

Molecular Photonics

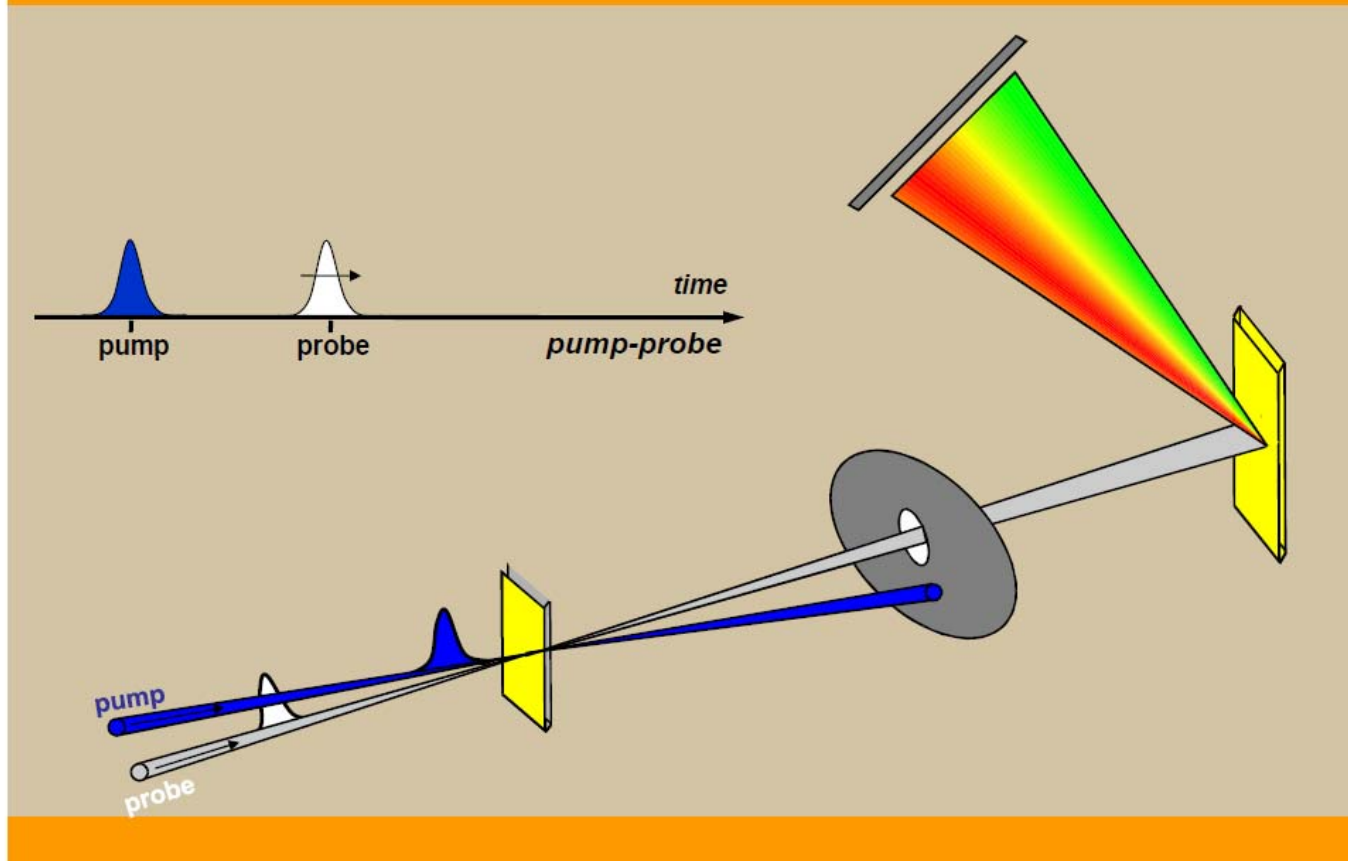
Lecture 7

Long-lived charge separation

Metal complexes photonics and OLEDs

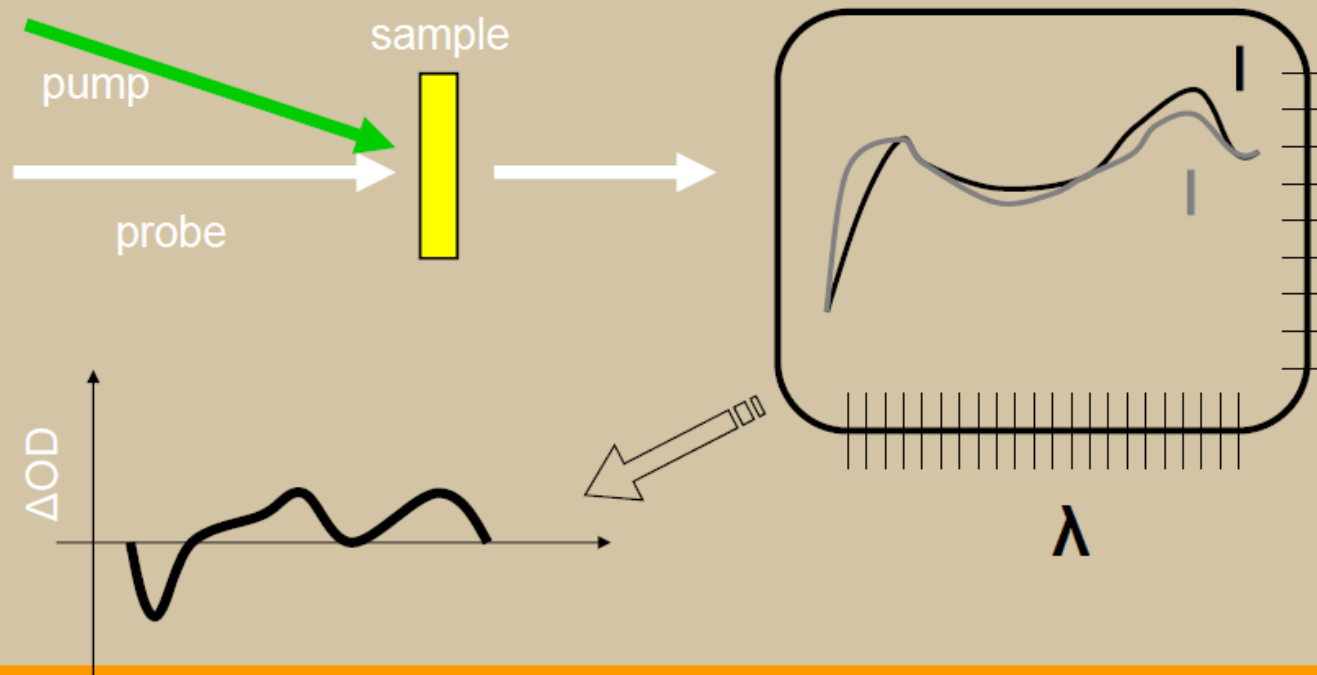
Transient absorption - ultrafast laser spectroscopy

Dispersed pump-probe

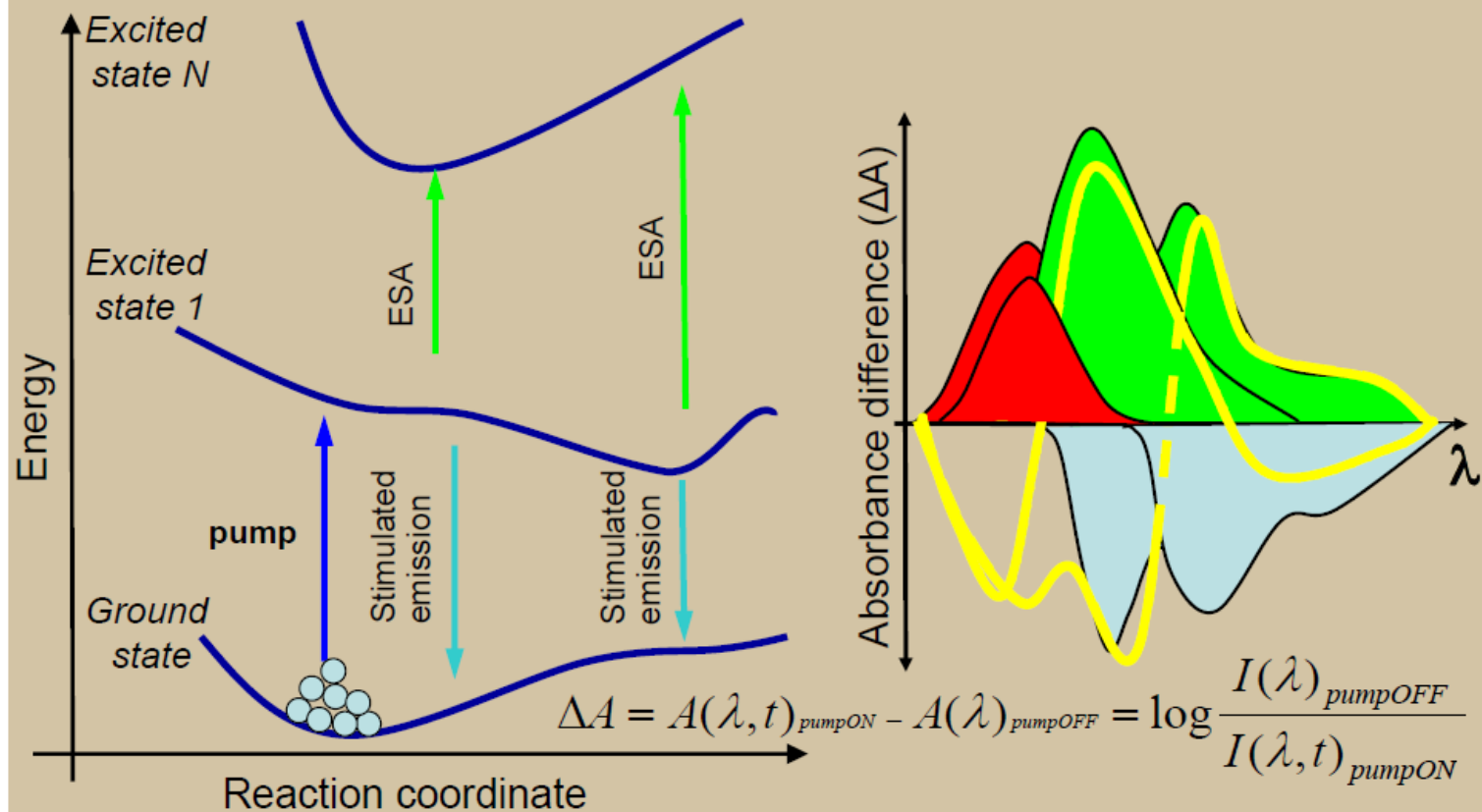


Absorbance changes

$$\Delta OD = OD(\lambda, t)_{pumpON} - OD(\lambda)_{pumpOFF} = \log \frac{I(\lambda)_{pumpOFF}}{I(\lambda, t)_{pumpON}}$$



