Structural DNA nanotechnology as a playground for plasmonics

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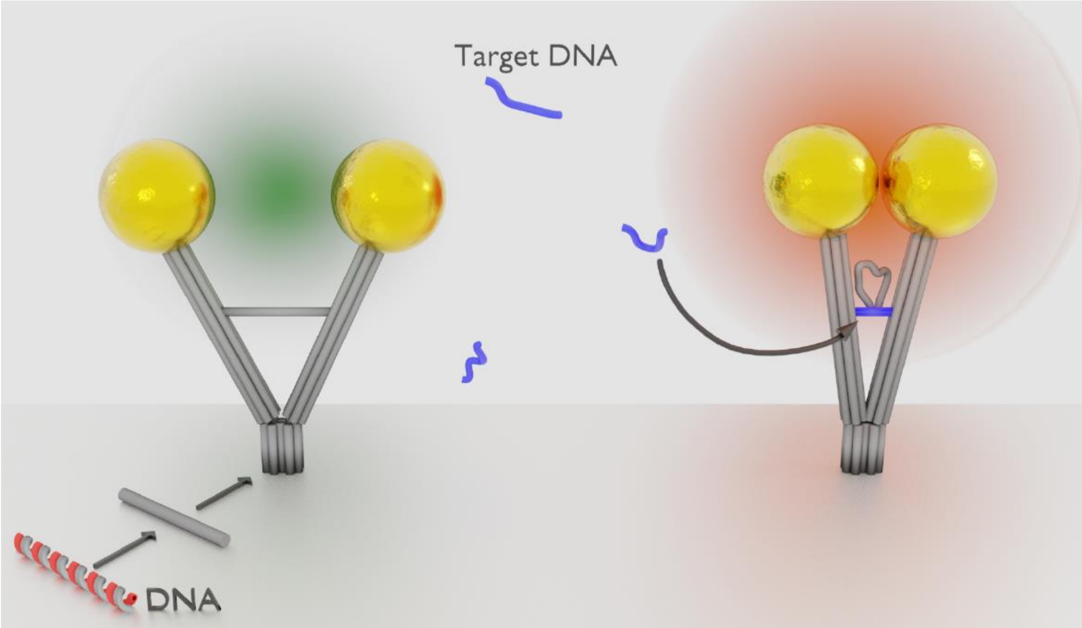
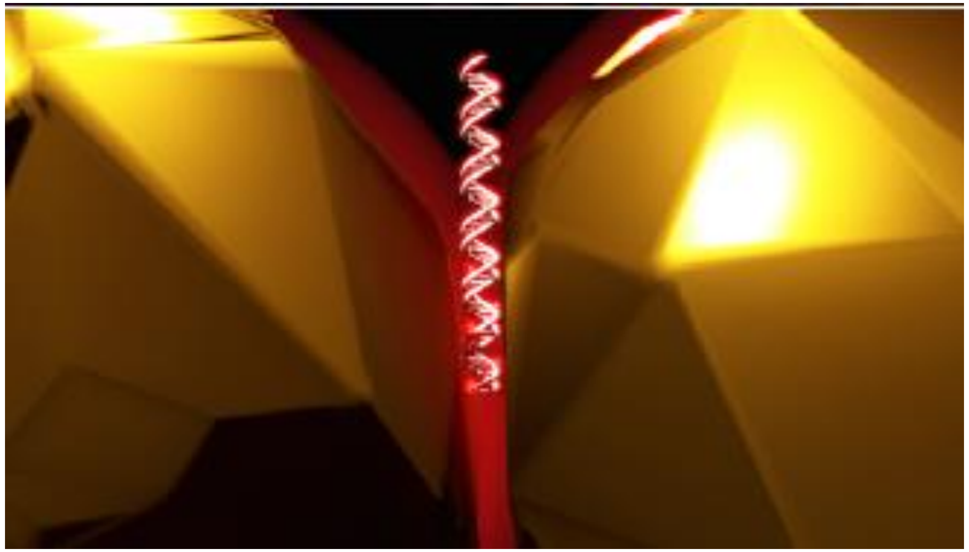
http://www.institut-langevin.espci.fr/optical_antennas

Why structural DNA nanotechnology?

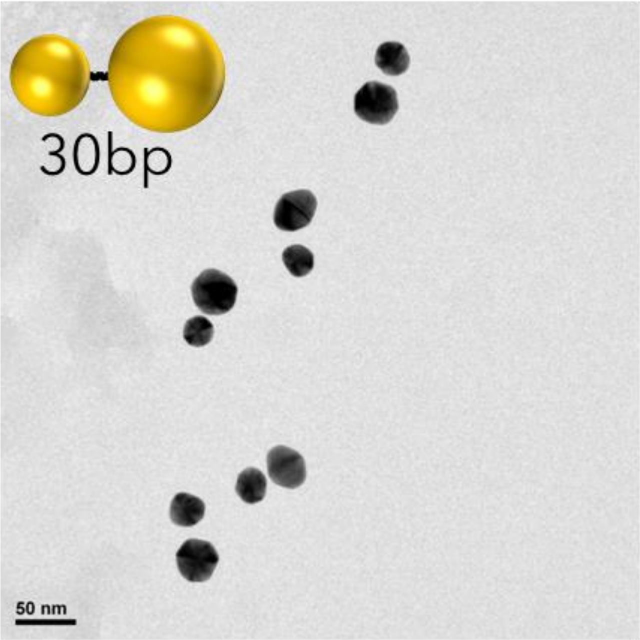




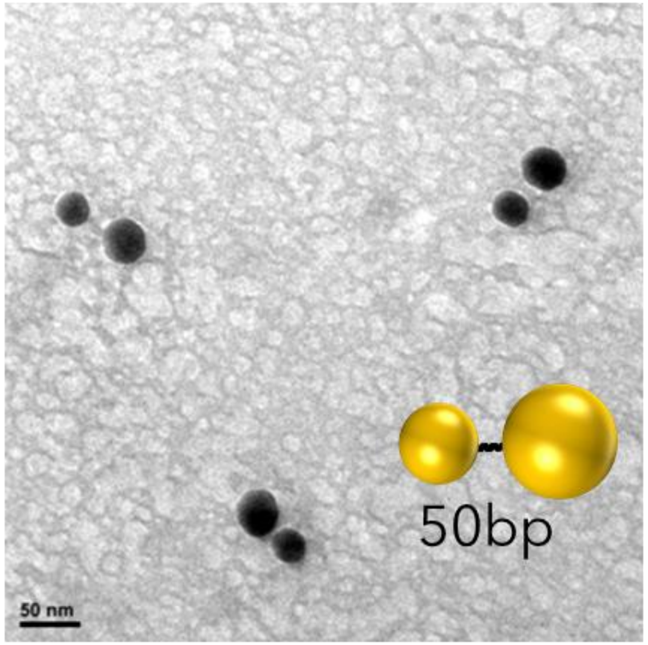
- Producing dynamic nanostructures whose morphology and optical properties can be actively and specifically modulated
- Introducing a controlled number of quantum emitters in the hot-spot of a plasmonic resonator

DNA linked gold nanoparticle dimers

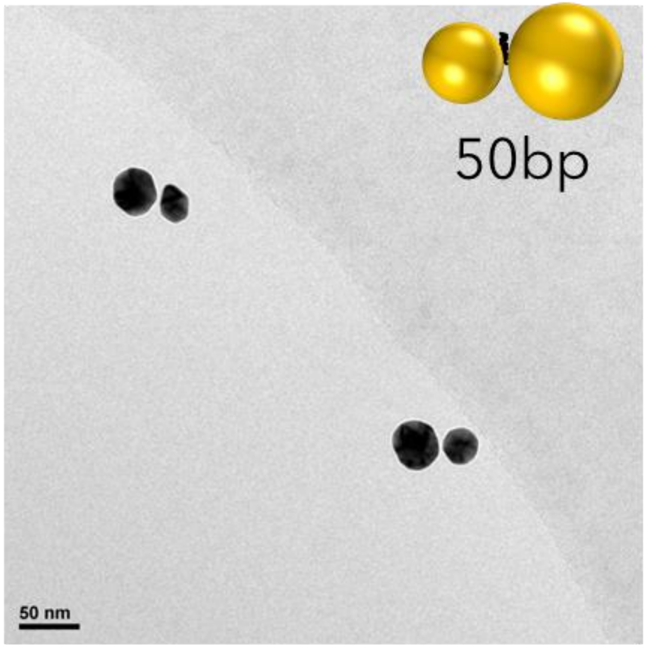
40 nm / 30 nm Au dimers:



d=13±2 nm



d=17.5±3 nm

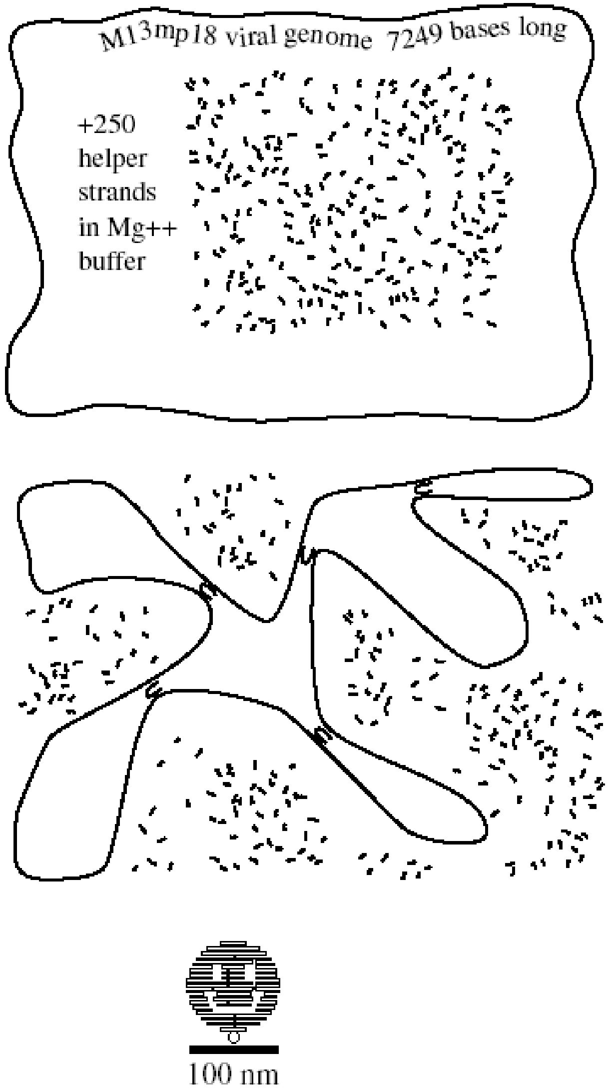


d=7±1 nm

cryo-EM imaging (to avoid drying effects)

