METAL-ENHANCED FLUORESCENCE
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METAL-ENHANCED FLUORESCENCE

Edited By

Chris D. Geddes

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Today conventional fluorescence spectroscopy, i.e. far-field fluorescence, is entrenched in the Biosciences. For over 150 years we have both observed and enjoyed an era of the growth of both the theory and applications of fluorescence. In nearly all examples of classical far-field fluorescence, a fluorophore is excited from the far field, optics enable the collection of light followed by detection. In these simple examples, the fundamental properties of the fluorophore, such as extinction coefficient or oscillator strength of a transition as well as the spatial distribution of emission remain for the most part unchanged. However, over the last 10 years, there has been intense research on the influences of near-field (less than 1 wavelength of light away) metallic nanoparticles on traditional far-field fluorescence properties. In contrast to traditional far-field fluorescence we know relatively little today concerning near-field fluorescence, although its potential applications look set to fuel yet another era in fluorescence, a likely paradigm shift in the ways we both think and use fluorescence spectroscopy today.

In about 2000, my laboratory started to study the interactions of fluorophores with metallic nanoparticles, both solution-based and surface-immobilized. Our findings agreed with other workers whom had observed increases in fluorescence emission coupled with a decrease in the fluorophores' radiative lifetime. Subsequently, we applied classical far-field fluorescence descriptions to these experimental observations, which ultimately suggested a modification in the fluorophores's intrinsic radiative decay rate, a rate thought to be mostly unchanged and only weakly dependent on external environmental factors. This simple description, coupled with what seemed like a limitless amount of applications led to a paper published by our laboratory in 2001 entitled "Metal-Enhanced Fluorescence", or MEF, a term now widely used today almost a decade later.

In 2005 and onwards we reported in numerous papers that the underlying mechanisms for MEF were potentially much more elegant than the simplistic radiative rate modifications, demonstrated by our group and others, which was approximated by a collection of modified far-field fluorescence rate equations on the emission side and an enhanced near-field absorption. In this new mechanistic description of MEF, a close-proximity excited fluorophore induces a mirror dipole in the metallic nanoparticle, which itself radiates with high efficiency the coupled quanta, resulting in significantly enhanced fluorescence. Today, near-field interactions have been extended to include enhanced chemiluminescence, phosphorescence as well as enhanced Bioluminescence signatures. The coupled fluorophore lifetime is also observed to be considerably shorter than the free-space or far-field fluorescence lifetime, reflecting the "surface plasmon" lifetime of the coupled emission. While this thinking is somewhat different than earlier descriptions, it has enabled new plasmonic discoveries, such as Plasmonic Electricity, by the Institute of Fluorescence, a digital form of metal-enhanced fluorescence and indeed far-field fluorescence with a plethora of potential applications. The enhanced absorption of fluorophores in close-proximity to plasmonics nanoparticles is also now further understood, with the wavelength dependence and distance from a metallic nanoparticle both modeled and experimentally verified.

While the mechanism/s of MEF is/are most certainly likely to be debated in the coming years, it is evident that the applications of MEF are forever growing. Subsequently, I have invited a collection of works from outstanding scientists around the world which have

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collectively contributed to our advancement of this new concept of near-field fluorescence, namely Metal-Enhanced Fluorescence, MEF, from both a theoretical and experimental perspective. At this time, I would like to thank the authors for their most timely cutting edge contributions and their willingness to share them with us, thank you. I would also like to thank members of my lab for helping me collate this volume, including, Caroleann Aitken, Rodd Pribik, Jeff Roeser, and Micah Weisenberg whom have spent many an hour typesetting the entire volume. Thanks also to Dr Jennie Hunter-Cevera, President of UMBI, for her support of the Institute of Fluorescence’s MEF programs. In closing, I hope you find this volume a valuable resource which attempts to reflect current thinking and trends in this new era of fluorescence spectroscopy.

