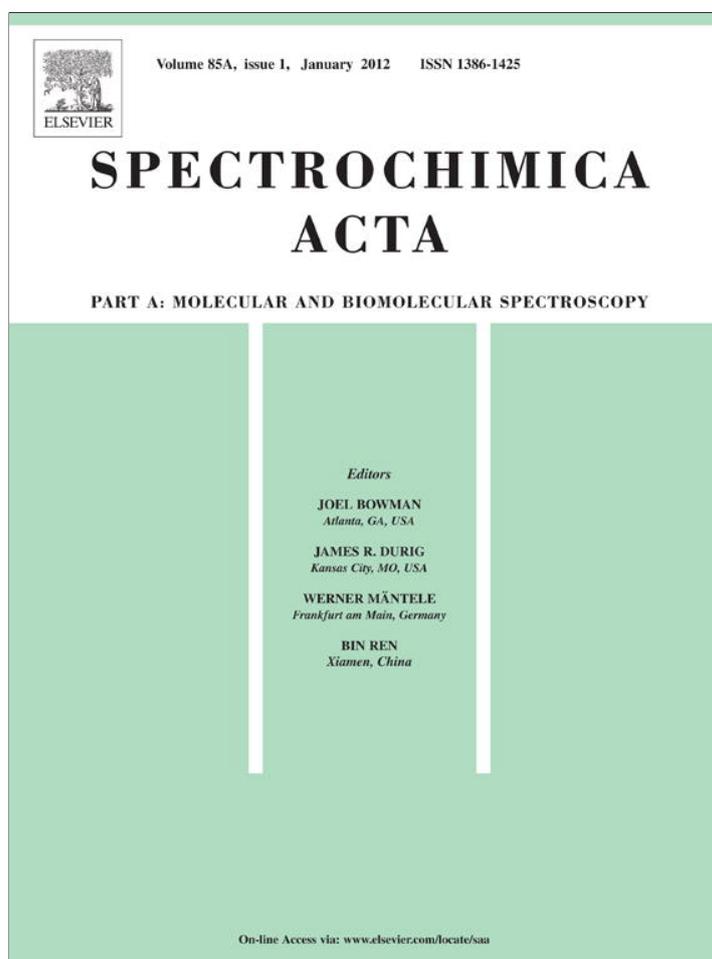


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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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## Metal-enhanced fluorescence exciplex emission

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### ABSTRACT

In this letter, we report the first observation of metal-enhanced exciplex fluorescence, observed from anthracene in the presence of diethylaniline. Anthracene in the presence of diethylaniline in close proximity to Silver Island Films (SIFs) shows enhanced monomer and exciplex emission as compared to a non-silvered control sample containing no silver nanoparticles. Our findings suggest two complementary methods for the enhancement: (i) surface plasmons can radiate coupled monomer and exciplex fluorescence efficiently, and (ii) enhanced absorption (enhanced electric near-field) further facilitates enhanced emission. Our exciplex studies help us to further understand the complex photophysics of the metal-enhanced fluorescence technology.

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### 1. Introduction

In past 10 years, there has been significant interest in using sub-wavelength sized metallic nanostructures such as silver [1], gold [2,3], copper [4], chromium [5], zinc [6], mixed metal substrates [7] and substrates which combine both dielectrics as well as metals [8]; different nanostructure architectures such as silver island films (SIFs) [9], silver colloids [10], silver nano-triangles [11], silver nano-rods [12] and fractal-like silvered surfaces [12], to favorably modify the spectral properties of fluorophores and to amplify the fluorescence emission [13], decrease fluorescence lifetimes [14] and protect against photobleaching [15]. Currently, there are several explanations for the near-field interactions of fluorophores with metallic nanoparticles. Fluorophore photophysical properties were originally thought to be modified by a resonance interaction by their close proximity to surface plasmons, which gives rise to a modification of the fluorophore radiative decay rate [16]. This description was fueled by workers who had shown increases in fluorescence emission coupled with a simultaneous drop in radiative lifetime [14]. However, metal enhanced fluorescence (MEF) described by Geddes, gave *raison d'être* to this effect, which is underpinned by a model whereby non-radiative energy transfer occurs from excited distal fluorophores, to the surface plasmon electrons in non-continuous films, in essence a fluorophore

