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The use of aluminum nanostructures as platforms for metal enhanced fluorescence of the intrinsic emission of biomolecules in the ultra-violet

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Abstract

We consider the possibility of using aluminum nanostructures for enhancing the intrinsic emission of biomolecules. We used the finite-difference time-domain (FDTD) method to calculate the effects of aluminum nanoparticles on nearby fluorophores that emit in the ultra-violet (UV). We find that the radiated power of UV fluorophores is significantly increased when they are in close proximity to aluminum nanostructures. We show that there will be increased localized excitation near aluminum particles at wavelengths used to excite intrinsic biomolecule emission. We also examine the effect of excited-state fluorophores on the near-field around the nanoparticles. Finally we present experimental evidence showing that a thin film of amino acids and nucleotides display enhanced emission when in close proximity to aluminum nanostructured surfaces. Our results suggest that biomolecules can be detected and identified using aluminum nanostructures that enhance their intrinsic emission. We hope this study will ignite interest in the broader scientific community to take advantage of the plasmonic properties of aluminum and the potential benefits of its interaction with biomolecules to generate momentum towards implementing fluorescence-based bioassays using their intrinsic emission.

Keywords

finite-difference time-domain; plasmonics; fluorescence; metal enhanced fluorescence; aluminum nanostructures; label free detection

1. INTRODUCTION

Fluorescence is a critically important technology in biological research and clinical medicine as exemplified by its wide use in cell imaging, medical diagnostics and biophysical research [1]. Almost all fluorescence based bioassays in use today require tagging biomolecules with external fluorescent probes. A more recent growth area of fluorescence in biomedical

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research is its use in protein and DNA arrays which involves tagging large number of biomolecules with external probes in hundreds or thousand of individual spots. The use of external labels has drawbacks because it requires chemical modification and washing steps which can perturb the native functionality of ligand-receptor interactions and also adds considerable expense and complexity to the techniques. One way to circumvent this problem is by exploiting the intrinsic emission of biomolecules. However this presents its own challenges because biomolecules absorb in the deep ultra-violet (UV) and emit in the UV with low quantum yields. Hence the presence of high background from biological media in the UV and the expenses involved in using quartz-based optical components presents significant challenges for exploiting the intrinsic emission of biomolecules in bioassays.

However, during the past several years we have shown that the quantum yields of fluorophores can be significantly increased by non-chemical through-space interactions with metallic surfaces and particles [1–6]. More recently we have shown that this effect can be extended to ultra-violet (UV) wavelengths [7–10]. Encouraged by these observations, we consider the possibility of using aluminum nanostructures for enhancing the intrinsic emission of biomolecules. We used the finite-difference time-domain (FDTD) method to calculate the effects of aluminum nanoparticles on nearby fluorophores that emit in the UV [8, 10, 11–13]. The FDTD method is a rigorous computational electrodynamics method that can be used quite accurately to describe plasmonic effects [8, 10, 11–16]. We find that the radiated power of UV fluorophores is significantly increased when they are in close proximity to aluminum nanostructures. We show that there will be increased localized excitation near aluminum particles at wavelengths used to excite intrinsic biomolecule emission. Additionally we present experimental results showing that a thin film of amino acids and nucleotides show enhanced emission when in close proximity to aluminum nanostructured surfaces.

It is important to note that our main goal is to present the most favorable effect of aluminum nanoparticles on fluorophores in their proximity. Hence we deliberately performed separate calculations for fluorophores oriented perpendicular relative to the nanoparticles and considered a variety of different system parameters. In all the quantitative calculations presented, it is assumed that the excitation stage of fluorescence has occurred and we only consider the emission side where the fluorophore is acting as a dipole source emitting radiation. These conditions are ideal in nature. It is expected that in actual experimental conditions fluorophore orientation effects, and effects arising from sample heterogeneity and the mode of sample excitation can arise that might prevent observation of some of the features reported here.

