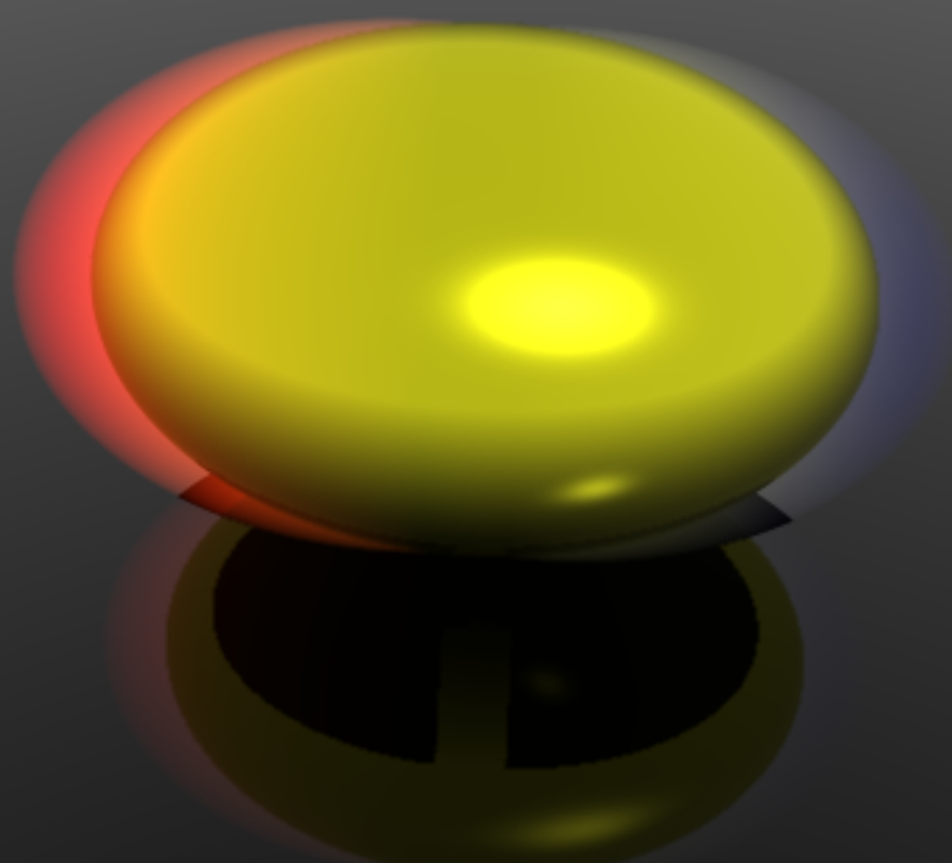
Light and chirality at the nanoscale

Baptiste Auguié

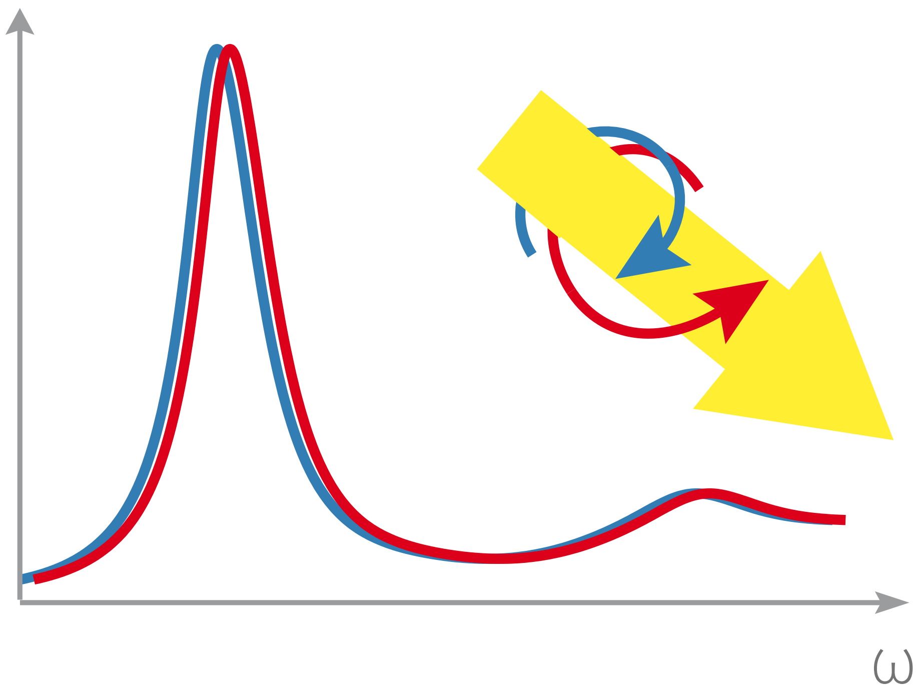
baptiste.auguie@gmail.com

"NANO ANTENNA"

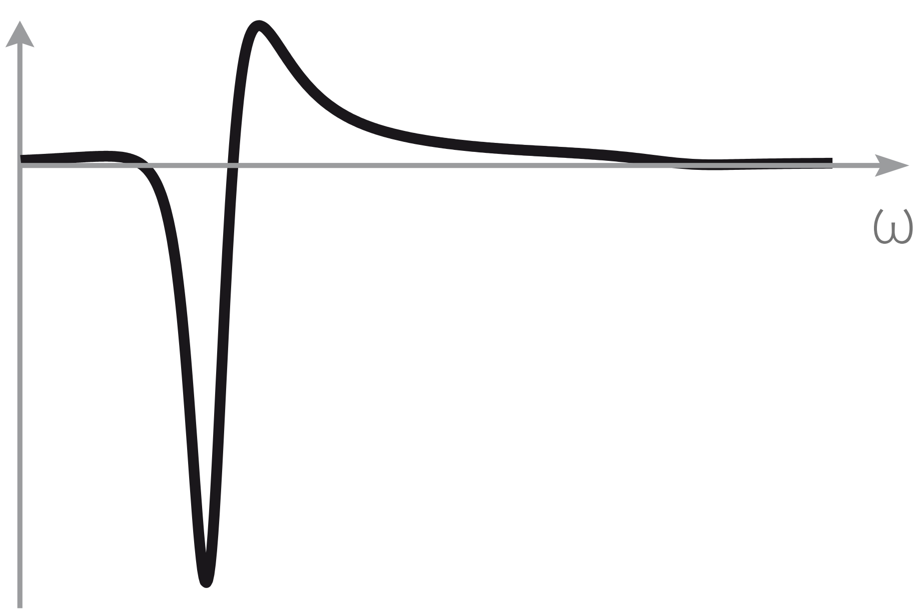


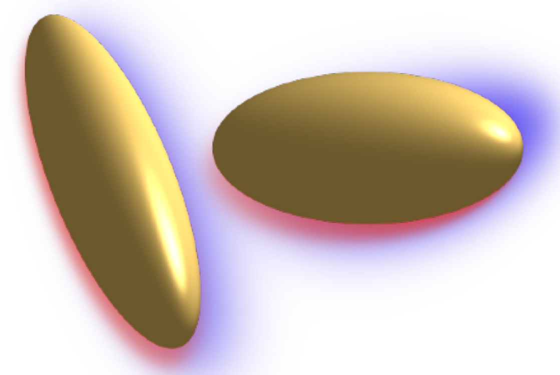
Fingers crossed (2011)

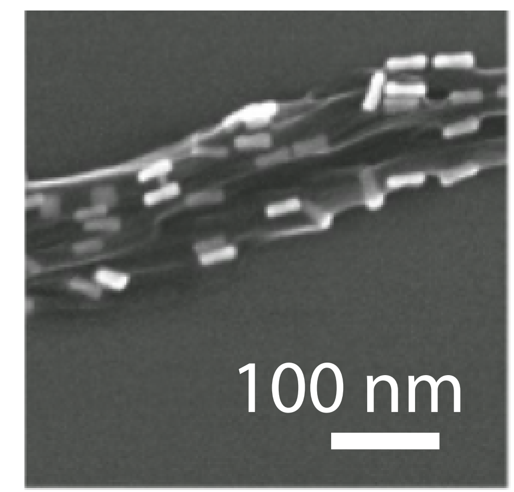
Absorbance



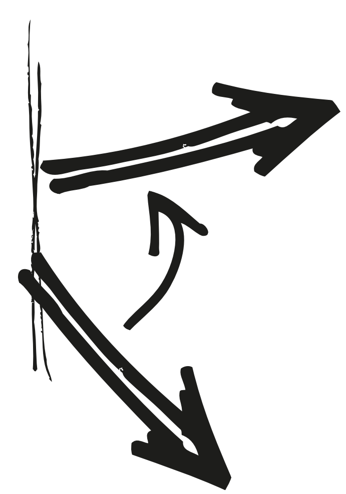
Circular dichroism

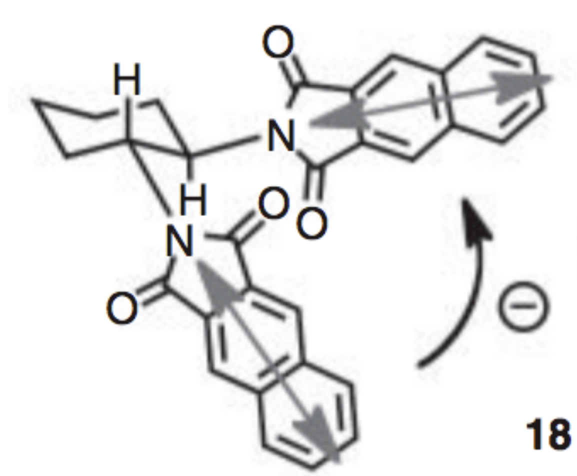






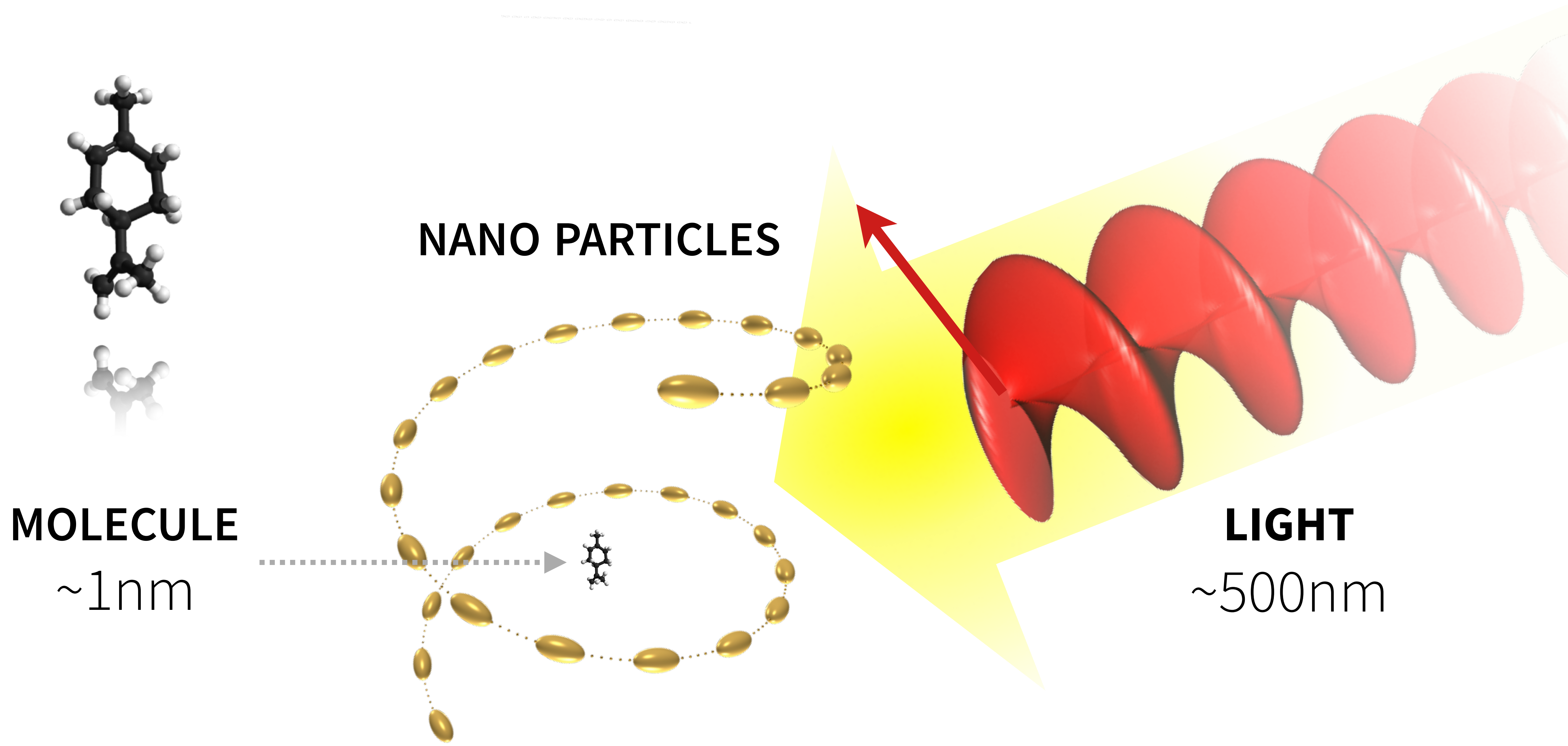
mimicking “*exciton coupling*”