Time-resolved absorption changes monitor photodynamics



<http://www.youtube.com/watch?v=mdNr6eVBJqk>

Electron transfer – case study

J. Phys. Chem. B **2002**, *106*, 1299–1306

1299

Biomimetic Electron Transfer Using Low Energy Excited States: A Green Perylene-Based Analogue of Chlorophyll *a*

Aaron S. Lukas, Yongyu Zhao, Scott E. Miller, and Michael R. Wasielewski*

*Department of Chemistry and Center for Nanofabrication and Molecular Self-Assembly,
Northwestern University, Evanston, Illinois 60208-3113*

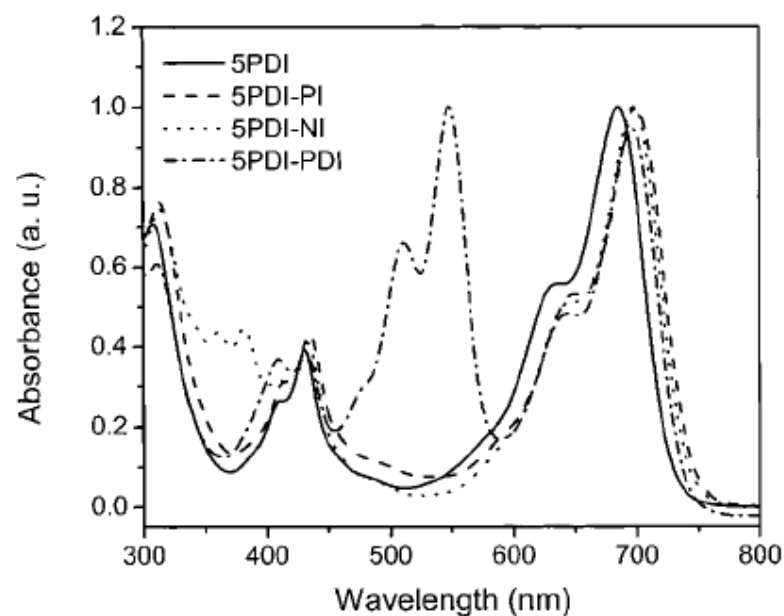
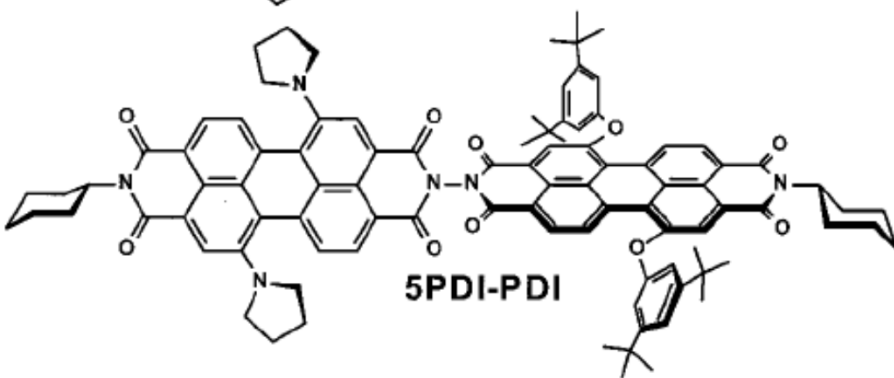
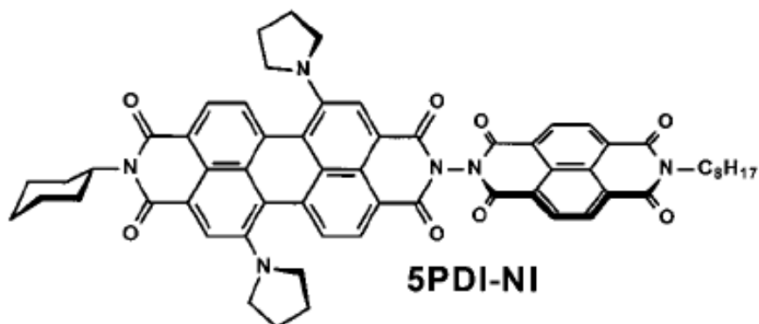
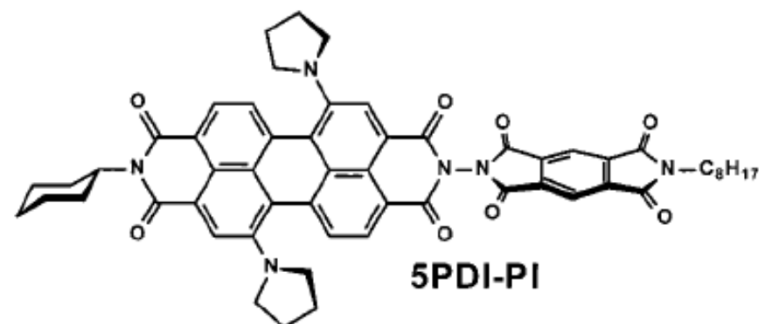
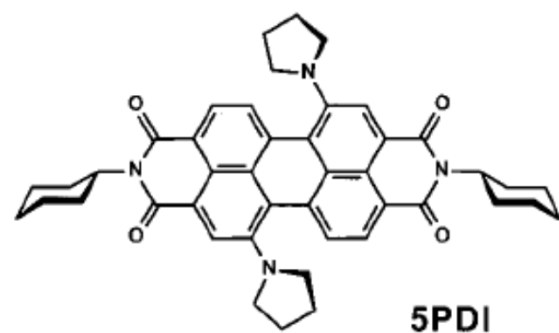


TABLE 1: Steady State Properties of Compounds

compd	toluene				MTHF			
	λ_{Abs}	λ_{Em}	E_S	Φ_F	λ_{Abs}	λ_{Em}	E_S	Φ_F
5PDI	686	721	1.77	0.35	683	733	1.76	0.28
5PDI-PI	696	740	1.73	0.21	697	745	1.73	0.01
5PDI-NI	696	735	1.73	0.01	696	744	1.73	<0.001
5PDI-PDI	695	742	1.74	0.13	695	742	1.73	<0.001

TABLE 2: Redox Potentials of Compounds in PrCN (V vs SCE)

compd	E_{5PDI}^{+1}	E_{5PDI}^{+2}	E_{5PDI}^{-1}	E_{5PDI}^{-2}	E_{ACC}^{+1}	E_{ACC}^{-1}
5PDI	0.68	0.75	-0.76	-0.94		
5PDI-PI	0.74	0.81	-0.62	-0.84	>2.0	-0.72
5PDI-NI	0.74	0.82	-0.71	-0.87	>2.0	-0.40
5PDI-PDI	0.75	0.82	-0.70	-0.89	>2.0	-0.47

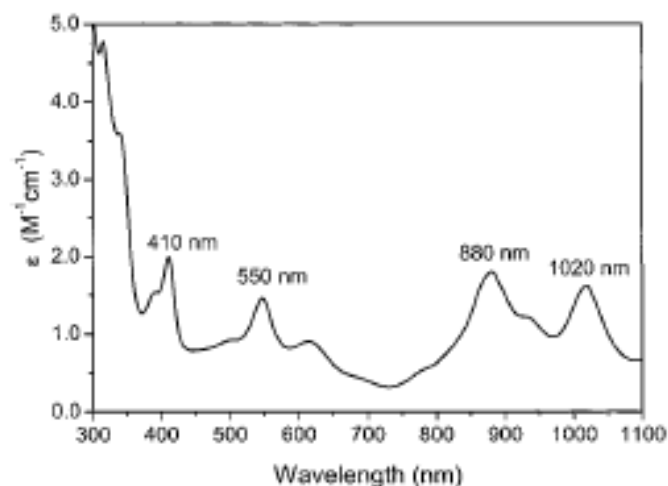


Figure 2. Electrochemically generated ground-state spectrum of the 5PDI⁺ in CH₂Cl₂.

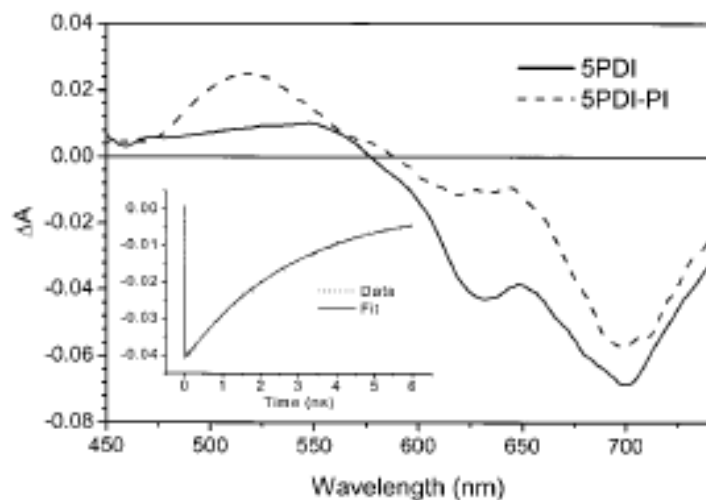


Figure 3. Transient absorption spectra of the indicated compounds in toluene at $\tau = 500$ ps following excitation with a 420 nm, 130 fs laser flash. Inset: Transient absorption kinetics monitoring changes in ΔA at 700 nm with the associated fits to the data.

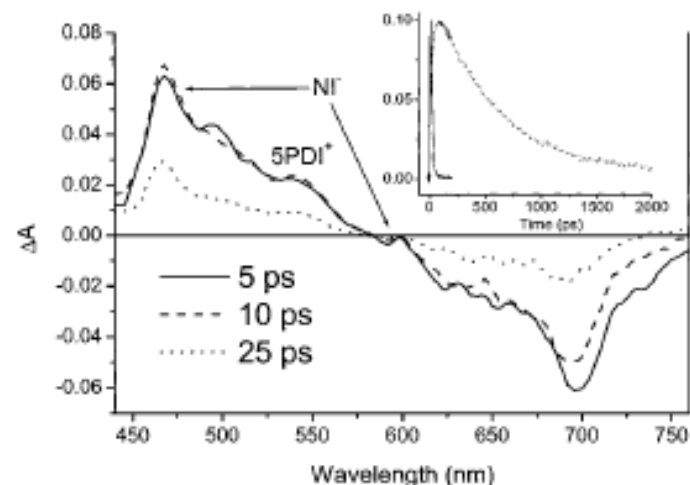
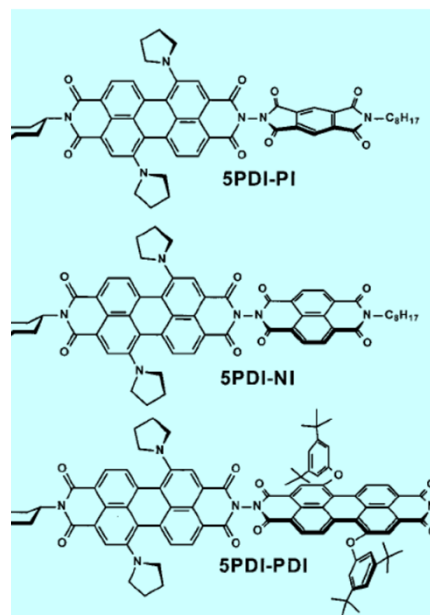


Figure 4. Transient absorption spectra of 5PDI-NI in MTHF at the indicated times following excitation with a 420 nm, 130 fs laser flash. Inset: Kinetics monitoring the rise and decay of the 470 nm absorption arising from the NI⁻ anion radical in toluene (---) and MTHF (—) with the associated fits to the data.

