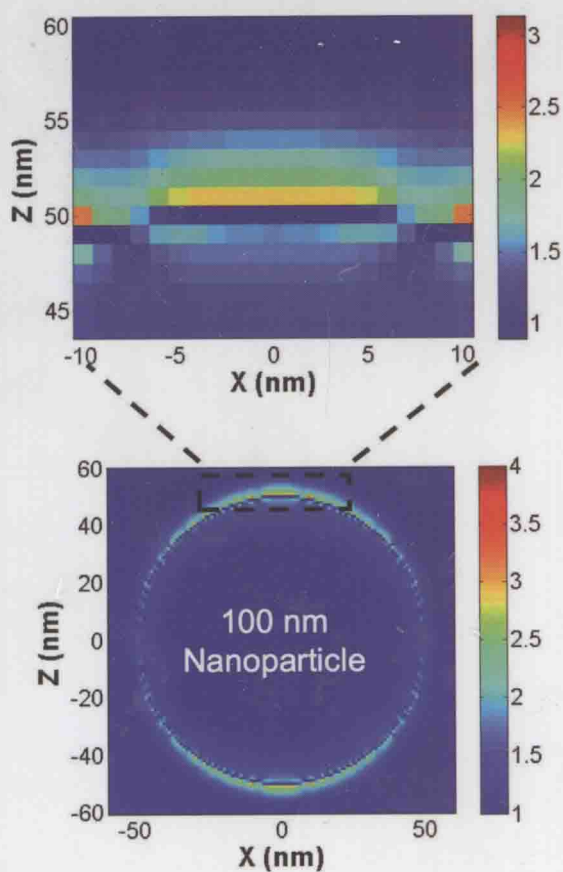


Metal-Enhanced Fluorescence

Edited by Chris D. Geddes



METAL-ENHANCED FLUORESCENCE

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Chris D. Geddes



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METAL-ENHANCED FLUORESCENCE

PREFACE

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

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
Baltimore, Maryland
18th August 2009*

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CONTENTS

Preface	vii
Contributors	ix
Metal-Enhanced Fluorescence: Progress Towards a Unified Plasmon-Fluorophore Description	1
<i>Kadir Aslan and Chris D. Geddes</i>	
Spectral Profile Modifications In Metal-Enhanced Fluorescence	25
<i>E. C. Le Ru, J. Grand, N. Félidj, J. Aubard, G. Lévi, A. Hohenau, J. R. Krenn, E. Blackie, P. G. Etchegoin</i>	
The Role Of Plasmonic Engineering In Potential Surface-Enhanced Fluorescence	67
<i>Daniel J. Ross, Nicholas P.W. Pieczonka, R. F. Aroca</i>	
Importance of Spectral Overlap: Fluorescence Enhancement by Single Metal Nanoparticles	91
<i>Keiko Munechika, Yeechi Chen, Jessica M. Smith and David S. Ginger</i>	
Near-IR Metal-Enhanced Fluorescence And Controlled Colloidal Aggregation	119
<i>Jon P. Anderson, Mark Griffiths, John G. Williams, Daniel L. Grone, Dave L. Steffens, and Lyle M. Middendorf</i>	
Optimisation Of Plasmonic Enhancement Of Fluorescence For Optical Biosensor Applications	139
<i>Colette McDonagh, Ondrej Stranik, Robert Nooney, Brian D. MacCraith</i>	
Microwave-Accelerated Metal-Enhanced Fluorescence	161
<i>Kadir Aslan and Chris D. Geddes</i>	
Localized Surface Plasmon Coupled Fluorescence Fiber Optic Based Biosensing	183
<i>Chien Chou, Ja-An Annie Ho, Chii-Chang Chen, Ming-Yaw, Wei-Chih Liu, Ying-Feng Chang, Chen Fu, Si-Han Chen, Ting-Yang Kuo</i>	
Surface Plasmon Enhanced Photochemistry	261
<i>Stephen K. Gray</i>	
Metal-Enhanced Generation of Oxygen Rich Species	277
<i>Yongxia Zhang, Kadir Aslan and Chris D. Geddes</i>	

Synthesis Of Anisotropic Noble Metal Nanoparticles	295
<i>Damian Aherne, Deirdre M. Ledwith, John M. Kelly</i>	
Enhanced Fluorescence Detection Enabled By Zinc Oxide Nanomaterials	363
<i>Jong-in Hahm</i>	
ZnO Platforms For Enhanced Directional Fluorescence Applications	393
<i>H.C. Ong, D.Y. Lei, J. Li, J.B. Xu</i>	
E-Beam Lithography And Spontaneous Galvanic Displacement Reactions For Spatially Controlled MEF Applications	419
<i>Luigi Martiradonna, S. Shiv Shankar, and Pier Paolo Pompa</i>	
Metal-Enhanced Chemiluminescence	439
<i>Yongxia Zhang, Kadir Aslan, Chris D. Geddes</i>	
Enhanced Fluorescence From Gratings	465
<i>Chii-Wann Lin, Nan-Fu Chiu, Jiun-Haw Lee, Chih-Kung Lee</i>	
Enhancing Fluorescence with Sub-Wavelength Metallic Apertures	489
<i>Steve Blair and Jérôme Wenger</i>	
Enhanced Multi-Photon Excitation of Tryptophan-Silver Colloid	529
<i>Renato E. de Araujo, Diego Rativa and Anderson S. L. Gomes</i>	
Plasmon-enhanced radiative rates and applications to organic electronics	543
<i>Lewis Rothberg and Shanlin Pan</i>	
Fluorescent Quenching Gold Nanoparticles: Potential Biomedical Applications	573
<i>Xiaohua Huang, Ivan H. El-Sayed, and Mostafa A. El-Sayed</i>	
Index	601