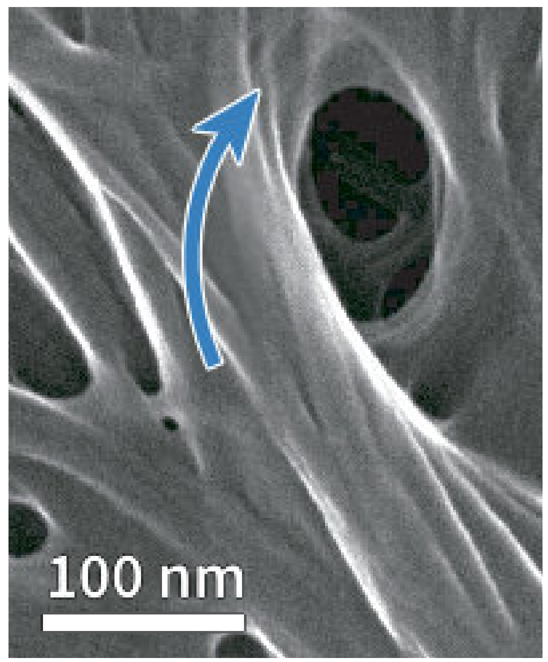


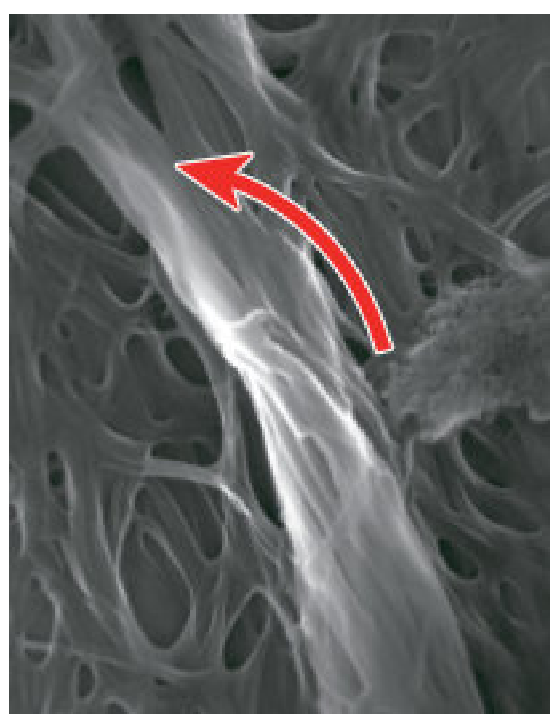
Squeezing out 3D molecular information

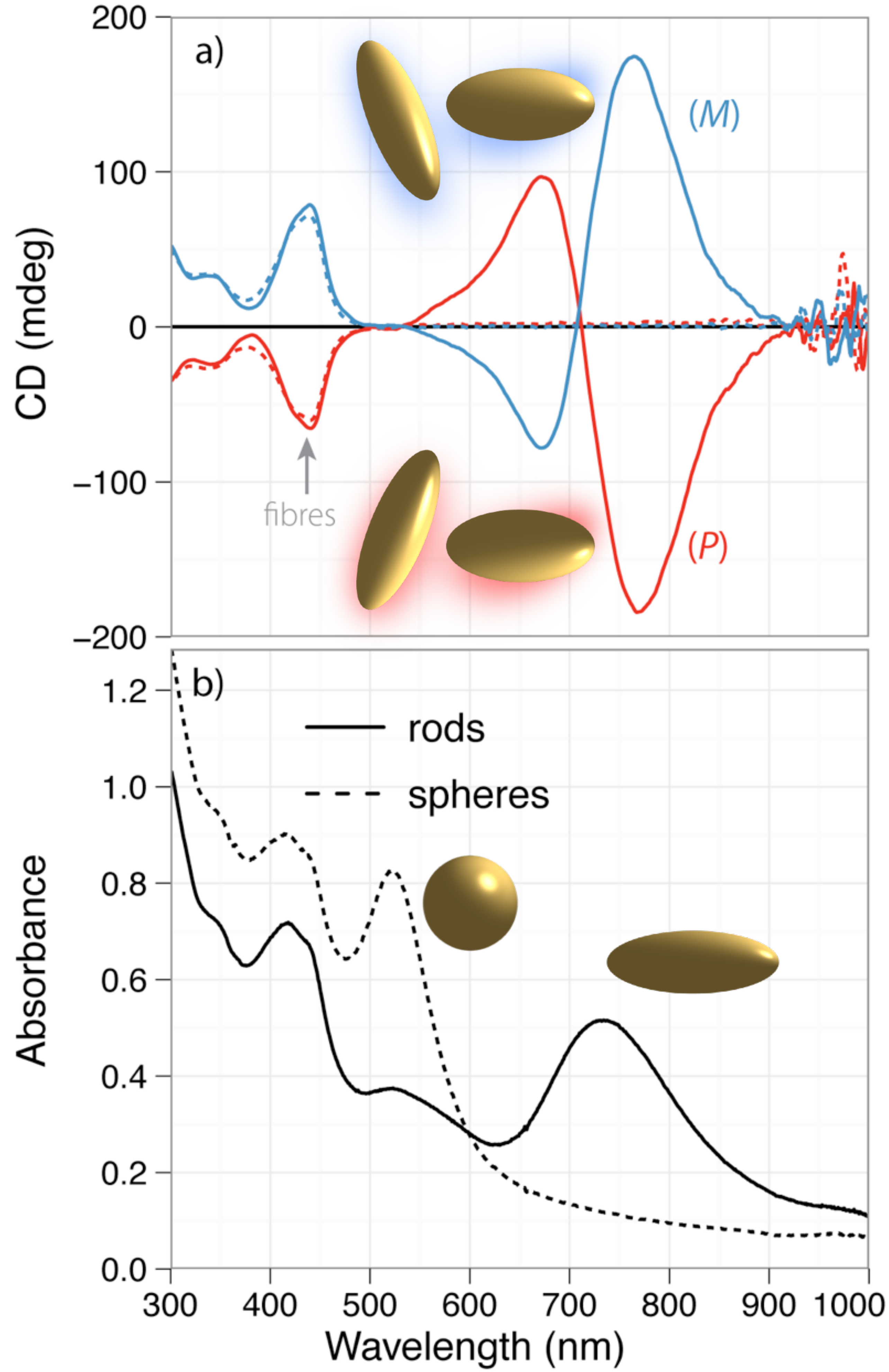
Using nano-antennae as chirality probes



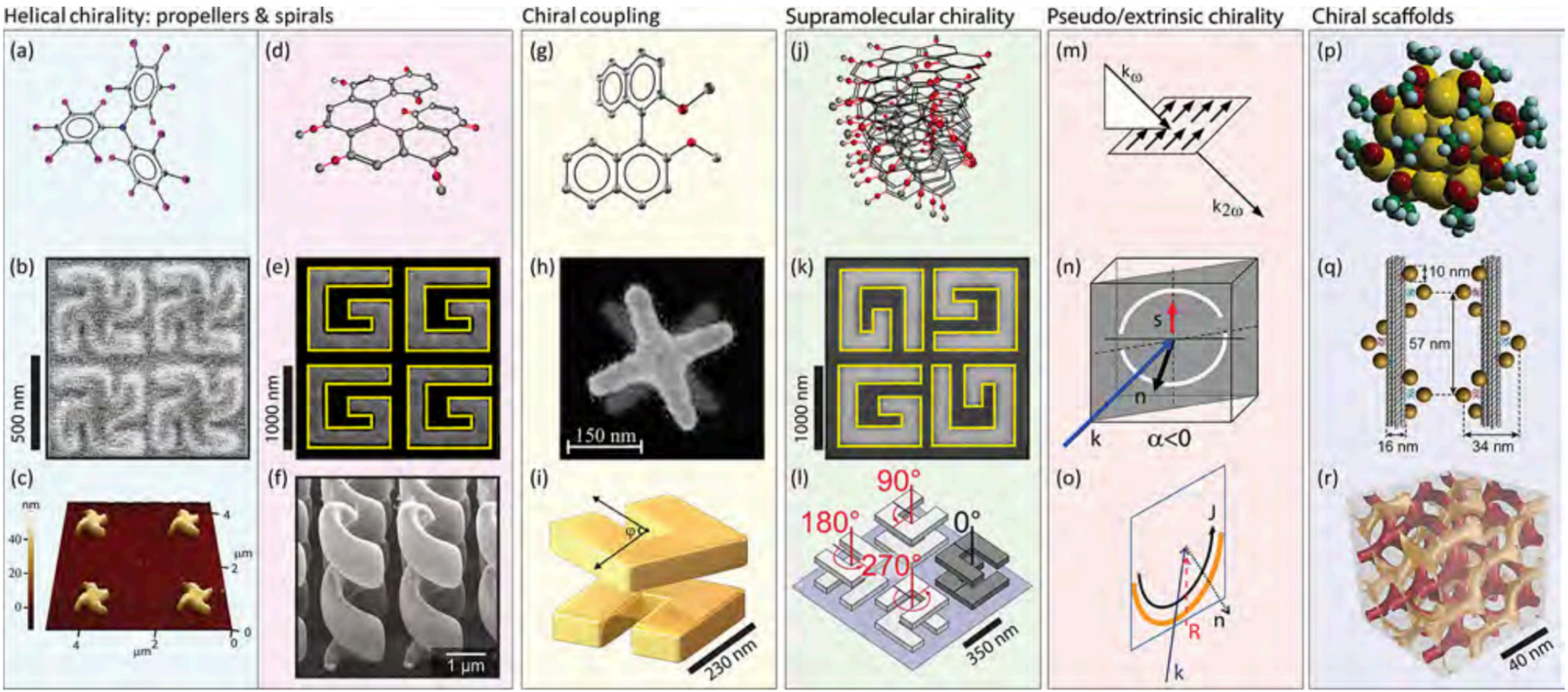
CD EXPERIMENTS





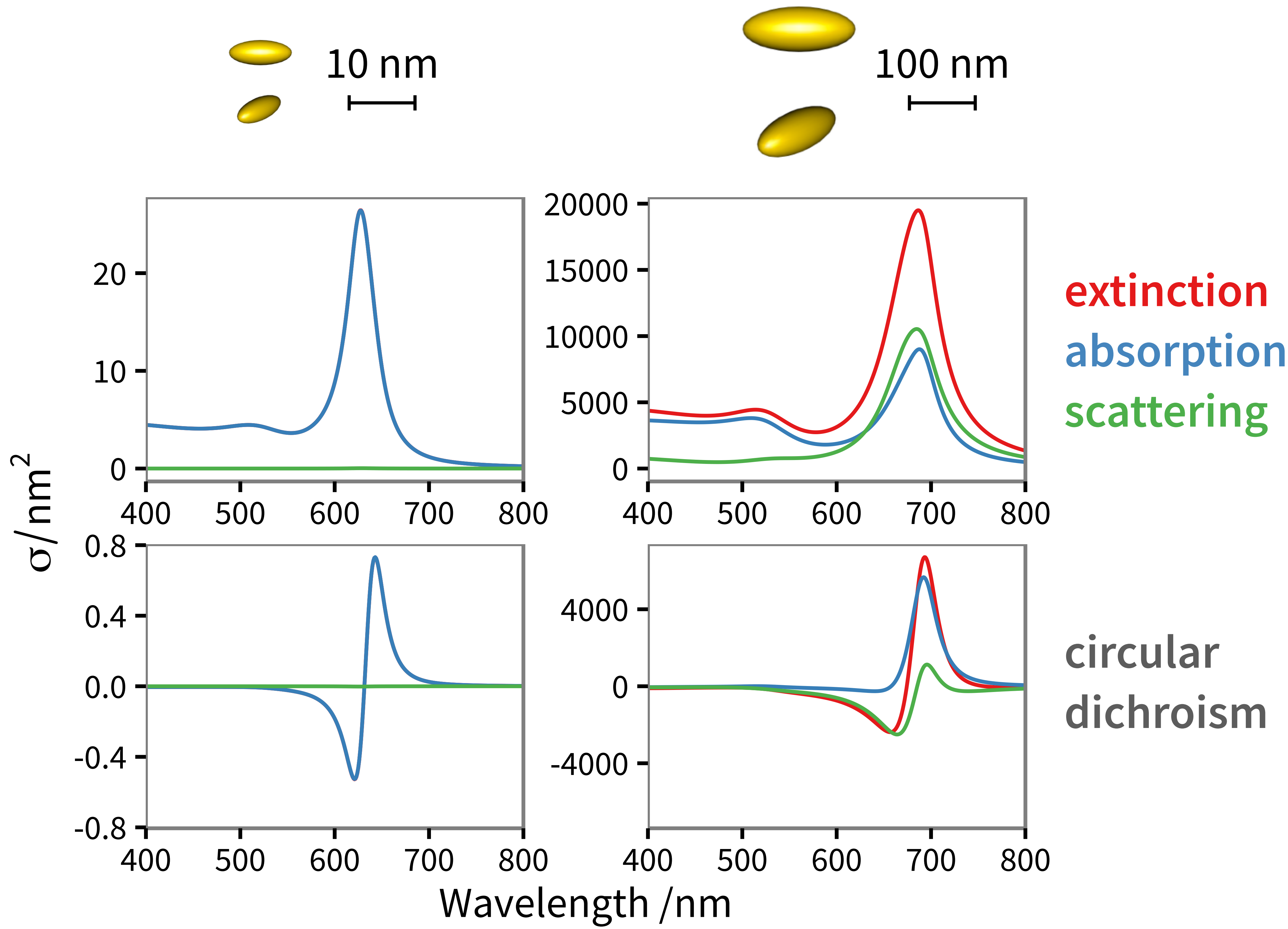


A TAXONOMY OF CHIROPTICAL SYSTEMS



Baumberg et al. Adv. Mater. 2013

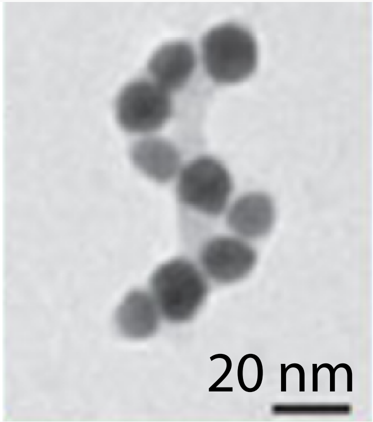
New physics in a chiral plasmonic dimer

