Nanoplasmonics and Metamaterials with Low Loss and Gain

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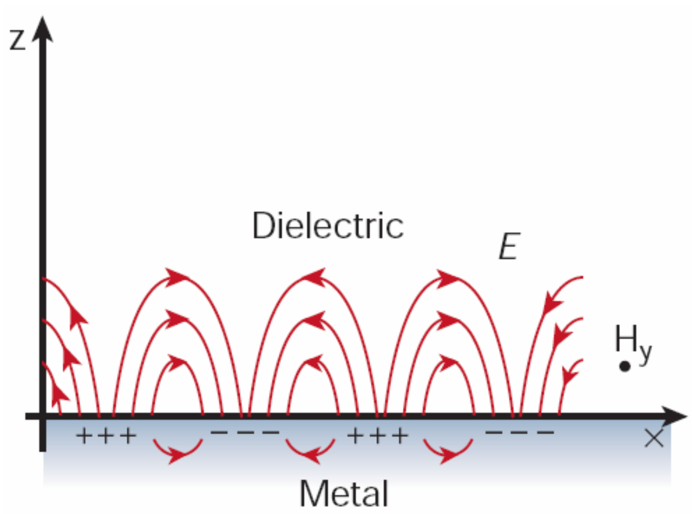
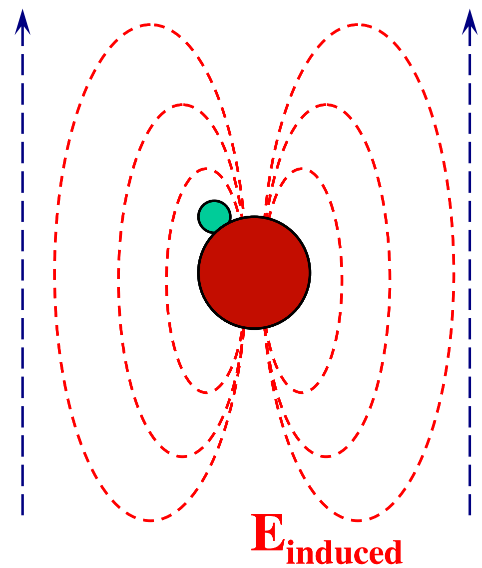
Outline

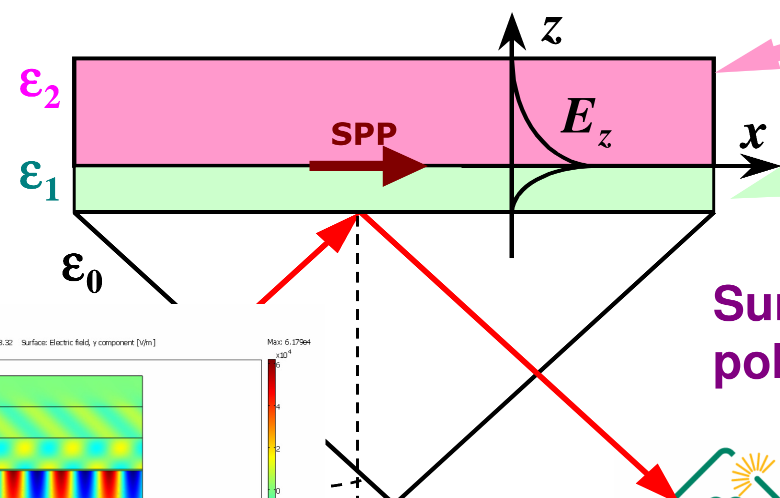
- **Introduction**
- **Enhancement of localized surface plasmon (SP) by gain**
  - ✓ **SPASER (Nanolaser)**
- **Enhancement of propagating surface plasmon polariton (SPP) by gain**
  - ✓ **Stimulated emission of SPPs**
- **Enhancement of SPP without Gain**
- **Metal-free optical materials with negative electric permittivity**
  - ✓ **Transparent conductive oxides**
  - ✓ **High concentrated laser dyes**
- **Summary**

Introductions





Localized surface plasmons (SP)

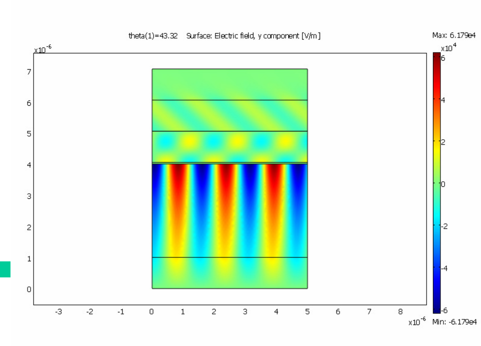


Dielectric

Metal

Surface plasmons polaritons (SPP)

- Electrons movement at metallic surface
- Oscillations of the movement upon an EM field interactions



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Introductions

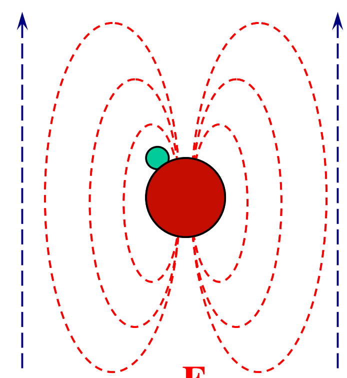
Areas and applications of nanoplasmonics:

- Surface Enhanced Raman Scattering
- Near- field microscopy and spectroscopy
- Negative Index Materials - Optical cloaking
- Medical applications, and many others …

Most of existing and potential applications of nanoplasmonics are suffered from the LOSS caused by metal absorption

Enhancement of localized SPs by gains

Enhancement of Localized surfac plasmon (LSP) in the presence of optical gain.



Theoretical predictions:

Localized SP in metallic sphere: Field enhancement in metallic sphere (R<<λ) with complex dielectric constant ε_1 surrounded by dielectric medium with complex dielectric constant ε_2:

Re=0; Im=0

$$\frac{E_{induced}}{E_0} \propto \left(\frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_1(\omega) + 2\varepsilon_2(\omega)}\right)$$

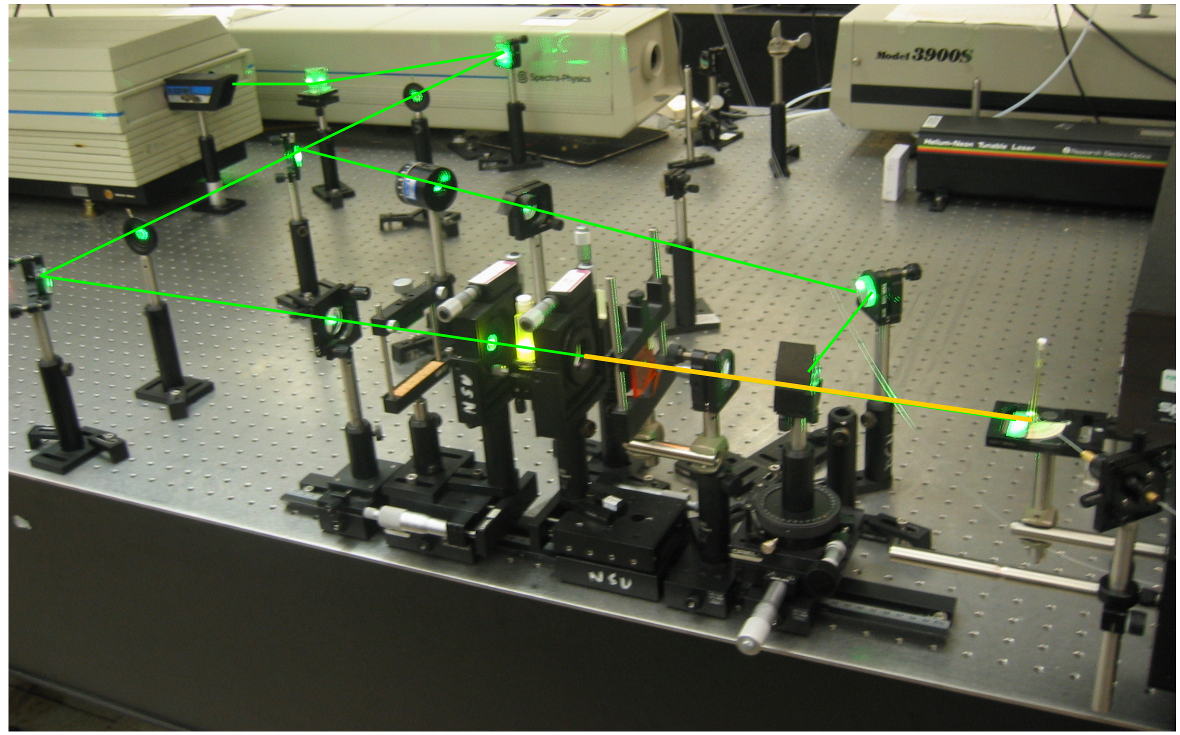
$$\varepsilon_1(\omega) + 2\varepsilon_2(\omega) = [\varepsilon_1'(\omega) + 2\varepsilon_2'(\omega)] + i[\varepsilon_1''(\omega) + 2\varepsilon_2''(\omega)]$$

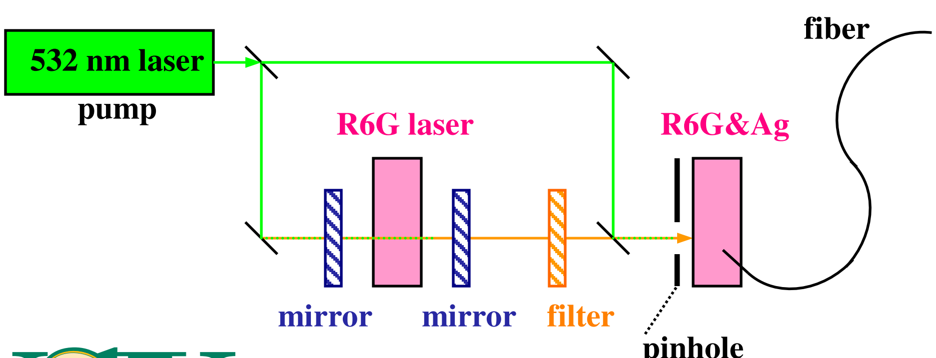
Lawandy, APL, 2004.

LSP enhancement in the presence of optical gain

The mixture of Ag aggregate and rhodamine 6G dye was pumped at 532 nm and probed at 560 nm.

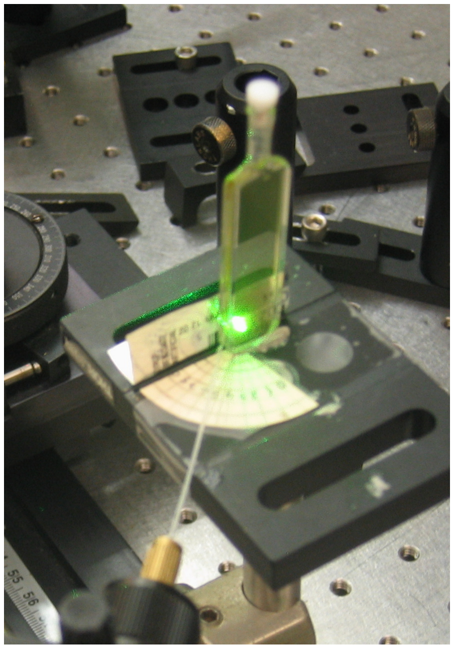
The scattering of the 560 nm light was studied as a function pumping.

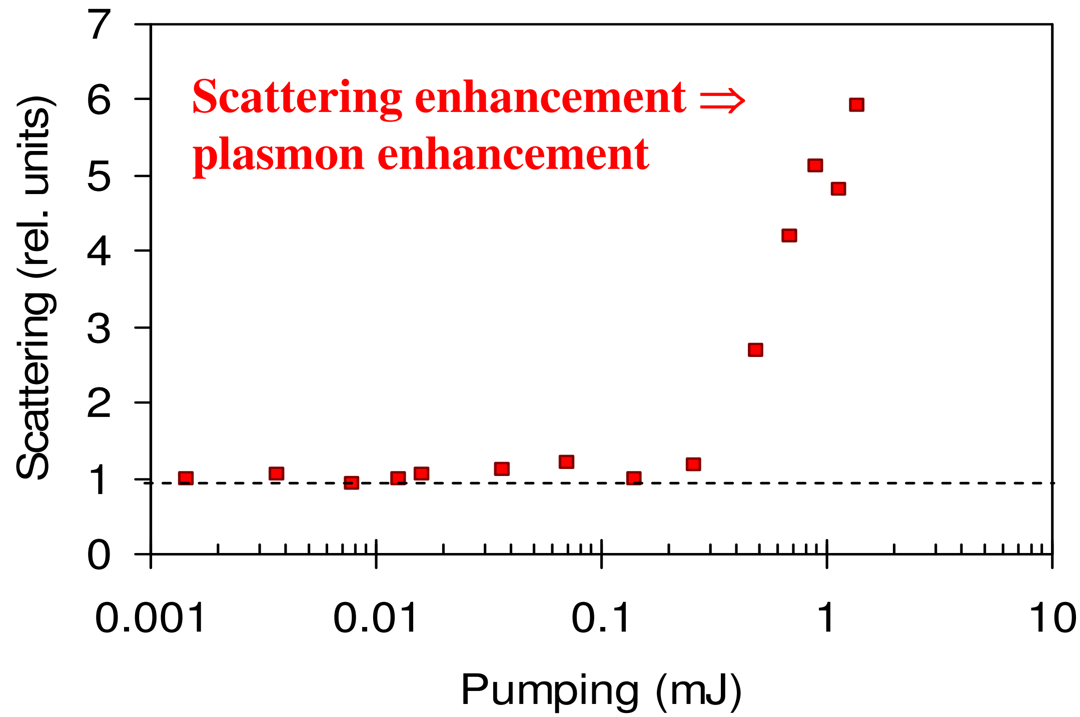




The enhanced scattering was used as the evidence of the plasmon enhancement.

LSP enhancement in the presence of optical gain





Six-fold enhancement of scattering was observed at the increase of the pumping.

[Noginov, Zhu *et.al.*, ArXiv, 2005; Appl. Phys B, 2006; Opt. Lett. 2006]

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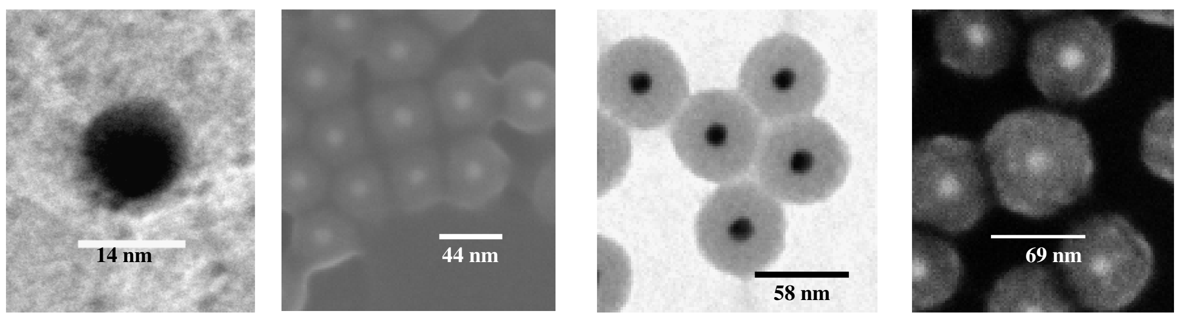
Demonstration of Spaser (nanolaser)

Surface Plasmon Amplification by Stimulated Emission of Radiation



TEM and SEM images of Au/silica particles before the fluorescent dye was added to the surface

