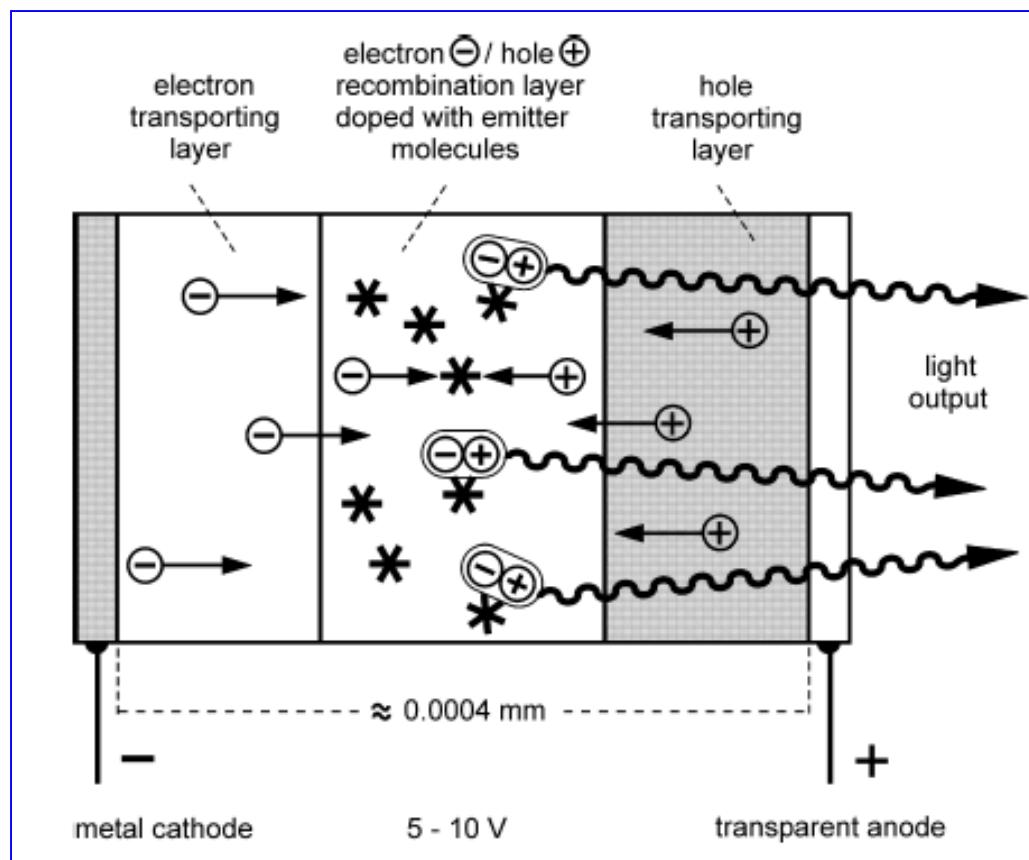


Molecular Photonics

Lecture 8
Metals/triplets/charge transfer

Exciton formation



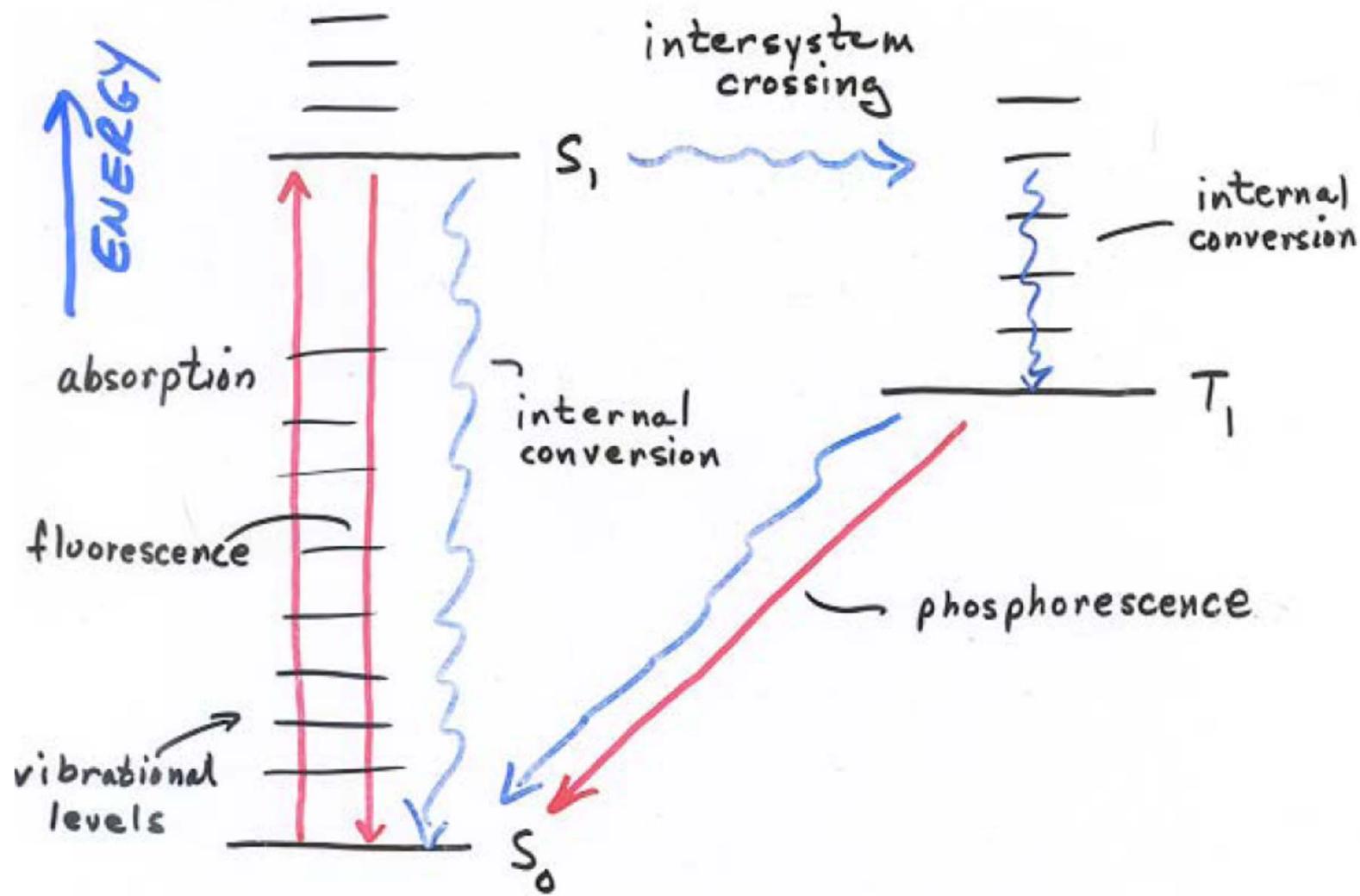
25% singlet and 75% triplet excitons
We want to harvest all of them!

How to get phosphorescence

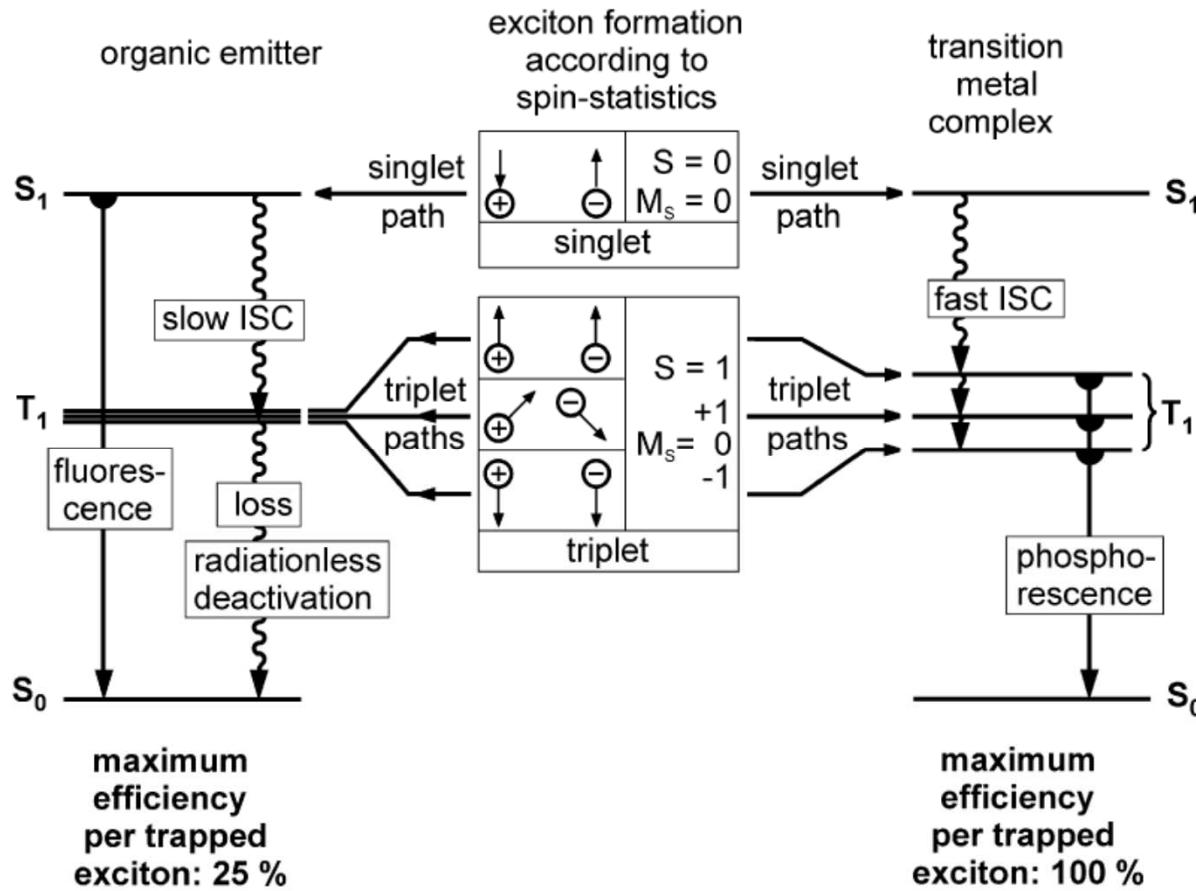
Many photophysical properties of the lowest excited triplet states and the corresponding transitions of organometallic compounds are essentially determined by the extent of metal participation in the wavefunctions. This **metal participation** not only alters the spatial extension of the wavefunctions, but also induces significant mixtures of singlet and triplet states by spin-orbit coupling (SOC) which is mainly carried by the metal orbitals. SOC leads to **phosphorescence**.

