Electronic Supporting Information

Controlled assembly of metal colloids on dye-doped silica particles to tune the photophysical properties of organic molecules.

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1. Computational background

The development of hierarchical assembly of gold nanoparticles is supported by computer simulations. The knowledge of the optical and electromagnetic behaviour of the metal nanoparticles is of fundamental importance in order to design advanced nanomaterials for specific applications. The mathematical modelling of such properties is a useful tool to support and guide the design of these materials. Discrete simulation, which implements finite element analysis, can be performed to model the electromagnetic behaviour of single particles and of complex particle structures, whose analytical simulation is not possible, like dimer, nanoparticles chain and planar distribution. Actually, by using mathematical simulations, the best configuration for the field enhancement and the trend of the absorption spectrum as a function of the relative distance among the particles can be derived. In particular, we were able to extrapolate the optical properties and the enhanced electric field generated by dimers, chains and planar distributions of gold nanoparticles (AuNPs).

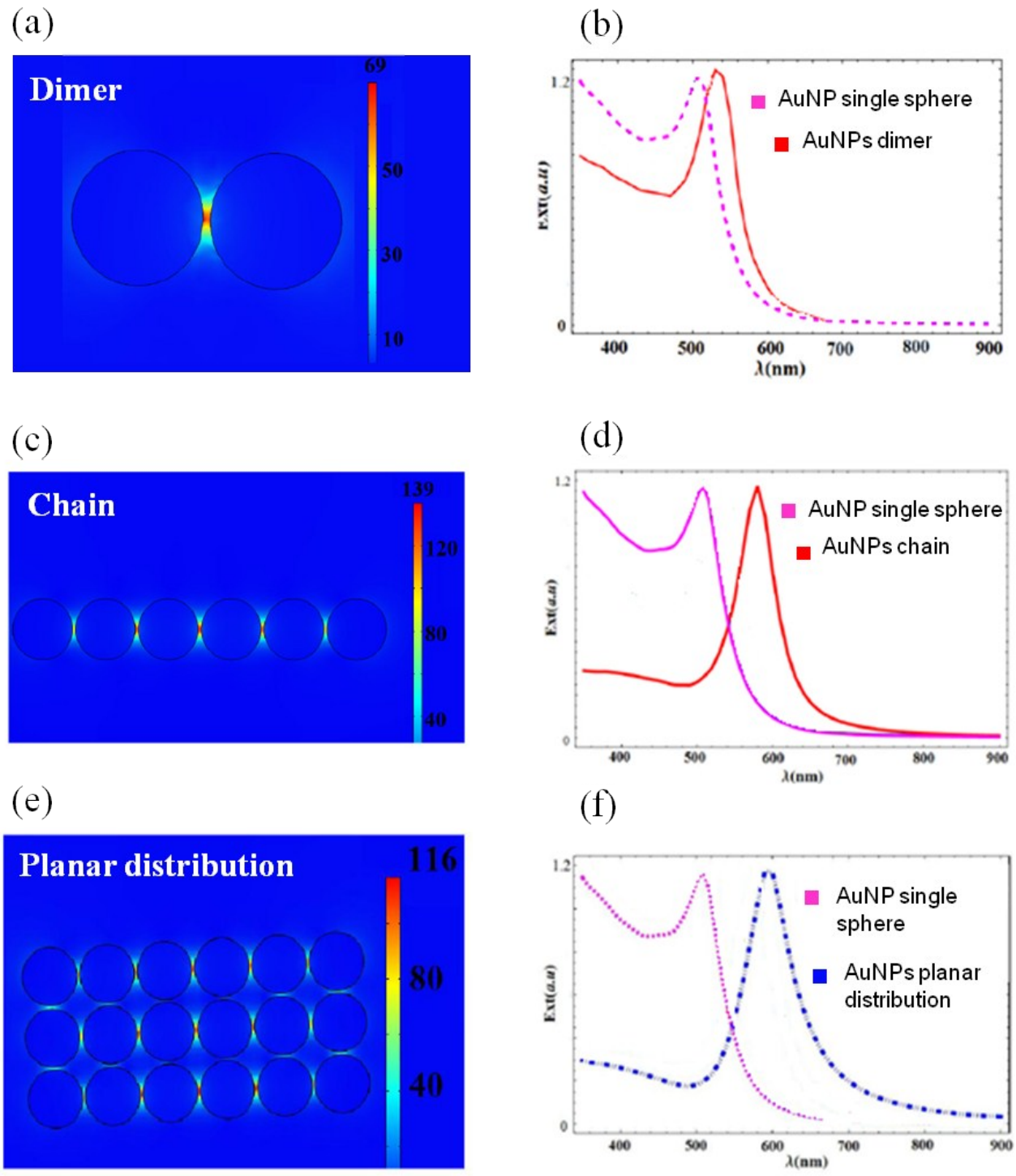

Figure S1. Electric field (V/m) plane distribution generated by AuNPs with 20 nm of radius and interparticle distance of 2 nm in dimer (a), chain (c) and planar (e) configuration; the calculated extinction spectra are also reported (b, d and f).

By analysing a dimer made of 20 nm radius-AuNPs and using an incident radiation with a linear polarization along the longitudinal alignment line of the spheres, the electric field between the spheres and the extinction spectrum were extrapolated (**Figure 1a-b**). The calculated field in the

