

# Optical Properties of Hybrid Nanomaterials

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**K. George Thomas**

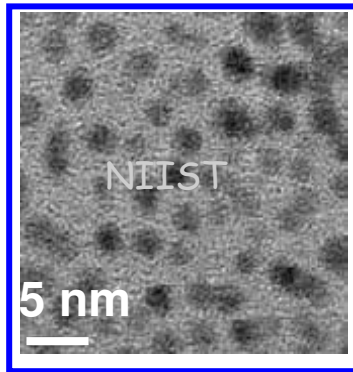
*Photosciences & Photonics Group  
National Institute for Interdisciplinary  
Science and Technology (NIIST), CSIR,  
Trivandrum- 695 019, INDIA  
([kgt@vsnl.com](mailto:kgt@vsnl.com))*

## Research Activities

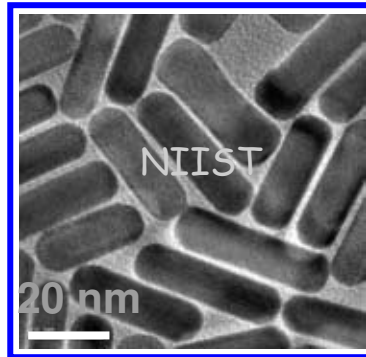
1. Hybrid nanomaterials for optoelectronic applications
2. Design and study of organic nanostructured materials
3. Light induced processes in functional molecular systems
4. Functional control of molecules on surfaces

## *Size and shape does matter....*

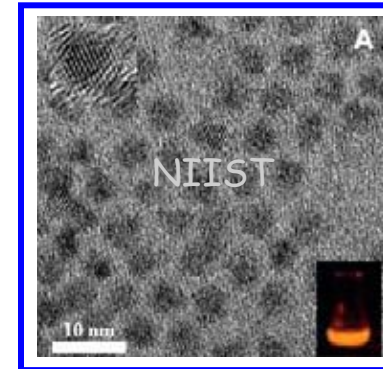
**Au nanoparticles**



**Au nanorods**

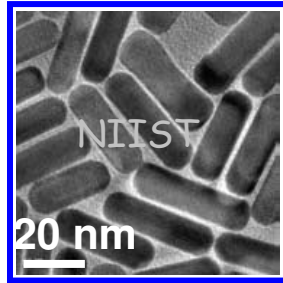
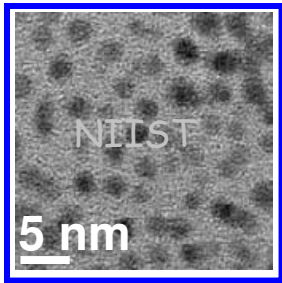


**Quantum dots**



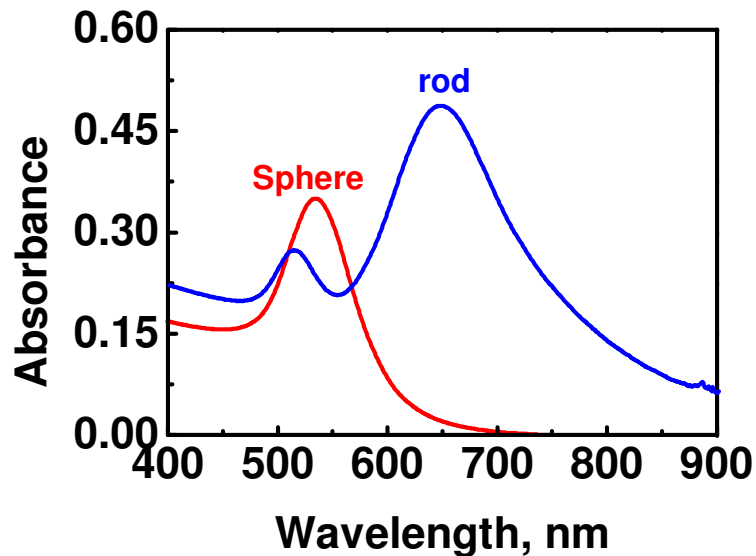
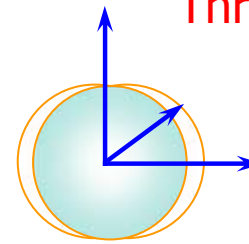
**Physical and chemical properties of matter in the nanometer scale are distinctly different than in the macroscopic scale**

# Gold nanoparticles and nanorods



Surface Plasmon (SP) is the collective oscillation of free electrons under the influence of electromagnetic radiation

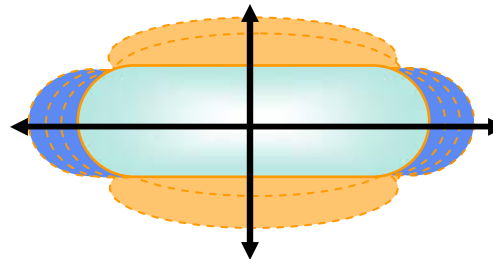
Three identical SP modes



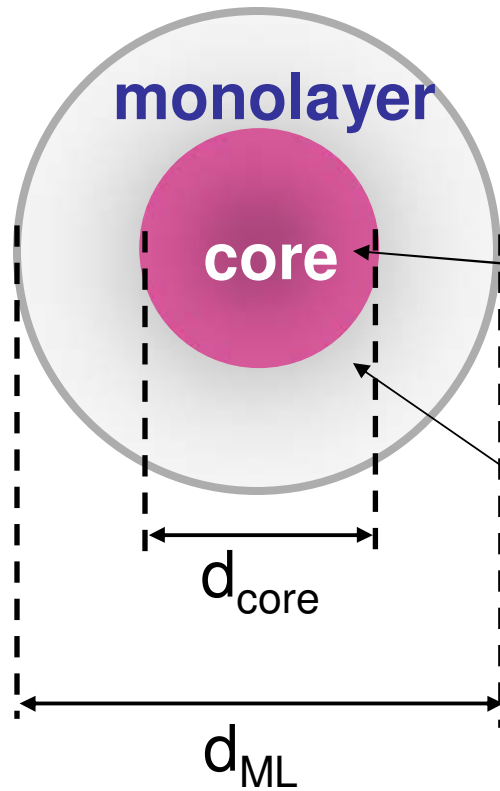
Shape anisotropy leads to the splitting of surface plasmon bands

Transverse absorption

Longitudinal absorption



Extinction Coefficient ( $\lambda_{\max}$  - 700 nm)  
 $0.53 \times 10^{10} \text{ M}^{-1}\text{cm}^{-1}$



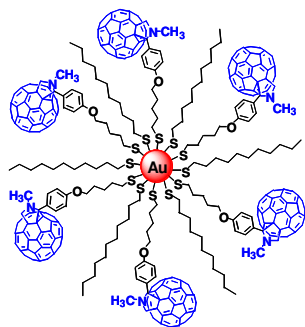
### Coupling of

the size and shape dependent optoelectronic properties of nanomaterials

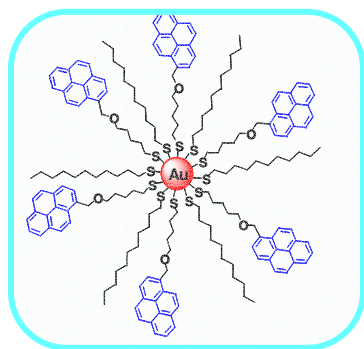
+

the intrinsic functionalities of molecular systems (binding, self-assembly, switching etc.)

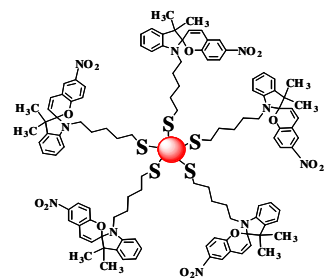
# Organic-inorganic hybrid nanomaterials



Nano Lett. 2002, 2, 29-35

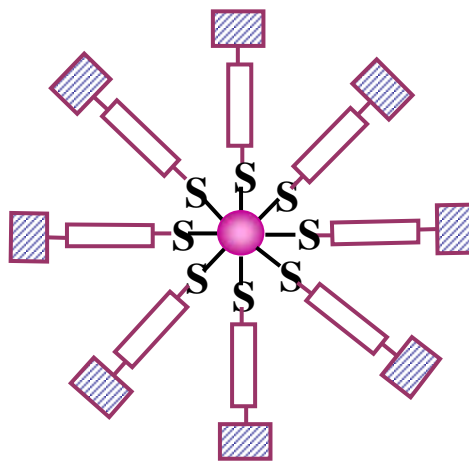


J. Phys. Chem. B 2002, 106, 18-21



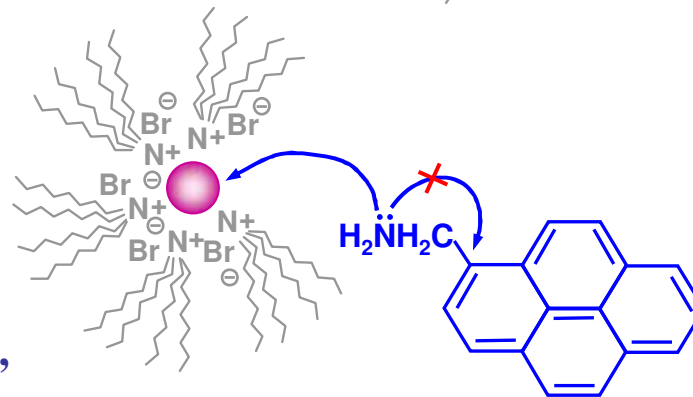
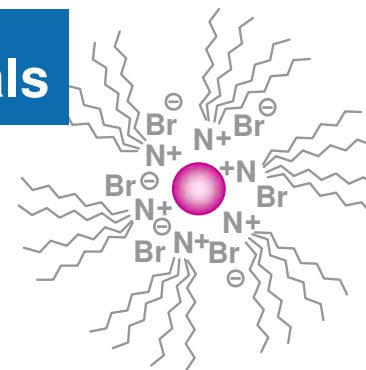
Au-SP