Institute of Fluorescence
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18th August 2009
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1.1. INTRODUCTION

Since the first experimental demonstration of the spontaneous emission rate of fluorescent species could be modified by changing the local photonic mode density (PMD) by metal surfaces by Drexhage and coworkers, there has been numerous studies to describe the interactions of fluorophores with metals placed in close proximity. Barnes provided an excellent detailed summary of fluorescence near interfaces in a review article in 1998. In recent years our laboratory has also both described and demonstrated many new favorable photophysical effects of electronically excited states (fluorophores / luminophores) in close-proximity to plasmon resonant particles. In these examples of Metal-Enhanced Fluorescence (MEF), it has become apparent that the true mechanism for MEF is far more elegant than the simple radiative decay rate description postulated by others. In fact MEF appears to be underpinned by the formation of a mirror dipole on the metallic nanoparticle, which itself radiates highly efficiently, effectively resulting in enhanced luminescence. Further, it is thought that the MEF effect is a consequence of an excited state coupling with the scattering mode of nanoparticles, which is thought to account for very fast MEF lifetimes, i.e. a coupled elastic scattering event. For metallic nanoparticles, the extinction spectrum is comprised of both an absorption and scattering component. For smaller particles (< 25 nm), then the extinction is for the most part dominated by absorption, while for larger particles, by scattering. For a fixed wavelength, this scales as the radius cubed and to the sixth power respectively. Given that MEF is thought to be the ability of a nanoparticle to plasmon scatter coupled quanta (i.e. fluorescence, phosphorescence etc), then concordantly larger particles have subsequently been shown to be ideal for MEF. It is this train of thought which readily accounts for the numerous reports of luminescence quenching by small metallic nanoparticles. While our mechanism for MEF is fairly new, we have reported compelling data in the recent past. In these reports, i) MEF is seen to be more pronounced for larger particles, ii) the wavelength dependence of MEF suggests a correlation between the scattering spectra of the nanoparticles and the emission spectra of the fluorophores, iii) MEF is angular
dependent, both from an observation and excitation perspective, similar to scattering by nanoparticles themselves, iv) metals ideal for MEF are those with high free electron densities and v) continuous metallic films have been shown to couple fluorophore emission, when fluorophores are positioned less than 100 nm from the surface. In addition, the coupled emission has been shown to be completely $p$-polarized, strongly indicating that the coupled-plasmon system is radiating.

In the opening chapter of this new exciting book, we aim to provide a broad overview of our interpretation of metal-fluorophore interactions, which exhibit the MEF concept with numerous experimental data. We hope this chapter will be useful in introducing the MEF concept to the newcomers to field, as well as interest to other researchers whom have already made contributions to this field.

![Figure 1.1](image.jpg) A schematic diagram of the unified plasmon/fluorophore description. Fluorophores induce surface plasmons in metals and energy is effectively transferred in a non-radiative fashion. This interaction of excited states with surface plasmons leads to a wealth of new fluorescence, chemiluminescence and phosphorescence phenomena and technologies we describe as a *Unified Description*.

### 1.2. METAL-ENHANCED FLUORESCENCE (MEF)

As briefly mentioned in the Introduction the MEF phenomenon is a result of the interactions between the excited states of the fluorophores and the induced surface plasmons of metal nanoparticles or roughened surfaces. Figure 1.2A depicts our laboratory’s interpretation of the processes involved in the interactions of fluorophores with metal nanoparticles in close proximity to one another. There are two main processes thought responsible in MEF 1) non-radiative coupling from the excited state of the fluorescent species to surface plasmons of the metallic
nanoparticles; which is subsequently radiated by the nanoparticles themselves and 2) enhanced absorption of light by fluorophores due to the increased electric fields between and around the metal nanoparticles. Fluorophores located in between the metal nanoparticles, where the electric fields are larger than the electric fields around the individual metal nanoparticles can contribute significantly to the MEF phenomenon. Figure 1.2B shows emission spectra of fluorescein isothiocyanate (FITC) placed on silver island films (SIFs) and on a blank glass slide. The emission peak at 520 nm of FITC on SIFs is \( \approx 5 \)-fold larger than that of FITC on glass. Real-color photographs (Figure 1.2B-inset) provides a visual evidence for the observation of increased fluorescence emission. In addition, it has also been reported that the decay time of the excited states is affected as a result of the interactions of fluorophores with metal nanoparticles. Figure 1.2C shows the fluorescence emission intensity decays for FITC on both SIFs and glass. The intensity decay for FITC on glass follows a single-exponential decay, corresponding to a fluorescence lifetime of \( \approx 3 \) ns, and follows a multi-exponential decay on SIFs, corresponding to a much shorter lifetime \( \approx 1.5 \) ns. The fact that one observes a multi-exponential decay on SIFs indicates the presence of multiple processes involved in the decay.

![Figure 1.2](image)

**Figure 1.2.** (A) A schematic diagram depicting the processes in close proximity to metals (< 10 nm) involved in Metal-Enhanced Fluorescence: enhanced absorption and coupling to surface plasmons. (B) Emission spectra of FITC deposited onto SIFs and glass. The inset shows the real-color photographs of FITC emission from these surfaces. (C) Intensity decays for FITC on both glass and SIFs. IRF: Instrument Response Function.