Nanoparticle synthesis –by Cornell

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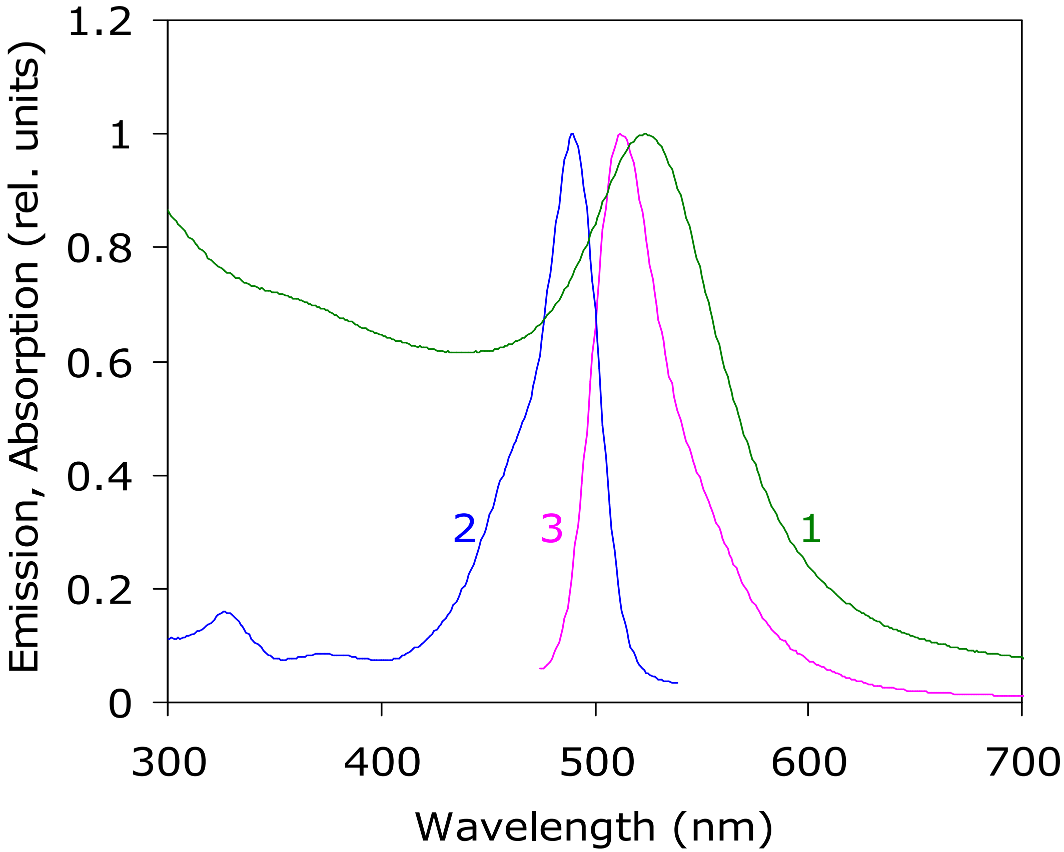
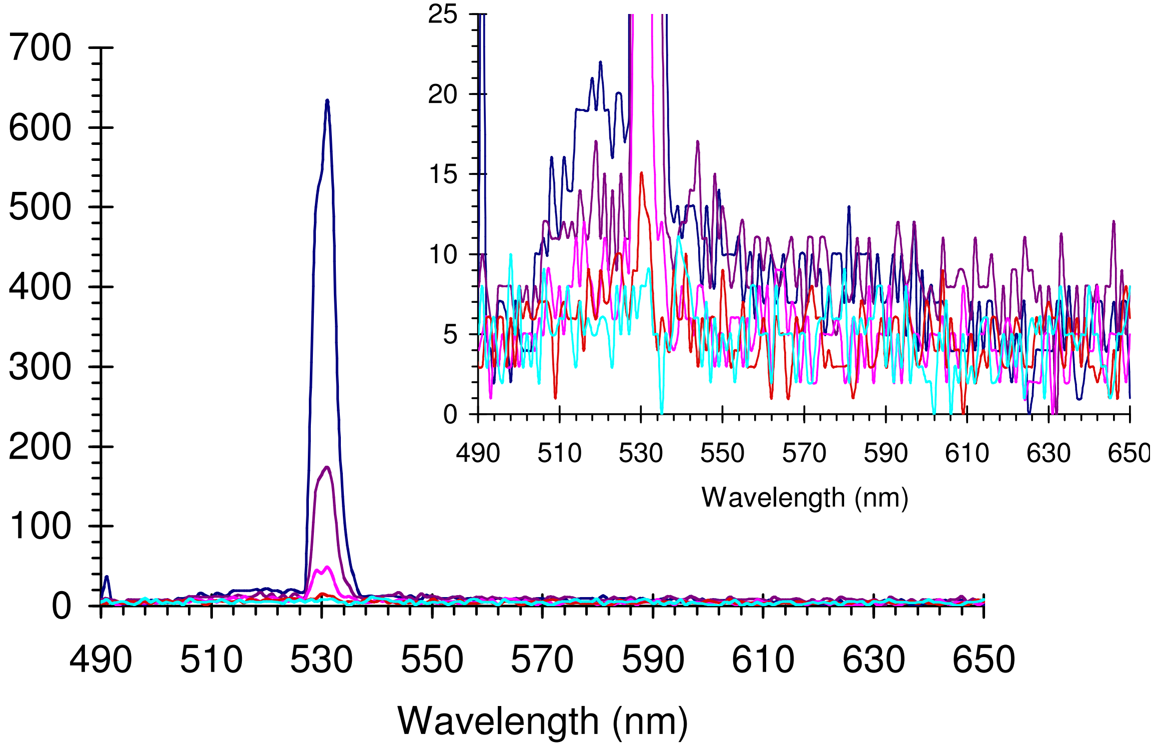
Absorption, Emission and Excitation



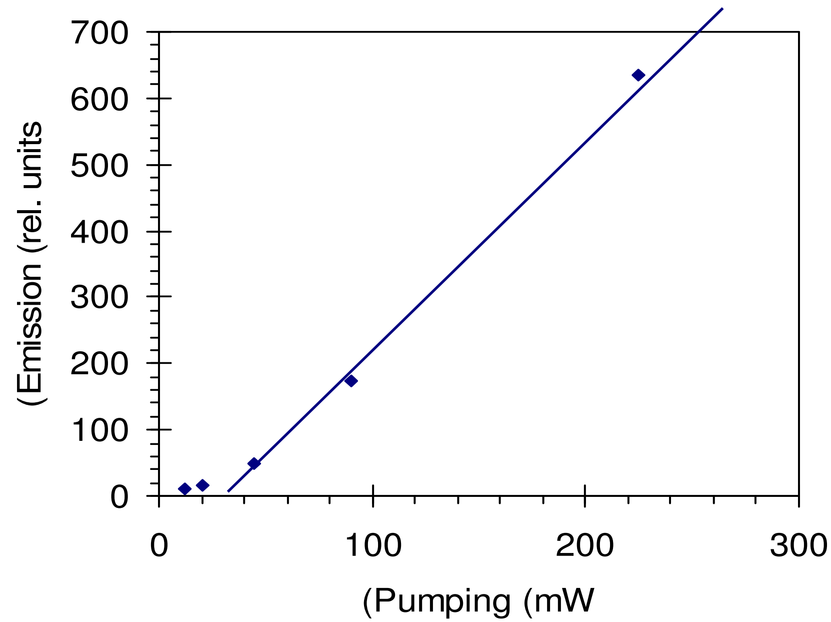
SP absorption overlaps with emission and excitation (absorption) of the Oregon Green 488 dye.

Absorption (1), excitation (2), spontaneous emission (3).

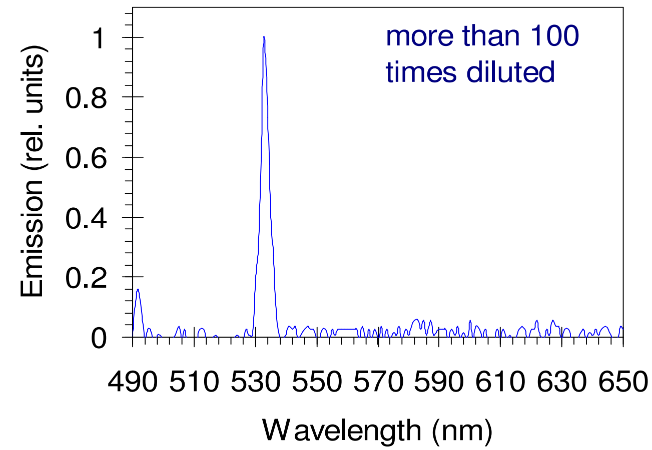
Demonstration of Spaser (nanolaser)



Pumping: λ=488 nm, $t_{pulse} \approx 5$ ns



At dilution, the signal decreased, but its shape and the ratio between the spontaneous and the stimulated emission did not ⇒
Emission occurs in single nanoparticles!



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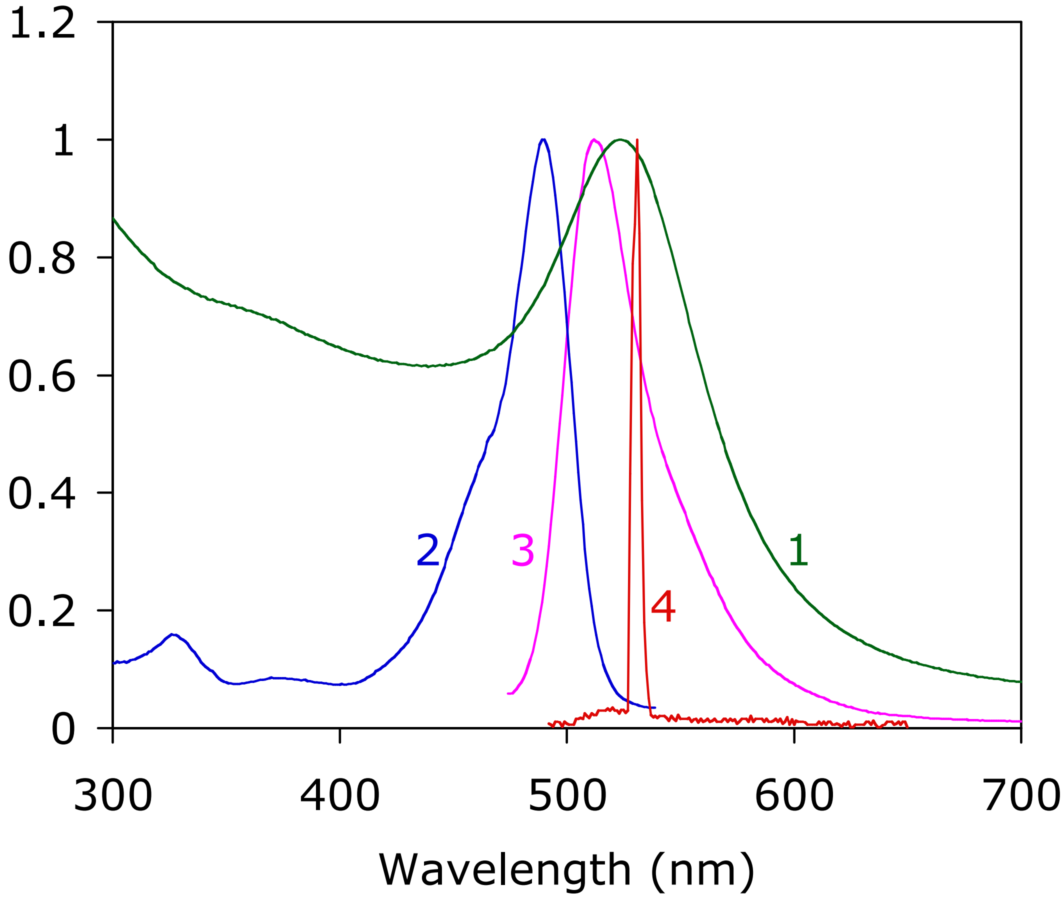
Position of the Spaser line



Absorption (1),
Exciatation (2),
Spontaneous emission (3).
Spaser line (4)

Dye absorption is low, emission and SP resonance are strong

[Noginov, Zhu, *et. al.*, *Nature 2009*]

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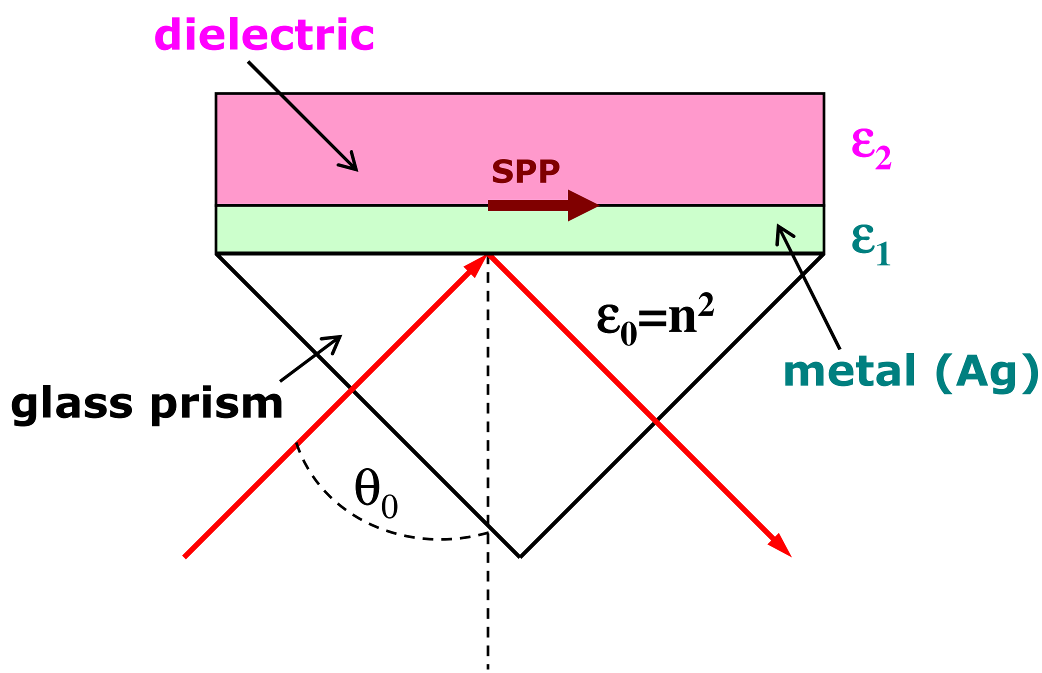
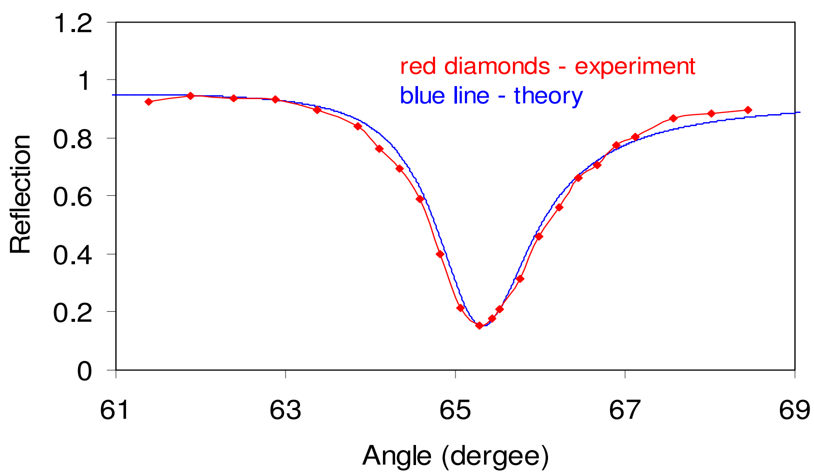
Surface Plasmon Polaritons (SPPs)

Surface Plasmon Polariton (SPP) is an electromagnetic wave propagating at the interface between metal and dielectric.

At critical angle θ_0, when $k_{phot}\sin\theta = k_{SPP}$, light wave excites SPP $\Rightarrow$ there is a "dip" in the reflection curve.

