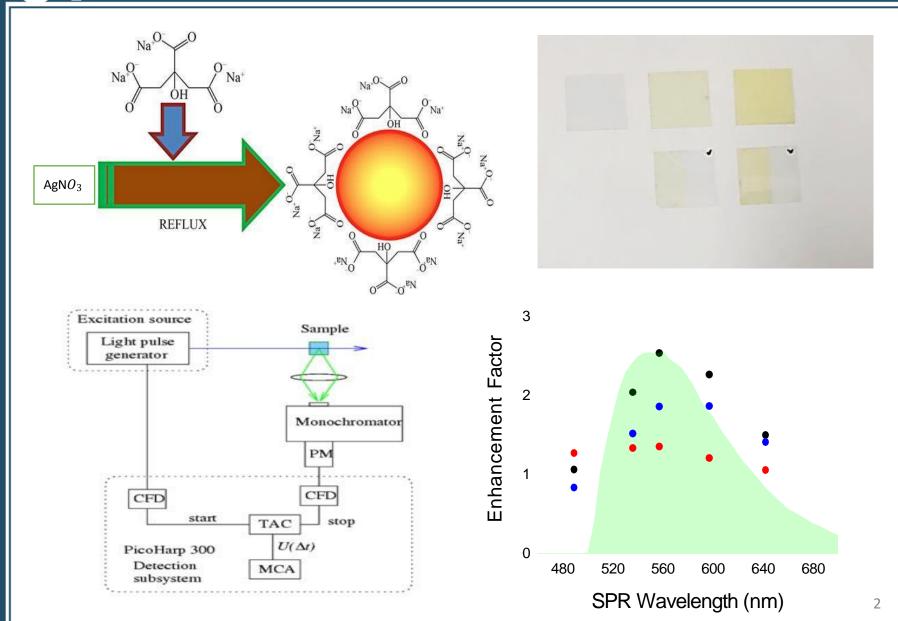
Metal-Enhanced Fluorescence of Dye Molecules using Ag Nano Particles

Haejung Koh 2019.08.09

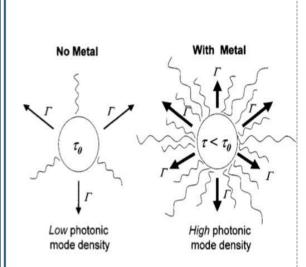
01 INTRODUCTION



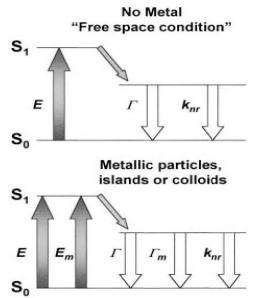
01 INTRODUCTION

Metal Enhanced Fluorescence





Low and high photonic mode densities in the absence and presence of metal, respectively.

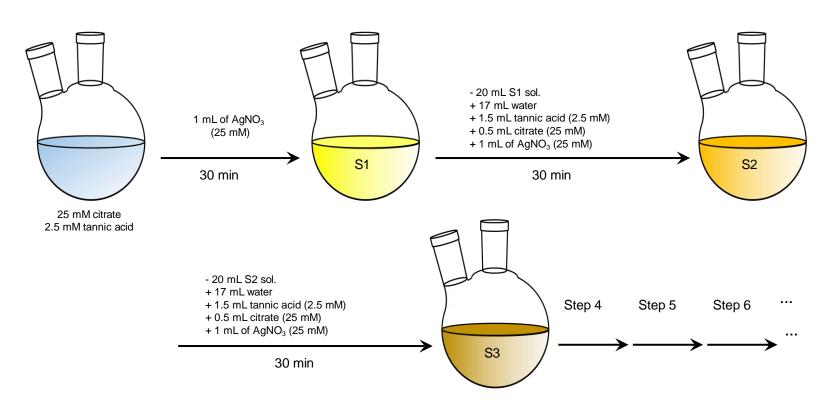


Classical Jablonski diagram for the free-space condition and the modified form in the presence of metallic particles, islands or radiative processes

- In the presence of the general dye, photochemical reactions decompose and cause a color of photosynthesis.
- Unlike normal organic light compounds, quantum dots are 100 to 1,000 times larger in absorbance coefficient than normal dyes and have higher quantum efficiency, which results in very high fluorescence.