In the publications on MEF to-date, silver has been the most studied metal as compared to other metals. Figure 1.3A shows the photographs of SIFs deposited onto glass and plastic supports, where the left-half of these supports was left intentionally blank to visually demonstrate the deposition of silver nanoparticles.
and utilize them as control surfaces in MEF experiments. A typical absorption spectrum of SIFs is shown in Figure 1.3B. Our research laboratory has also shown MEF from copper, \(^{23}\) gold \(^{24}\) and zinc nanostructures. \(^{25}\) The reader is referred to the specific publications for detailed information regarding MEF from metals other than silver. As shown in Figure 1.3B, the surface plasmon resonance (SPR) peak for SIFs occur at \(\approx 420\) nm; the SPR peak depends on the type, size and the shape of the metal deposited onto the solid support. The surface morphology of SIFs on glass and plastic supports studied by atomic force microscopy, Figures 1.3C and 1.3D, show SIFs were deposited onto glass as individual particles of size \(\approx 100\) nm in a homogeneous fashion. On the other hand, AFM images of SIFs on plastic support reveal that the deposition was more heterogeneous, which stems from the fact the surface of the plastic was chemically modified and was not smooth as the glass surfaces.

**Figure 1.3.** (A) Photographs of silver island films (SIFs) deposited onto glass and plastic supports. (B) Normalized absorbance of zinc, copper, gold and silver nanostructured particles on a glass support. Atomic force microscope images of SIFs on (C) glass (D) plastic support.

It is well known that several different modes of surface plasmons can be created in a single metal nanoparticle by changing the shape of the nanoparticle itself. \(^{26,27}\) That is, while a single surface plasmon mode typically exists in a spherical nanoparticle for \(\lambda/10\) since all the electrons in the metal oscillate with the same energy, the presence of a secondary path or an axis on the metal, e.g., a longer longitudinal axis in rod-shape nanoparticle, a secondary surface plasmon mode occurs. In a rod-shaped nanoparticle, electrons can oscillate at two different frequencies giving rise to an additional SPR peak which is red-shifted with respect to the SPR peak as a result of the electron oscillations on the shorter axis. One can also observe additional SPR peaks for a triangular shaped nanoparticle, etc. The presence of multiple SPRs in a single nanoparticle results in a greater probability of coupling
excited states of fluorophores, e.g. fluorophores randomly oriented near nanoparticles have greater probability of coupling to one or multiple SPR modes. In addition, electric fields in between these anisotropic nanoparticles are significantly stronger as compared to the electric fields in between isotropic (e.g., spherical) nanoparticles, which could result in further increases in the extent of light absorbed by the fluorophores. In this regard, our research laboratory has recently demonstrated MEF from anisotropic silver structures.\textsuperscript{26, 27} Figures 1.4A and 1.4B show the AFM images of silver nanorods and triangles deposited onto glass supports, respectively. Figures 1.4C and 1.4D show the emission spectra of indocyanine green (ICG) from these surfaces. Figures 1.4C and 1.4D also show that emission intensities from anisotropic silver structures are significantly larger than from control surfaces and also depends on the extent of loading of anisotropic silver structures on the surfaces.

![Figure 1.4](image)

**Figure 1.4.** Atomic Force Microscope Images of (A) silver rods and (B) triangles deposited onto glass substrates. (C) and (D) Fluorescence emission spectra of Indocyanine Green (ICG) deposited onto both surfaces, respectively.

In nearly all the applications of MEF, the excitation and emission observation have been on the same side of the assay platform as the incoming excitation. It is well known that when fluorophores are near interfaces with different refractive indices (such as air and glass), a significant part of the fluorescence can be coupled into the medium of higher refractive index,\textsuperscript{28} with a unique angular dependence peaking at the critical angle.\textsuperscript{29} Moreover, the fluorescence emission through the high refractive index medium (and in air) could further be increased, when metallic nanoparticles are placed between the fluorophores and the interface. This phenomenon arises from the fact that metallic nanoparticles (especially silver, gold and copper) are known to scatter light efficiently and in an angular-dependent
In fact, 30 nm silver nanoparticles scatter light (at 530 nm) ~ 9 and 124 times more efficiently than 30 nm gold and polystyrene nanoparticles, respectively.\textsuperscript{14} Subsequently, light scattering by silver and gold nanoparticles can be detected at concentrations as low as $10^{-16}$ M.\textsuperscript{14} It was previously shown that scattered light by metallic nanoparticles is highest at observation angles of 0 and 180° with respect to the incident light, i.e., backward and forward scatter. Thus, when silver (also gold or copper) nanoparticles are placed between the fluorophores and the interface (glass substrate), coupled light originated from the fluorophore will be preferentially scattered in backward and forward directions by the silver nanoparticles. The forward scattered light then couples to glass and is subsequently emitted from the back of the glass substrate, while the backward scattered light is emitted into free space. In addition, the angular-dependent scattered light from metallic nanoparticles depends on the size, shape and composition of the nanoparticles, as well as the refractive index of the suspending medium and is significantly different than the light scattered by planar glass.\textsuperscript{14}