induced mirror dipole in the metal [17–19]. The surface plasmons in turn, radiate the emission of the coupling fluorophores [19]. This explanation has been further facilitated by the observation of metal-enhanced chemiluminescence, which having no excited electric field component, further confirmed the presence of two discrete absorption and emission components in the metal enhanced chemiluminescence/fluorescence technology [19].

To date, all of our previous studies of MEF were exclusively focused on intramolecular monomer or the intermolecular *excimer* fluorescence emission [20]. In this work, we show that surface plasmons can also radiate and amplify molecular complex fluorescence, i.e. exciplex emission. We subsequently report our observations of anthracene in presence of diethylaniline at various concentrations, which is well-known to form an excited state complex, in close proximity to SiFs. We have observed both enhanced monomer and exciplex fluorescence emission from SiFs as compared to a quartz control substrate, which contains no silver nanodeposits and therefore cannot facilitate MEF. When in close proximity to silver nanostructures, we observed a shorter exciplex (excited state complex) fluorescence lifetime, which suggests that the enhanced exciplex emission is in part due to *coupling-to* and *emission-from* silver surface plasmons, consistent with current MEF thinking [18].

### 2. Experimental

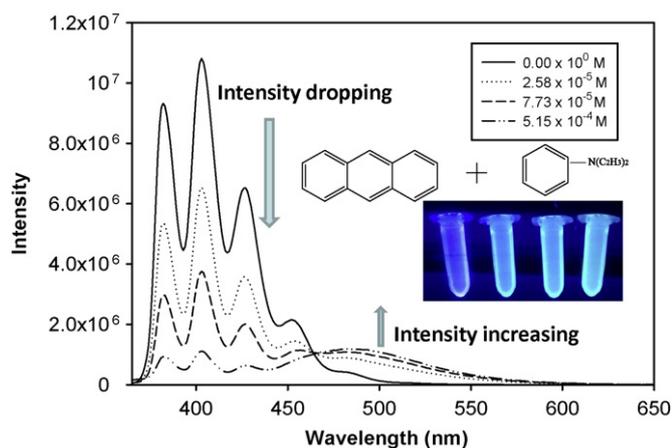
#### 2.1. Materials

Silver nitrate (99.9%), sodium hydroxide (99.996%), ammonium hydroxide (30%), D-glucose, Toluene, anthracene, Diethylaniline

Abbreviations: MEF, Metal enhanced fluorescence; Exciplex, Excited state complex.

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**Fig. 1.** Fluorescence spectra of anthracene ( $3 \times 10^{-4}$  mol/L) in the presence of diethylaniline at various concentration in toluene, 1: 0 mol/L; 2:  $2.58 \times 10^{-5}$  mol/L; 3:  $7.73 \times 10^{-5}$  mol/L; 4:  $5.15 \times 10^{-4}$  mol/L. Real color photographs of anthracene with various concentrations of diethylaniline (insert).

were obtained from Sigma-Aldrich. Quartz (75 mm  $\times$  25 mm) slides were bought from Ted Pella Inc. All chemicals were used as received.

### 3. Methods

Silver Island Films (SIFs) were prepared as we have previously published [1]. 100  $\mu$ L of anthracene ( $3.0 \times 10^{-4}$  M) in presence of diethylaniline at various concentrations in toluene was sandwiched between both the quartz slides and silver island films coated quartz slides, respectively. Fluorescence spectra were collected on a Fluoramax4 fluorometer at an angle of  $45^\circ$  to the surface. Excitation light was incident to the bottom of the slides surface with an excitation of 351 nm. The monomer and exciplex fluorescence spectra were collected in the fluorescence mode.