Organo-transition-metal compounds (triplet emitters) are attractive for optimizations of organic light emitting diodes (OLEDs). This is a consequence of significantly higher efficiencies and chemical stabilities obtainable with these compounds as compared to organic emitters.

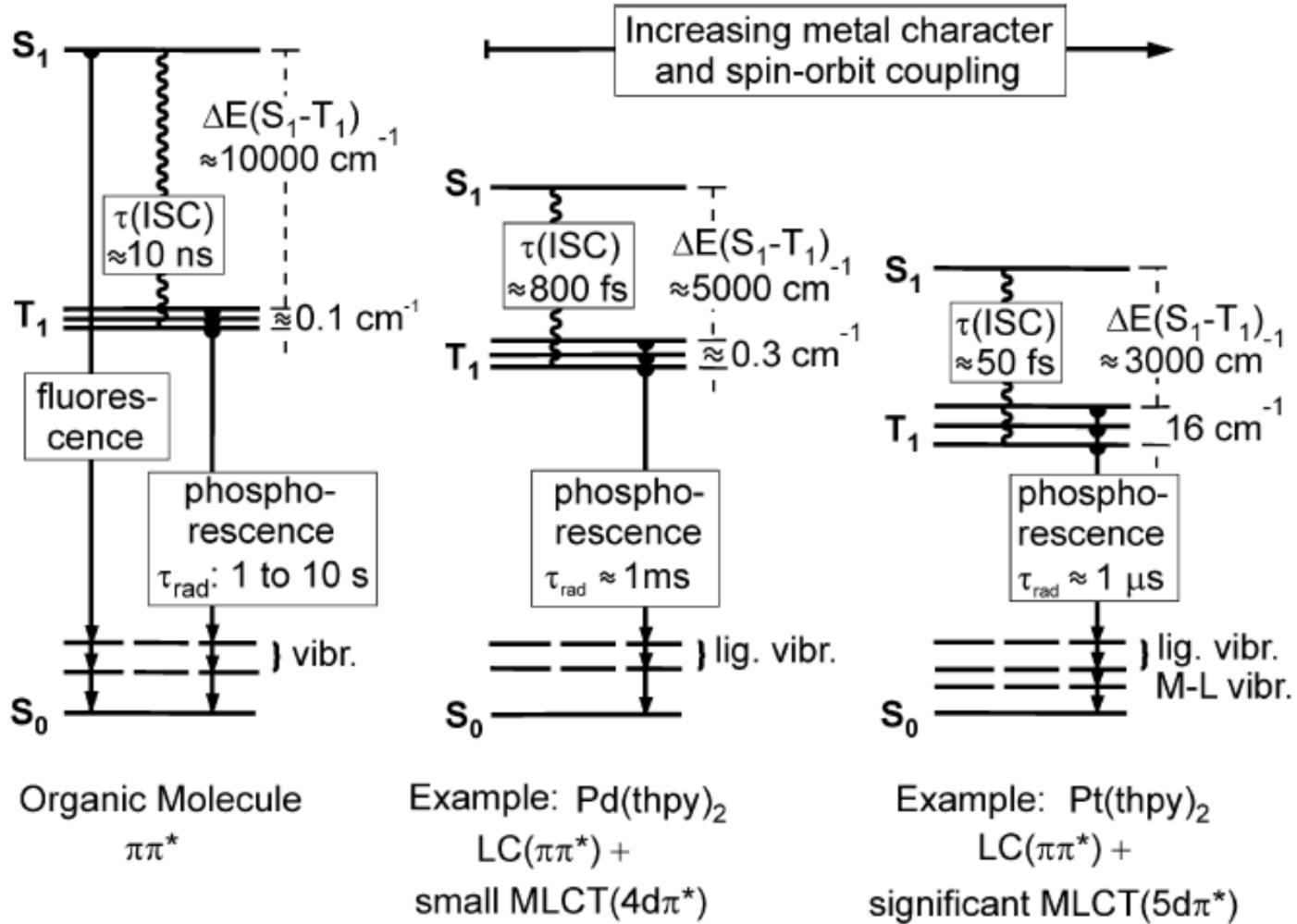
JABLONSKI DIAGRAM



Organic vs. Metal Complex Emitter



Due to spin-statistics, electron-hole recombination leads to 25% singlet and 75% triplet state population. In organic molecules, only the singlets emit light (fluorescence), while the triplet excitation energy is transferred into heat (left hand side). Organometallic compounds with transition metal centers do not exhibit fluorescence, but show a fast intersystem crossing (ISC) to the lowest triplet state. Thus, the triplet harvests singlet and triplet excitation energy and can efficiently emit. In principle, a triplet emitter can exhibit a four times higher electroluminescence efficiency than a singlet emitter



- <http://www.adsdyes.com/oled-s-electrophosphorescent.html>

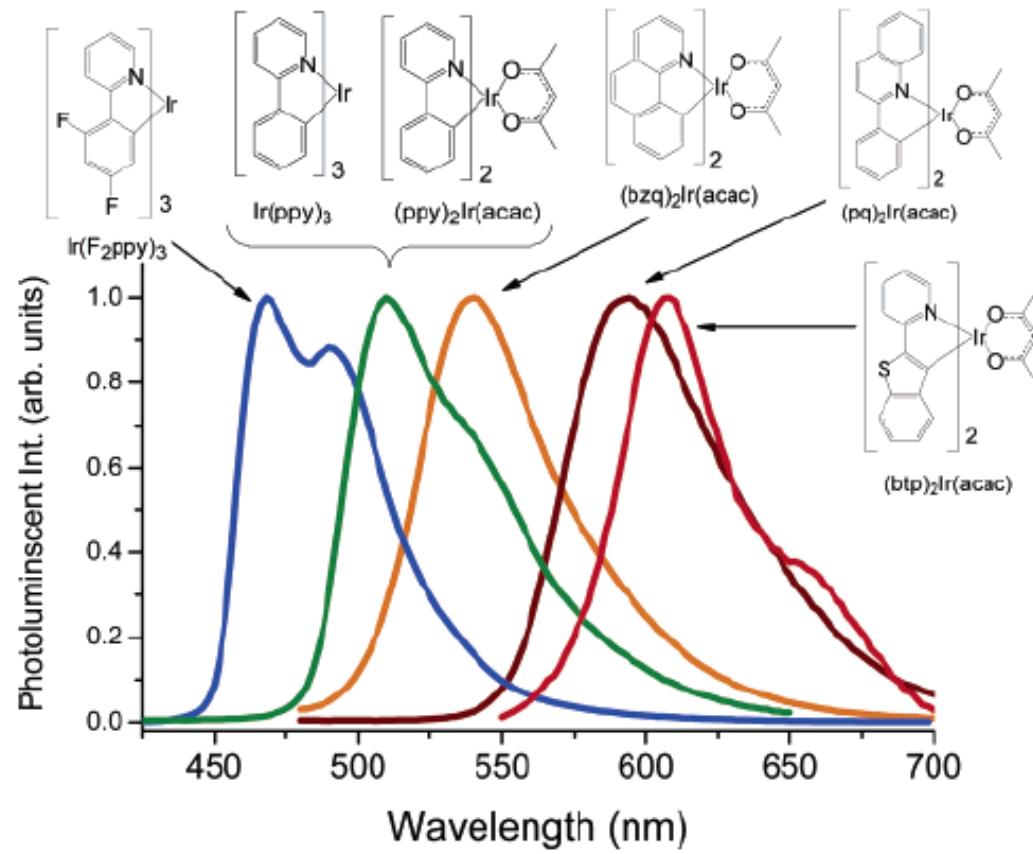


Figure 1. Photoluminescence spectra of Ir phosphors (room temperature, 2-MeTHF solutions).

Thompson and Forrest
Inorg. Chem. **2005**, *44*, 7992-8003

Conclusions

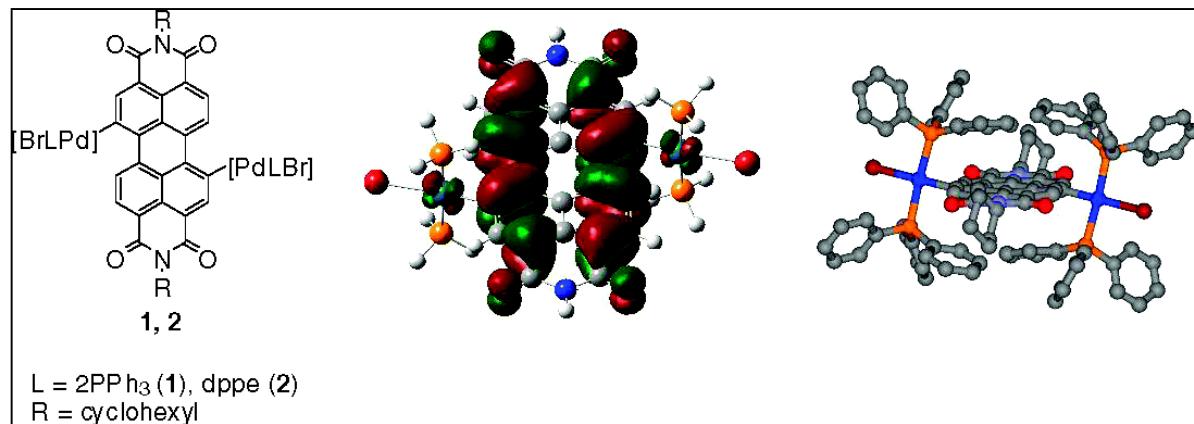
To develop LEDs:

- One has to know molecular photophysics
- One has to have easily tunable system

Case Study

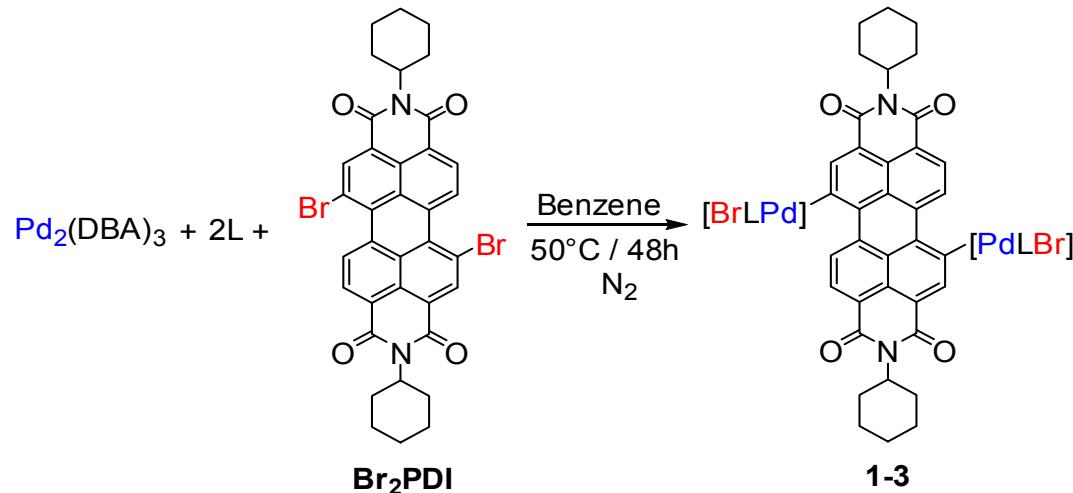
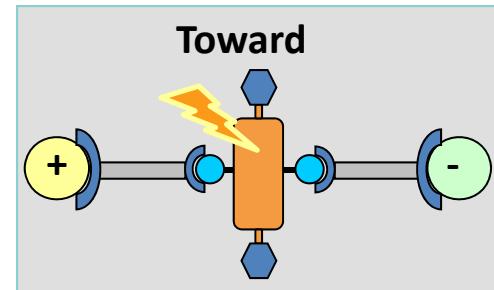
Pd-PDI organometallic chromophores

σ -Bonded Palladium-PDI complexes



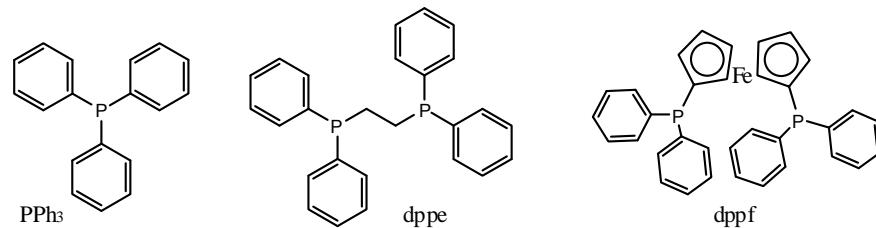
Novel Photofunctional Systems with Tunable Properties

Connecting Transition Metals to the Aromatic Core of PDI: Novel Photofunctional Systems with Tunable Properties

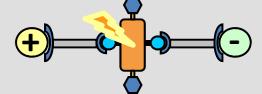


DBA = dibenzylideneacetone

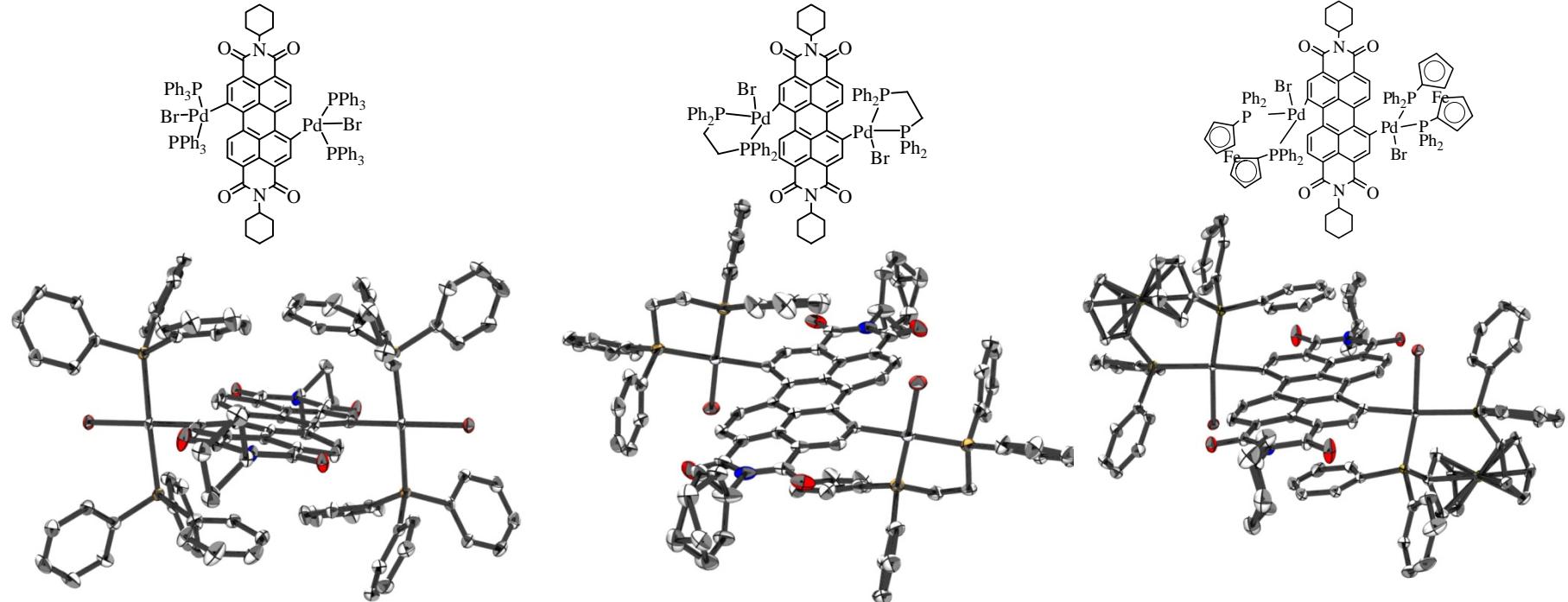
L = 2PPh_3 (1), dppe (2), dppf (3)



Toward



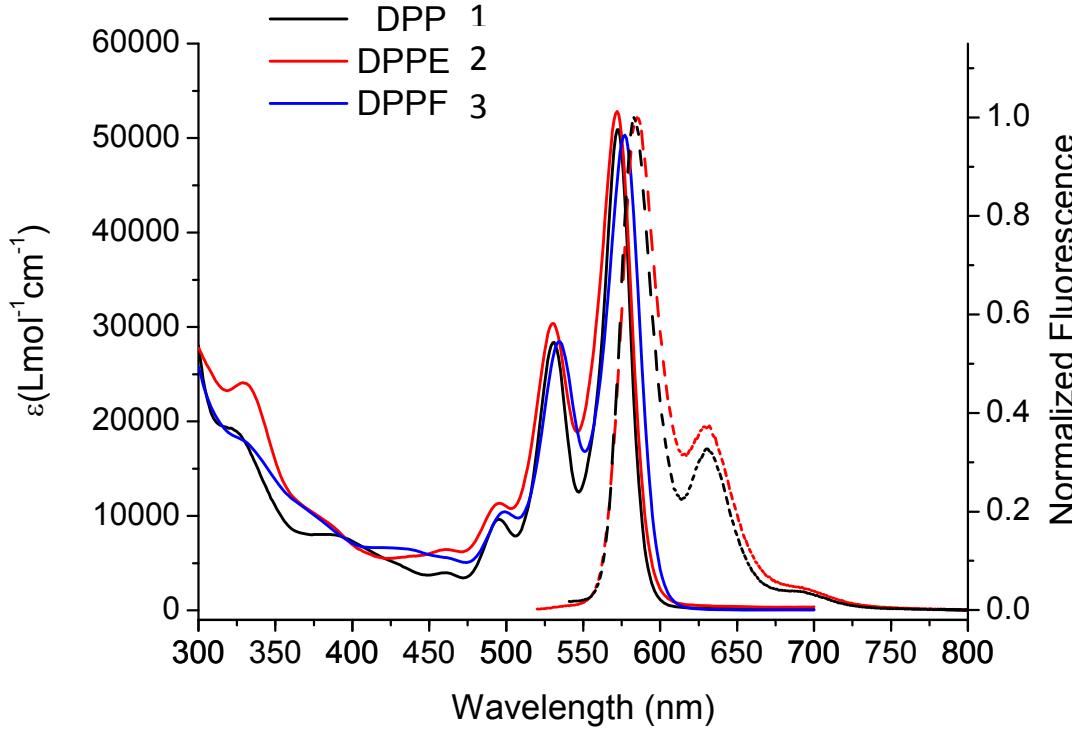
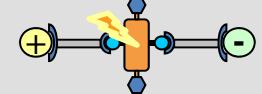
X-Ray Structures and Emission Characteristics