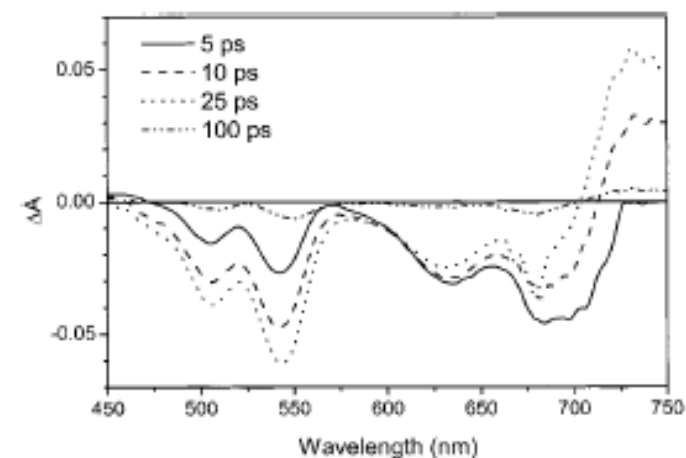


Figure 5. Transient absorption spectra of 5PDI-PDI in toluene at the times indicated following excitation with a 420 nm, 130 fs laser flash.

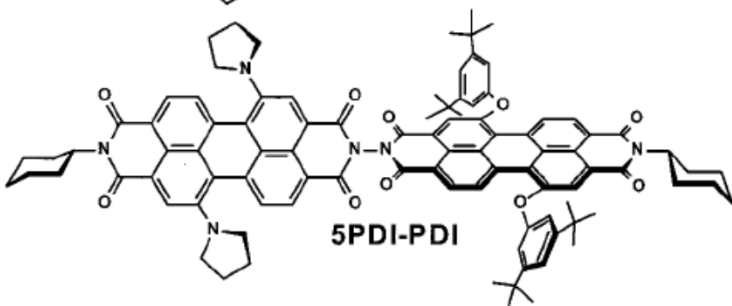
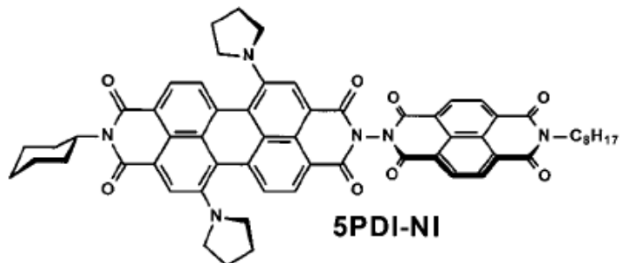
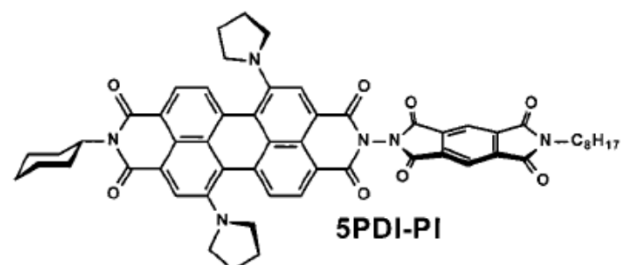
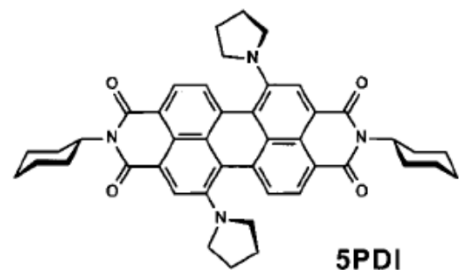


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TABLE 3: Free Energies and Time Constants for CS and CR

	ΔG_{CS} (eV)	τ_{CS} (ps)	ΔG_{CR} (eV)	τ_{CR} (ps)
Toluene				
5PDI-PI	0.00	8100	-1.73	
5PDI-NI	-0.32	40	-1.41	550
5PDI-PDI	-0.29	50	-1.45	2000
MTHF				
5PDI-PI	-0.24	50	-1.49	370
5PDI-NI	-0.56	6	-1.17	13
5PDI-PDI	-0.49	13	-1.24	300

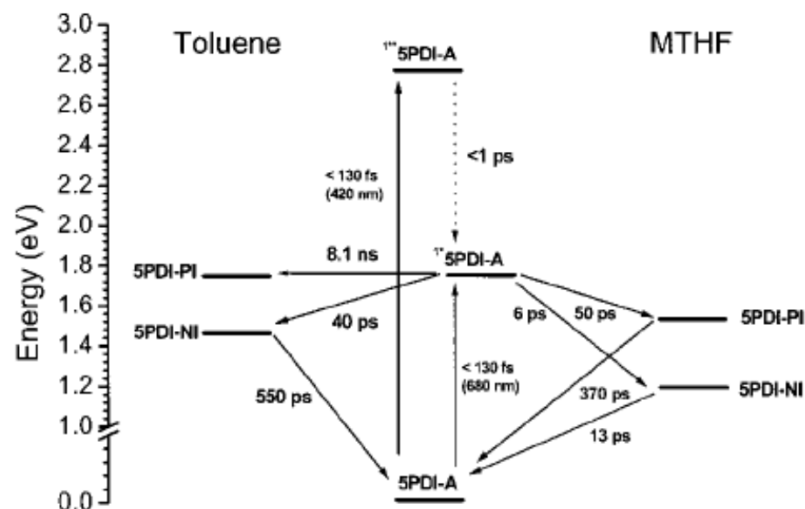


Figure 9. Energy level diagram for 5PDI-PI and 5PDI-NI in toluene and MTHF.

