

Steering and Separating Excitons in Organic Thin Films and Devices (Solar Cells)

Mark Thompson

Department of Chemistry
University of Southern California

Outline



Good efficiency: 16-20%
Moderately high cost

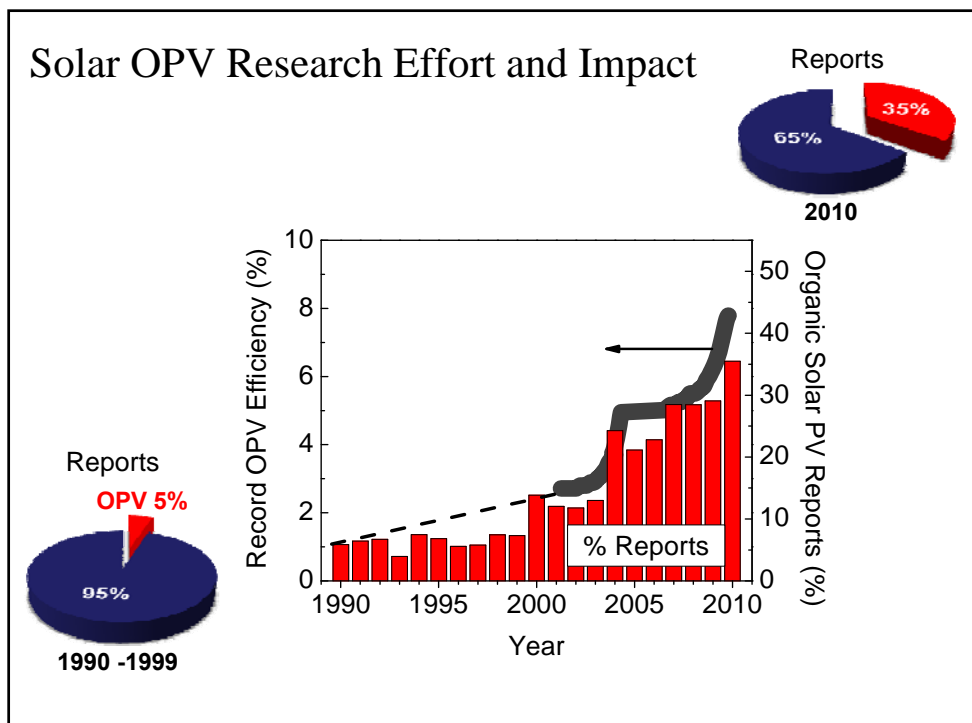
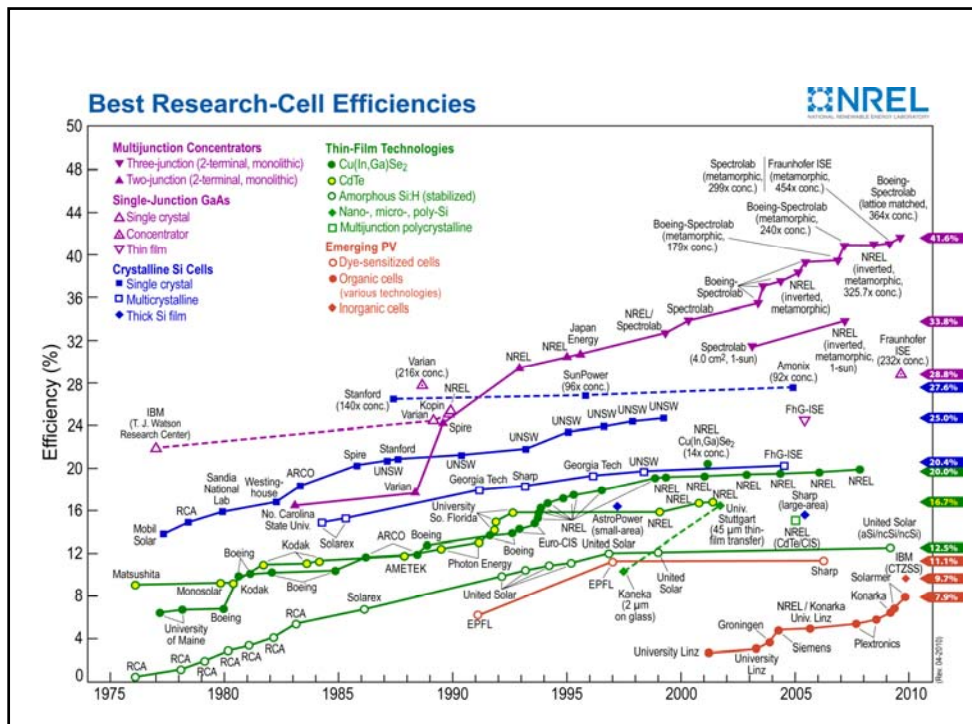


San Francisco bus stop

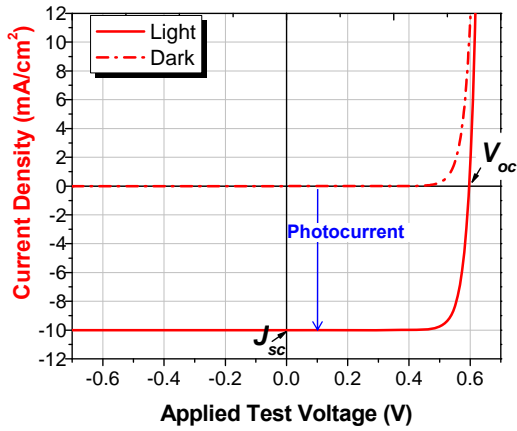
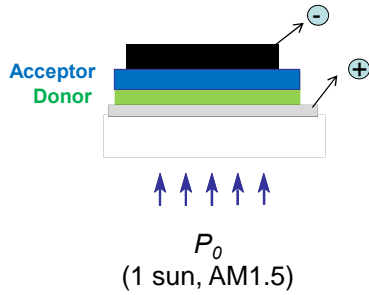
Promise of low cost
Low efficiency: panel = 3%,
Laboratory cell record = 8%

Today's talk:

- Issues with organic photovoltaics
- Open circuit voltage and what to do about it
- Exciton transfer and steering in organic materials



