

Metal-enhanced fluorescence

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Fluorescence spectroscopy is entrenched throughout the life sciences today and is used for a variety of applications, including the detection of chemical or biological analytes/species, in reporting molecular events or for the understanding of microenvironments, such as local viscosity, polarity and voltage measurements, to name but just a few. In the majority of these fluorescence-based measurements, fluorophore brightness (quantum yield) and photostability are the primary concerns and limitations to the fluorescence technique, with little opportunity existing to tune favorably the photophysical properties of the fluorophore. In addition, in nearly all the uses of fluorescence, the fluorescent molecule (fluorophore) is both excited and emits into a homogenous environment, with little consideration for the complex interaction which fluorophores can undergo in the near-field, *i.e.* when a dipole is located < one wavelength of light away from a substrate.

However, the use of metallic surface plasmon supporting materials to modify favorably the brightness and photostability of fluorophores in the near-field, has found notable traction in recent years and offers some opportunities to alleviate some of the classical photophysical constraints of fluorophores. The term “Metal-Enhanced Fluorescence (MEF)”, was first introduced by Geddes in 2002,¹ although others have

called the same MEF effect Surface-Enhanced Fluorescence (SEF), Plasmon-Enhanced Fluorescence and Metal-induced Fluorescent Enhancement (MIFE) since then.² MEF occurs when fluorophores are positioned in the near-field, typically less than 10 nm from a metal and is characterized by an increased fluorescence intensity and a decreased fluorescence lifetime, where the decreased lifetime often lends itself to an enhanced fluorophore photostability, as the fluorophores spend less time “on average”, in an excited state, prior to their return to the ground state, and are subsequently less prone to photodestruction. It is this enhancement factor coupled with an enhanced photostability, which has attracted workers to implement MEF into analytical and microscopy applications, where an increased brightness and enhanced photostability are highly favored.²

It is not only the practical applications of MEF which have attracted interest. The actual MEF mechanism today is still discussed and debated. Over a decade ago, Geddes and Lakowicz proposed¹ that the MEF mechanism was underpinned by a radiative rate modification of the fluorophore when in close proximity to metallic nanoparticles, although Geddes has since proposed that it is the metal itself that radiates the coupled quanta,³ and that the fluorophore and metal are coupled in both the ground and excited state.³ While this is a only a subtle difference in mechanism, Geddes has suggested that the fluorophore radiates through the scattering mode of the

nanoparticle, which is also shown experimentally by the fact that the red-edge of the emission spectrum can be distorted,⁴ due to the inefficient overlap of the fluorophore emission spectrum and the scattering portion of the nanoparticle extinction.⁴

To address this growing and what has become an important area of spectroscopy, I have subsequently invited a selection of perspective and research articles from my colleagues around the world. The articles not only review past work, but comment on the limitations of MEF, the types of structures which can result in MEF as well as the direction the “MEF Field” is heading. I would like to take the opportunity to thank all my colleagues for their significant and excellent contributions, thank you.

References

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