiral dyes films with surface densities of 70µgcm\(^{-2}\) deposited upon them (black) are compared with spectra from bare crosses (red). In the lower panels are the absorption spectra of solutions (1 mM) of the two dyes.
Figure 12S In panel A is an AFM image of a drop casted FMN film with a surface density of 70 µm gcm$^{-2}$ deposited on the nanostructured substrate. Panels B, C and D, display the height (z) profiles for the red, blue and green lines shown in A.
Figure 13S The upper panel is an AFM image of a FMN film (surface density of 70\(\mu g \text{ cm}^{-2}\)) which had been deposited next to an abrupt edge, which was subsequently removed. This procedure allow a well defined step to be produced in the film, enabling the thickness of the film to be determined with AFM. The lower panel show the height profile of the red line in the AFM image. The film display a thicker region close to the abrupt edge, but then this rapid tails off to produce a film of uniform thickness (912±53 nm).
Figure 14S A CD spectrum collected from a FMN film (surface density 70mg cm\(^{-2}\)) deposited on a crystal violet film (surface density 70mg cm\(^{-2}\)) on a quartz substrate. The spectrum is identical to one collected from a FMN film deposited on quartz (see Figure 1 D).