In a recent paper, our research laboratory has demonstrated the angular-dependent nature of MEF from silver nanoparticles deposited onto glass support.\textsuperscript{15,24} Figure 1.5A shows the experimental setup, where the excitation was normal to the surface, a common angle in fluorescence spectroscopy, and the fluorescence emission was collected at all angles (0-360 degrees). Real-color photographs of FITC on SIFs and glass, collected separately at 225 degrees, show the emission is more intense from SIFs than from glass at the same angle. The quantitative interpretation of the observed angular-dependent MEF can be accomplished by MEF enhancement factors (emission intensity at 517 nm (I517) on silver colloids divided by I517 on glass) were calculated at all observation angles and are shown in Figure 1.5B. MEF enhancement factors of 3-4 and 7-9 can be seen for FITC emission on silver colloids with low and medium loading, respectively. One can see that when silver colloids were present between the fluorophores and the interface, the fluorescence emission from the air and back side, increased to a similar extent. Clearly, the enhanced fluorescence was significantly greater from surfaces with a higher degree of colloid loading (OD = 0.4). The utility of this observation lies in the fact that one can construct a bioassay on the silvered surfaces and measure a concentration-dependent response at a chosen angle, i.e. angular-ratiometric assays.\textsuperscript{15} The angular-ratiometric intensity measurements are independent of initial intensity and fluctuations in the excitation light, colloid loading and also the loading of the fluorophore. Thus, angular-ratiometric measurements combined with the use of more sensitive detectors should further enhance the capability of MEF-based surface assays.\textsuperscript{15}
In addition to the benefits of MEF from metal nanostructures deposited onto solid supports that are very useful in surface bioassays, MEF can also be observed from individual nanostructures in bioassays carried out in solution. In this regard, fluorophores and metal nanostructures can be assembled in core-shell architecture and can be used as fluorescent nanoparticles as indicators in biological applications such as imaging of cellular activity or single-molecule sensing.

In a recent paper, our research laboratory have developed core-shell (silver core-silica shell) nanoparticles with various shell thicknesses featuring a variety of fluorophores, to show the versatility of the core-shell architecture, and have demonstrated their applicability for MEF and single nanoparticle sensing. The broad potential applications of these fluorescent nanostructures were demonstrated by employing near-infra red emitting probes (Rh800) for potential applications in cellular imaging and the use of highly photostable long lifetime (μS) lanthanide probes, probes suitable for off-gating biological auto fluorescence. In addition, a commonly used long-wavelength fluorophore, Alexa 647, was also incorporated into these core-shell nanostructures to demonstrate that fluorophores can be readily covalently linked to the core-shell particles also, for MEF applications.

Figures 1.6A and 1.6B show the fluorescence emission intensity from Eu-TDPA-doped Ag@SiO₂ and Rh800-doped Ag@SiO₂ and from the corresponding fluorescent nanobubbles (control samples), Eu-TDPA-doped SiO₂ and Rh800-doped SiO₂. The emission intensity was approximately 8-fold and 20-fold higher for Eu-TDPA-doped Ag@SiO₂ and Rh800-doped Ag@SiO₂ than Eu-TDPA-doped SiO₂ and Rh800-doped SiO₂, respectively. Figure 1.6C shows representative scanning confocal images of individual fluorescent core-shell nanoparticles, Alexa 647 Ag@SiO₂, and the corresponding nanobubbles, Alexa 647@SiO₂. The bright spots in Figure 1.6C-
represents fluorescence emission from the single fluorescent core-shell nanoparticles, while the dimmer spots in Figure 1.6C-2 represent the single nanobubbles. The significant differences in the peak intensities of the two images are immediately evident from Figure 1.6C. For fluorescent core-shell nanoparticles the average value of the peak intensity was approximately 10-fold higher than that of the nanobubbles.