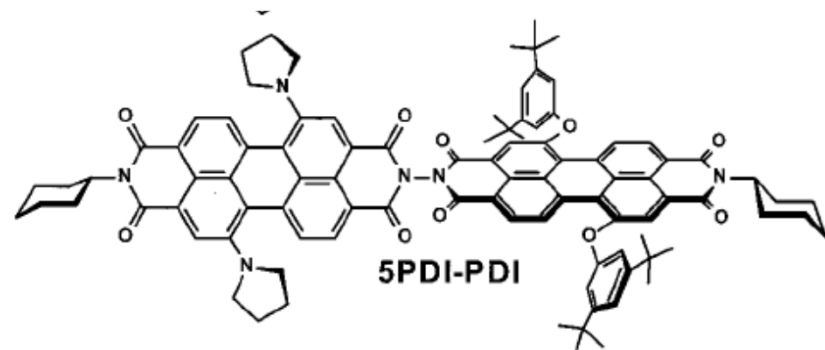


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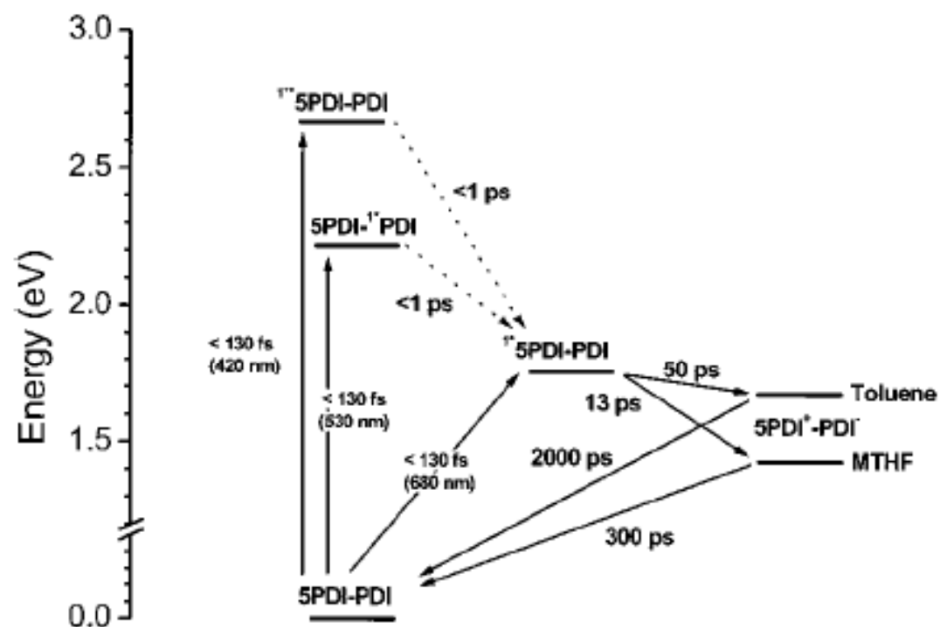
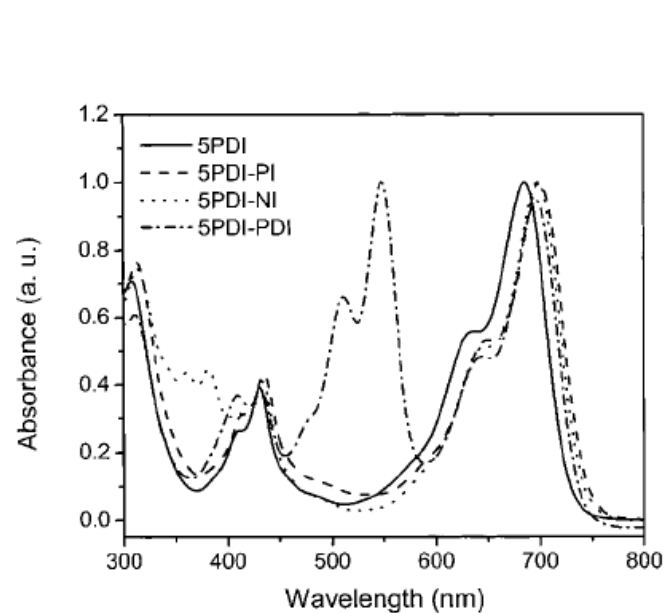
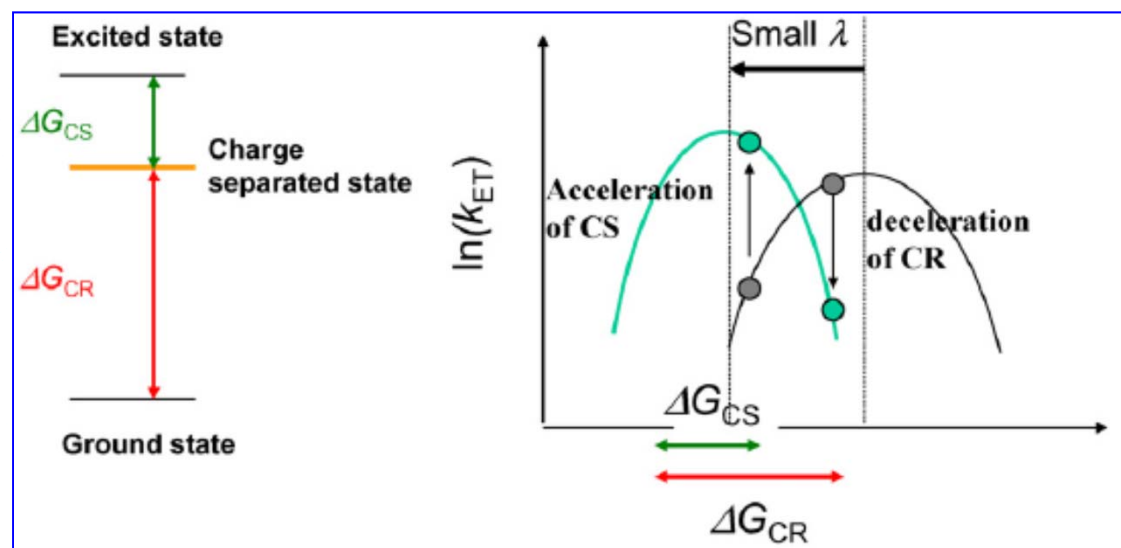
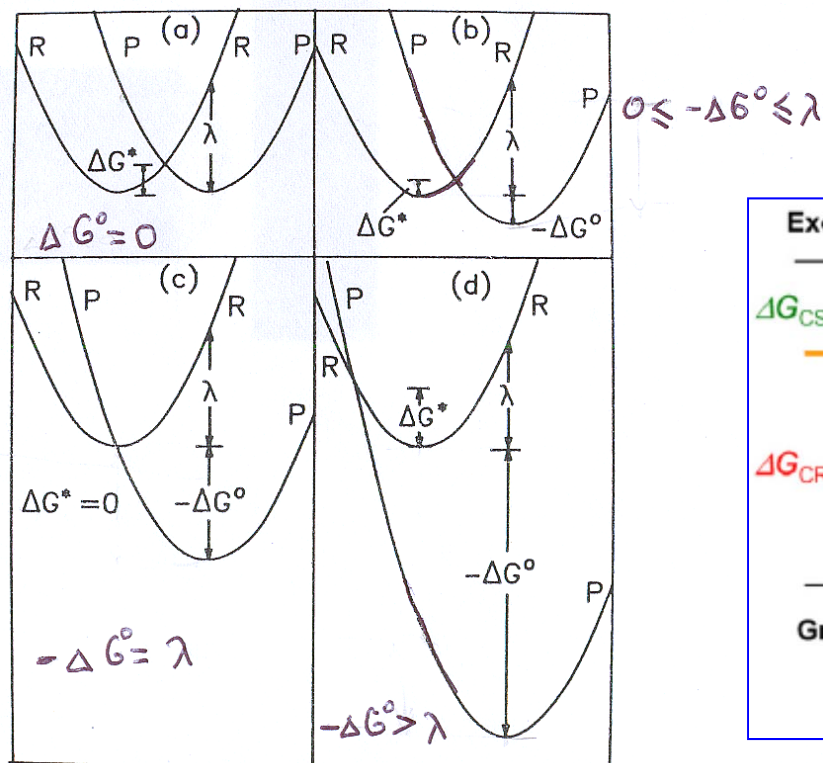


Figure 10. Energy level diagram for 5PDI-PDI in toluene and MTHF.

Small reorganization energy

The thermodynamic maximum ($-\Delta G_{ET} = \lambda$) and, therefore, access to the 'inverted-region' ($-\Delta G_{ET} > \lambda$) should be reached with relative ease if λ is **low**. Now, it is easier to get strongly exothermic shifts deep into the 'inverted-region', as charge-recombination processes typically are, and their rate is largely slowed-down. An additional benefit of a small λ value is that the 'normal-region' ($-\Delta G_{ET} < \lambda$) becomes steeper, which is expected to accelerate the charge separation.



Reorganization energies (including solvent reorganization) for C_{60} are not exceeding 0.6 eV, while other acceptors show 1-1.2 eV

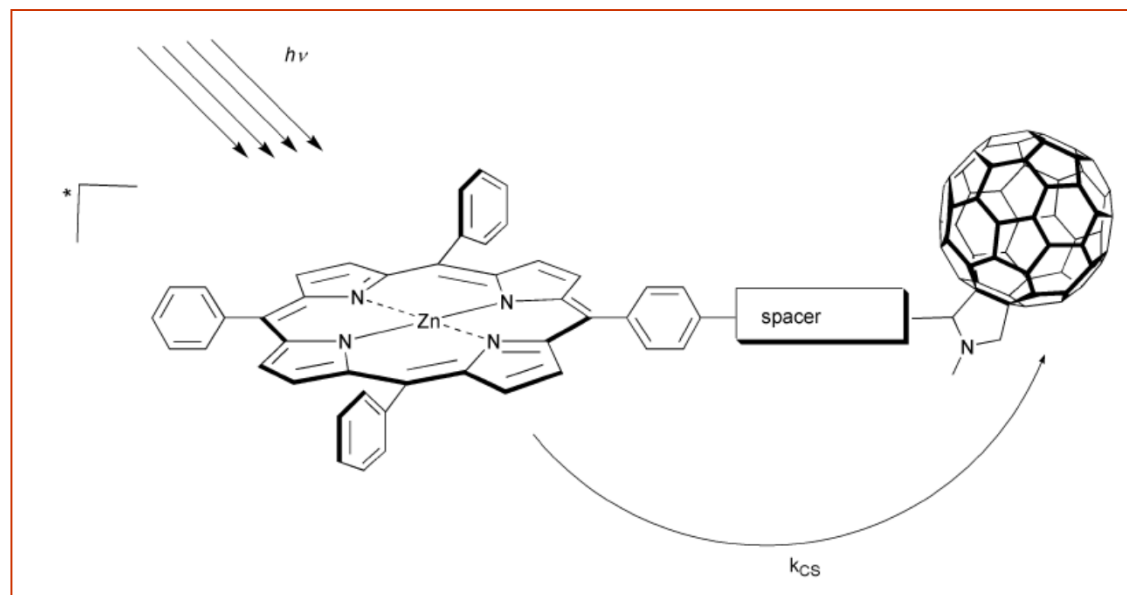
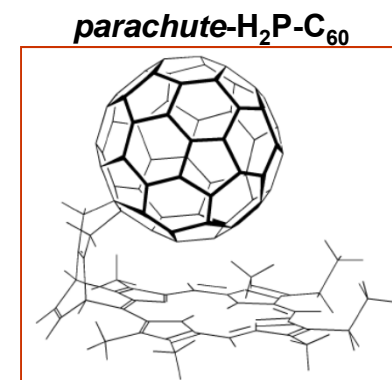


Table 1 Lifetimes of charge-separated states in various (ZnP/ C_{60})-based donor-acceptor ensembles at room temperature

Compound	THF	Benzonitrile	DMF	Solvent polarity
<i>trans</i> -2-ZnP- C_{60}	385 ps	38 ps		
<i>parachute</i> -ZnP- C_{60}	99 ps	69 ps	56 ps	
<i>parachute</i> -H ₂ P- C_{60}	314 ps	155 ps	107 ps	
<i>pyrrole</i> -ZnP- C_{60}		50 ps		
<i>pyrrole</i> -H ₂ P- C_{60}		290 ps		
<i>equatorial</i> -ZnP- C_{60}	2.6 μ s	1.1 μ s	0.21 μ s	
<i>meta</i> -ZnP- C_{60}	215 ns	113 ns	99 ns	
<i>para</i> -ZnP- C_{60}	236 ns	149 ns	133 ns	
<i>norbornylogous</i> -ZnP- C_{60}		420 ns		
<i>amide</i> -ZnP- C_{60}	2.7 μ s	0.78 μ s	0.57 μ s	
ZnP-H ₂ P- C_{60}	34 μ s	21 μ s	20 μ s	
Fc-ZnP- C_{60}	3.7 μ s	7.5 μ s	16 μ s	

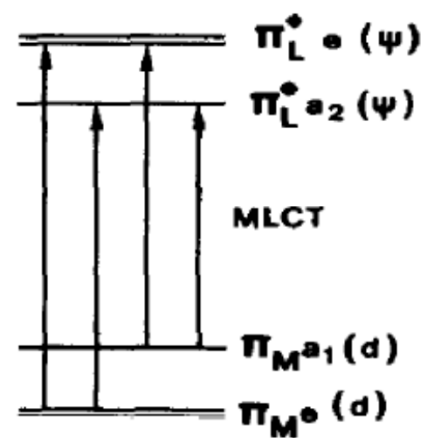
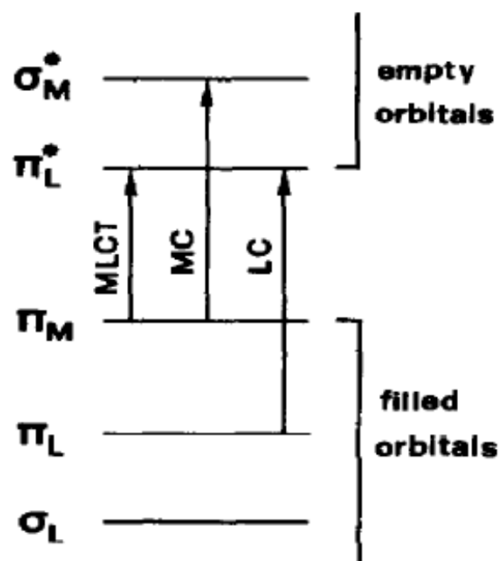
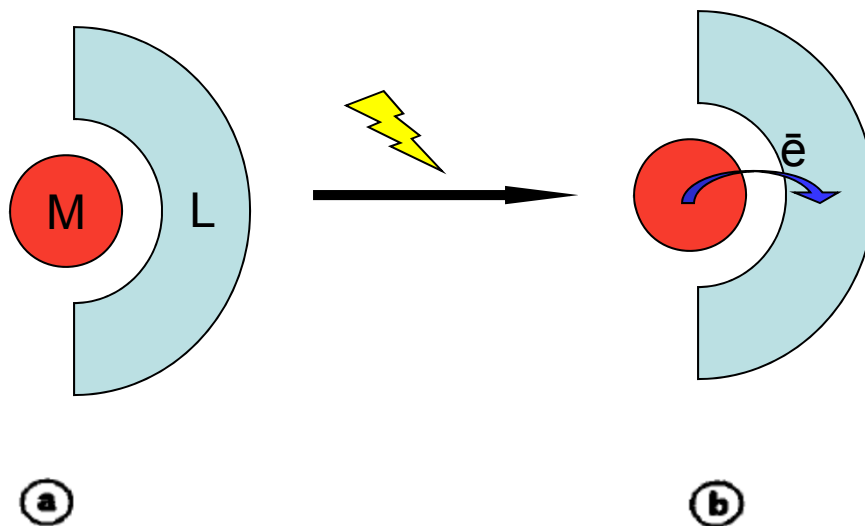