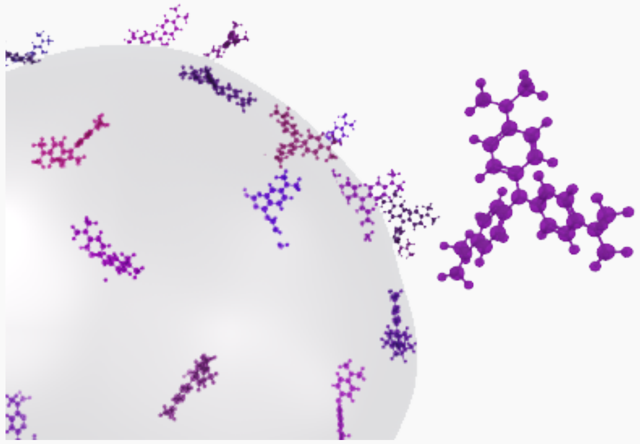


RDF PROJECT OVERVIEW

EXPERIMENTS

CHIRAL NANO STRUCTURES & MOLECULES

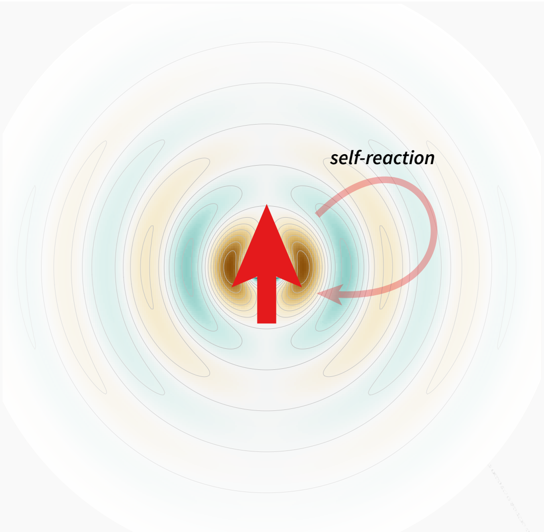




- **Circular dichroism**
  individual aggregates
- **Raman and fluorescence**
  enhanced signals

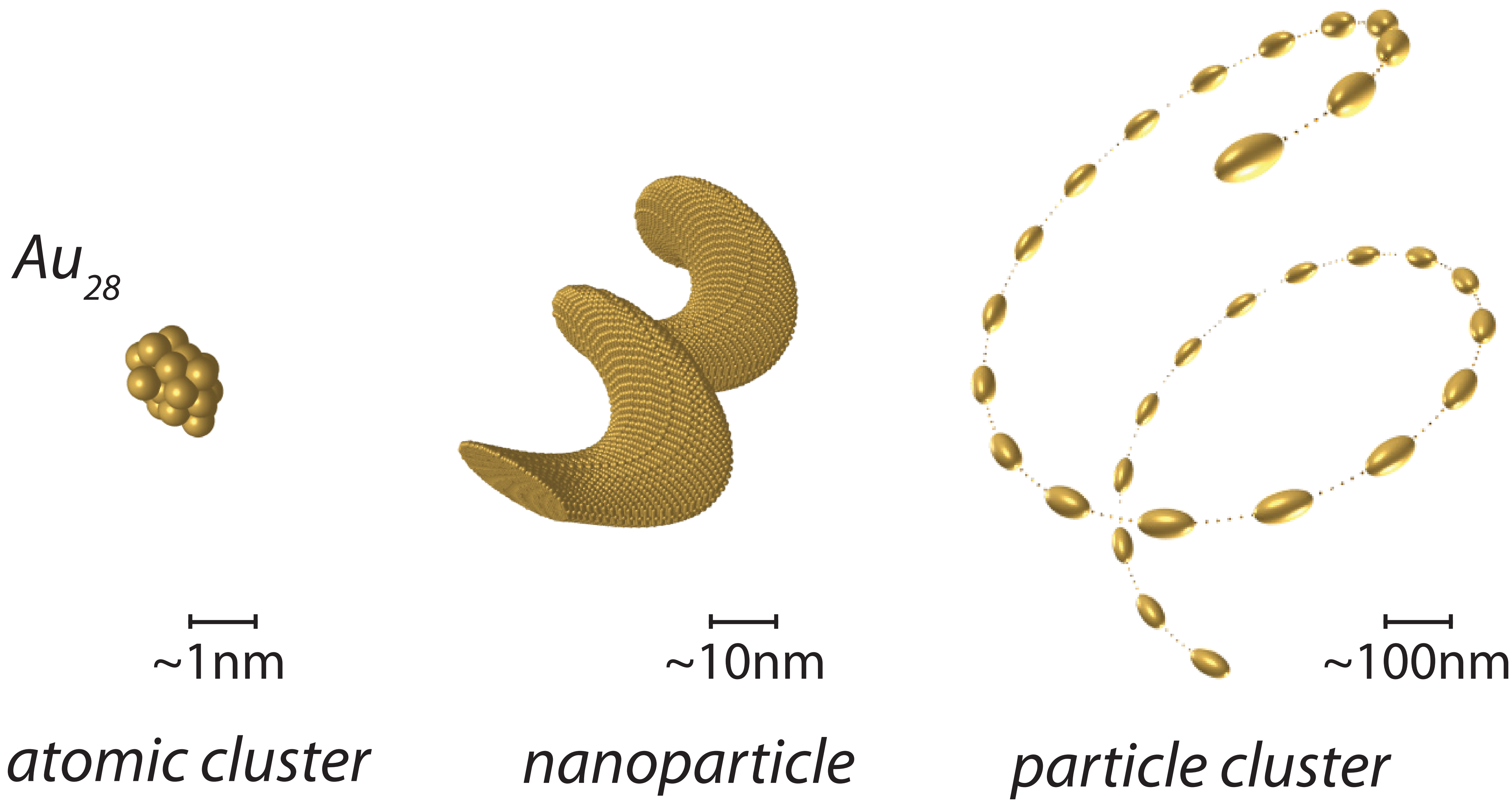
THEORY

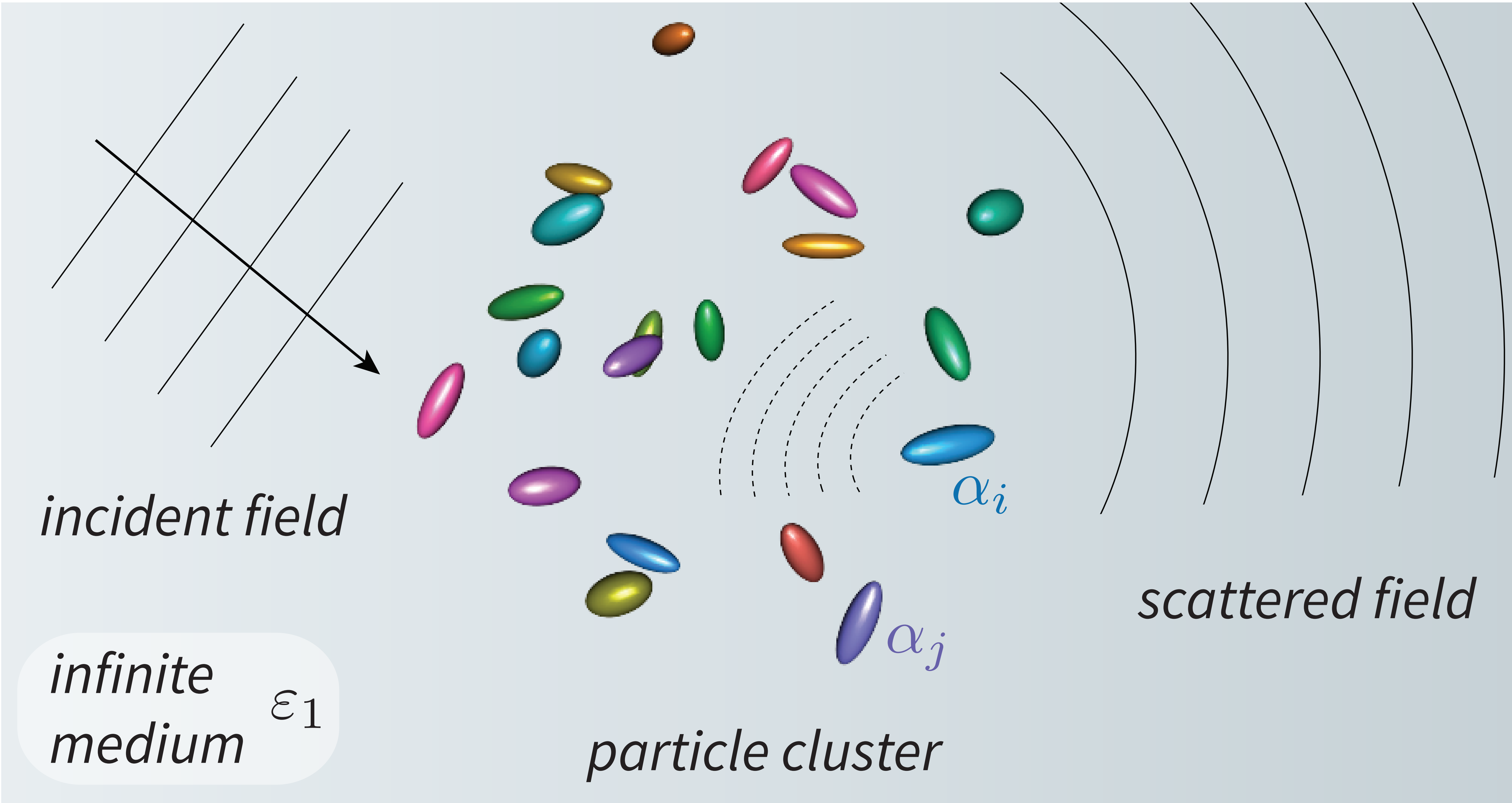
COUPLED DIPOLE & MULTIPOLE THEORY



- **Optimisation**
  geometry, super-chiral fields
- **T-matrix framework**
  fast, accurate, insightful