![Figure 1.6](image)

**Figure 1.6.** Fluorescence emission intensity of (A) Eu-TDPA-doped Ag@SiO₂ and (B) Rh800-doped Ag@SiO₂ and from the corresponding fluorescent nanobubbles (control samples), Eu-TDPA-doped SiO₂ and Rh800-doped SiO₂. The diameter of the Ag is 130±10 nm and the thickness of the shell is 11±1 nm for all the samples. (C) Scanning confocal images (20x20 mm) of (1) Alexa 647 Ag@SiO₂, (2) Alexa 647@SiO₂, (3) zoomed in version of (B). Intensity counts in the scale were normalized to 1.

In a recent publication, our research laboratory has studied another interesting phenomenon observed in fluorescence: emission from a second excited state (S₂) level. It is well-known that the azulene molecule emits fluorescence from S₂ upon excitation, instead of emitting from the normal S₁ that is observed for almost all fluorophores. Since its discovery azulene has been used in tracking cellular activity due to its affinity towards binding DNA and tubulin of the cytoplasm. On the other hand, azulene’s S₂ emission is still weak. In this regard, our research laboratory has demonstrated that azulene’s S₂ emission can be further increased by placing azulene in close proximity to silver nanoparticles. Figure 1.7A shows the graphical representation of metal-enhanced S₂ emission, where the interactions of azulene’s second excited state level of with surface plasmons of silver nanoparticles are enhanced. Figure 1.7B shows the S₂ fluorescence emission spectra of
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Azulene from SIFs and from glass at room temperature, where a ≈1.5-fold increase is observed. It is important to note that the true enhancement factor is ≈37-fold. This is because the MEF phenomenon is distance dependent, where with a sample thickness of ≈1 μm, and an enhanced interaction region <20 nm, then only 4% of the sample is within the MEF enhancement region. In addition, the effect of temperature on S₂ emission was also studied, where > 2-fold enhancement of fluorescence from SIFs at 77K was observed, Figure 1.7C.

Figure 1.7. (A) Graphical representation of our laboratory's current interpretation of Metal-Enhanced S₂ emission (Bottom). IC-Internal Conversion, VR-Vibrational energy relaxation. Ag-Silver nanoparticle (SIFs), TCP-Transfer/coupling to Plasmons, MES₂-Metal Enhanced S₂ Emission. Energy level spacing not drawn to scale. Fluorescence emission spectra, lex = 338 nm, of Azulene sandwiched between two SiFs and unsilvered slides at room temperature (B) Room Temperature, RT and (C) at 77K.

In all the examples summarized above, fluorescence emission of fluorophores was unstructured, where excitation of fluorophores with a single or wide range of wavelengths generates an entire range of allowed transitions that populate the vibrational energy levels, Figure 1.8A-top. There exist some fluorophores with several vibrational structures emitted over a range of wavelengths, that is, the transitions from the lowest vibrational level of an excited state to several vibrational levels of the ground state usually have a much higher degree of probability than others, and when combined, constitute the structured emission spectrum of that molecule. In this regard, amplification of vibrational structures may yield better analysis of intra- and intermolecular interactions as well as very detailed finger print for the discrimination of chemical substances with subtle differences, or in slightly difference physical states and surroundings can be achieved. In a recent publication,¹² enhancement of structured emission of perylene, a fluorophore with
structured absorption and emission bands (Figures 1.8B and 1.8C) in close proximity to SIFs was reported. It is thought that the vibrational bands of perylene can couple to surface plasmons of silver nanoparticles and subsequently be emitted at a increased intensity, Figure 1.8A-bottom. Since the fluorophores placed close proximity to SIFs experience increased electric fields and they absorb more light than as shown in Figure 1.8B. Figure 1.8C shows the structured fluorescence emission spectra of perylene on SIFs and glass. Perylene shows significant structure due to transitions from the lowest vibrational level of the excited $S_1$ state to several vibrational levels of the ground state, those having a much higher degree of probability than others. Figure 1.8C also shows the enhanced structured fluorescence intensity was $\approx 2$-fold brighter from the silver, as compared to glass. An additional experiment was undertaken to verify that the structured emission is plasmon enhanced: SIFs were replaced by a continuous silver film (50 nm thick), where the fluorescence emission was heavily quenched. Since the generation of surface plasmons in continuous metal films occurs only under certain unique conditions, as compared to metallic nanoparticles, the observation of quenching supports the notion that the structured emission on SIFs is indeed plasmon-enhanced.