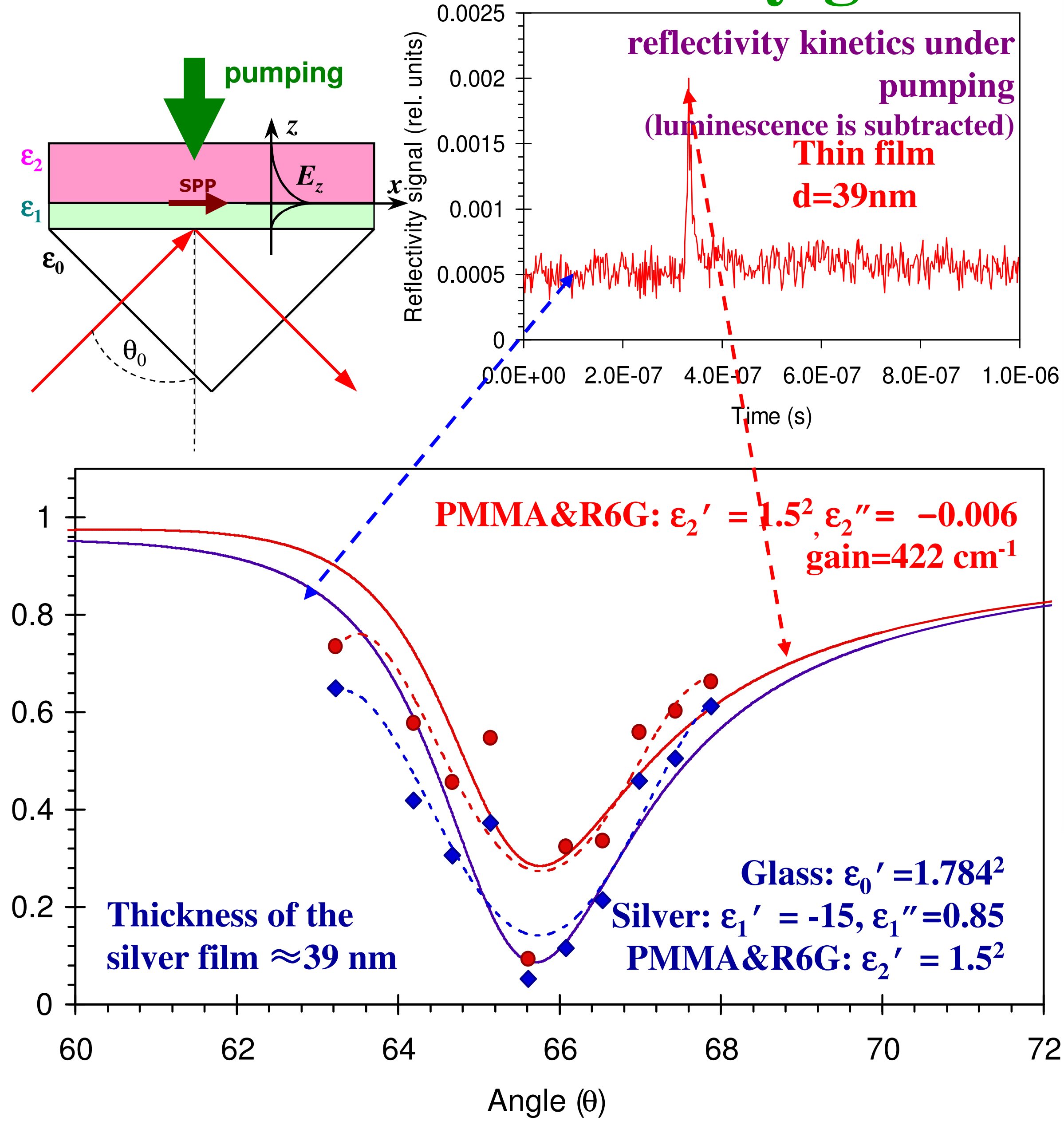


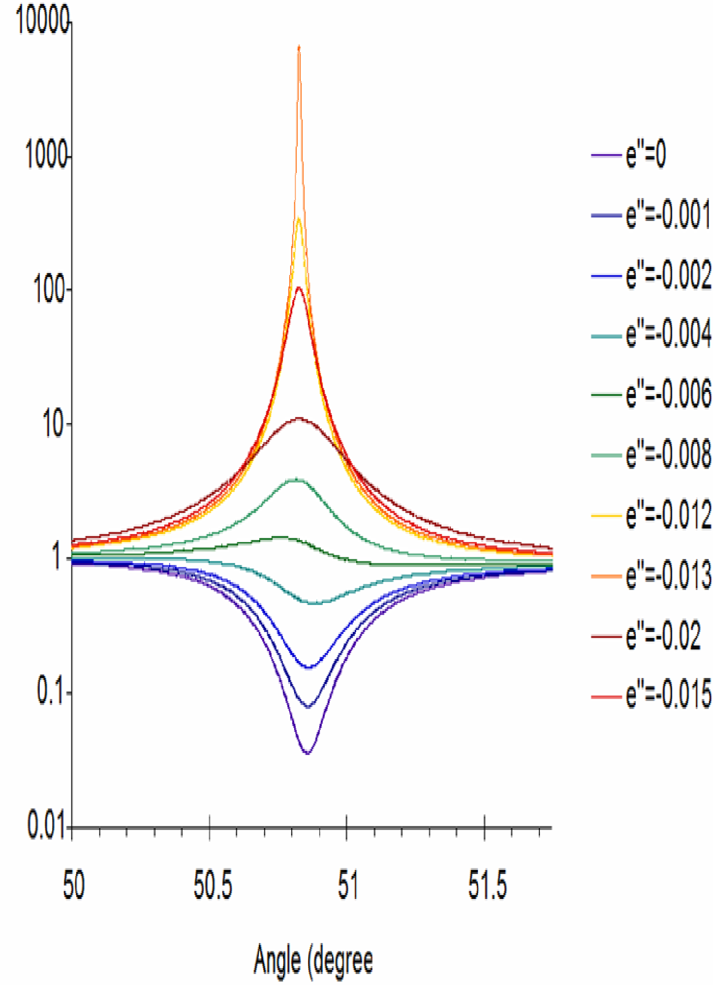


k_{phot} $\qquad$ k_{SPP}

$$\frac{\omega}{c} \cdot n \cdot \sin\,\theta_0 = \frac{\omega}{c} \cdot \sqrt{\frac{\varepsilon_1 \cdot \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$

Enhancement of SPPs by gains





Relative enhancement of the reflectivity signal as high as 280% !

[Noginov, Zhu, *et. al.*, *Optics Express 2008*]

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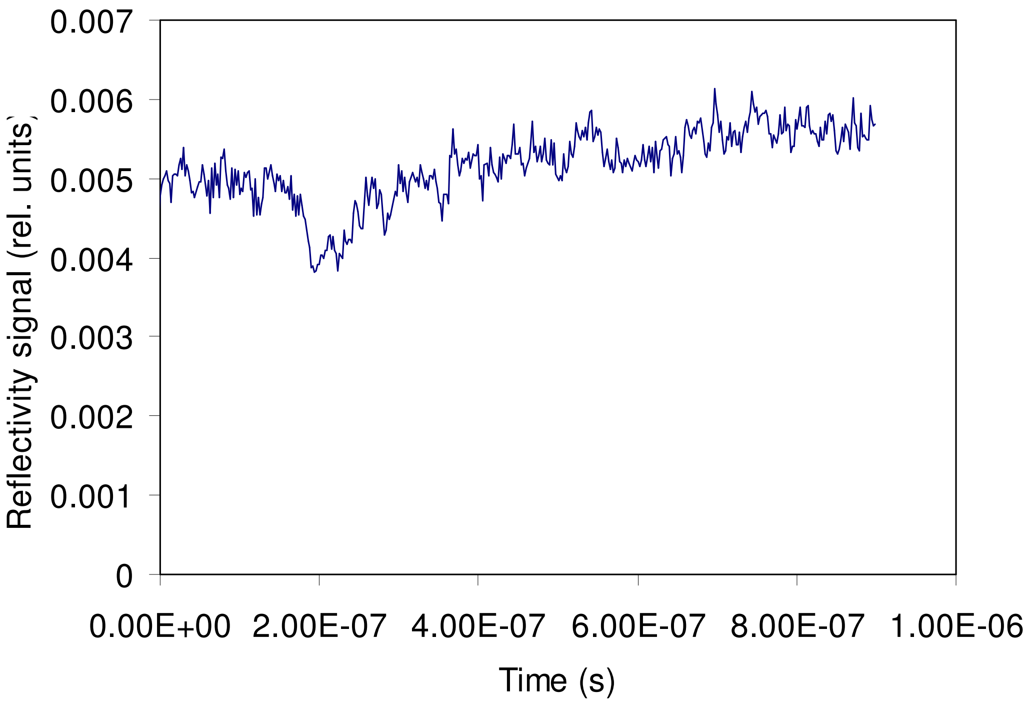
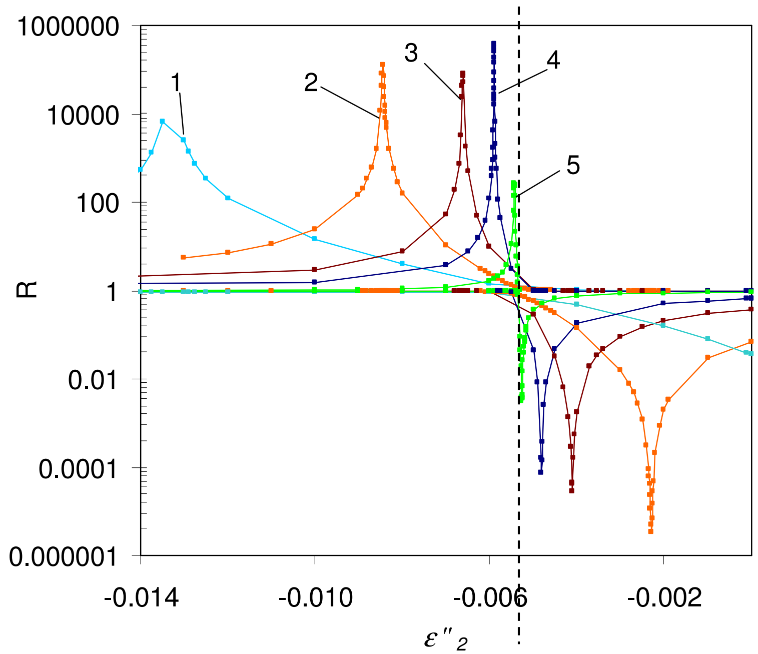
SPPs with optical gain





Thickness of the silver film is ~ 90 nm

Trace #1 - 50nm; trace #2 - 60nm; trace #3 - 70nm; trace #4 - 80nm; trace #5 - 100nm.

Experimental result is just as the model predicted !

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[Noginov, Zhu, *et. al.*, *Optics Express 2008*]

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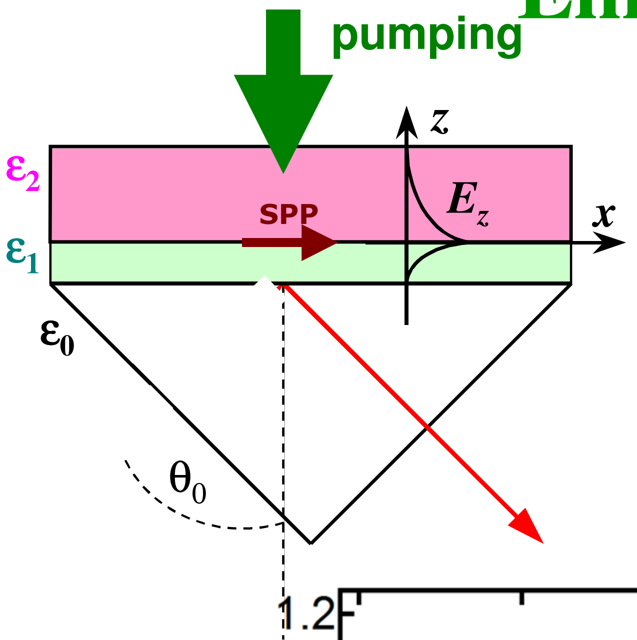
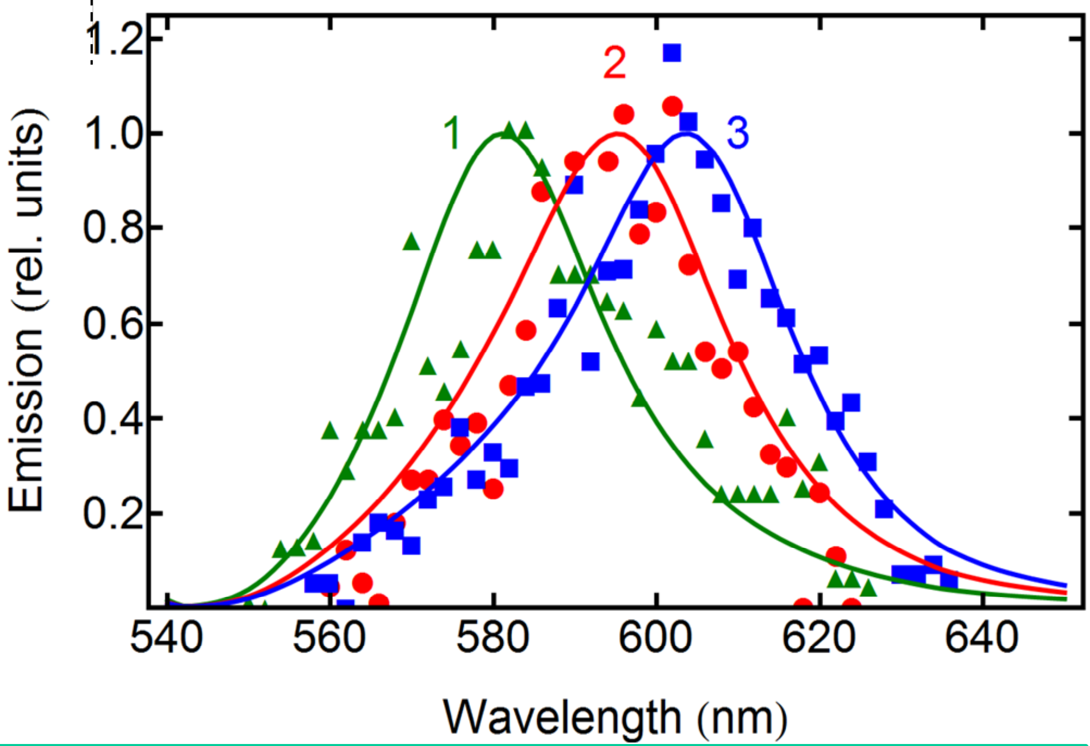
Emission of SPPs

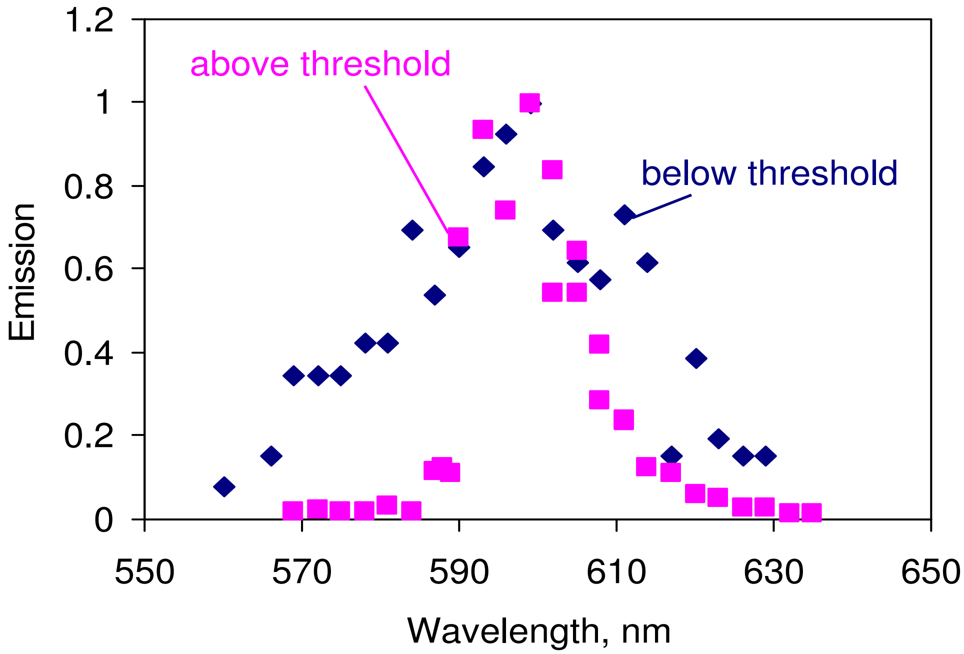


SPPs can be excited *via* ***emission*** of R6G molecules in the **R6G-PMMA film**



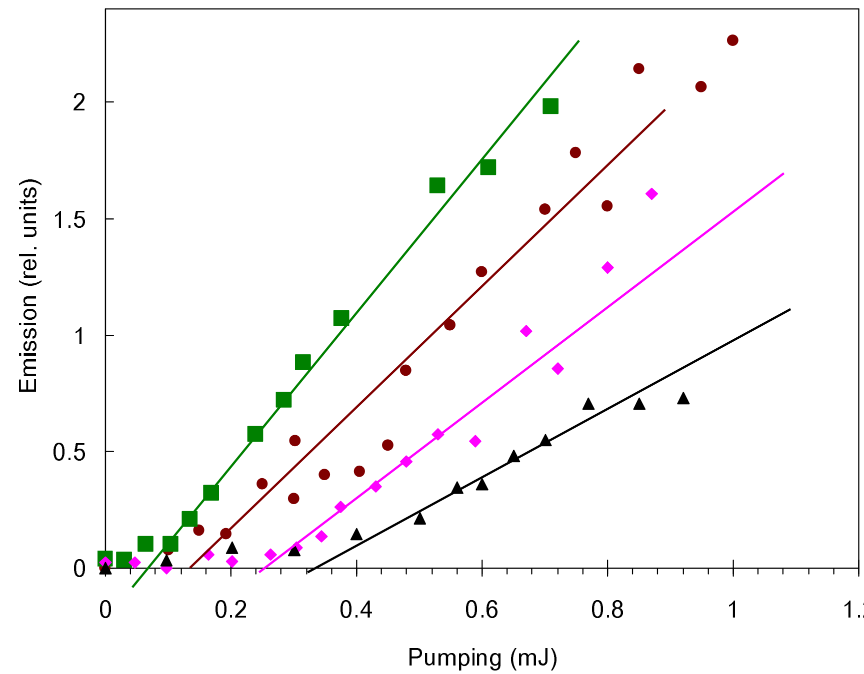
SPP spectra recorded at different decoupling angles

Stimulated emission of SPPs



Emission spectra considerably narrowed in comparison to those at low pumping.