Metal-Enhanced Fluorescence: Progress Towards a Unified Plasmon-Fluorophore Description

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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,^{1, 2} there has been numerous studies to describe the interactions of fluorophores with metals placed in close proximity.^{3, 4} Barnes provided an excellent detailed summary of fluorescence near interfaces in a review article in 1998.⁵ 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.⁶⁻⁸ 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.⁹ 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 (Figure 1.1).^{8, 10-12} In this regard, our research laboratory has been working a “Unified Fluorophore-Plasmon Description”, which is summarized in Figure 1.1 and which describes the effects of fluorophores in a broad range of fluorescence disciplines. The coupled fluorophore lifetime is also observed to be much shorter than the “free-space lifetime”, reflecting the very fast “plasmon” lifetime of the coupled quanta.⁵⁻⁷ 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.^{8, 13} For metallic nanoparticles, the extinction spectrum is comprised of both an absorption and scattering component.¹⁴ 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.¹⁴ Given that MEF is thought to be the ability of a nanoparticle to plasmon scatter coupled quanta (i.e. fluorescence, phosphorescence etc),⁸ then concordantly larger particles have subsequently been shown to be ideal for MEF.^{8, 13} 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,⁸ 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

MEF: Progress towards a Unified Plasmon Fluorophore Description

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dependent,¹⁵ both from an observation and excitation perspective, similar to scattering by nanoparticles themselves,¹⁶ iv) metals ideal for MEF are those with high free electron densities¹⁷ 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.^{18, 19}

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.

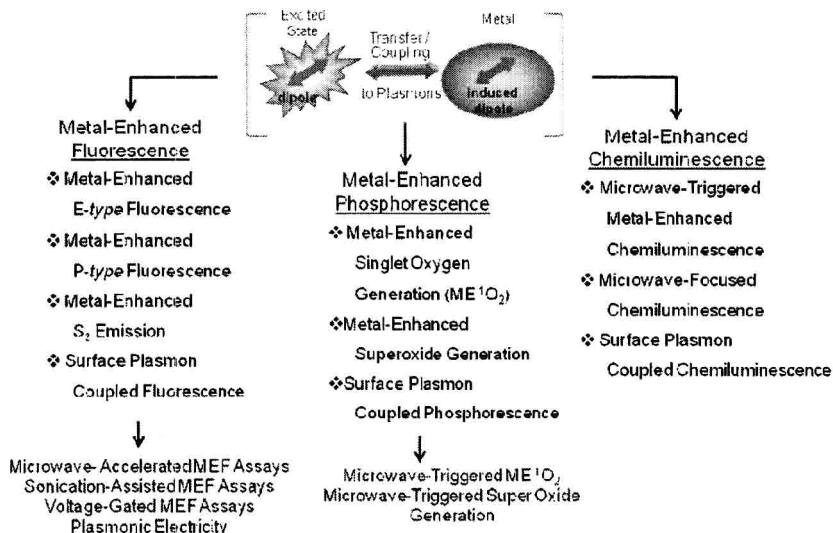


Figure 1.1 A schematic diagram of the unified plasmon/fluorophore description. Fluorophores induce surface plasmons in metals and energy is effectively transferred in a non-radiative fashion. This interaction of excited states with surface plasmons leads to a wealth of new fluorescence, chemiluminescence 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.²⁰ 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.²⁰ 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 ≈ 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.⁷ 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 ≈ 3 ns, and follows a multi-exponential decay on SIFs, corresponding to a much shorter lifetime ≈ 1.5 ns. The fact that one observes a multi-exponential decay on SIFs indicates the presence of multiple processes involved in the decay.