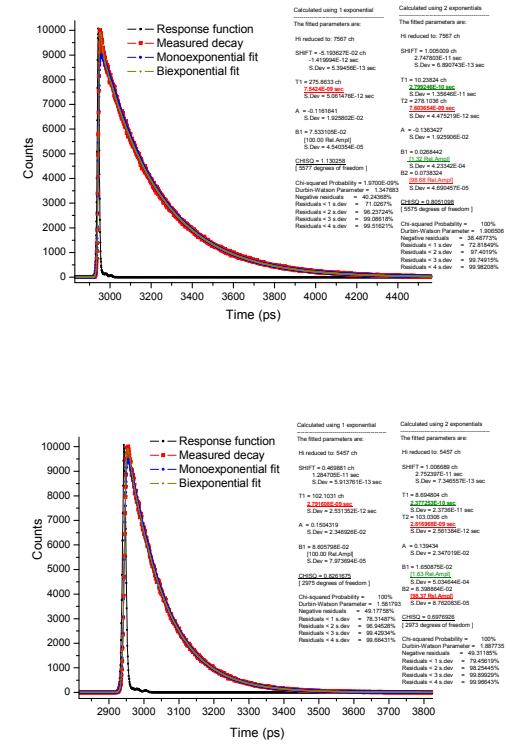
	1	2	3
Φ_f	0.65	0.22	~0.002
T_f/ns	7.5	2.8	-

Absorption and Emission Spectra

Toward

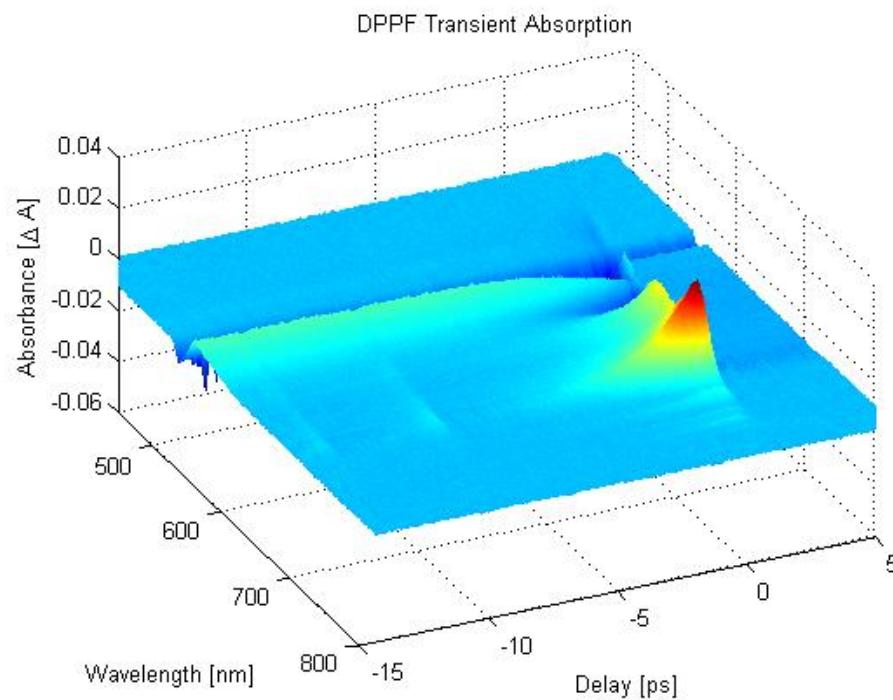
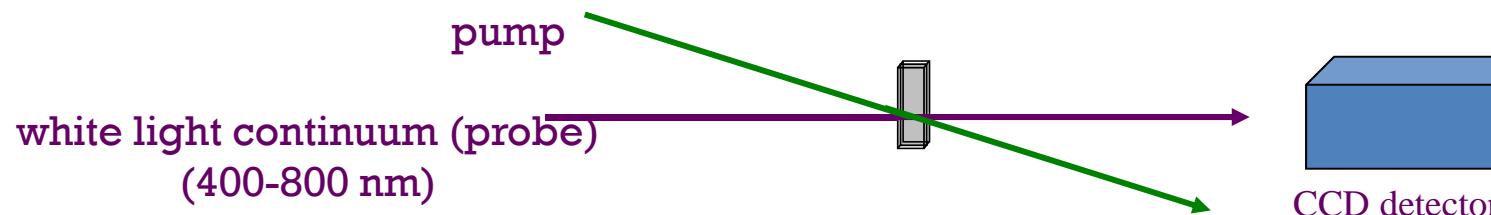
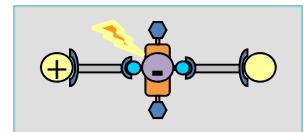


	$\lambda_{\text{abs}}/\text{nm}$	$\varepsilon/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Φ_f	τ_f/ns	$E_{1/2}^{\text{RED}}/\text{V}$	$E_{1/2}^{\text{OX}}/\text{V}$
1	573	50900	584	0.65	7.5	-0.96	1.28
2	572	52800	584	0.22	2.8	-1.01	1.08
3	577	50300	588	~0.002	-	-1.02	1.13 (PDI)

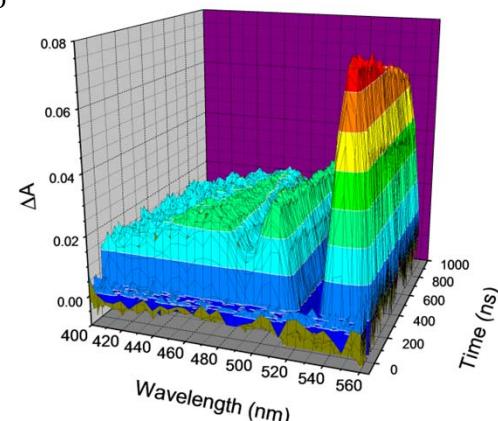
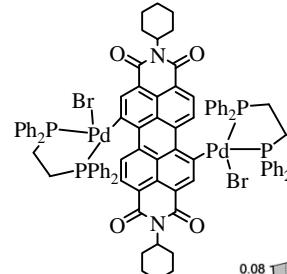
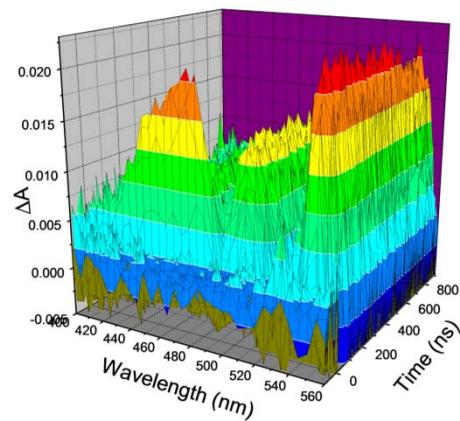
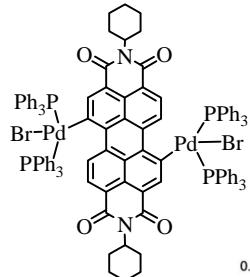
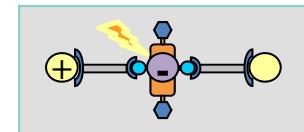


Fluorescence Life Time measurements for **1** (top) and **2** (bottom). The decays are monoexponential with time constants of 7.5 and 2.8 ns respectively

Transient Absorption Spectroscopy

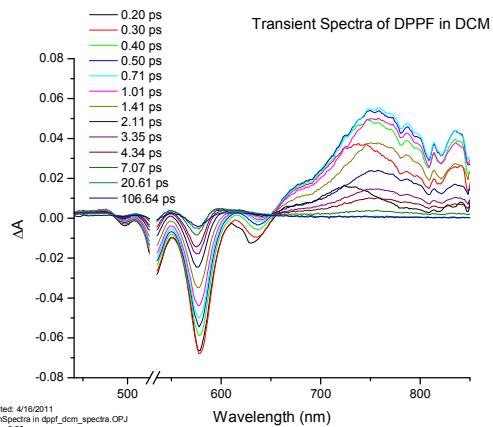
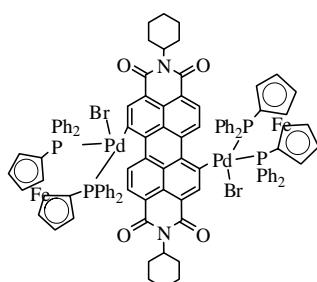
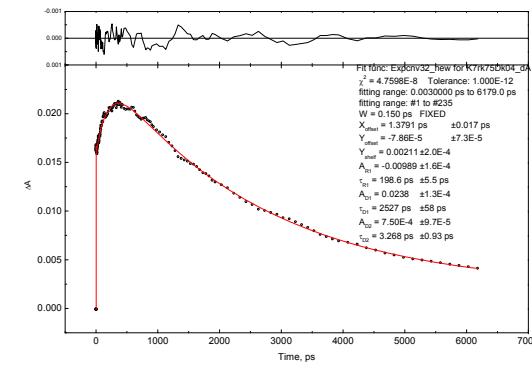
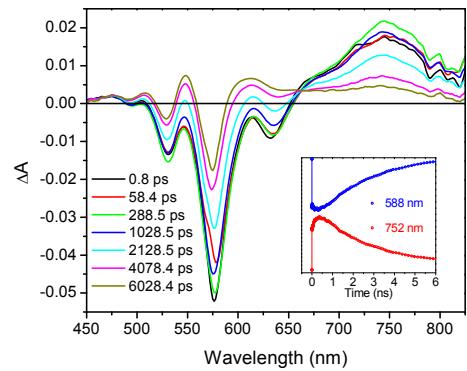
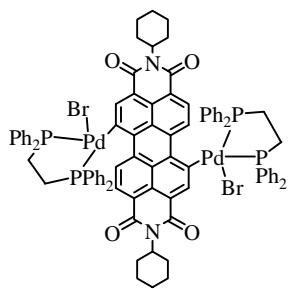
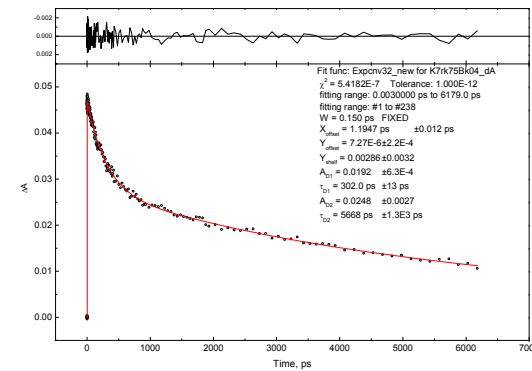
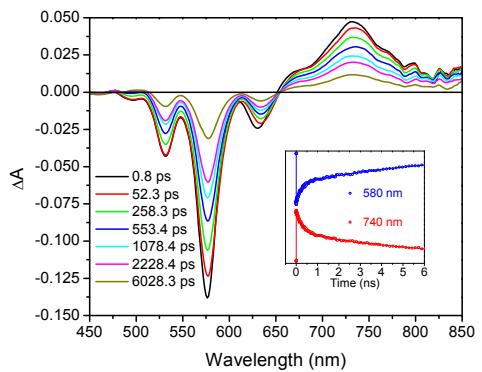
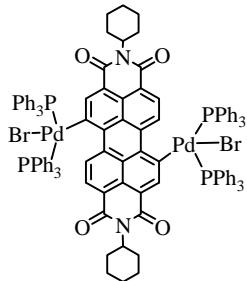