2. METHODS

2.1 FDTD Computational Details

Three-dimensional FDTD simulations were performed using the program *FDTD Solutions* (version 5.0) from Lumerical Solutions, Inc., (Vancouver, Canada) [8, 10, 13–15]. The calculations were performed with the parallel FDTD option on a Dell Precision PWS690 Workstation with the following components: Dual Quad-Core Intel Xeon E5320 processors at 1.86 GHz, and 8 GB RAM. Additional post-processing of the FDTD Solutions data was

performed using *MATLAB* (version 7.0) from Mathworks (Natick, MA), and OriginPro 7 from Originlab Corporation (Northampton, MA). The fluorophore is modeled as a time-windowed, oscillating point source for the electric field, with frequency content spanning the spectral range (100–700 nm) of interest and polarization perpendicular to the metal nanoparticle surface. Additionally, we also used a time-windowed dipole source, radiating at a fixed wavelength of 350 nm was used to mimic the emission of a tryptophan and proteins. Further details of our computational technique can be found in our previous reports [8, 10, 14–15]. After testing for convergence, we employed a grid size of 0.5 nm for the 20 nm metal nanoparticles, and 1 nm for the 40, 80, 100 and 140 nm metal nanoparticles. Typically the durations of our simulations were 400 fs.

Figure 1 is a schematic illustration of the system studied where: d is the diameter of the aluminum nanoparticle, $2s$ is the surface-surface distance between dimers. For the case of the single nanoparticle (monomer) – s is spacing between the fluorophore to the surface of the particle), θ is the polar angle from the z -axis where $0 \leq \theta \leq \pi$ and Φ is the azimuthal angle in the x - y plane from the x -axis with $0 \leq \Phi < 2\pi$. The fluorophore is placed at the origin and a spherical aluminum nanoparticle or nanoparticle dimer is placed near the fluorophore along the x -axis. It is assumed the excitation stage of fluorescence has occurred and the fluorophore is now emitting dipole radiation. We calculate the enhancement of the total power radiated by the various fluorophore-nanoparticle systems with the dipoles oriented perpendicular to the aluminum surface (dipole along the x -axis). The enhancement of the total power radiated indicates increases in the relative radiative decay rates of the fluorophore-nanoparticle system when compared to the isolated fluorophore. The enhancement in the total radiated power is inferred by integrating the normal flux passing through a closed surface containing the system. It is represented as:

$$P_{rad}/P_0 \quad (1)$$

where P_0 is the radiated power of a classical dipole in a homogeneous background which in our case is air/vacuum, and P_{rad} is radiated power of the dipole in proximity of the metal nanoparticles. Eq. (1) is inferred from integrals of the Poynting vector over a surface enclosing the system or equivalent volume integrals [8, 10, 15–16]. Enhancement occurs when $P_{rad}/P_0 > 1$. An enhancement in the total radiated power by a system (system = dipole-nanoparticle complex) when compared to an isolated dipole is indicative of a corresponding increase in the relative radiative decay rate of the system and vice-versa [8, 10, 15–16]. This correspondence between quantum and classical theory is valid if normalized quantities are considered, and is given by [8, 10, 15–16]:

$$\frac{\gamma_{rad}}{\gamma_{rad}^0} = \frac{P_{rad}}{P_0} \quad (2)$$

where γ_{rad}^0 and γ_{rad} are respectively the radiative decay rate of an isolated classical dipole in a homogeneous background (which in our case is air/vacuum), and the radiative decay rate of the dipole in proximity of the metal nanoparticles [15–17]. In our implementation of FDTD, we use a set of six frequency domain surface monitors to create a box around the system, and measure the total power radiated by the system by integrating the real part of the

Poynting vector over all six surfaces. This power is then normalized to the analytic expression for the power radiated by a dipole in a homogeneous dielectric (in this case, air) to get the relative change in power radiated as described in Eq. 1.

2.2 Experimental Details

Aluminum slugs, silicon monoxide, N-acetyl-L-tryptophanamide (NATA), Guanosine 3',5'-cyclic monophosphate sodium salt (GMP), and low molecular weight polyvinyl alcohol (PVA, MW 13000–23000) were purchased from Sigma-Aldrich and used as received. Distilled water (with a resistivity of 18.2 M Ω -cm) purified using Millipore Milli-Q gradient system was used for sample preparation. Aluminum was deposited on quartz slides using an Edwards Auto 306 Vacuum Evaporation chamber under high vacuum ($<5 \times 10^{-7}$ Torr). In each case, the metal deposition step was followed by the deposition of 5 nm of silica via evaporation without breaking vacuum. This step served to protect the metal surface as well as it adds a spacer layer between the metal surface and fluorophore. The deposition rate was adjusted by the filament current and the thickness of film was measured with a quartz crystal microbalance. An aliquot of approximately 500 μ l of 0.25 wt % aqueous solution of low molecular weight PVA containing separately dissolved NATA, and GMP was spin coated at 3000 rpm (Specialty coating system Inc., Speedline Technologies, Indiana) on the surface of the aluminum and quartz substrates respectively. This composition of PVA forms approximately 10 nm thick film. The steady-state fluorescence spectra were carried out using front face illumination with a Varian Cary Eclipse Fluorescence Spectrophotometer. Emission spectra were measured through bandpass interference filters. Magic angle observation was used in the emission path for reducing the scattered light of the excitation wavelength without significant distortion of the emission spectra.