Figure 1.8. (A) Current interpretation Metal-Enhanced unstructured (Top) and structured emission (Bottom). F-Fluorophore. MEF- Metal Enhanced Fluorescence. (B) Absorption spectra of Perylene sandwiched between two silvered and unsilvered slides respectively (Sandwich experimental geometry (Top Insert). (C) Fluorescence emission spectra of Perylene sandwiched between two silvered, unsilvered slides, 50 nm thick continuous Ag films, respectively.

Previous MEF studies were exclusively focused on *prompt* fluorescence emission, where excited singlet state populations rapidly decayed to ground states. E-type fluorescence is well-known to arise from thermal activation of the $S_1$ state.
from the T\textsubscript{1} state (reverse intersystem crossing), and hence its decay time (excited state lifetime) is underpinned by the decay of the T\textsubscript{1} state, which typically has a long decay time in the millisecond range.\textsuperscript{32} Because of its long decay time, e-type delayed fluorescence has been widely used to investigate the rotational diffusion time of biological macro-molecules in membranes on micro – millisecond time scales.\textsuperscript{33} Our research laboratory has also studied whether E-type fluorescence can be enhanced by SIFs when placed in close proximity.\textsuperscript{34} Figure 1.9A shows e-type fluorescence and phosphorescence spectra after Argon purging in a cuvette at different temperatures. One can observe not only e-type delayed fluorescence at $\approx 550$ nm, which is spectrally identical to prompt $S_1$ fluorescence, but also the phosphorescence emission peak is evident at $\approx 690$ nm. The delayed emission band readily disappears if the solution is not deoxygenated. The e-type fluorescence peak readily increases with increased temperature, while the phosphorescence peak subsequently decreases. On SIFs we have observed different extents of e-type fluorescence and phosphorescence from both glass slides and SIFs at different temperatures, with Argon purging. Figure 9-insert shows e-type fluorescence is $\approx$2.5-fold brighter as compared to phosphorescence, $\approx$ 1.9-fold brighter on SIFs. Visual evidence for metal-enhanced e-type fluorescence is provided in Figure 1.9C; eosin fluorescence emission intensity on glass is a light greenish; on SIFs it is brighter than on glass due to the MEF effect. After heating the sample for 2 minutes, the eosin fluorescence emission on glass is much brighter than the pre-heating emission. This indicates more e-type fluorescence with increased temperature. The eosin emission is even more pronounced on SIFs after heating, indicating that e-type fluorescence emission was enhanced by surface plasmons.

Figure 1.9. (A) E-type Fluorescence and phosphorescence emission spectra, $\lambda_{ex} = 473$ nm, of Eosin in a cuvette at different temperatures. Insert Eosin immobilized in PVA sandwiched between two silvered and unsilvered slides at 25\textdegree C EF - Enhancement Factor. RT - Room Temperature. (B) experimental sample geometry. (C) Real-color photographs of Eosin emission from glass and SIFs, before and after 2 mins heating. $\lambda_{ex} = 473$ nm. SIFs - Silver Island Films. The real-color photographs were taken through an emission filter (488 nm razor edge).
Fluorescence can also be used to track intermolecular interactions of molecules. These interactions can result in the formation of an “excimer” abbreviation for an excited state dimmer, which is formed between the ground state (M) and lowest electronically excited singlet state (M*) of a species, Figure 1.10A. The aromatic molecule pyrene is well-known for forming an excimer. Pyrene has been used to probe RNA folding and DNA duplex formation by monitoring the monomers and excimer emission fluctuations that arise from local base stacking and the quenching effect. Pyrene has also been used for the selective detection of cellular mRNA by yielding a strong excimer emission at 485 nm in the presence of the target. However, the sensitivity of these approaches of the singly labeled pyrene probe is typically more dependent on the excimer emission, due to the inherently high biological autofluorescence in the pyrene monomer emission region. In a recent publication, our research laboratory has studied MEF from pyrene when placed in close proximity to SIFs (Figure 1.10B and 1.10C). Due to transitions from the lowest vibrational level of the monomer excited state to several vibrational levels of the ground state, the fluorescence emission spectrum of the monomer of pyrene from quartz and SIFs has fine structured bands at 370 nm, while the broad excimer emission yields an unstructured band at 470 nm. Enhanced monomer emission (≈1.5 fold brighter) and excimer fluorescence emission (≈ 2.5 fold brighter) was typically observed from the SIFs as compared to a quartz control substrate (Figure 1.10C), containing no silver nanoparticles. These findings of metal-enhanced monomer and excimer fluorescence of pyrene are consistent with our research laboratory’s previous reported findings for structured and unstructured S₁ emission for fluorophores sandwiched between silver nanostructures. Metal-enhanced excimer fluorescence can also be seen visually (Figure 1.10C-inset) from real-color photographs taken through a 450 nm long-pass filter.