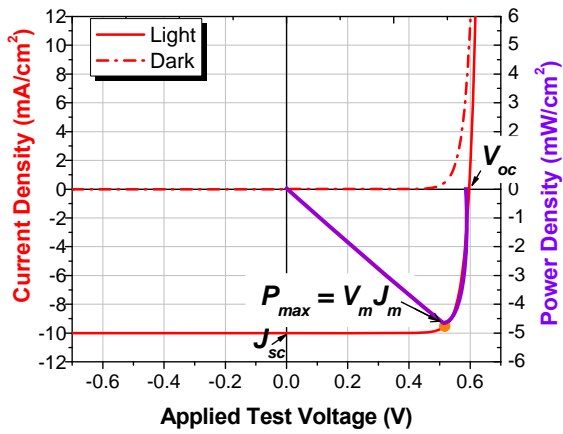
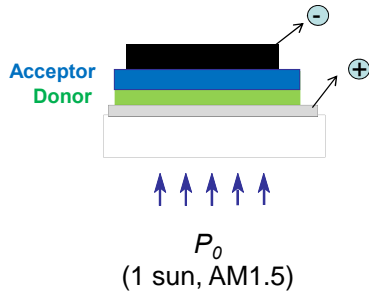
Solar Cell Efficiency



$$\text{Cell Efficiency} = \eta_p = \frac{J_{sc} \times V_{oc} \times FF}{P_o}$$

USC

Solar Cell Efficiency

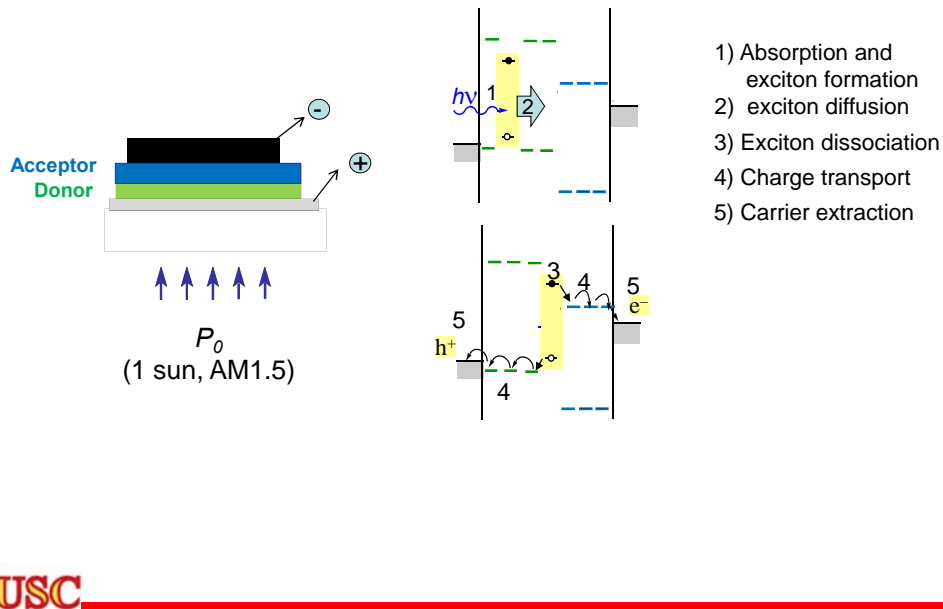


$$\text{Fill Factor} = FF = \frac{J_m V_m}{J_{sc} V_{oc}}$$

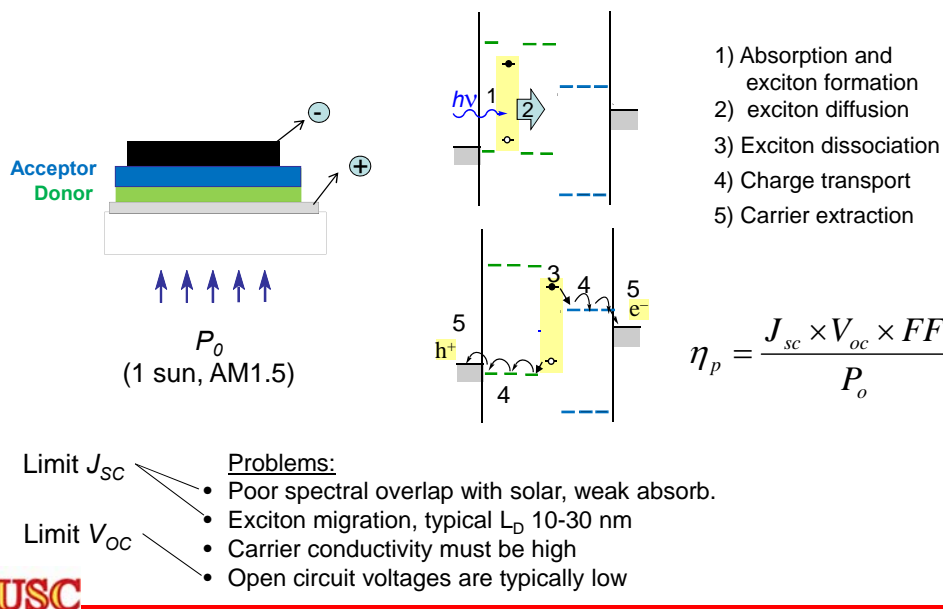
$$\text{Cell Efficiency} = \eta_p = \frac{J_{sc} \times V_{oc} \times FF}{P_o}$$

USC

Excitonic Mechanism for Organic photovoltaics

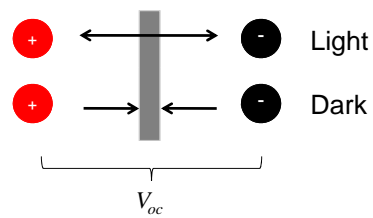
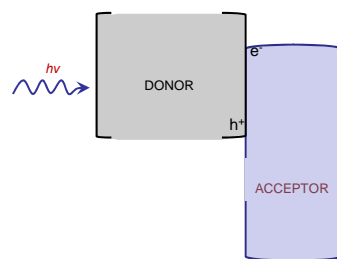
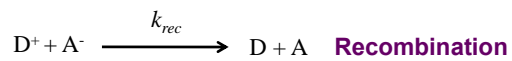


Limitations of Organic Photovoltaics



Kinetic Control of V_{OC}

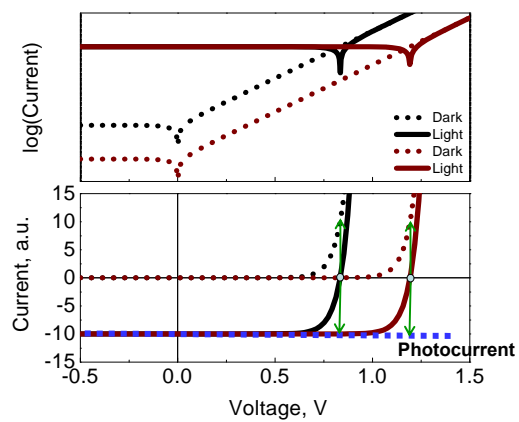
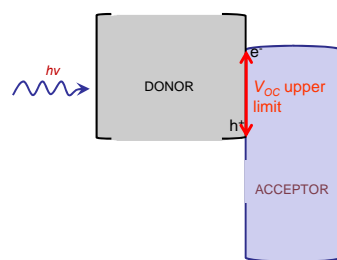
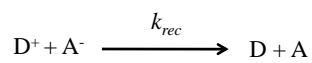
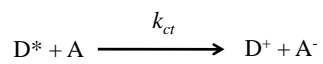
At V_{OC} the photocurrent is cancelled out by the injected current: steady state



USC

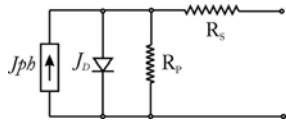
Kinetic Control of V_{OC}

At V_{OC} the photocurrent is cancelled out by the injected current: steady state