Charge transfer in metal complexes

MLCT

LUMO
(π^* of the
ligand)

HOMO
(metal based)



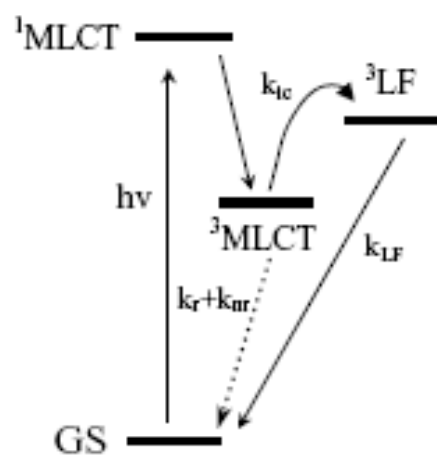
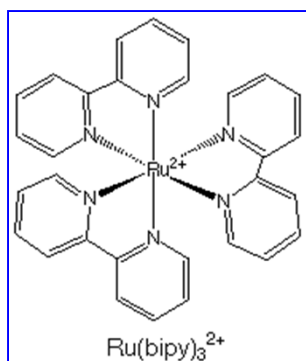


Fig. 1. State diagram for $[\text{Ru}(\text{bpy})_3]^{2+}$.

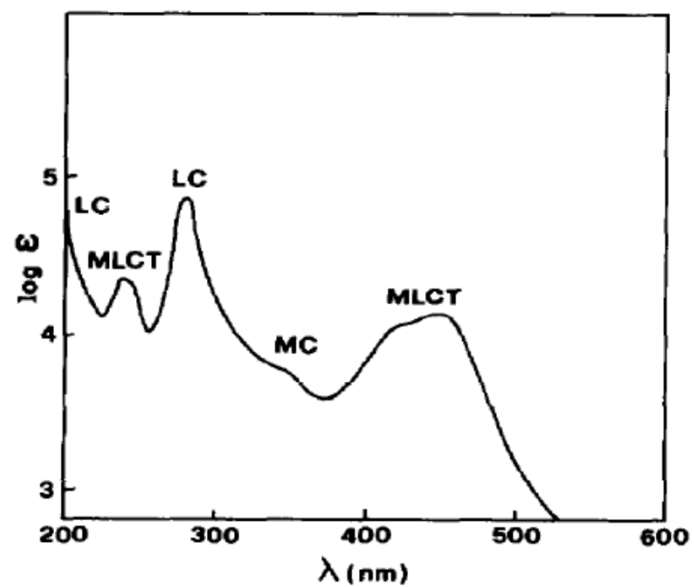
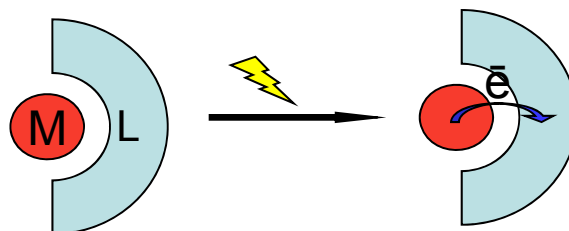


Fig. 17. Electronic absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$.



Organic Light Emitting Diodes and Metal Complexes

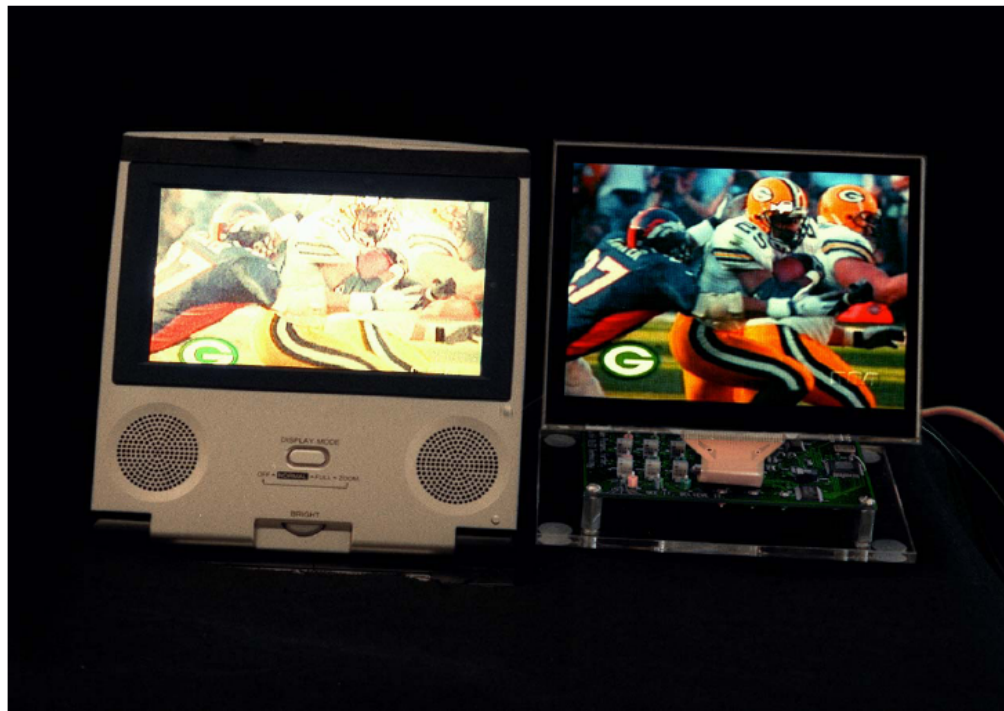
Sony 13" full color display



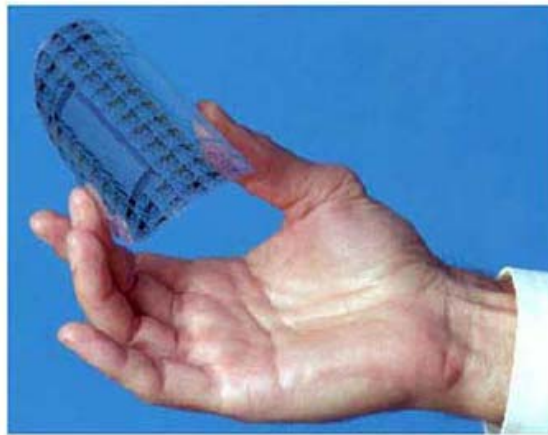
The largest OLED display prototype as of May 2005, at 40 inches.

Organic Light Emitting Diodes

are thin-film, light-emitting devices that typically consist of a series of organic layers between two electrical contacts



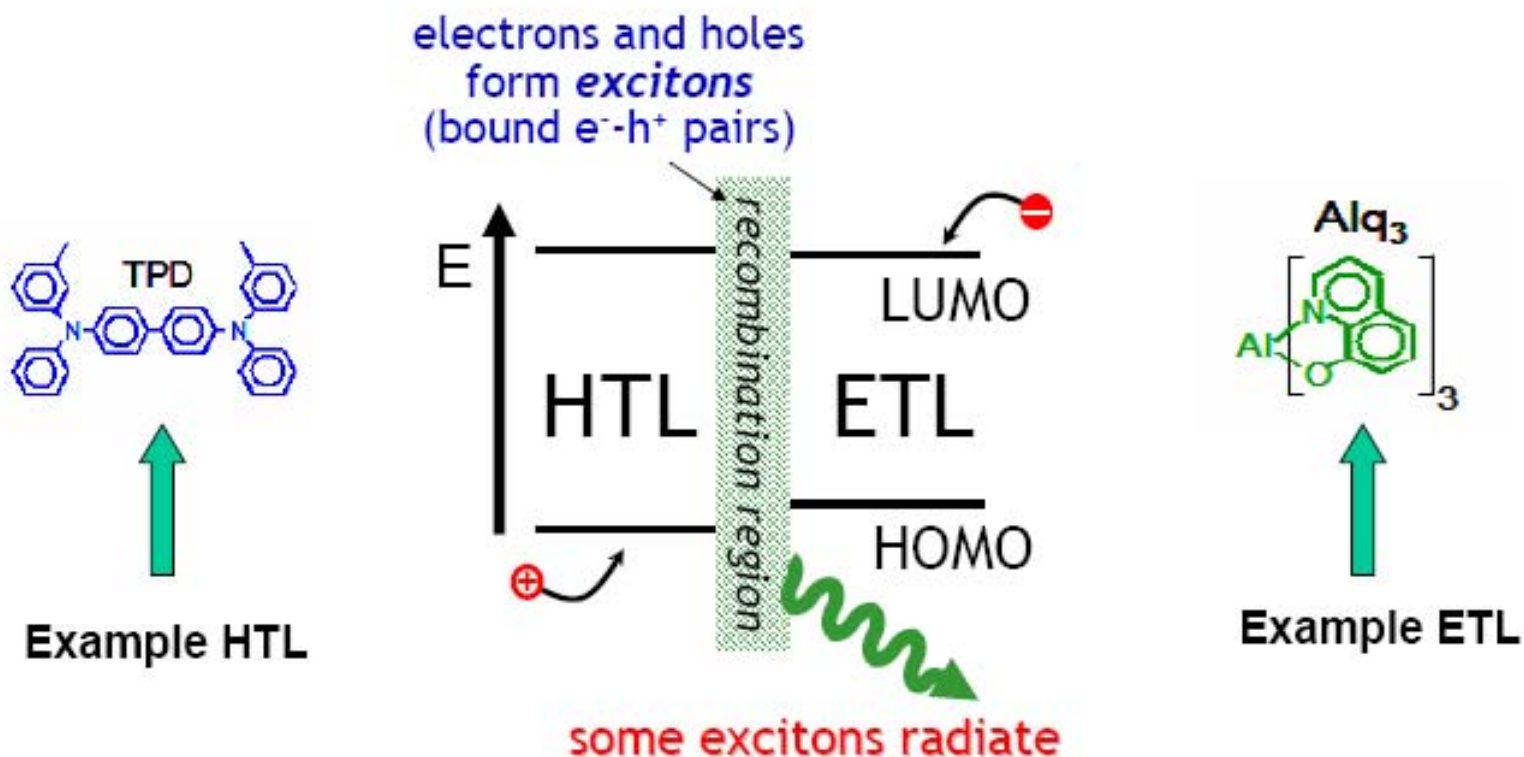
Products



Technology

- Small Molecule OLED technology was developed by **Eastman-Kodak** and is usually referred to as "small-molecule" OLED. The production of small-molecule displays requires vacuum deposition which makes the production process expensive and not so flexible. The term OLED traditionally refers to this type of device, though some are using the term SM-OLED.
- A second technology, developed by **Cambridge Display Technologies or CDT**, is called LEP or Light-Emitting Polymer, though these devices are better known as polymer light-emitting diodes (PLEDs). No vacuum is required, and the emissive materials can be applied on the substrate by a technique derived from commercial inkjet printing. This means that PLED displays can be made in a very flexible and inexpensive way.
- Recently a third hybrid light-emitting layer has been developed that uses nonconductive polymers doped with light-emitting, conductive molecules. The polymer is used for its production and mechanical advantages without worrying about optical properties. The small molecules then emit the light and have the same longevity that they have in the SM-OLEDs.