The dependence of the emission intensity shows strongly nonlinear with the distinct threshold.



[Noginov, Zhu, *et. al.*, *PRL 2009*]

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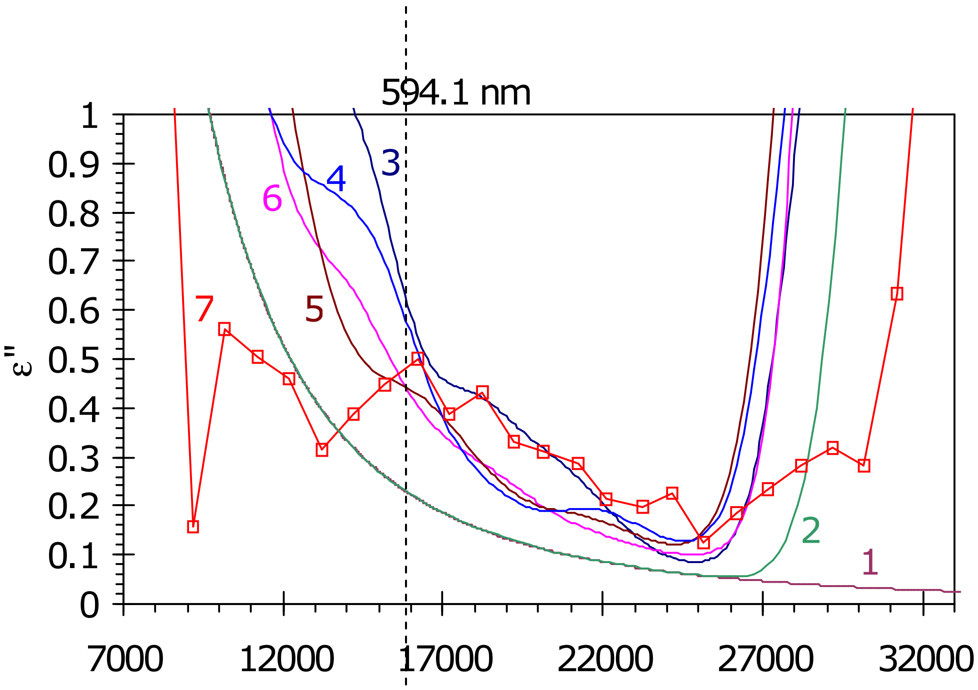
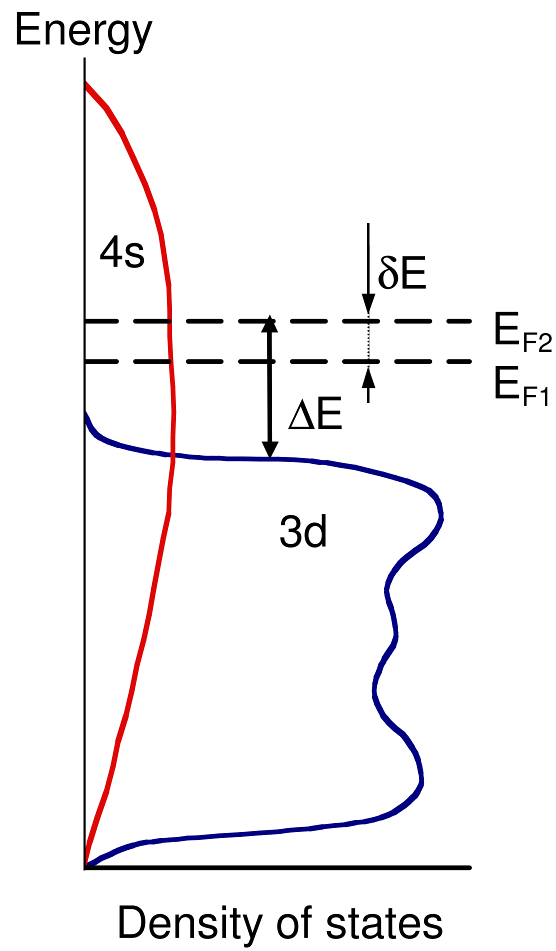
Enhancement of SPs w/o optical gain

Modifying surface states of bound electrons



Trace #1, according to the Drude model
Trace #2, from the first principles for bulk silver;
Traces #3-6, for the surface of silver slabs consisting of 7, 10, 13, and 16 monolayers. .

Changing Fermi level of a metallic layer



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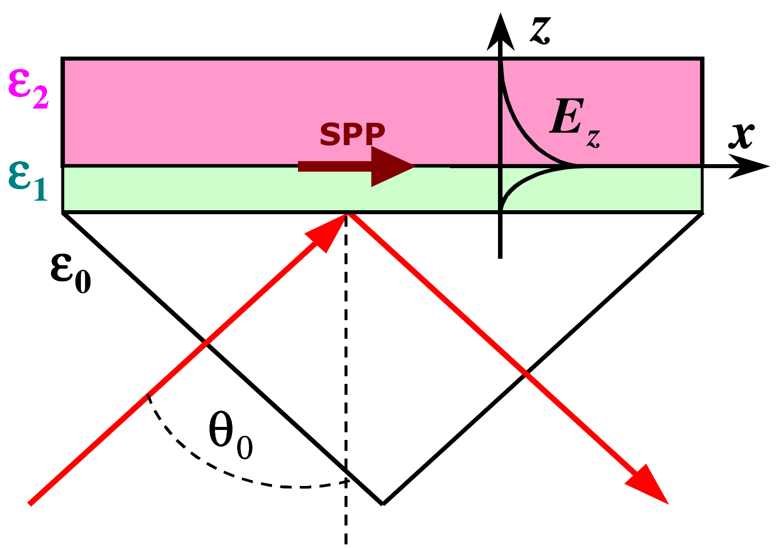
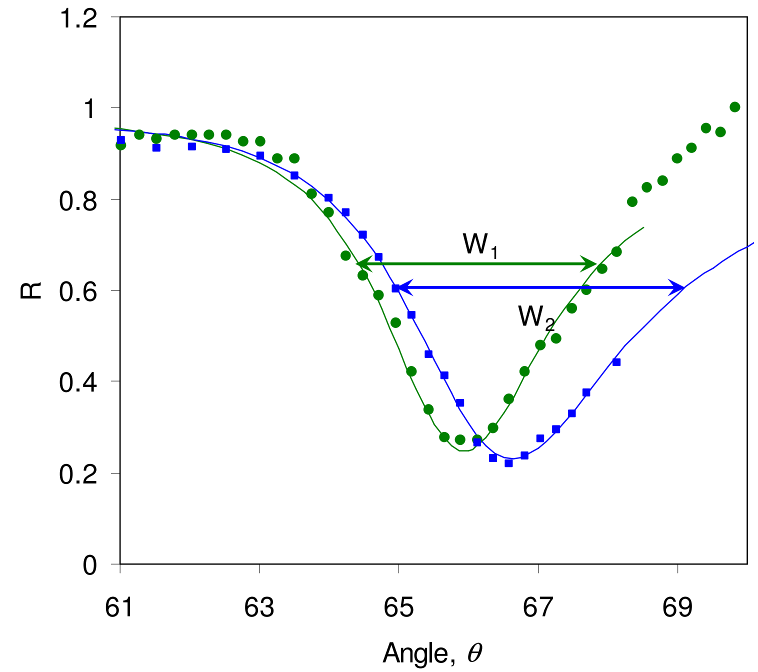
Elongation of propagation length of SPs – modify the interface

PMMA film with high concentration of R6G dye was deposited on the silver film.





~ 30% elongation of the SPP propagation length when the dye conc. is about *30* g/l !

[Zhu, *et. al., APL 2009*]

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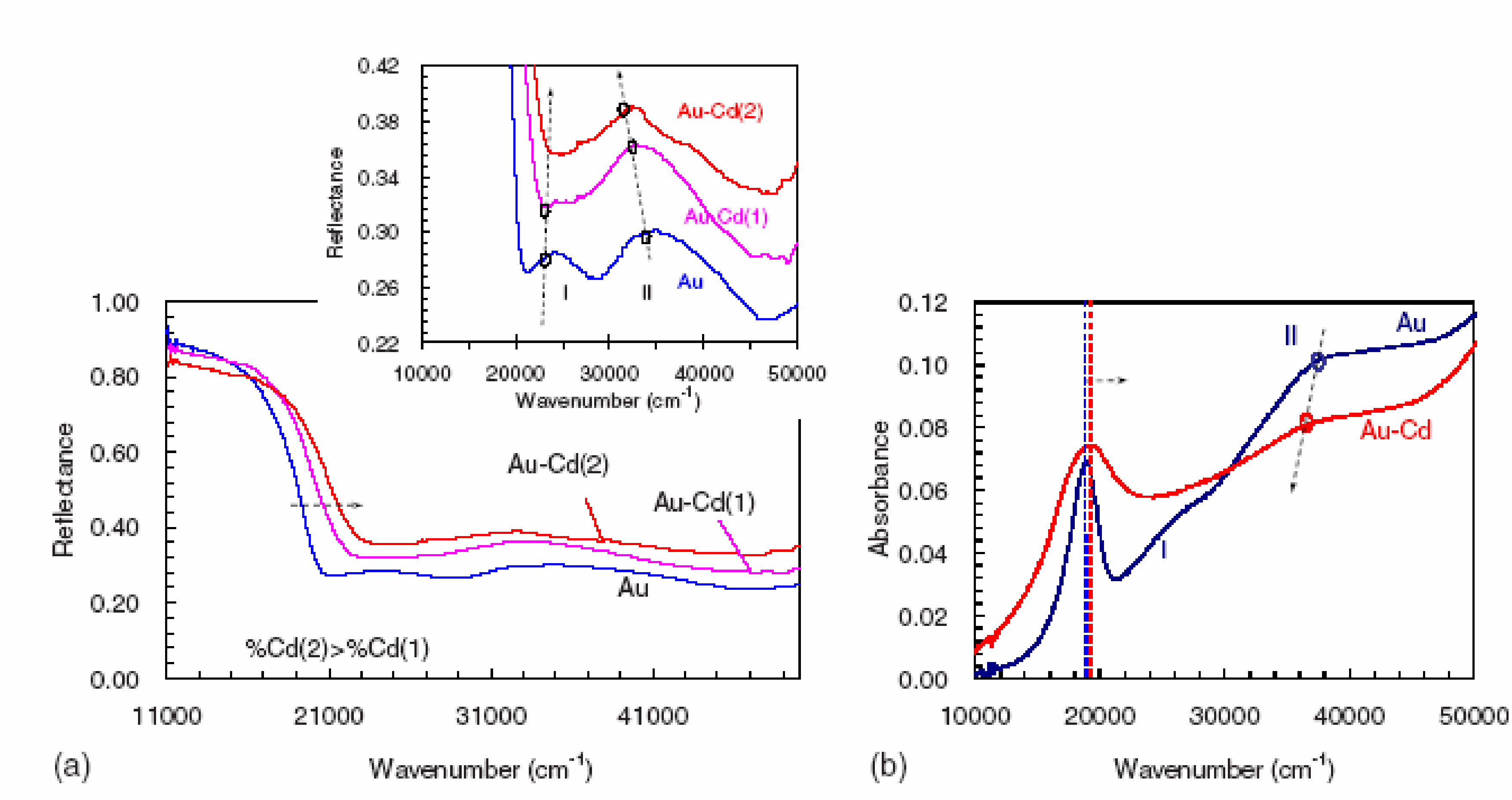
Elongation of propagation length of SPs – mechanical alloy



[Bobb, Zhu, *et. al.*, *APL 2009*]

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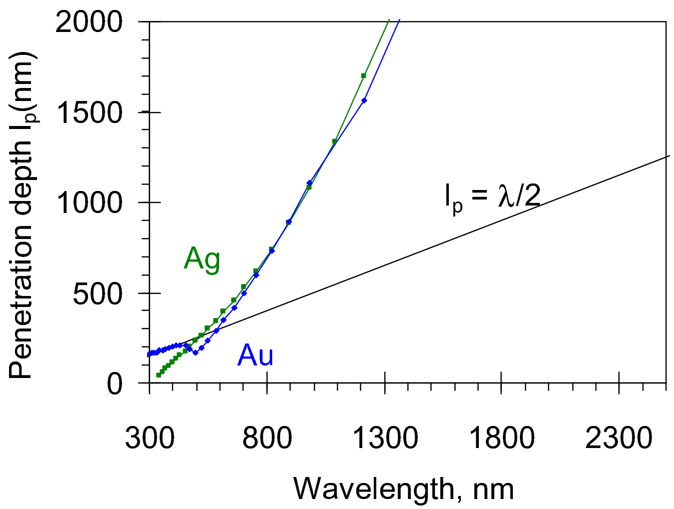
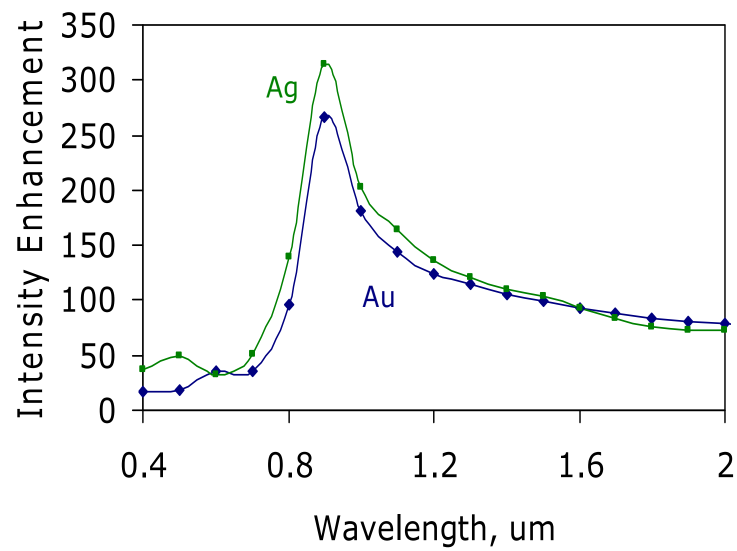
Metal-free plasmonic materials ~ IR range

Plasmonics based on silver and gold loss their compactness above 539 nm and 660 nm respectively.

$$l_{d,m} = \frac{1}{\mathrm{Im}\left(k_{d,m}^{z}\right)} = \mathrm{Im}\left(\frac{\lambda}{2\pi}\sqrt{\frac{\varepsilon_d + \varepsilon_m}{\varepsilon_{d,m}^{2}}}\right)$$



Maximal SPP field enhancements of silver and gold centered ONLY around 900nm, very lower at mid-infrared.



A search for plasmonic materials with higher compactness and efficient in the infrared, is of high importance.