USC

Solar cell physics



$$J = \frac{R_p}{R_s + R_p} \left\{ J_s \left[\exp\left(\frac{q(V - JR_s)}{nkT}\right) - 1 \right] + \frac{V}{R_p} \right\} - J_{ph}(V)$$

$$R_p \rightarrow \infty$$

$$J = J_s \left[\exp\left(\frac{q(V - JR_s)}{nkT}\right) - 1 \right] - J_{ph}$$

$$\text{at } V = V_{oc}, J_{ph} = J_{sc}$$

$$V_{oc} \approx \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_s}\right)$$

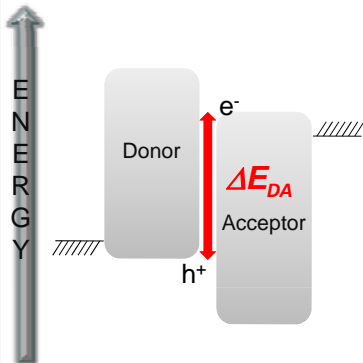
Light
Dark

- **R_s , Series resistance** : carrier mobilities, contact resistance
- **R_p , Parallel resistance**
- **J_D , Diode current** : Shockley equation)
- **J_{ph} , photocurrent**: illumination
- **J_s , saturation dark current**
- **n , diode ideality factor**

USC

Fahrenbruch, A. L.; Aranovich, J., *Solar Energy Conversion - Solid-State Physics Aspects*. (1979).
B. P. Rand, et. al., *Phys. Rev. B* (2007)

Controlling V_{oc}



- V_{oc} should correlate with the energy gap: acceptor LUMO - donor HOMO
 - $V_{oc} \propto \Delta E_{DA}$
 - Observed for OPVs (polymer & molecular)
- ΔE_{DA} controls the dark current

$$J_s \propto \exp(-\Delta E_{DA})$$

$$V_{oc} \approx \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_s}\right)$$

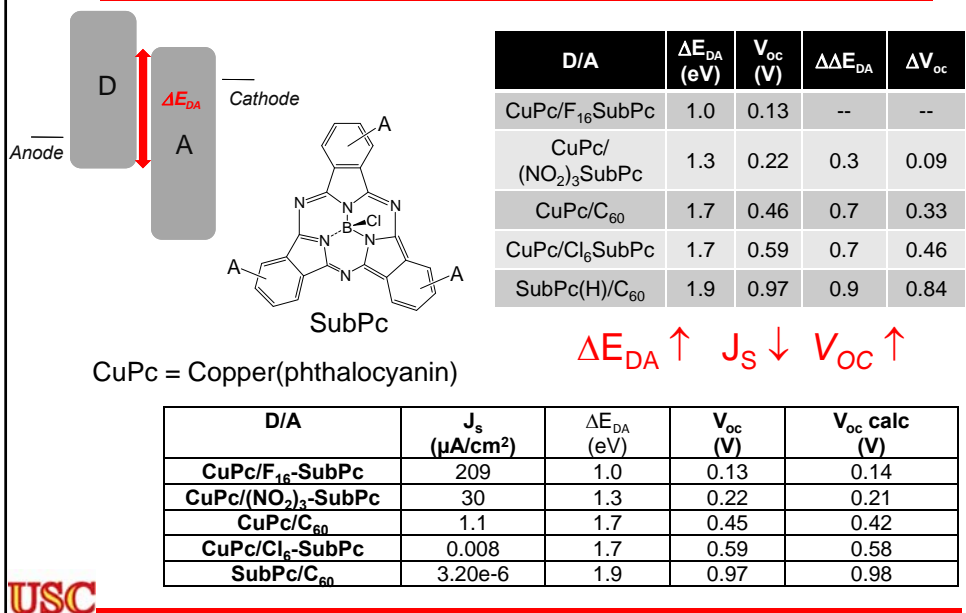
Light
Dark

$$\Delta E_{DA} \uparrow \quad J_s \downarrow \quad V_{oc} \uparrow$$

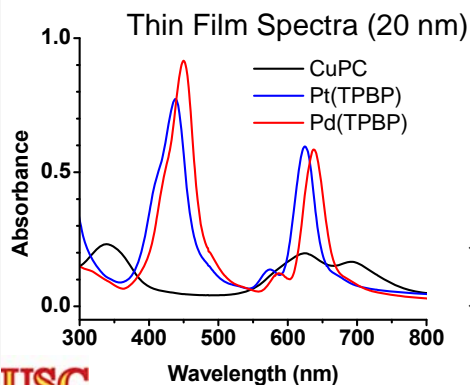
USC

Fahrenbruch, A. L.; Aranovich, J., *Solar Energy Conversion - Solid-State Physics Aspects*. (1979).
B. P. Rand, et. al., *Phys. Rev. B* (2007)

Device Performance of subPCs



Motivation for using Pt(TPBP) in photovoltaics



$$\alpha_{Pt} = 5.9 \times 10^5 \text{ cm}^{-1}$$

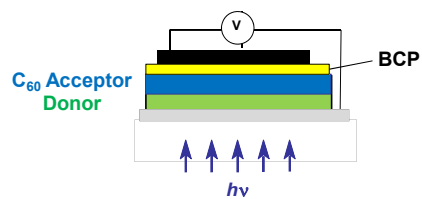
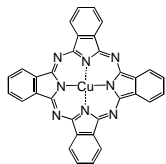
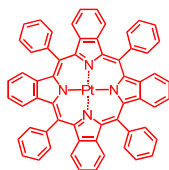
$$\alpha_{Pd} = 6.0 \times 10^5 \text{ cm}^{-1}$$

$$\alpha_{CuPc} = 2.1 \times 10^5 \text{ cm}^{-1}$$

- ✓ High absorption coefficient: initial interest was in the intense absorption not V_{oc}
- ✓ Soret, Q-band at similar (high) intensity

USC

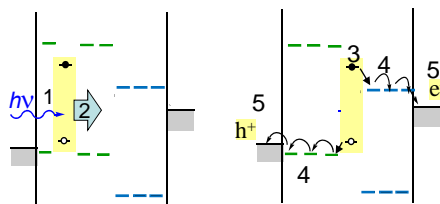
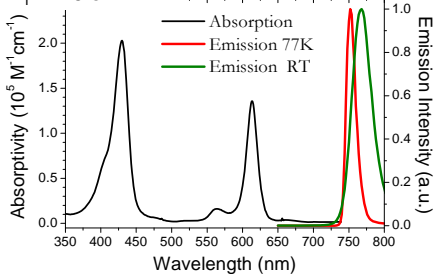
Motivation for using Pt(TPBP) in photovoltaics



