Supporting Information for:
Electromagnetic Interactions of Dye Molecules Surrounding a Nanosphere

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Figure S1: Simulated spectra of a 30 nm radius silver sphere in water, compared to the experimentally-derived absorption cross-section of the dye Rhodamine 6G (orange line, scaled up by a factor $10^5$). The solid lines represent extinction (red), absorption (green) and scattering (blue) cross-sections. The dashed black line, with corresponding scale on the right side of the plot, presents the surface-averaged local-field intensity enhancement factor $\langle M_{loc} \rangle$. The dye absorbance peaking at 526 nm is well-detuned from the plasmon resonances, and the enhancement factor is around 13 at that wavelength.

We reproduce for completeness in Fig. S1 the simulated optical response of a 30 nm radius silver sphere in water calculated with Mie theory (far-field absorption, scattering, and extinction cross-sections (left scale), and surface-averaged local-field intensity enhancement factor $M_{loc}$ (right scale)). For comparison, the spectrum of a single Rhodamine 6G dye is displayed, with a scaling factor of $10^5$. Note the large detuning between the dye absorption maximum (526 nm) and the plasmon resonance (around 429 nm for the dipole resonance). Most figures in the manuscript focus on the changes in the dye’s spectrum due to dipole-dipole and dipole-sphere electromagnetic interactions, rather than the plasmon resonances.

S2 Coupled dipole equations

We summarise below the standard equations of coupled-dipole theory in the more general case where the embedding medium is not necessarily vacuum/air, as no single convention exists for the various prefactors affecting the definition of polarisability and other quantities.

We consider a collection of $N$ point electric dipoles $p_i$ located at $r_i$ and embedded in a homogeneous infinite medium characterised by a dielectric function $\varepsilon_1$. The dipoles are subject to an incident macroscopic field $E^{inc}$. The response of the point dipoles $p_i$ is assumed local and linear and described by a polarisability tensor (possibly different for each molecule)
as:
\[ p_i = \tilde{\alpha}_i E_i, \]  
(S1)

where \( E_i \) denotes the macroscopic field at the dipole position.

At a microscopic level, a dipole reacts to the applied field with an intrinsic polarisability \( \tilde{\alpha}^\mu \). The applied field is enhanced by a local-field correction \( L \) arising from the polarisation of the embedding medium (Eq. S33 below). In turn, such a dipole moment produces a field which is enhanced by the same local field factor, from a reciprocity argument. We may therefore deduce the effective macroscopic polarisability \( \tilde{\alpha} \) as
\[ \tilde{\alpha} = L^2 \tilde{\alpha}^\mu. \]  
(S2)

The macroscopic electric field created by such a dipole \( p_i \) at a general point \( r \) also depends linearly on that dipole moment,
\[ E_{pi}(r) = \tilde{G}(r_i, r) p_i, \]  
(S3)

where the Green’s tensor \( \tilde{G} \) characterises the electric field at \( r \) created by a unit point dipole at \( r_i \).

A given dipole responds to a net macroscopic field that is the sum of the incident field and the field scattered by its neighbours. With the above conventions, the coupled dipole equations take the form,
\[ p^i = \tilde{\alpha}_i \left( E^{\text{inc}}(r_i) + \sum_{j \neq i} \tilde{G}_{ij} p^j \right), \]  
(S4)

where \( E^{\text{inc}}(r_i) \) is the incident field, and \( \tilde{G}_{ij} = \tilde{G}(r_i, r_j) \) is the Green’s tensor for the field created by dipole \( j \) at the location of dipole \( i \) in the infinite surrounding medium,
\[ \tilde{G}_{ij} = \beta^{-1} e^{ik_1 r_{ij}} \left\{ k_1^2 \left[ \tilde{I} - \tilde{r}_{ij} \otimes \tilde{r}_{ij} \right] \right. \left. - \left( \frac{1}{r_{ij}^2} - \frac{ik_1}{r_{ij}} \right) \left[ \tilde{I} - 3 \tilde{r}_{ij} \otimes \tilde{r}_{ij} \right] \right\}. \]  
(S5)

\( k_1 \) is the wave vector in the embedding medium, and we introduced the prefactor \( \beta = 4\pi \varepsilon_0 \varepsilon_1 \) which may be simplified throughout in practice by defining suitably-normalised quantities.