3. RESULTS AND DISCUSSION

Figure 2 shows the wavelength dependent radiated power enhancement for a dipole located $s = 5$ nm away from single aluminum nanoparticle with diameters $d = 20, 40$ and 80 nm respectively. In these calculations, the dipole was oriented perpendicular to the tangential aluminum surface (along the x -axis). We see that the enhancement in the radiated power peaks at approximately $\lambda = 155$ nm for the $d = 20$ nm particle size [8]. For the $d = 40$ nm particle size, the radiated power enhancement shows a dipolar peak at $\lambda = 180$ nm and we also see a quadrupolar enhancement peak at $\lambda = 137$ nm [8]. This indicates that higher order radiation modes become relevant when the radiating dipole and the metal surface are in very close proximity. Finally, for the $d = 80$ nm particle size the radiated power enhancement peaks at $\lambda = 310$ nm - a 130 nm red shift from the corresponding peak of the $d = 40$ nm particle. Additionally we also see sharp higher order mode peaks at $\lambda = 172$ nm and $\lambda = 141$ nm [8]. This result further corroborates the fact that higher order radiation modes arise when the radiating dipole and the metal surface are in very close proximity. The enhancements observed in Figure 2 can be expected because when the dipole is oriented perpendicular to the metal surface, the fluorophore's dipole induces a dipole in the aluminum nanoparticle in a configuration that allows the dipoles to align along the x -axis head to tail, leading to a much larger effective radiating dipole than in the case of an isolated fluorophore – and hence the enhancements. We have deliberately included FDTD results with dipoles oriented

perpendicular to the metal surface to present the best case scenario. Previous studies done from laboratory have demonstrated that dipoles oriented parallel to the metal surface induce significant quenching of the emission and hence we did not choose the parallel orientation case for this study [8, 15]. The radiation enhancement of a spherical nanoparticle/dipole system can also be analytically solved and we have validated our FDTD results by comparison with those solutions [8]. However the dimer systems to be discussed later do not admit such analytical solutions.

It is important to investigate the effect of the aluminum nanoparticle size on the enhancement of the radiated power of fluorophores in the biologically relevant UV range. This was done by integrating the area under the radiated power enhancement spectra for the fluorophore near the $d = 20$ nm, 40 nm, 80 nm, 100 nm and 140 nm aluminum nanoparticles between the wavelength range of 300–420 nm and dividing it by the corresponding area under the curve for the isolated dipole [8]. This wavelength region was chosen because it is the typical region for the intrinsic fluorescence emission of biological molecules. For these calculations, the dipole-aluminum distance was kept constant at $s = 5$ nm. Figure 3 shows these results which indicate that there is a clear dependence of the radiation enhancement with particle size, with the 80 nm aluminum nanoparticle giving the maximum enhancement of about 12-fold [8].

We also studied the effect of fluorophore-aluminum distance on the extent of enhancement observed for the case of a fluorophore next to a single aluminum as well as in between two aluminum particles in a dimer system. Figure 4 shows a visual comparison of the enhancement in the radiated power for all the $d = 80$ nm aluminum particle monomer and dimer systems studied with the perpendicular dipole orientation. The calculations were performed in a manner similar to Figure 3 i.e. in the wavelength range of 300–420 nm. We investigated fluorophore-metal distances of $s = 1$ nm, 2 nm, 5 nm, 10 nm and 20 nm for the single particle case and dimer spacing of $2s = 2$ nm, 4 nm, 10 nm, 20 nm and 40 nm respectively. For the dimer case, the fluorophore is located exactly the midpoint of the dimer axis. i.e. equidistant from each aluminum nanoparticle. The first five values in the x -axis ($s = 1, 2, 5, 10$ and 20 nm) of Figure 4 denotes the single nanoparticle system or monomer, whereas the last five values ($2s = 2, 4, 10, 20$ and 40 nm) represents the dimer case. The y -axis of Figure 4 is plotted in a semi-logarithmic scale (base 10 along the y -axis) for convenience of observation. We see that extent of enhancement decreases with increasing fluorophore-metal distance – an observation that is expected as the increasing distance will reduce the strength of the induced dipole in the aluminum nanoparticles. The major conclusion that can be drawn from Figure 4 is that the presence of the dimer creates a significant increase in the enhancement of the radiated power when compared to an isolated dipole, up to a maximum of over 3,500-fold for the dimers with a surface-surface spacing of $2s = 2$ nm [8]. Additionally it is also seen that the degree of enhancement observed from the dimer system decreases with increasing dimer spacing. This huge enhancement for the dimer case occurs because in the perpendicular orientation the fluorophore's dipole induces two dipoles, one in each of the nanoparticles in the dimer system: in this configuration allows all the three dipoles to align along the x -axis head-to-tail, leading to a much larger effective radiating dipole than in case of the isolated dipole and the single nanoparticle system and