J. Am. Chem. Soc. 2003, 125, 7174-7175

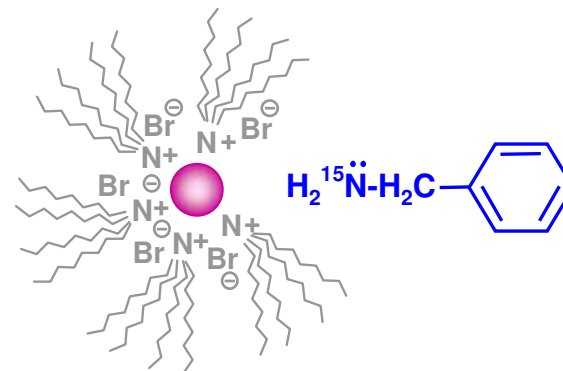
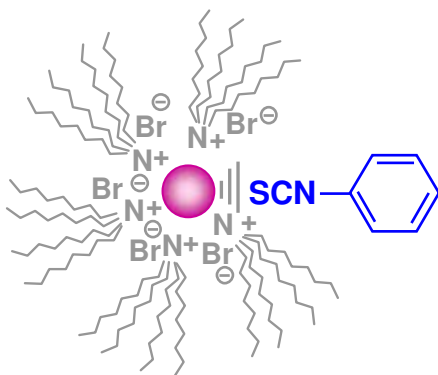


George Thomas and P. V. Kamat, *Acc. Chem. Res.* 2003, 888

George Thomas, Binil and Sudeep, *Pure & Appl Chem.* 2002, 74, 1731

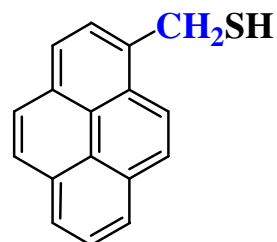
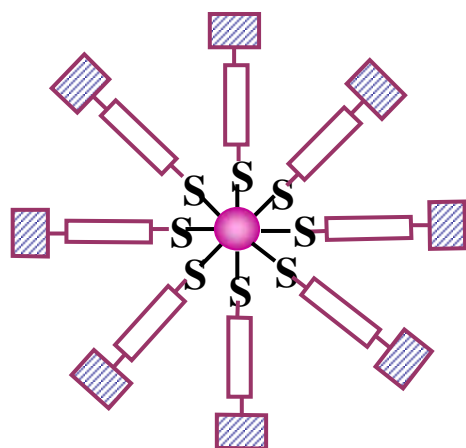


J. Am. Chem. Soc. 2000, 122, 2655-2656

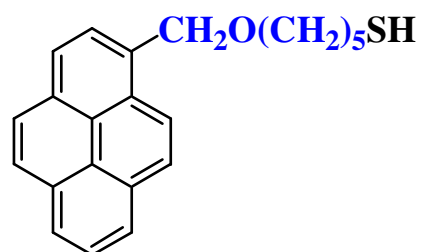


Langmuir 2002, 18, 3722-3727.

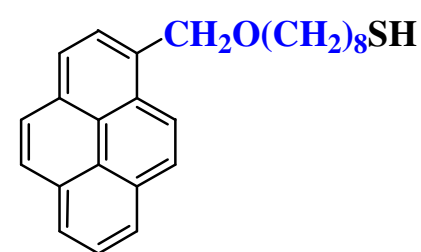
# How polar is Au nanoparticle surface ?



III/I peak = 0.89



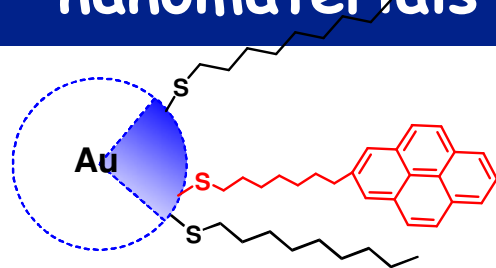
III/I peak = 0.98



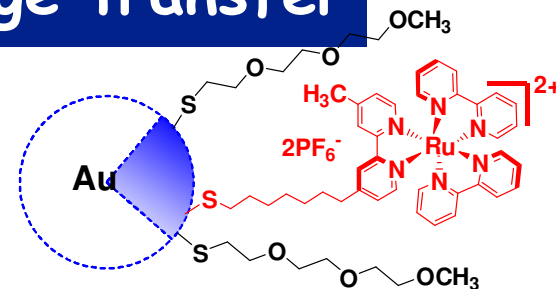
III/I peak = 1.18

Binil and K. George Thomas *J. Phys. Chem. B*, 108, 13265 (2004)

# Hybrid nanomaterials for charge transfer



*J. Phys. Chem. B.*, 106, 18 (2002)



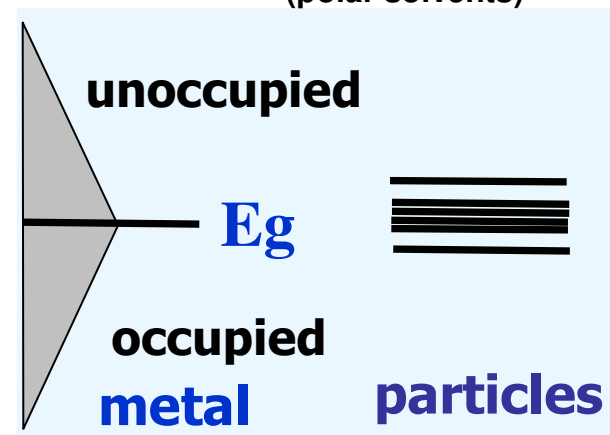
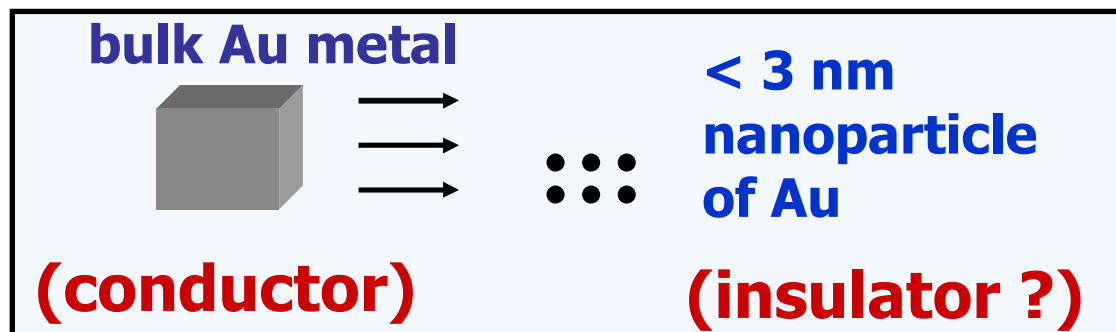
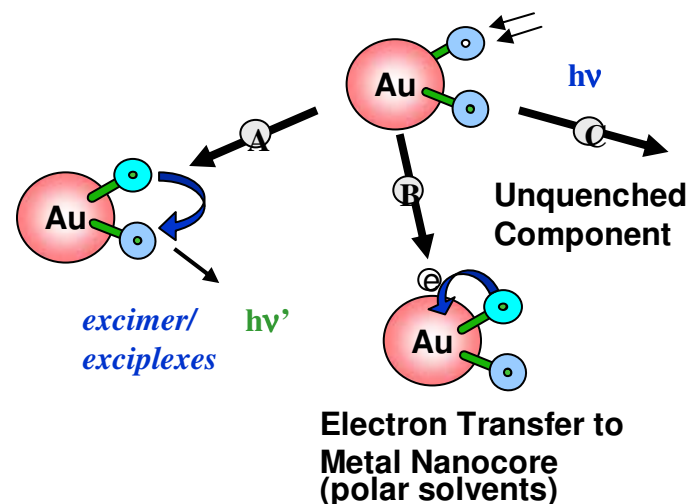
**Au-Ru<sup>2+</sup>**

*J. Phys. Chem. B.*, 110, 20737 (2006)  
*J. Phys. Chem. B.* 111, 6839-6844 (2007)

# What are the main deactivation pathways of the photoexcited fluorophore bound to a metal nanoparticle/QD's ?

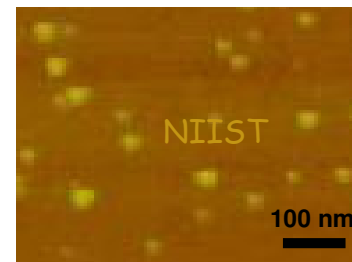
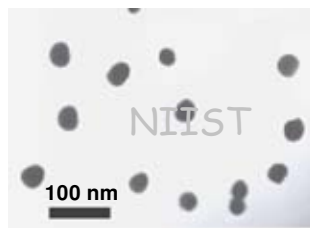
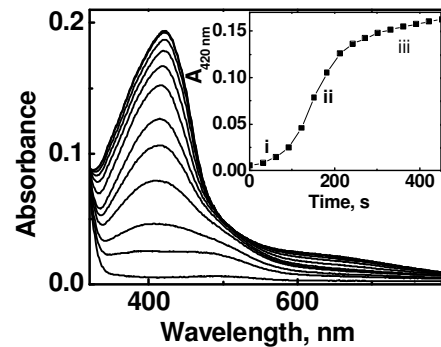
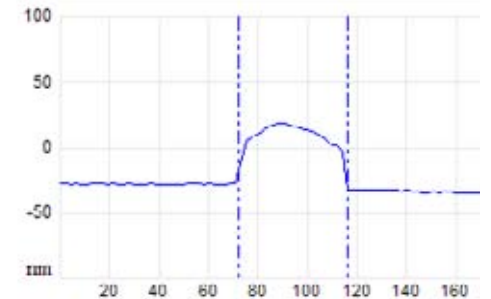
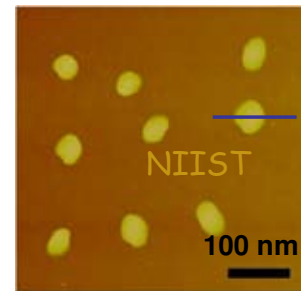
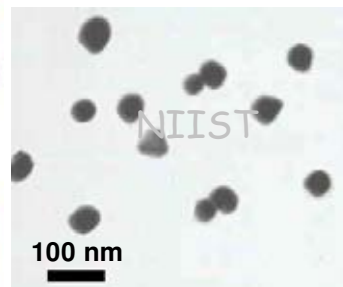
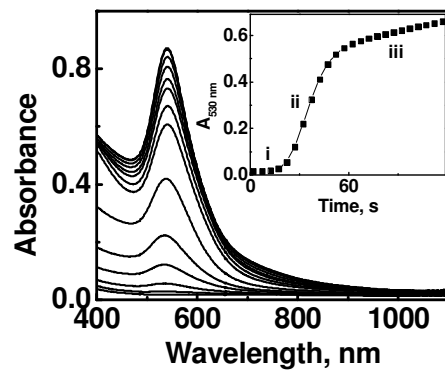
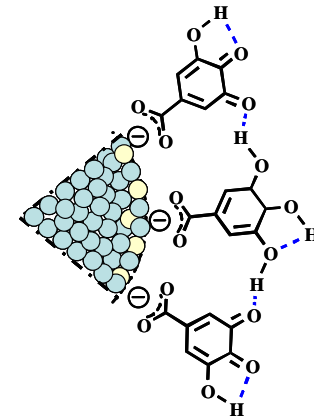
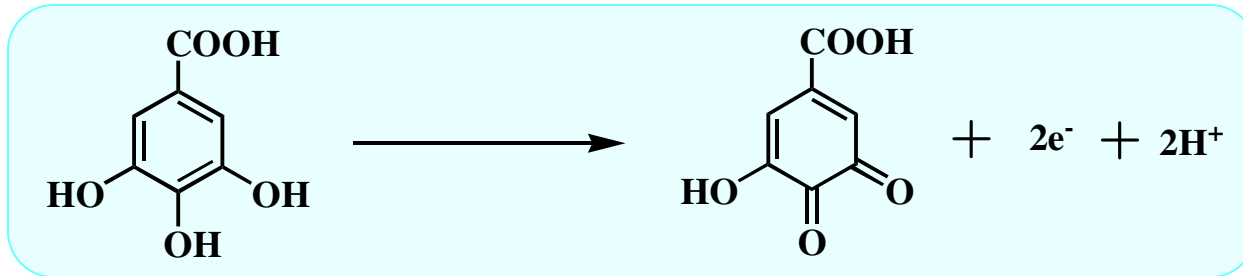
## Chromophore Functionalized Metal/QD's