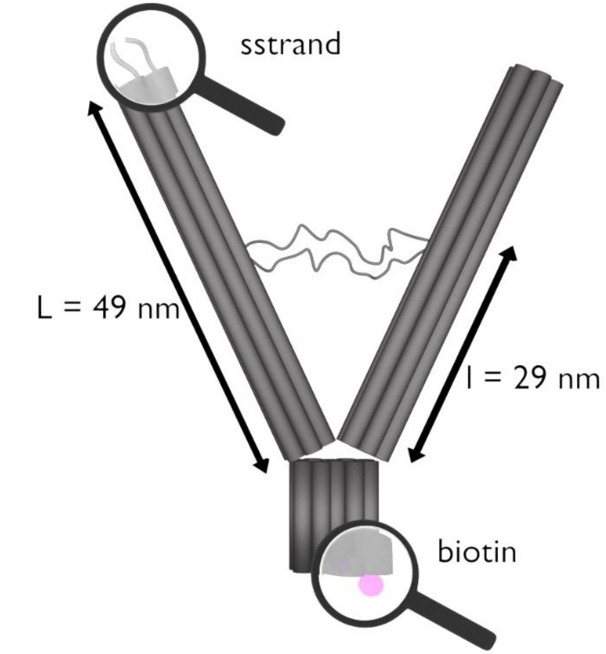
M. P. Busson et al, Nano Lett. 2011

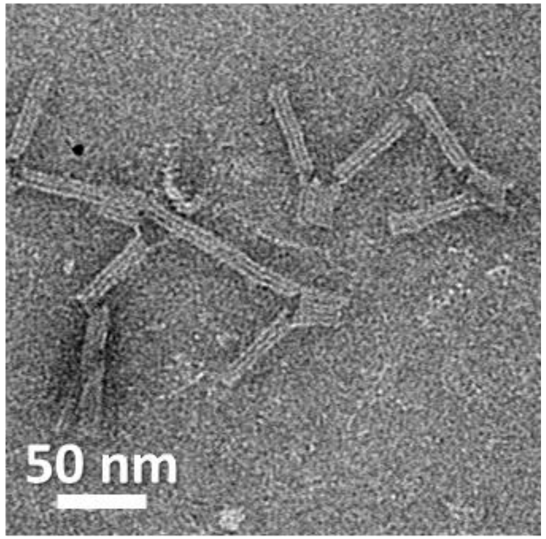
DNA origami templates



P.K. Rothemund, Nature 2006

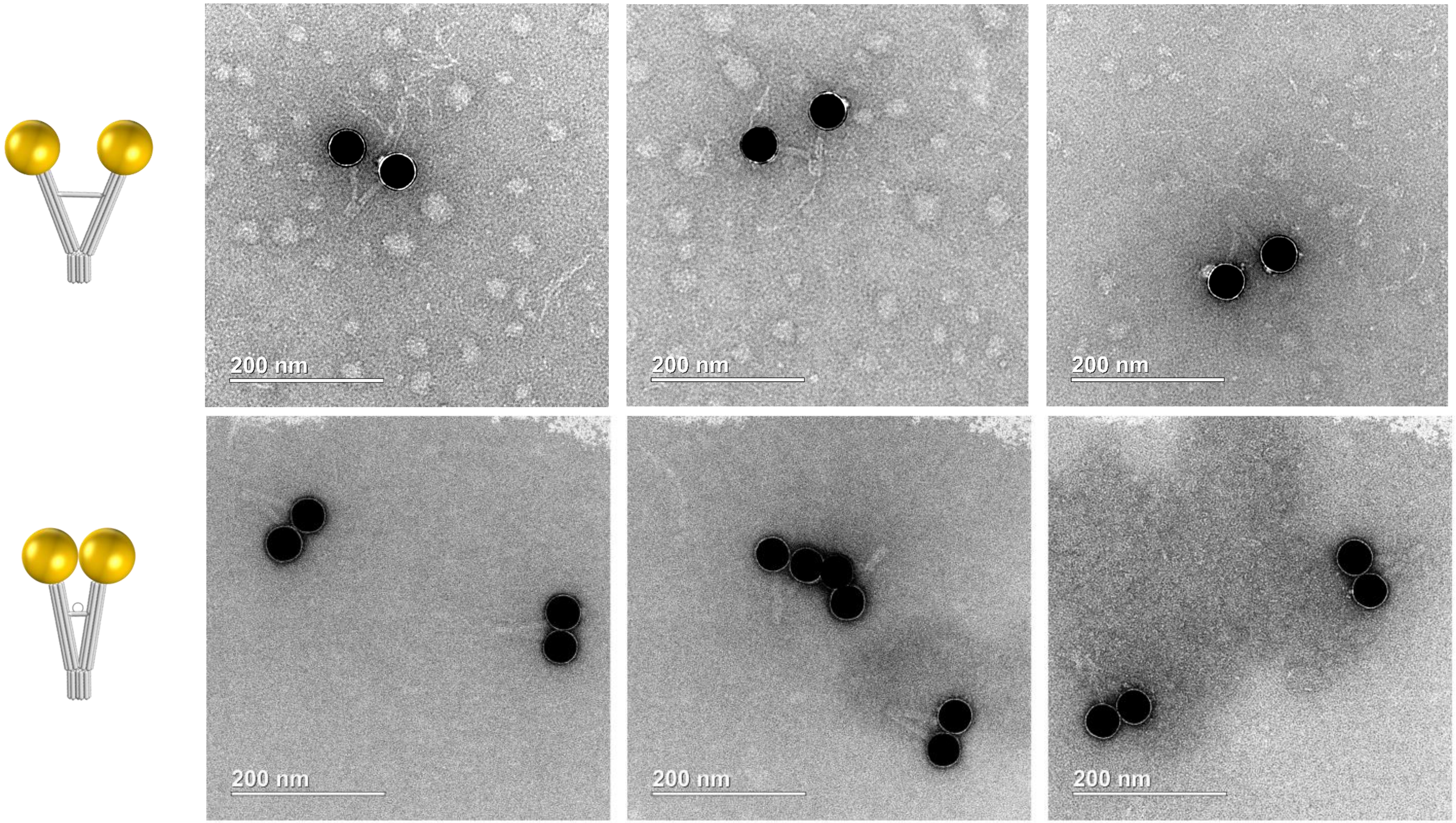
S. M. Douglas et al, Nature 2009 & H. Dietz et al, Science 2009





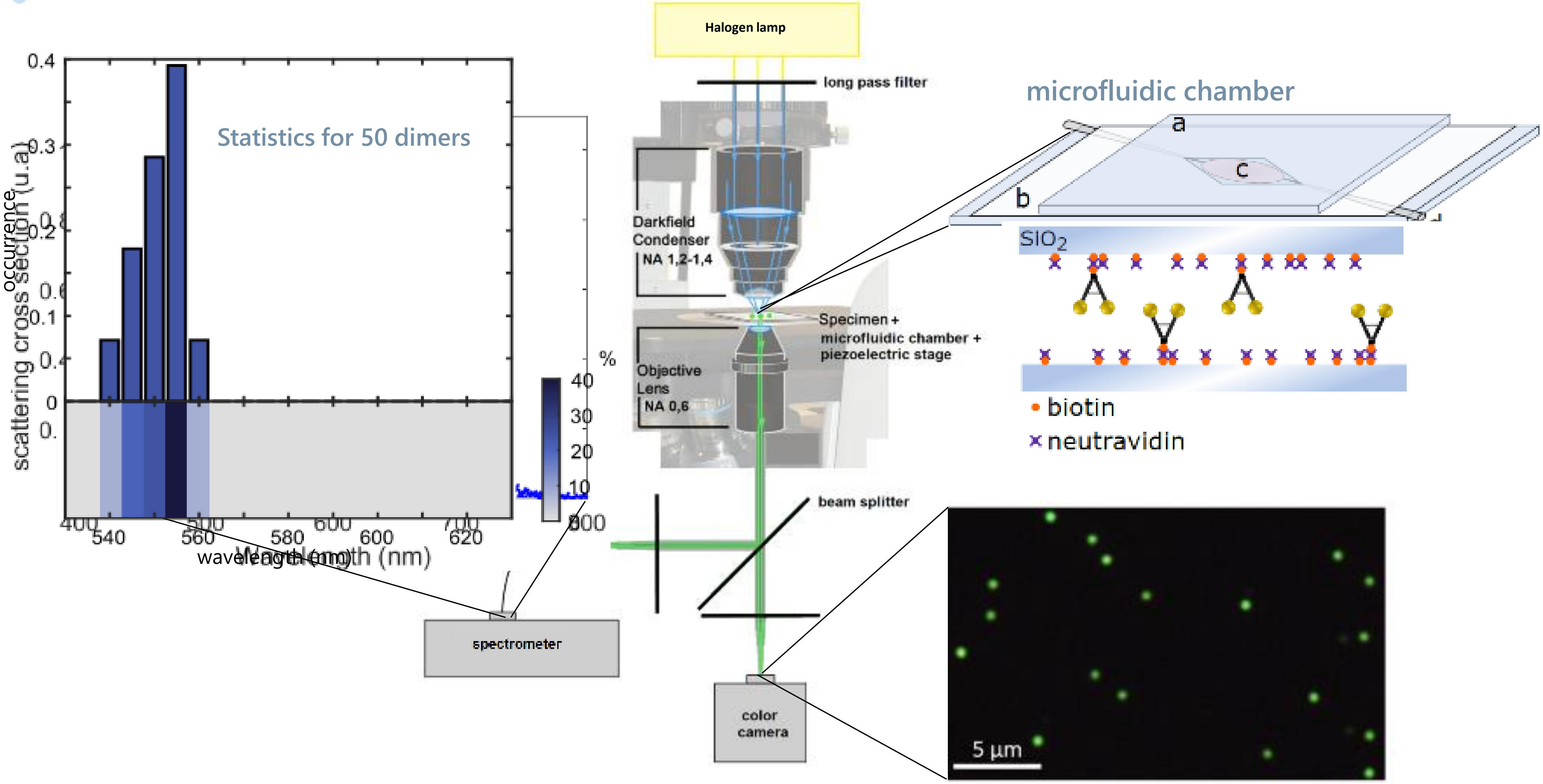
G. Bellot & coworkers (CBS, Montpellier)

Gold nanoparticle dimers on DNA-origami templates

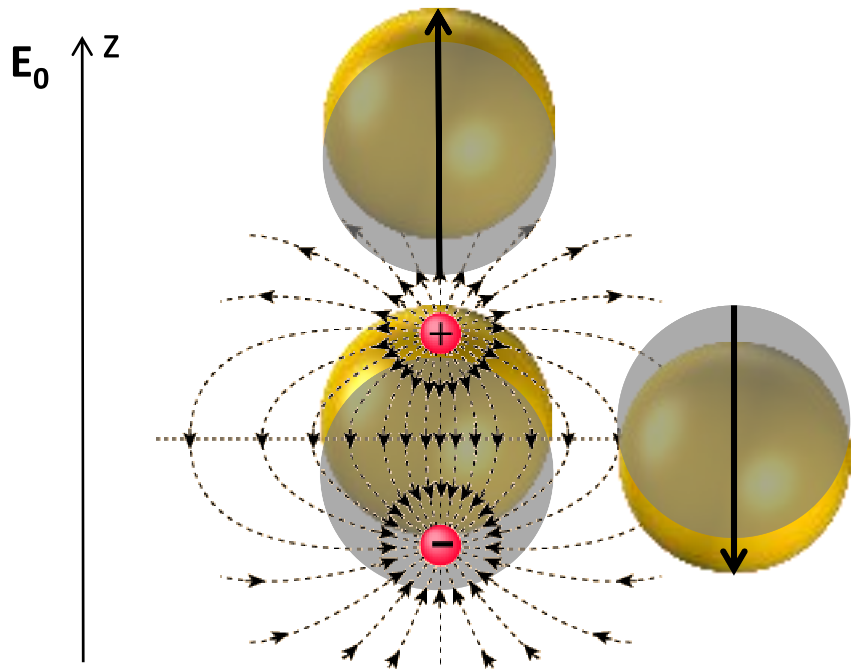


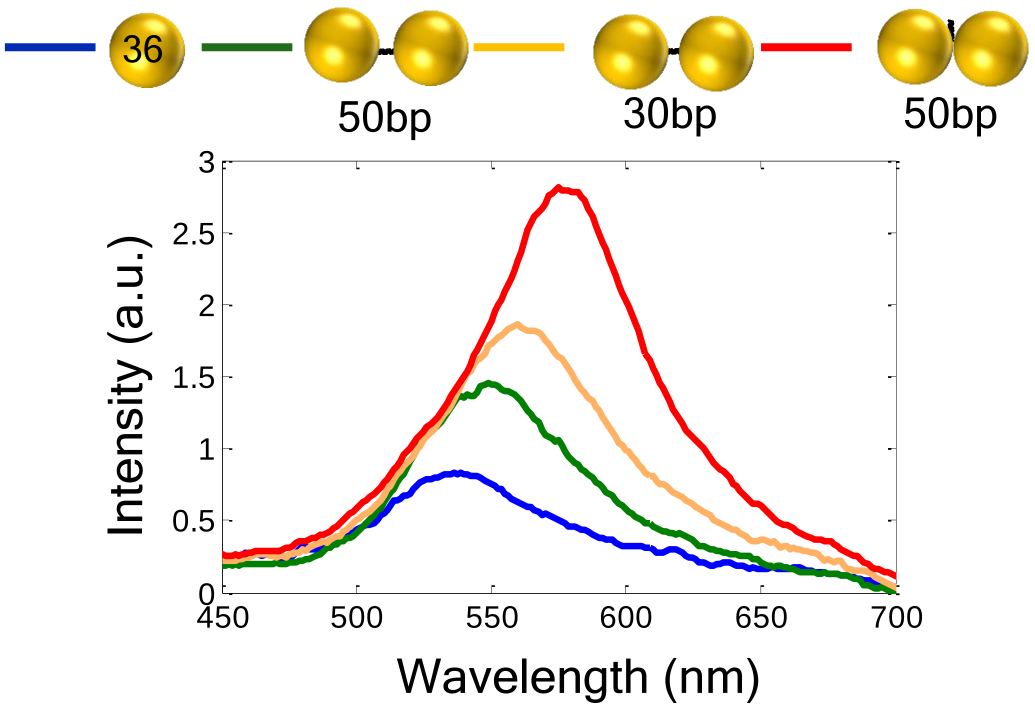
Chemically etched gold nanospheres: S. Marguet (NIMBE, Saclay)