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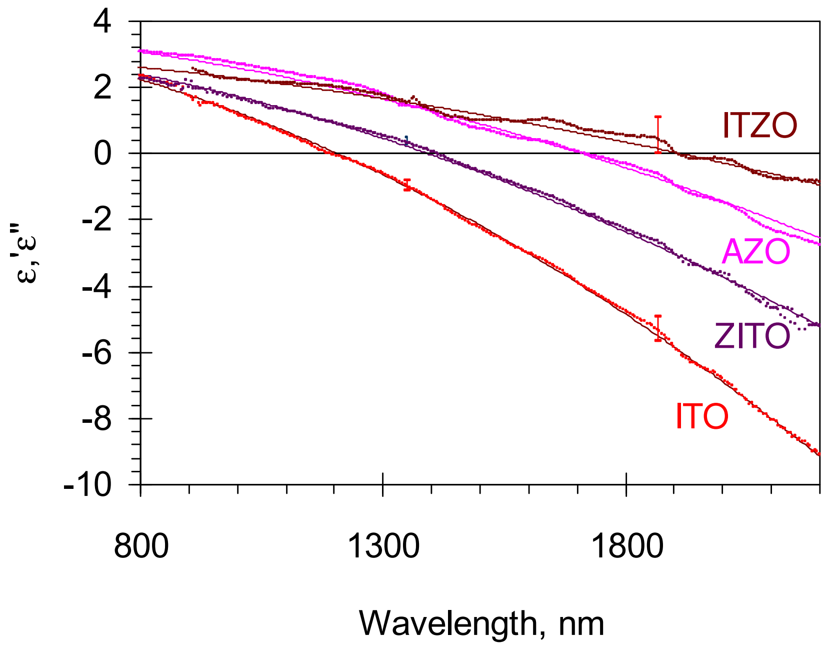
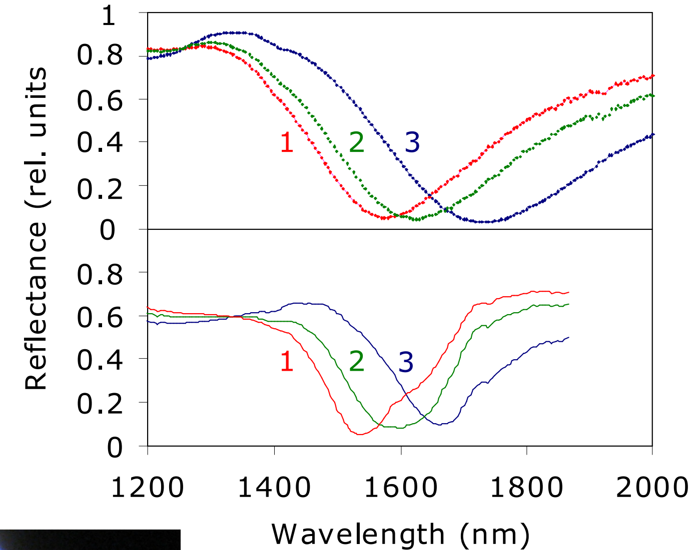
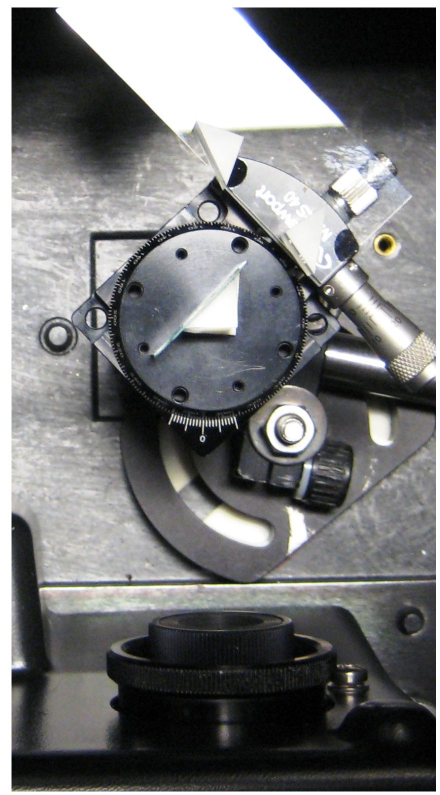
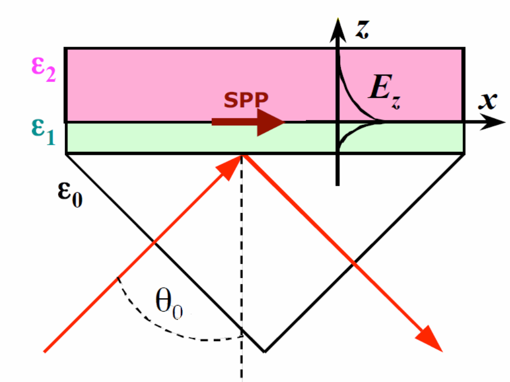
Metal-free plasmonic materials



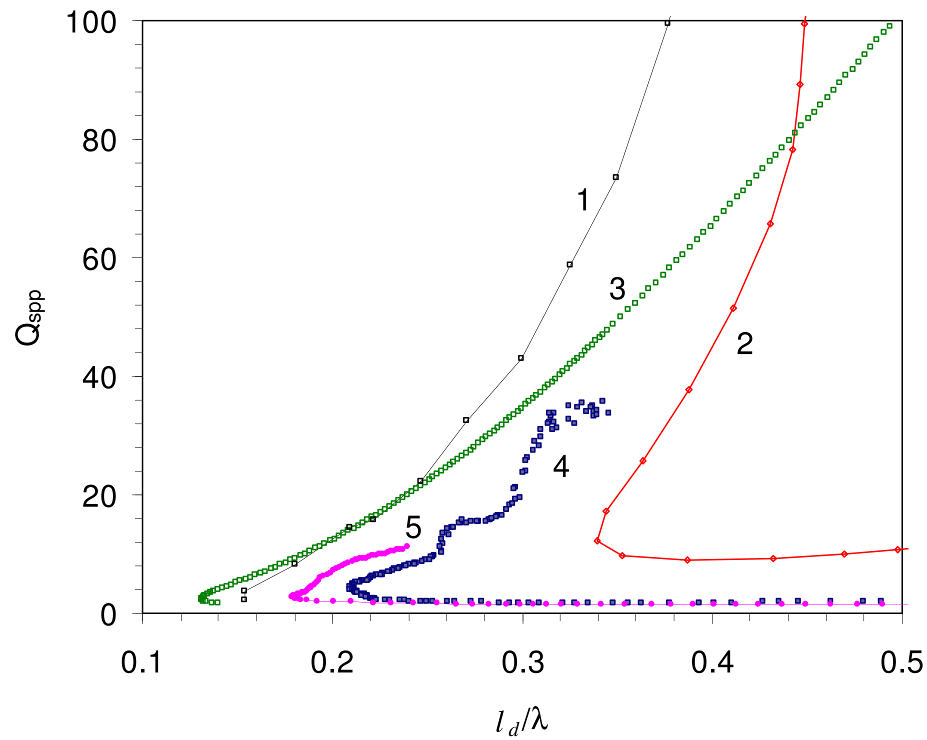






Heavily doped degenerate wide-band-gap semiconductors in near-infrared spectral range with strong confinement of SPPs and low loss.

Metal-free plasmonic materials-Semiconductors



SPP Q-factor on *lp*/*λ* for silver (1), gold (2), ITO (3), ZITO (4) and AZO (5).

[Noginov, Gu, Zhu, et. al, OSA 2010, accepted by APL, 2011]

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Theoretical predictions

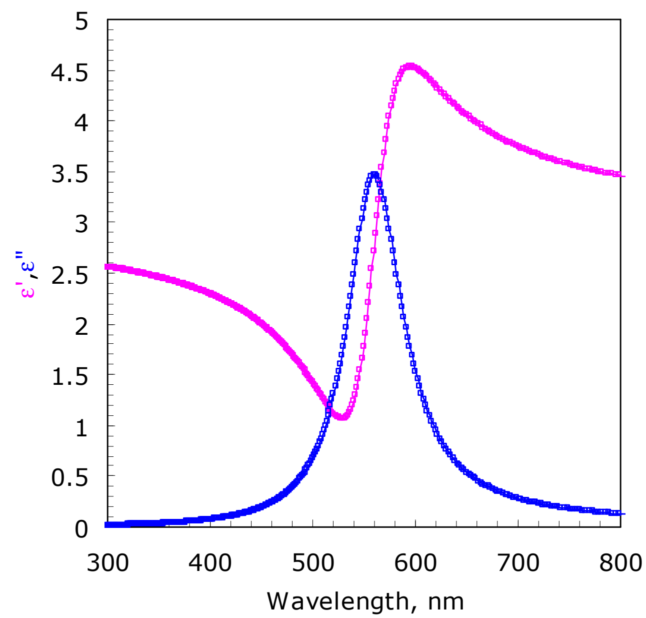
Kramers-Kronig Relations

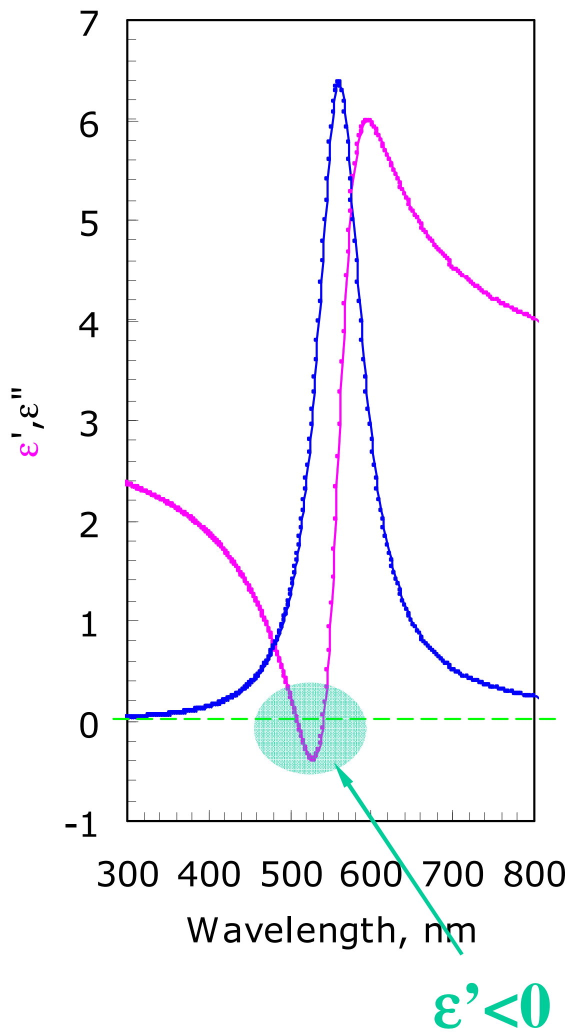
Increase of peak absorption leads to negative permittivity

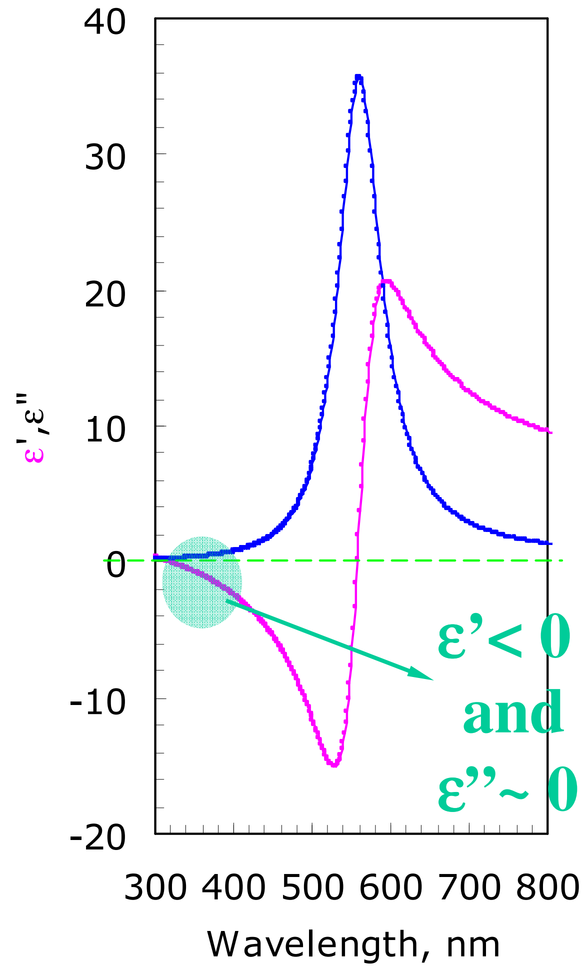
$$\mathrm{Re}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = 1 + \frac{1}{\pi} P\int_{-\infty}^{\infty} \frac{\mathrm{Im}\left(\frac{\varepsilon(\omega')}{\varepsilon_0}\right)}{\omega' - \omega} d\omega'$$

$$\mathrm{Im}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = -\frac{1}{\pi} P\int_{-\infty}^{\infty} \frac{\mathrm{Re}\left(\frac{\varepsilon(\omega')}{\varepsilon_0}\right) - 1}{\omega' - \omega} d\omega'$$

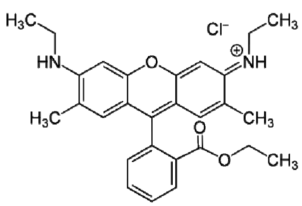
$$\varepsilon(\omega) = \mathrm{Re}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) + i\,\mathrm{Im}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$



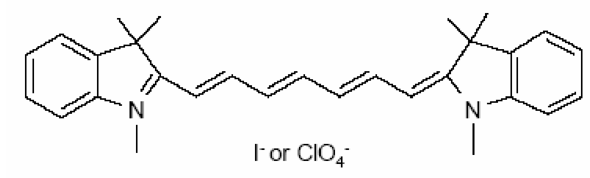




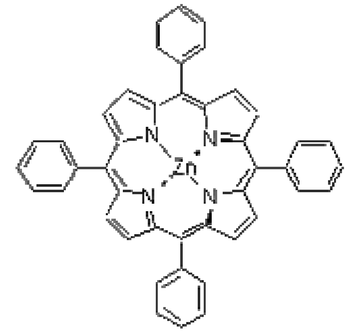
Experimental samples: Films of several laser dyes



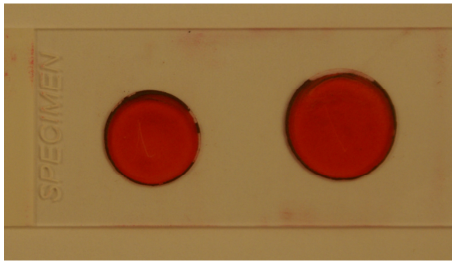
Rhodamine-6G ($C_{28}H_{31}N_2O_3Cl$)



HITC ($C_{29}H_{33}N_2I$)



Zn-TPP



Rhodamine-6G film

Films preparation:

Dissolved in a solvent

↓

Deposited onto a glass substrate

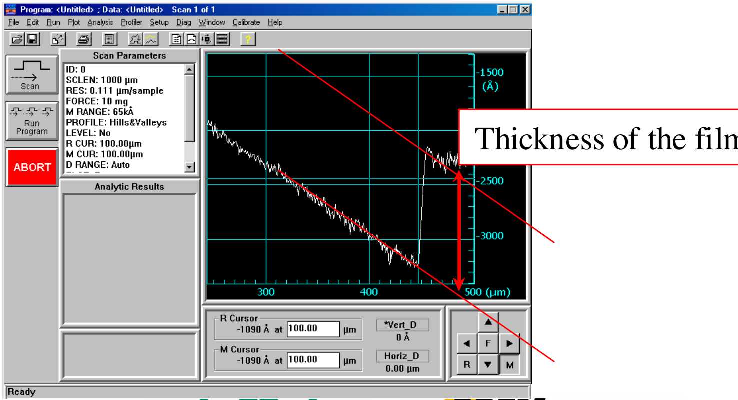
↓

Dried to a solid state.