hence we observe the higher enhancements. The enhancement values for all the monomer and dimer cases plotted in Figure 4 are tabulated in Table 1.

The results discussed thus far have been instructive in providing us with an insight on the possible use of aluminum nanoparticles as MEF substrates for the label free detection of biological molecules. But this effort cannot be complete without an attempt to examine of the electromagnetic near-field distributions around the aluminum nanoparticles that are created by both excitation light as well as excited-state fluorophores. Figures 5(a) shows the enhancement in the near-fields ($E^2 = E_x^2 + E_y^2 + E_z^2$) around a $d = 60$ nm dimer spaced $2s = 10$ nm apart that was created by the interaction with a plane wave of wavelength 280 nm. All the near-field calculations shown are performed along a single plane, that is, the x - y plane running through the center of the fluorophore-aluminum nanoparticles. A wavelength of 280 nm was chosen because it is typical for excitation of protein fluorescence. Figure 5(a) shows there is intense near-field enhancements in the region in between the particles. In this case the plane wave was propagating along the z -axis and polarized along the x -axis. The areas of high near-field enhancements in between the particles means that a protein or any other biomolecule once localized between the dimers will experience a much higher excitation field than if it were isolated and directly excited only by the incident light. This will lead to higher excitation rates of the fluorophore, which leads to greater excitation-emission cycles in a given time period. In Figure 5(b) we present the near-field enhancements around a $d = 80$ nm aluminum dimer system spaced $2s = 10$ nm apart that are induced by a fluorophore radiating at 350 nm. We chose a fluorophore radiating at 350 nm because it is the typical emission region for proteins and nucleotides. In Figure 5(b), only a small area between the two aluminum nanoparticles shows quenching. Interestingly this is the area where the excited-state fluorophore is physically located. The overwhelmingly large portion of the image depicts significant near-field enhancements in the region immediately surrounding the dimer. It is important to note that the near-fields calculated in Figure 5(b) do not necessarily represent propagating radiation. They could either be propagating fields or localized evanescent fields that are non-propagating. However, we believe these near-field enhancements are somehow related to the enhancements in the far-field propagating emission (radiation) as shown in Figures 2–4. Such spatial variations in the near-field enhancements are not easily inferred from calculations involving changes in the total radiated power. They provide a unique insight into the nature of metal enhanced fluorescence that is interesting from the perspective of applications involving molecular spectroscopy and designing specific fluorophore-metal nanoparticle systems.

We also performed experiments to corroborate the theoretical predictions presented above concerning the efficiency of aluminum nanostructures to detect unlabeled biomolecules such as amino acids and/or nucleotides using their intrinsic emission. We spin-coated a 10 nm layer of PVA containing dissolved NATA and GMP separately on a 10 nm thick aluminum film (sitting on top of a quartz substrate) and compared its fluorescence emission intensity an identical sample on a quartz substrate [8,10]. Figure 6(a) shows that for a 10 nm thick PVA film containing NATA, the 10 nm thick aluminum substrate gives an emission intensity enhancement of approximately 11-fold when compared to the quartz (control). Similarly Figure 6(b) shows that for a 10 nm thick PVA film containing GMP, the 10 nm

thick aluminum substrate gives an emission intensity enhancement of approximately 11-fold when compared to the quartz (control). We have also reported the emission enhancement from a number of amino acids and DNA bases in addition to NATA and GMP [8, 10]. The experimental results of Figure 6 corroborate the validity of our theoretical predictions that aluminum nanoparticles can be used to efficiently enhance the intrinsic emission of various biomolecules in the UV region, and so suggest the possibility of designing bioassays based on intrinsic biomolecule fluorescence, thus potentially avoiding the pitfalls involved in additional external labeling steps that are currently limit biological experiments.