dimer centre showed a remarkable enhancement, due to the coupling of the plasmon resonances that induces the red-shift of the extinction spectrum of the dimer system (if compared to the one of the isolated AuNPs). The collective and coherent motion of electrons led to the increase of the electric field near the metal and the highest value was reached in the central point between the nanoparticles, being more evident in the case of nanoparticles close together (near-field), with an interparticle distance of 2 nm.

The calculation was then carried out for structures with more than two nanoparticles, *i.e.* a finite Au nanoparticles chain and a nanoparticles planar distribution (limited to 18 nanoparticles), maintaining constant the interparticle distance of 2 nm and using a propagation direction of the incident wave normal to the chain and to the plane respectively. In the case of a single chain (**Figure 1c-d**), an enhanced field, doubled with respect to the dimer system, was found in the central point of the chain, which progressively decreased going from the central point to the chain edges: such effect has been attributed to the collective effect of the 6 nanoparticles, whose effect is summed to the central point. Moreover, the interaction among a distribution of closely spaced nanoparticles increased the red-shift of the LSPR and narrowed the band. Such effects were even more evident in the planar distribution of AuNPs (**Figure 1e-f**), whose field distribution displayed the same edge effect observed for the chain configuration, with a maximum field enhancement in the central point between nanoparticles, along with an extinction spectrum characterized by an additional red-shift due to the interaction of more ordered particles.

These results suggested that arrays of AuNPs on silica surface might strongly affect the photophysical behaviour of a nearby dye, thanks to the enhanced antenna effect obtained by the sum of the contribution of the plasmon of isolated spheres.

2. Evaluation of nanoparticles size distributions

2.1 Effect of plasmonic nanoparticles on the fluorescence of organic dyes

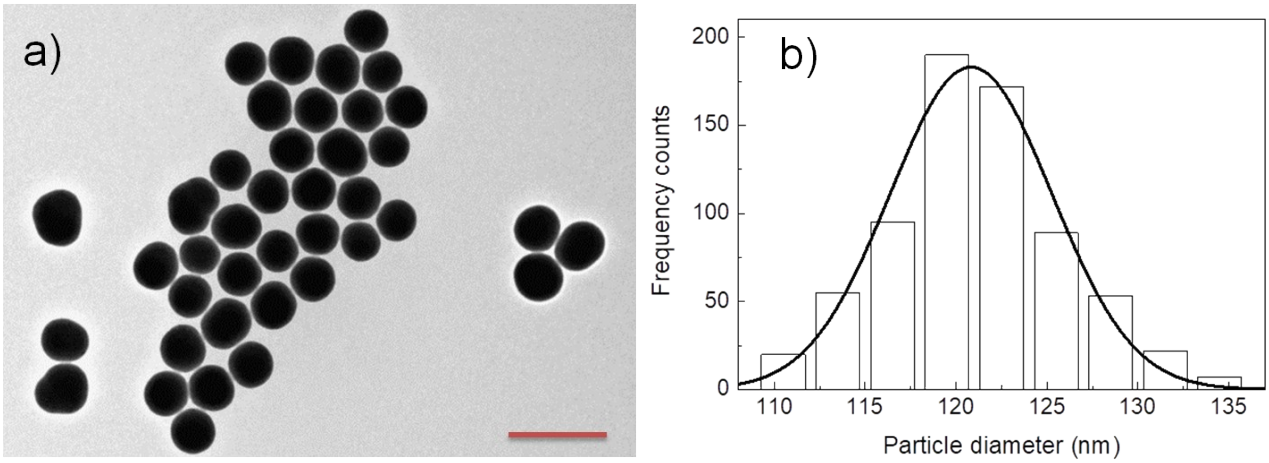

Figure S2. (a) Representative TEM image (b) and size distribution of silica nanoparticles subsequentially functionalized with different fluorescent dyes. Scale bar 200 nm.