Background: Organic Light-Emitting Devices



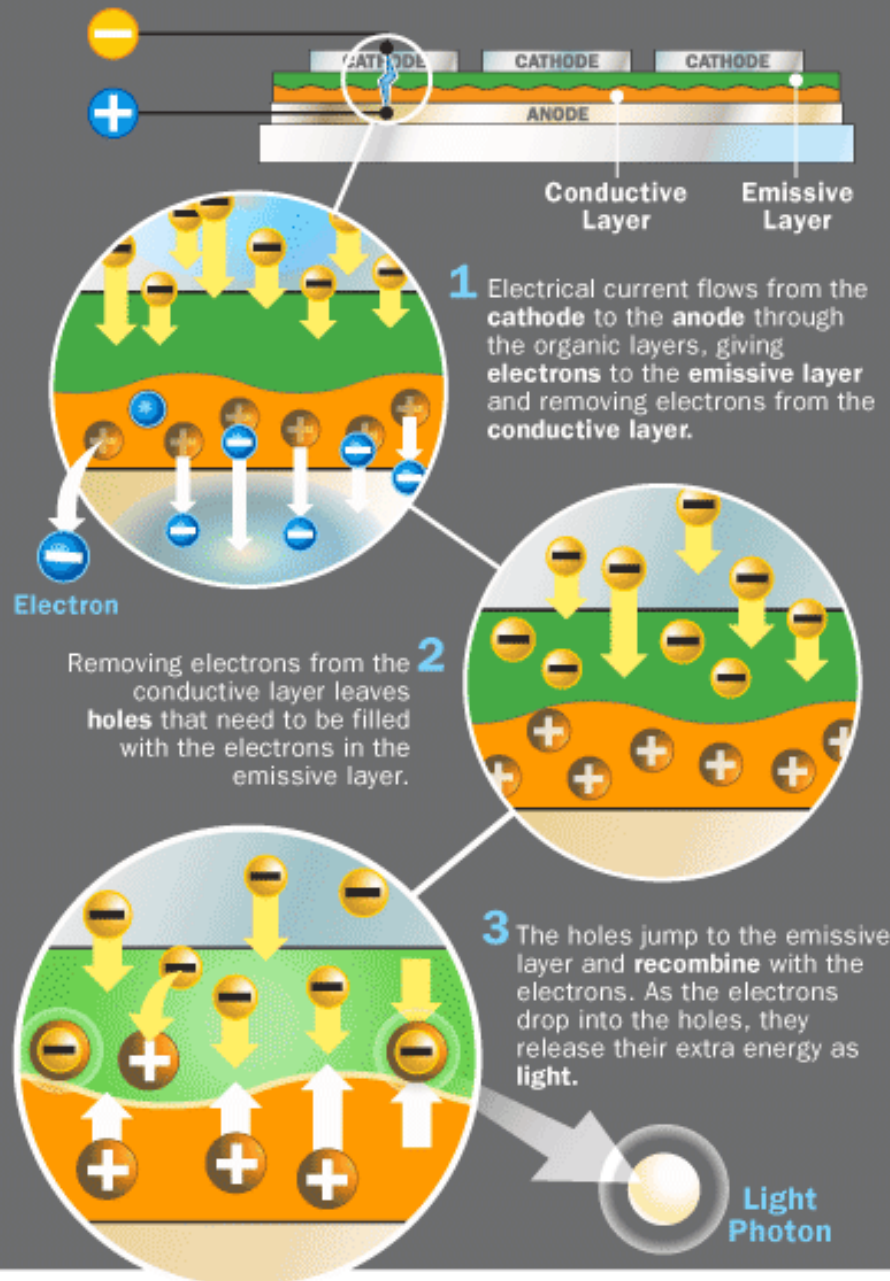
<http://www.adsdyes.com/oled-s-holetransport.html>

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

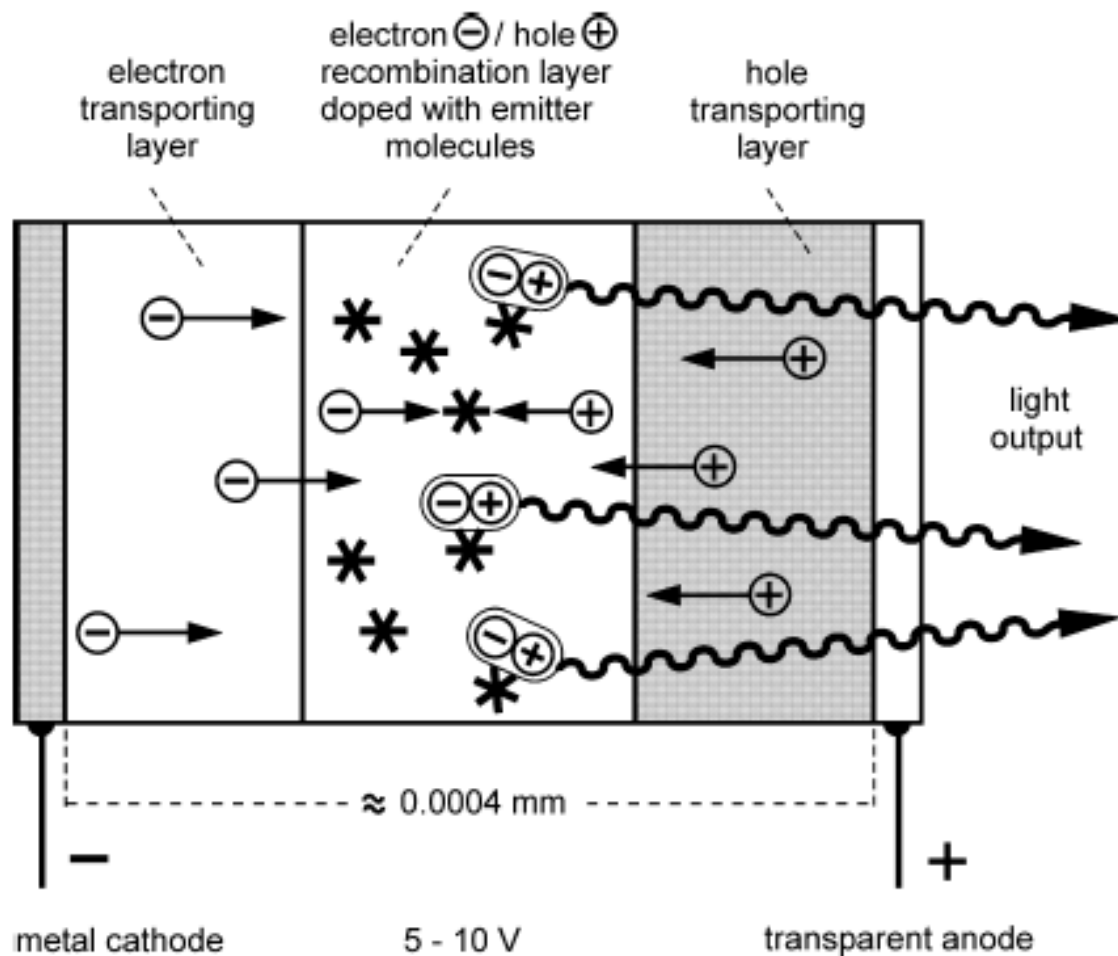
<http://www.adsdyes.com/oled-s-oligomers.html>

OLED Creating Light

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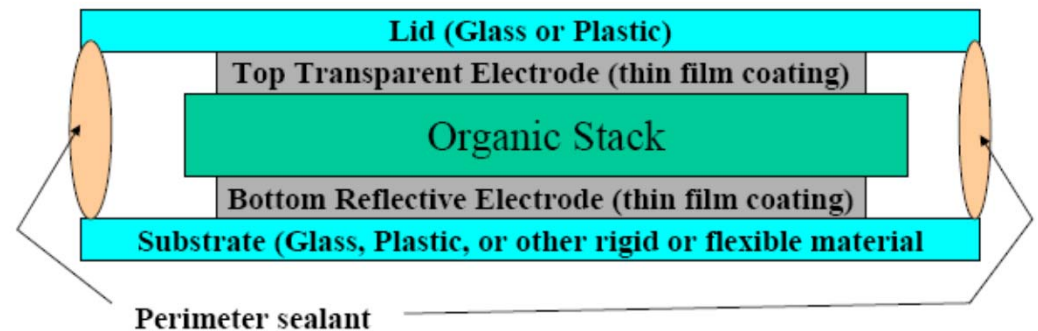
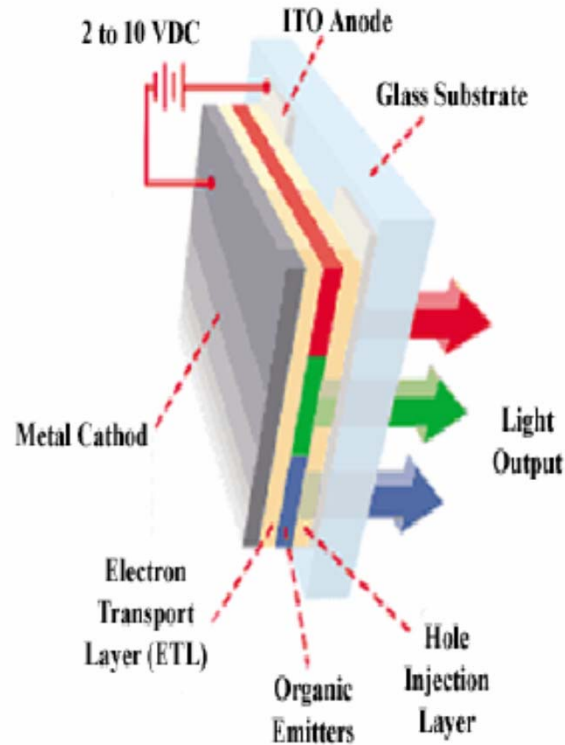
Device Architecture