4. CONCLUSION

We presented computational and experimental studies showing the effect of aluminum nanoparticles on the emission of fluorophores in the UV region of the spectrum. The excited fluorophore was modeled as a radiating dipole source, and a variety of nanoparticle sizes (20 nm – 140 nm) and fluorophore-particle distances were studied. Our computational results show that spherical aluminum nanoparticles enhance the radiated power of a fluorophore to varying degrees. The peak enhancement wavelength is a function of the nanoparticle size, with larger nanoparticles showing greater enhancements at longer wavelengths. We observe that the maximum theoretical enhancement by a single aluminum particle is approximately 12-fold when compared to an isolated fluorophore. This change in the radiated power is indicative of changes in the radiative decay rates of the fluorophore-nanoparticle system. We also see that the extent of enhancement in the radiated power is a function of the fluorophore-metal distance, with larger separation distances showing lower enhancements. Another important result that we present is that the degree of the computed enhancement in the radiated power of a fluorophore increases significantly when the fluorophore is placed in between aluminum dimers with maximum enhancement of over 3,500-fold. We show that both incident plane waves and excited-state fluorophores can induce enhancements in the near-fields around an aluminum nanoparticle. An inspection of intensity patterns in the near-field reveal very specific regions around the nanoparticles that experience field enhancements. This type of result is not easily inferred from far-field observations and is relevant to potential applications that would involve spatially resolved molecular spectroscopy or detection using fluorescence. Finally, we presented preliminary experimental results that show that thin aluminum films can significantly enhance the emission intensity of a layer of PVA film containing separately neutral derivatives of tryptophan (NATA) and Guanosine 3',5'-cyclic monophosphate sodium salt (GMP). These experimental observations corroborate our theoretical predictions that aluminum nanostructures can serve as efficient substrates for metal-enhanced fluorescence applications in the ultra-violet region. This can make aluminum a valuable tool for developing modalities for the label free detection of bio-molecules in a variety of sensing and imaging applications.

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References

1. Lakowicz, JR. Principles of Fluorescence Spectroscopy. 3. Kluwer Academic/Plenum Publishers; New York: 2006.
2. Lakowicz J. Radiative Decay Engineering: Biophysical and Biomedical Applications. Anal Biochem. 2001; 298:1–24. [PubMed: 11673890]
3. Lakowicz JR, Shen Y, D'Auria S, Malicka J, Fang J, Gryczynski Z, Gryczynski I. Radiative Decay Engineering. 2. Effects of Silver Island Films on Fluorescence Intensity, Lifetimes, and Resonance Energy Transfer. Anal Biochem. 2002; 301:261–277. [PubMed: 11814297]
4. Lakowicz JR. Radiative decay engineering 3. Surface plasmon-coupled directional emission. Anal Biochem. 2004; 324:153–169. [PubMed: 14690679]
5. Lakowicz JR. Radiative Decay Engineering 5: Metal-Enhanced Fluorescence and Plasmon Emission. Anal Biochem. 2005; 337:171–194. [PubMed: 15691498]
6. Lakowicz JR, Ray K, Chowdhury M, Szmajcinski H, Fu Y, Zhang J, Nowaczyk K. Plasmon-Controlled Fluorescence: A New Paradigm in Fluorescence Spectroscopy. Analyst. 2008; 133:1308–1346. [PubMed: 18810279]
7. Ray K, Chowdhury MH, Lakowicz JR. Aluminum Nano-structured Films as Substrates for Enhanced Fluorescence in the Ultraviolet - Blue Spectral Region. Anal Chem. 2007; 79:6480–6487. [PubMed: 17685553]
8. Chowdhury MH, Ray K, Gray SK, Pond J, Lakowicz JR. Aluminum Nanoparticles as Substrates for Metal-Enhanced Fluorescence in the Ultraviolet for the Label-Free Detection of Biomolecules. Anal Chem. 2009; 81:1397–1403. [PubMed: 19159327]
9. Ray K, Szmajcinski H, Lakowicz JR. Enhanced Fluorescence of Proteins and Label-Free Bioassays Using Aluminum Nanostructures. Anal Chem. 2009; 81:6049–6054. [PubMed: 19594133]
10. Chowdhury MH, Ray K, Johnson Michael L, Gray SK, Pond J, Lakowicz JR. On the Feasibility of Using the Intrinsic Fluorescence of Nucleotides for DNA Sequencing. J Phys Chem C. 2010 in press.
11. Taflov, A.; Hagness, SC. Computational Electrodynamics: The Finite-Difference Time-Domain Method. 3. Artech House; Norwood: 2005.
12. Sullivan, DM. Electromagnetic Simulation Using the FDTD Method. IEEE Press; Piscataway: 2000.
13. Lumerical Solutions Inc. Reference Guide for FDTD Solutions™ Release 5.0. 2007 <http://www.lumerical.com/fdtd>
14. Chowdhury MH, Gray SK, Pond J, Geddes CD, Aslan K, Lakowicz JR. Computational study of fluorescence scattering by silver nanoparticles. J Opt Soc Am B. 2007; 24:2259–2276. [PubMed: 19777118]
15. Chowdhury MH, Pond J, Gray SK, Lakowicz JR. Systematic computational study of the effect of silver nanoparticle dimers on the coupled emission from nearby fluorophores. J Phys Chem C. 2008; 112:11236–11249.
16. Kaminski F, Sandoghdar V, Agio M. Finite-Difference Time-Domain Modeling of Decay Rates in the Near Field of Metal Nanostructures. J Comput and Theoret Nanoscience. 2007; 4:635–643.