Film thickness

45nm -180 nm

(Dektak-6M profilometer)



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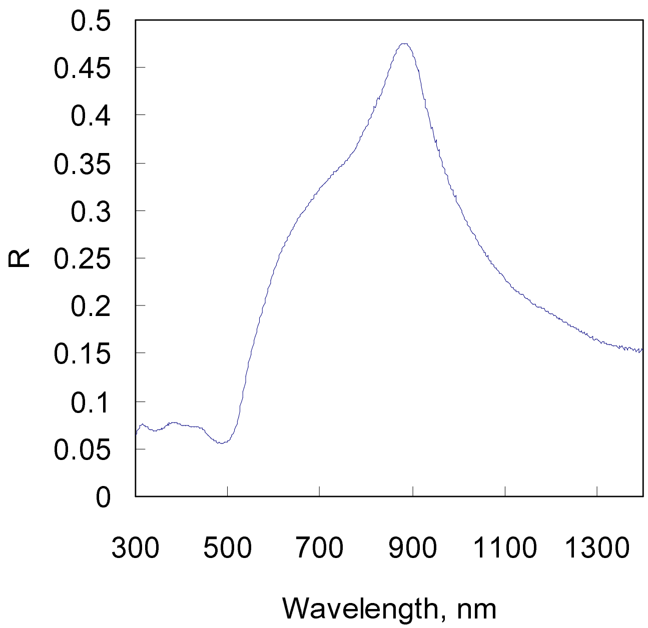
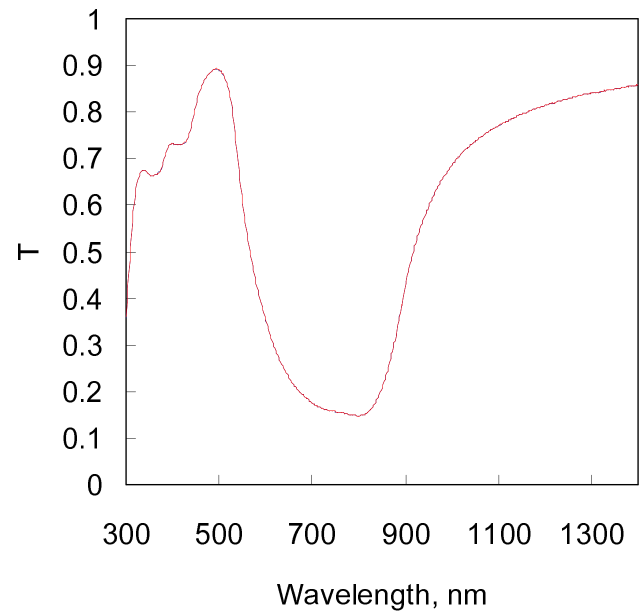
Reflection and transmission spectra

HITC film: thickness ~ 63nm





Reflection is as high as 47% (λ = 874nm)

$$R(\lambda)=F_1(\varepsilon',\varepsilon'');T(\lambda)=F_2(\varepsilon',\varepsilon'')$$

$$\varepsilon'(\lambda)=f_1(T,R);\varepsilon''(\lambda)=f_2(T,R)$$

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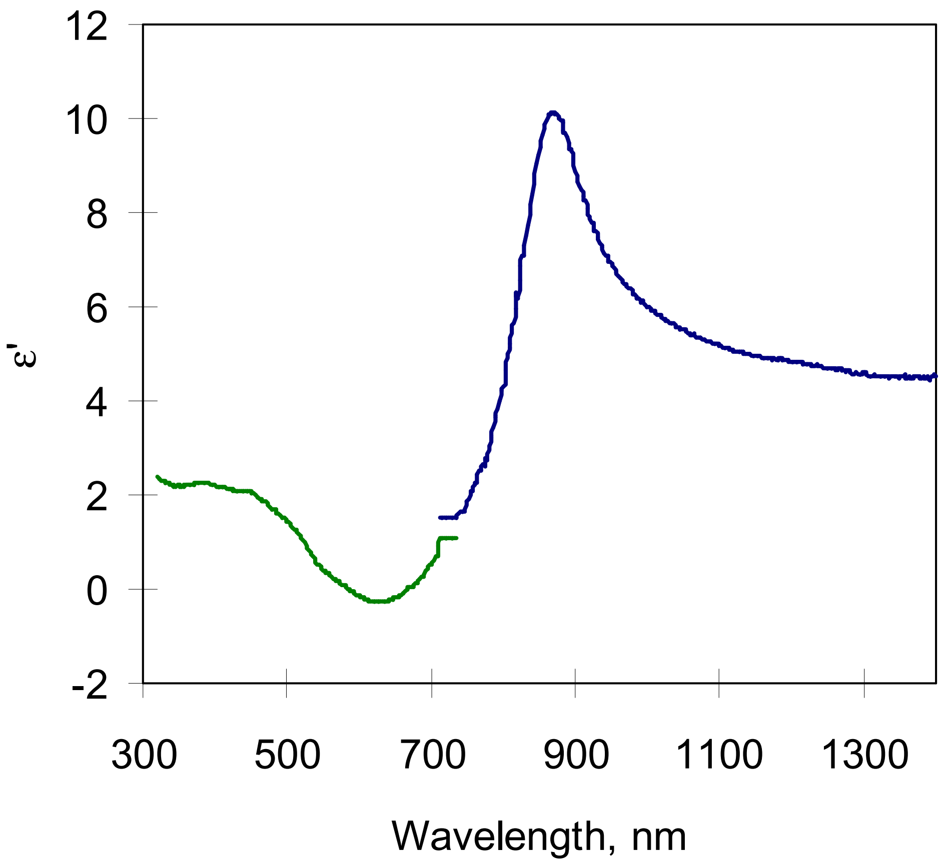
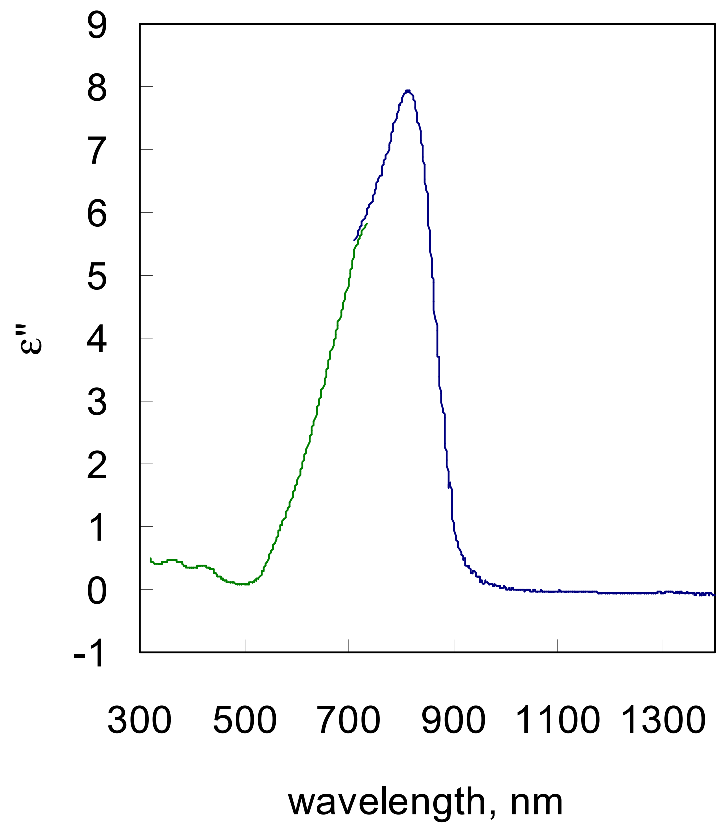
Permittivity (HITC) extracted from R(λ) and T (λ)





ε''_{max} = 7.98 at λ = 844nm

ε'_{max} = 10.2 at λ = 864nm

ε'_{min} = -0.2 at λ = 606nm

M. Mayy, Zhu, …, Noginov, JAP, 2009

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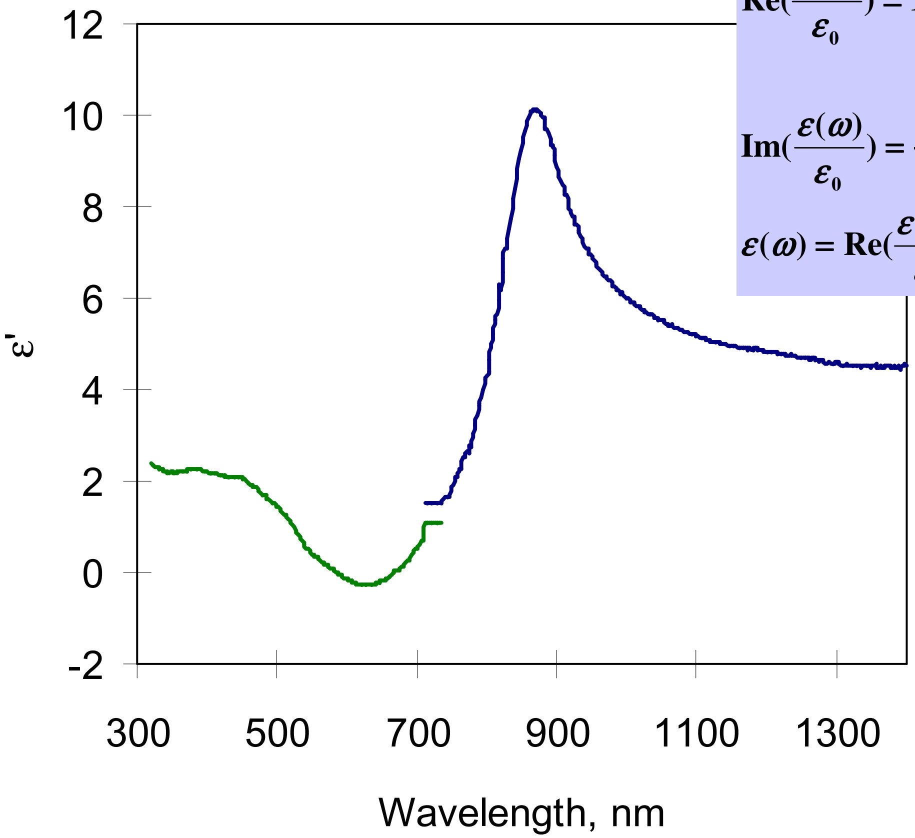
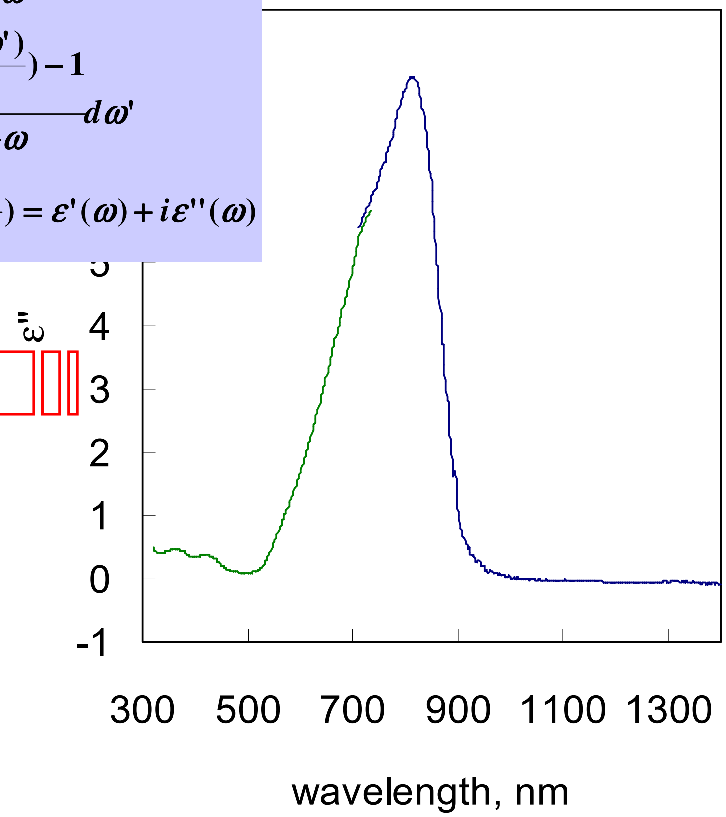
Permittivity (HITC) extracted from R(λ) and T (λ)

$$\mathrm{Re}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = 1 + \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{Im}\left(\frac{\varepsilon(\omega')}{\varepsilon_0}\right)}{\omega' - \omega} d\omega'$$

$$\mathrm{Im}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{Re}\left(\frac{\varepsilon(\omega')}{\varepsilon_0}\right) - 1}{\omega' - \omega} d\omega'$$

$$\varepsilon(\omega) = \mathrm{Re}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) + i\,\mathrm{Im}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$





$\varepsilon'_{max} = 10.2$ at $\lambda = 864$nm

$\varepsilon'_{min} = -0.2$ at $\lambda = 606$nm

$\varepsilon''_{max} = 7.98$ at $\lambda = 844$nm

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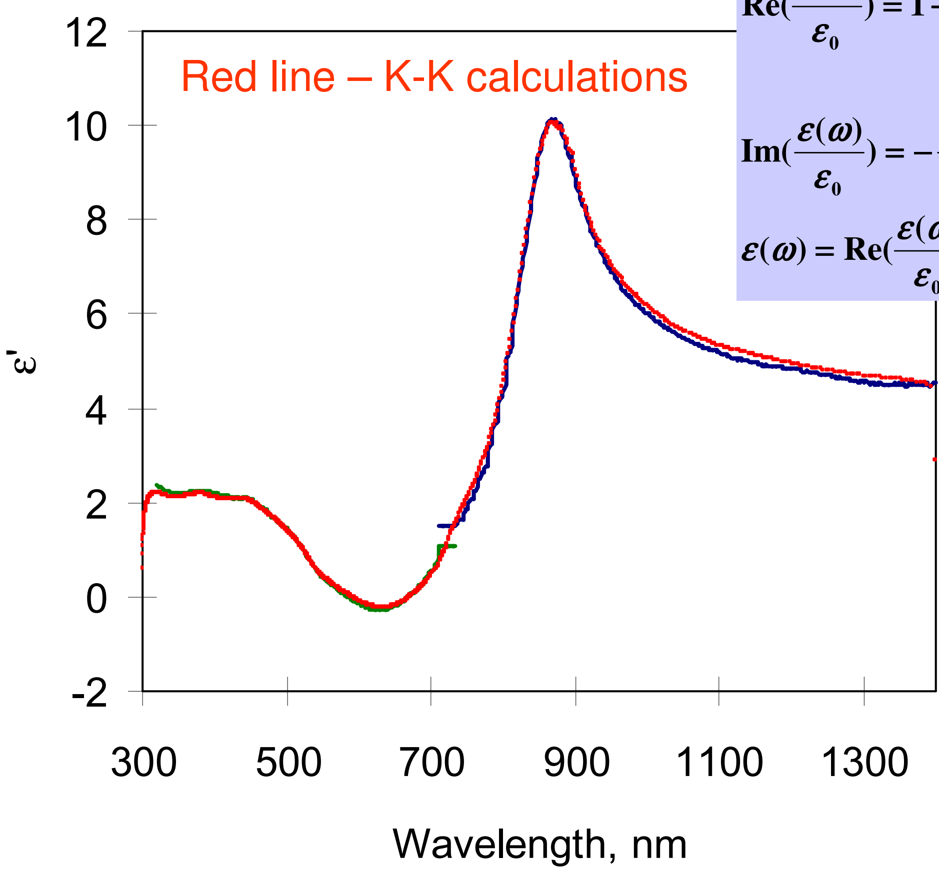
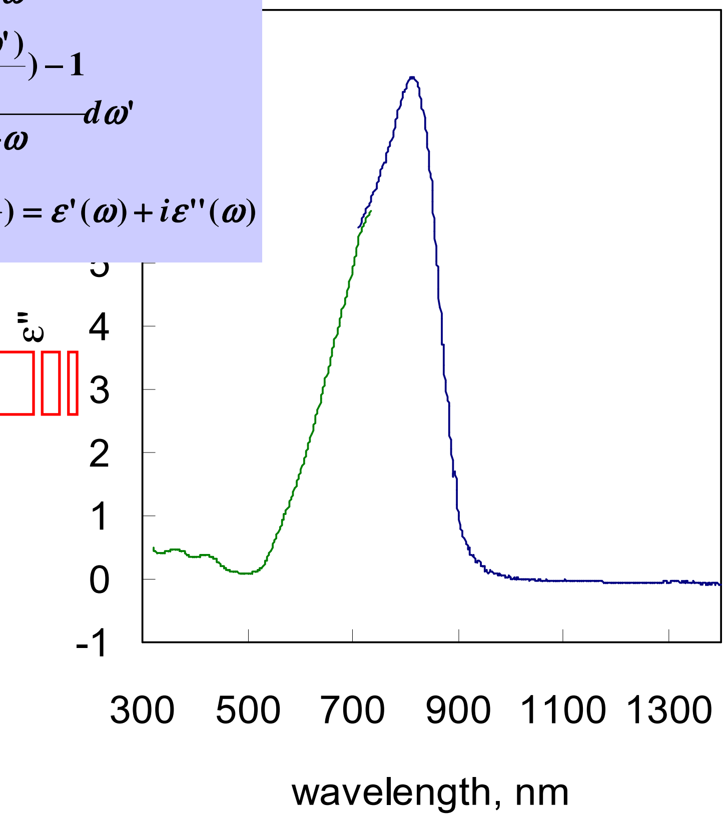
Permittivity (HITC) extracted from R(λ) and T (λ)

$$\mathrm{Re}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = 1 + \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{Im}\left(\frac{\varepsilon(\omega')}{\varepsilon_0}\right)}{\omega' - \omega} d\omega'$$

$$\mathrm{Im}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\mathrm{Re}\left(\frac{\varepsilon(\omega')}{\varepsilon_0}\right) - 1}{\omega' - \omega} d\omega'$$

$$\varepsilon(\omega) = \mathrm{Re}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) + i\,\mathrm{Im}\left(\frac{\varepsilon(\omega)}{\varepsilon_0}\right) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$