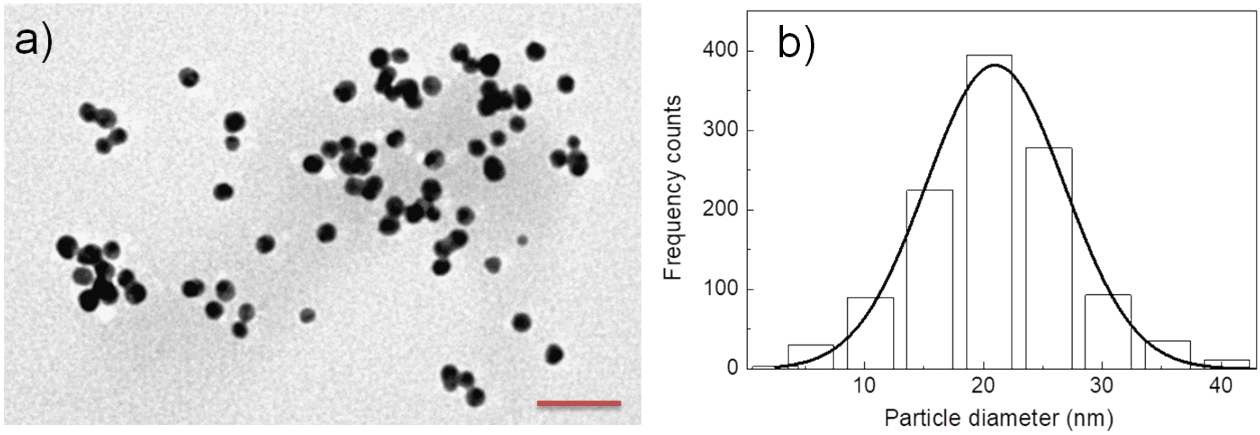

Figure S3. (a) Representative TEM image (b) and size distribution of gold nanoparticles subsequentially adsorbed onto different fluorescent dye-silica nanoconjugates. Scale bar 100 nm.

The analysis of TEM size distributions enables the determination of average diameters of 121 nm (σ = 4.4 nm) for silica nanoparticles and 20.9 nm (σ = 5.8 nm) for gold nanoparticles.

2.2 Effect of plasmonic nanoparticles on the photo-induced formation of ROS

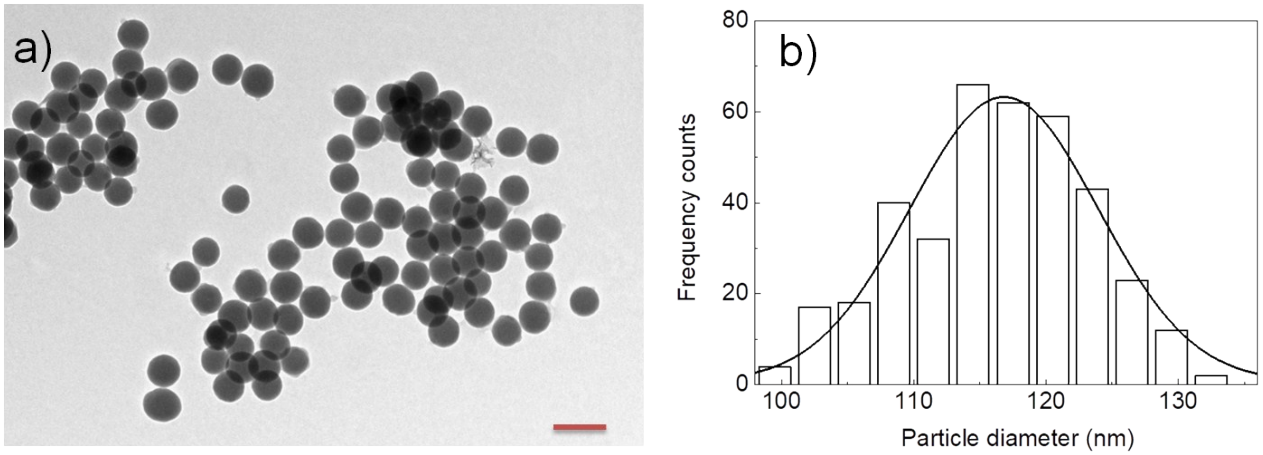

Figure S4. (a) Representative TEM image (b) and size distribution of silica nanoparticles used to anchor PpIX for the photo-induced formation of ROS. Scale bar 200 nm.