Scattering spectroscopy



Near-field plasmon coupling





Reducing the interparticle distance induces a wavelength redshift of the longitudinal plasmon mode of the dimers and increases the scattering cross-section of the antenna

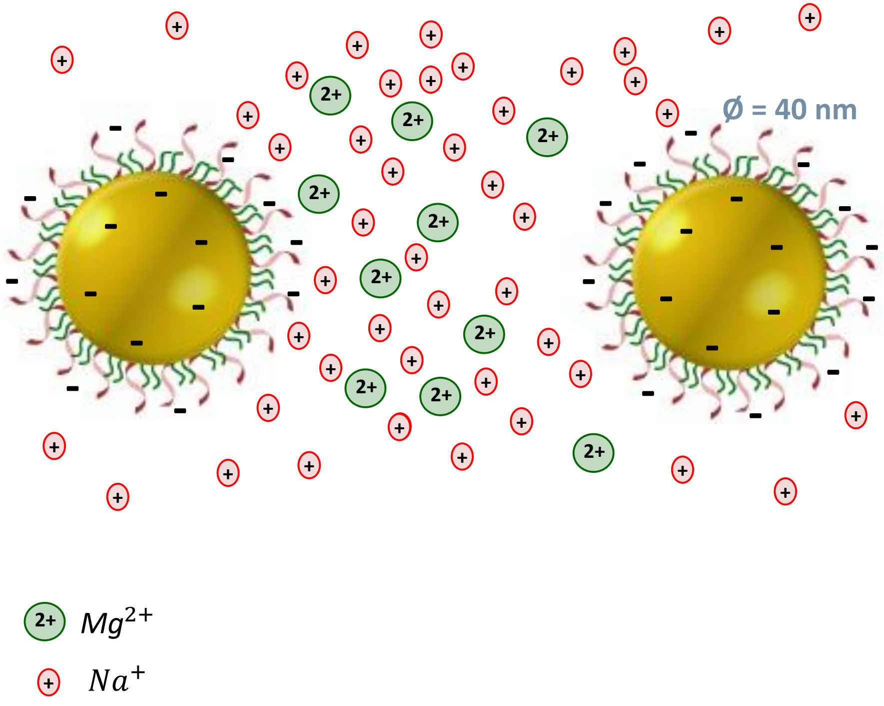
Monitoring the longitudinal plasmon resonance allows a **nanoscale analysis of the interparticle distance**

M. P. Busson et al, Nano Lett. 2011

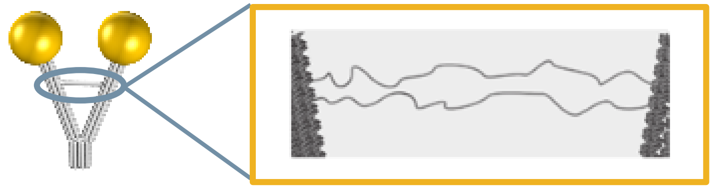
Actively tuning the interparticle distance

Ionic strength [M]

$$I = \frac{1}{2}\sum_i c_i z_i^2$$



Single-stranded active site

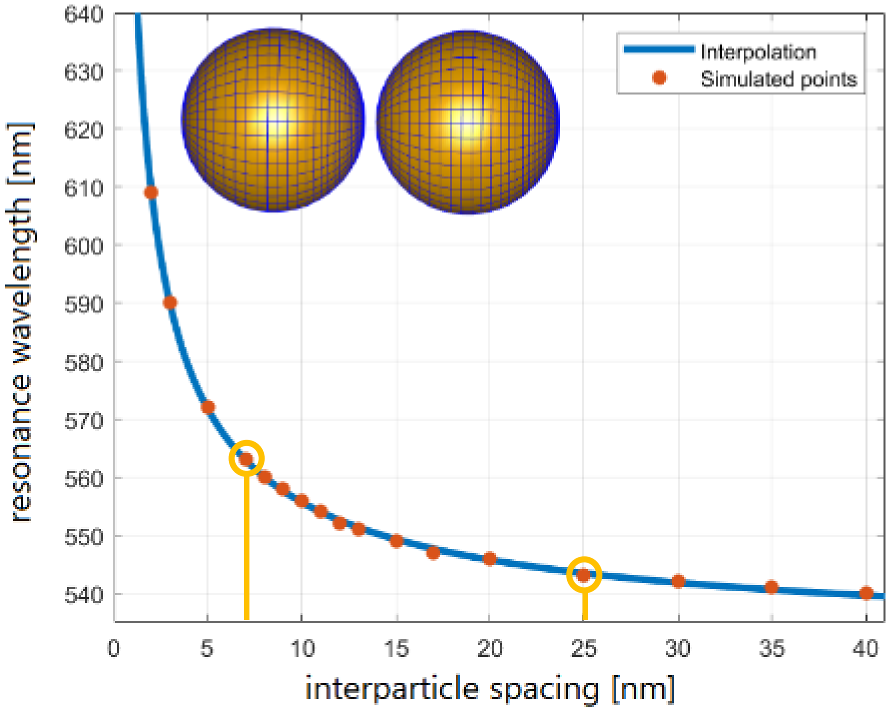


Actively tuning the interparticle distance

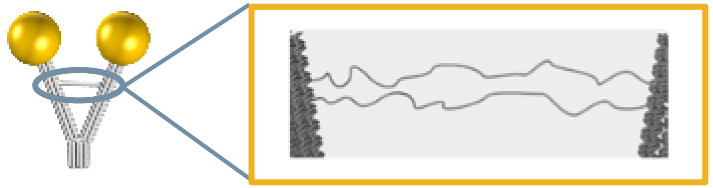
Ionic strength [M]