02 Experimental Method

Specific protocols for Ag nanoparticle synthesis ▼

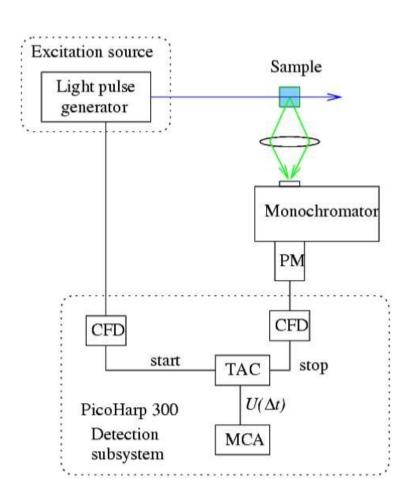


¥ Neus G. et al. Chem. Mater. 2014, 26, 2836-2846,

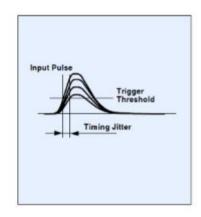
02 Experimental Method

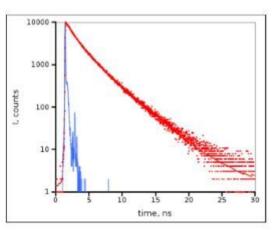
Time-correlated Single Photon Counting (TCSPC)





CFD; constant fraction discriminator

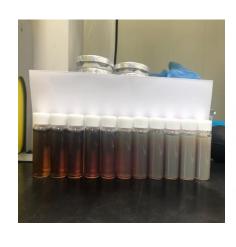


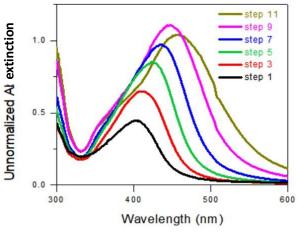


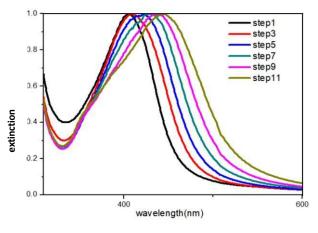
03Results & Discussion

Color change in visible light & UV-Vis spectra









color change in visible light (chronological order from left to right)

UV-Vis spectra of the samples in Figure 8 (Left-unnormalized, Right-Normalized)

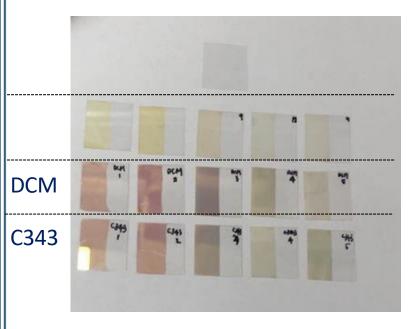
Sample	Step 1	Step 3	Step 5	Step 7	Step 9	Step 11
UV-Vis wavelength (nm)	402.9	411.1	424.2	433.9	447.0	456.8
Diameter (nm)	19.7	28.0	41.2	55.8	71.4	79.0

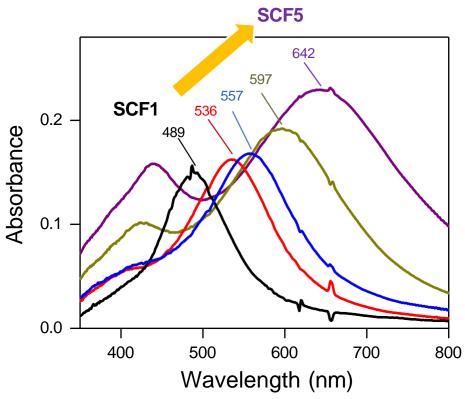
[¥] Neus G. et al. Chem. Mater. 2014, 26, 2836-2846,

O 3 Results & Analysis

Polystyrene (PS) coated Ag NPs arrays





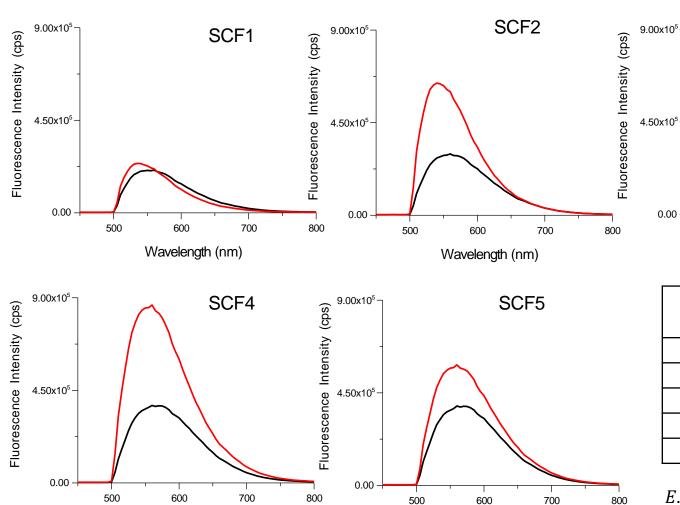


- Silver colloidal films (SCFs) coated by PS contatining DCM & C343 were fabricated for MEF study.
- The SPR bands are broadened and red-shifted as the size of Ag NPs increase.

