Supporting Information for “Silver nanoparticle aggregates as highly efficient plasmonic antennas for fluorescence enhancement”

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I. EXPERIMENTAL DETAILS

Reproducibility of measurements:

Unlike single molecules experiment on SEF, were shot noise and other noise source are significant compared to the signal level, in this system all our signals are rather high. This provides a very low intrinsic noise level to our measurements, and as we have shown previously, we can get less than 1% coefficient of variation (CV) on repeat experiments. From a practical point of view, because of the limited dynamic range of photodetectors, when the enhanced fluorescence is below the saturation level of the detector, the fluorescence measurement of the water sample and the dye only sample are low and suffer from noise. However these two samples are not changing with time, so we average the different time measurements on these samples to get high accuracy. One factor that is important in the measurement is the temperature. The dependence of aggregation on temperature is known from literature, and therefore we conduct all our experiments at room temperature, which is kept constant at the lab at 22°C. It is important to note that it is not the optimal temperature, since in several experiments where the stock solutions were used when they are still cold from the fridge, the intensity enhancement factor was measured to be 10-15% higher that the result reported in this paper. However, in such experiments, the correlation to the aggregation kinetics that was measured independently (and at probably a slightly different temperature of the reactants) was not as good as when all were measured at the same (room) temperature.

Time resolved fluorescence measurements on Silver nanoparticle-dye complexes

In order to confirm that we can use the scattering beam as our instrument response function (IRF), we compared the decay curve of A655-DNA in the presence of silver nanoparticles and aggregating agent to the time response of pinacyanol in methanol (measured under the same conditions) which was previously determined to have a 6 ps lifetime. As can be seen in Figure S1, the decay of A655-DNA, which gives a lifetime of 6 ps when the scattering curve is used as the IRF, overlaps with the decay curve of pinacyanol.
Figure S1: Decay curves of 680 nm±10 nm. A655 with Ag-NPs and spermine (black), pinacyanol (red), and Ag scattering (blue). For comparison, all traces are normalized to their maxima and horizontally shifted from the original data to the same starting point.

Figure S2 shows the emission spectra of A655-DNA co-aggregated with Ag-NPs as measured in the fluorescence spectrometer, in comparison to that measured by the streak camera. A good agreement is found between the two. In the streak camera system, when the second 645 nm long pass filter is removed, a very strong scattering peak (~100× stronger than the fluorescence peak at 680 nm) with a spectral dependence that corresponds to the laser, rather than the fluorescence emission is detected (Figure S2, black line). The time decay of this data around 615 nm was used as the IRF of the instrument.

Figure S2: Spectrum of A655-DNA with Ag-NPs and spermine: as measured on the Tecan Safire II spectrometer (blue), as measured by the streak camera using both a 630nm and a 645nm long pass filter (red) and as measured by the streak camera with only the 630nm long pass filter (black).
Excitation and emission wavelength position when measuring SEF compared to the absorption and emission spectra of A655-DNA

**Figure S3:** Excitation and emission spectra of the A665-DNA. The purple line marks the center position of the excitation monochromator used in the SEF experiments (650nm) and the orange line marks the center position of the emission monochromator used in the SEF experiments (690nm).

Control experiments

**Figure S4:** Time dependence of fluorescence readout for a) pure water; b) no aggregating agent and no silver control (only dye); c) no silver control (dye and aggregating agent); d) full experiment containing dye-labeled
DNA, aggregating agent and silver nanoparticles; e) no-DNA control (only spermine and Ag nanoparticles); f) no dye control (unlabelled DNA, spermine and Ag nanoparticles). In all experiments final dye concentration is 0.5 nM, final spermine concentration is 100 µM and final silver concentration is 100 pM.
II. THEORETICAL CONSIDERATIONS

Finite Element Modeling electromagnetic calculations

In order to understand the effect of increasing aggregation of nanoparticles, simulations were carried out using the commercial software COMSOL[http://www.comsol.com/, version 4.2]. This software uses Finite Element Modeling to calculate electromagnetic properties. The simulations were carried out in 3D, using the frequency domain study of the Electromagnetic Waves physics interface, which is implemented in the RF module. The spheres in the simulation were of radius \( r = 17 \text{ nm} \), with gaps of \( g = 1.5 \text{ nm} \). The simulations used the dielectric function of silver from Ref. \(^4\) and NPs were embedded in water with \( n = 1.33 \). The spheres are arranged in a linear chain for simplicity, and the incident field is polarized along the chain axis and is propagating perpendicular to it. The chain was enclosed in a spherical bounding box of radius 680 nm, which was surrounded by a spherical perfectly matched layer (PML) with 6 layers and total thickness of 520 nm. The purpose of the PML is to eliminate reflections from the boundary of the simulation volume. Convergence of the results was tested by comparing the results from the dimer to exact results obtained from generalized Mie theory\(^5-7\).