- (i) Effect of spacer
- (ii) Core size
- (iii) Redox properties

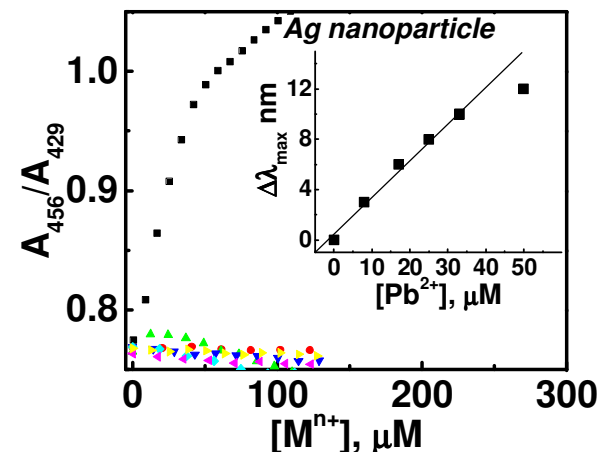
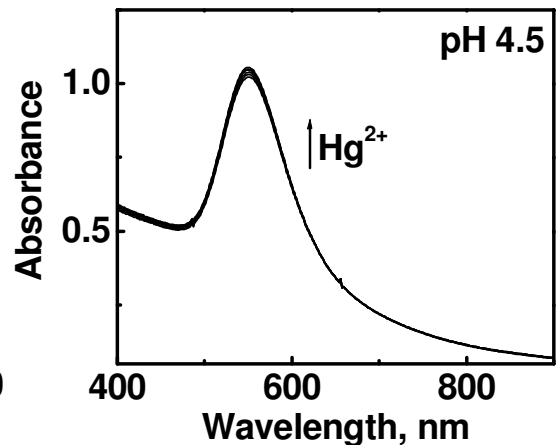
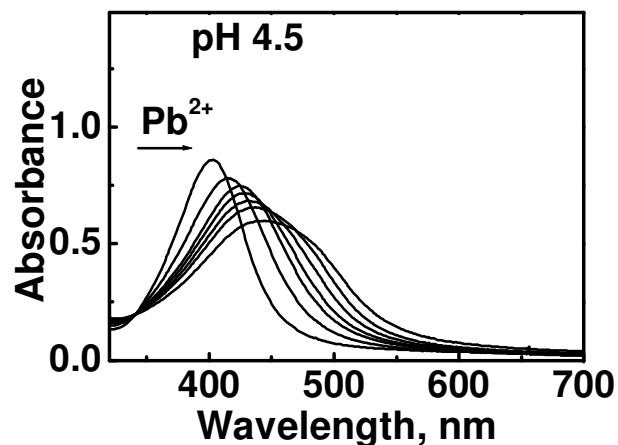


# Hybrid nanomaterials as biosensors

## In Situ Synthesis of Metal Nanoparticles



# Selective 'Naked-Eye' Detection of Lead Ions from Aqueous Media



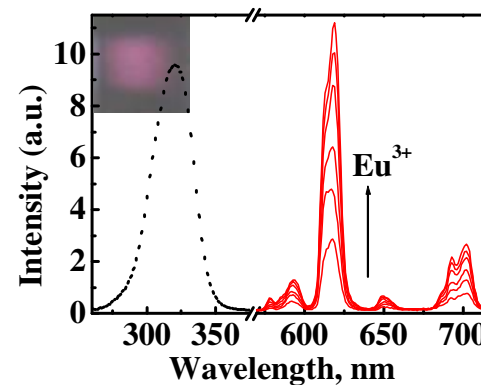
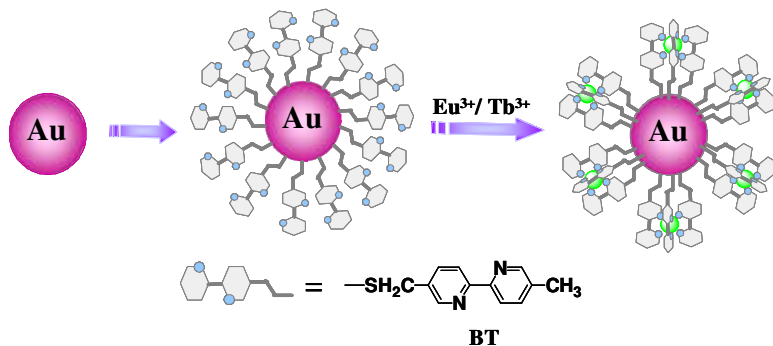
**Fe<sup>3+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup> & Ca<sup>2+</sup>.**



Pb<sup>2+</sup> ions (i) variable co-ordination number up to 12  
(ii) flexible bond length (up to 3 Å) and co-ordination geometry.

**Yoosaf, Binil, Suresh and George Thomas,  
*J. Phys. Chem. C* 111, 12839 (2007)**

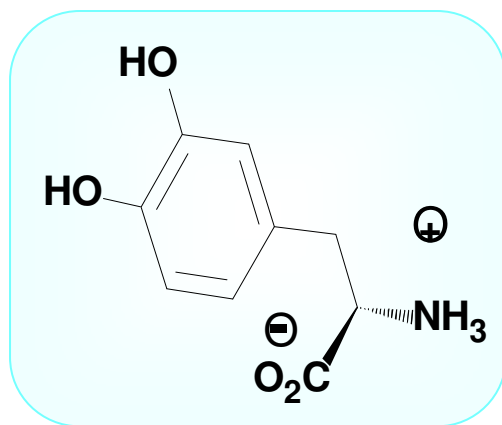
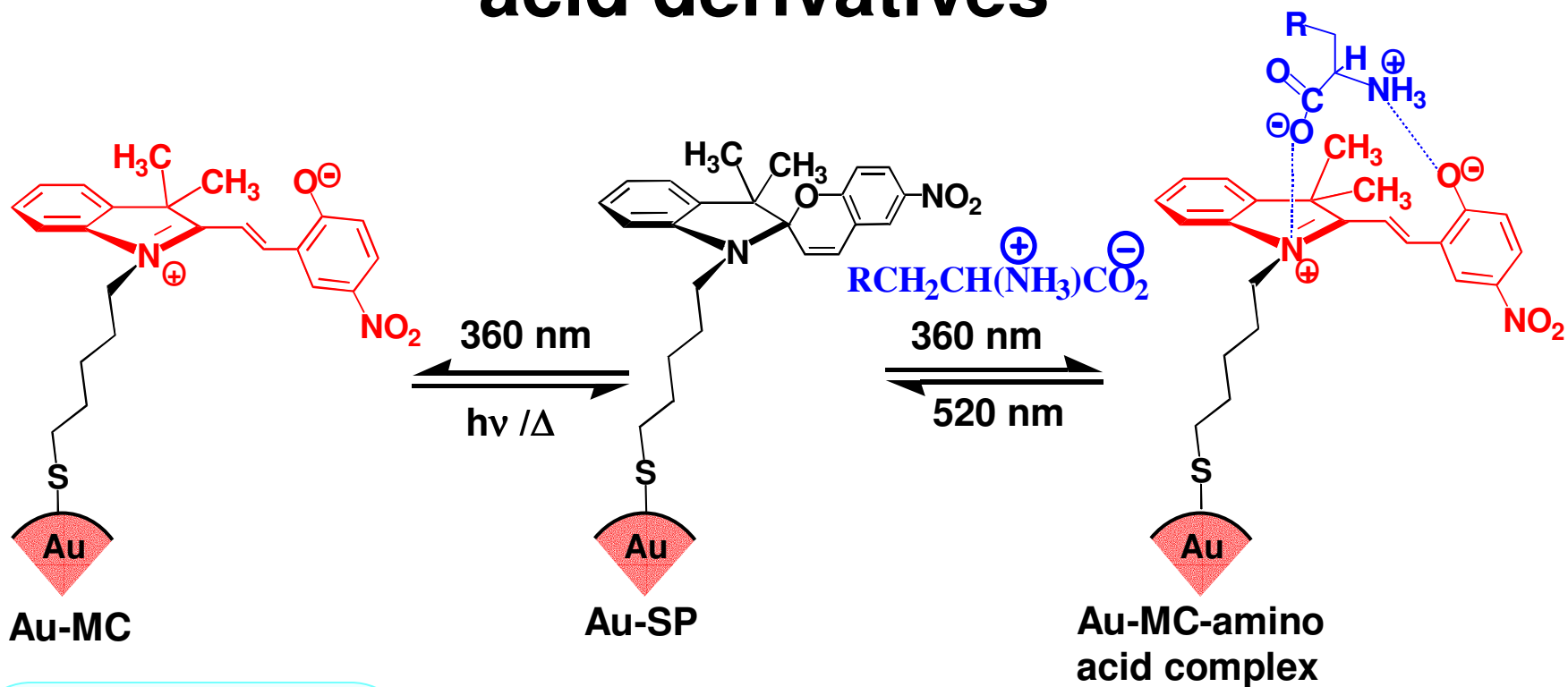
# Phosphorescent nanomaterials as biosensors



**B. I. Ipe, K. Yoosaf, George Thomas**  
*J. Am. Chem. Soc.* 128, 150 (2006)

Complex	$\Phi$	$\tau$ , ms
Eu-AuBT	0.009	0.4
Tb-AuBT	0.038	0.56

# Light-mediated binding and release of amino acid derivatives



DOPA

Binil, Mahima and George Thomas  
*J. Am. Chem. Soc.* 125, 7174 (2003)

## Miniaturizing of devices-propagation of light at nanoscale

Surface plasmons are not diffraction limited



Nanostructures of noble metals can convert photons into surface plasmon and within the propagation length, the surface plasmon modes can be decoupled back to light.