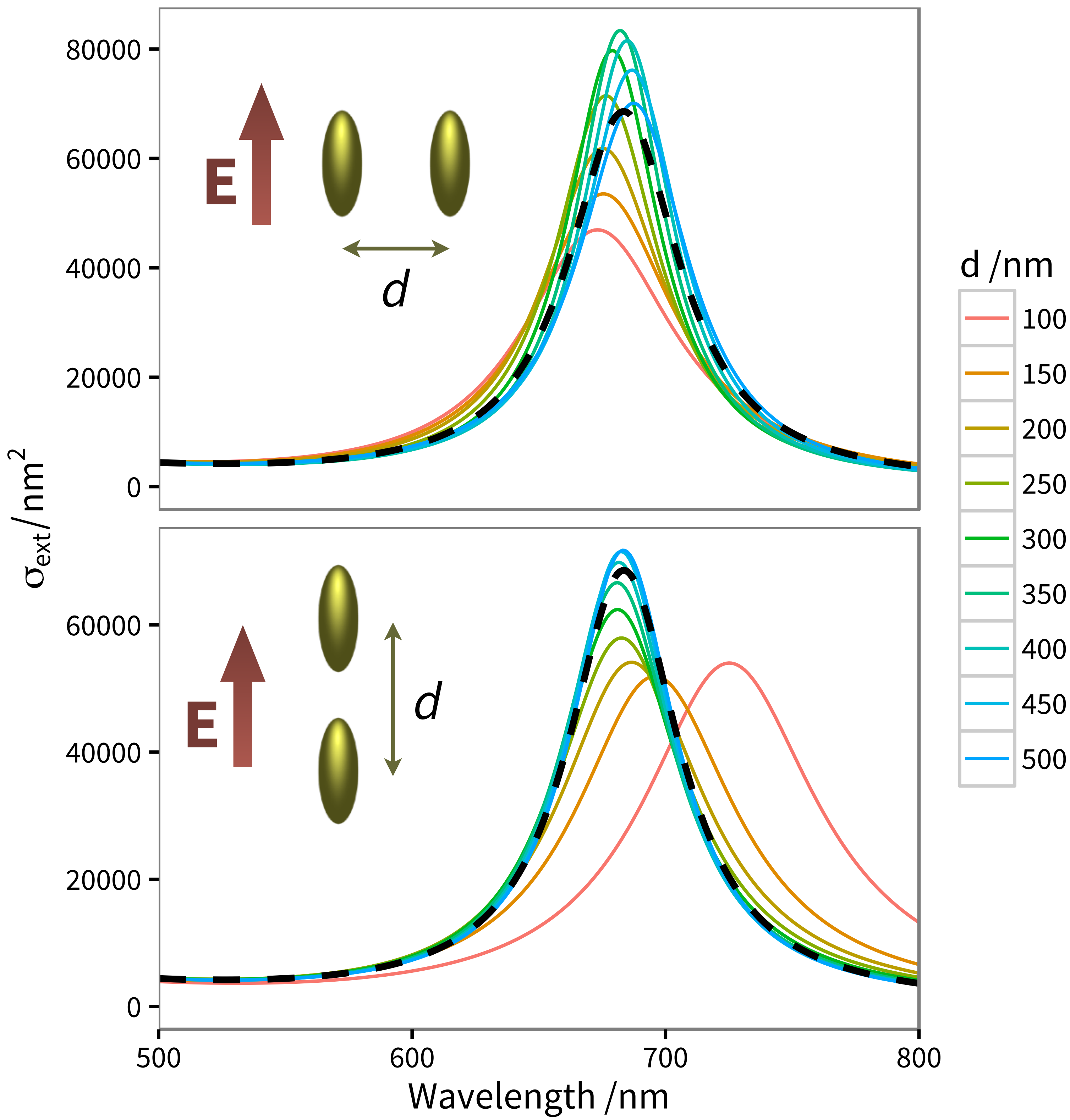
Coupled Dipole Approximation



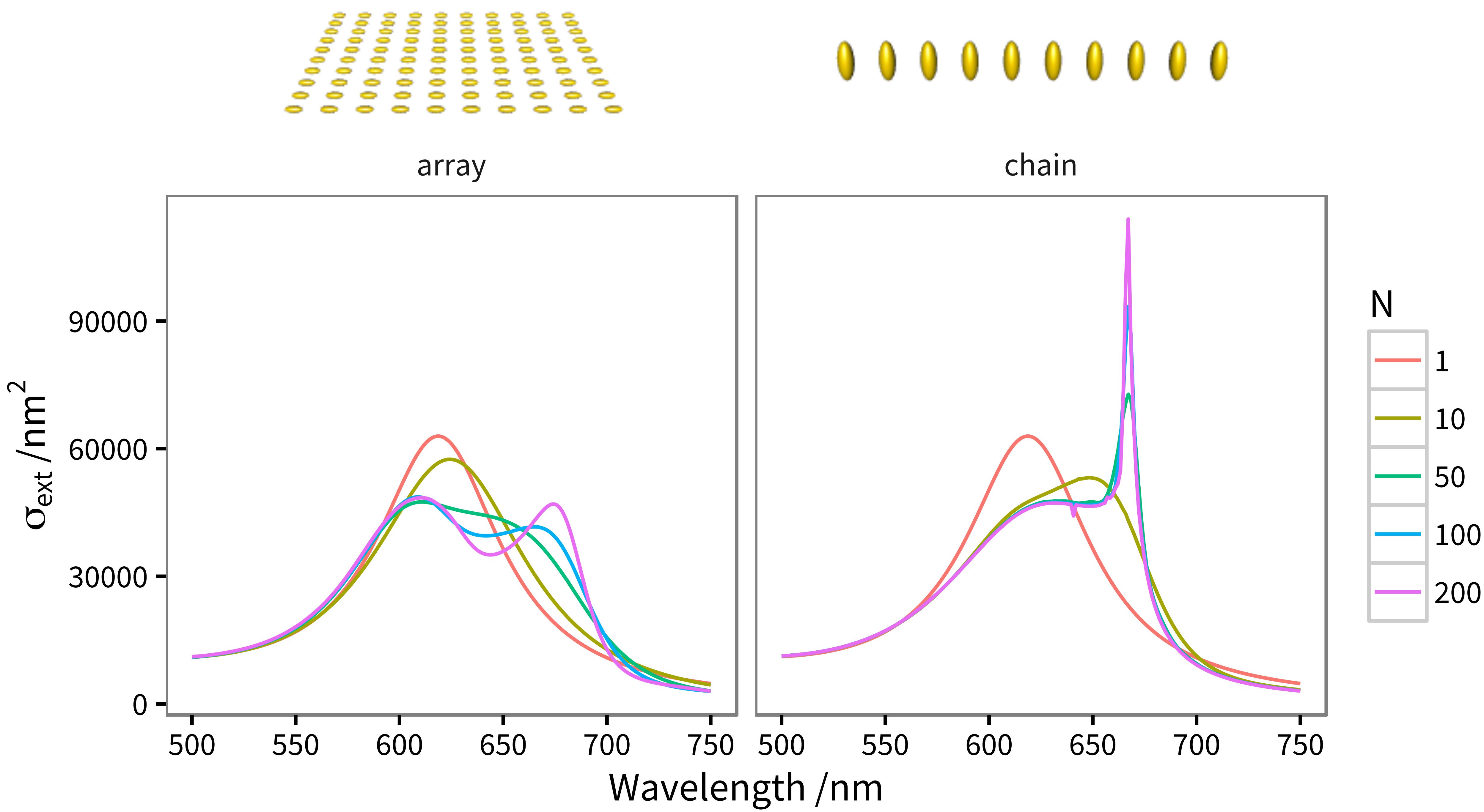


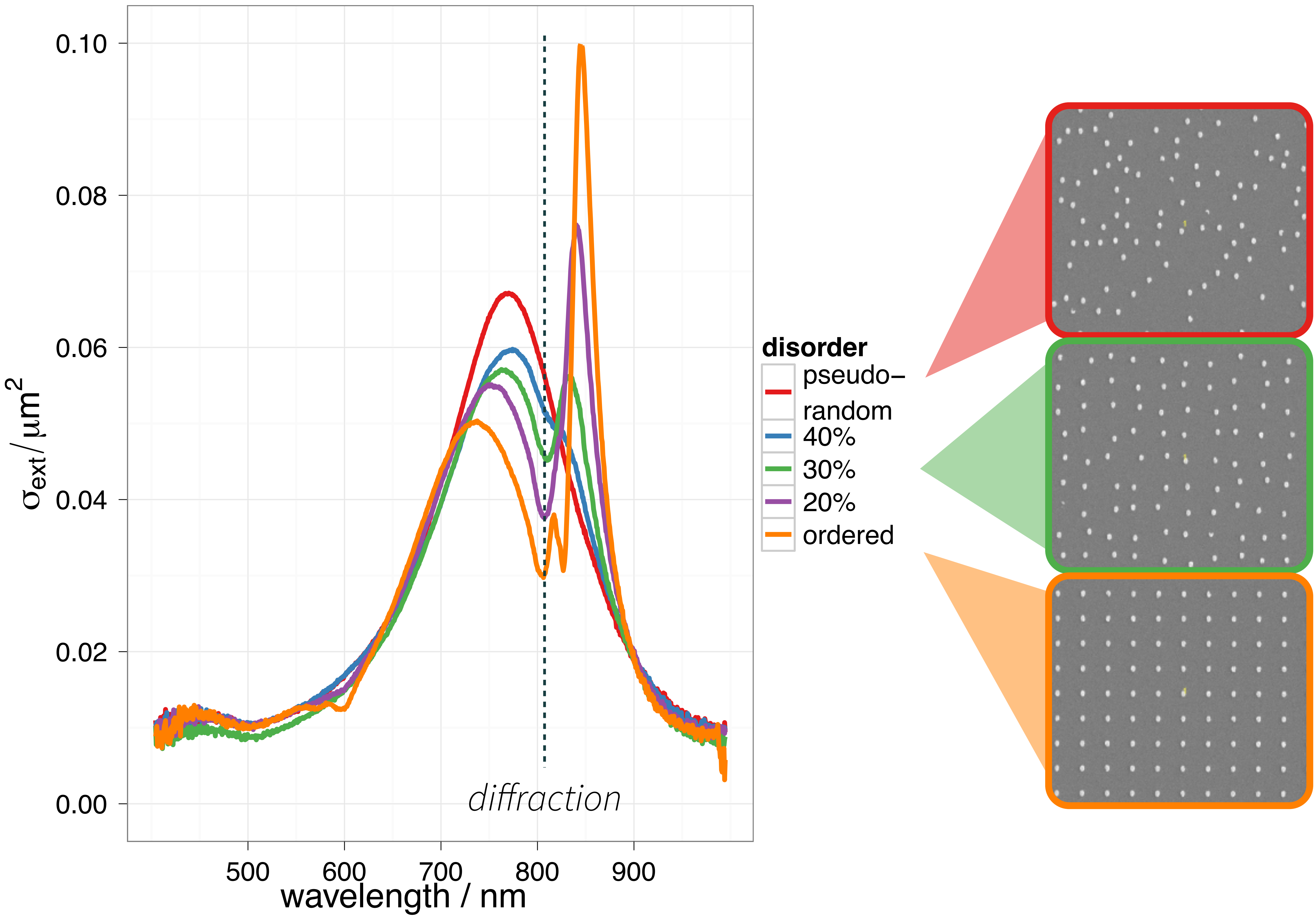
$$\mathbf{E}^i = \mathbf{E}^i_{\text{inc}} + \sum_{j \neq i} \mathbb{G}_{ij} \alpha_j \mathbf{E}^j$$