Fluorescence lifetime analysis. Fluorescence lifetimes were measured using a Horiba Jobin Yvon Tem-Pro fluorescence lifetime system employing the time-correlated single photon counting (TCSPC) technique, with a TBX-04 picosecond detection module. The excitation source was a pulsed LED source of wavelength 351 nm having maximum repetition rate 1.0 MHz and pulse duration  $\approx 1.1$  nanosecond (FWHM). The intensity decays were analyzed

by decay analysis software (DAS) version 6.4. Intensity decays were analyzed in terms of the multi-exponential model:

$$I(t) = \sum_i \alpha_i \exp\left(-\frac{t}{\tau_i}\right) \quad (3)$$

where  $\alpha_i$  are the amplitudes and  $\tau_i$  are the decay times,  $\sum_i \alpha_i = 1.0$ .

The fractional contribution of each component to the steady-state intensity is given by

$$f_i = \frac{\alpha_i \tau_i}{\sum_j \alpha_j \tau_j} \quad (4)$$

The mean lifetime of the excited state is given by

$$\bar{\tau} = \sum_i f_i \tau_i \quad (5)$$

and the amplitude-weighted lifetime is given by

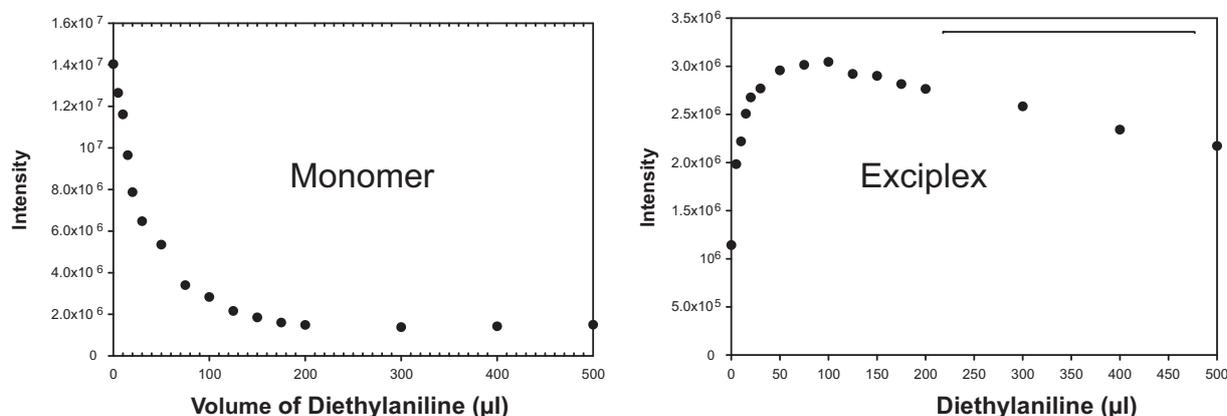
$$\langle \tau \rangle = \sum_i \alpha_i \tau_i \quad (6)$$

The values of  $\alpha_i$  and  $\tau_i$  were determined by nonlinear least squares impulse reconvolution with a goodness-of-fit  $\chi^2$  criterion.