Electromagnetic calculations based on the dimer model

In order to understand, at least semi-quantitatively, the main features of the electromagnetic model for SEF in our system, we have used the model system of a dimer of two closely-spaced silver nanoparticles. This provides a simplified model of our aggregates, which nevertheless captures the most important physical phenomena associated with gap-containing nanostructures. For this model, all the necessary electromagnetic properties can be calculated efficiently and accurately within the framework of generalized Mie theory (see \(^5-7\) for details). In aggregates bigger than a dimer, plasmon resonances are typically redshifted (as in the example of a chain also studied in this work) and damped. As a result, this simplified model cannot predict the position of the plasmon resonance and is also likely to overestimate local field enhancements. With these provisos in mind, it does however allow us to clarify and illustrate on simple examples the concepts that are discussed in the main paper. It is with this
goal in mind that we provide the following figures and discussion (see also the supplementary information of 8 for further details).

The parameters used for the calculations have been chosen to match those estimated in our real system. We therefore consider silver spheres (with the dielectric function of \( \varepsilon \)) of radius \( a = 17 \) nm (34 nm diameter), separated by a gap of \( g = 1.5 \) nm and embedded in water (\( n = 1.33 \)). The incident wavelength, \( \lambda_L \), is the main parameter. We here only consider excitation polarized along the dimer axis (and propagating perpendicular to it). This is the situation where a maximum coupling to the main (most redshifted) plasmon resonance of the dimer occurs. In reality, orientation averaging should be carried out, which would typically result in lower average enhancements 9, 10.

We first compare in Figure S5 the spectral profile of the extinction \( Q_{\text{Ext}}(\lambda_L) \) of such a dimer and that of the local field intensity enhancement factor (LFIEF) \( M_{\text{Loc}}(\lambda_L) \) in the gap (where it is maximum). As can be seen in Figure S6, at least close to the interaction plasmon resonance (at 520 nm), \( M_{\text{Loc}}(\lambda_L) \) and \( Q_{\text{Ext}}(\lambda_L) \) correlate very closely (up to a proportionality factor). It should be noted that when comparing different systems, the actual value of the extinction coefficient may not be correlated with the magnitude of the LFIEF 9, but for a given system, the wavelength dependence of the extinction coefficient usually provides a good approximation to the spectral profile of \( M_{\text{Loc}}(\lambda_L) \). This approximation has in fact been used in the past in similar contexts 11-13.

![Normalized extinction (blue), and normalized field enhancement (red) spectra for the case of a dimer of 34 nm diameter silver particles with 1.5 nm gap embedded in water.](image)

**Figure S5:** Normalized extinction (blue), and normalized field enhancement (red) spectra for the case of a dimer of 34 nm diameter silver particles with 1.5 nm gap embedded in water.
We now focus on the spectral dependence of the surface-enhanced fluorescence enhancement factor, $M_{SEF}(\lambda_L, \lambda_R)$ for an emitter at a distance $d$ from the metal surface. As explained in the main text, this factor can be approximated as:

$$M_{SEF} = M_{Loc}(\lambda_L)\eta(\lambda_R)/Q_0$$  \hspace{1cm} (S1)

Where $\eta$ is the modified quantum yield given by:

$$\eta(\lambda_R) = M_{Rad}(\lambda_R)/M_{Tot}$$  \hspace{1cm} (S2)

$M_{Tot}$ can moreover be decomposed into a radiative contribution, given by $M_{Rad}$ and a non-radiative contribution $M_{NR}$. The latter can itself be decomposed into two distinct non-radiative contributions:

$$M_{NR} = M_{NR}^{LSP} + M_{NR}^{SPP}$$  \hspace{1cm} (S3)

$M_{NR}^{SPP}$ represents coupling into non-radiative surface-plasmon polariton waves of the metal surface. This contribution is strongly distance-dependent and does not depend much on the geometry. In fact, it is well approximated$^8,14-16$ by the case of an emitter on a flat metal surface for which:

$$M_{NR}^{SPP} \approx \frac{3}{8(\kappa_M d)^3} \text{Im} \left( \frac{\epsilon - \epsilon_M}{\epsilon + \epsilon_M} \right)$$  \hspace{1cm} (S4)

where $\epsilon$ ($\epsilon_M$) is the dielectric function of the metal (embedding medium), $\kappa_M$ is the wavevector in the embedding medium, and $d$ is the distance to the surface. The expression above applies to a dipole perpendicular to the surface (a factor $1/2$ should be added for a parallel dipole). Also, for very small distances, $d<1$ nm, non-local effects are expected to become important, and the above expression underestimates the real non-radiative rates. In any case, as illustrated in Figure S7, this factor varies dramatically with the distance, owing to the $1/d^3$ dependence, but not much with wavelength.