The absorption cross-section is given by:
\[ \sigma_{\text{abs}} = \frac{4\pi \beta^{-1} k_1}{|E_0|^2} \sum_i \left( 3 [p_i \cdot E_i^*] - \frac{2\beta}{3} k_1^3 |p_i|^2 \right). \]  
(S6)

**S3 Generalised Coupled Dipole Method (GCDM)**

We now describe the additional terms introduced in the generalised coupled-dipole system (Eq. 2 of the main manuscript) by the introduction of the sphere, as well as the calculation of far-field cross-sections for the combined system in the framework of generalised Mie theory.
Figure S2: Schematic representation of the light scattering problem under study. (a) An incident plane wave with associated electric field \( E^{\text{inc}} \) impinges on a spherical nanoparticle of radius \( R \) surrounded by polarisable dipoles in arbitrary positions and orientations at a distance \( d \) above the sphere. Each dipole responds to a net exciting field that comprises the incident plane wave, the scattered field from the sphere \( E^{\text{sph}} \), and the scattered field from all neighbouring dipoles in the presence of the sphere. (b) For convenience, in numerical calculations, the response of the dipoles to a plane wave is modelled by rotating the coordinates such that the incident wave propagates with wave vector along the \( z \) axis. (c) Similarly, the coupling between two dipoles is treated by considering the source dipole placed along the \( z \) axis, with appropriate rotations, and its decomposition along two orthogonal unit dipoles (normal and tangential to the sphere).

S3.1 Exciting field due to the sphere.

The net incident field on the collection of dipoles (source term in the linear system of Eq. 2) is augmented by the contribution \( E^{\text{sph}} \). For a given external incident field, such as a plane wave propagating along an arbitrary direction, we use the Mie theory\(^3\) to compute the electric field scattered by the bare sphere at any point in space, and in particular at the location of each dipole. In practice, the calculation simplifies considerably and is therefore much more efficient when the plane wave is incident along the \( z \) axis (Fig. S2b). Our strategy is therefore to compute the electric field for a plane wave incident along the \( z \) axis on a fine grid of locations around the sphere and interpolate the (complex) vector components of this electric field distribution at the location of the dipoles in a suitably-rotated coordinate system for each required direction of incidence and polarisation.

S3.2 Coupling mediated by the sphere.

The Green tensor’s contribution \( \tilde{S}_{ij} \) expresses the field created at location \( \mathbf{r}_j \) by a unit dipole at \( \mathbf{r}_i \) due to scattering by the sphere. We calculate this \( 3 \times 3 \) matrix using a generalised Mie theory, where the field of the exciting dipole \( \mathbf{p}_i \) is decomposed in a basis of vector spherical
wavefunctions (VSWFs) centred on the sphere,\textsuperscript{1,4,5}

\[
E_{i,\text{DIP}}^{\text{L}} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} a_{mn}^{i,\text{DIP}} M^{(1)}(k_1, \mathbf{r}) + b_{mn}^{i,\text{DIP}} N^{(1)}(k_1, \mathbf{r}), \quad r \leq r_i, \tag{S7}
\]

\[
E_{i,\text{DIP}}^{\text{I}} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} e_{mn}^{i,\text{DIP}} M^{(3)}(k_1, \mathbf{r}) + f_{mn}^{i,\text{DIP}} N^{(3)}(k_1, \mathbf{r}), \quad r \geq r_i. \tag{S8}
\]

\((N^{(3)}, M^{(3)}), (N^{(1)}, M^{(1)})\) are the regular and irregular VSWFs, respectively, \(a_{mn}^{i,\text{DIP}}, b_{mn}^{i,\text{DIP}}, e_{mn}^{i,\text{DIP}}, f_{mn}^{i,\text{DIP}}\) are expansion coefficients with known analytical expressions in terms of \(p_i\) (given in Sec. S2). The second expansion in terms of irregular waves will be used in the calculation of cross-sections.

The field scattered by the sphere from this dipolar excitation follows from Mie theory,

\[
E_{\text{SCA}} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} p_{mn} M^{(3)}(k_1, \mathbf{r}) + q_{mn} N^{(3)}(k_1, \mathbf{r}) \tag{S9}
\]

with

\[
p_{mn}^{i,\text{DIP}} = \Gamma_n a_{mn}^{i,\text{DIP}}, \tag{S10}
\]

\[
q_{mn}^{i,\text{DIP}} = \Delta_n b_{mn}^{i,\text{DIP}}, \tag{S11}
\]

where \(\Gamma_n\) and \(\Delta_n\) are the standard electric and magnetic multipolar Mie susceptibilities.\textsuperscript{1,3}

Calculating this field for each dipole at all the other dipole positions can become too computationally intensive and impractical for a large number of coupled dipoles. We therefore again adopt an interpolation scheme to speed up this step: as with the case of plane wave illumination, the VSWF series simplify greatly if the source dipole is placed along the \(z\)-axis; we therefore evaluate the scattered field around the sphere for two independent unit dipoles placed along the \(z\) axis, and oriented radially or tangentially, respectively (Fig. S2c). For each dipole, we then perform the required rotations to bring it along the \(z\) axis and interpolate the field components at the location of the other dipoles, before rotating them back to the common reference frame.