Exciton energies

$$S_1 = 1.9 \text{ eV}$$

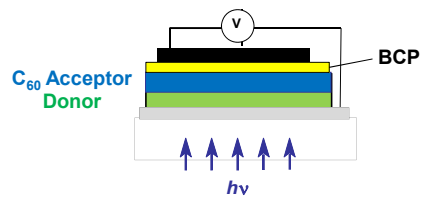
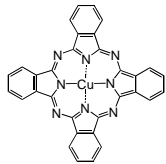
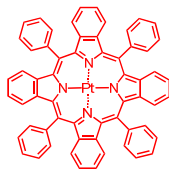
$$T_1 = 1.6 \text{ eV}$$



$$L_D = 6 \text{ nm}$$

USC

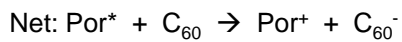
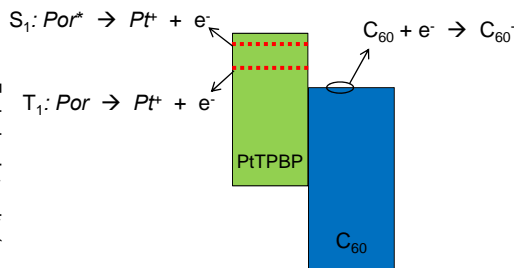
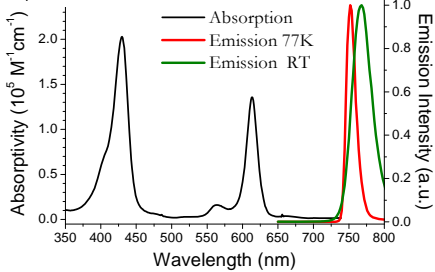
Motivation for using Pt(TPBP) in photovoltaics



Exciton energies

$$S_1 = 1.9 \text{ eV}$$

$$T_1 = 1.6 \text{ eV}$$

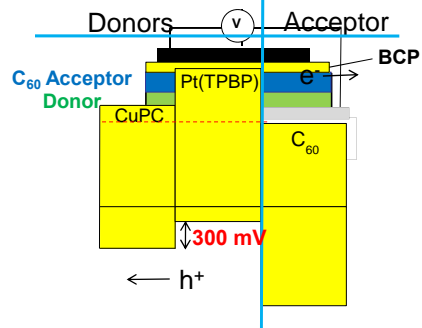
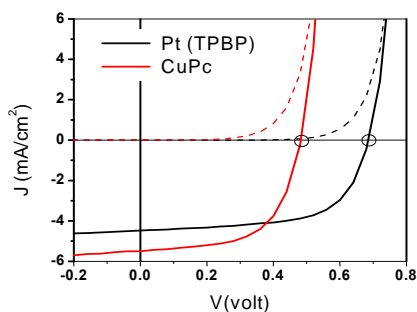


Driving force for exciton separation:

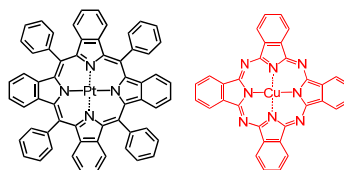
$$S_1 = 0.5 \text{ eV}, T_1 = 0.2 \text{ eV}$$

USC

Pt(TPBP) OPV performance

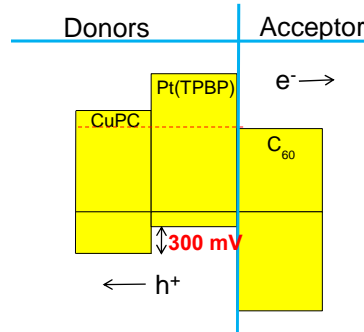
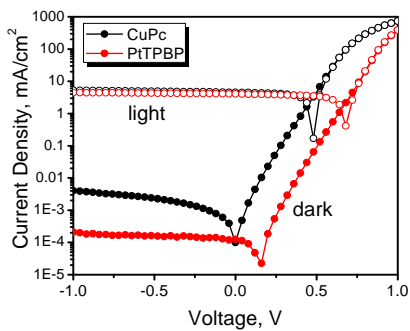


	J_{sc}	V_{oc}	FF	$\eta(\%)$
CuPc	5.51	0.482	0.60	1.59
PtTPBP	4.48	0.685	0.63	1.93



USC

Pt(TPBP) OPV performance



	J_{sc}	V_{oc}	FF	$\eta(\%)$	ΔE_{DA}	J_s ($\mu A/cm^2$)
CuPc	5.51	0.482	0.60	1.59	1.7	1.1
PtTPBP	4.48	0.685	0.63	1.93	1.4	0.02

$\Delta E_{DA} \downarrow \quad J_s \downarrow$

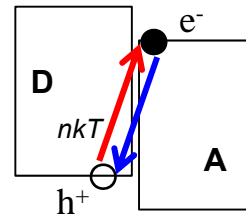
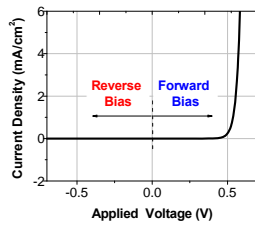
USC

Dark currents

- Source of J_S depends on the origin of dark current
 - For OPVs, recombination/generation dominates the dark current

$$J_S = J_{SO} \exp\left(\frac{-E_g}{nkT}\right)$$

$$J_S = J_{SO} \exp\left(\frac{-\Delta E_{DA}}{2nkT}\right)$$



$$\Delta E_{DA} = \text{HOMO}_D - \text{LUMO}_A$$

USC

Fahrenbruch, A. L.; Aranovich, J., *Solar Energy Conversion - Solid-State Physics Aspects*. (1979). Bube, H. R.; Fahrenbruch, A. L., *Advances in Electronics and Electron Physics*. (1981).

V_{oc} dependence

$$V_{oc} \approx \frac{nkT}{q} \ln\left(\frac{J_{SC}}{J_S}\right)$$

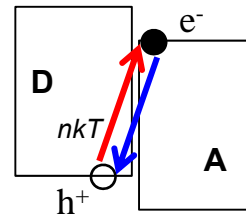
$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{SC}}{J_{SO}}\right) + \frac{\Delta E_{DA}}{2q}$$

$$J_S = J_{SO} \exp\left(\frac{-\Delta E_{DA}}{2nkT}\right)$$

⇒ What determines J_{SO} ?