ε'_{max} = 10.2 at λ = 864nm

ε'_{min} = -0.2 at λ = 606nm

ε''_{max} = 7.98 at λ = 844nm

[M. Mayy, Zhu, et. al., JAP, 2009]

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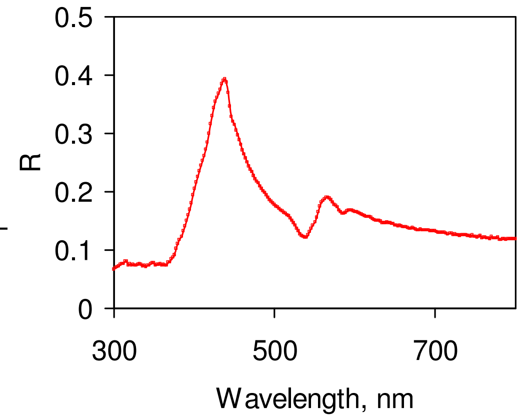
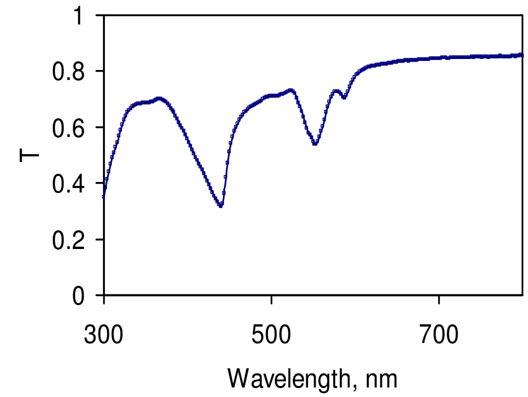
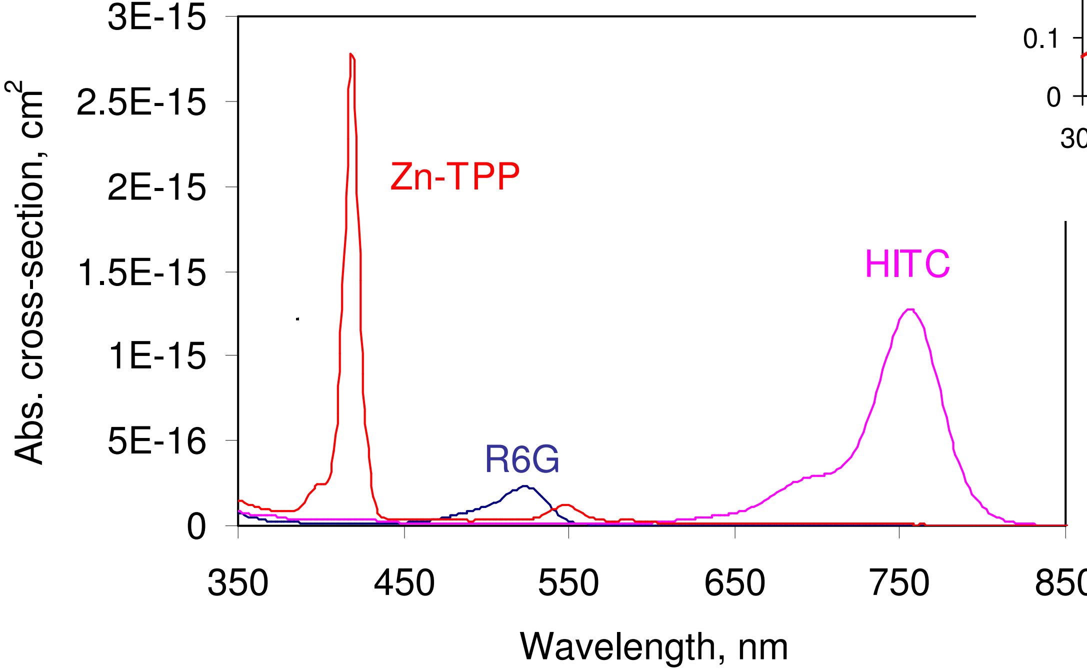
Zn-TPP Dye



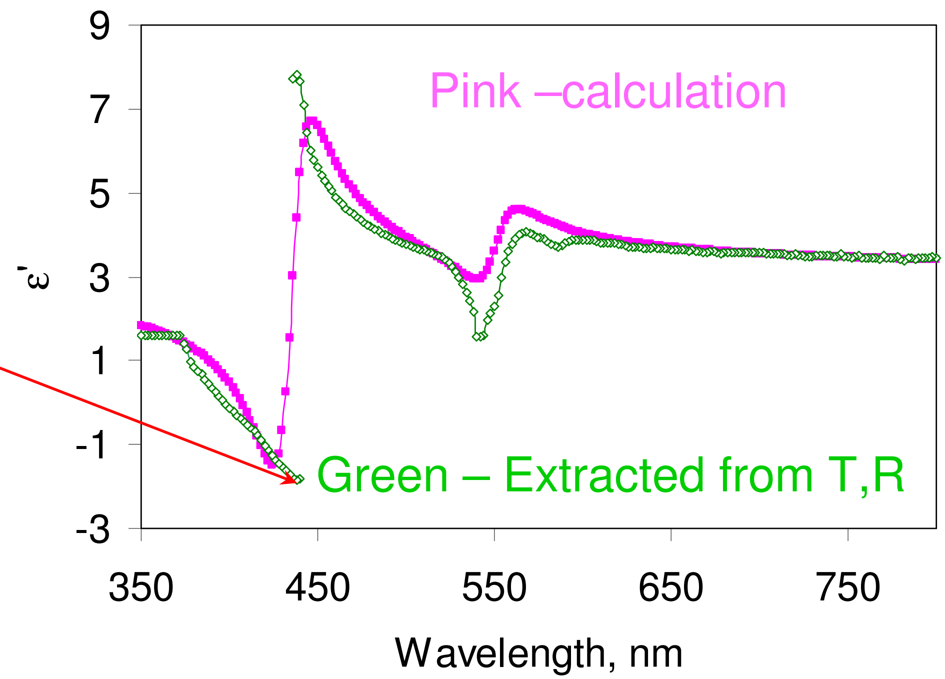




$\varepsilon'_{ZnTPP}(\lambda)$

$R(\lambda)$ and $T(\lambda)$ of Zn-TPP

$\varepsilon'_{ZnTPP}(\lambda=434\text{ nm}) = -1.8$



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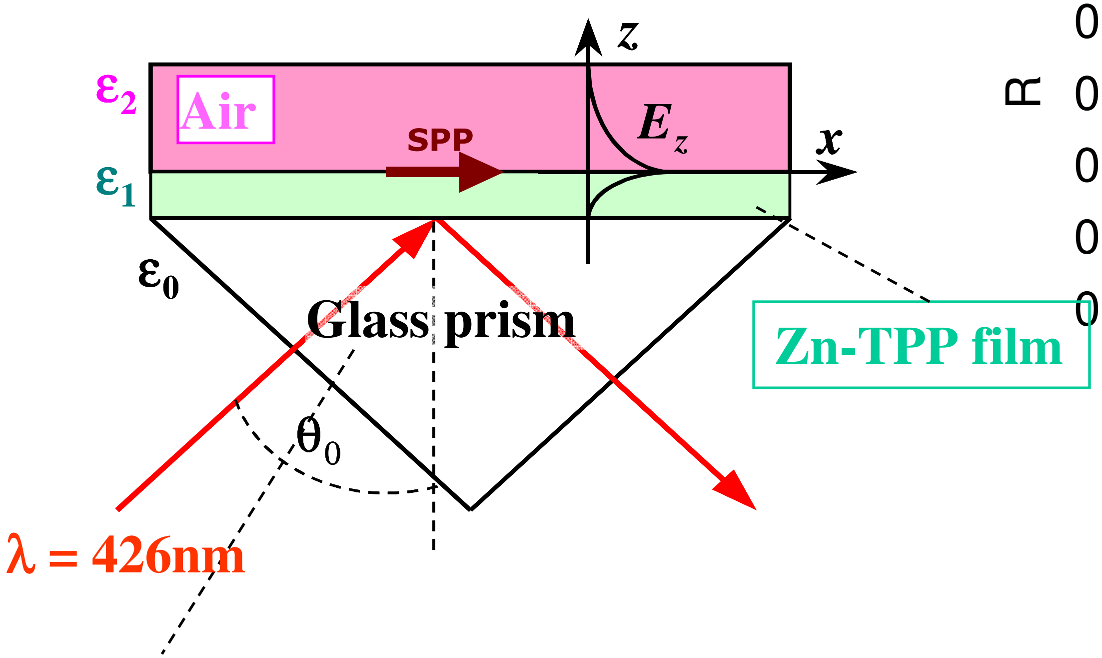
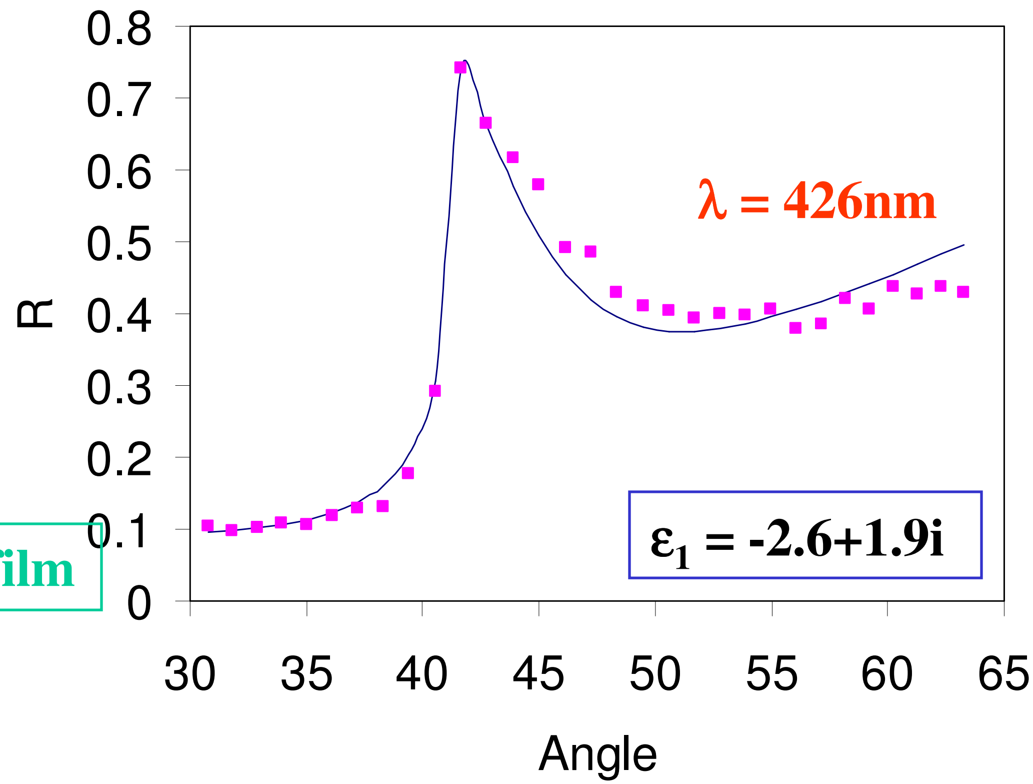
SPP excited in ZnTPP





Squares: Experiment result

Solid line : Fitting

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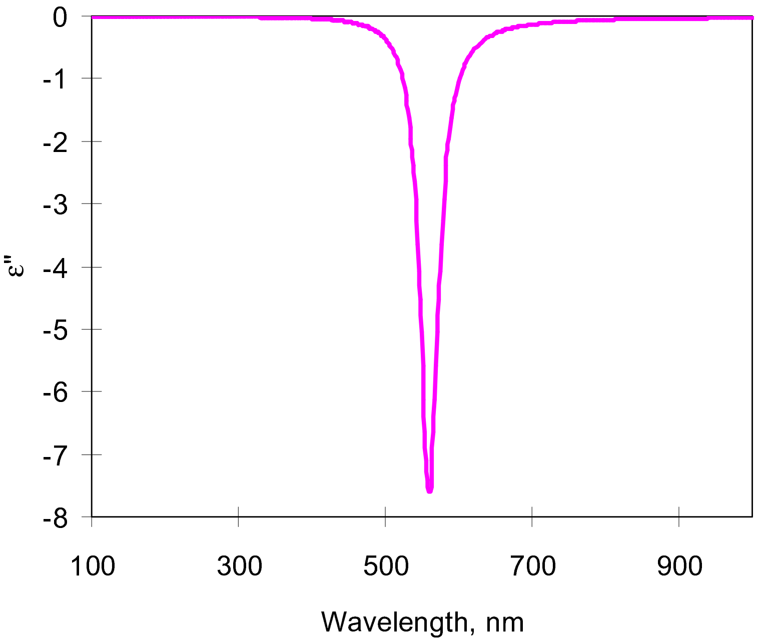
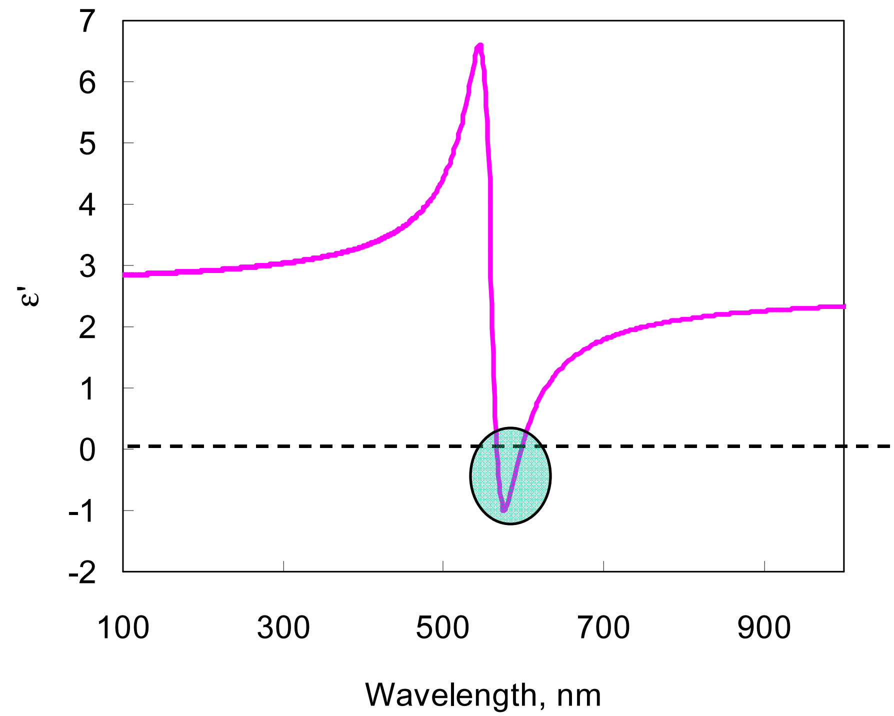
Dye film with gain ----- Predictions

In the presence of pumping, the dye film shows emission rather than absorption.