DIMER • PLASMON HYBRIDISATION



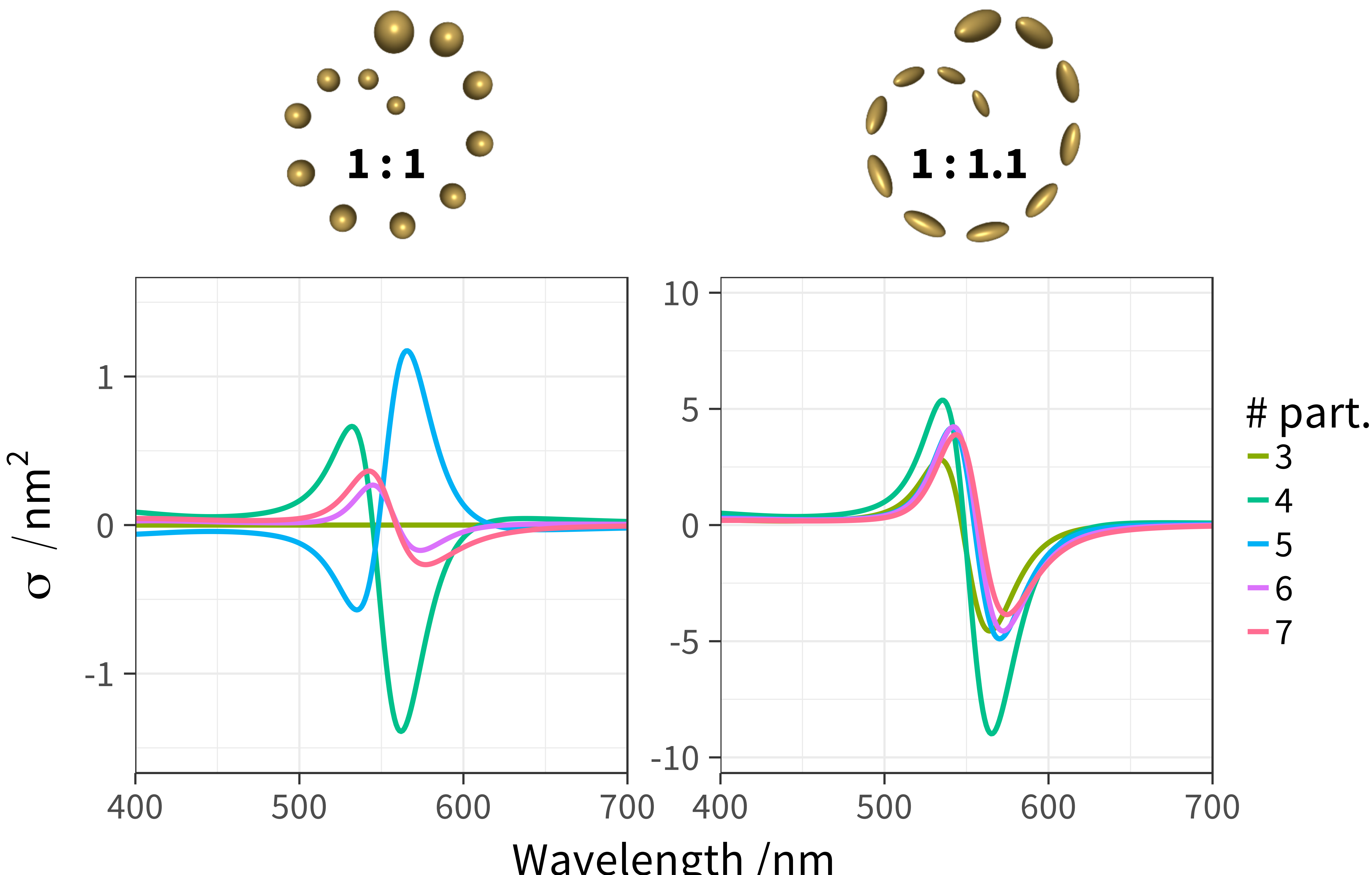
Diffractive arrays of nanorods

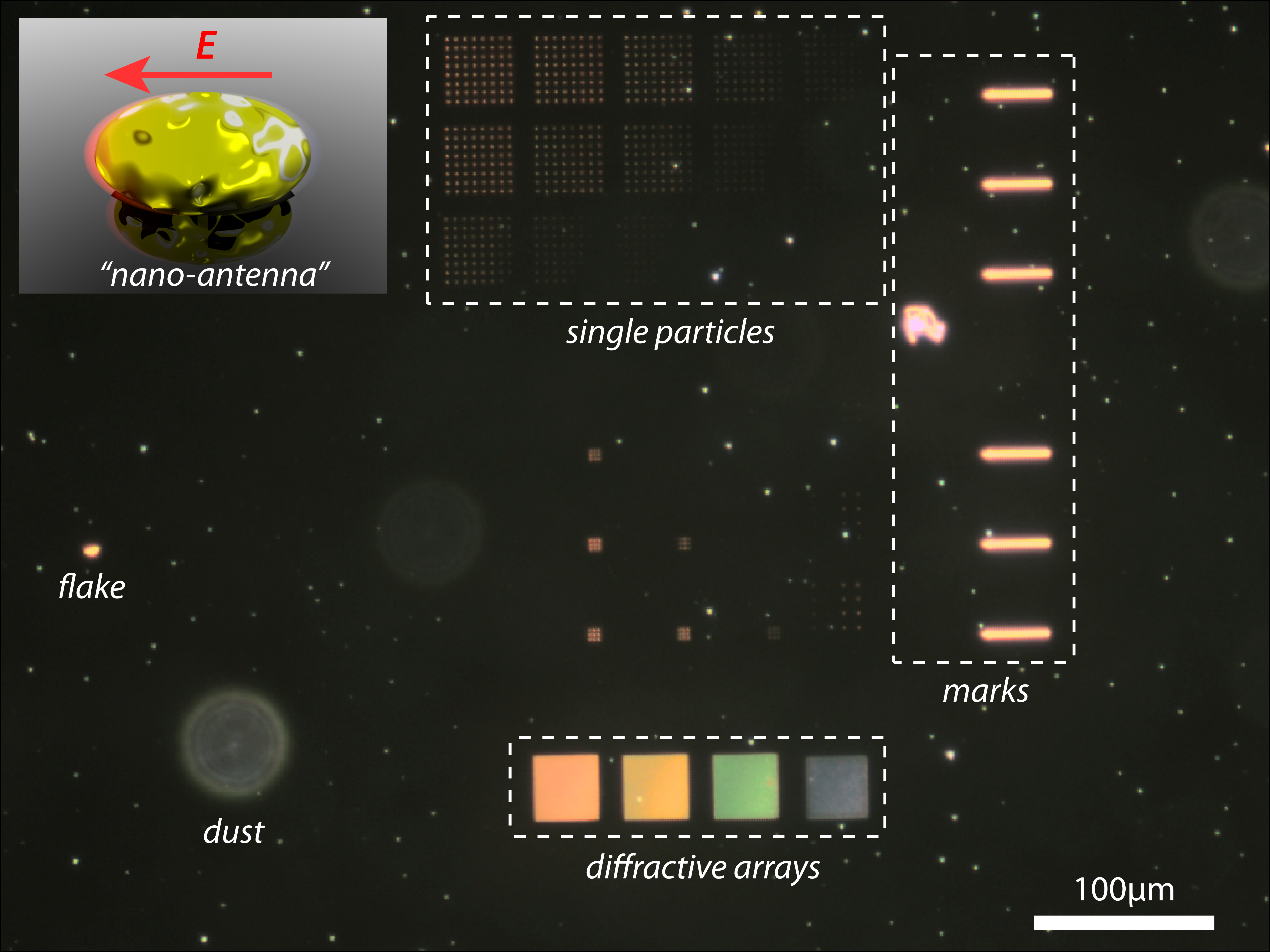




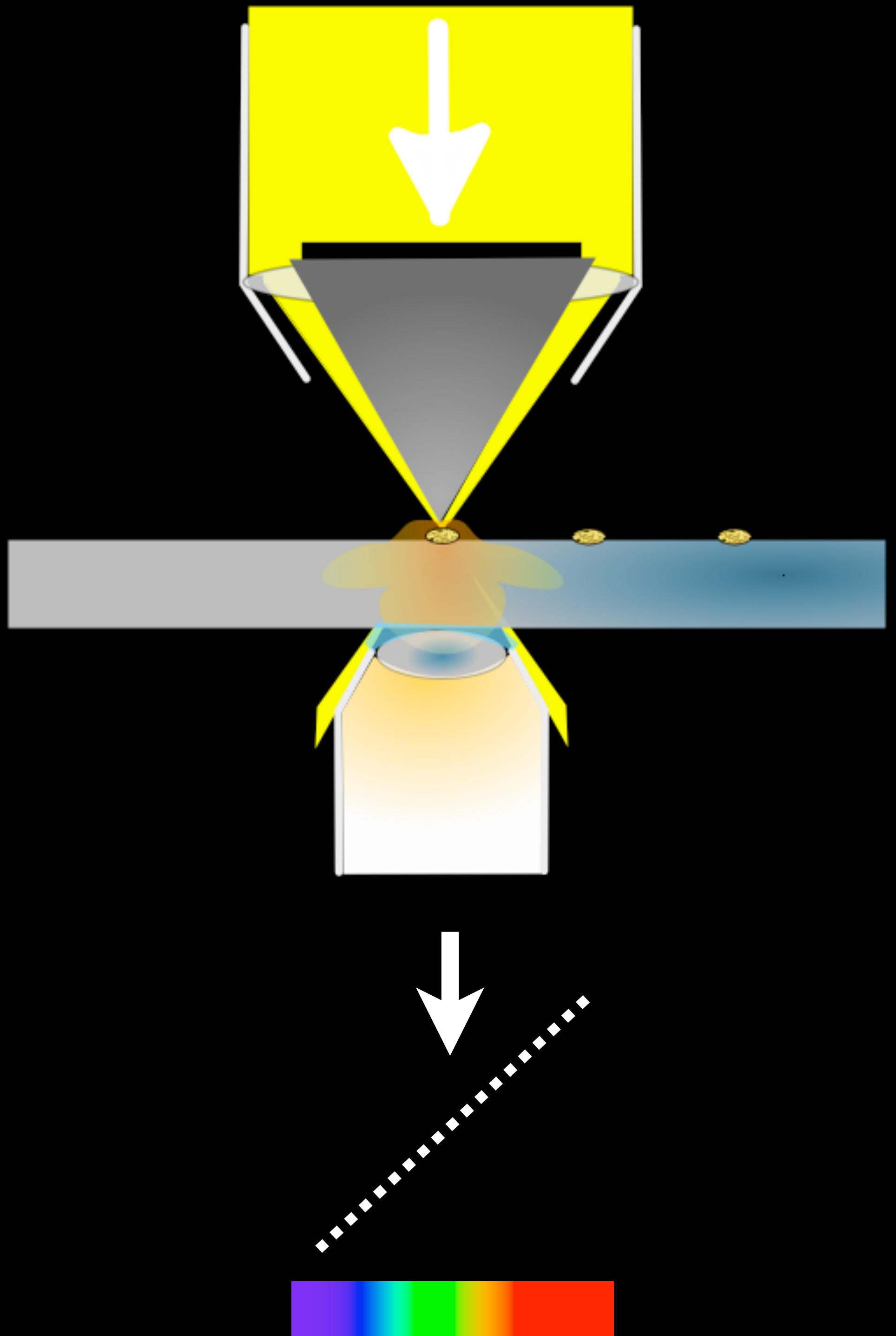
0.10
0.08
0.06
0.04
0.02
0.00
$\sigma_{ext}/\mu m^2$
500
600
700
800
900
wavelength / nm
diffraction
disorder
pseudo–random
40%
30%
20%
ordered