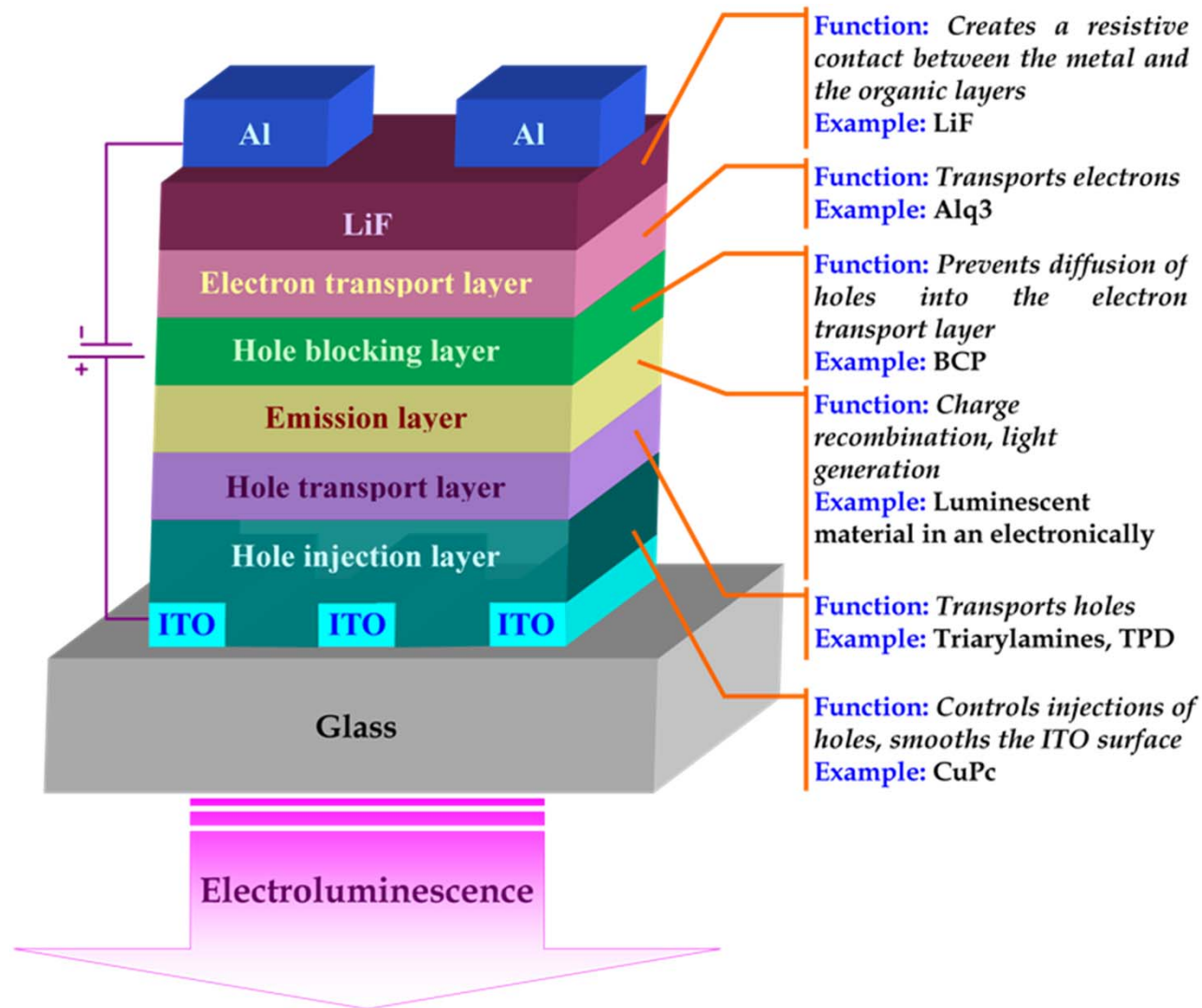
Hartmut Yersin

Top Curr Chem (2004) 241:1-26

Engineering

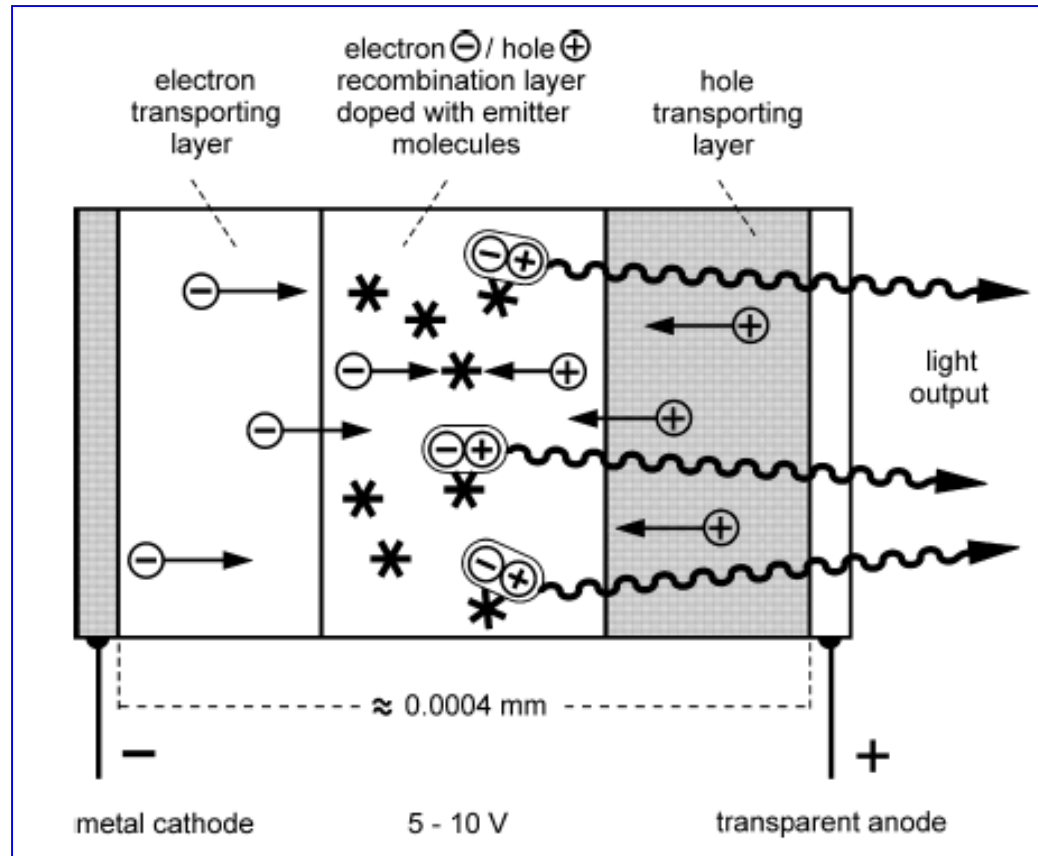


The biggest technical problem left to overcome has been the limited lifetime of the organic materials. Particularly, current materials used as blue OLEDs typically have lifetimes of around 1,000 hours when used for flat panel displays, which is lower than typical lifetimes of LCD or Plasma technology. However, recent experimentation has shown that it's possible to swap the **fluorescent** chemical component for a more stable **phosphorescent** one.



Schematic illustration of multi layer structure of small molecule based OLED

Exciton formation



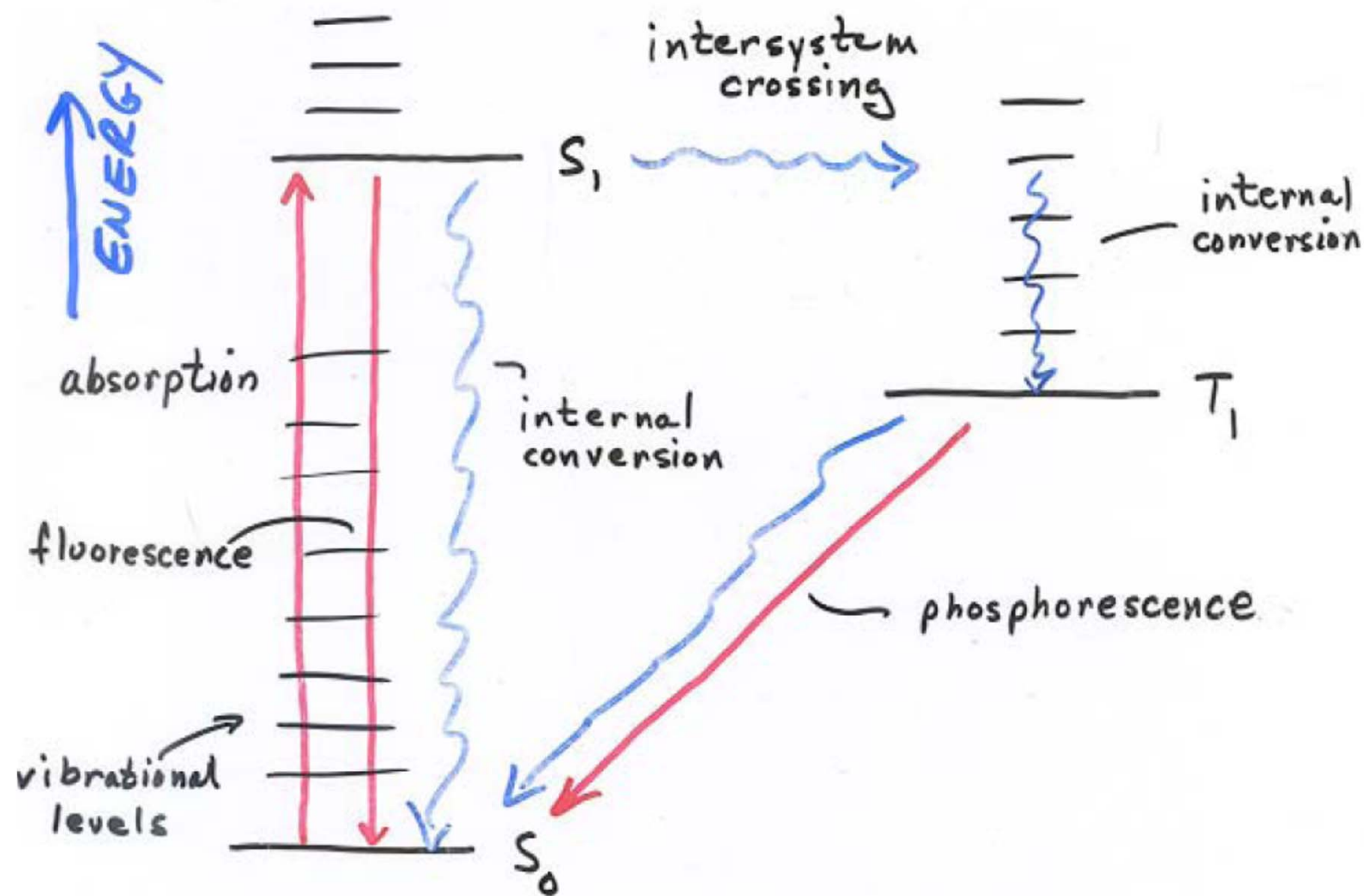
25% singlet and 75% triplet excitons
We want to harvest all of them!