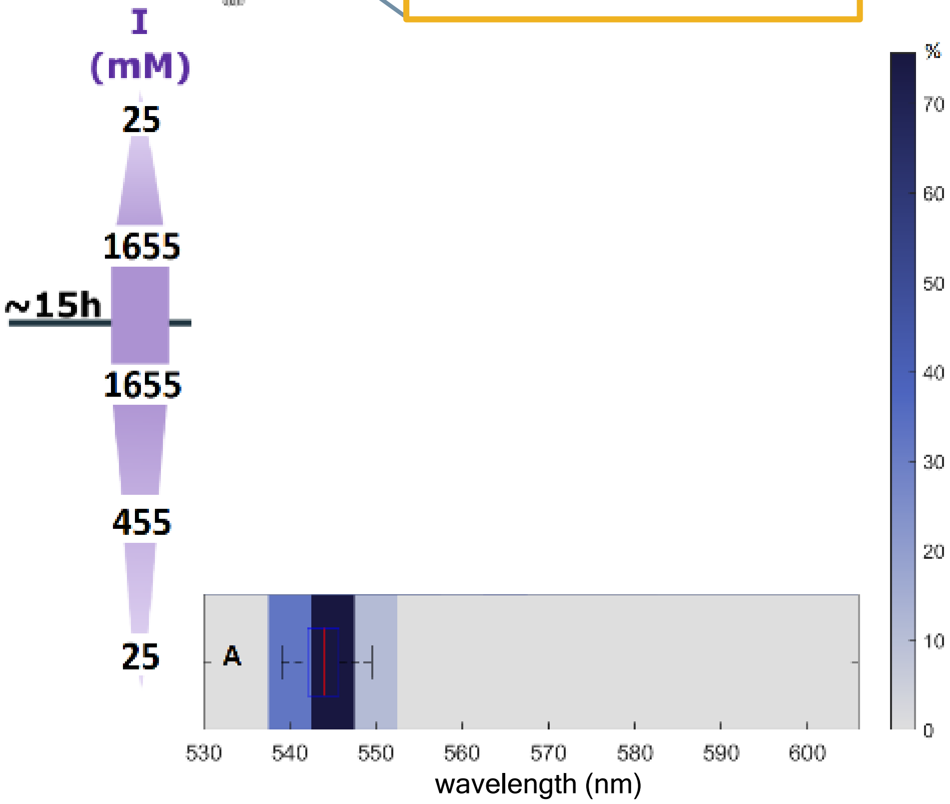
$$I = \frac{1}{2}\sum_i c_i z_i^2$$

calibration curve

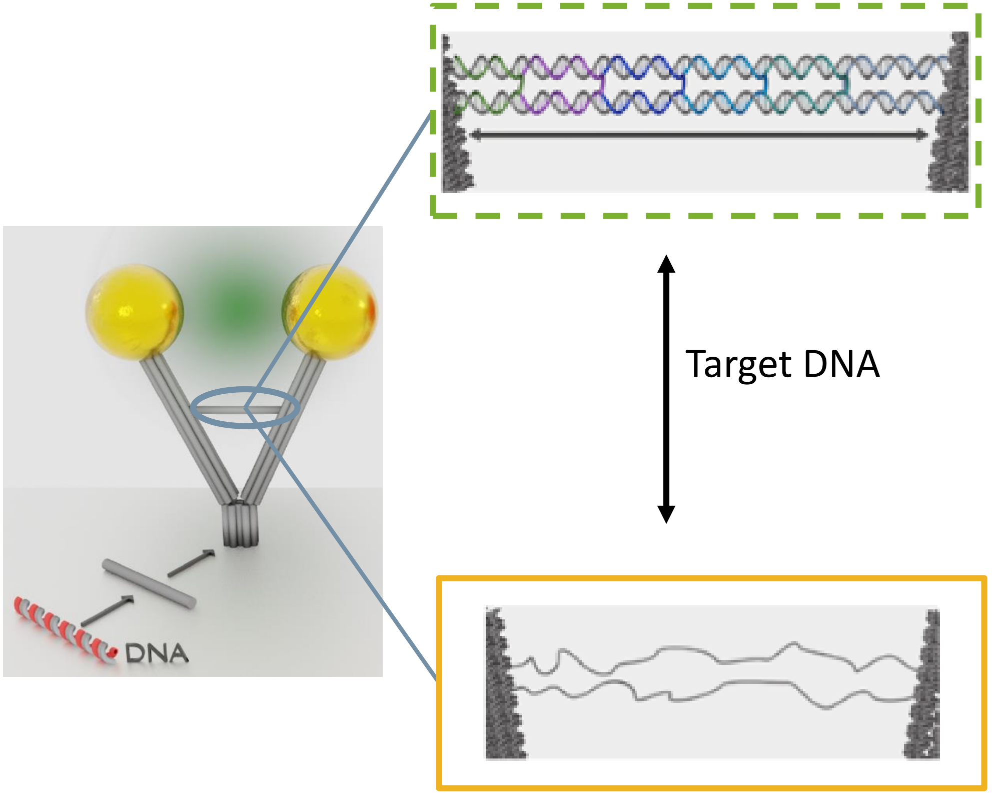


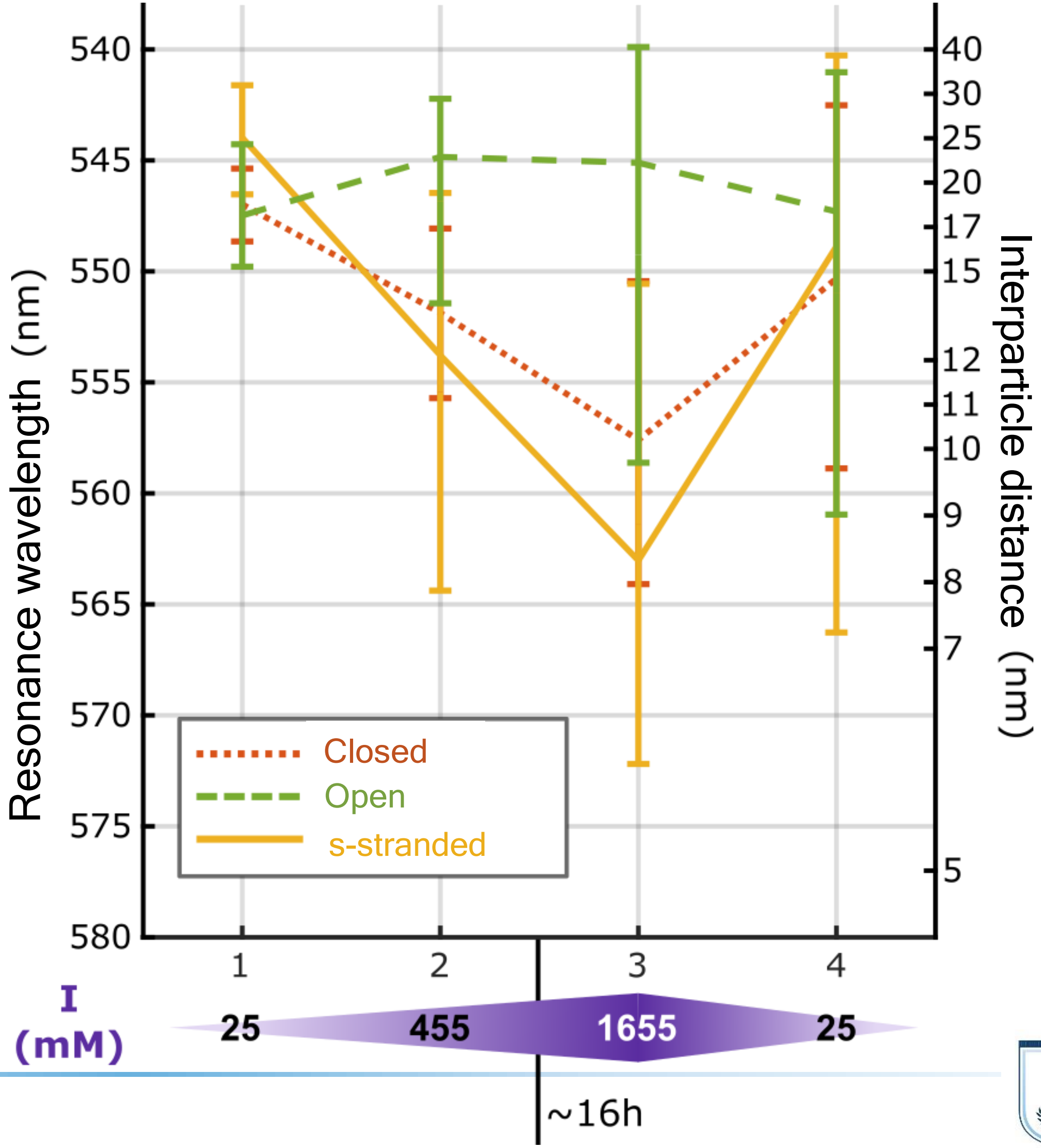
Single-stranded active site





Tuning the rigidity of the origami

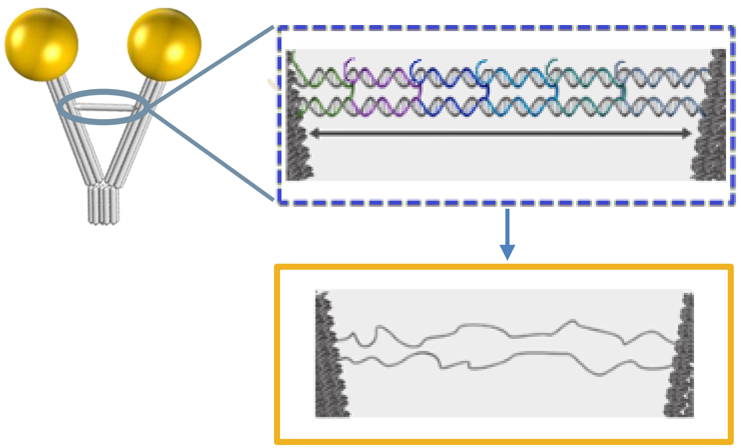


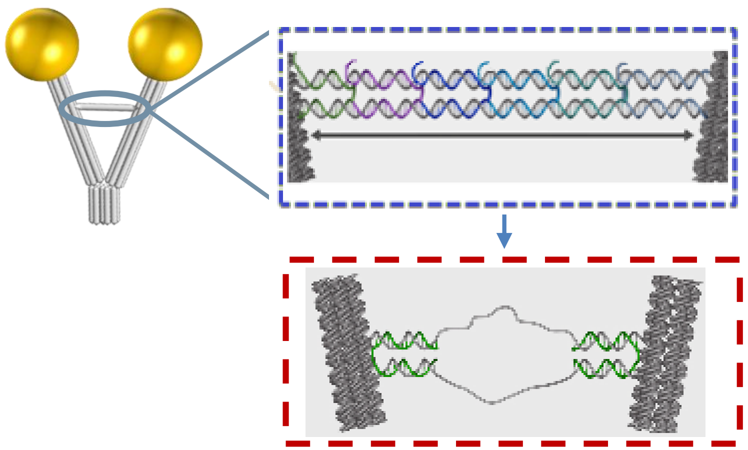


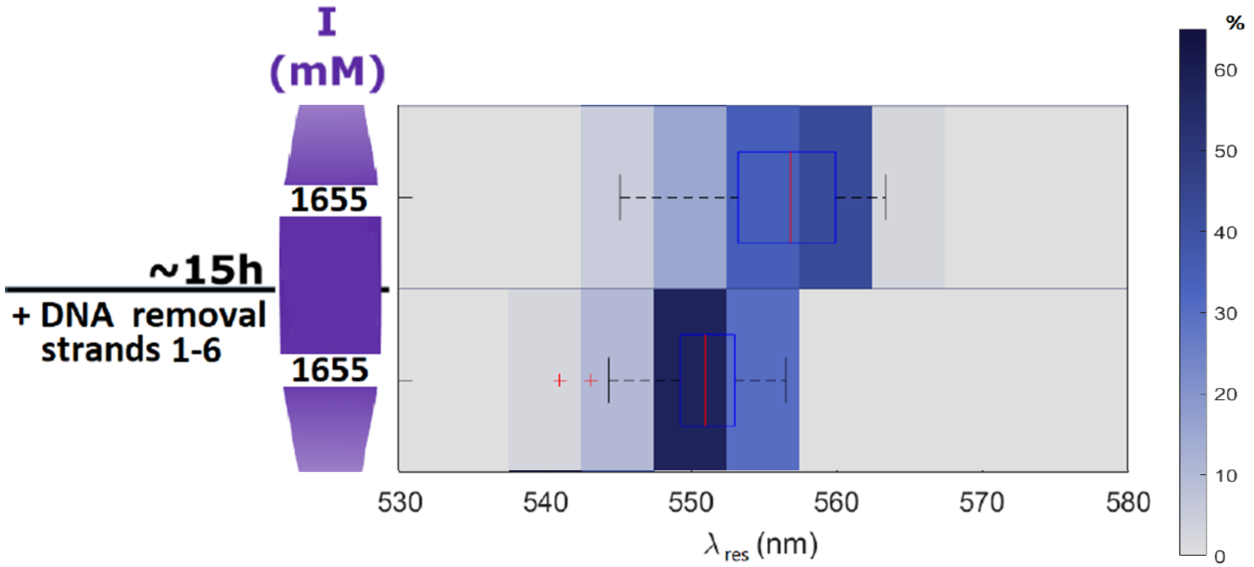
The geometry and rigidity of the DNA origami control the flexibility of the hybrid nanostructure