Wavelength (nm)

Fluorescence Enhancement of DCM molecules with SCFs





Wavelength (nm)

500	600 700			
Wavelength (nm)				
With	Enhancement			
	Factor			
SCF1	1.07			
SCF2	2.04			
SCF3	2.54			
SCF4	2.27			

SCF3

$$E.F. = \frac{I_{fluor}(SCFs \ surface)}{I_{fluor}(bare \ surface)}$$

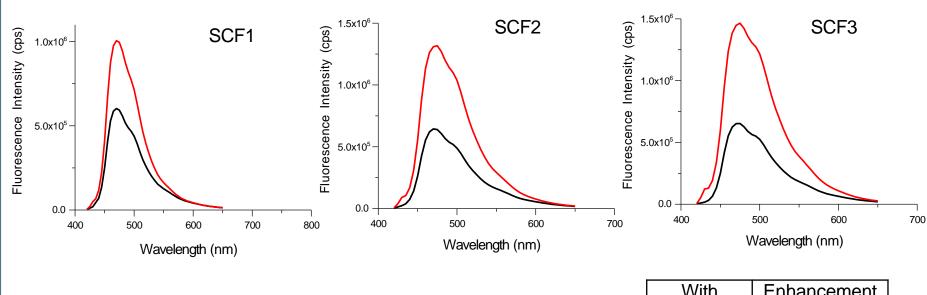
SCF5

1.51

800

Fluorescence Enhancement of C343 molecules with SCFs





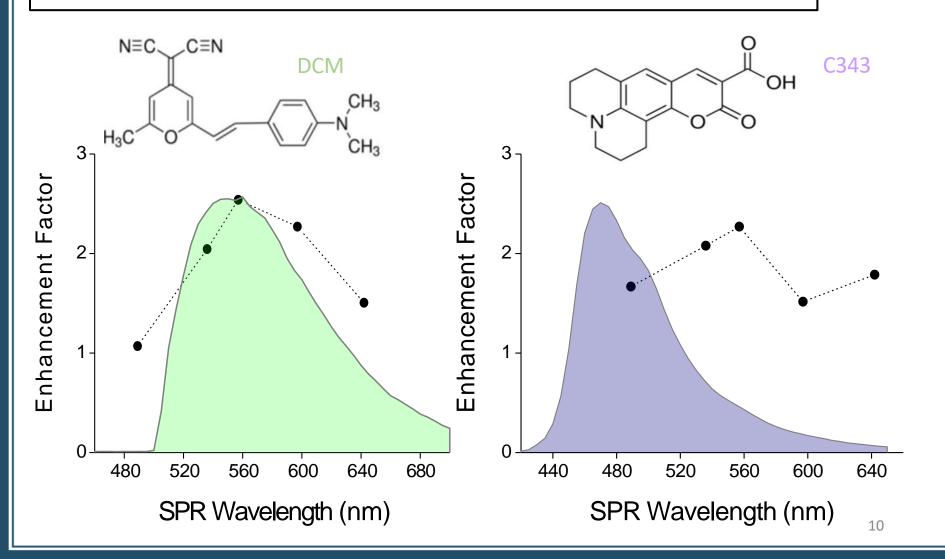
90 1.5x10 ⁶	SCF4	(ඉස් 1.5x10 ⁶	SCF5	
1.0x10 ⁶ –	\wedge	Intensity 1.0x10 ^e –		
Huorescence 2.0x10 ⁵ –		5.0x10⁵ –		
0.0		0.0	500 600	700
400	500 600 Wavelength (nm)	700	Wavelength (nm)	700

	_
With	Enhancement
	Factor
SCF1	1.67
SCF2	2.08
SCF3	2.27
SCF4	1.52
SCF5	1.79

$$E.F. = \frac{I_{fluor}(SCFs \ surface)}{I_{fluor}(bare \ surface)}$$

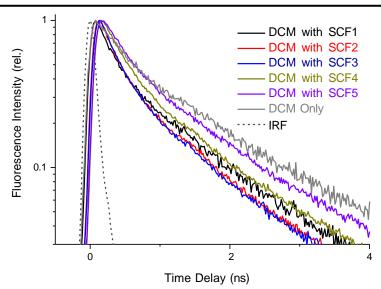
Fluorescence enhancement factors of DCM in thin PS films with SCFs as a function of maximum (dipolar) plasmon wavelength of the SCFs