- Density of States at the band edge
- Intermolecular coupling at the DA interface

Strongly related to the kinetics of charge generation/recombination:
Small J_{SO} = slow recombination



$$\Delta E_{DA} = \text{HOMO}_D - \text{LUMO}_A$$

USC

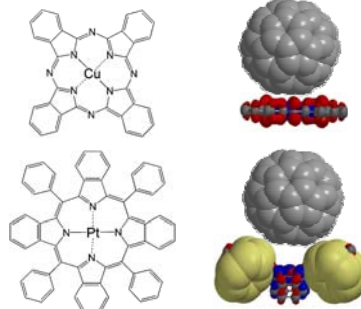
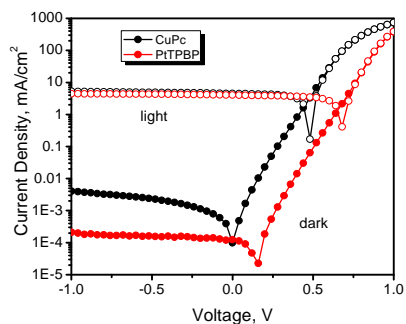
M.D. Perez, *et. al.*, *J. Am. Chem. Soc.*, **2009**
 W. J. Potscavage, *et. al.*, *Appl. Phys. Lett.* **2008**

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_s}\right)$$

J_{SO} : CuPc vs. PtTPBP

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_{so}}\right) + \frac{\Delta E_{DA}}{2q}$$

ITO/Donor/C₆₀(400Å)/BCP(100Å)/Al(1000Å)



Donor	J_{so} (mA/cm ²)	$\frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_{so}}\right)$ (V)	$\Delta E_{DA}/2q$ (V)	V_{oc} exp (V)
CuPc	1.5×10^4	-0.41	0.85	0.48
PtTPBP	12	-0.05	0.70	0.69

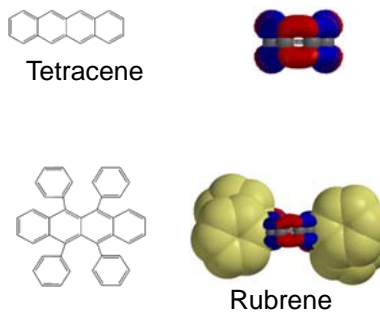
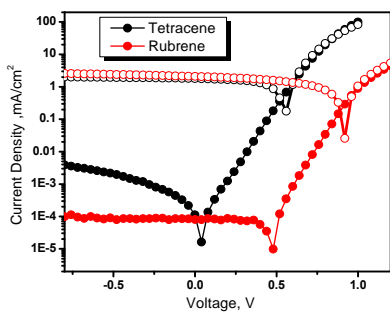
USC

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_s}\right)$$

J_{SO} : rubrene vs. tetracene

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_{so}}\right) + \frac{\Delta E_{DA}}{2q}$$

Donor/C₆₀(400Å)/BCP(100Å)/Al(1000Å)

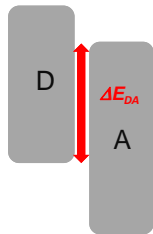


Donor	J_{so} (mA/cm ²)	$\frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_{so}}\right)$ (V)	$\Delta E_{DA}/2q$ (V)	V_{oc} exp (V)
Tetracene	150	-0.24	0.80	0.55
Rubrene	1.1	0.05	0.90	0.90

USC

Molecular shape , morphology and J_{SO}

Donor /C₆₀(400Å)/BCP(100Å)/Al(1000Å)



Donor	J_s ($\mu\text{A}/\text{cm}^2$)	J_{SO}	ΔE_{DA} (eV)	$V_{oc,exp.}$
subPC	3×10^{-3}	0.8	1.9	0.98
Rubrene	2.7×10^{-3}	1.1	1.8	0.9
NPD	5.17×10^{-3}	11	1.9	0.85
PtTPBP	0.020	12	1.4	0.69
Tetracene	0.077	150	1.6	0.55
PtOEP	0.081	5.1×10^3	1.8	0.52
CuPc	1.1	1.5×10^4	1.7	0.48

Nonplanar molecules increase D-A separation and slow carrier recombination.

High steric bulk = low J_{SO}

V_{OC} is largely unrelated to ΔE_{DA}

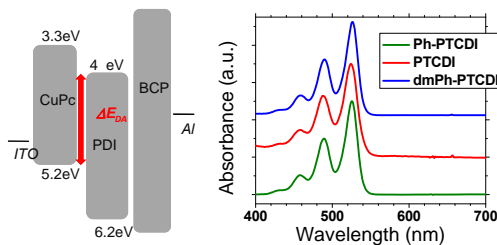
USC

M.D. Perez, et. al., *J. Am. Chem. Soc.*, 2009

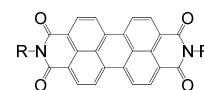
Acceptor variation

- Donor sterics controls V_{OC} how about acceptors?
- Perylene-diimides

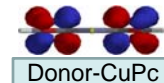
Acceptor	IPES (eV) ¹	DFT LUMO (eV) ²
PTCDI	4.04	3.7
Ph-PTCDI	3.95	3.6
dmPh-PTCDI	-	3.6



1: D.R.T. Zahn, et. al., *Chem. Phys.* 2006
2: P.I. Djurovich, et. al., *Org. Elect.* 2009

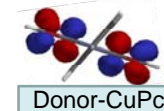


PTCDI
-H



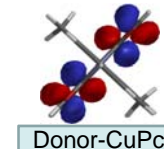
Ph-PTCDI

Dihedral = 60°



dmPh-PTCDI

Dihedral = 89°

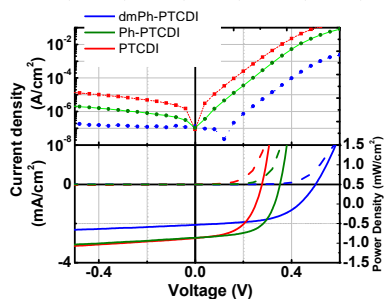


USC

Acceptor variation

- Donor sterics controls V_{OC} how about acceptors?

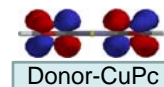
ITO/CuPc(200Å)/PDI(200Å)/BCP(100Å)//Al



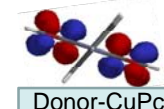
Acceptor	V_{OC}	J_{SO}	J_{SC}	FF	EQE
PTCDI	.28	1500	3.21	.54	.49
Ph-PTCDI	.35	710	2.73	.60	.59
dmPh-PTCDI	.50	9	2.07	.55	.57



PTCDI
-H

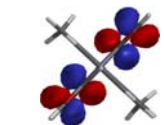


Ph-PTCDI



Dihedral = 60°

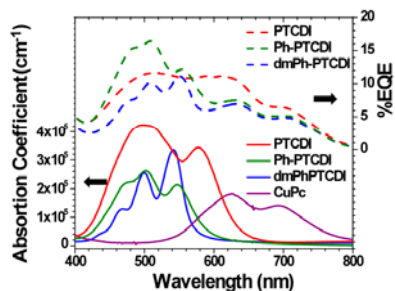
dmPh-PTCDI



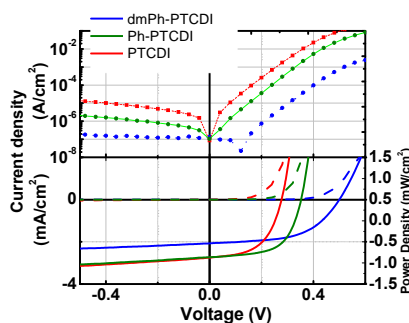
Dihedral = 89°

USC

Steric bulk of acceptor ↑: V_{OC} ↑



ITO/CuPc(200Å)/PDI(200Å)/BCP(100Å)//Al



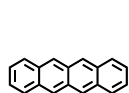
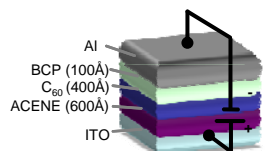
Acceptor	V_{OC}	J_{SO}	J_{SC}	FF	EQE
PTCDI	.28	1500	3.21	.54	.49
Ph-PTCDI	.35	710	2.73	.60	.59
dmPh-PTCDI	.50	9	2.07	.55	.57