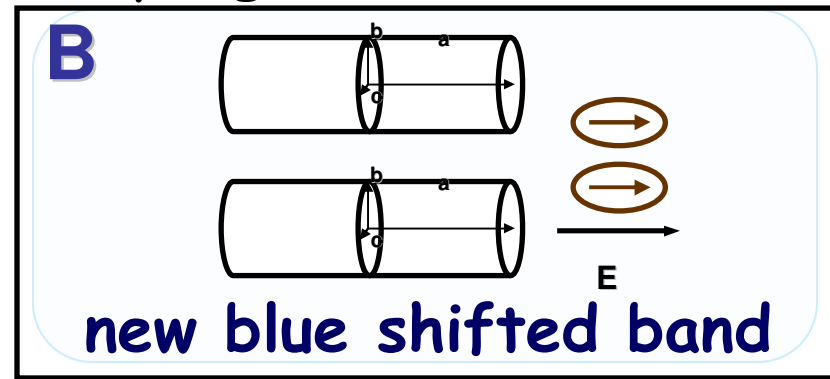
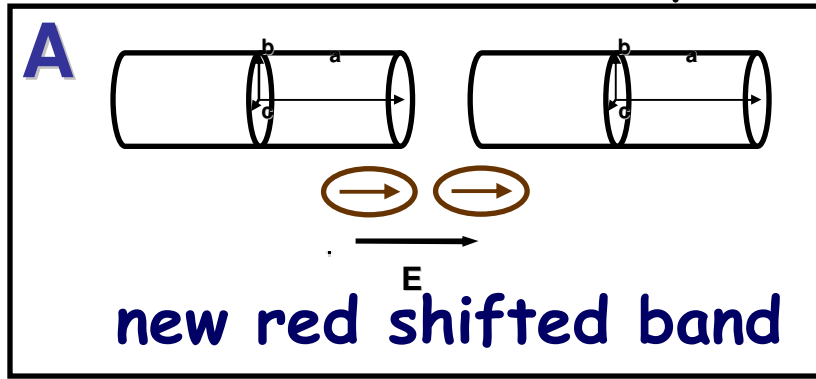
**Design of nanoscale optoelectronic and photonic devices**

Atwater and coworkers *Nature materials*, 2003, 2, 229

# Can we integrate nanorods into higher order assemblies and tune their optical responses ?



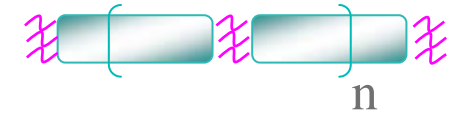
## Theoretical studies on plasmon coupling



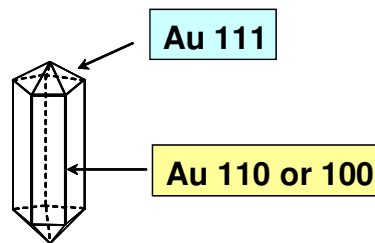
Gludenis and Foss, *J. Phys. Chem. B* 106, 9484 (2002).

- Also refer –
- Schatz and coworkers
  - El-Sayed and coworkers
  - Liz-Marzán and coworkers
  - Mulvaney and coworkers
  - Cortie and coworkers
  - Murphy and coworkers

# Hierarchical integration of nanomaterials



## Crystallographic facets of Au nanorods



- The end faces of Au nanorods are dominated by {111} planes and the side facets by {100} and {110} plane

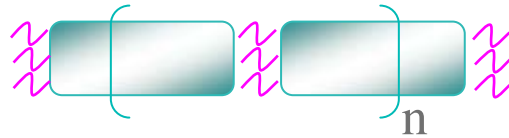
*(El-Sayed and coworkers  
Murphy and coworkers)*

- Thiols preferentially bind to the {111} planes of the Au rods

Murphy and coworkers; *J. Am. Chem. Soc.*, 125, 13914 (2003)

- supramolecular approach
- covalent linking

# Hierarchical integration of nanomaterials and plasmon coupling



## George Thomas and coworkers

J. Phys. Chem. B, 108, 13066-13068 (2004).

J. Am. Chem. Soc., 127, 6516-6517 (2005).

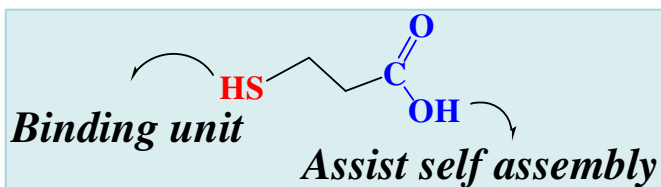
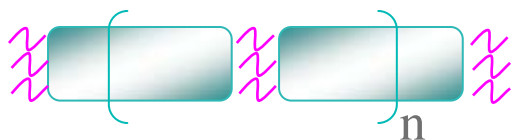
J. Phys. Chem. B, 110, 150-157 (2006).

J. Am. Chem. Soc. 129, 6712-6713 (2007).

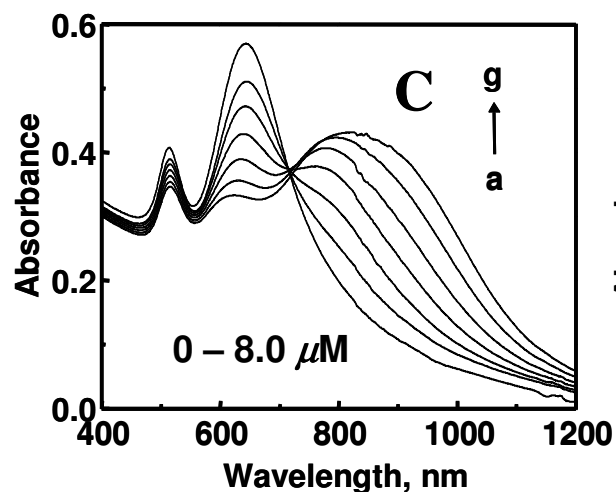
Adv. Mater. (2008) (DOI: 10.1002/adma.200703057)

Thomas, K. G., chapter entitled "Surface plasmon resonances in nanostructured materials," in Nanomaterials chemistry: Novel aspects and new directions, Rao, C.N.R.; Mueller. A.; Cheetham A. K. (Eds.) Wiley-VCH (2007) pp 185-216.

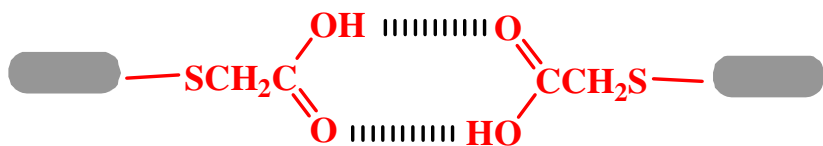
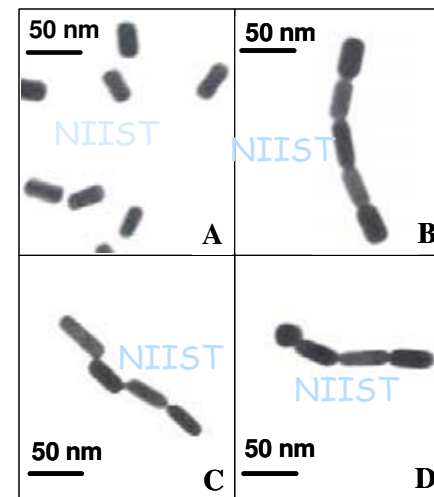
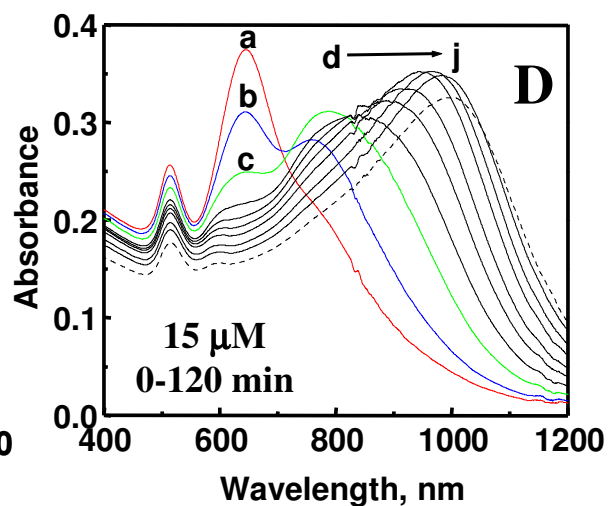
# Connecting nanorods-supramolecular approach



with concentration

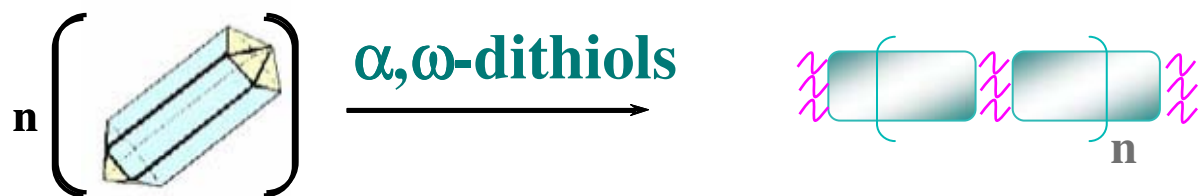


with time



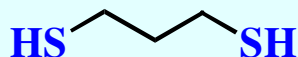
George Thomas et al.,  
*J. Phys. Chem. B* 2004, 108, 13066

# Connecting nanorods-covalent approach

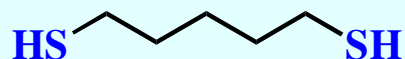


~0.12 nM of Au nanorods

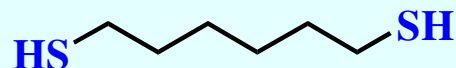
S. T. S. Joseph, B. I. Ipe, P. Pramod and  
K. George Thomas,  
*J. Phys. Chem. B.*, 110, 150 (2006)



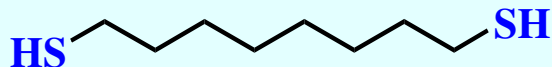
1,3-propanedithiol (C3-DT)