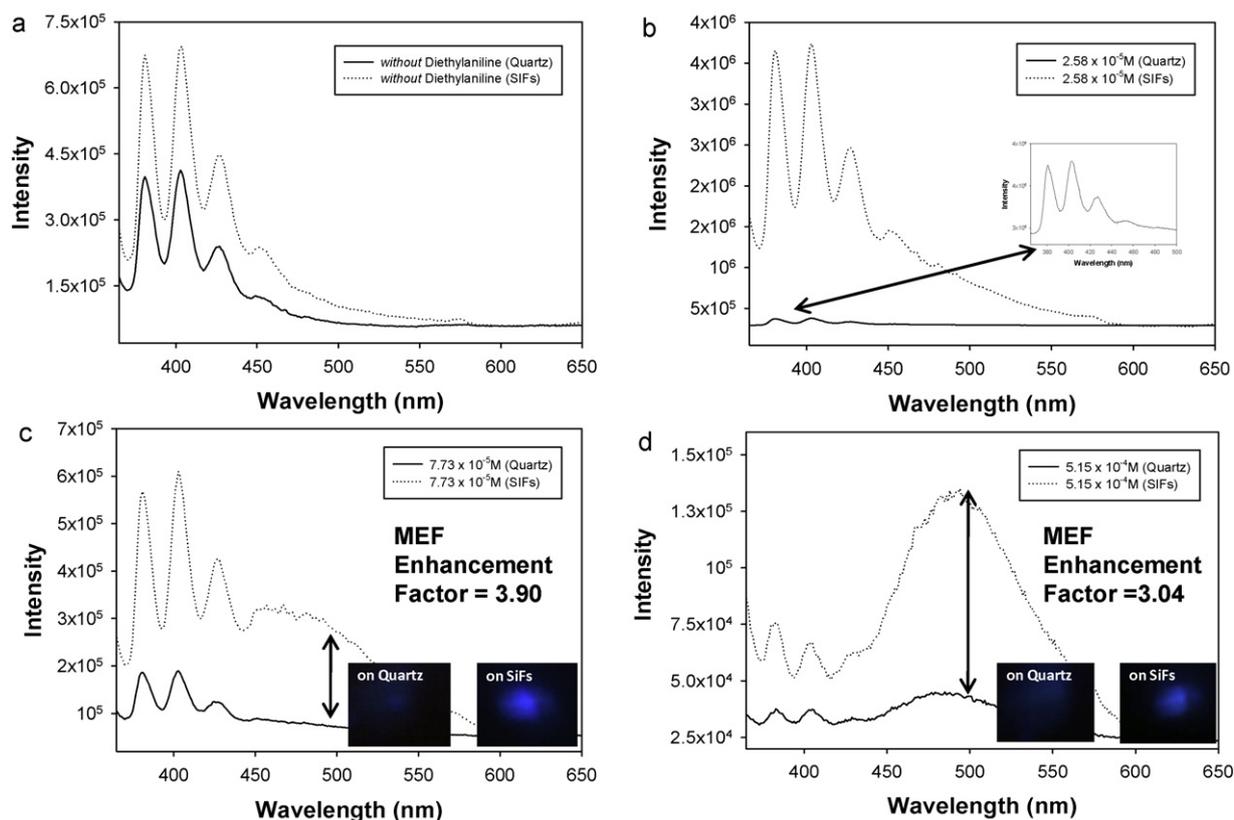
### 4. Results and discussion

Fig. 1 shows the spectra of anthracene in the presence of diethylaniline at various concentrations (0 mol/L,  $2.58 \times 10^{-5}$  mol/L,  $7.73 \times 10^{-5}$  mol/L,  $5.15 \times 10^{-4}$  mol/L) in toluene. Due to transitions from the lowest vibrational level of the monomer excited states to several vibrational levels of the ground state, the fluorescence emission spectra of the monomer of anthracene has fine structured bands at  $\approx 400$  nm. The structured emission is a mirror image of the absorption spectrum of anthracene. The unstructured emission at longer wavelength  $\approx 500$  nm, which is referred to as exciplex emission, is due to the formation of a charge-transfer complex during the excited state of anthracene and diethylaniline [21]. From the Fig. 1 inserts we can see the real color change of the emission of anthracene as a function of the various concentrations of diethylaniline. In Fig. 2, the peak intensities show that by increasing the concentration of diethylaniline, the structured emission of anthracene was decreased, while the unstructured exciplex emission intensity increased and then plateaued.