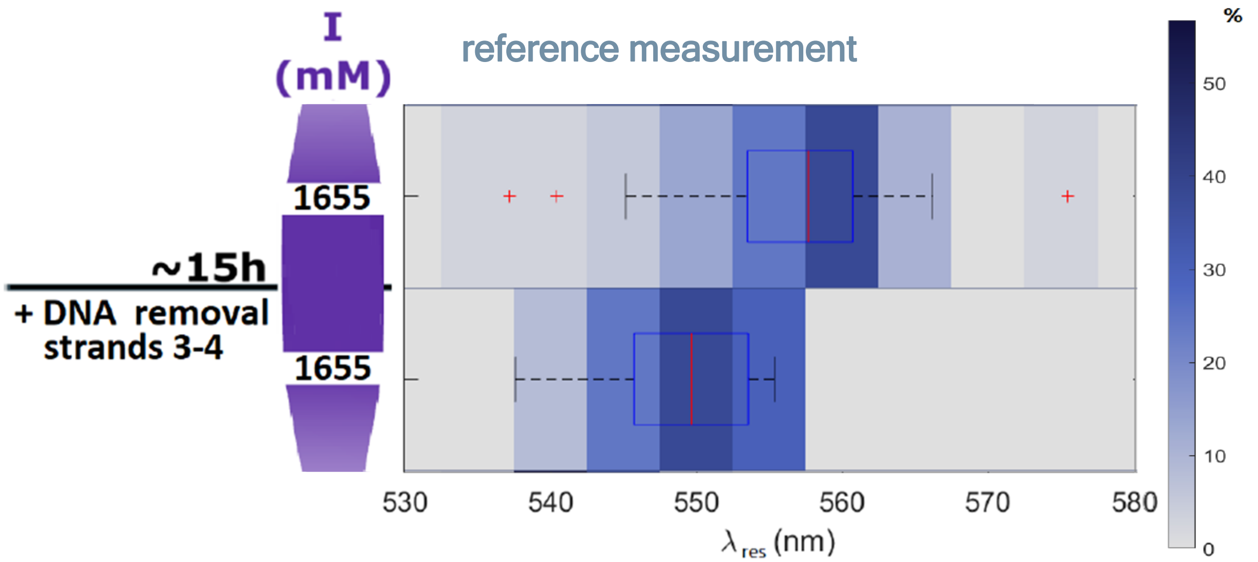
E. Y. Gayet et al, in preparation

Optical detection of a DNA strand displacement reaction



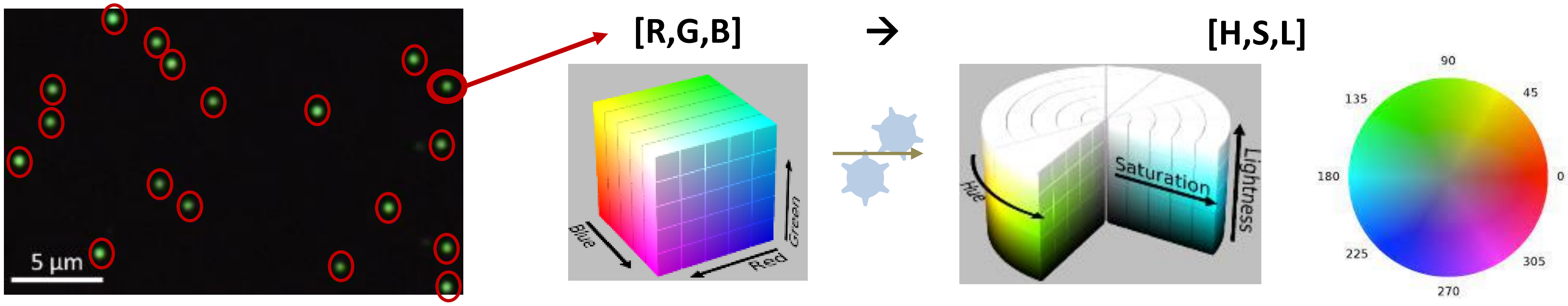


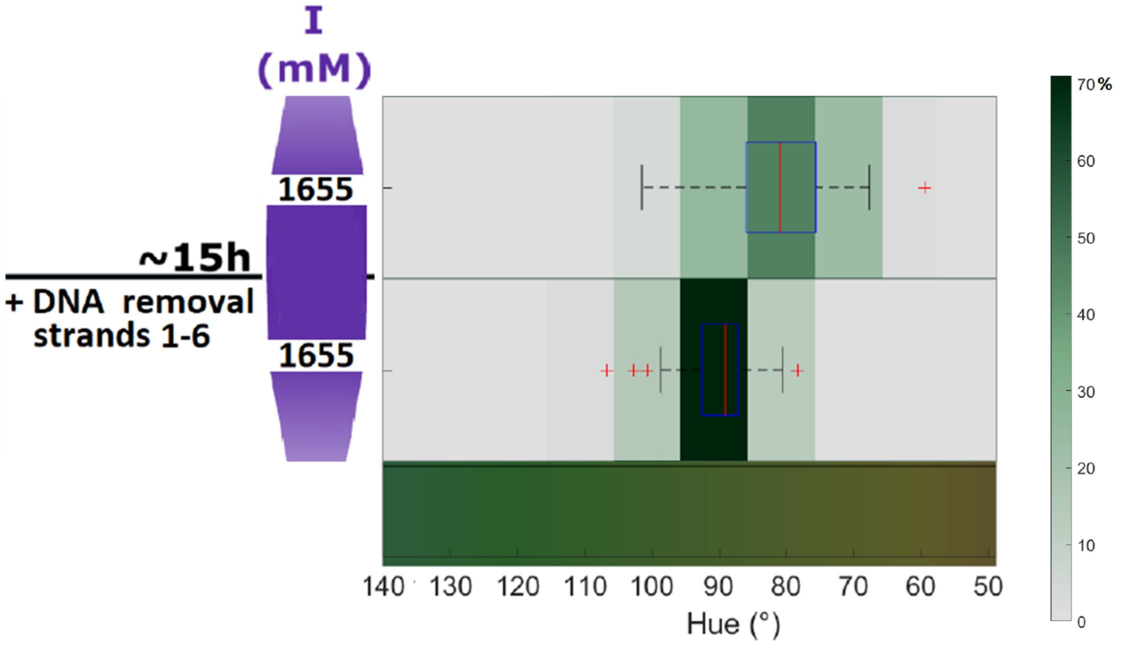


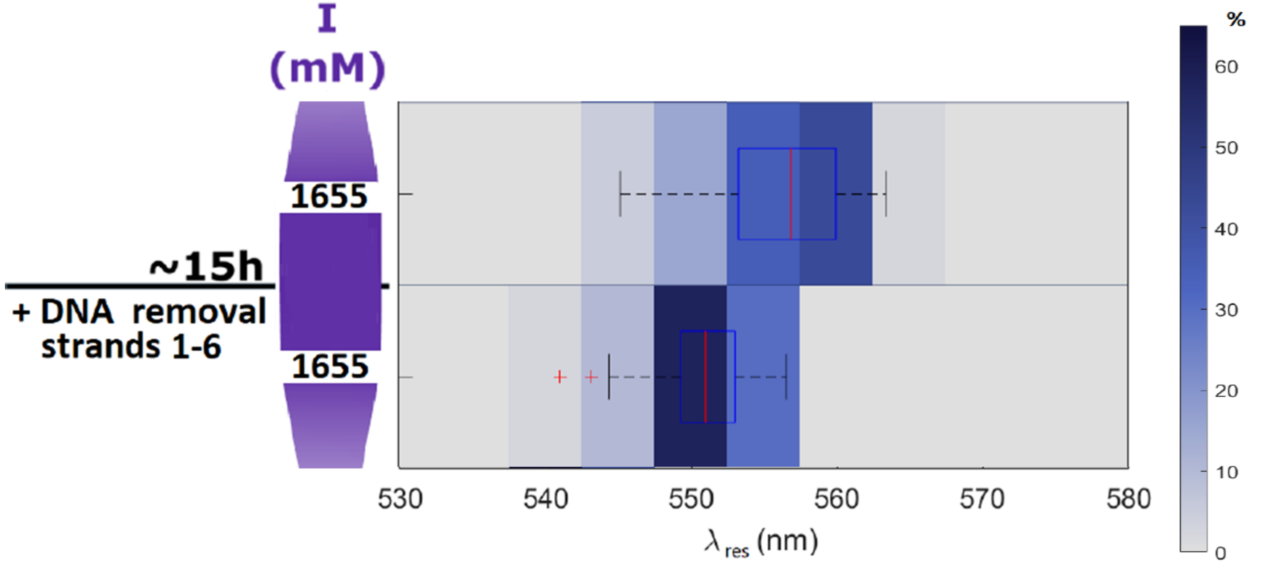


Strand displacement induces spectral redshift of ~7nm

Colorimetric detection of a DNA strand displacement reaction

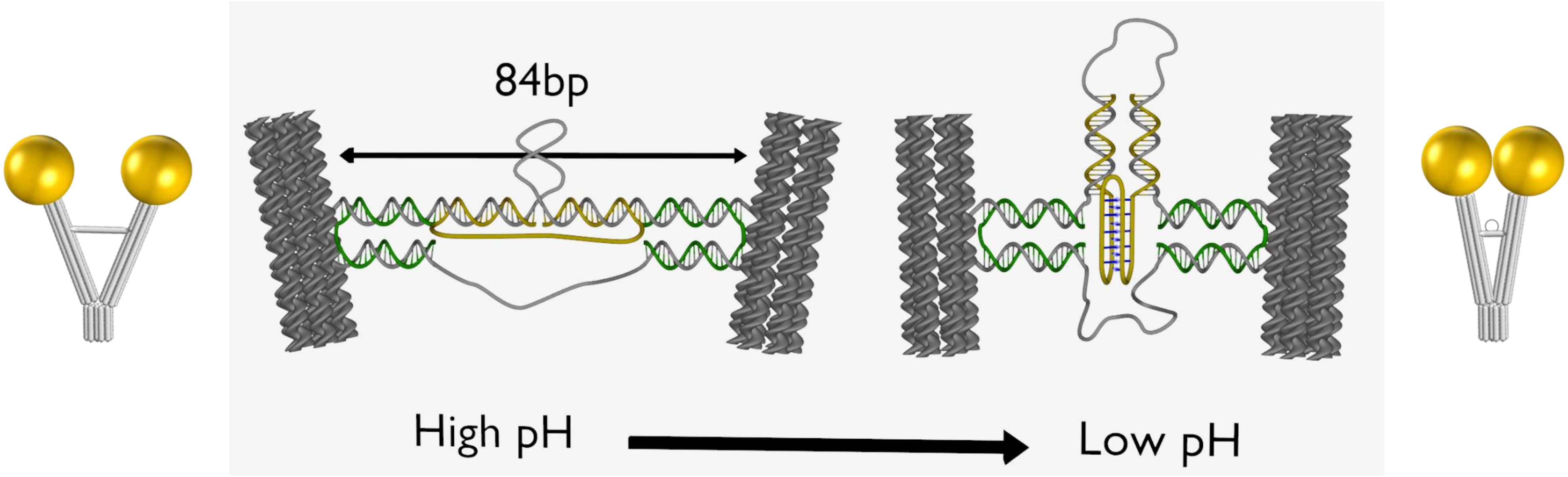




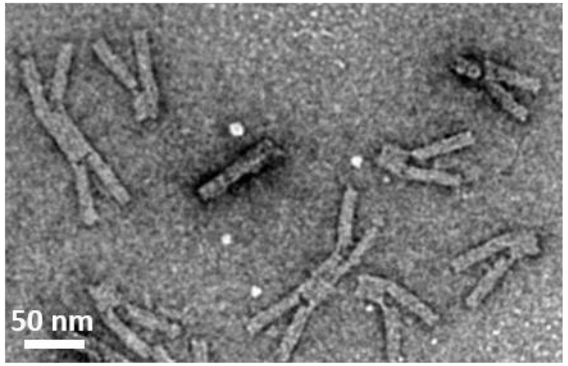


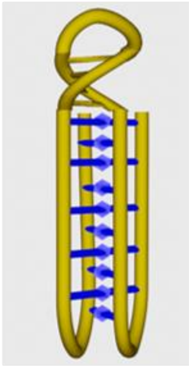
Colorimetric detection of strand displacement similar to data collected via spectrometer

pH-sensitive hybrid nanostructures

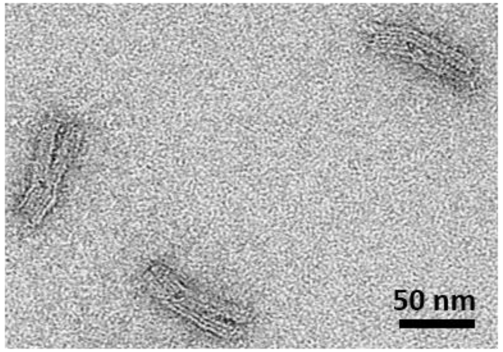


pH
8.5





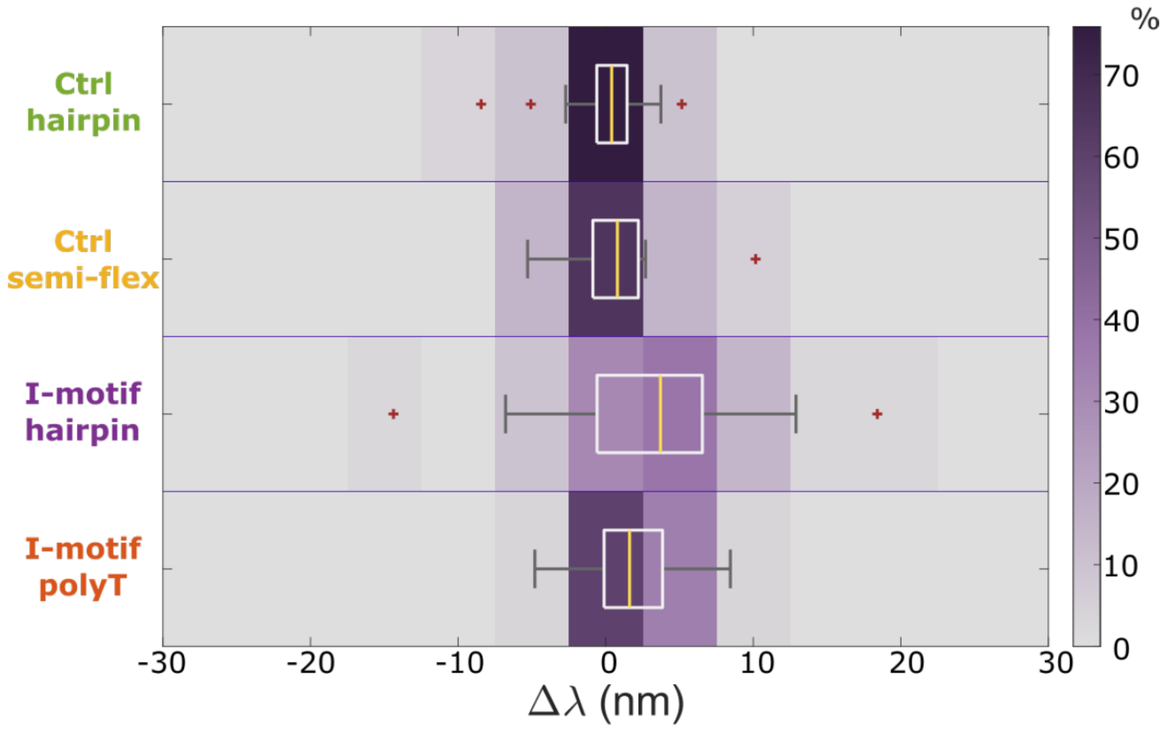
Hairpin:
4 bp (1 AT, 3GC)

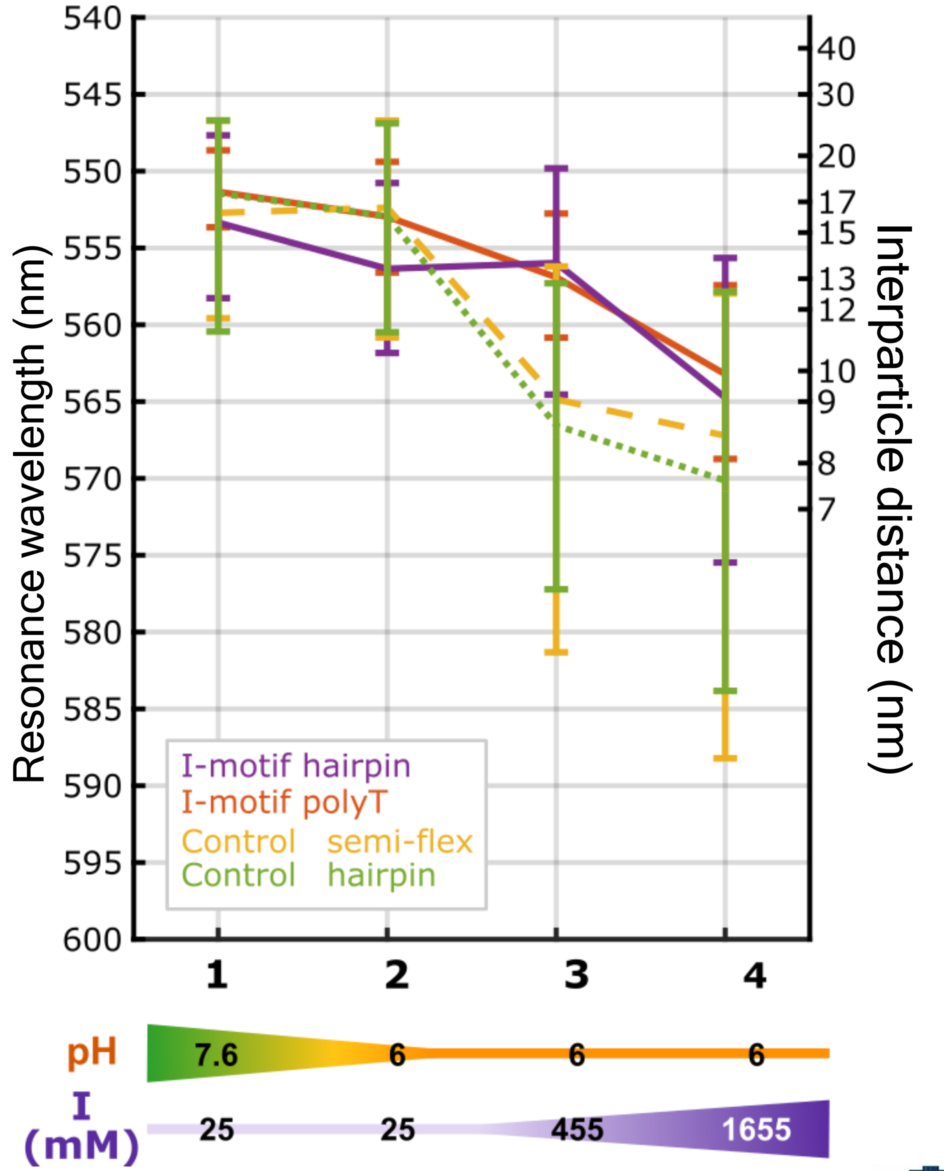


pH
5.6

E. Y. Gayet et al, in preparation

pH-sensitive hybrid nanostructures



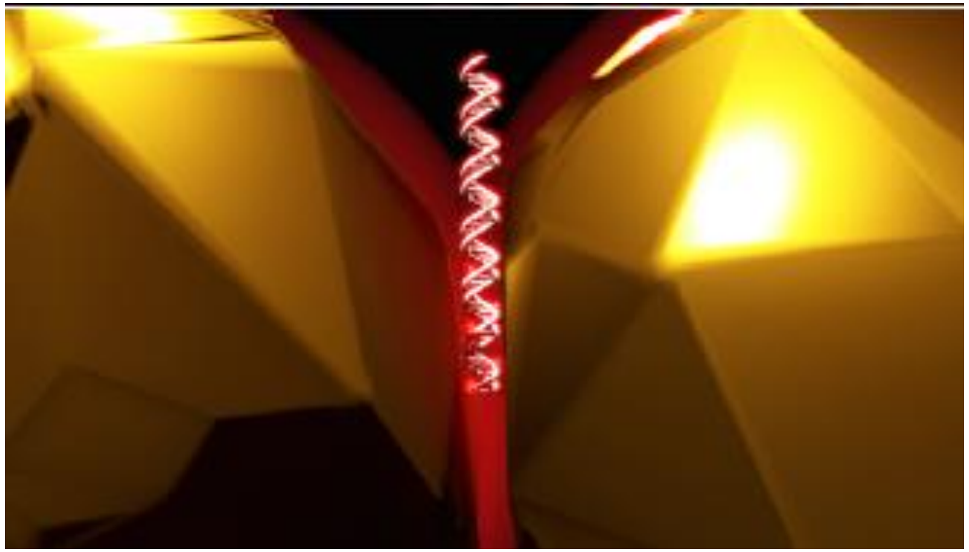


Small redshift due to DNA i-motif during the pH transition

Large modification of the rigidity of the hybrid nanostructure

E. Y. Gayet et al, in preparation

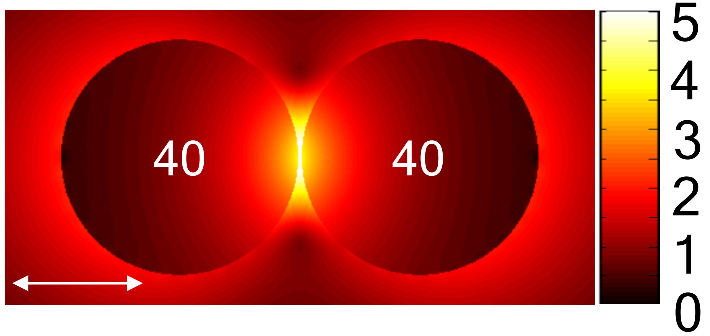
Why structural DNA nanotechnology?



- Producing dynamic nanostructures whose morphology and optical properties can be actively and specifically modulated
- Introducing a controlled number of quantum emitters in the hot-spot of a plasmonic resonator

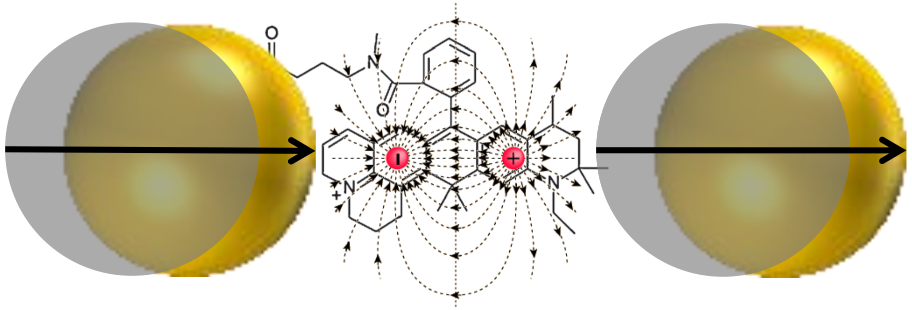
Coupling broadband emitters and resonators

Enhancing excitation



$$P_{0\to 1} = \sigma_{abs}(\omega_{exc}) \cdot \left|\mathbf{E}(\mathbf{r}) \bullet \mathbf{u}_p\right|^2$$

Modifying the local density of states



$$F_p = \frac{\rho_p(\mathbf{r},\omega)}{\rho_0} = \frac{\mathrm{P}}{\mathrm{P}_0} = \frac{\Gamma}{\Gamma_0}$$

(classical dipole) (quantum weak coupling regime)

Reciprocity in weak coupling $\Rightarrow \dfrac{\left|\mathbf{u}_p\cdot\mathbf{E}\right|^2}{\left|\mathbf{u}_p\cdot\mathbf{E}_0\right|^2} \approx \dfrac{\Gamma_R}{\Gamma_{R0}}$

P. Bharadwaj et al, Adv. Opt. Photon. 2009

Enhancing the fluorescence signal

$$\frac{I_{fluo_{enhanced}}(\mathbf{r},\mathbf{u}_p)}{I_{fluo_{ref}}} = \frac{\left|\mathbf{E}(\mathbf{r}) \bullet \mathbf{u}_p\right|^2}{\left|\mathbf{E}_0 \bullet \mathbf{u}_p\right|^2} \cdot \frac{\varphi(\mathbf{r},\mathbf{u}_p)}{\varphi_0}$$

Coupling regimes

Emitter (ω_0,γ_0) and resonator (ω_p,γ_p) as two coupled damped harmonic oscillators

Coupling rate g: complex eigenfrequencies of the coupled system are inferred by diagonalizing

$$\begin{pmatrix} \omega_0 - i(\gamma_0 - \Gamma_0)/2 & g \\ g & \omega_p - i\gamma_p/2 \end{pmatrix} \quad \text{with } g = \sqrt{F_p \Gamma_0 \gamma_p / 4}$$

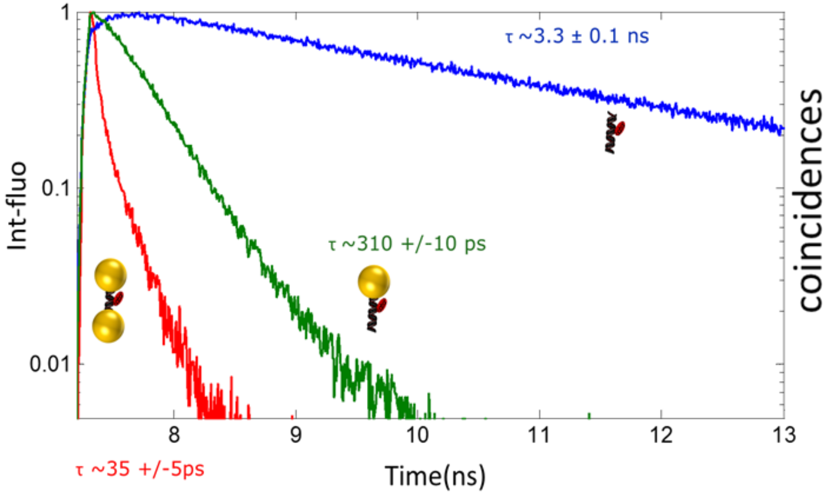
Eigenmodes $\begin{cases} \omega_\pm = \frac{1}{2}(\omega_0 + \omega_p) \pm \sqrt{\left(\frac{\omega_0 - \omega_p}{2}\right)^2 + g^2} \\ \gamma_\pm = \frac{(\gamma_0 - \Gamma_0) + \gamma_p}{2} \end{cases}$