USC

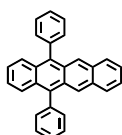
Intermolecular interaction strongest for PTCDI: lowest V_{OC}

Classic Solar Cell Problem

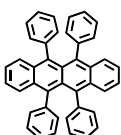
- Increased V_{OC} with substitution



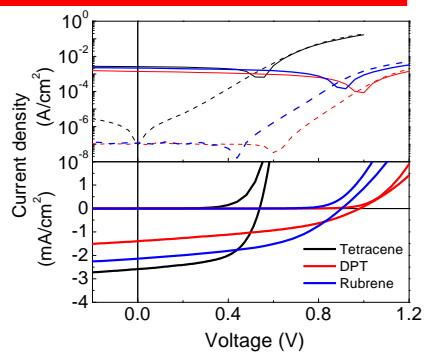
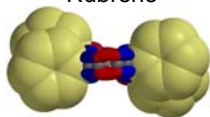
Tetracene



DPT



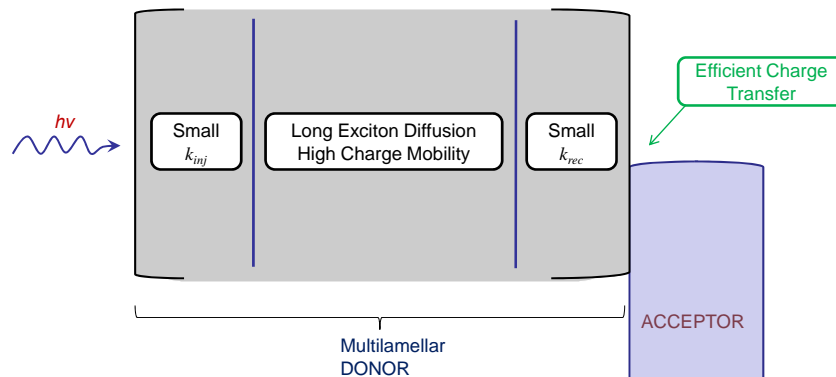
Rubrene



- Improve One Thing - Screw Up Another
- Increased steric bulk = higher V_{OC}
- But:
 - Higher resistance: lower FF, J_{SC}
 - Lower density: lower optical density and J_{SC}

USC

Lamellar Donor for Tailored Interfaces

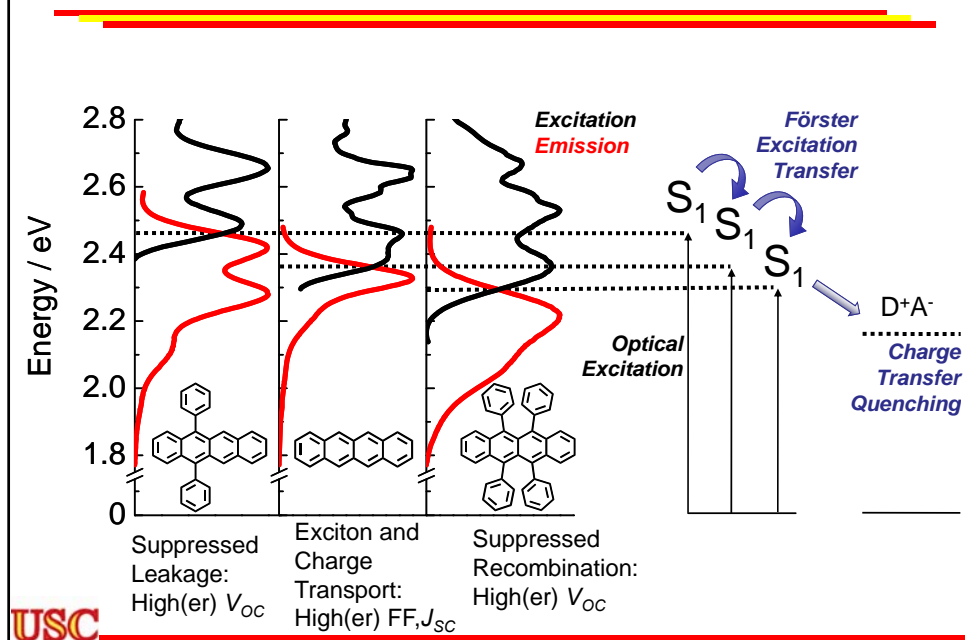


Requirements:

- Hole Transport Energy Alignment
- Slightly Cascading Exciton Energy

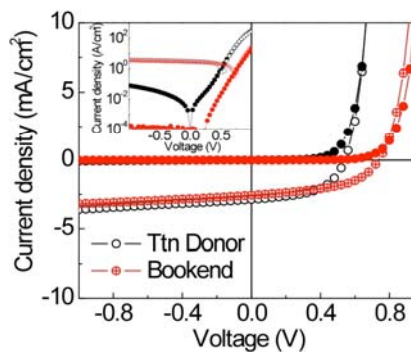
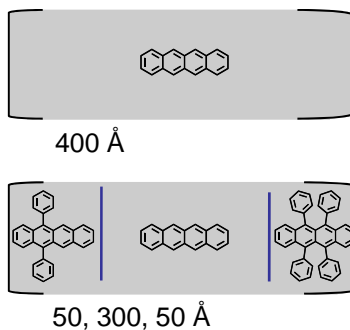
USC

Exciton Energy Cascade



Photovoltage Enhancement

- 200 mV Enhancement
 V_{oc} : 0.55 V \Rightarrow 0.75 V

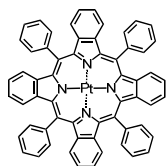


Multilamellar Donor:

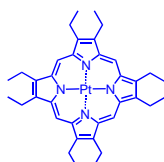
- Enhanced V_{oc}
- J_{sc} retained
- $\Delta E_{DA} = 1.7$ eV

Donor	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η
Ttn	0.54	2.86	0.54	0.83
Dpt/Ttn/Rbn	0.75	2.55	0.50	0.95

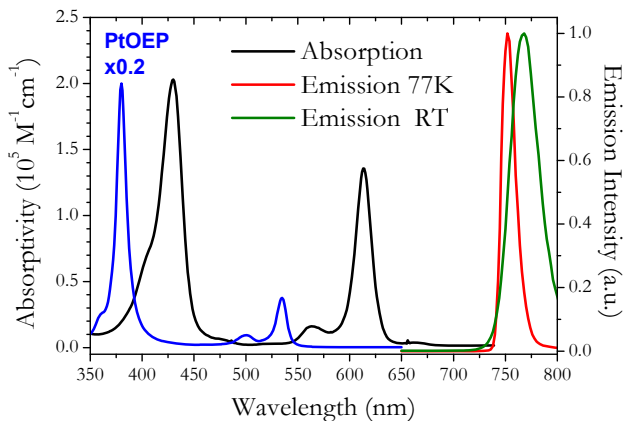
Absorption & Emission Spectra PtTPBP



PtTPBP



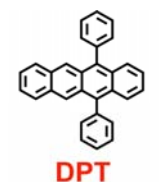
PtOEP



- Benzannulation red shifts Soret and Q, remain fairly narrow
- Very small S_1 - T_1 gap: $S_1 = 1.9$ eV; $T_1 = 1.6$ eV
- Filling the gap between Soret and Q
- How about extending conjugation at the meso positions??