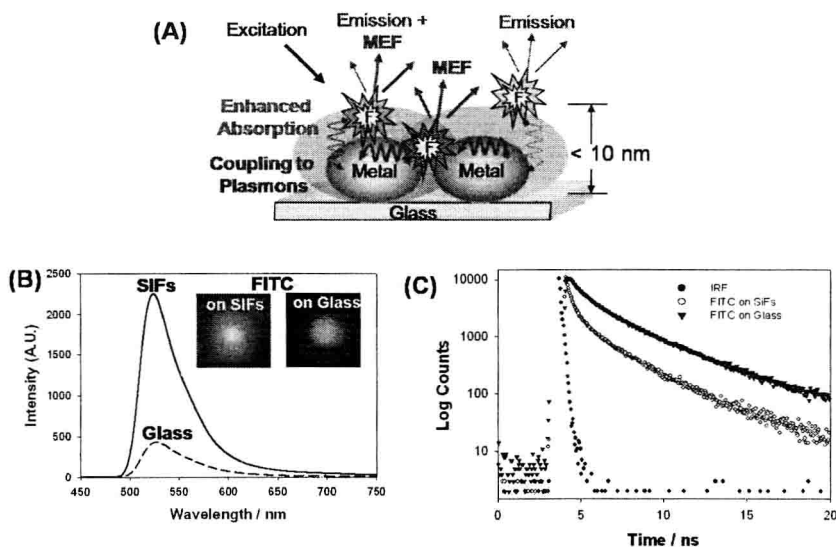


Figure 1.2. (A) A schematic diagram depicting the processes in close proximity to metals (< 10 nm) involved in Metal-Enhanced Fluorescence: enhanced absorption and coupling to surface plasmons. (B) Emission spectra of FITC deposited onto SIFs and glass. The inset shows the real-color photographs of FITC 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,^{7, 21, 22} 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 gold²⁴ 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 ≈ 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 ≈ 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.

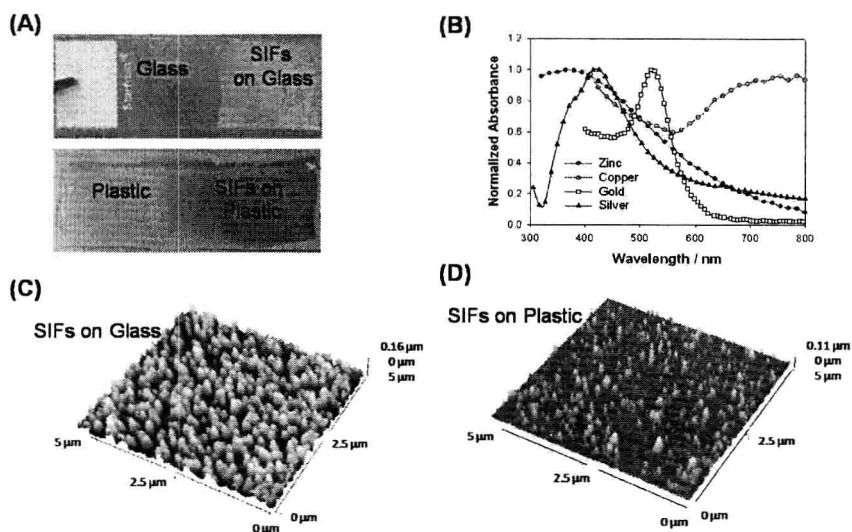


Figure 1.3. (A) Photographs of silver island films (SIFs) deposited onto glass and plastic supports. (B) Normalized absorbance of zinc, copper, gold and silver nanostructured particles on a glass support. Atomic force microscope images of SIFs on (C) glass (D) plastic support.

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-shaped 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.^{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.

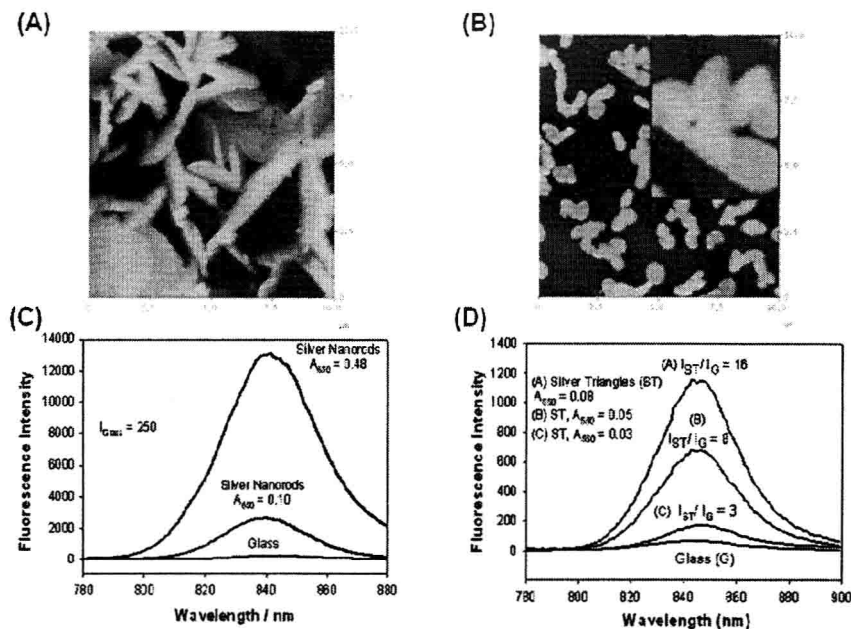


Figure 1.4. Atomic Force Microscope Images of (A) silver rods and (B) triangles deposited onto glass substrates. (C) and (D) Fluorescence emission spectra of Indocyanine Green (ICG) deposited onto both surfaces, respectively.

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,²⁸ with a unique angular dependence peaking at the critical angle.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