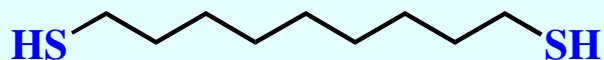
1,5-pentanedithiol (C5-DT)



1,6-hexanedithiol (C6-DT)

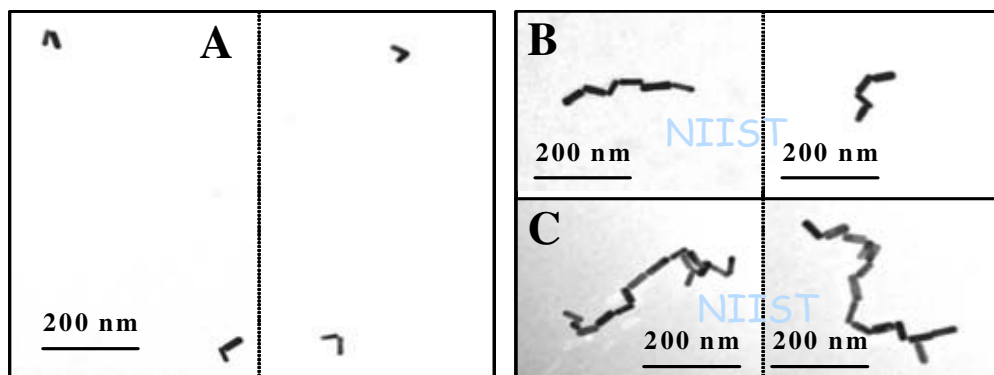
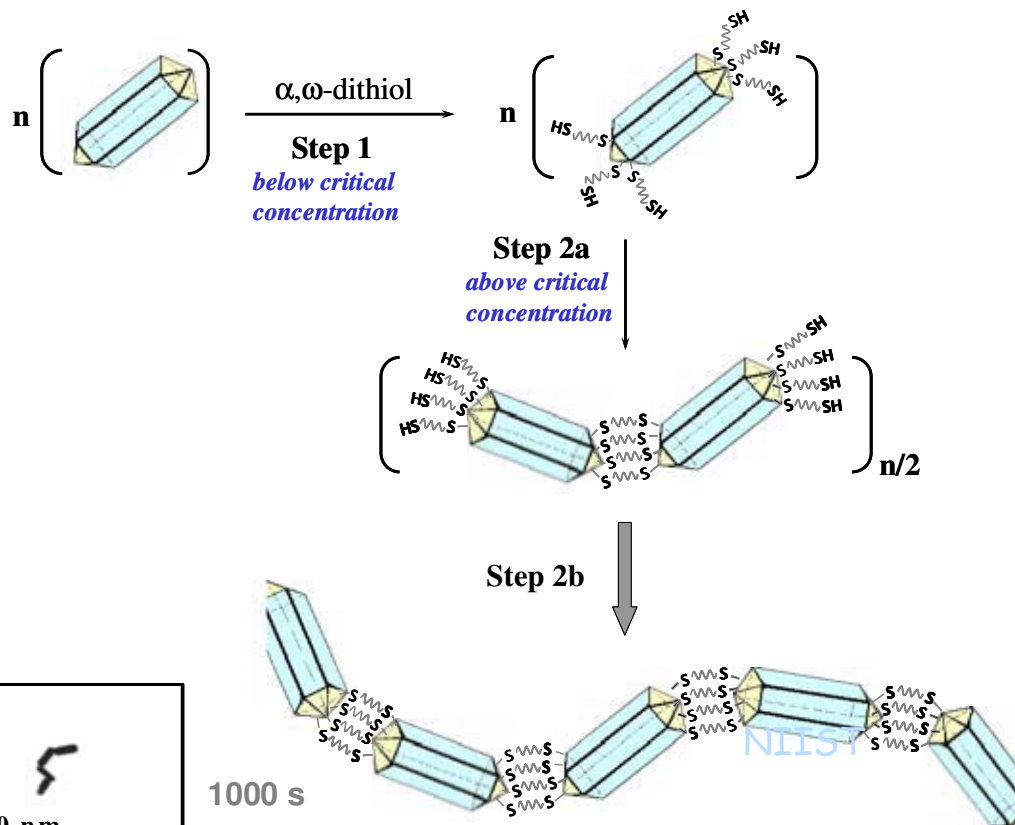
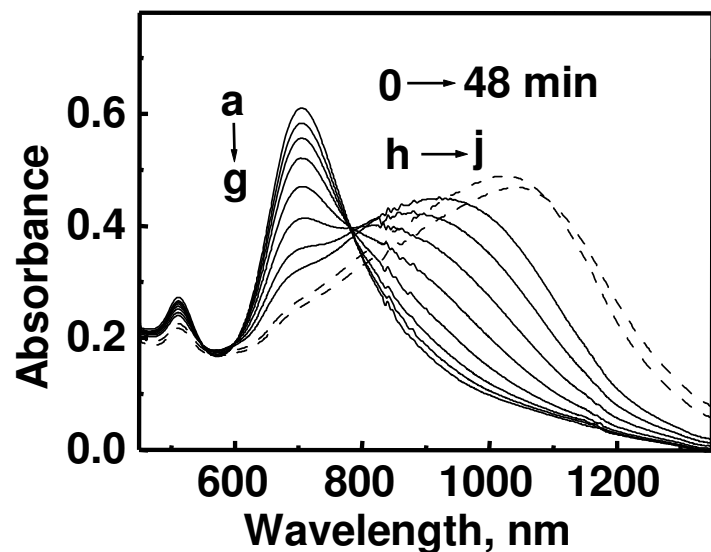


1,8-octanedithiol (C8-DT)



1,9-nonanedithiol (C9-DT)

# Gold nanorods to nanochains



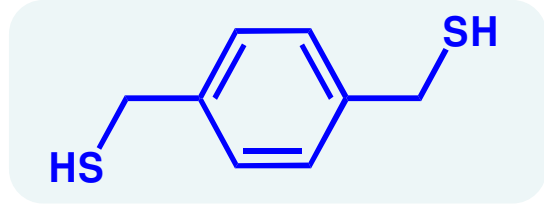
1000 s

1500 s

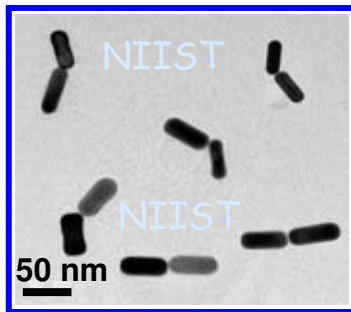
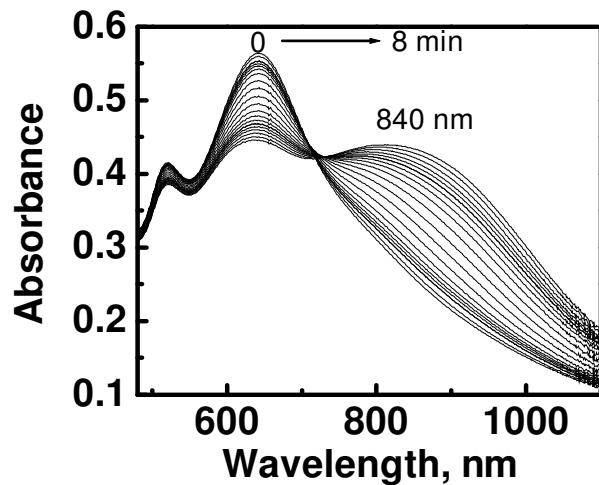
500 s

Shibu, Binil, Pramod, George Thomas, *J. Phys. Chem. B* 2006, 110, 150

# Effect of linker group



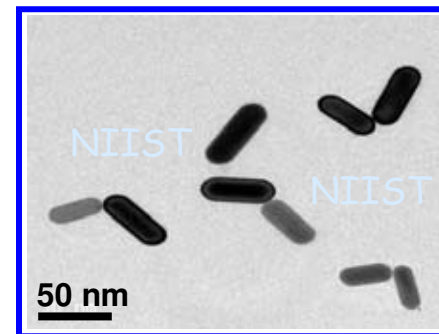
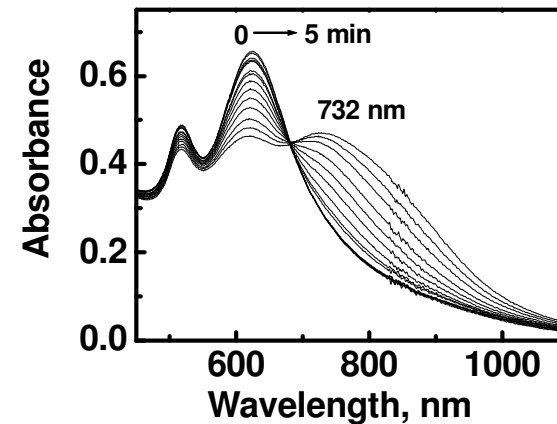
1,4-phenylenedimethanethiol; PDT  
(~0.9 nm)



Av. angle = 146°



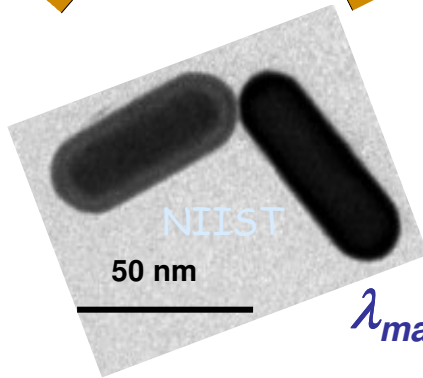
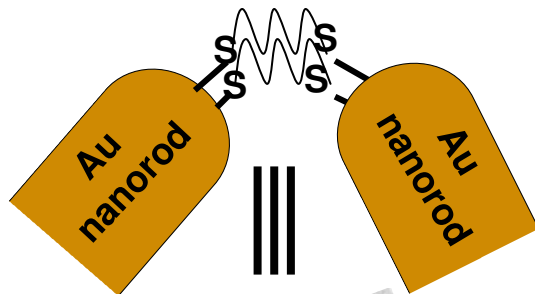
1,6 hexane dithiol; C6DT  
(~0.84 nm)