The second non-radiative contribution, $M_{NR}^{LSP}$, relates to coupling to the (mostly radiative) localized surface Plasmon resonance, which also contributes to $M_{Rad}$. As a result, $M_{NR}^{LSP}$ is of the same order as $M_{Rad}$, and follows the same resonance profile and is not very distance-dependent.
Given this, we can identify two limiting cases for the modified quantum yield:

- SPP-dominated regime, i.e. when $M_{NR}^{SPP}$ dominates over $M_{NR}^{LSP}$. This regime will apply for the shortest distances. In this case, $M_{Tot} \approx M_{NR}^{SPP}$ and has only a mild wavelength dependence in the region of the LSP resonance. As a result, the spectral profile of $\eta(\lambda_R)$ is governed by the factor $M_{Rad}(\lambda_R)$ and is also typically much smaller than 1.

- LSP-resonance-dominated regime, i.e. when $M_{NR}^{LSP}$ dominates over $M_{NR}^{SPP}$. This regime will apply for the largest distances. In this case, $M_{Tot} \approx M_{NR}^{LSP} + M_{Rad}$ and follows the same resonance profile as $M_{Rad}(\lambda_R)$. This resonant wavelength-dependence therefore cancels out in the ratio to obtain $\eta(\lambda_R)$, which therefore has only a mild wavelength dependence in the region of the LSP resonance ($\eta \approx 0.4$ in the example of Figure S6).

The distance from the surface, $d$, is the primary factor influencing which of these two regimes applies. The cross-over from one regime to the other occurs when $M_{NR}^{SPP} \approx M_{Rad}$ and will therefore occur at shorter distances when local field enhancements (and therefore $M_{Rad}$) are large.

These ideas are further illustrated in the theoretical calculations summarized in Figure S6, using parameters relevant to the experiments presented in the main paper. In order to be able to vary the distance from the surface, we consider emitters on a line angled at $\alpha \approx 21^\circ$ from the dimer axis as shown in Figure S6(a). The maximum distance from the surface is therefore $d=2$ nm (in the 1.5 nm gap exactly between the spheres, the maximum distance is only 0.75 nm). As shown in Figure S6(a), the factor $M_{Rad}(\lambda_R)$ exhibit a resonance associated with the localized Plasmon resonance of the dimer, but its magnitude is not strongly dependent on distance over the small range investigated here. In contrast, $M_{NR}^{SPP}$ is not very wavelength dependent but varies over several orders of magnitude as $d$ changes (see Figure S6(b)). In the greyed area (short distances), it entirely dominates $M_{Tot}$ as shown explicitly in Figure S6(c). As a result, the modified quantum yield $\eta(\lambda_R)$ follows closely the spectral profile of $M_{Rad}(\lambda_R)$ in this regime (short distances). For larger distance, however, $\eta(\lambda_R)$ is of the order of 0.4 around the resonance and exhibit a much less pronounced wavelength dependence (Figure S6(d)).
Figure S6: The influence of distance on the spectral profile and magnitude of the enhancement factors influencing the modified quantum yield in SEF conditions. All quantities are obtained from generalized Mie theory calculations on a dimer of silver spheres, with a dipole perpendicular to the surface positioned at a distance \( d \) from the surface along a line angled at \( \alpha \approx 21^\circ \) from the dimer axis, as shown in the schematics in (a). We show in particular:

(a) the radiative enhancement factor \( M_{\text{Rad}} \). (b) the SPP contribution to the non-radiative enhancement factor, \( M_{\text{NR}}^{\text{SPP}} \) (Eq. S4), also compared to \( M_{\text{Rad}} \). Depending on their relative contributions, two regimes can be identified for the total decay rate enhancement \( M_{\text{Tot}} \): SPP-dominated (greyed area) at short distances, and LSP-dominated (yellow area) at larger distances. This is also evident when comparing the predicted \( M_{\text{Tot}} \) and \( M_{\text{NR}}^{\text{SPP}} \) as shown in (c). The resulting modified quantum yield, \( \eta = M_{\text{Rad}}/M_{\text{Tot}} \) is shown in (d). Its spectral profile is the same as that of \( M_{\text{Rad}} \) in the SPP-dominated regime (small \( d \)), but is much less pronounced around the resonance (0.4) in the LSP-dominated regime (larger \( d \)).
References: