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Surface Plasmons Control the Dynamics of Excited Triplet States in the Presence of Gold Nanoparticles

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A molecule irradiated in the proximity of a metal nanoparticle can be viewed as undergoing transmitter/receiver antenna interactions;[1,2] the process has also been described as analogous to a lightning rod effect.[3] In our case, methylene blue (MB) interacts with aqueous gold nanoparticles (AuNPs). Laser excitation produces the readily detectable MB triplet state, ^{3}MB*, in both the presence and absence of AuNPs, but the ^{3}MB* yield and dynamics change significantly as a result of the MB−AuNP interactions in both the ground and excited states. A molecule in its excited state located near an optical antenna can be viewed as a transmitter; similarly, a molecule (e.g., MB) in its ground state and being excited by the localized plasmon field in the vicinity of the AuNP antenna acts as a receiver.[2] The antenna can be used to enhance molecular fluorescence; enhanced fluorescence is simply the reflection of an increased excited state concentration near the nanoparticle, and similar effects should be anticipated in the case of triplet states produced via intersystem crossing (ISC) from the excited singlet state.[4]

In our system ^{3}MB* is readily detectable by its transient absorption at 420 nm,[5] while the excited singlet state decays very rapidly with a lifetime of ∼380 ps[6] as a result of a rapid ISC. The aqueous ∼15 nm AuNPs selected for this study were prepared photochemically, as reported earlier;[7,8] their surface is largely unprotected (see Supporting Information); in contrast with thiol-modified AuNPs,[9] our AuNPs do not give a signal under laser excitation. The lifetime of triplet MB was 82 μs under N_2 in the absence of AuNPs and 11.8 μs in the presence of 1.2 nM AuNPs, Figure 1. Plotting the reciprocal ^{3}MB* lifetime against [AuNP], Figure 1C, one obtains a quenching rate constant, k_q, of 6.4×10^{13} $M^{-1}\ s^{-1}$ from the slope. An estimation using Debye's equation gives a diffusional rate constant of 7.4×10^9 $M^{-1}\ s^{-1}$ in water at 25 °C.[10] In the case of metal nanoparticles this value would require a correction to take into account that the AuNP diffusion is negligible compared with the dye and another to account for the bigger target (large diameter) that the AuNP represents. This can lead to estimated diffusional rate constants of $\sim 10^{11}$ $M^{-1}\ s^{-1}$, nearly three orders of magnitude below that observed.

The ^{3}MB* decay reveals that in the absence of AuNP the process can be reasonably fit with a single exponential, while in the presence of AuNP a biexponential fit is required; this is illustrated in Figure 1B for short time scales. Two things are apparent from these data: (a) the overall triplet absorption at least doubles at short time scales, and (b) the short decay component ($\tau \approx 25$ ns) is only observed in the presence of AuNPs. Traces at different AuNP concentrations reveal that while the signal amplitude due to this fast decay depends upon the AuNP concentration, the short lifetime (±25%) is largely unchanged. We attribute this fast decay component to MB molecules that are bound to the nanoparticle surface at the time of excitation, i.e., a static AuNP quenching component, that may incorporate some self-quenching.[5]

Triplet quenching with a rate constant of 6.4×10^{13} $M^{-1}\ s^{-1}$ is inconsistent with our understanding of dynamic quenching but is reminiscent of transient phenomena described by Noyes,[11] for cases where the results (transient quenching) correspond to a nonrandom distribution of reactants, i.e., when there is a rich concentration of ^{3}MB* in the proximity of the AuNP. We attribute the anomalous quenching rate constant ($>10^{13}$ $M^{-1}\ s^{-1}$) to formation of a large triplet concentration in the vicinity of the AuNP due to plasmon enhancement effects; thus, laser excitation effectively leads to a ^{3}MB* "transient shell" spatially set up for easy quenching.

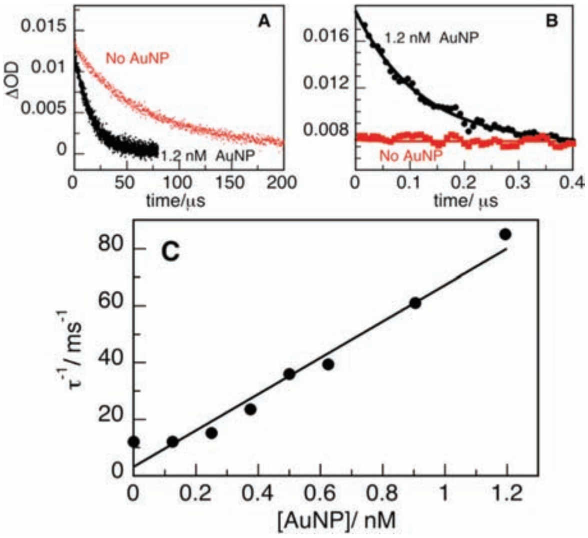

Figure 1. Decay of ^{3}MB* at 420 nm in the absence and presence of 1.2 nM AuNP in long (A) and short (B) time scales ([MB] = 5 μM). MB triplet (monitored at 420 nm) following 650 nm laser excitation. (C) the slope is the bimolecular rate constant for ^{3}MB* quenching by AuNP.

We were concerned with possible electrostatic effects that could lead to a nonrandom MB distribution, given that MB is positively charged and AuNPs normally show a negative zeta potential.[7] To explore this, we measured the zeta potential as a function of [MB] for two concentrations of AuNPs. Two important observations can be derived from Figure 2: first, that at [MB] = 5 μM, as used in most experiments, AuNP are essentially neutral as a result of MB surface attachment of the same MB population responsible for static quenching (i.e., the 25 ns decay of Figure 1B); second, that only a small fraction of the MB is "fixed" at the AuNP surface; otherwise the black curve would be much steeper reflecting surface saturation at a much lower MB concentration. We note that while AuNP colloids are stable for years,[7] once MB has been added, they are only stable for hours, as expected once charge repulsions have been eliminated.

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For the model proposed to be applied, one must expect an enhanced MB triplet production. This is observed, as illustrated in Figure 3, based on data acquired on short time scales with data points separated by 8 ns, where the steep change in absorbance is responsible for the large error bars; the transient absorbance increases by a factor ∼2.2 upon addition of AuNPs. A recent study suggests larger enhancements of the MB ground state absorbance;[12] this is not inconsistent with our data, since ground state enhancements will lead to excited singlet enhancements, but a portion of these singlets will be quenched quickly, before ISC, and thus not populate the triplet state.

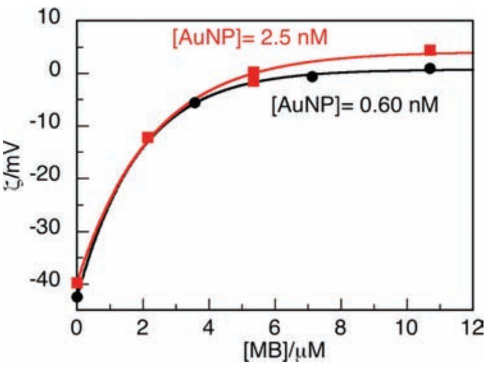

Figure 2. Changes in zeta potential upon addition of MB for two different concentrations of AuNP.

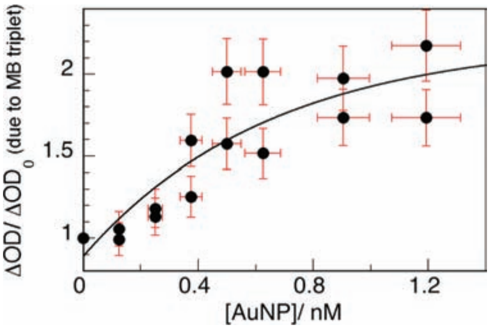

Figure 3. Relative change of the relative transient absorbance due to MB triplet recorded at 420 nm and immediately after the 650 nm laser excitation pulse for [MB] = 5 μM. The extrapolated plateau level is at 2.2.

One can ask if the slow (μs) triplet decay of Figure 1A should not show more complex kinetic behavior, since the signal should also incorporate the remote unaffected molecules (see Figure 4) whose triplet lifetime should remain largely unchanged. This is probably the case, but kinetic analysis of multiple decay exponentials with similar lifetimes is usually difficult and it is likely that the modest signal-to-noise in these traces masks its true complexity (see Figure S4). If this is the case, it would mean that quenching of the enhanced population would be slightly faster than suggested.

We believe that this is the first report on the dynamics of triplet states influenced by plasmon field interactions in the vicinity of a nanostructure. Our results fit well the paradigm of a transmitter−receiver antenna that provides a framework for the interpretation of these phenomena.[2,13] Thus at the excitation stage, the AuNP is the antenna, enhancing the absorption of receiver MB,[12] and leading to an increased population of dye excited singlets. These in turn partition between surface quenching and ISC; in monitoring directly ^{3}MB* our results do not report on possible effects on the ISC rate. The yield of detectable triplets is more than doubled by AuNP plasmon interactions. At 1.2 nM AuNPs about half the triplets decay with a lifetime of ∼25 ns (a reduction of a factor >10 000), due to surface quenching, i.e., now ^{3}MB* is the transmitter and the AuNP the receiver. The longer ^{3}MB* lifetime compared the singlet state[1] probably results from the need for electron exchange interactions for triplet quenching by AuNPs.[10]

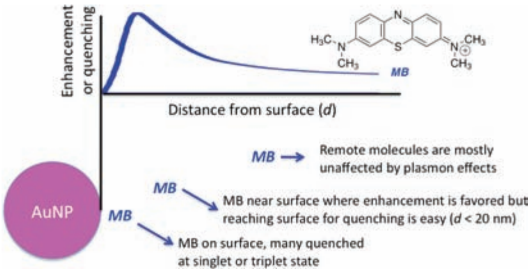

Figure 4. Schematic representation of the interaction of MB with the AuNP surface. Qualitative curve modeled after reported plasmon effects.[1]

The long-lived MB triplets are quenched by AuNPs with an anomalous rate constant of 6.4×10^{13} M^{-1}s^{-1}, attributed to a nonrandom distribution (see Figure 4) caused by plasmon antenna interactions. We show that plasmon field interactions in the vicinity of AuNPs produce an enhancement doubling the ^{3}MB* population. Surface plasmon sensitization due to antenna effects opens an exciting field based on the noncovalent interaction of metallic nanoparticles and excited triplets.

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Supporting Information Available: Experimental details, UV−visible and transient spectra, calculation of AuNP concentration, SEM and size distribution of AuNP. This material is available free of charge via the Internet at http://pubs.acs.org.

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