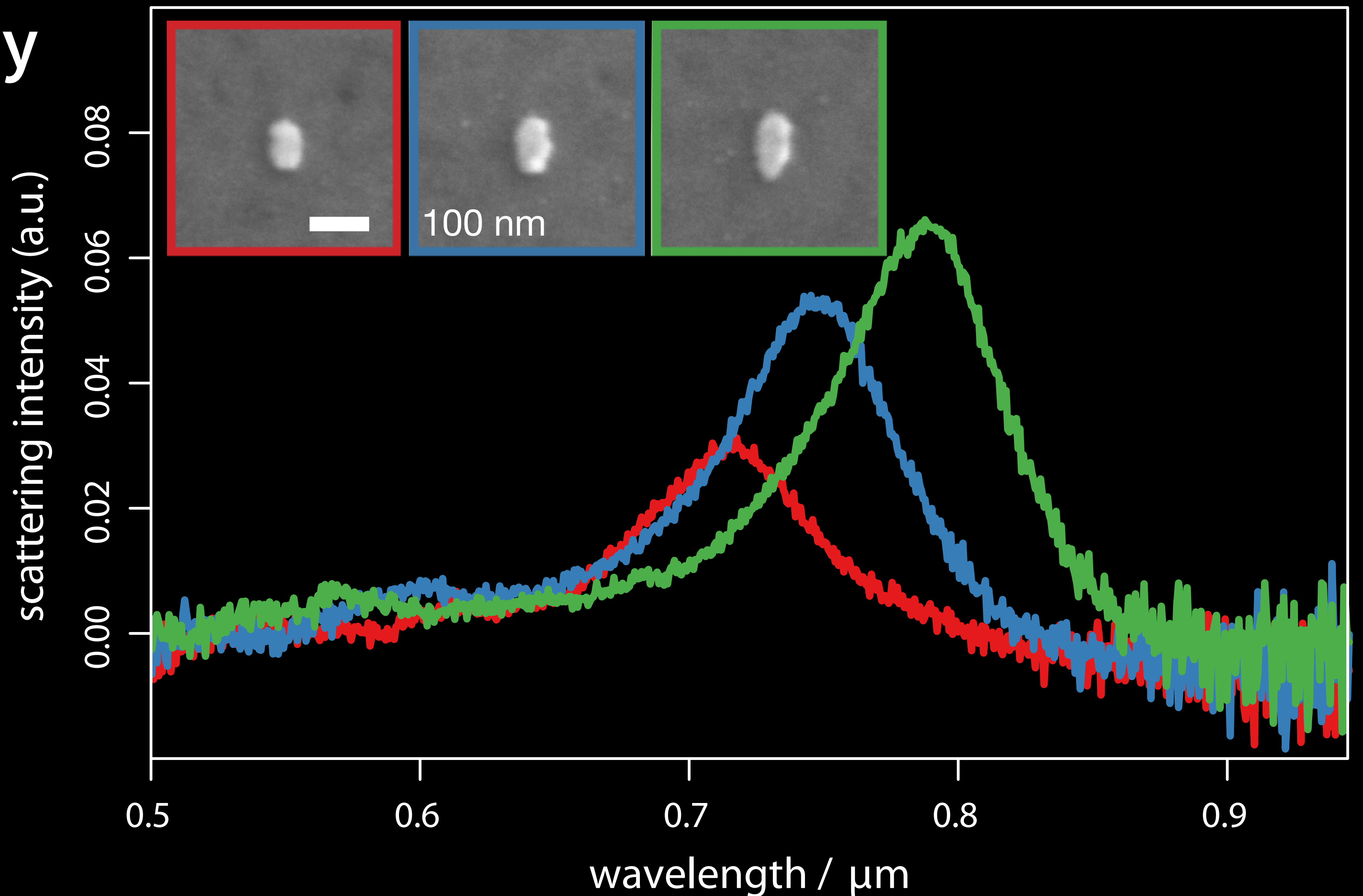
OPTIMISING OPTICAL ACTIVITY

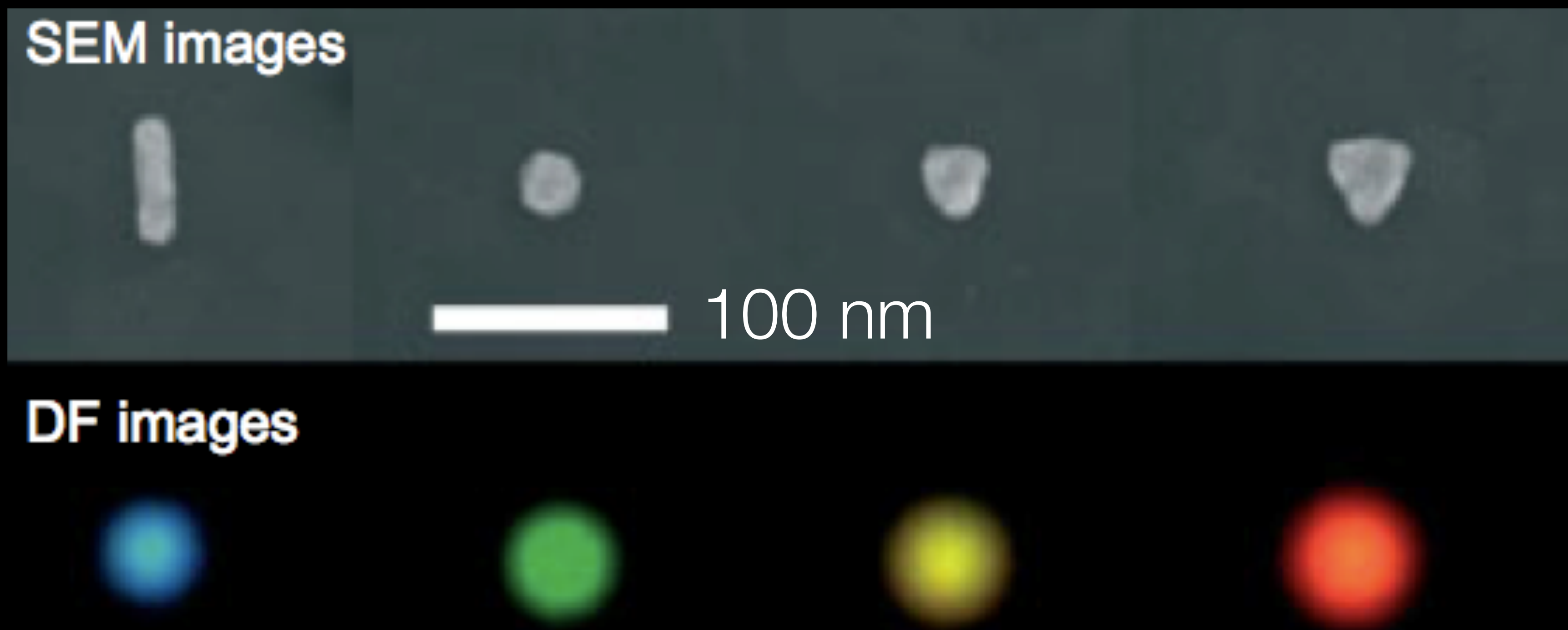



E
"nano-antenna"
single particles
marks
flake
dust
diffractive arrays
100µm

Dark-Field Spectroscopy







Dream 1: Probing individual chiral clusters?

Volume 93, Number 3 PHYSICAL REVIEW LETTERS week ending 16 JULY 2004

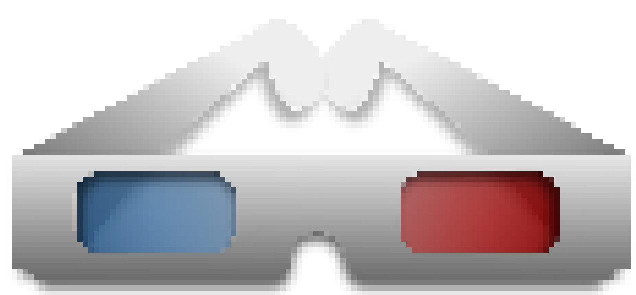
Detection and Spectroscopy of Gold Nanoparticles Using Supercontinuum White Light Confocal Microscopy

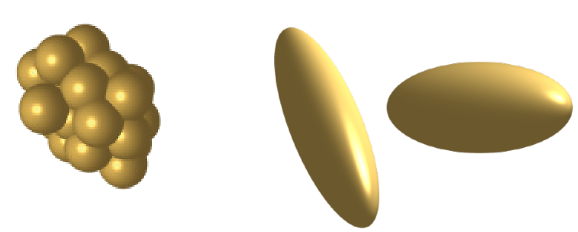
K. Lindfors,* T. Kalkbrenner,† P. Stoller, and V. Sandoghdar‡

Laboratory of Physical Chemistry, Swiss Federal Institute of Technology (ETH), CH-8093 Zurich, Switzerland

(Received 26 November 2003; published 15 July 2004)

We combine confocal microscopy using supercontinuum laser illumination and an interferometric detection technique to identify single nanoparticles of diameter below 10 nm. Spectral analysis of the signal allows us to record the plasmon resonance of a single nanoparticle. Our results hold great promise for fundamental studies of the optical properties of single metal clusters and for their use in biophysical applications.





DREAM 2: *SUPERCHIRAL* FIELDS?

PRL **104,** 163901 (2010) PHYSICAL REVIEW LETTERS week ending 23 APRIL 2010

Optical Chirality and Its Interaction with Matter

Yiqiao Tang and Adam E. Cohen*

Departments of Chemistry and Chemical Biology and of Physics, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, USA

(Received 22 November 2009; published 19 April 2010)

We introduce a measure of the local density of chirality of the electromagnetic field. This *optical chirality* determines the asymmetry in the rates of excitation between a small chiral molecule and its mirror image, and applies to molecules in electromagnetic fields with arbitrary spatial dependence. A continuity equation for optical chirality in the presence of material currents describes the flow of chirality, in a manner analogous to the Poynting theorem for electromagnetic energy. "Superchiral" solutions to Maxwell's equations show larger chiral asymmetry, in some regions of space, than is found in circularly polarized plane waves.

$$C \equiv \frac{\epsilon_0}{2}\mathbf{E} \cdot \nabla \times \mathbf{E} + \frac{1}{2\mu_0}\mathbf{B} \cdot \nabla \times \mathbf{B}$$

CONCLUSIONS

- Rich new physics to explore with chiral plasmonics
- Enhanced chiroptical spectroscopies – *the new SERS*?
- Experiments & theory – get in touch!

THANKS

- Luis Liz-Marzán’s group (Spain), Bill Barnes’ group (UK)
- Eric Le Ru’s group (VUW)

SUPPLEMENTARY INFO

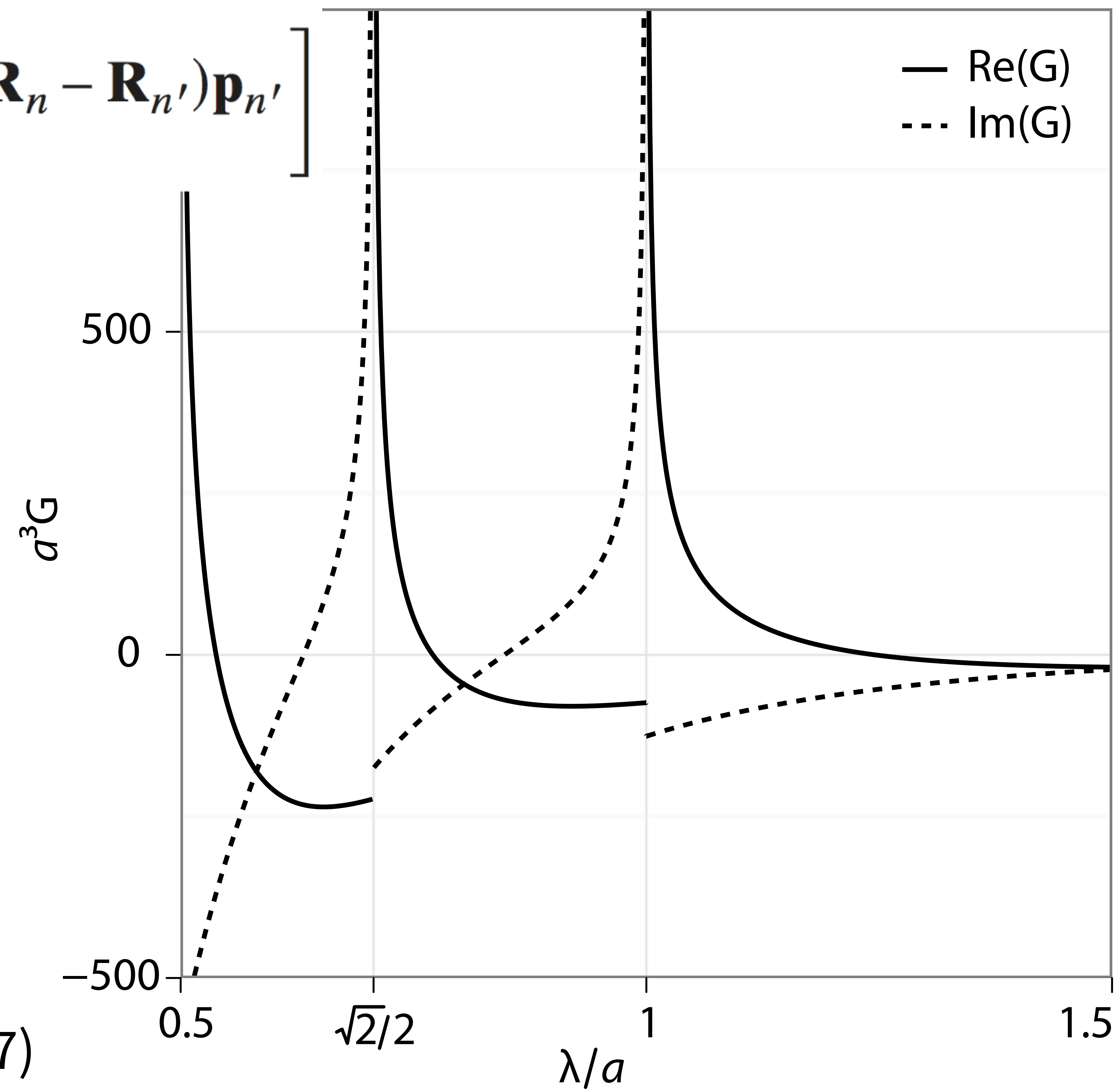
Lattice sums in electromagnetism…

$$\mathbf{p}_n = \alpha_E \left[\mathbf{E}^{\text{ext}}(\mathbf{R}_n) + \sum_{n' \neq n} \mathcal{G}^0(\mathbf{R}_n - \mathbf{R}_{n'})\mathbf{p}_{n'} \right]$$