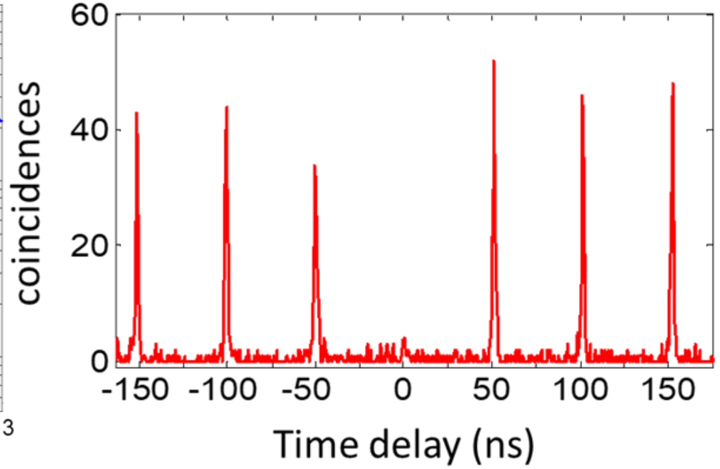
Weak coupling regime if $|\tilde{\omega}_0 - \tilde{\omega}_p|^2 \gg 4g^2$ then $\omega_+ = \omega_0$ and $\omega_- = \omega_p$

Strong coupling regime if $|\tilde{\omega}_0 - \tilde{\omega}_p|^2 < 4g^2$

Enhancing emission in the weak coupling regime

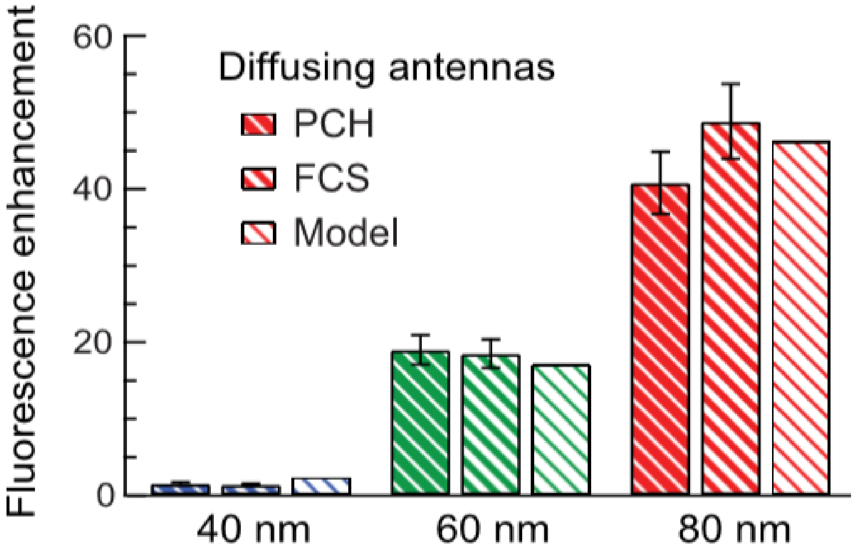
Accelerating emission





M. P. Busson et al, Nat. Commun. 3, 962 (2012)

Fluorescence enhancement



S. Bidault et al, ACS Nano , 10, 4806−4815 (2016)

$\varphi\sim 15\%$ $\varphi\sim 45\%$ $\varphi\sim 70\%$

High brightness and quantum yields

Fluorescence intensity up to **×330** (**×44 average**)

Emission rates up to **×760** (**×72 average**)

Typical antenna yields in **40 % - 70 %** range

Coupling regimes

Emitter (ω_0,γ_0) and resonator (ω_p,γ_p) as two coupled damped harmonic oscillators

Coupling rate g: complex eigenfrequencies of the coupled system are inferred by diagonalizing

$$\begin{pmatrix} \omega_0 - i(\gamma_0 - \Gamma_0)/2 & g \\ g & \omega_p - i\gamma_p/2 \end{pmatrix} \quad \text{with } g = \sqrt{F_p \Gamma_0 \gamma_p / 4}$$

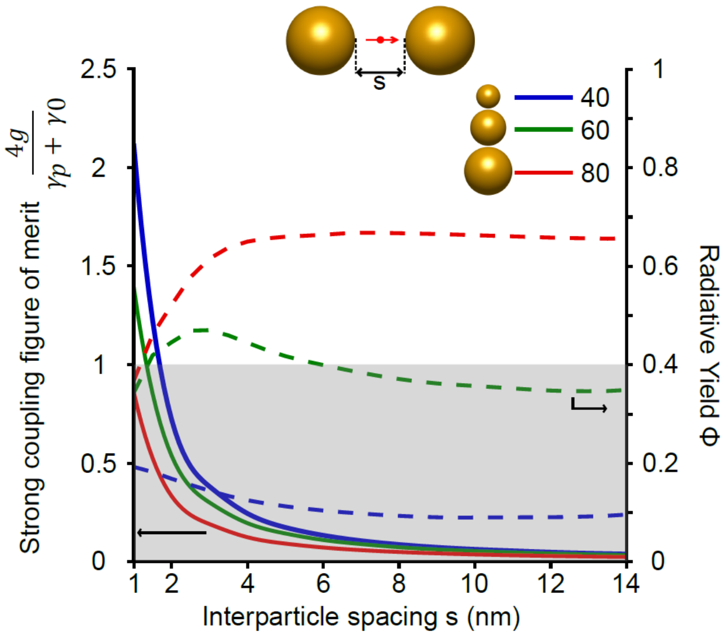
Eigenmodes $\begin{cases} \omega_\pm = \frac{1}{2}(\omega_0 + \omega_p) \pm \sqrt{\left(\frac{\omega_0 - \omega_p}{2}\right)^2 + g^2} \\ \gamma_\pm = \frac{(\gamma_0 - \Gamma_0) + \gamma_p}{2} \end{cases}$

Weak coupling regime if $\left|\tilde{\omega}_0 - \tilde{\omega}_p\right|^2 \gg 4g^2$ then $\omega_+ = \omega_0$ and $\omega_- = \omega_p$

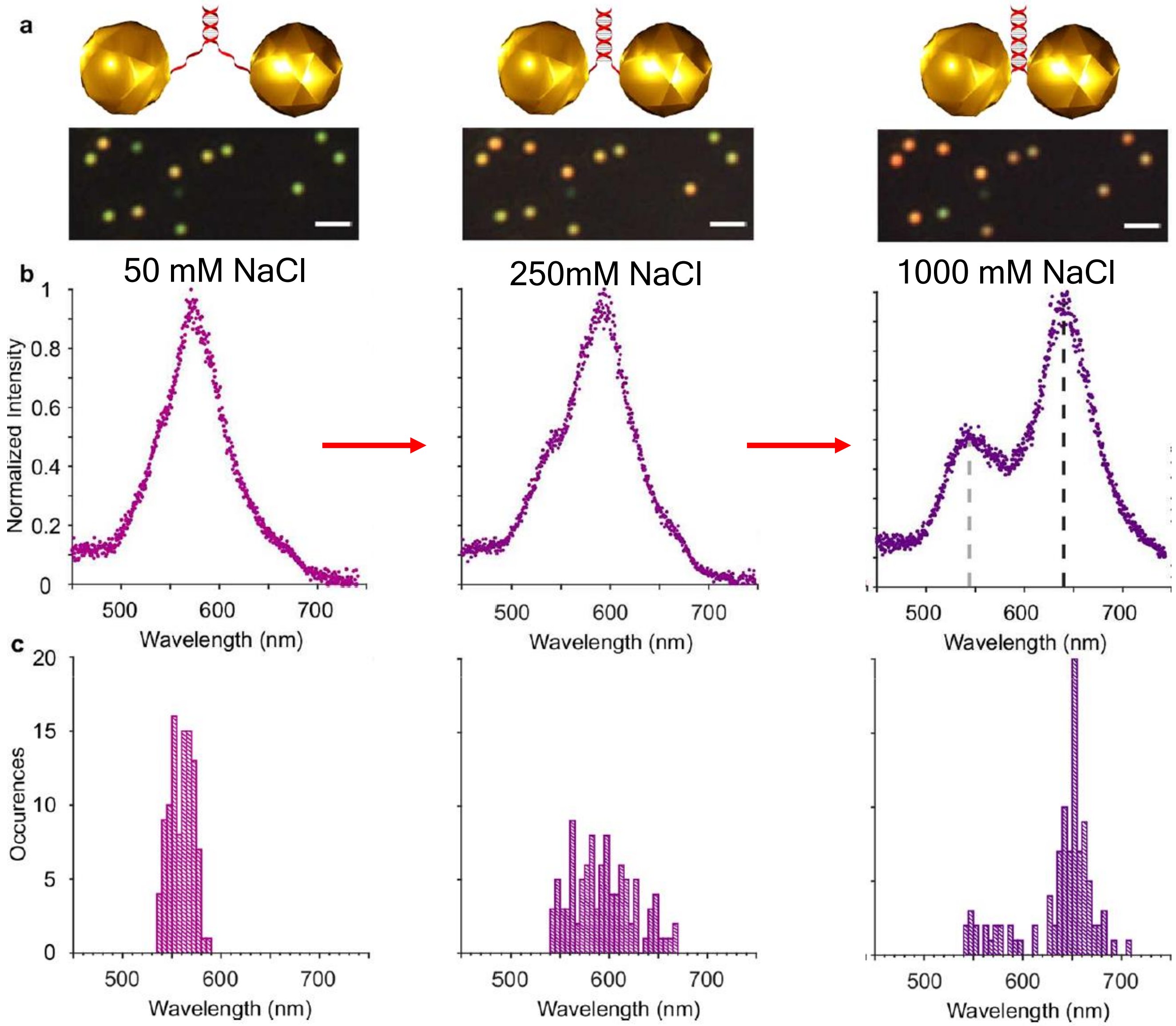
Strong coupling regime if $\left|\tilde{\omega}_0 - \tilde{\omega}_p\right|^2 < 4g^2$

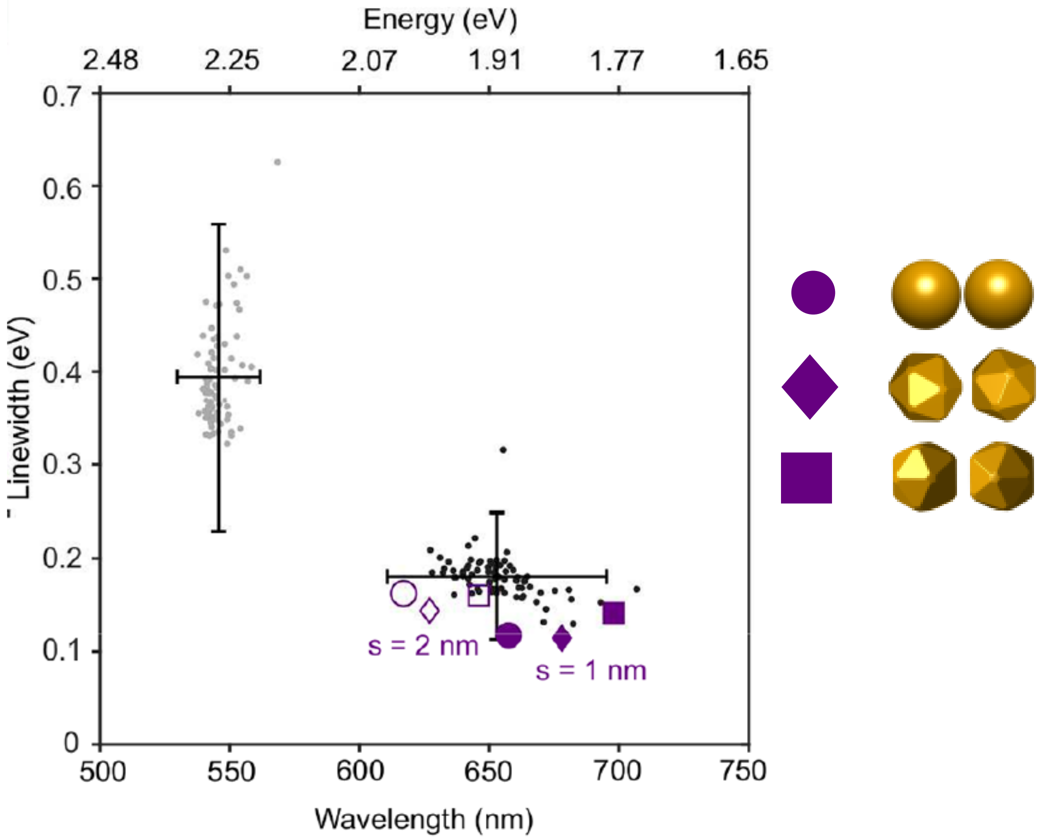
Two strongly coupled hybrid resonances are observed if the coupling rate is larger than all decay rates in the coupled system: $2g >$ $\gamma_p/2+\gamma_0/2$