Enhanced monomer emission and exciplex fluorescence emission were observed in all cases from the SIFs, as compared



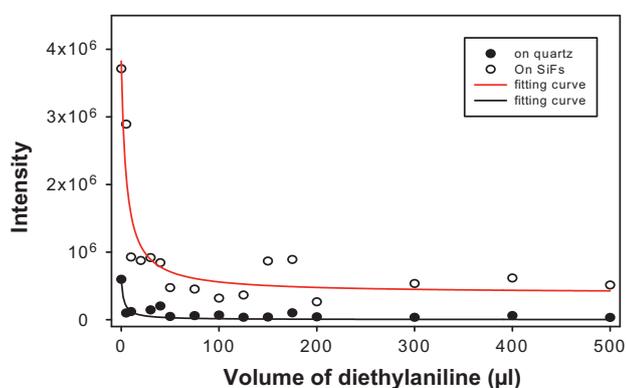
**Fig. 2.** The fluorescence intensity of anthracene (monomer (403 nm) and Exciplex (477 nm)) in the presence of diethylaniline at various concentrations (in toluene), measured in a cuvette.



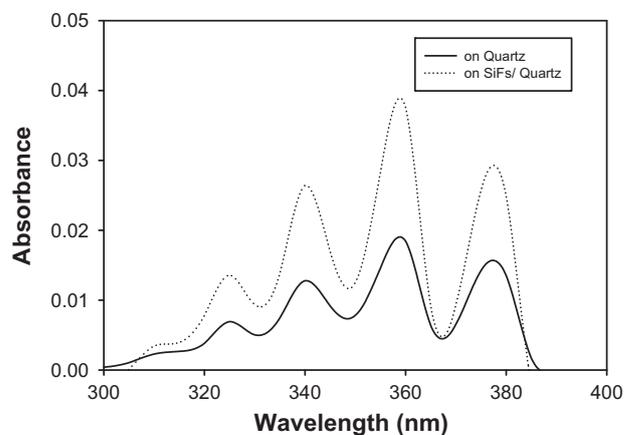
**Fig. 3.** Fluorescence spectra of  $3 \times 10^{-4}$  mol/L anthracene in the presence of diethylaniline at various concentrations in toluene, sandwiched between two quartz slides and one quartz and SiFs control Quartz, respectively. (a) 0 mol/L; (b)  $2.58 \times 10^{-5}$  mol/L; (c)  $7.73 \times 10^{-5}$  mol/L; (d)  $5.15 \times 10^{-4}$  mol/L.

to a quartz control substrate, containing no silver nanoparticles deposits (Fig. 3). Fig. 3 shows the structured monomer and unstructured exciplex emissions were enhanced when an anthracene and Diethylaniline solutions were sandwiched between SiFs. Metal-enhanced monomer and exciplex fluorescence can also be seen visibly (Fig. 3 insert), where the photographs were taken through a 400 nm longpass filter. These findings of metal-enhanced monomer and exciplex fluorescence of anthracene are consistent with our previous reported findings for structured and unstructured  $S_1$  emission for fluorophores sandwiched between silver nanostructures [22]. In Fig. 3c and d, both monomer and exciplex are both plasmon-enhanced considerably. Interestingly, the exciplex enhancement factor is larger than the monomer

enhancement factor. This result can be explained according to the current interpretation of MEF [18], whereby the exciplex emission has better spectral overlap with the scattering portion of the metal particle extinction spectra at this wavelength [23], which is thought to underpin the observed intensities in metal-enhanced fluorescence [18]. Fig. 4 shows the maximum fluorescence intensity of anthracene at 403 nm in the presence of diethylaniline at various concentrations in toluene with and without SiFs. The intensity of anthracene from the glass substrate was fitted by the function:  $y = 585937 / (1 + 0.3760x)$ ,  $R = 0.87$ . Intensity of anthracene from the SiFs substrate was fitted to the function:



**Fig. 4.** The fluorescence intensity of anthracene at 403 nm in the presence of diethylaniline at various concentrations in toluene. SiFs – Silver Island Films. On Quartz – a control sample containing no silver and therefore no metal-enhanced fluorescence (MEF).