How to get phosphorescence

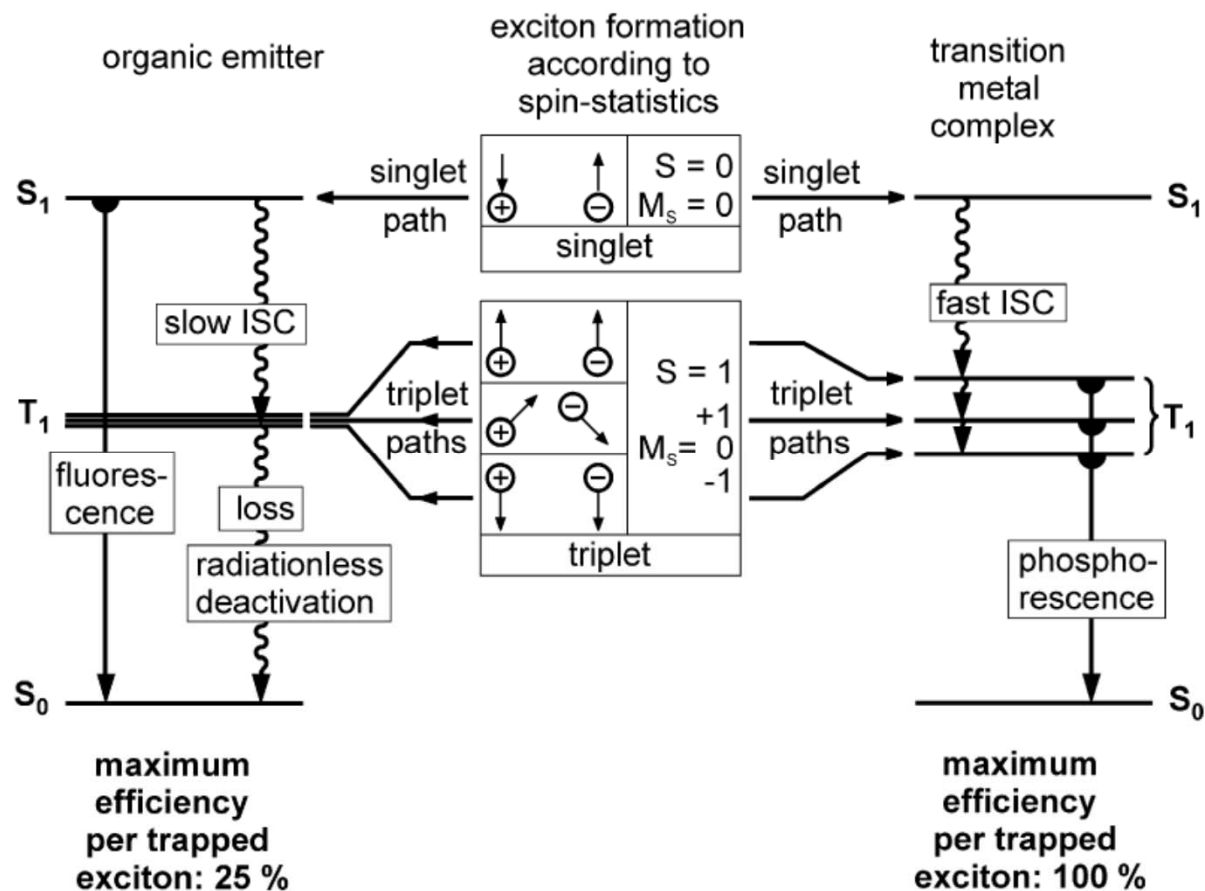
Many photophysical properties of the lowest excited triplet states and the corresponding transitions of organometallic compounds are essentially determined by the extent of metal participation in the wavefunctions. This **metal participation** not only alters the spatial extension of the wavefunctions, 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.

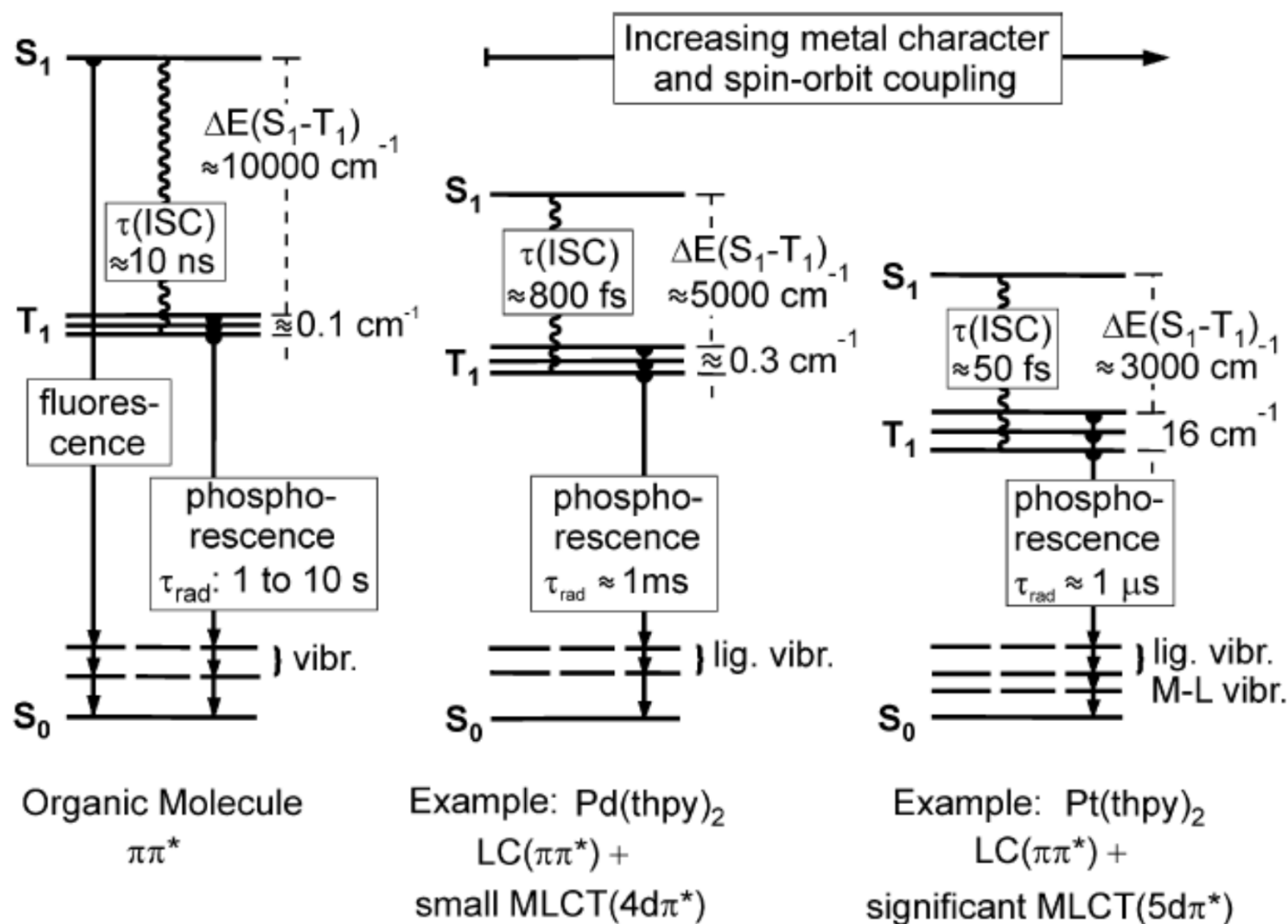
JABLONSKI DIAGRAM



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>

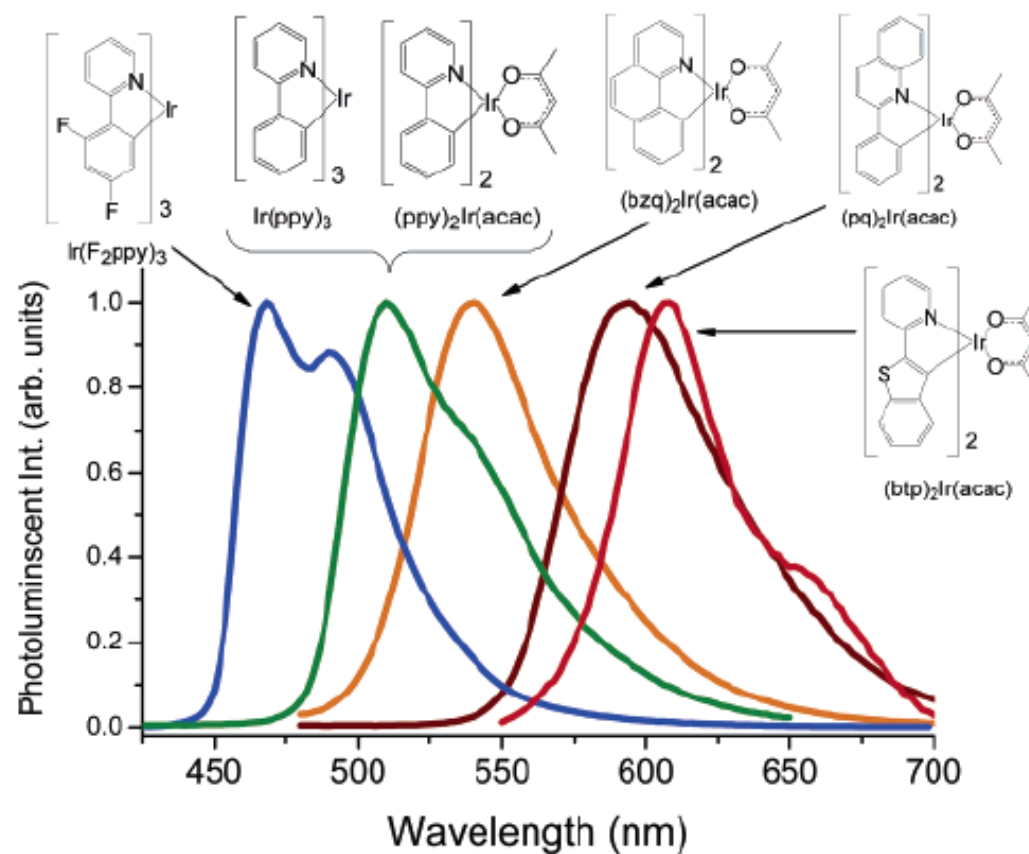


Figure 1. Photoluminescence spectra of Ir phosphors (room temperature, 2-MeTHF solutions).

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