Figure 1.

Schematic of the model radiating fluorophore/metal nanoparticle system studied where: the arrow represents the fluorophore, the fluorophores will be oriented along the x axis; d is the diameter of the aluminum nanoparticle, $2s$ is the surface to surface distance between dimers (for the monomer case – s is the space between the fluorophore and the surface of the particle), θ is the polar angle from the z -axis where $0 \leq \theta \leq \pi$ and Φ is the azimuthal angle in the x - y plane from the x -axis with $0 \leq \Phi < 2\pi$. AI NP = aluminum nanoparticle.

Figure 2.

Wavelength dependent radiated power enhancement for dipoles spaced $s = 5$ from $d = 20, 40$ and 80 nm aluminum nanoparticles calculated using FDTD. The dipoles are oriented perpendicular to the metal surface (oriented along the x -axis).

Figure 3.

Total radiated power enhancement in the $\lambda = 300\text{--}420$ nm range for dipoles at a distance of $s = 5$ nm from the surface of aluminum nanoparticles of varying diameters ($d = 20, 40, 80, 100$ and 140 nm).

Figure 4.

Computed total radiated power enhancement of emission (integrated around a closed surface containing the system) for different $d = 80$ nm monomer and dimer aluminum nanoparticles with the perpendicular fluorophore orientation. For the dimer systems, the fluorophore is located midway between the two aluminum particles. Note the enhancement is represented in the log scale (base 10). F = fluorophore.

Figure 5.

(a) Near-field image of the field enhancement around a $d = 60$ nm aluminum nanoparticle dimer spaced $2s = 10$ nm apart by its interaction with the plane wave with wavelength 280 nm propagating along the z -axis and polarized along the x -axis; (b) Near-field image of the field enhancement around a $d = 80$ nm aluminum nanoparticle dimer spaced $2s = 10$ nm apart by its interaction with a dipole radiating at 350 nm located in the middle of the dimer. The dipole is oriented along the x -axis. Note all images are displayed in the log scale (base 10).

Figure 6. Experimental fluorescence spectra of a 10 nm thick PVA film on top of a 10 nm thick aluminum film, and on a quartz control that contain: (a) NATA; (b) GMP.

Table 1

Computed enhancement/quenching of the total power radiated in the 300–420 nm range (integrated around a closed surface containing the Al-dipole system) by the various $d = 80$ nm aluminum nanoparticle systems studied with the dipoles oriented perpendicular to the metal surface. The enhancement of the total power radiated indicates changes in the relative radiative decay rates of the aluminum-dipole system when compared to the isolated dipole. s is the space between the dipole and the surface of the nanoparticles for the all the monomer systems. For the dimer systems, the space between the two nanoparticles is $2s$ and the dipole is located exactly midway between the Al nanoparticles [8].

	Enhancement Factor
Monomer, $s = 1$ nm	14.90
Monomer, $s = 2$ nm	14.39
Monomer, $s = 5$ nm	12.02
Monomer, $s = 10$ nm	8.34
Monomer, $s = 20$ nm	4.52
Dimer, $2s = 2$ nm	3565
Dimer, $2s = 4$ nm	874
Dimer, $2s = 10$ nm	153
Dimer, $2s = 20$ nm	41.33
Dimer, $2s = 40$ nm	11.30