Nanosecond Transient Absorption Spectroscopy

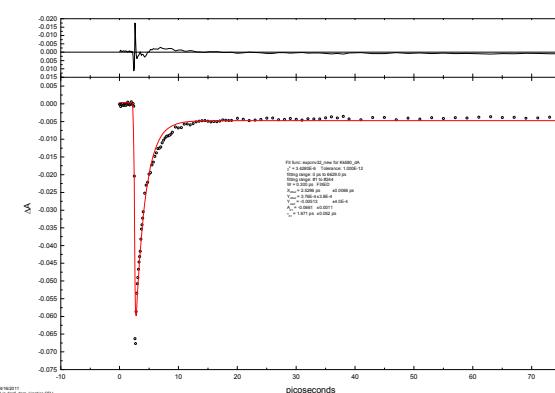


Nanosecond transient absorption spectra of complexes **1** and **2** showing the PDI triplet features which decay with time constants of ca. 2.6 μ s and 3.2 μ s.
The estimated triplet quantum yields are 6 and 20% for **1** and **2** respectively

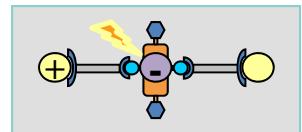
Femtosecond Transient Absorption Spectroscopy



Printed: 4/6/2011
FemSpectra in dppf_dcmn_spectra.QPJ
Data: 0.20 ps



Thermodynamics of Electron Transfer



Gibbs free energy for photoinduced charge separation

E_{ox} and E_{red} are the oxidation potential of the donor and the reduction potential of the acceptor respectively, E_s is the lowest excited singlet state energy of the system, e is the charge of the electron, r_{DA} is the ion pair distance, r_D and r_A are the ionic radii, ϵ_s is the dielectric constant of a particular solvent, and ϵ_p is the dielectric constant of the solvent in which the electrochemistry was done

$$\Delta G_{cs} = E_{ox} - E_{red} - E_s - \frac{e^2}{\epsilon_s r_{DA}} + e^2 \left(\frac{1}{2r_D} + \frac{1}{2r_A} \right) \left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_p} \right)$$

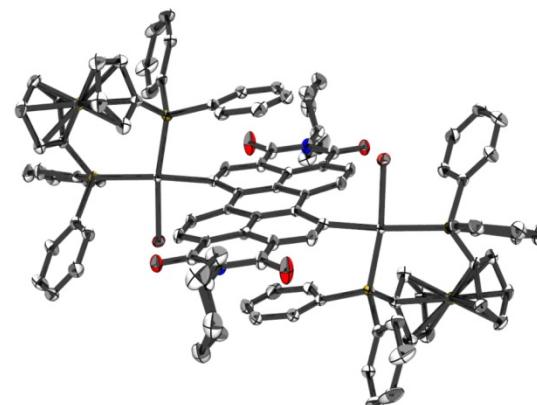
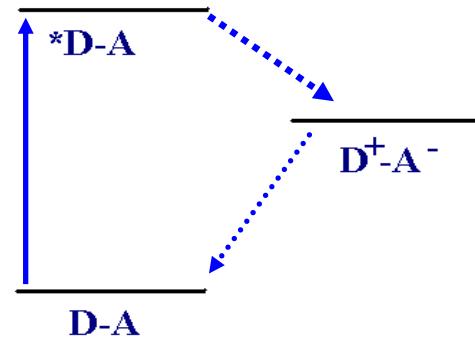
For complex 3:

$E_{ox} \sim 0.65$ V, $E_{red} \sim -1$ V

$E_{s1} = 577$ nm = 2.15 eV

Solvent term < 0.5 eV

→ ΔG_{cs} is negative



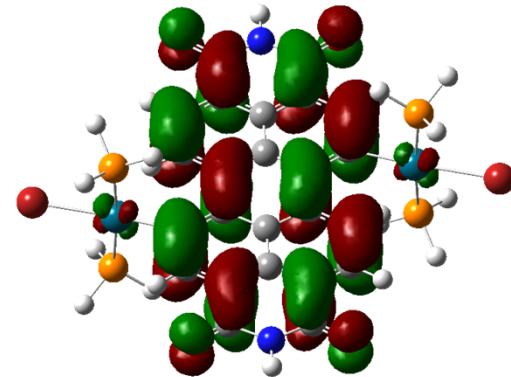
Rationalization of the Influence of Pd Centers

Toward

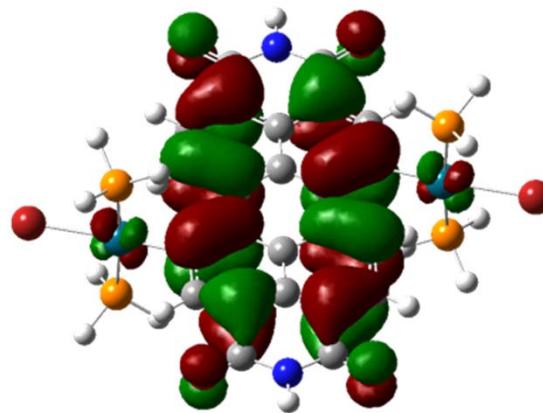


TD-DFT derived contour surfaces of HOMO and LUMO for Pd-PDI model system

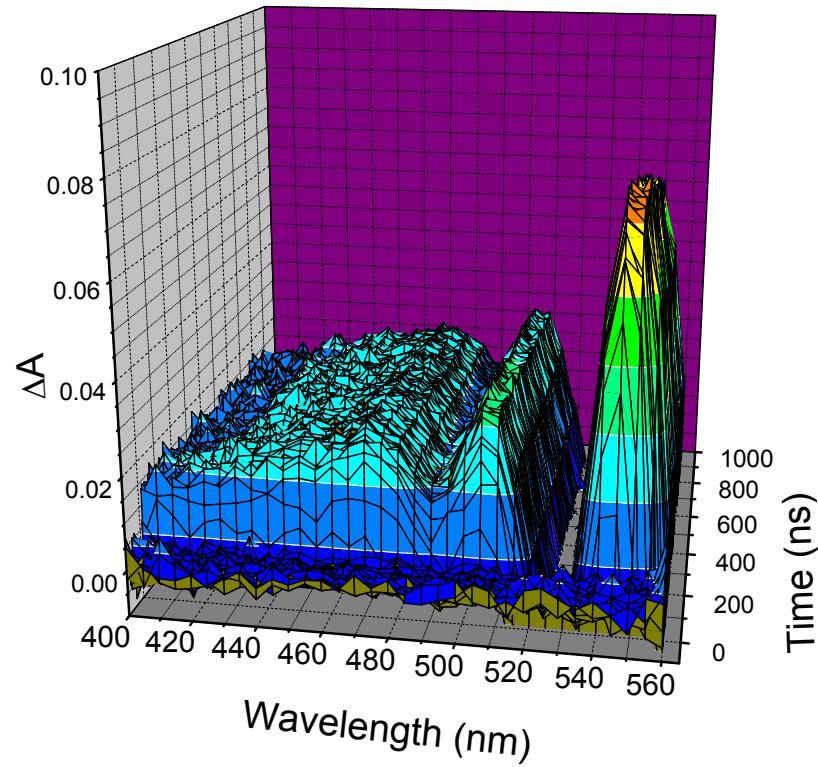
LUMO
-3.54eV



HOMO
-5.93eV



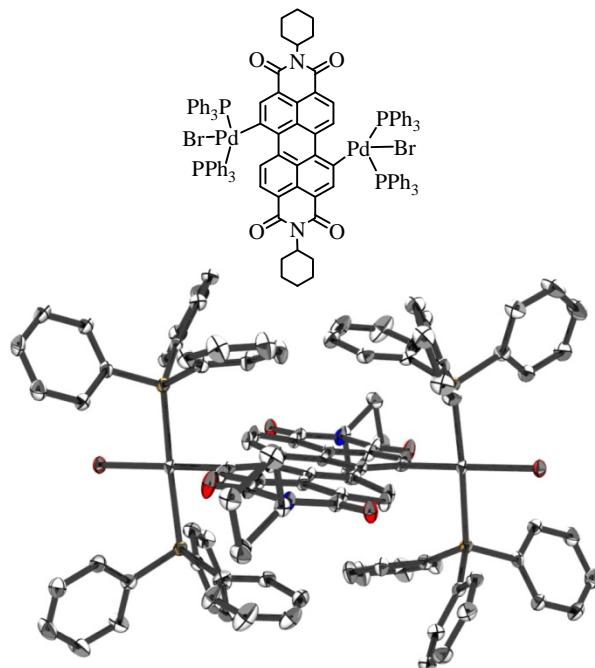
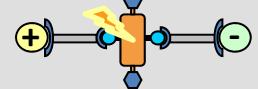
Pd Centers Have Little Influence on the Electronic Communication between the Ligands and PDI



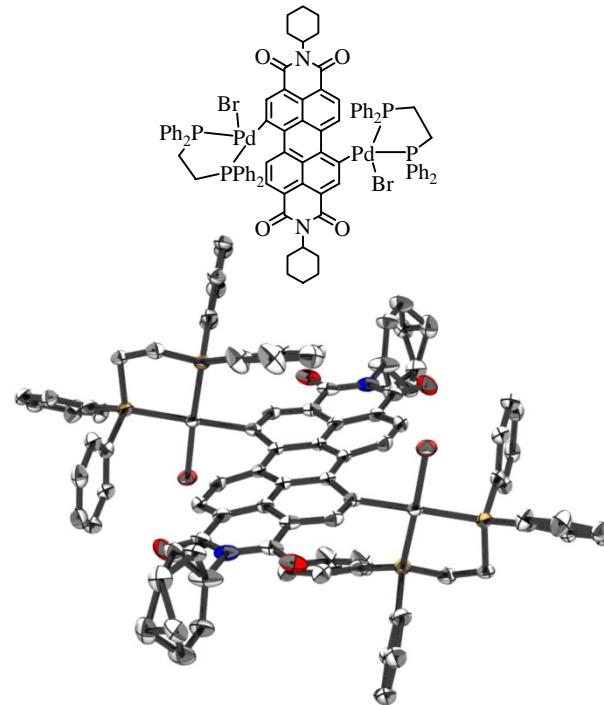
Nanosecond transient absorption spectra
of complex **2** showing the PDI triplet peaks.
The triplet features decay with a time
constant of ca. 3.2 μ s.