and with N identical emitters $g_N = \sqrt{N} g$



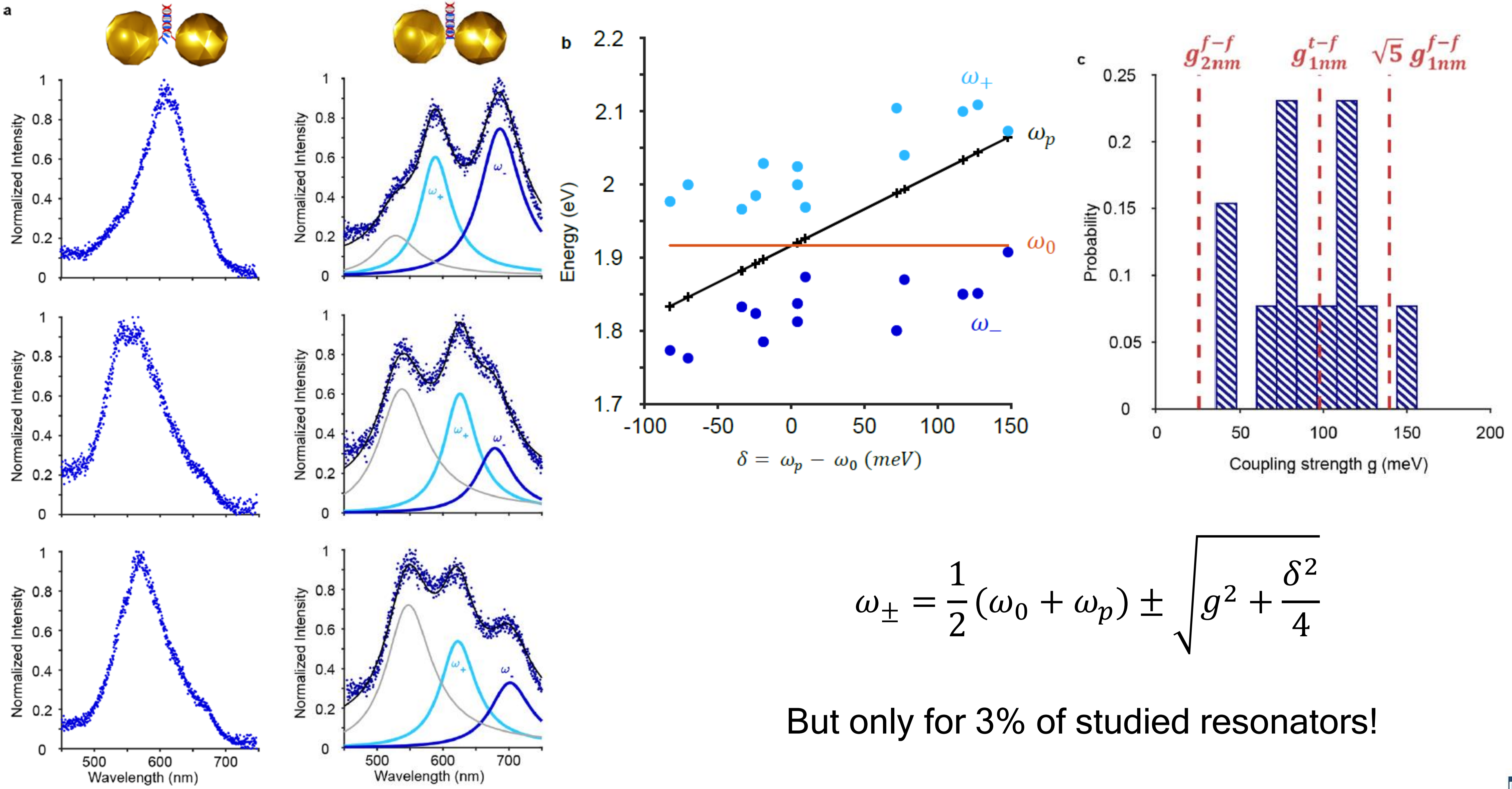
Reaching sub-2nm gaps reproducibly





J. Heintz et al, ACS Nano 2021

Visible strong-coupling with 5 ATTO647N molecules

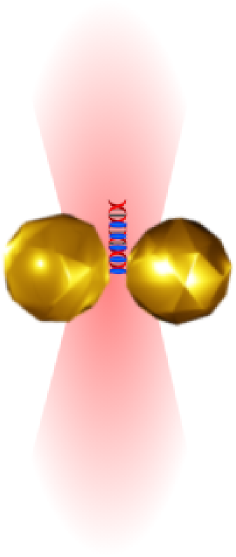


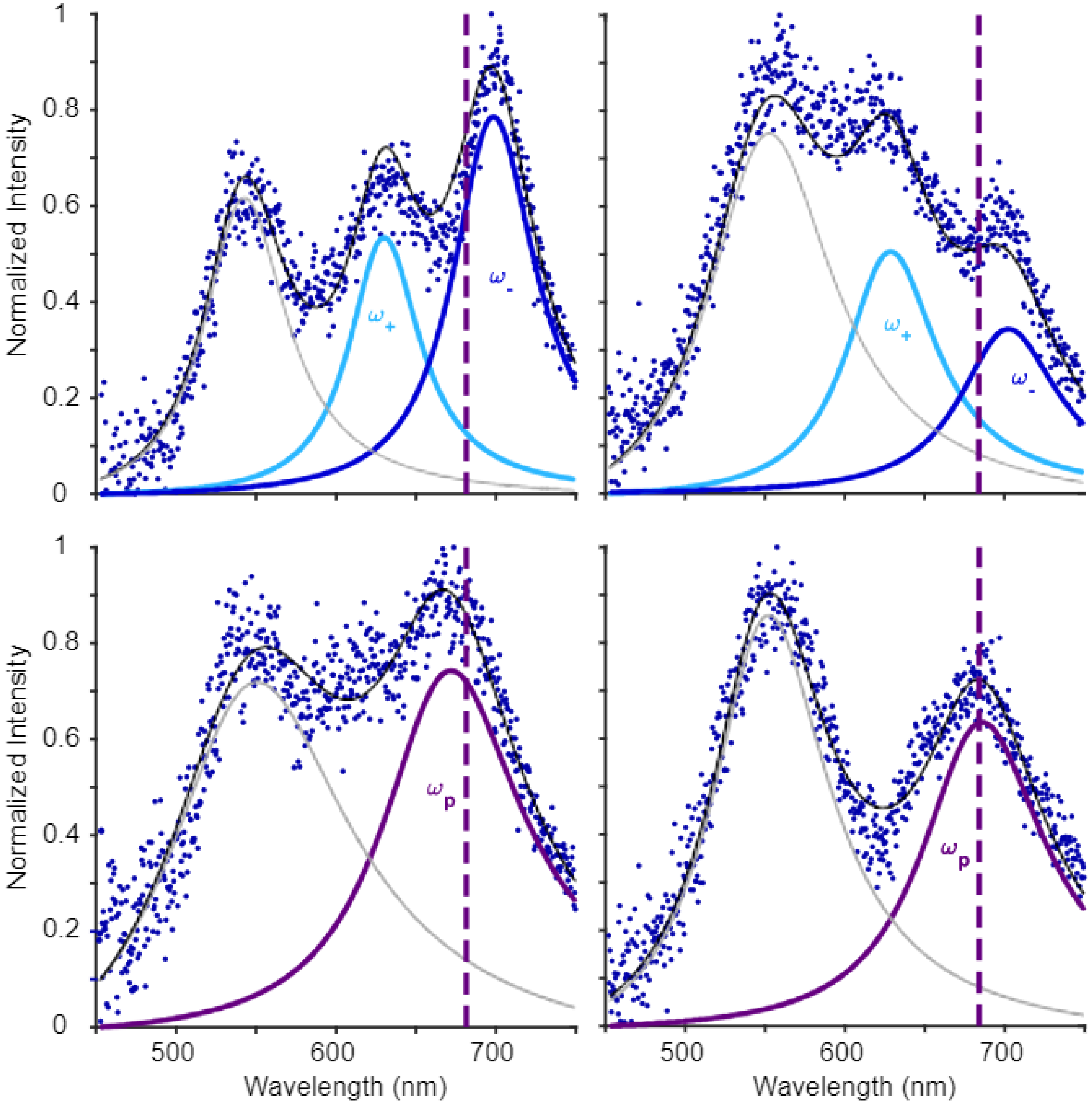
$$\omega_\pm = \frac{1}{2}(\omega_0 + \omega_p) \pm \sqrt{g^2 + \frac{\delta^2}{4}}$$

But only for 3% of studied resonators!

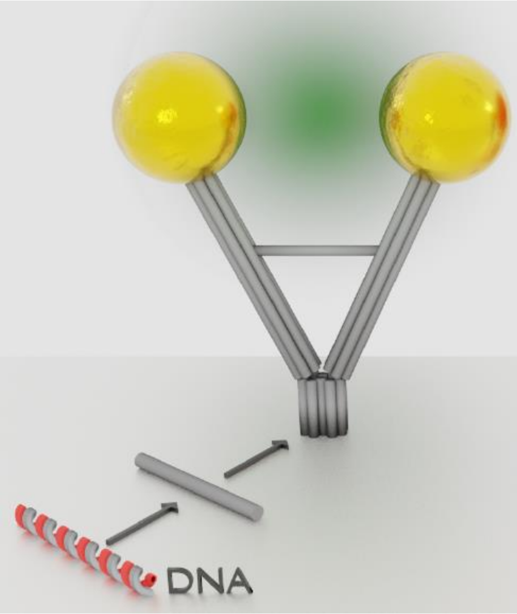
J. Heintz et al, ACS Nano 2021

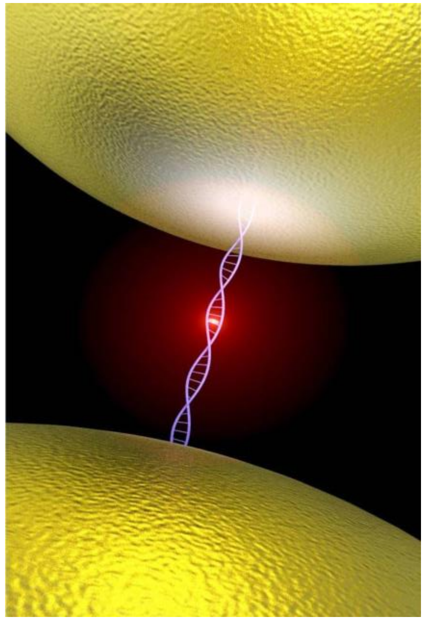
Photoinduced disappearance of hybrid modes





Conclusions





- DNA-based nanofabrication techniques allow the development of plasmonic resonators with an excellent control over their chemical environment
- An active control of the interparticle distance is possible by tuning interparticle interactions or the shape of the DNA scaffold

- DNA-templated dimers enhance both the fluorescence intensity and decay rate of single molecules by nearly 2 orders of magnitude (average) and up to 3 (max)
- It is possible to reach a strong-coupling regime with a controlled number of emitters but with low reproducibility

Acknowledgements

- PhD students & post-docs

Mickaël Busson, Laurent Lermusiaux, Nemanja Markesevic, Elise Gayet, Jeanne Heintz, Claudia Corti






- N. Bonod, J. Wenger & coworkers (Fresnel, Plasmonic resonators)
- G. Bellot & coworkers (CBS, DNA origamis)
- Sylvie Marguet (CEA, gold nanoparticles)