Electronic Supplementary Information (ESI)

For

Photochromic control of a plasmon – quantum dots coupled system

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This ESI consists of the six parts listed below:

- Characteristics of the silver nanocylinders
- Characteristics of the photochromic molecules
- Coupling between photochromic molecules and metallic nanoparticles
- Setup details
- FRET characterisation
- Coupling between quantum dots and metallic nanoparticles

1. Characteristics of the silver nanocylinders

The Figure S1a shows a SEM image of the nanoparticles which are randomly distributed in an array. During the design task, we started from a regular square array with a constant filling factor of 10% and we used a macro to randomly shift the NPs of at least two radius from their origins. The Figure S1b represents the plasmonic resonance of four diameters (70 nm, 100 nm, 130 nm and 160 nm) and the QDs emission spectrum.



Figure S1 – (a) SEM image of disorder nanoparticle array (160 nm-diameter) – (b) Fitted plasmonic resonance of the 70 nm (green curve), 100 nm (red curve), 130 nm (blue curve) and 160 nm (purple curve) diameter silver nanoparticles and fitted QDs emission (dashed black curve)

2. Characteristics of the photochromic molecules

Under UV irradiation, the C-O link breaks, followed by a cis/trans isomerisation leading to the merocyanine MC form (Figure S2a). The initial form, spiropyran (SP), is uncoloured and absorbs between 200 nm and 400 nm, while the photo-induced form, MC, is coloured and absorbs in the visible between 500 nm and 800 nm; the absorbance maximum being around 570 nm (Figure S2b).



Figure S2 – (a) Structural transformation induced by the photochromic transition – (b) Spiropyran (red dashed curve) and merocyanine (green curve) absorbance – (c) Ellipsometric measurements of the change of refractive index Δn (solid red curve) and extinction coefficient Δk (solid blue curve) between the two photochromic states

3. Coupling between photochromic molecules and metallic nanoparticles

The normalized extinction spectra of silver NPs presenting different diameters, before and after the photochromic transition, are displayed on Figure S3. It is worth to note that the extinction spectra recorded above the NPs have been normalized by the extinction spectra of the background, either in the SP or in the MC isomers. Unlike our previous study (R1), we covered the silver NPs with a 5 nm thick silica layer to avoid the silver oxidation. It seems that the silica layer thickness avoid any coupling between the LSPR and the excited state of the PM molecules. As a consequence, studying the extinction spectra (Figure S3), we do not observe any shift of the plasmonic resonance after the photochromic transition.



Figure S3 – Extinction spectra of the nanocylinders in Spy (red curve) and in MC (green curve) for the diameter (a) 70 nm - (b) 100 nm - (c) 130 nm - (d) 160 nm

4. Setup details

The custom-built confocal microscope is based on an inverted RM21 (MadCityLabs - MCL) equipped with a micro and nanoscanning stage (MCL). The Microscope objective is a Nikon CFI FluorPlan ® (100x, NA1.3). The pulsed excitation source is a 467 nm picosecond laser operated at 20 MHz repetition rate (Hamamatsu ®), an APD (MPD) with small (50 µm) active detection area was placed in confocal detection configuration. A 483 nm dichroic filter mirror was used to reflect the laser excitation beam towards the sample, while the fluorescence emission signal was collected in epifluorescence mode with a 473 nm long pass filter (Semrock ®) placed in front of the APD detector. To reject fluorescence emission from activated photochromic molecules (PM) a 439/156 nm band pass filter (Semrock ®) was used. For Time

Correlated Single Photon Counting (TCSPC) measurements, the SYNC and the detector output were connected to a SPC130 correlation card (Becker and Hickl R) allowing Fluorescence Lifetime Imaging Microscopy (FLIM). A 385 nm LED source was used to induce the photochromic change of PM. Power of the picosecond laser was adjusted using a gradient gray filter and set about 10 μ W. The repetition rate of the laser is 20 MHz, *ie.* one pulse every 50 ns. The collection time is set to 0.2 ms per pixel. The collected photons which are time tagged using the single photon counting technology are either collected in form of photon arrival time histograms or data is integrated over the collection time interval to obtain intensity values.

5. FRET characterisation

We recall that the Förster radius R_0 is defined as the distance at which the energy of the donor is transferred to the acceptor with a probability of 0.5. It can be calculated by (R2):

$$R_0^6 = \frac{9 (ln10)\phi_D \kappa^2 J(\lambda)}{128\pi^5 N_A n^4} = (8.79 \times 10^{-28} \ mol) n^{-4} \phi_D \kappa^2 J(\lambda)$$
(E1)

where φ_D is the PL quantum yield of the donor, N_A is Avogadro's number, n is the refractive index of the medium, J(λ) is the spectral overlap integral and κ^2 is the orientation factor between the electronic dipoles of the donor and the acceptor. The spectral overlap integral measures the degree of resonance between the donor emission spectrum and acceptor absorption spectrum. It is defined by:

$$J(\lambda) = \frac{\int F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int F_D(\lambda)d\lambda}$$
(E2)

where $F_D(\lambda)$ is the wavelength-dependent fluorescence intensity of the donor, $\epsilon(\lambda)$ is the wavelength-dependent molar absorption coefficient for the acceptor and λ is the wavelength. By calculating the spectral overlap integral J (λ), we find a Förster radius R₀ of 5.23 nm. Finally, we calculated the FRET efficiency E_{FRET} given by the equation E3, where τ_D and τ_{DA} represent respectively the lifetime of the donor in absence and in presence of acceptors.

$$E_{FRET} = 1 - \frac{\tau_{DA}}{\tau_D} \tag{E3}$$

We find that the FRET efficiency is about 79%, which shows that the FRET between the QDs and the MC is very efficient.

6. Coupling between quantum dots and metallic nanoparticles

The Figure S4 shows the PL (a) and the lifetime (b) images of the QDs diluted in a PMMA layer and spin-coated onto the NP arrays. We can see that the PL and the lifetime are quenched above all nanocylinder arrays. It seems there is no influence of the nanocylinder diameter.



Figure S4 - (a) PL image – (b) FLIM image - recorded on the silver nanocylinders coupled to QDs. In image (a) are written the diameter of the nanocylinders.

Références

(R1) Baudrion, A.L.; Perron, A.; Veltri, A.; Bouhelier, A.; Adam, P.M.; Bachelot, R.; *Nano Letters* 13, nº 1, **2013**, 282-86. <u>https://doi.org/10.1021/n13040948</u>.

(R2) Algar, W. R.; Kim, H.; Medintz, I.L.; Hildebrandt, N.; *Coordination Chemistry Reviews*, 263-264, 2014. https://doi.org/10.1016/j.ccr.2013.07.015.