Av. angle = 96°

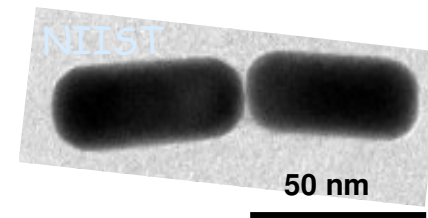
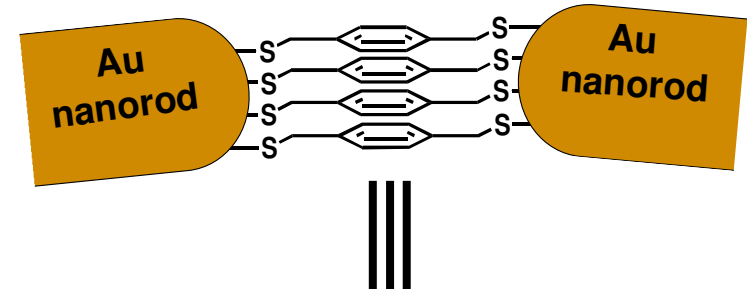
# Probing nanomaterial-molecule junctions

*Flexible linker*



$$\lambda_{\max} = 730 \text{ nm}$$

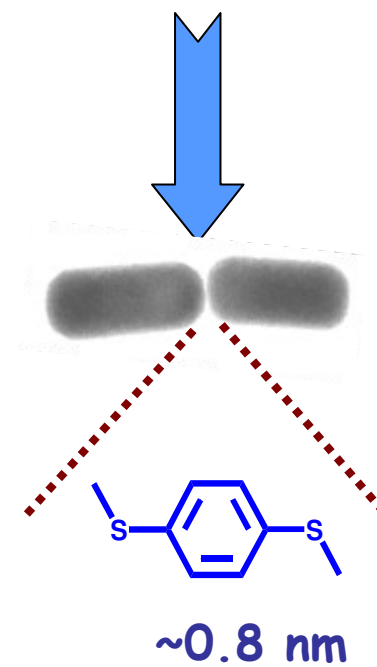
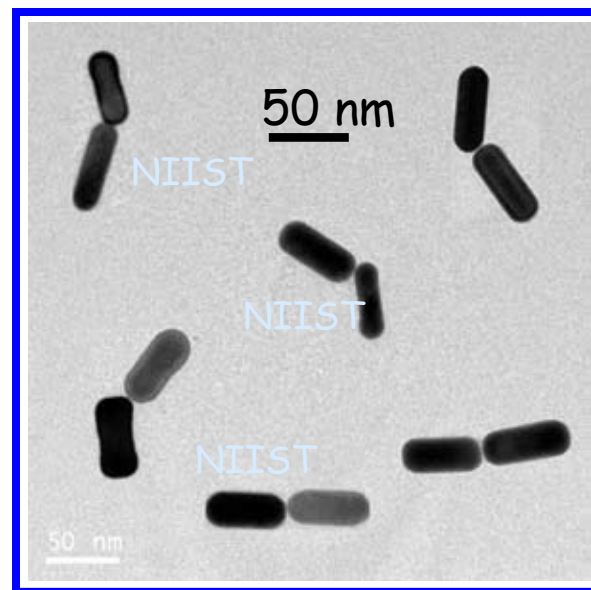
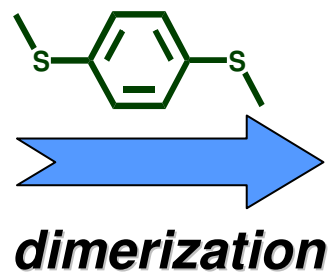
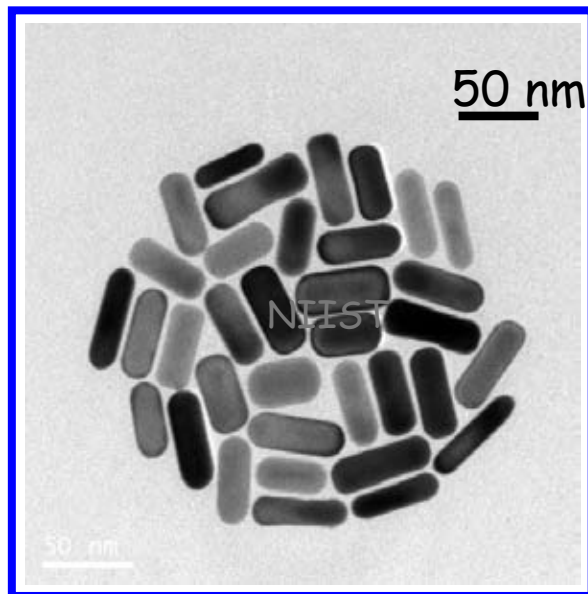
*Rigid linker*



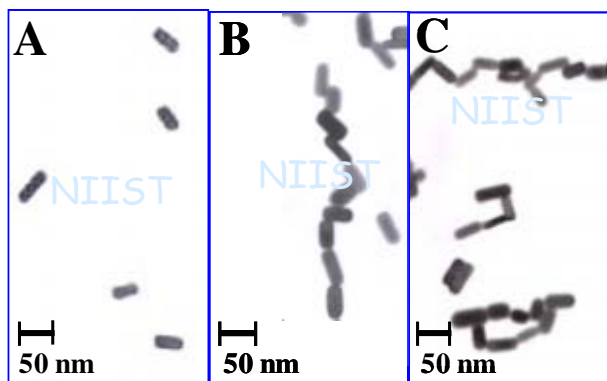
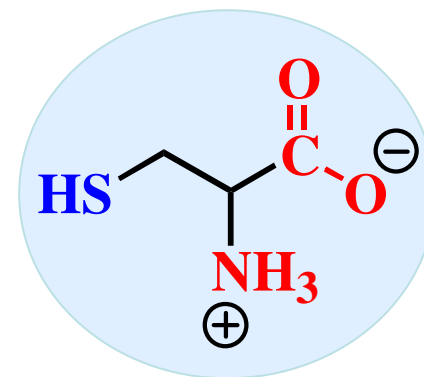
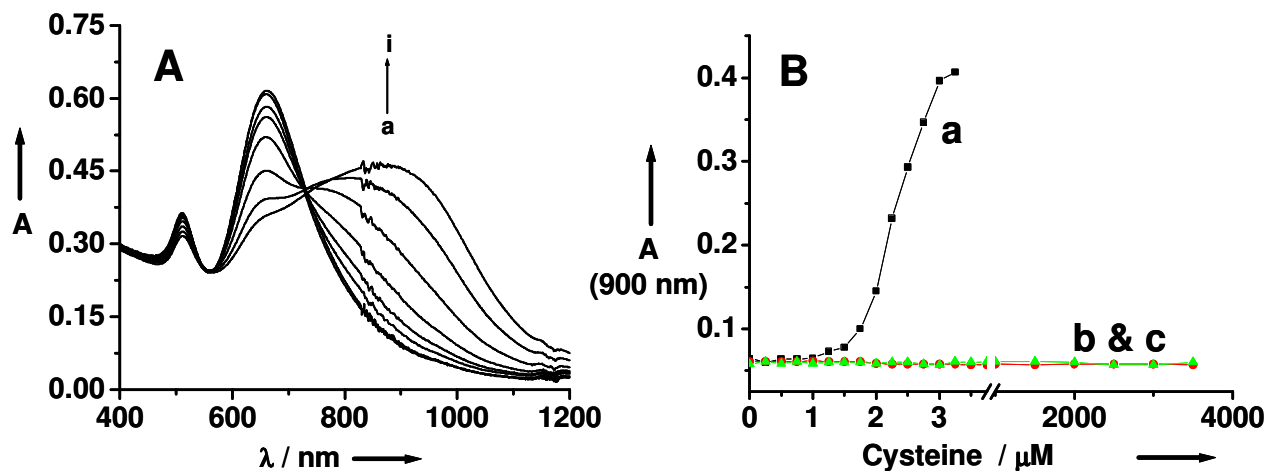
$$\lambda_{\max} = 840 \text{ nm}$$