"Metal" with gain ⇒ Unique properties
Fantastic applications

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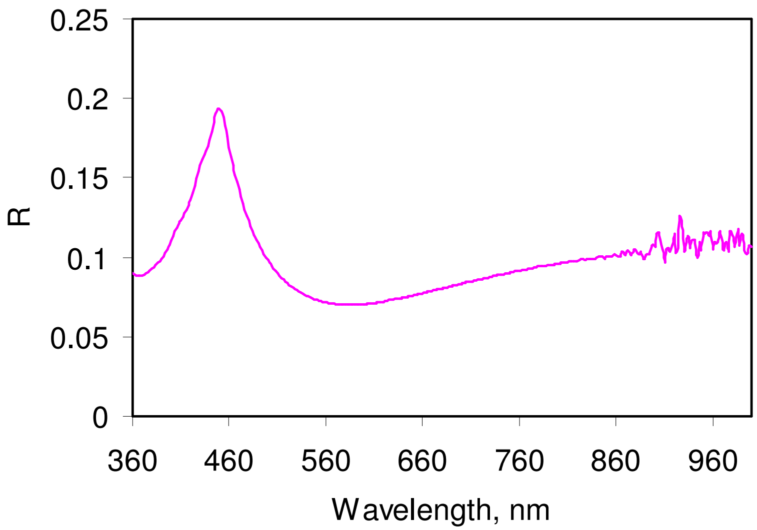
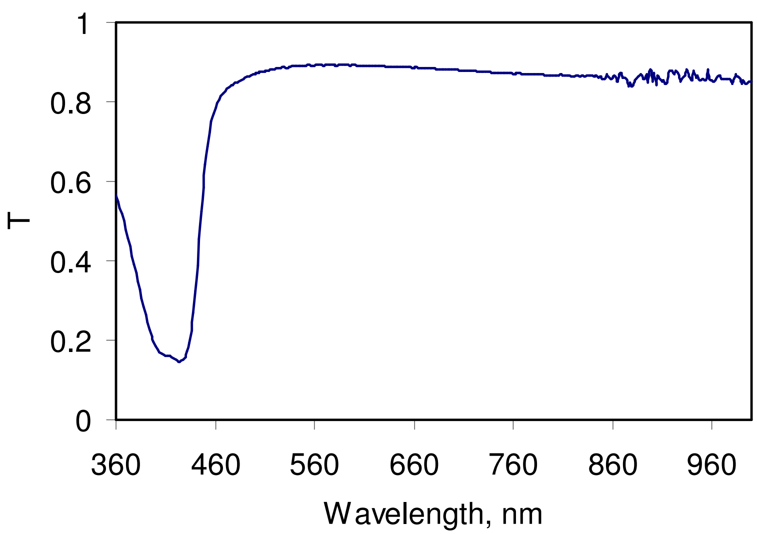
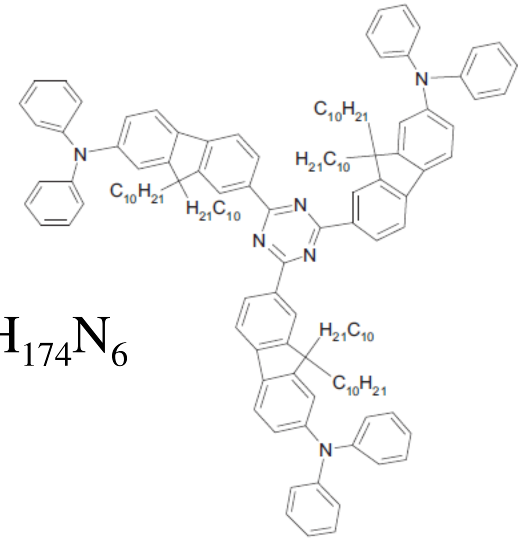
AF455

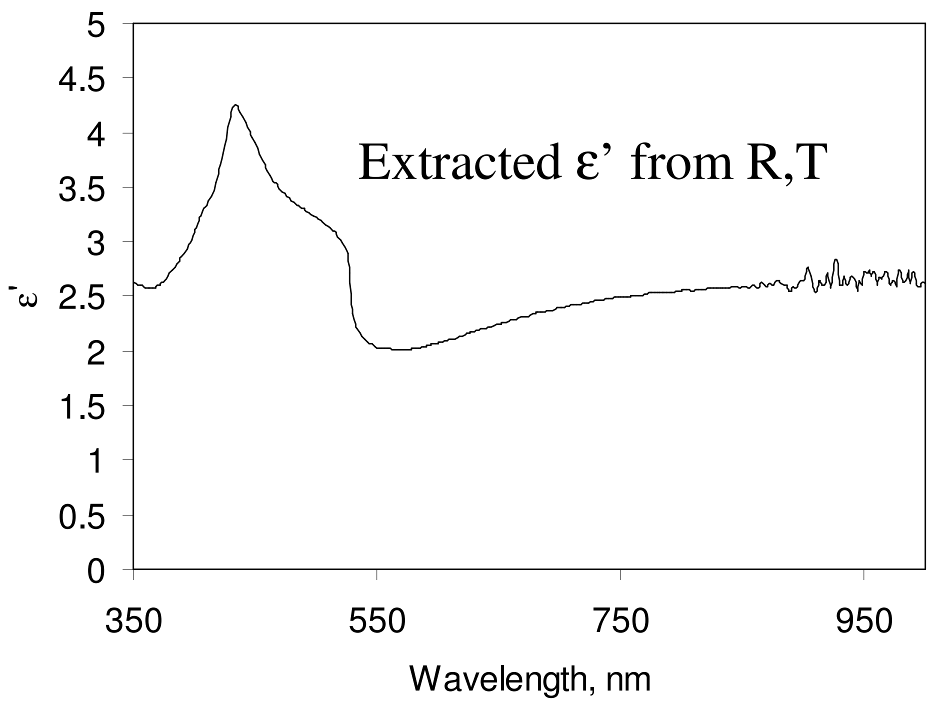
Dye molecules separated by alkyl side chains







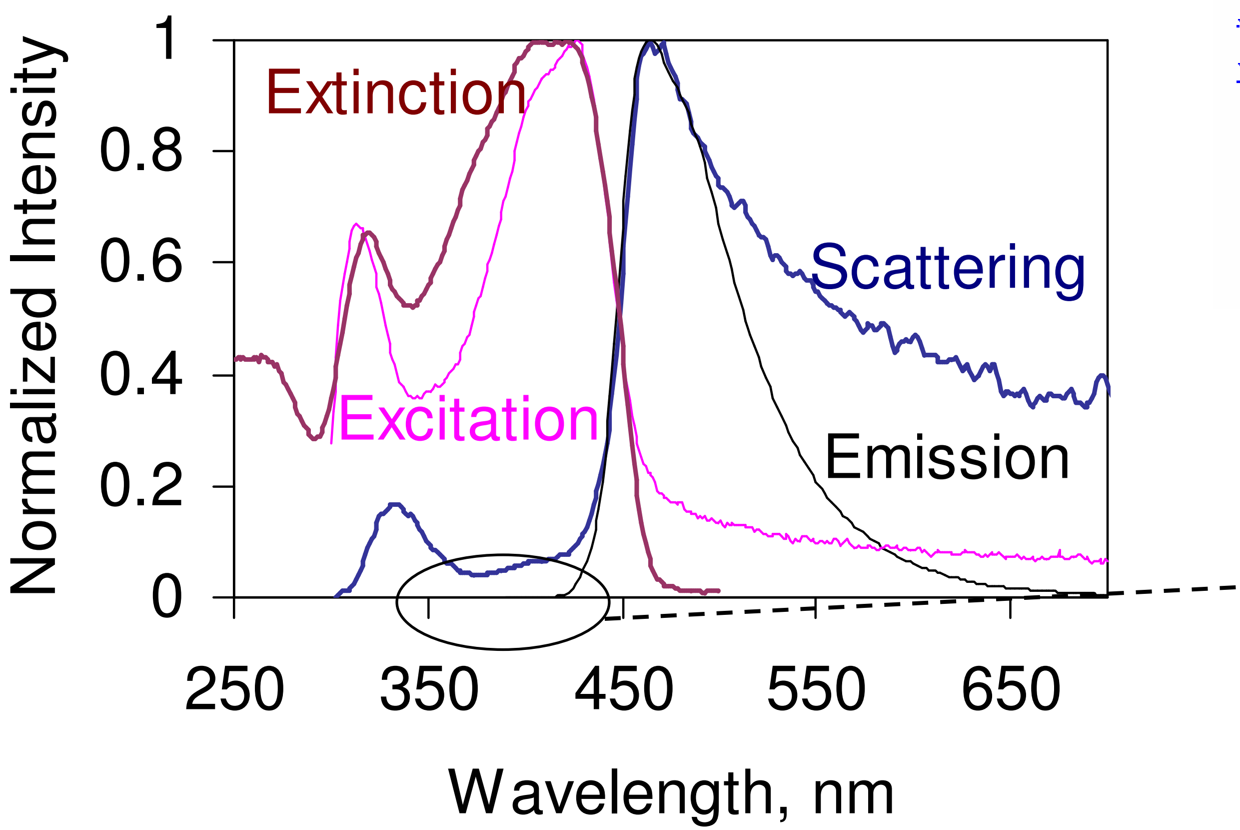
$C_{138}H_{174}N_6$

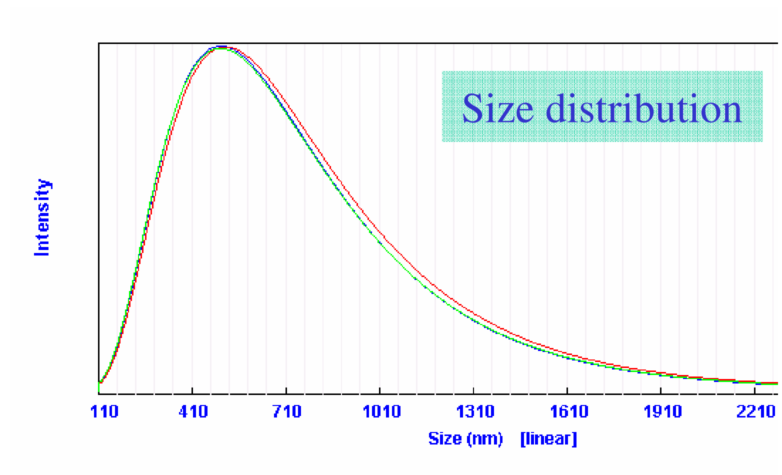


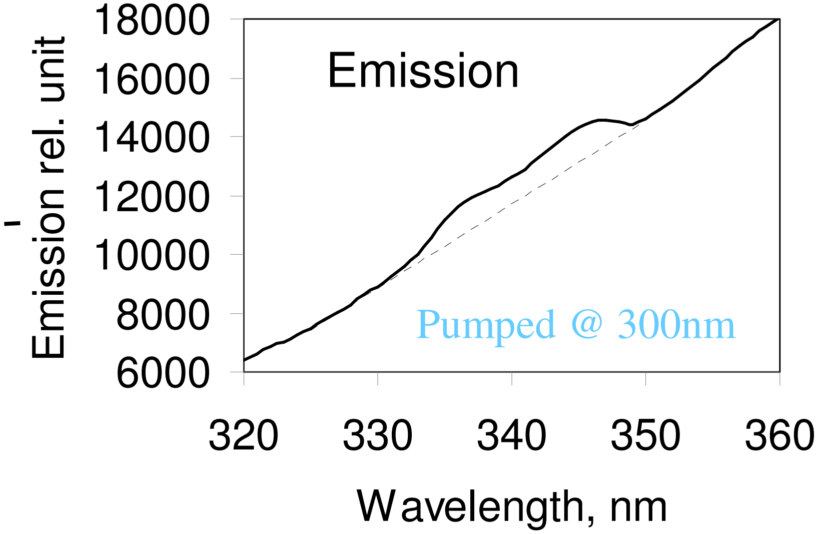
G.S. He, et al., Chem. Mater. 16, pp.185-194 (2004).

H. Kasai, et al.,." Jpn. J. Appl. Phys., Part 2 31, L1132 (1992).

Spectroscopy study of AF455 solution







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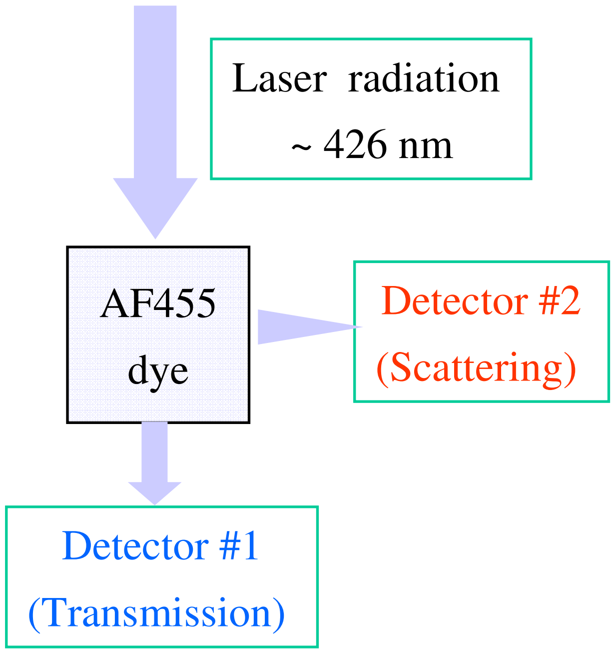
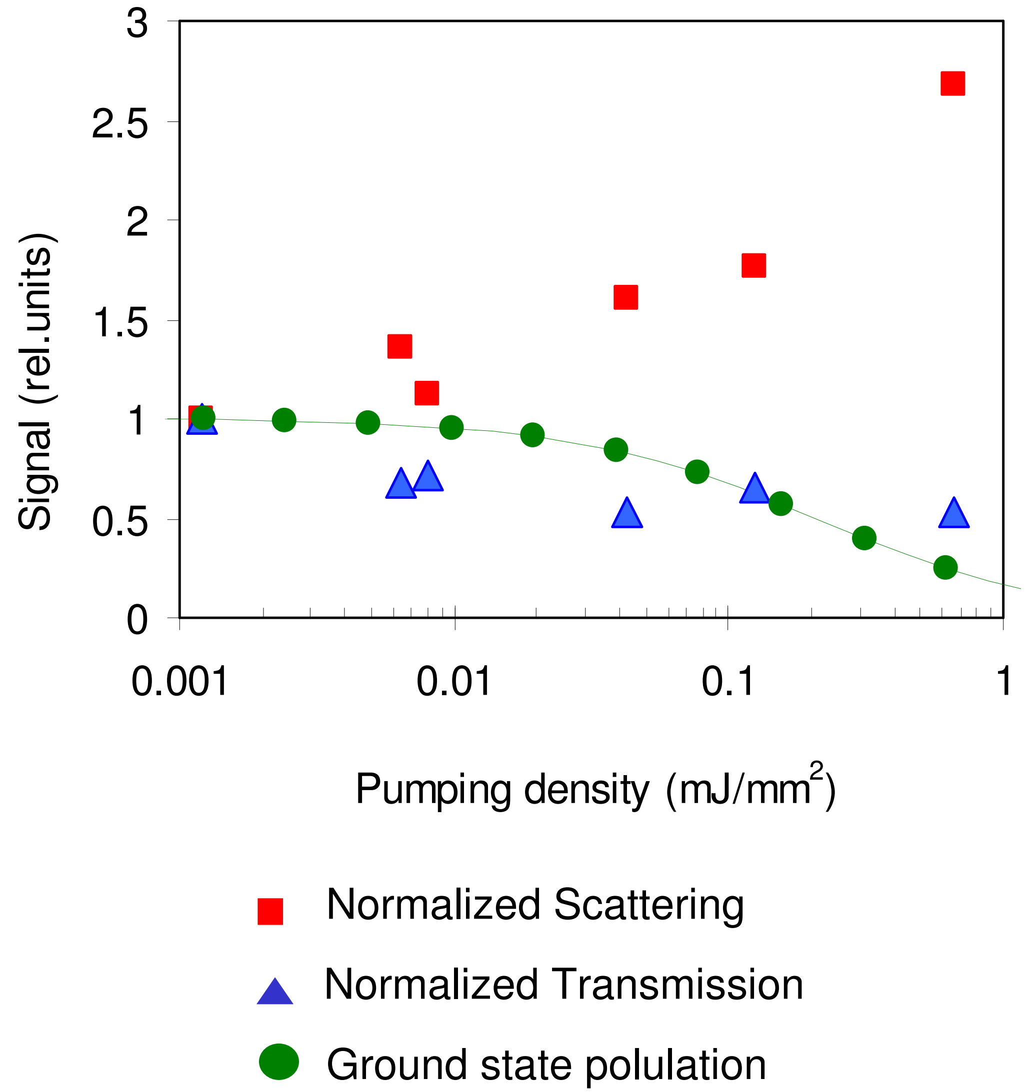
Transmission/Scattering with optical pumping



$$\frac{n^*}{N}(P) = \frac{\dfrac{P}{h\omega \cdot s}\sigma_{abs}}{\dfrac{P}{h\omega \cdot s}\sigma_{abs} + \dfrac{1}{\tau}}$$



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Summary

(1) Complete compensation of the SPP loss by gain

(2) Stimulated emission of SPPs and Spaser nanolaser

(3) Enhancement of SPPs without gain

(4) Metal-free plamonics

active plasmonics matematerials

The results pave the road to many practical applications of nanoplasmonics and metamaterials

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