Figure 1.10. (A) Graphical representation of current interpretation for Metal-Enhanced P-type Fluorescence. (B) Experimental sample geometry. (C) Fluorescence emission spectra and photographs of pyrene emission from quartz (control sample) and SIFs.
1.3. METAL-ENHANCED CHEMILUMINESCENCE (MEC)

In recent years, our research laboratory has also studied the interactions of chemically excited states (i.e., chemiluminescence) with metal nanoparticles extensively, metal-enhanced chemiluminescence.11, 37, 38 The reader is referred to Chapter 15 of this book for a detailed summary of MEC. The authors intend to provide a short introduction to MEC within the context of the current Chapter. Unlike fluorescence excited states which are induced by an external excitation source, the excited states in chemiluminescence are created as a result of chemical reactions. Once the optically inactive chemicals are activated (creation of excited states) by chemical reactions, these excited states can interact with surface plasmons in metal nanoparticles in a similar fashion to their fluorescence counterparts. It is also important to note that, in addition to enhancement of chemiluminescence, metal nanoparticles are thought to act as catalyst of the chemical reactions that produce light. Figure 1.11A depicts the current interpretation of the MEC phenomenon, where chemically excited states couple to surface plasmons of the metals and chemiluminescence is in turn enhanced by the metals. A simple experimental geometry as shown in Figure 1.11B can be used to study MEC. Here the chemiluminescent solution is placed in between two metal-coated glass slides and the emission is measured. In this experimental geometry, the gap between the slides was estimated to be ≈1 μm. Figure 1.11C shows the emission spectra of green chemiluminescence material placed in between two SIFs. Left-half of each silvered glass slide is left intentionally blank to demonstrate the benefits of using silver. Figure 1.11C shows the emission from SIFs is significantly brighter than from glass, as also can be seen visually from the real-color photographs of chemiluminescence material placed in between two SIFs.

![Figure 1.11](image-url)

**Figure 1.11.** (A) Graphical representation of our current interpretation for Metal-Enhanced Chemiluminescence. (B) Experimental sample geometry. (C)
Chemiluminescence emission spectra and real-color photographs of green chemiluminescence emission from glass and SIFs. M- Metal.

Based on our research laboratory’s observations of MEF from metals other than silver, MEC from chromium, copper, nickel and zinc was also studied. Figure 1.12 shows the enhancement factors for green chemiluminescence from these metals with various thicknesses. A typical enhancement factor of 2-3-fold is observed from all metal surfaces, which implies that chemically excited states can couple to these plasmon resonant metal particles. It is interesting to note that the chemiluminescence emission is dependent on the amount of reactants in the solution and diminishes once one of the reactants is used up. To test whether the remainder of the inactive chemiluminescent dye can be excited with an external light source and still emit luminescence, additional experiments were undertaken where the chemiluminescence solution was excited with a laser at 473 nm. Interestingly, the inactive chemiluminescence dye can be optically excited and still emit luminescence with enhancement factors similar to the chemically excited conditions being observed. A detailed investigation of MEC from different metals is currently underway and will be reported in due course.

![Figure 1.12](image)

**Figure 1.12** - Enhancement factor versus metal deposition thickness for (A) chromium (Cr), (B) copper (Cu), (C) nickel (Ni), (D) zinc (Zn) for both a green chemiluminescence solution and the same solution after reaction completion optically excited at $\lambda_{ex} = 473$ nm.