$$\mathcal{G}^0(\mathbf{r}) = (k^2 + \nabla\nabla)\frac{e^{ikr}}{r}$$

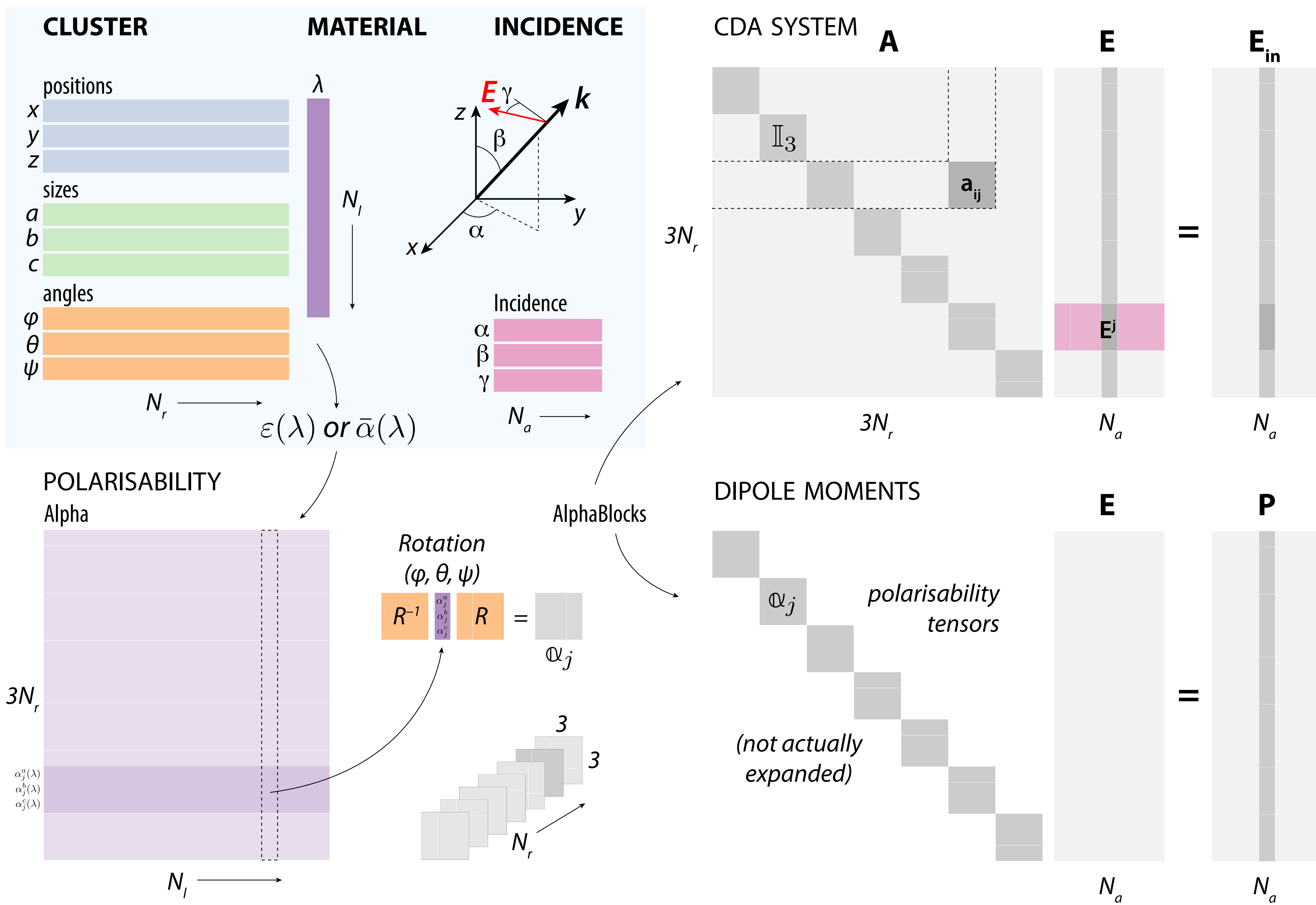
$$\mathbf{p} = \frac{1}{1/\alpha_E - G(\mathbf{k}_\parallel)}\mathbf{E}^{\text{ext}}$$

$$G(\mathbf{k}_\parallel) = \sum_{n \neq 0} \mathcal{G}^0(\mathbf{R}_n) e^{-i\mathbf{k}_\parallel \cdot \mathbf{R}_n}$$



F. J. García de Abajo
Rev. Mod. Phys. 79, 1267 (2007)

Matrix layout



$$\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{inc}} + \sum_{\text{dipoles}\setminus\text{itself}} \mathbf{E}_{\text{dip}} \qquad \mathbf{p}_{\text{dip}} = \alpha \mathbf{E}_{\text{loc}}$$

$$\mathbf{E}^{\text{dipole}} = \frac{e^{i\omega r/c}}{4\pi\varepsilon_0} \left\{ \frac{\omega^2}{c^2 r} \hat{\mathbf{r}} \times \mathbf{p} \times \hat{\mathbf{r}} + \left(\frac{1}{r^3} - \frac{i\omega}{cr^2} \right) [3(\hat{\mathbf{r}} \cdot \mathbf{p})\hat{\mathbf{r}} - \mathbf{p}] \right\}$$

$$A\mathbf{P} = \text{E}_{\text{inc}}$$

$$A_{ij} = \frac{e^{(ikr_{ij})}}{r_{ij}} \left\{ k^2 (\hat{\mathbf{r}}_{ij} \otimes \hat{\mathbf{r}}_{ij} - \mathbb{I}) + \frac{ik\mathbf{r}_{ij} - 1}{r_{ij}^2} (3\mathbf{r}_{ij} \otimes \mathbf{r}_{ij} - \mathbb{I}) \right\}$$

$$\sigma_{\text{ext}} = \frac{4\pi k}{|\text{E}_{\text{inc}}|^2} \Im(\mathbf{E}_{\text{inc}}{}^* \cdot \mathbf{P}) \qquad \sigma_{\text{CD}} = \langle \sigma_L \rangle_\Omega - \langle \sigma_R \rangle_\Omega$$

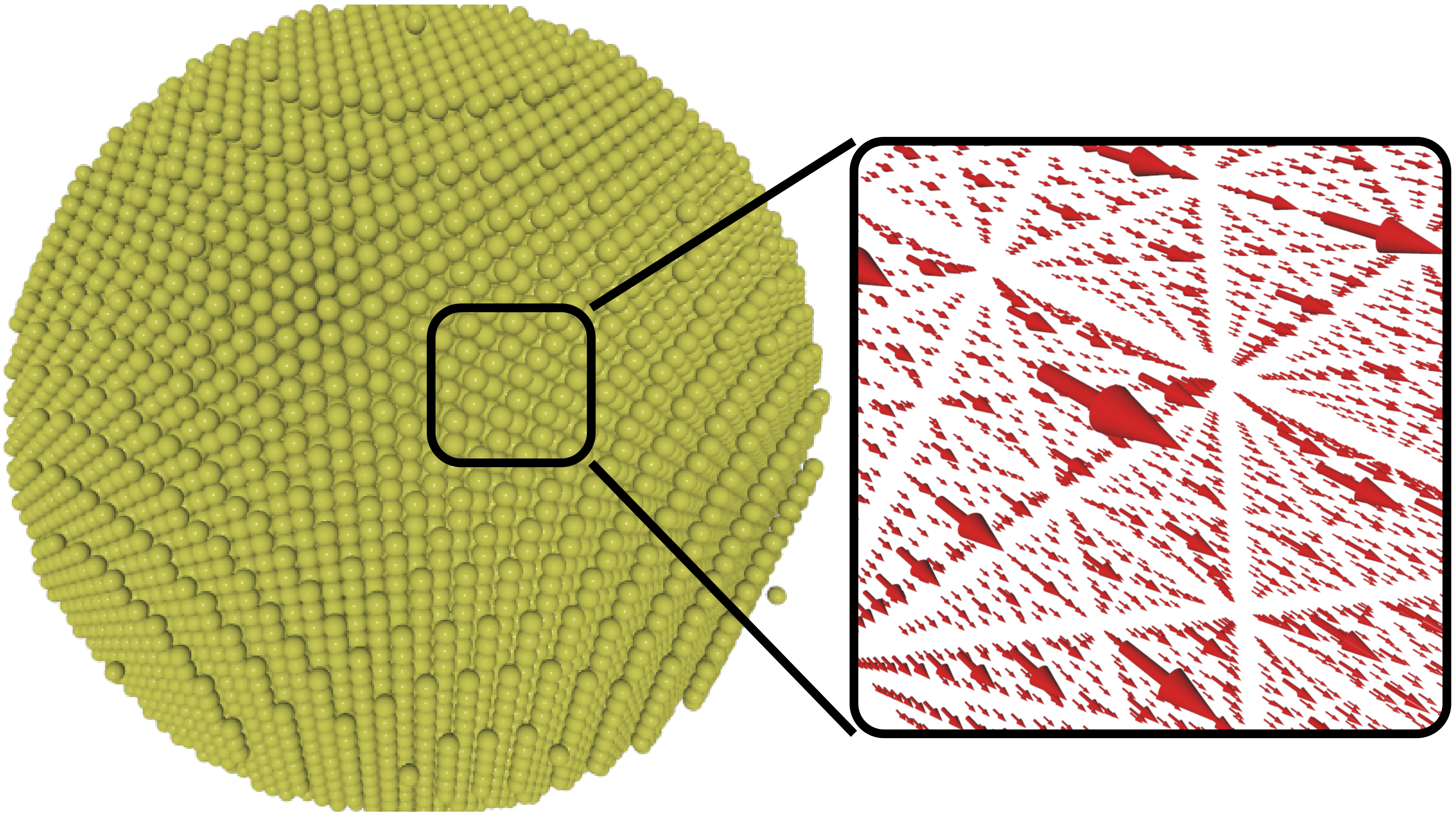
$$\mathbf{E}_{\text{inc}} = \frac{\exp i(\omega t - k_x x)}{\sqrt{2}} \begin{pmatrix} 0 \\ i \\ 1 \end{pmatrix} \qquad \textit{(right-handed)}$$