*Effective dipolar overlap*

*Pramod and George Thomas Adv. Mater. 2008  
(DOI: 10.1002/adma.200703057)*

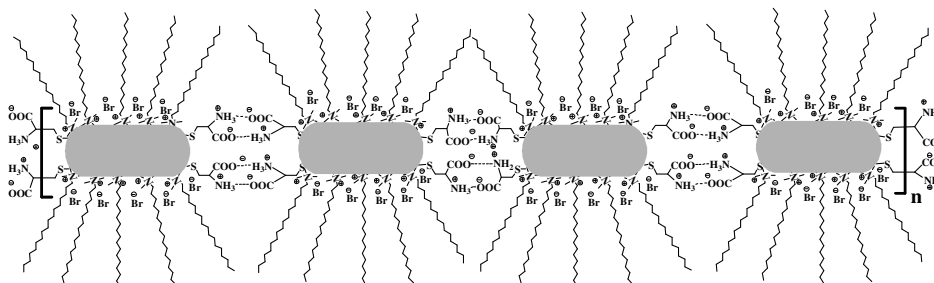


# Selective Detection of Cysteine



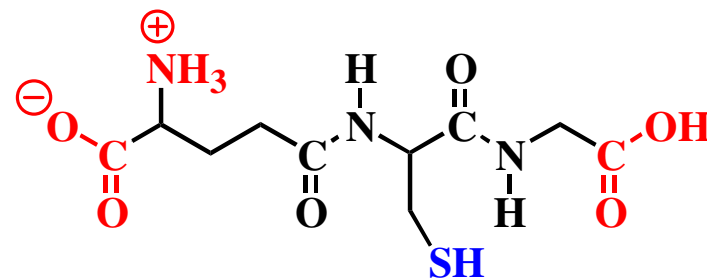
Two point electrostatic interaction

Oligomerization of gold nanorod through end to end self-assembly

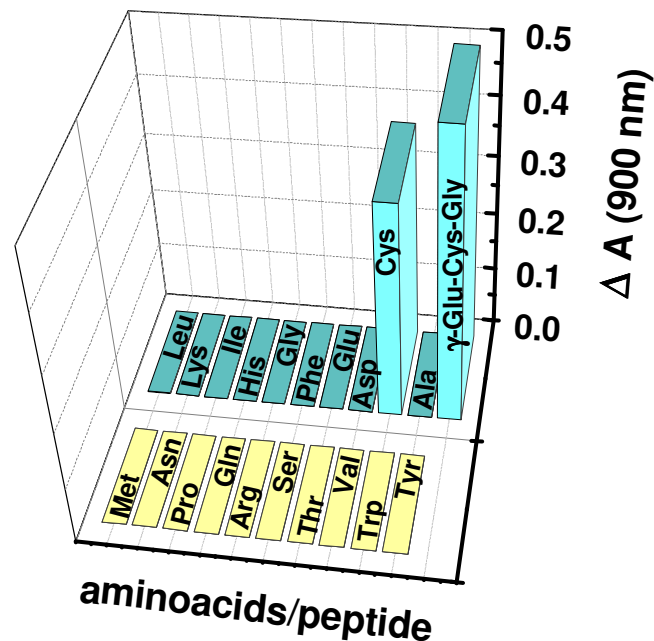
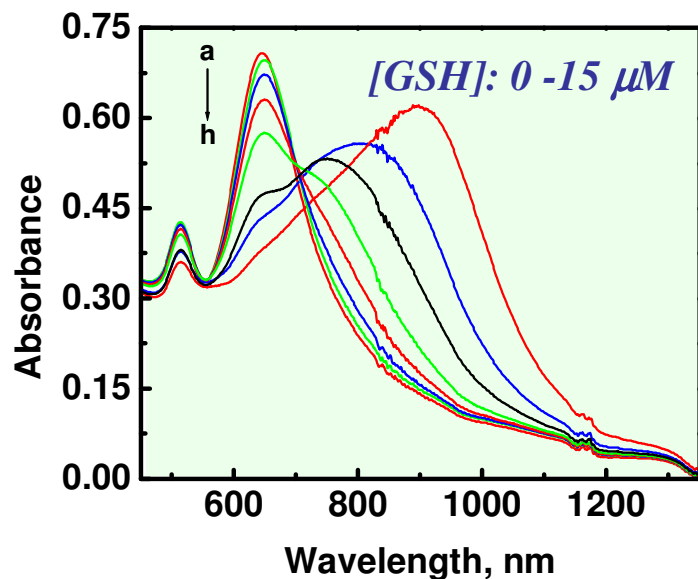


# Detection of Glutathione

i) keeping the cysteine thiol group in proteins in the reduced state and (ii) protecting the cells from oxidative stress by trapping free radicals that damage DNA and RNA.

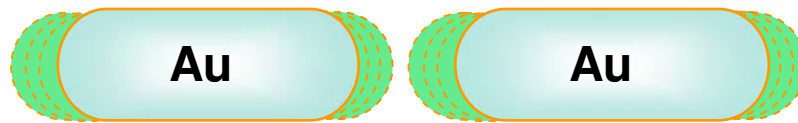
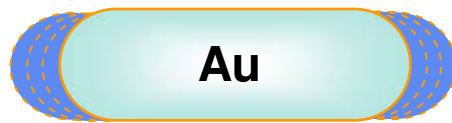
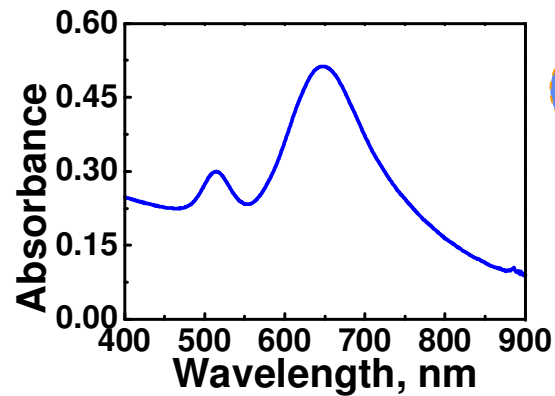


*Protects body from oxidative stress*

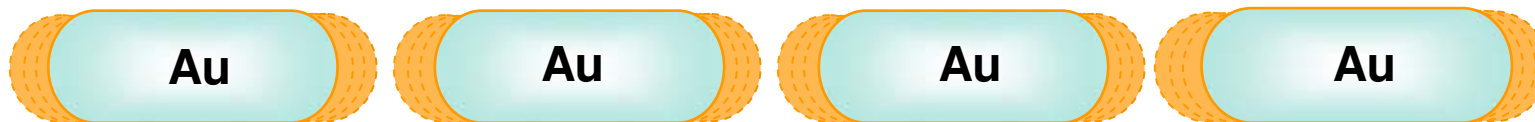
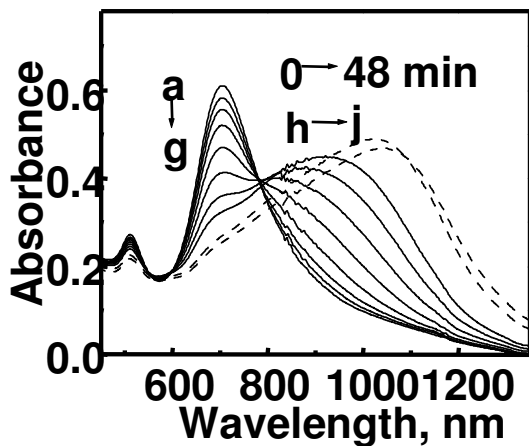
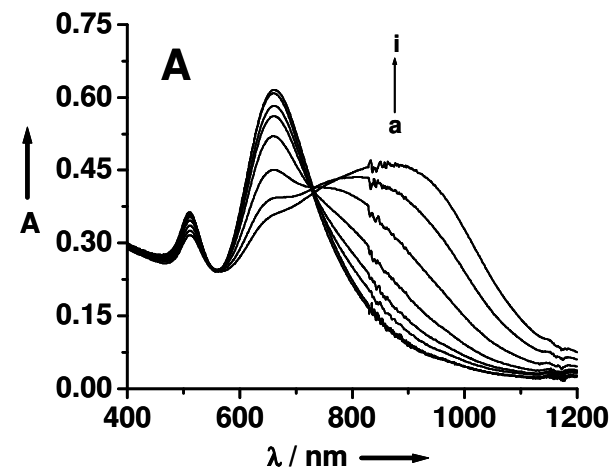


**P. K. Sudeep, S. T. S. Joseph and K. George Thomas,  
*J. Am. Chem. Soc.*, 127, 6517 (2005).**

# Plasmon coupling in Au nanorods



Dimerization



Oligomerization

# Edge effect

## Divergence of electric field and charge accumulation at the edges or corners

### Tasting Edge Effects

Bocquet, *Am. J. Phys.* 2007, 75, 148.

### Electric-field-intensity enhancement in nanoparticles and nanorods- FDTD calculation

Wang and co workers, *small* 2007, 3, 2103

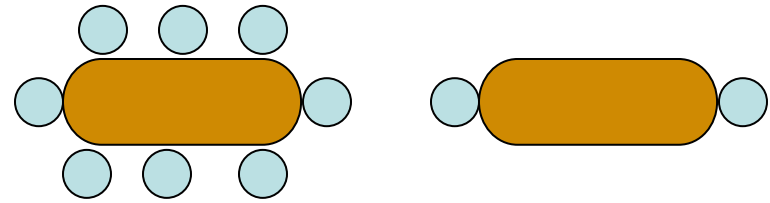
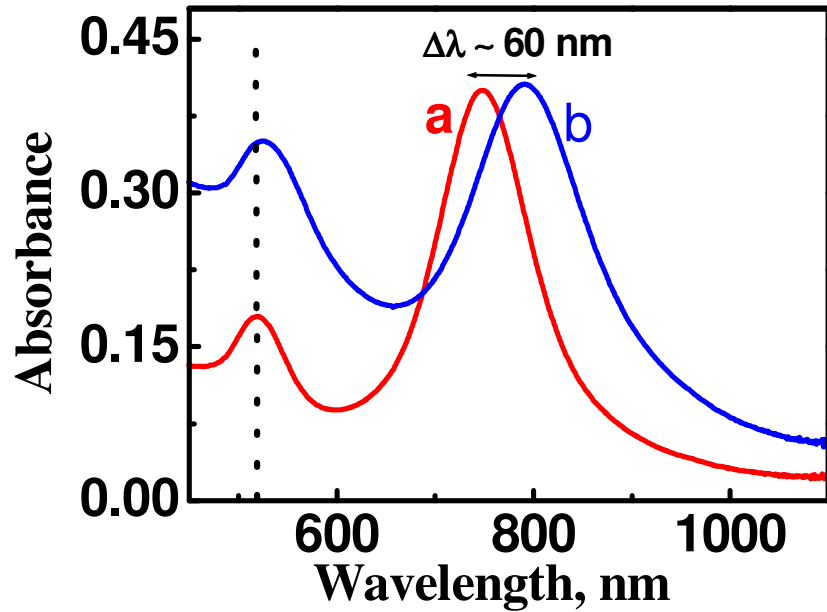
### Identification of active edge sites for electrochemical H<sub>2</sub> evolution from MoS<sub>2</sub> nanocatalysts

Thomas F. Jaramillo, *et al Science* 2007, 317, 100

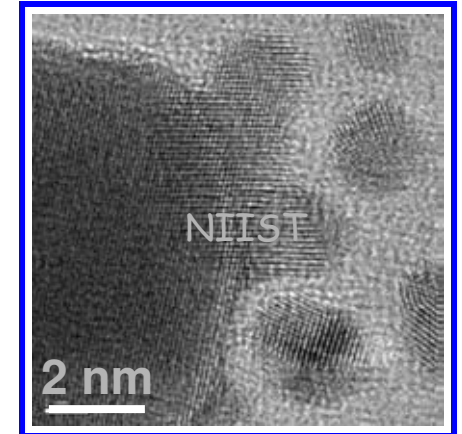
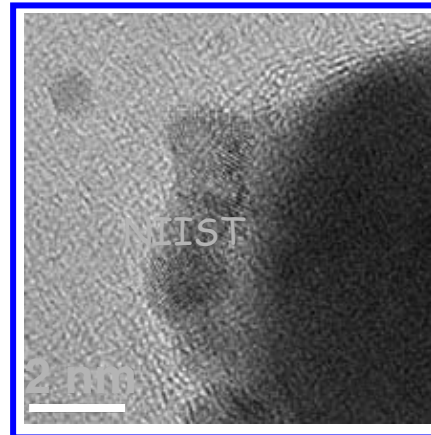
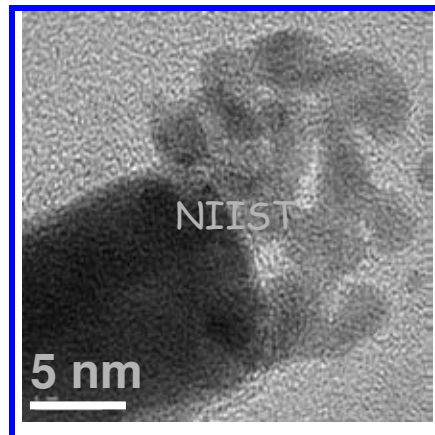
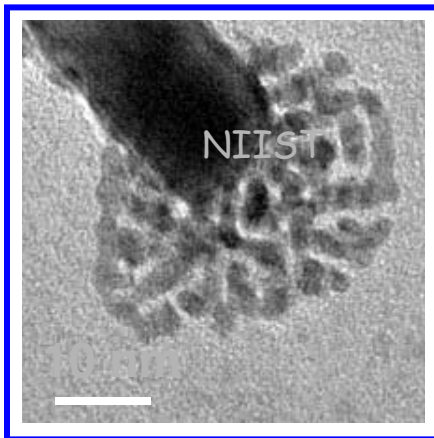
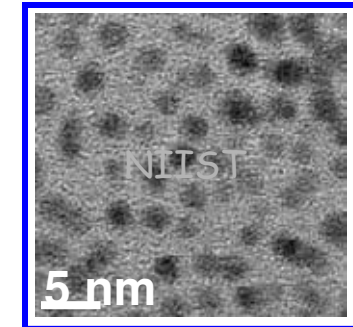
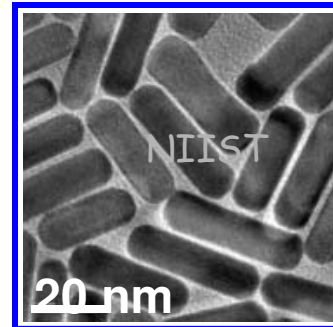
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***Edges are very reactive***