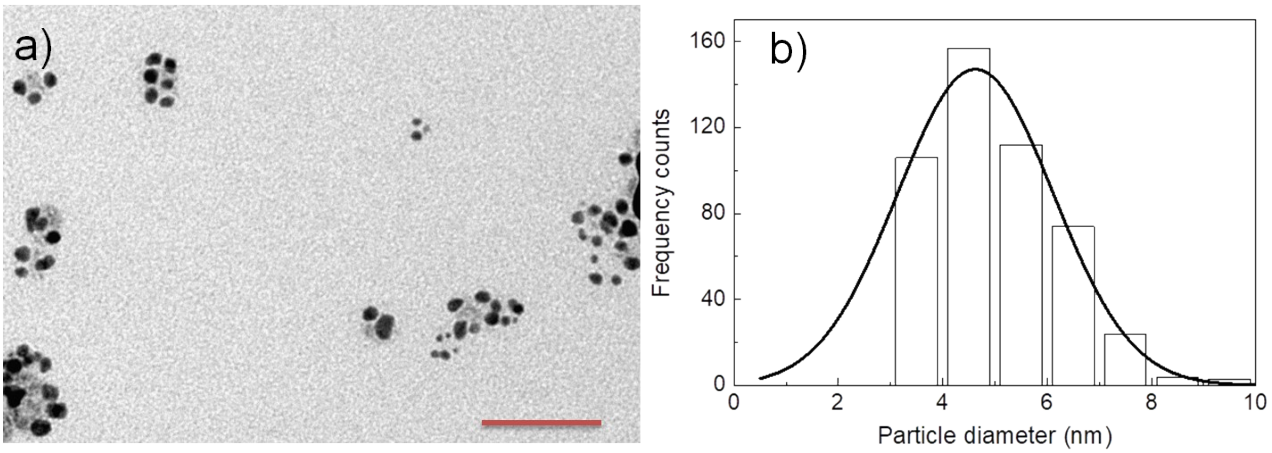

Figure S5. (a) Representative TEM image (b) and size distribution of gold nanoparticles subsequentially adsorbed onto Si-PpIX nanoparticles for the photo-induced formation of ROS. Scale bar 50 nm.

The analysis of TEM size distributions enables the determination of average diameters of 117 nm (σ = 7 nm) for silica nanoparticles and 4.6 nm (σ = 1.5 nm) for gold nanoparticles.

3. Instrumentations

3.1 Morphological and structural characterization of the nanoparticles

The morphology of silica, aminated silica and gold nanoparticles was investigated by a Philips 208 transmission electron microscope (TEM) operating at 80 kV of beam acceleration. For each sample, a drop of the suspension was deposited on a 300 square mesh Formvar-coated copper grid and then the solvent was left to evaporate in air at room temperature. The size distribution was obtained from the analysis of at least 300 nanoparticles using Image J software and the mean diameters were calculated from the best fitting of the experimental histograms with a Gaussian function.

3.2 Spectroscopic techniques

A Cary 8454 UV-VIS Diode Array spectrophotometer was used to collect the absorption and extinction spectra.

The corrected fluorescence emission spectra, collected at specific wavelengths depending on the analyzed dye, were acquired through a Fluorolog-2 (Spex, F112AI) fluorimeter.

Fluorescence decay times τ_F were measured by the time-correlated single photon counting (TCSPC) method using an Edinburgh Instrument 199S setup, by using as excitation source proper wavelength nanoLEDs, depending on the analyzed dye, with a pulse duration < 1.1 ns and a Hamamatsu R7400U-03 detector for the acquisition of the decay times. The least squares method was used to evaluate the goodness of the deconvolution fitting procedures; in particular the time-resolved data were deconvoluted from the source profile and reproduces through monoexponential or biexponential functions, from which decay times and relative amplitudes were determined. The reduced chi-squared value and the distribution of the calculated residuals were used to judge the quality of the fit.