USC

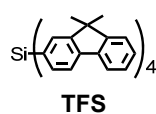
Mixed Materials to Fill the Porphyrin Gap



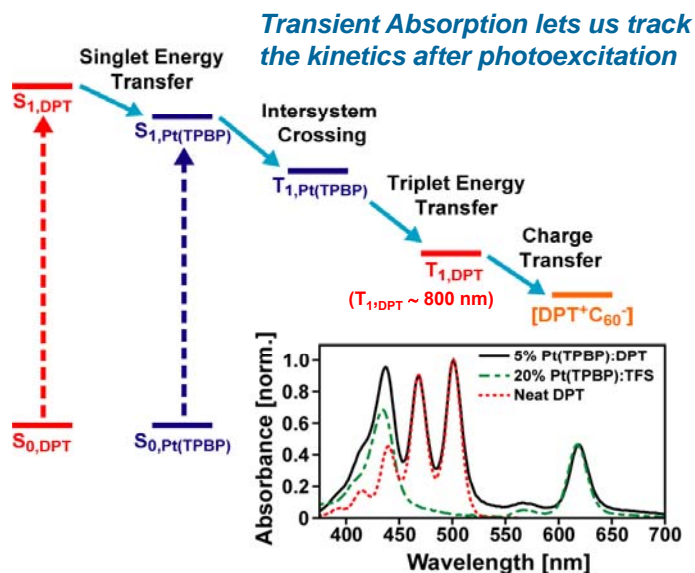
DPT



Pt(TPBP)

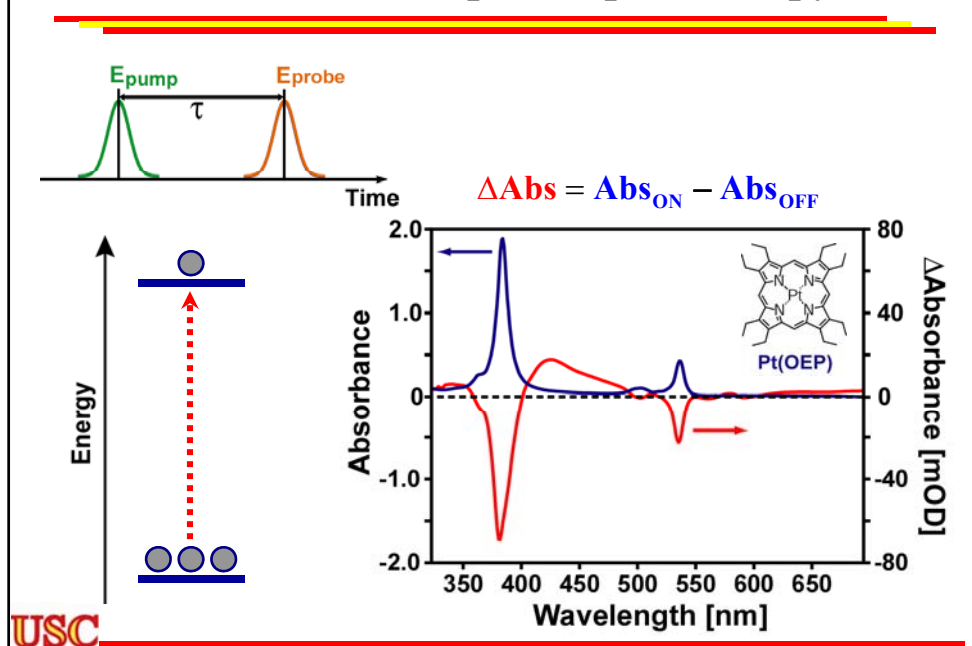


TFS

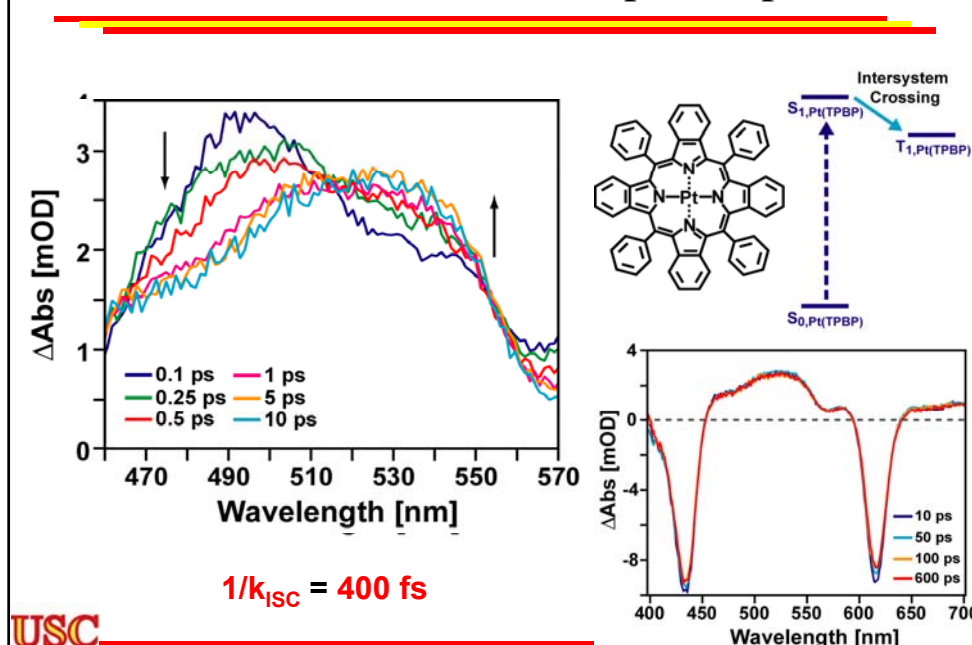


USC

Transient Absorption Spectroscopy

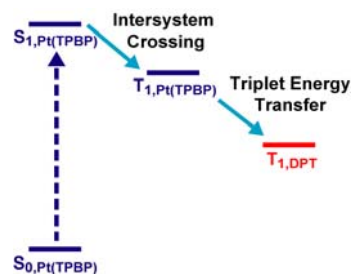
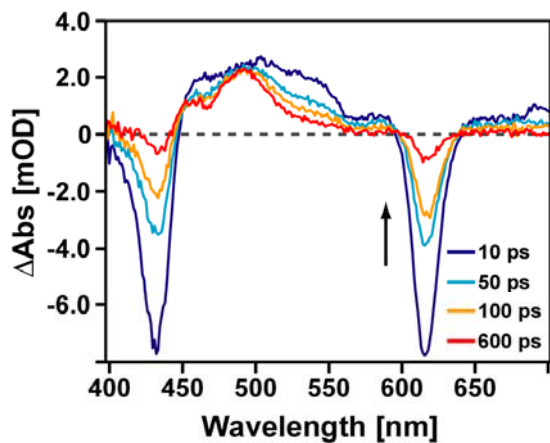