\section*{S3.3 Far-field cross-sections.}

A similar formal expansion to Eq. S7 is used for the plane wave illumination at arbitrary incidence (with different, known coefficients\textsuperscript{5}) corresponding to the incident field,

\[
E_{\text{INC}} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} a_{mn}^{\text{PW}} M^{(1)}(k_1, \mathbf{r}) + b_{mn}^{\text{PW}} N^{(1)}(k_1, \mathbf{r}). \tag{S12}
\]
The sum of both incident and dipole fields forms the net exciting field for the sphere,

\[ E_{\text{exc}} = E_{\text{dip}} + E_{\text{inc}} \]

\[ = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} a_{mn}^{\text{exc}} M^{(1)}(k_1, r) + b_{mn}^{\text{exc}} N^{(1)}(k_1, r) \]  \hspace{1cm} (S13)

where we simply sum all dipole coefficients to those of the incident plane wave,

\[ a_{mn}^{\text{exc}} = a_{mn}^{\text{pw}} + \sum_i a_{mn}^{i,\text{dip}}, \quad \text{and} \]
\[ b_{mn}^{\text{exc}} = b_{mn}^{\text{pw}} + \sum_i b_{mn}^{i,\text{dip}}. \]  \hspace{1cm} (S14)

The coefficients for the field scattered by the sphere from the combined excitation follow from Mie theory,

\[ p_{mn} = n a_{mn}^{\text{exc}}, \]
\[ q_{mn} = \Delta_n b_{mn}^{\text{exc}}. \]  \hspace{1cm} (S15, S16)

The total scattering cross-section is obtained by summing the total field scattered by the sphere, and that directly radiated by the dipoles (Eq. S8), both expressed in a basis of irregular VSWFs.

\[ \sigma_{\text{sca}} = \frac{1}{k^2} \sum_{n=1}^{\infty} \sum_{m=-n}^{n} |e_{mn}^{\text{dip}} + p_{mn}^{\text{SPH}}|^2 + |f_{mn}^{\text{dip}} + q_{mn}^{\text{SPH}}|^2 \]  \hspace{1cm} (S17)

For the extinction cross-section we invoke the optical theorem, where the incident field is a plane wave excitation along a specific direction, and the scattered field is given by the superposition of the dipole sources and the total field scattered by the sphere, which results in:

\[ \sigma_{\text{ext}} = -\frac{1}{k^2} \sum_{n=1}^{\infty} \sum_{m=-n}^{n} \Re \left( a_{mn}^{\text{pw}} a_{mn}^{*} + a_{mn}^{\text{pw}} e_{mn}^{*\text{dip}} \right) + \Re \left( b_{mn}^{\text{pw}} q_{mn}^{*} + b_{mn}^{\text{pw}} f_{mn}^{*\text{dip}} \right). \]  \hspace{1cm} (S18)

The absorption cross-section is then deduced as

\[ \sigma_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{sca}}. \]  \hspace{1cm} (S19)

### S3.4 Numerical implementation

We summarise our approach as follows:

- obtain the self-consistent macroscopic fields \( E_i \) and dipole moments \( \mathbf{p}_i \) via the extended coupled-dipole system (Eq. 2)
- for each dipole \( \mathbf{p}_i \), now considered as a source, calculate its expansion coefficients \( a_{nm}^{i}, b_{nm}^{i}, e_{nm}^{i}, f_{nm}^{i} \)
• define the total exciting field as the sum of expansion coefficients from all dipoles (Eq. S14), added to those corresponding to the incident plane wave

• multiply these incident field coefficients by the Mie susceptibilities $\Delta_n$ and $\Gamma_n$ to obtain the scattered field coefficients $(p_{nm}, q_{nm})$ in response to this composite exciting field

• the optical cross-sections follow from these coefficients using Eqs. S17–S19.