1.4. METAL-ENHANCED PHOSPHORESCENCE (MEP)

Photodynamic therapy (PDT) has potential in the diagnosis and treatment of several diseases such as diabetes, peripheral vascular diseases, cerebrovascular and cardiovascular. In all PDT treatments, the main focus is on inducing cell death
when a suitable dye (lumophore), light and oxygen are combined. Three primary processes are known to be involved in the photodynamic effect: Firstly, the ground state of the dye (S₀) is optically excited to an excited singlet state. Then a population from the excited state is typically transferred to the dye’s lowest triplet state by intersystem crossing. Finally, collisional energy transfer from the triplet dye to ground-state molecular oxygen (¹O₂) produces highly reactive singlet oxygen, returning the dye to its original ground state. The singlet oxygen can react readily with many biological targets and destroy a wide variety of cells. However, modern PDT is limited by an insufficient quantity of singlet oxygen, while reacting with biological targets. Since singlet oxygen plays a very important role for cell damage, an abundant supply of oxygen is very important.⁴⁰ If the consumption of oxygen by the photodynamic process is faster than it can be resupplied, it causes oxygen depletion. An alternative method to resolve this problem is to populate high-lying triplet excited states of several dyes which produce oxygen-independent damage. If these excited triplet states obtain sufficient energies to allow for the cleavage of one of the molecular bonds, then radicals that are even more reactive than singlet oxygen can be produced. The production of these radicals does not require the presence of oxygen. But both mechanisms, i.e. ¹O₂ and radical, do require high phosphorescence (triplet) quantum yields.

In recent years, our research laboratory has published several papers on the increase of phosphorescence,⁴¹ singlet oxygen⁴², ⁴³ and superoxide generation⁴⁴ within close proximity to metal nanoparticles. A summary of these reports are provided in this section. The current interpretation of metal-enhanced phosphorescence (MEP) is depicted in Figure 1.13A, where the phosphorescence emission is thought to couple to surface plasmons of metal nanoparticles and is subsequently increased. Figure 1.13B shows the experimental geometry used in MEP experiments. In this regard, a solution of rose bengal was placed in between two SIFs and the phosphorescence emission was measured. It is important to note that phosphorescence is not readily observed at room temperature because of collisional deactivation by oxygen and the presence of quenching impurities. However, phosphorescence emission can be observed at low temperatures and in media where the diffusion of both the luminophore and oxygen is negligible. Figure 1.13C shows the phosphorescence emission spectra and real-color photographs of rose bengal emission from glass and SIFs. From Figure 1.13C the enhanced phosphorescence intensity was ≈5-fold brighter from the SIFs, as compared to glass (497 vs 110 A.U.). The photograph inserts of Figure 1.13C also show the enhanced phosphorescence visibly from both glass and SIFs. The emission intensity is clearly brighter from between the SIFs, but much weaker from the glass control slide. Since fluorescence and phosphorescence are competitive processes, one would not expect to observe MEP. We have presented two possible explanations for the occurrence of both MEF and MEP in the same system. 1) enhanced net system absorbance, which would increase the net singlet and triplet yields, and 2) reverse intersystem crossing, i.e. Tₙ → Sₙ, where the triplet state is directly populated and the back intersystem crossing facilitates MEP. Further information can be found in the corresponding publication.⁴⁵
Molecular oxygen has a unique electronic configuration characterized by a partially filled set of antibonding π* orbitals. As predicted by Hund’s rule, the lowest energy state of the molecular oxygen has maximum multiplicity, i.e. is a triplet ground state. Molecular oxygen has two excited singlet states, $^1\Sigma_g^+$ and $^1\Delta_g$, whose electronic energies are 158 and 95 kJ/mol higher than that of the triplet ground state $^3\Sigma_g^-$, respectively. The electronic configuration of $^1\Sigma_g^+$ is very similar to that of the ground state, except the fact that the last two electrons in $^1\Sigma_g^+$ have antiparallel spins while these electrons in the ground state have parallel spins. The other excited singlet state, $^1\Delta_u$, is commonly called singlet oxygen ($^1\text{O}_2$) and is more important than $^1\Sigma_g^+$ because of its longer lifetime (lifetime of $^1\Delta_u$ is 45 minutes and of $^1\Sigma_g^+$ is 7-12 sec). Since singlet oxygen can readily react with many biological targets and destroy a wide variety of cells, the photosensitized production of singlet oxygen has significance in a range of areas, especially in PDT.

It is widely accepted that singlet oxygen is the primary cytotoxic agent responsible for photobiological activity. Since singlet oxygen plays a very important role in cell damage, an abundant supply of oxygen is required. In addition, photodynamic therapy is currently limited by the insufficient generation of singlet oxygen while reacting with biological targets. A method to possibly resolve these problems is to increase the triplet yield of sensitizers, by coupling to surface plasmons, which invariably results in more singlet oxygen generation. Our research laboratory has reported the first observation of metal-enhanced singlet oxygen generation (ME$^0$O$_2^*$). A photosensitizer (rose bengal) sandwiched between SIFs enables more singlet oxygen to be produced due to the enhanced triplet excited state yield of the sensitizer, Figure 1.14A.

Figure 1.14B and 1.14C show the fluorescence emission spectra of a mixture of GR and Rose Bengal solutions on glass and SiFs, before and after UV