Summary: The Influence of the Auxiliary Ligands

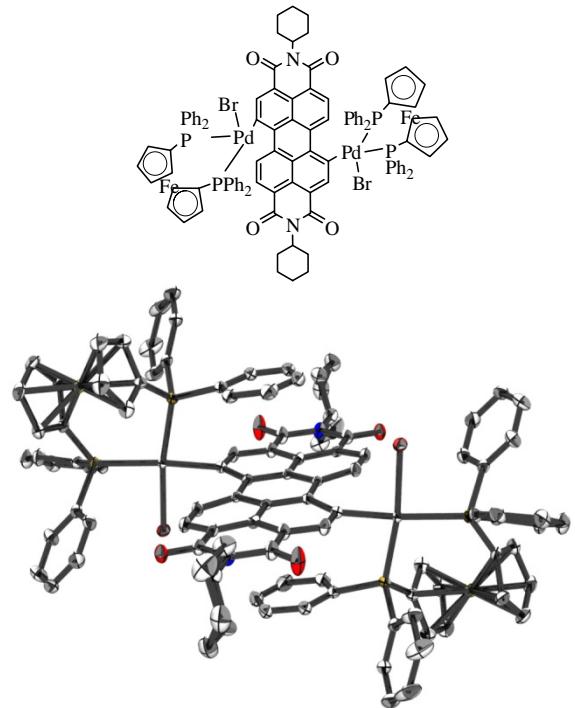
Toward



High Fluorescence



Enhanced Triplet Yield



Charge Separation

	1	2	3
Φ_F	0.65	0.22	-0.002
Φ_{ST}	0.06	0.20	-
T_f/ns	7.5	2.8	-

Auxiliary Ligand Choice Modifies Photophysical Characteristics of Chromophore

A different kind of metal...

- Why is gold yellow? Metals exhibit their characteristic shininess as the delocalized electron sea in the metallic bonds are able to absorb and re-emit photons over a wide range of frequencies. Thus the reflectance spectra of most metals appears fairly flat and they appear silver in color.
- A few metals, such as copper and gold, have a reflectance spectrum where the red end (400–700nm) dominates. Why is this so?

Why is Gold Golden?

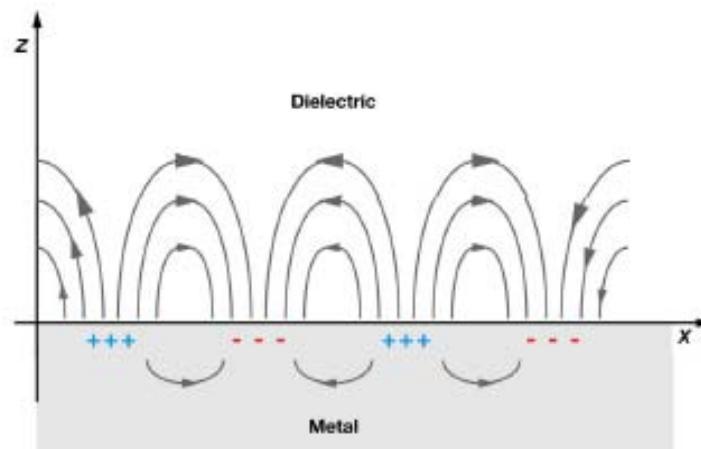


Silver



Gold

- **Plasmon** – collective oscillation of electrons against fixed metal cations in an electric field
- **Plasma frequency** – collective oscillation of electrons against fixed metal cations in an electric field



The colour of metals such as silver and gold is mainly due to absorption of light when a d electron jumps to an s orbital. For silver, the $4d \rightarrow 5s$ transition has an energy corresponding to ultraviolet light, so frequencies in the visible band are not absorbed. With all visible frequencies reflected equally, silver has no colour of its own; it's *silvery*. In gold, however, relativistic contraction of the s orbitals causes their energy levels to shift closer to those of the d orbitals (which are less affected by relativity). This, in turn, shifts the light absorption (primarily due to the $5d \rightarrow 6s$ transition) from the ultraviolet down into the lower energy and frequency blue visual range. A substance which absorbs blue light will reflect the rest of the spectrum: the reds and greens which, combined, result in the yellowish hue we call *golden*.

Why is Gold Golden?



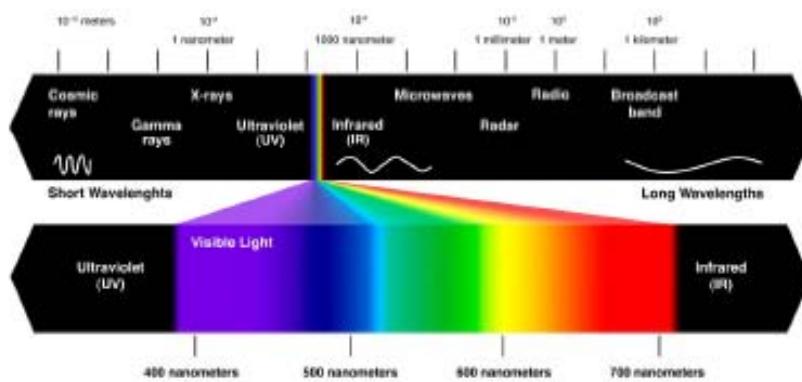
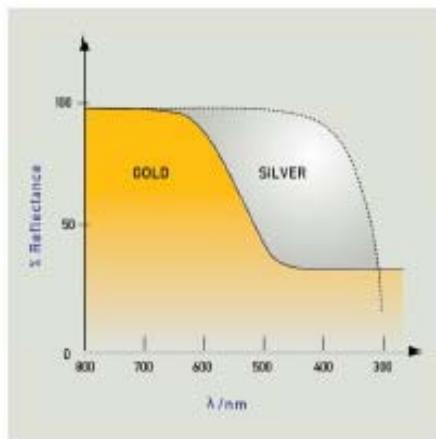
Silver



Gold



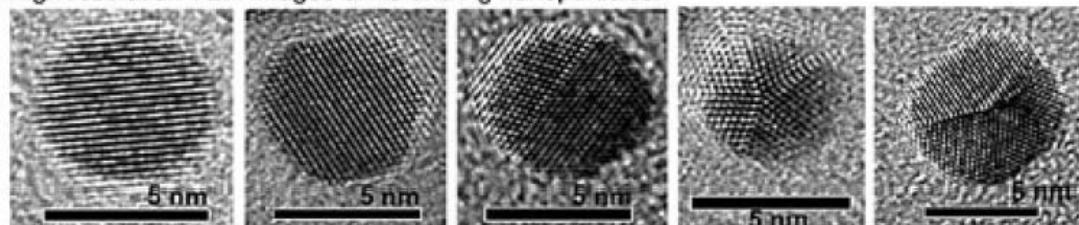
Copper



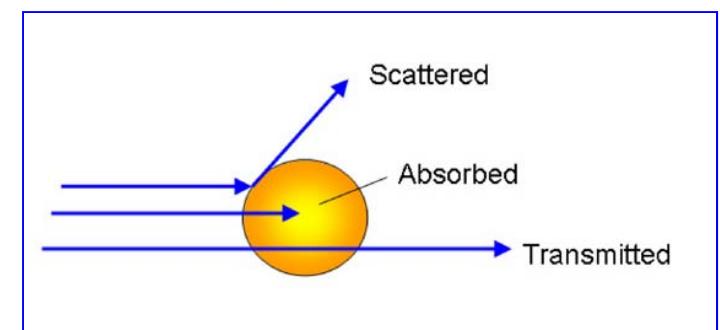
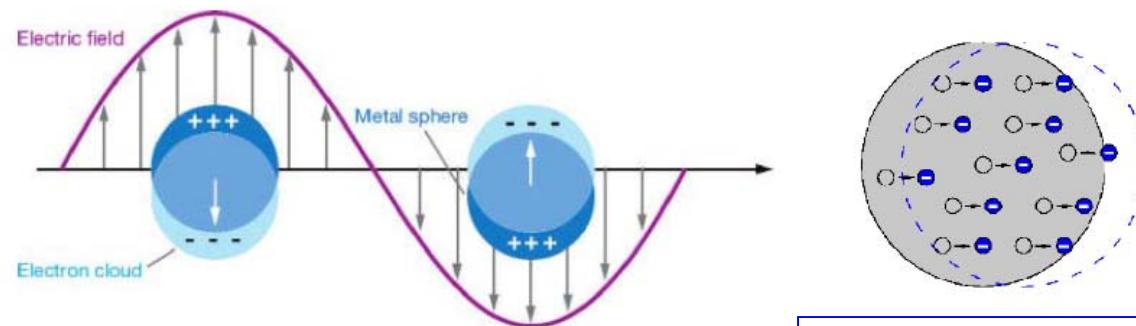
Metal Nanoparticles