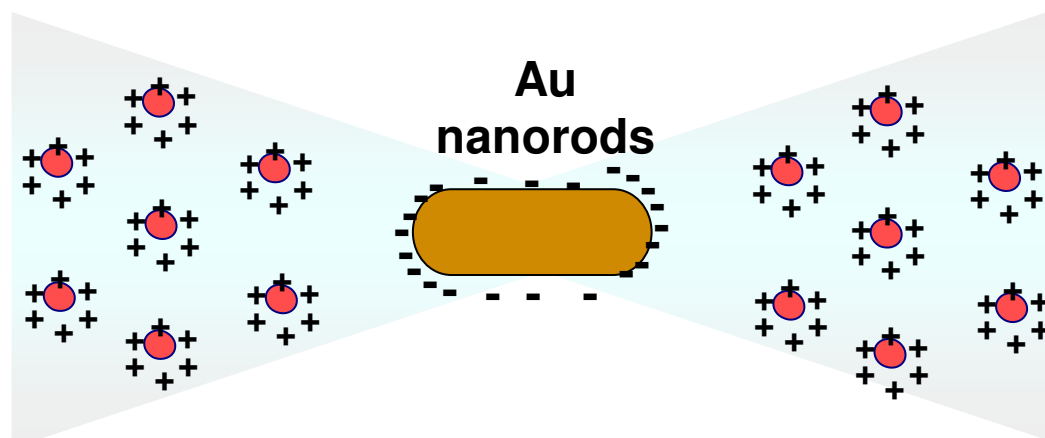
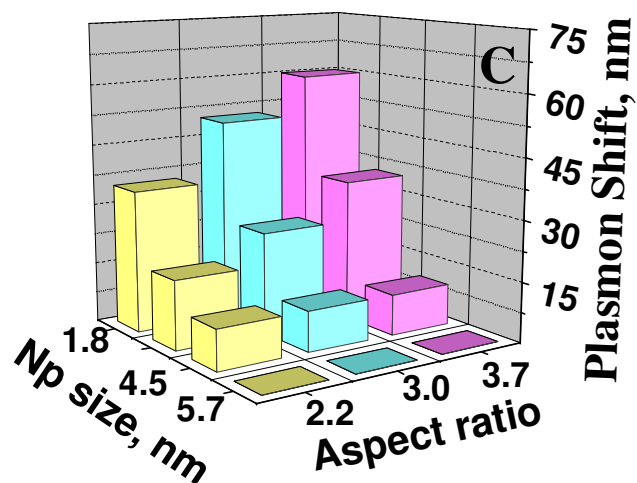
# Electric field at the edges of anisotropic nanostructures



## - HRTEM studies +

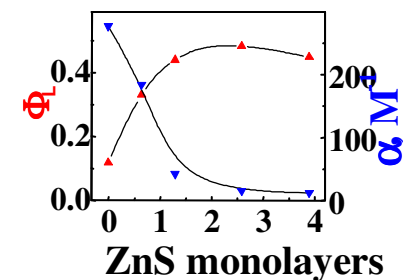
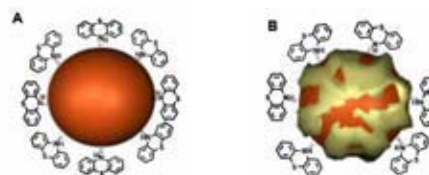
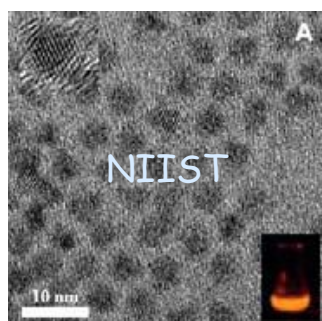


## Electric field at the edges



Pramod, Shibu and George Thomas  
*J. Am. Chem. Soc.* , 129, 6712 (2007)

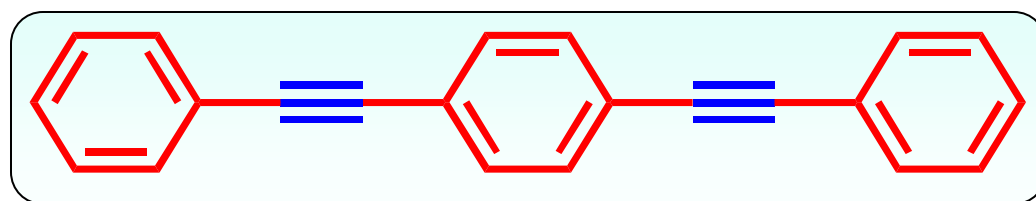
## Optimizing the shell thickness of Quantum dots



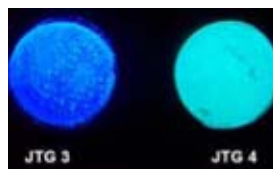
Vinayakan. Shanmugapriya, Nair, Ramamurthy, George Thomas  
*J. Phys. Chem. C* 111, 10146 (2007)

# Self-organization of molecules on surface

## Phenyleneethylenes.....



**Rigid  
molecules**



**Maintains  $\pi$ -  
conjugation**

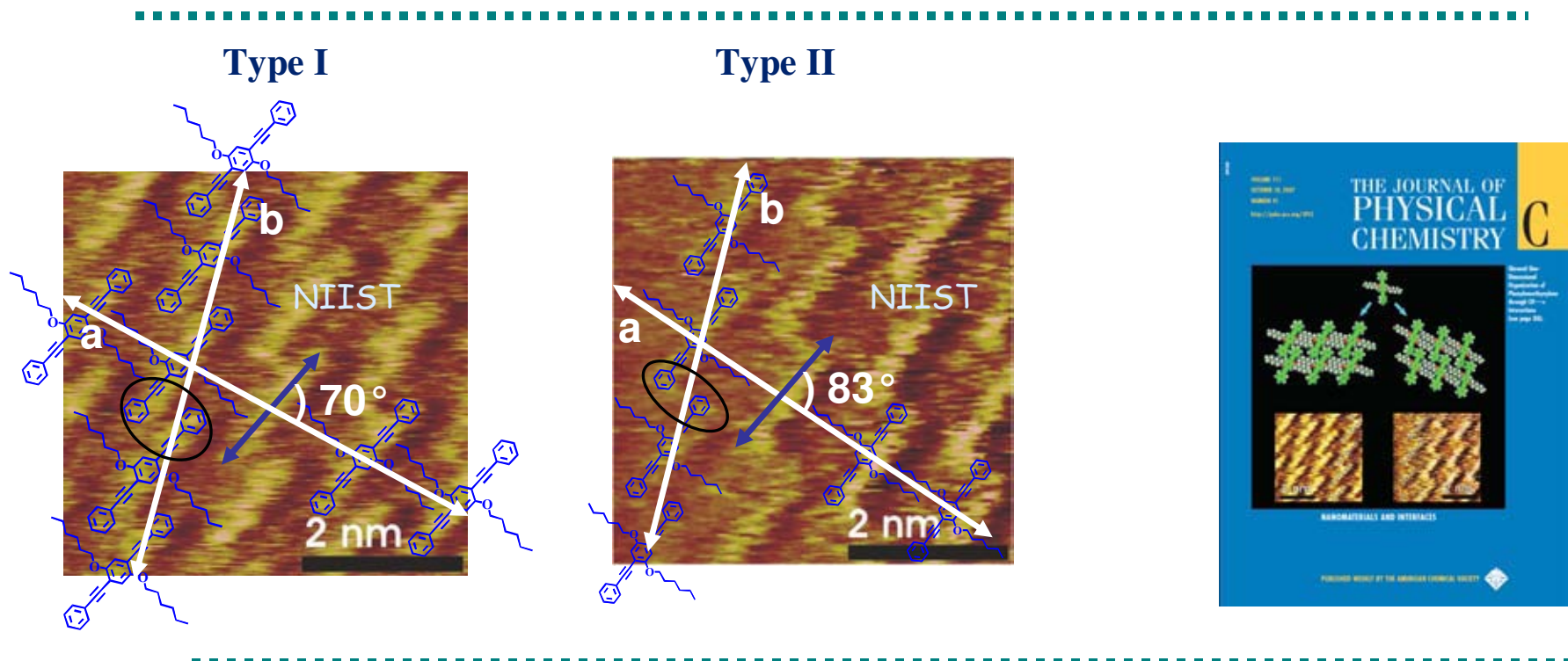
**George Thomas and coworkers**

**J. Phys. Chem. A 110, 4329-4337 (2006)**

**J. Phys. Chem. A, 110, 5642-5649 (2006).**

**Can the optoelectronic properties of same molecules  
on surface modulated by varying their organization**

# Functional control of molecules on surfaces - STM studies



Yoosaf, James, Ramesh, Suresh, and George Thomas,  
J. Phys. Chem. C. 111, 14933-14936 (2007).

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**Dr. P. K. Sudeep**

**Dr. S. T. Shibu Joseph**

**Dr. P. V. James**

**Dr. P. Pramod**

**Dr. K. Yoosaf**

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**R. Vinayakan**  
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**Former Directors of NIIST**

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**Dr. P. Ramamurthy (University of Madras)**



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**(ii) Nanoscience and Technology Initiative of DST  
(Government of India)**

Thank you