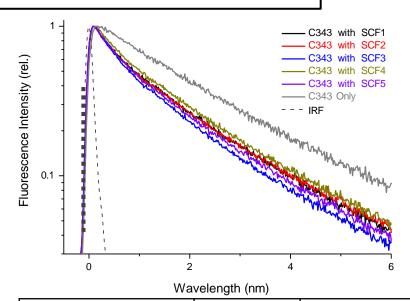


Time-resolved emission kinetics of DCM & C343 probed at 405nm in coated thin PS films with SCFs





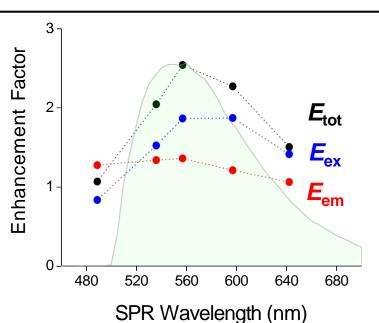
Sample	Lifetime	Enhancement	
	(ns)	Factor	
DCM Only	1.59	-	
DCM with SCF1	1.19	1.07	
DCM with SCF2	1.11	2.04	
DCM with SCF3	1.09	2.54	
DCM with SCF4	1.30	2.27	
DCM with SCF5	1.50	1.51	



Sample	Lifetime	Enhancemen	
	(ns)	Factor	
C343 Only	2.36	-	
C343 with SCF1	2.15	1.67	
C343 with SCF2	2.25	2.08	
C343 with SCF3	2.21	2.27	
C343 with SCF4	2.04	1.52	
C343 with SCF5	2.06	1.79	

Quantum Yields of DCM & C343 probed at 405nm in coated thin PS films with SCFs





DCM with SCF5

1.50

0.50

$$Q_0 = \frac{\Gamma_0}{\Gamma_0 + k_{\rm nr}} = \tau_0 \Gamma_0$$

$$Q_{\rm m} = \frac{\Gamma_{\rm m}}{\Gamma_{\rm m} + k_{\rm nr,m}} = \tau_m \Gamma_{\rm m}$$

$$m{E}_{m{em}} = rac{Q_{
m m}}{Q_0}$$

 Q_0 of DCM in PS = 0.47

1.06

1.51

Semi-empirical model

$$Q_{0} = \frac{\Gamma_{0}}{\Gamma_{0} + k_{\text{nr}}} = \tau_{0} \Gamma_{0}$$

$$Q_{\text{m}} = \frac{\Gamma_{\text{m}}}{\Gamma_{\text{m}} + k_{\text{nr}}} = \tau_{\text{m}} \Gamma_{\text{m}}$$

$$\Gamma_{\text{m}} = \frac{1}{\tau_{\text{m}}} - k_{\text{nr}} = \frac{1}{\tau_{\text{m}}} - \frac{(1 - Q_{0})}{\tau_{0}}$$

$$Q_{\text{m}} = 1 - \frac{\tau_{\text{m}}}{\tau_{0}} (1 - Q_{0})$$

$$E_{\text{m}} = \frac{Q_{\text{m}}}{\tau_{0}}$$

$$E_{\text{m}} = \frac{P_{\text{tot}}}{T_{0}}$$

1.41

	Lifetime	Quantum	Emission	Total	Excitation
	(ns)	Yield, Q _m	Enhancement	Enhancement	Enhancement
	` '		Factor, <i>E</i> em	Factor, E tot	Factor, <i>E</i> ex
DCM Only	1.59	0.47	-	-	-
DCM with SCF1	1.19	0.60	1.28	1.07	0.84
DCM with SCF2	1.11	0.63	1.34	2.04	1.53
DCM with SCF3	1.09	0.64	1.36	2.54	1.87
DCM with SCF4	1.30	0.57	1.21	2.27	1.87

04Conclusions

- Synthesized Ag nano particle in terms of size
- Fabricated homogeneous and well-dispersed polymer films with Ag nano particles
- Learned and arranged the TCSPC
- MEF tested of DCM & C343 dyes using several sizes of Ag nano particles prepared
- earned positive correlation between fluorescence enhancement with the extent of Surface Plasmon Resonance

O SAcknowledgement

- Advised by Professor Yoonsoo Pang
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(http://femto.gist.ac.kr)

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T H A N K Y O U