In a practical numerical implementation, all the infinite series expansions must be truncated. We chose to truncate them at a maximum multipolar order $n_{\text{max}}$ and include all $j_m j_n$. The value of $n_{\text{max}}$ was chosen such that the resulting cross-sections have converged to a good accuracy, i.e. do not vary with higher $n_{\text{max}}$. We note that, although the Mie theory provides a rigorous analytical solution to the scattering problem, in practice the computation of the series can be problematic, as a large number of terms needs to be included for dipoles very close to the surface of the sphere (as many as $n_{\text{max}} = 1000$ multipoles).\textsuperscript{1,6,7} In order to alleviate the numerical difficulties in computing the Mie coefficients at very large order (which results in overflow when computing spherical Bessel functions), we use a fast-convergent electrostatic approximation\textsuperscript{7} for terms above $n = 50$, and combine this solution to the exact Mie coefficients for $n < 50$. This is justified because the spherical Bessel functions $z_n(x)$ can be well approximated by their small-argument ($x \to 0$) approximation for $x \lesssim n$. Our tests indicate that this approximation yields results that have a relative accuracy better than $10^{-3}$. A truncation value of $n_{\text{max}} = 500$ was sufficient to reach results of comparable accuracy in all the calculations presented here.

### S3.5 Expansion coefficients for plane wave and dipole

Our definitions for the vector spherical wavefunctions follow Mishchenko et al.;\textsuperscript{5} we summarise below for convenience the expansion coefficients for a plane wave illumination\textsuperscript{5} and a dipole source,\textsuperscript{1} with reference to the equation number in the original source,

\begin{align*}
a_{mn}^{\text{pw}} & = 4\pi (-1)^m i^r r_n e^{-im\phi} \hat{e} \cdot C_m^e(\theta) \quad \text{[C.57] in Ref. 5} \quad (S20) \\
b_{mn}^{\text{pw}} & = 4\pi (-1)^m i^{r-1} r_n e^{-im\phi} \hat{e} \cdot D_m^e(\theta) \quad (S21) \\
a_{mn}^{\text{dip}} & = E_p(1)^m \hat{p} \cdot M_m^{(3)}(r, \theta, \phi) \quad \text{[H.84] in Ref. 1} \quad (S22) \\
b_{mn}^{\text{dip}} & = E_p(1)^m \hat{p} \cdot N_m^{(3)}(r, \theta, \phi) \quad (S23) \\
e_{mn}^{\text{dip}} & = E_p(1)^m \hat{p} \cdot M_{-m}^{(1)}(r, \theta, \phi) \quad \text{[H.86] in Ref. 1} \quad (S24) \\
f_{mn}^{\text{dip}} & = E_p(1)^m \hat{p} \cdot N_{-m}^{(1)}(r, \theta, \phi) \quad (S25)
\end{align*}

where we defined

\[ r_n = \sqrt{\frac{2n + 1}{4\pi n(n + 1)}}, \quad (S26) \]
and \( \mathbf{\hat{p}} \) and \( \mathbf{\hat{e}} \) are unit vectors in the direction of \( \mathbf{p} \) and \( \mathbf{E} \), respectively. The prefactors for both fields are

\[
E_0 = 1, \quad \text{(we assume a unit incident field throughout)} \tag{S27}
\]

\[
E_{p0} = \frac{ik_1^3 p}{\varepsilon_0 \varepsilon_1} = 4\pi i k_1^3 \beta^{-1} p, \quad \text{[H.83] in Ref. 1} \tag{S28}
\]

## S4 Model dye polarisability

The model dye polarisability is the same as the one used in our previous study of dye interacting in the absence of the nanosphere. We recall it here for completeness.\(^8\)

The polarisability tensors considered in the main manuscript for coupled-dipole simulations are either isotropic,

\[
\bar{\alpha} = \begin{pmatrix} \alpha_d & 0 & 0 \\ 0 & \alpha_d & 0 \\ 0 & 0 & \alpha_d \end{pmatrix}, \tag{S29}
\]

or uniaxial,

\[
\bar{\alpha} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 3\alpha_d \end{pmatrix}. \tag{S30}
\]

These tensors are expressed in their natural frame (where they are diagonal), and need to be rotated depending on molecular orientations. The factor of 3 in the second case ensures that the trace remains the same and that the orientation-averaged absorption is the same in both cases.