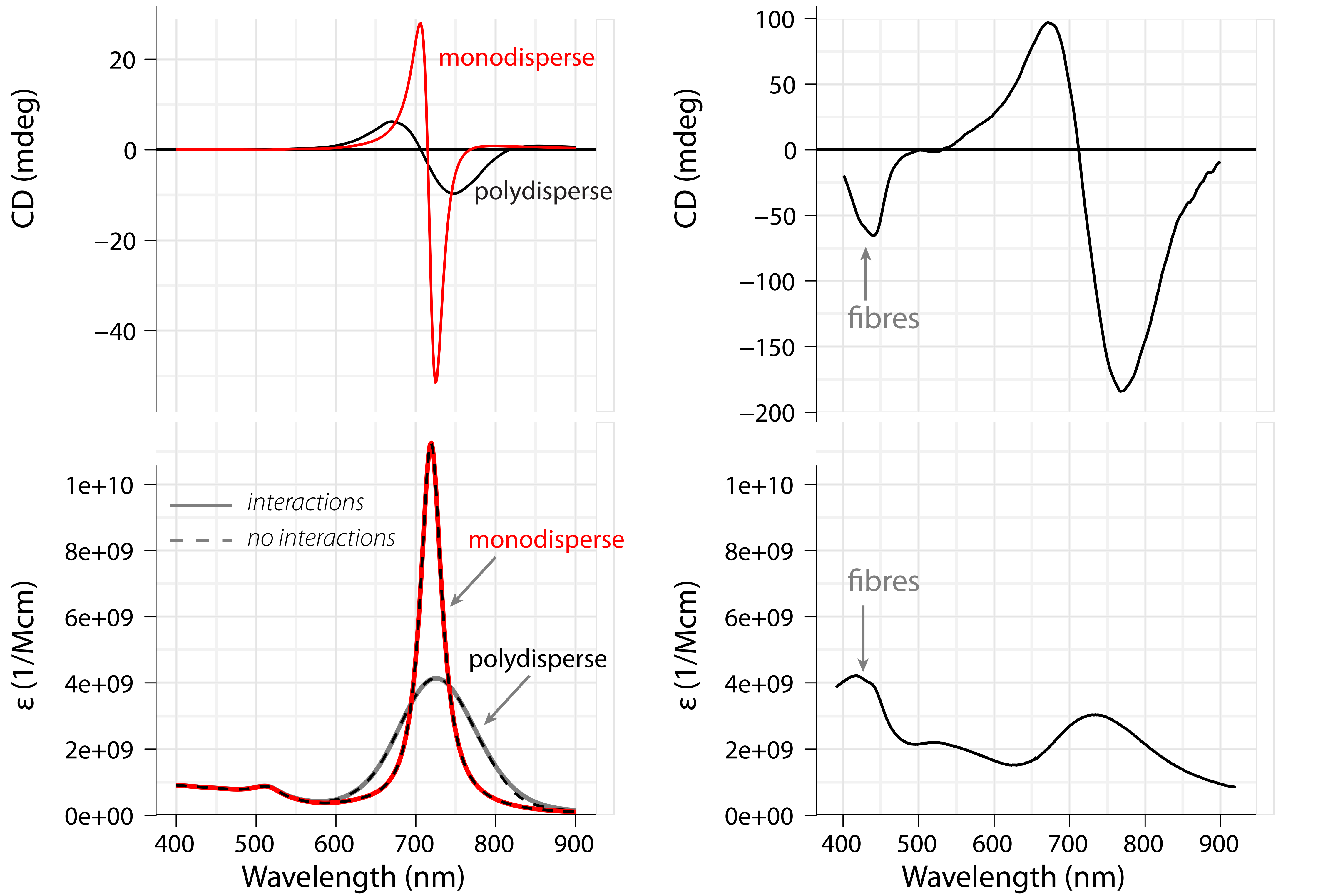
$$\mathbf{E}_{\text{inc}} = \frac{\exp i(\omega t - k_x x)}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ i \end{pmatrix} \qquad \textit{(left-handed)}$$

RADIATIVE CORRECTION & SELF-REACTION

	Radiative correction	Self-reaction
total field	$\mathbf{E}^i = \mathbf{E}_{\text{inc}} + \sum_{j \neq i} \mathbb{G}_{ij} \alpha_j \mathbf{E}^j$	$\widetilde{\mathbf{E}}^i = \mathbf{E}^i + \mathbf{E}^{\text{SR}} = \mathbf{E}^i + \mathbb{G}_{ii} \alpha_i \mathbf{E}^i$
dipole moment	$\mathbf{p} = \alpha \mathbf{E}$	$\mathbf{p} = \alpha^0 \widetilde{\mathbf{E}} = \alpha^0 (\mathbf{E} + \mathbf{E}^{\text{SR}})$
polarisability	$\alpha = \frac{1}{\frac{1}{\alpha^0} - G}$ (RC)	α^0 (*static*)
absorption	$P_{\text{abs}} = \frac{\omega}{2} \left(\Im(\alpha) \lvert \mathbf{E} \rvert^2 - \Im(G) \lvert \mathbf{P} \rvert^2 \right)$	$P_{\text{abs}} = \frac{\omega}{2} \Im(\alpha^0) \lvert \widetilde{\mathbf{E}} \rvert^2$

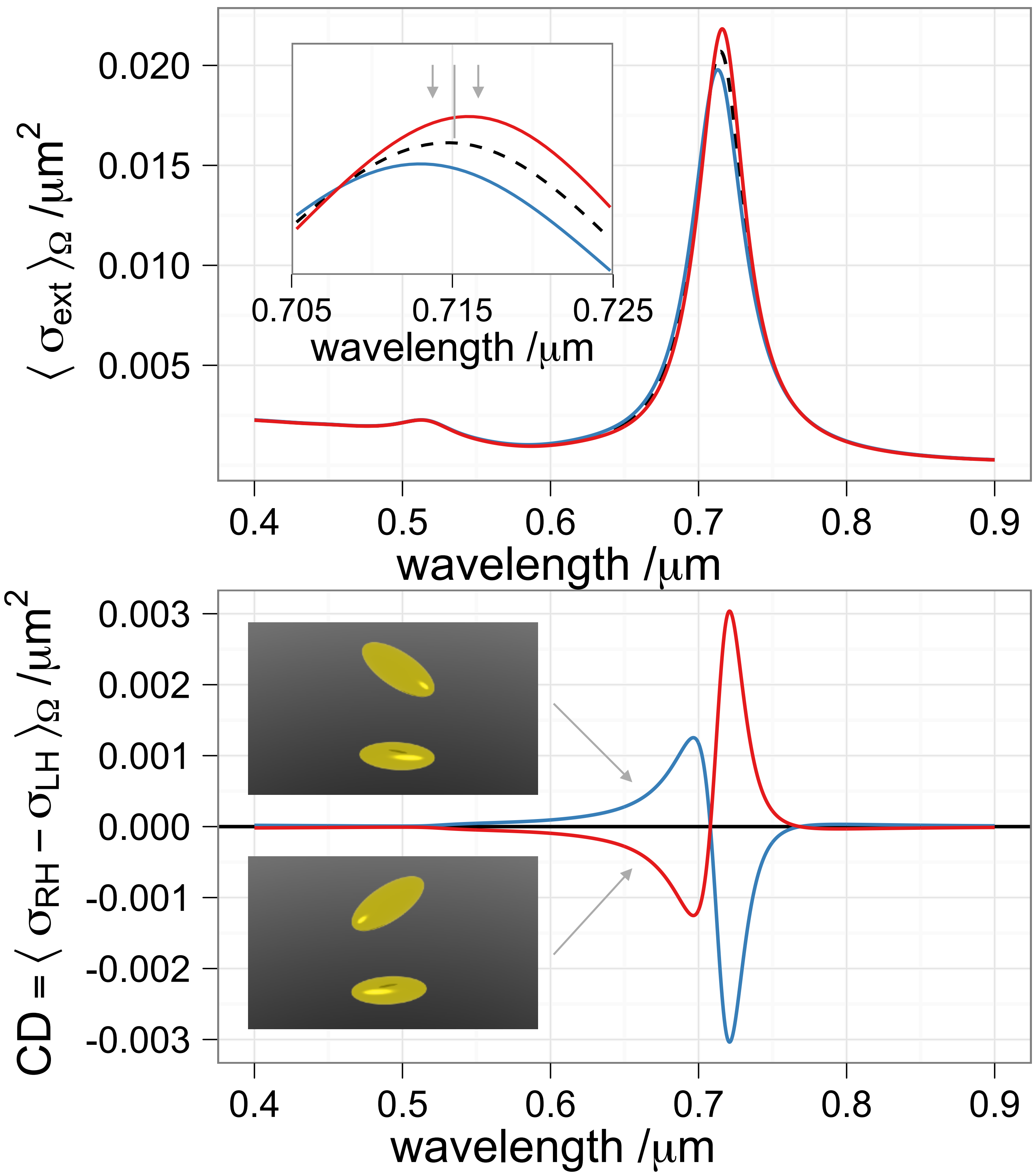
(Related topic) Discrete Dipole Approximation

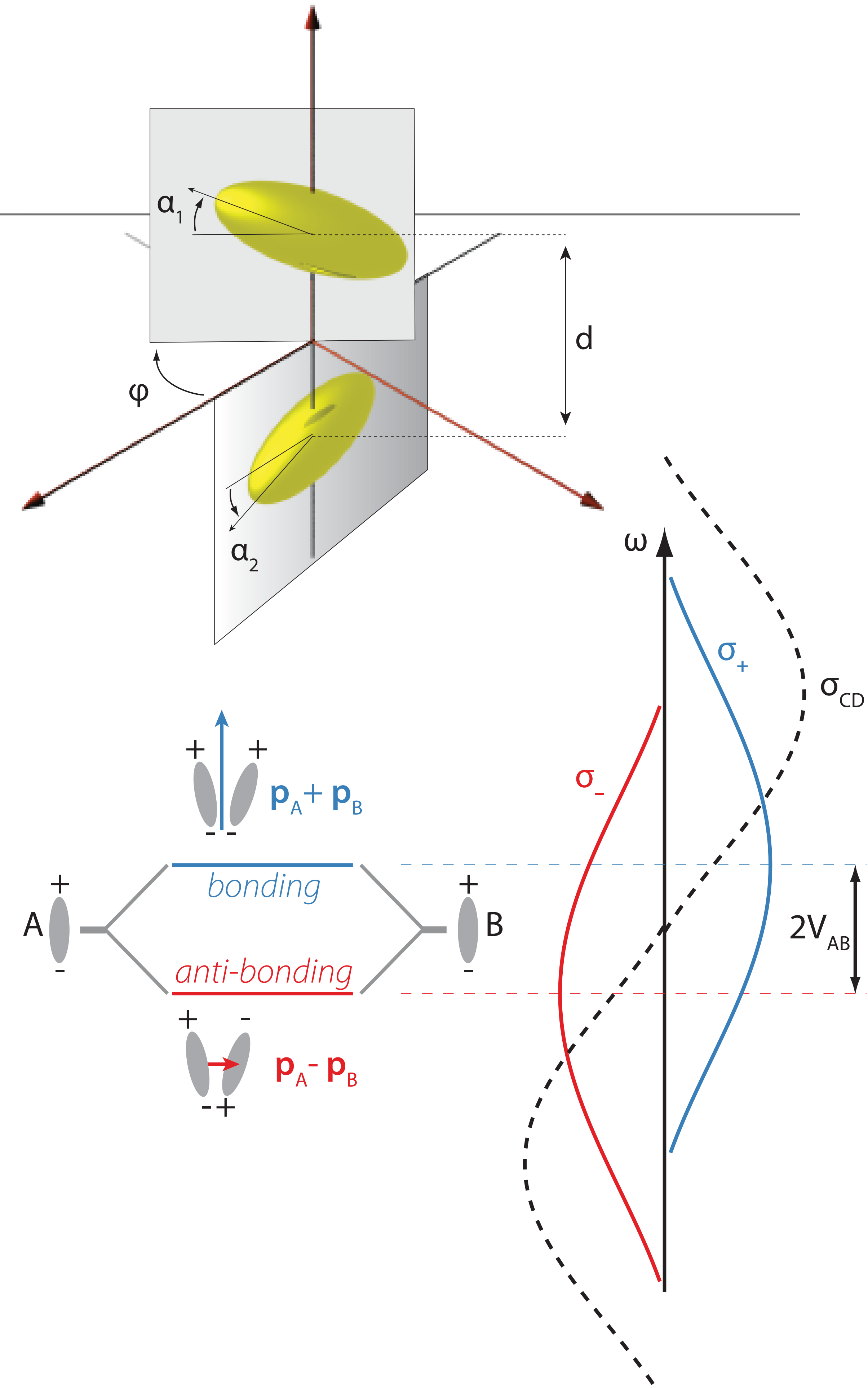




CD (mdeg)
20
0
−20
−40
monodisperse
polydisperse
100
50
0
−50
−100
−150
−200
fibres
ε (1/Mcm)
1e+10
8e+09
6e+09
4e+09
2e+09
0e+00
interactions
no interactions
monodisperse
polydisperse
fibres
400
500
600
700
800
900
Wavelength (nm)

Chiral plasmon hybridisation





Project *West Ford* (1961–1963)

- **500 000 000** copper needles
- Nature 192 (1961); Science 134, (1961) Adv. Space Res. 35, (2005) …
- Ignited some debate (astronomers…)

"At various times, apprehension has been expressed concerning several possible deleterious effects which might result from such a dipole belt"