**Fig. 5.** Absorption spectra of anthracene sandwiched between two quartz slides and one quartz and SiFs on Quartz respectively. (molar extinction of anthracene in toluene on SiFs is  $4222 \text{ M}^{-1} \text{ cm}^{-1}$ . Cross section of anthracene in toluene on SiFs is  $16 \text{ \AA}^2$  (angstrom<sup>2</sup>), Cross section of anthracene in toluene on Quartz is  $7 \text{ \AA}^2$  (angstrom<sup>2</sup>).

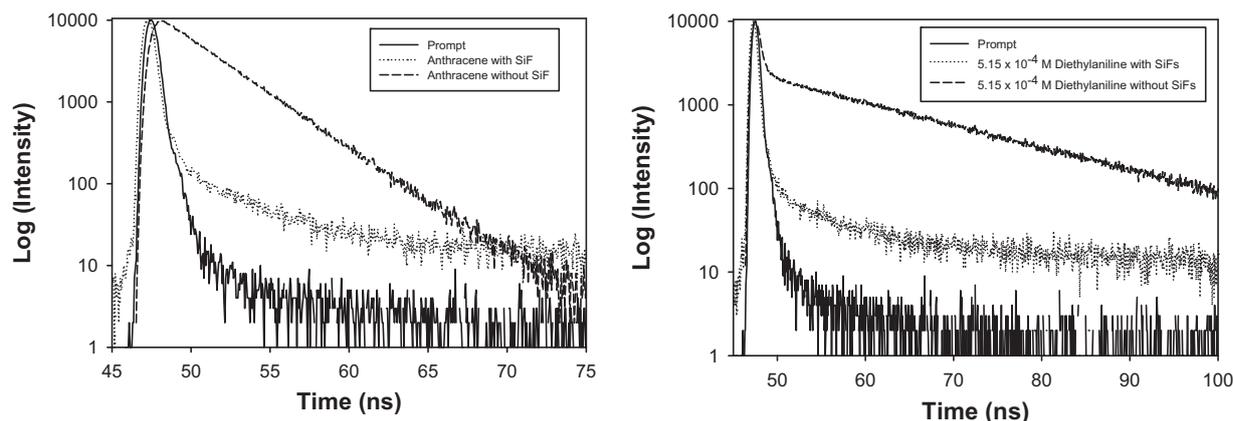


Fig. 6. Fluorescence intensity decay of anthracene with (right) and without diethylaniline ( $5.15 \times 10^{-4}$  mol/L) (Left).

Table 1

Fluorescence intensity decay analysis of anthracene with and without diethylaniline.  $\langle \tau \rangle$  – a lifetime less than the time resolution of the instrument. SiFs – Silver Island Films.

	(ns)	$\alpha_1$	(ns)	$\alpha_2$	$\langle \tau \rangle$ (ns)	$T$ (ns)	$\chi^2$
Anthracene without SiFs	6.31	0.76%	3.22	99.24%	3.23	3.26	1.09
Anthracene with SiFs		100%			$< \tau_R$	$< \tau_R$	1.15
Anthracene with $5.15 \times 10^{-4}$ mol/L diethylaniline without SiFs	0.31	21.66%	15.8	78.34%	12.3	15.7	1.03
Anthracene with $5.15 \times 10^{-4}$ mol/L diethylaniline with SiFs	$< \tau_R$	100%			$< \tau_R$	$< \tau_R$	1.18

$y = (3824727 + 76579x)/(1 + 0.1954x)$ ,  $R = 0.94$ . As we can see from Fig. 4, for the monomer anthracene, the greatest enhancements are observed in the absence of diethylaniline, i.e. the ratio of the SiFs curve: quartz control curve and for small sample volumes. For volumes above 100  $\mu\text{L}$  diethylaniline, the enhancement factor for anthracene remains for the most part constant, noting that the concentration of anthracene used in the sample sandwiched was  $\approx 100 \mu\text{L}$ , and a 1:1 complex is formed. In addition, MEF is a near-field effect, and for larger volumes used, then more material is distal from the metal and not surface plasmon enhanced [18].