- Crystalline nature of metallic nanoparticles:

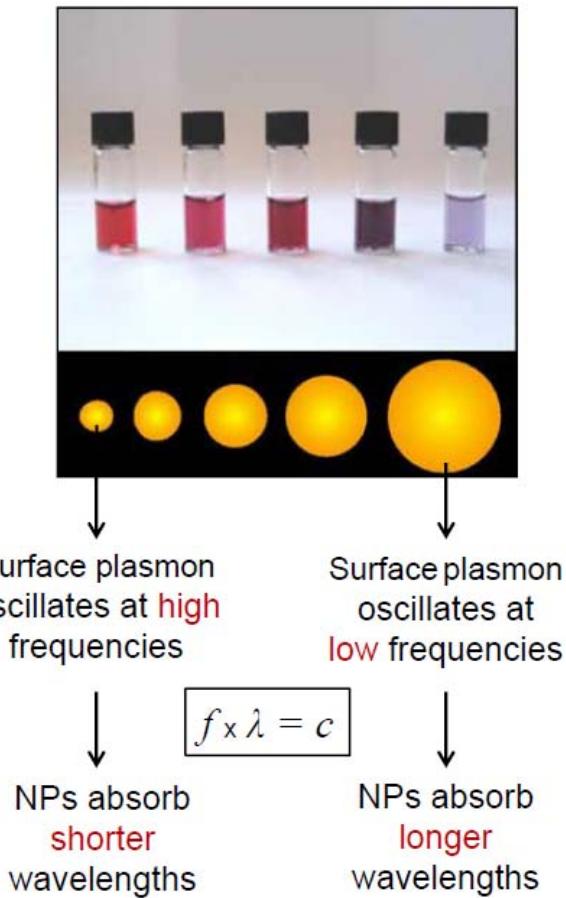
High resolution TEM images of Au and Ag nanoparticles:



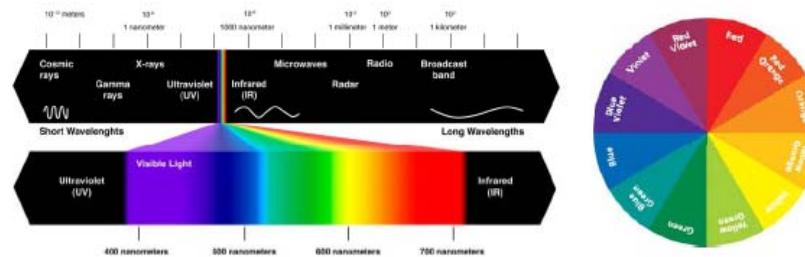
- Surface plasmons in nanosized particles:



Surface Plasmon Resonance of Gold Nanoparticles

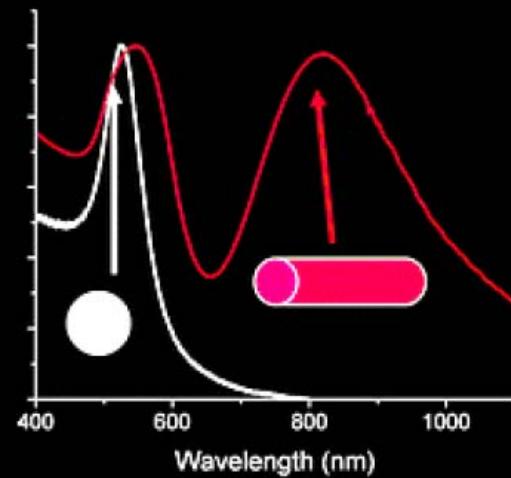
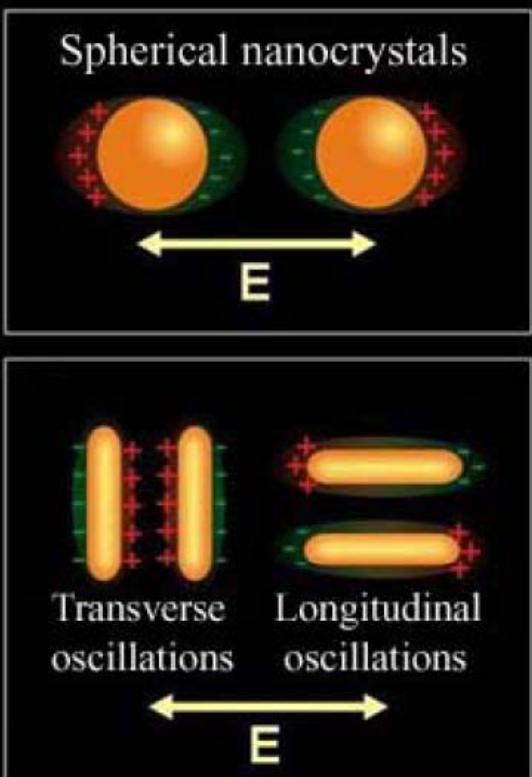


- In order to satisfy the condition of SP Resonance (= frequency of electron oscillations corresponding to the frequency of light), **smaller** particles will absorb **shorter** wavelengths of light



Nanoparticles of Different Shapes

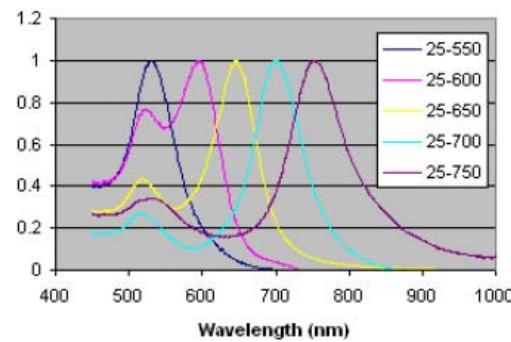
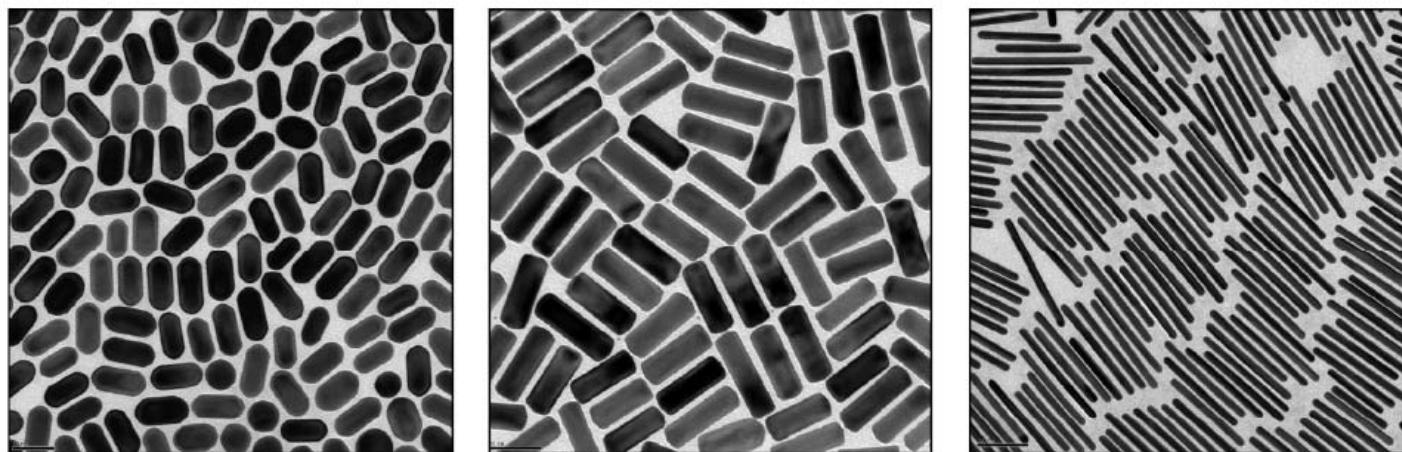
- 1D nanorods (as opposed to 0D nanospheres) have an additional vibration mode



- As a result, an additional absorption band appears in the UV-Vis spectra of nanorods

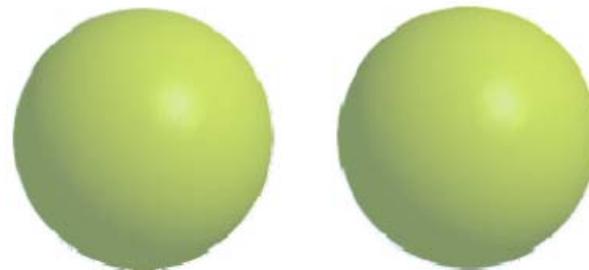
The Case of Nanorods

- Representative TEM images and UV-Vis spectra of gold nanorods:

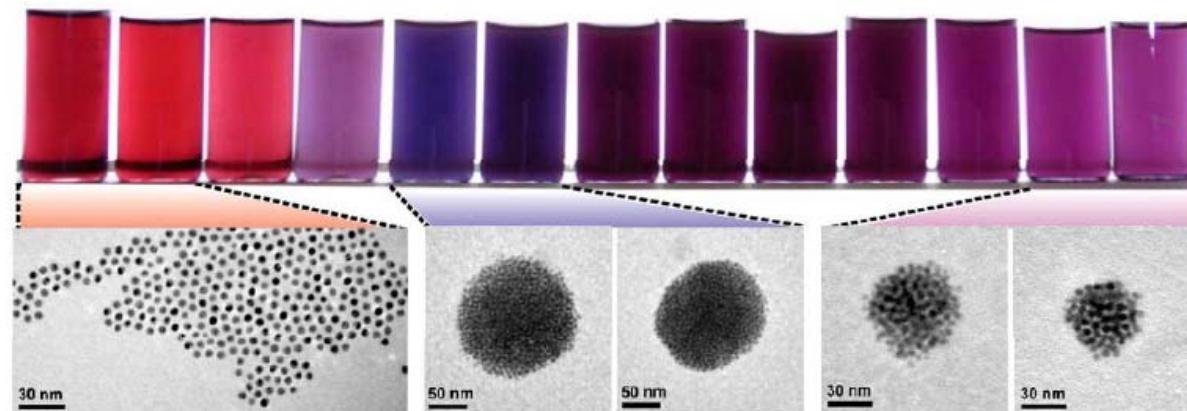


Interparticle Coupling of Surface Plasmons

- Collective oscillation of electrons in a given nanoparticle can assist surface plasmon of a neighboring particle:



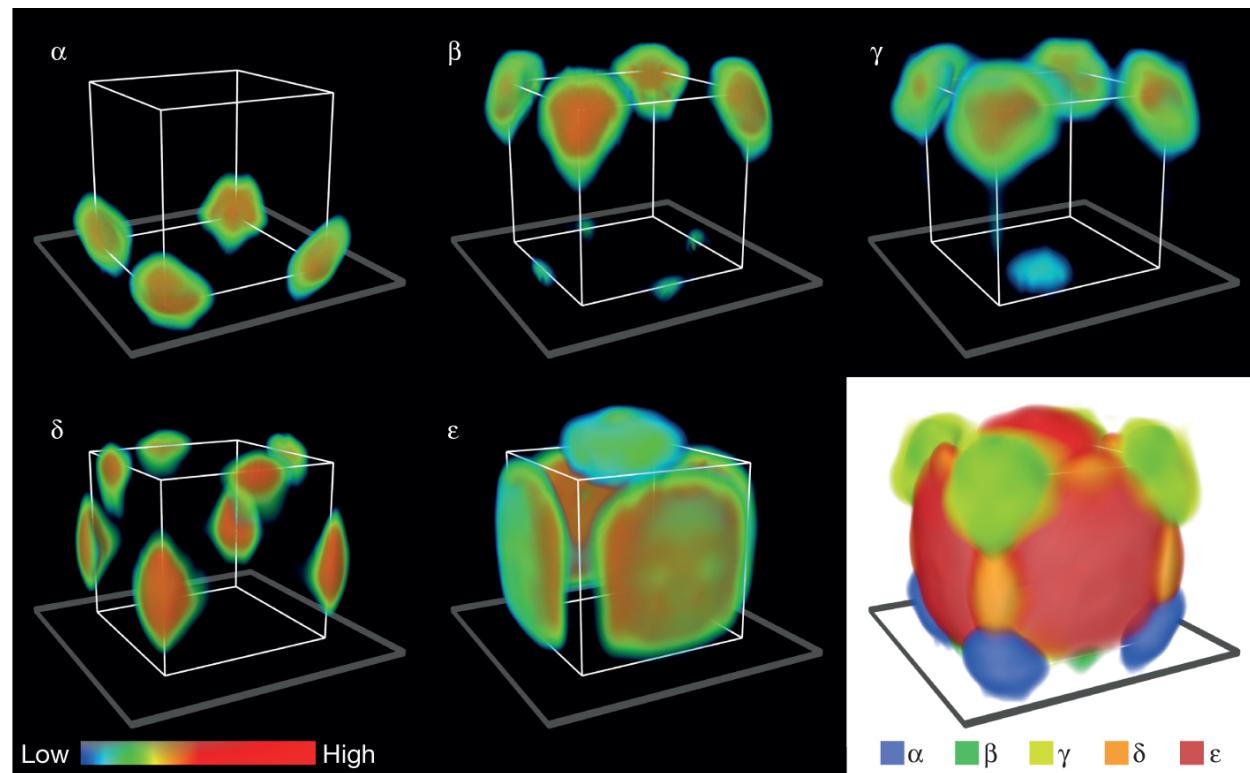
- The consequence of this coupling is the lengthening of the wavelength of light required to achieve the resonance condition



Three-dimensional imaging of localized surface plasmon resonances of metal nanoparticles

Olivia Nicoletti^{1*}, Francisco de la Peña^{1*}, Rowan K. Leary¹, Daniel J. Holland², Caterina Ducati¹ & Paul A. Midgley¹

3D visualization of the LSPR components of a silver nanocube.



O Nicoletti *et al.* *Nature* **502**, 80-84 (2013) doi:10.1038/nature12469

nature

FEATURE ARTICLE

The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment**K. Lance Kelly, Eduardo Coronado, Lin Lin Zhao, and George C. Schatz****Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113**Received: August 9, 2002*

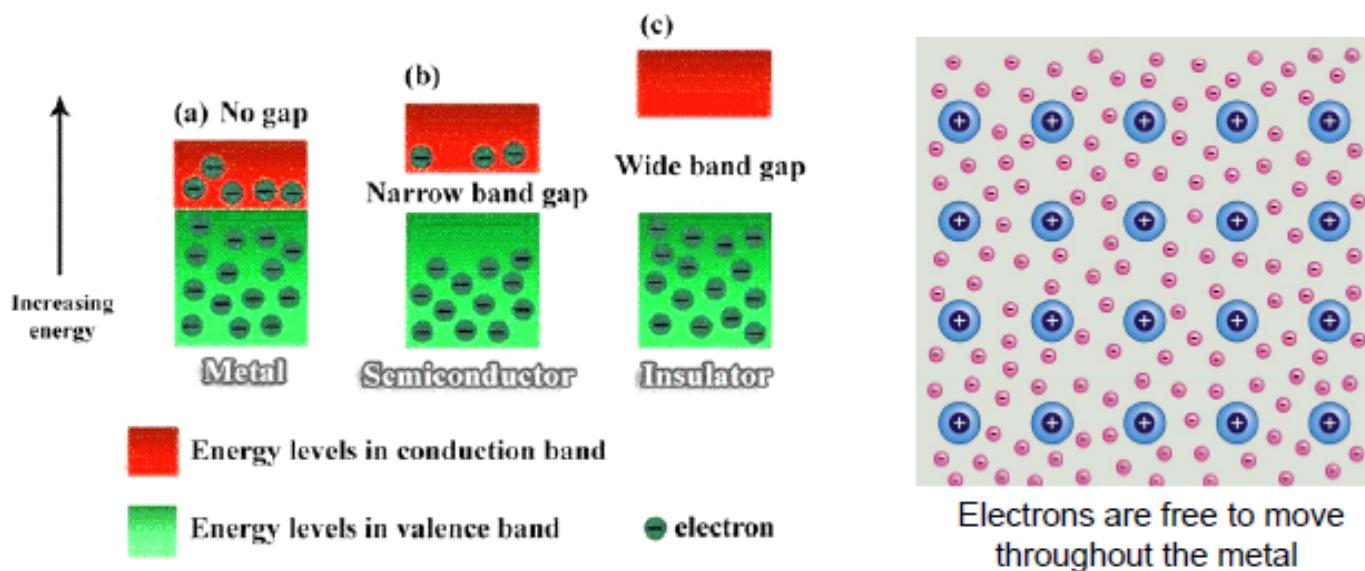
FDTD Studies of Metallic Nanoparticle Systems***Ariel L. Atkinson, Jeffrey M. McMahon, and George C. Schatz**

N. Russo et al. (eds.), *Self-Organization of Molecular Systems: From Molecules and Clusters to Nanotubes and Proteins*, NATO Science for Peace and Security Series A: Chemistry and Biology, © Springer Science+Business Media B.V. 2009

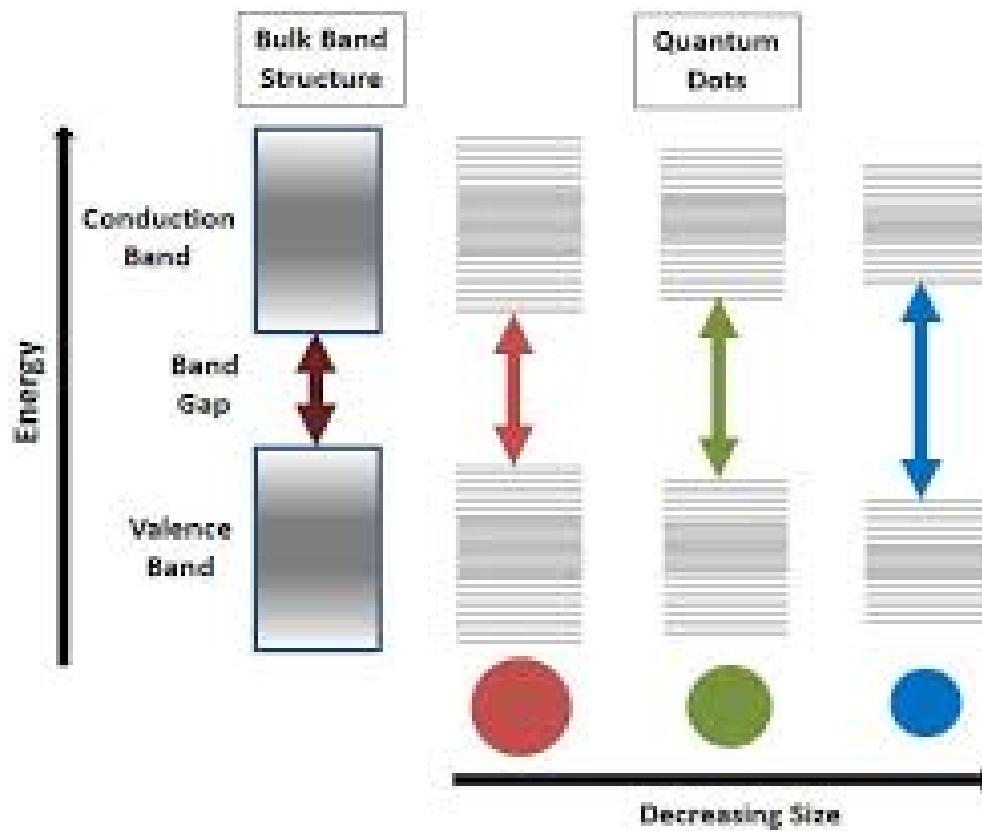
Semiconductor NPs

Quantum dots

Band Theory of Conductivity



Quantum confinement



<http://www.youtube.com/watch?v=B195U--HI8A>

Size dependent absorption and emission