We take the following model (single Lorentzian) to describe the microscopic polarisability of a dye in a vacuum,

\[
\alpha_d = \alpha_\infty + \frac{\alpha_1 \lambda_1}{\mu_1} \left[ \frac{1}{1 - \frac{\lambda^2}{\lambda_1^2} - i \frac{\lambda^2}{\lambda_1 \mu_1}} - 1 \right] \tag{S31}
\]

For a simplified model of a dye resembling Rhodamine 6G, we use \( \alpha_\infty = 3.2 \times 10^{-39} \) [SI], \( \alpha_1 = 1.92 \times 10^{-38} \) [SI], \( \lambda_1 = 526 \) nm, \( \mu_1 = 10^4 \) nm. We emphasise that for the concentration-dependence to be meaningful the magnitude of \( \alpha_d \) must be correct. In many studies, this is freely adjusted to match experimentally-observed spectral shifts. Here, we instead use the experimentally measured absorption cross-section to determine the absolute \( \alpha_d \), as discussed in Ref. 9. Taking into account the local-field enhancement of the solvent (of refractive index \( n = \sqrt{\varepsilon_1} \)), the absorption cross-section of an isolated dye in water is given by\(^1,9\)

\[
\sigma_{\text{abs}}(\lambda) = \frac{2\pi}{\lambda \varepsilon_0 \sqrt{\varepsilon_1}} L^2 \text{Im} (\alpha_d(\lambda)) \tag{S32}
\]

with the local field factor

\[
L = \frac{\varepsilon_1 + 2}{3}. \tag{S33}
\]
Self-reflected field in the electrostatic-planar approximation

The self-reflected field is given by the field created by the dipole image,\(^1\)\(^{10}\)

\[
E^{\text{SR}} = \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \right) \frac{2p_\perp + p_\parallel}{4\pi\varepsilon_0\varepsilon_1(2d)^3}, \quad (S34)
\]

where \(p_\perp\) and \(p_\parallel\) are the components of the dipole normal or tangential to the metal surface. This is equivalent to the approximation:

\[
\tilde{S}_{11} \approx \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \right) \frac{1}{4\pi\varepsilon_0\varepsilon_1(2d)^3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \quad (S35)
\]

For a general external field \(E^{\text{EXT}}\), the induced dipole is \(p_1 = \tilde{\alpha}_1(E^{\text{EXT}} + E^{\text{SR}})\), and we may describe the net response in terms of an effective polarisability: \(p_1 = \tilde{\alpha}_{\text{eff}}E^{\text{EXT}}\), with

\[
\tilde{\alpha}_{\text{eff}} = (\vec{I} - \tilde{\alpha}_1\tilde{S}_{11})^{-1}\tilde{\alpha}_1. \quad (S36)
\]

Substituting Eq. S35 into Eq. S36, we can predict the modified absorbance of a single dipole (proportional to \(\Im(\tilde{\alpha}_{\text{eff}})\)) in the electrostatic-planar approximation.

Effect of the dye orientation and coverage uniformity

In Fig. 7 of the main manuscript we present a comparison with experimental data for a chosen configuration with uniaxial dyes oriented at \(\theta = 75^\circ\) from the normal to the surface, and a random coverage of the sphere surface. We provide in Fig. S3 further simulations to explore the influence of both parameters. The non-uniform coverage of the surface broadens the spectral features, and shows an onset of spectral shifts at a lower concentration than with a more uniform coverage; this is expected because randomly-chosen positions yield a broader range of pair-wise distances between nearest neighbours, and in particular shorter distances responsible for the more prominent spectral shifts. The molecule’s orientation with respect to the surface normal is an important parameter for the simulations; it affects the intensity of the local field, and therefore the differential absorbance (compare the scale of panels (a) and (e)), but also the spectral shifts through dye-dye interactions. Comparing the predicted absorbance spectra to those observed experimentally suggests that an adsorption geometry of around 75° yields the closest agreement.

References

Figure S3: Differential absorbance spectra for uniaxial dipoles titled by an angle \( \theta \) from the surface normal with either uniform coverage (Top row a–e) or random positions on the sphere with a minimal exclusion distance of 0.7 nm between any two neighbours (Bottom row f–j). We vary the tilt angle from 5° to 85°, and the surface concentration \( \rho \). The dashed line, common to all panels, is the absorption of the isolated dye in the embedding medium without the sphere. For ease of comparison of the spectral shape, the dotted line presents the same data rescaled to the maximum of the low-concentration predictions with the sphere.