#### 4.1. Interpretation of the results in terms of metal-enhanced fluorescence

We suggest two complementary effects for the observed enhancements: (i) surface plasmons can radiate coupled-excimer fluorescence efficiently, and (ii) enhanced absorption facilitates enhanced emission. In this regard, we studied the absorption of anthracene in the presence and absence of SiFs (Fig. 5). SiFs and glass without fluorophore were used as reference backgrounds for the anthracene absorption measurements, respectively. It can be seen that anthracene has a much larger absorbance on SiFs as compared to that on quartz for the same concentration of anthracene. When a fluorophore is placed near-to metal, there is often a very strong net absorption effect caused by the localized enhanced electromagnetic field of the incident excitation field [18]. In essence, conducting metallic particles can modify the free space absorption condition in ways that increase the incident electric near field felt by a fluorophore [18]. Since enhanced electromagnetic fields in proximity to metal nanoparticles are the basis for the increased system absorption in MEF [18], then we attribute part of the enhanced observed emission to the enhanced absorption [18]. A simple calculation suggests that the anthracene absorption cross section changes from  $\approx 7 \text{ \AA}^2$  to about  $\approx 16 \text{ \AA}^2$  in the presence of SiFs. It should be noted that an enhanced e-field only influences the excitation rate (Absorption) of a fluorophore by an effective change in its absorption cross-section in the metal-fluorophore coupled system, which does not influence the emission rate or the emission lifetime, which are underpinned by a 2nd MEF mechanism [19].

Subsequently, we have also measured the fluorescence lifetime, which is only affected by a modified system emission rate [18] when in close proximity to SiFs. The respective lifetimes were calculated from the decay curve data (Fig. 6), using an exponential decay curve analysis. Since a 400 nm long pass filter was used during the measurement, we expect that the recovered lifetime is comprised of both monomer and excimer excited state decay lifetimes. We observed a very short amplitude weighted lifetime ( $\langle \tau \rangle$ ) and average lifetime ( $\langle \tau \rangle$ ) of anthracene ( $\langle \tau \rangle$  on SiFs  $< \tau_R$ ,  $\langle \tau \rangle$  on quartz  $< \tau_R$ , i.e.  $<$  the time resolution ( $\tau_R$ ) of the instrument) for fluorophores near-to silver as compared to the quartz control sample ( $\langle \tau \rangle$  on quartz = 3.23 ns,  $\langle \tau \rangle$  on quartz = 3.26 ns). The amplitude weighted lifetime and average lifetime of Anthracene with diethylaniline are 12.3 ns and 15.7 ns respectively, while the amplitude weighted lifetime and the average lifetime were reduced to a very short value near-to silver (Table 1). These findings are highly consistent with our previously reported findings and trends for fluorophores sandwiched between silver nanostructures [18], and suggest that in addition to an enhanced absorption, anthracene and the excimer emission is also plasmon coupled and radiated by the nanoparticles themselves [18], as evidenced by the very short measured lifetimes. These findings are also consistent with those observed for MEF Pyrene based excimer emission [20], giving us confident in our interpretation.

## 5. Conclusions

In this paper, we report the first observation of metal-enhanced excimer fluorescence, which is thought to be due to both an enhanced absorption and surface plasmons radiating excimer fluorescence efficiently. Anthracene molecules in close proximity to Silver Island Films (SiFs) can undergo enhanced monomer and Excimer fluorescence, as compared to an identical control sample containing no silver. These observations of enhanced excimer formation not only suggest the use of Metal-Enhanced Fluorescence (MEF) for following surface kinetics with a much improved fluorescence sensitivity, but also further contribute to our collective knowledge of the photophysics of fluorophores near-to metals.

## Acknowledgements

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