Pt(TPBP) Transient Absorption Spectra



DPT Doped with Pt(TPBP)

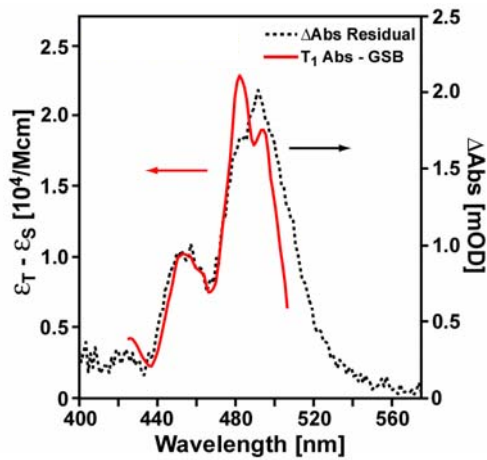
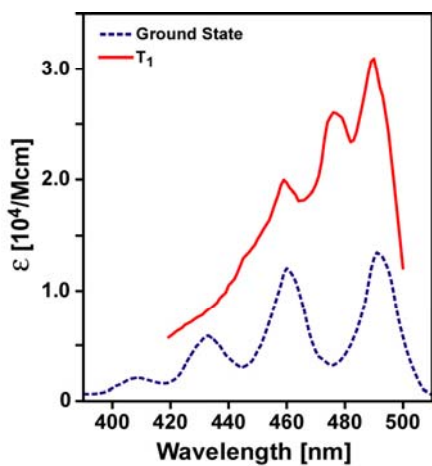
$$1/k_{TT} = 35 \text{ ps}$$



USC

DPT Triplet Yield

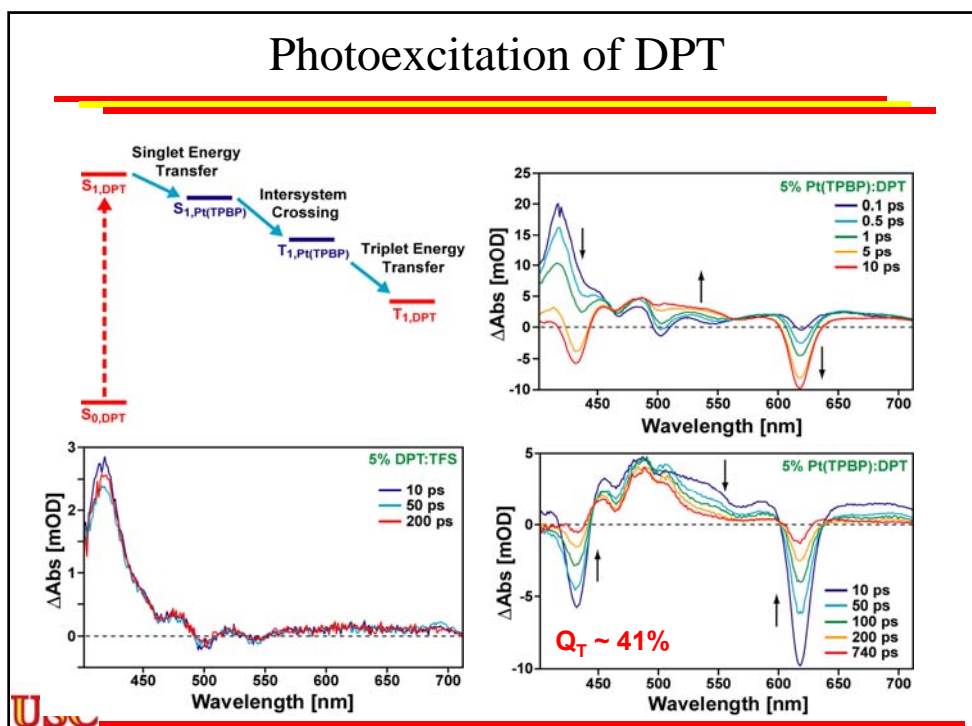
$$1/k_{TT} = 35 \text{ ps} \quad Q_T = 85 \pm 6\%$$



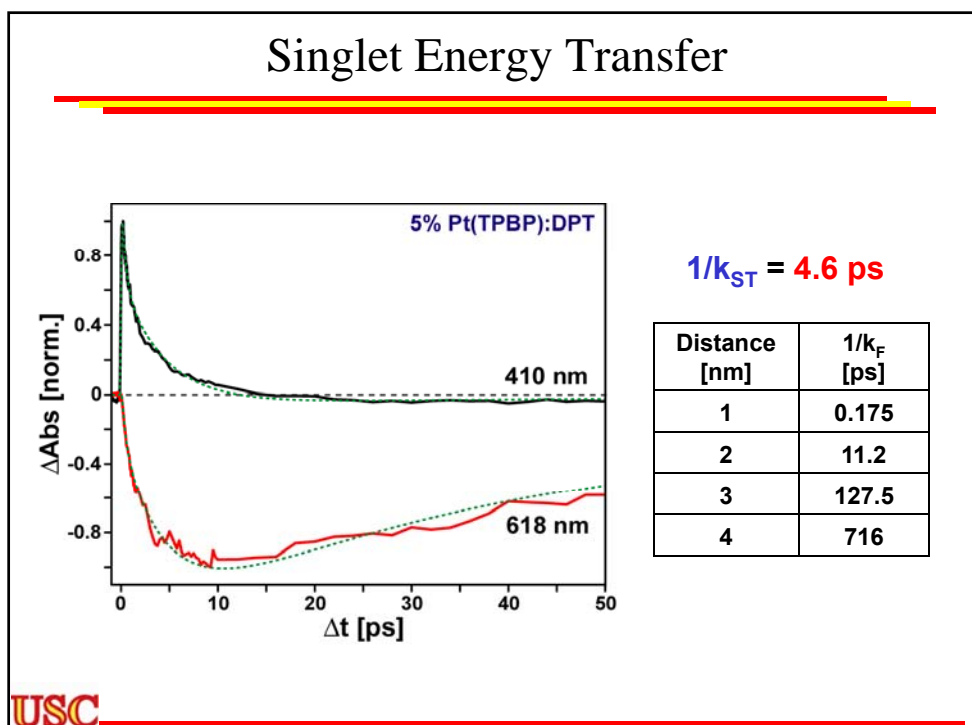
C. Burgdorff et. al. *Spectrochim. Acta.* **44A** (1988) 1137.

USC

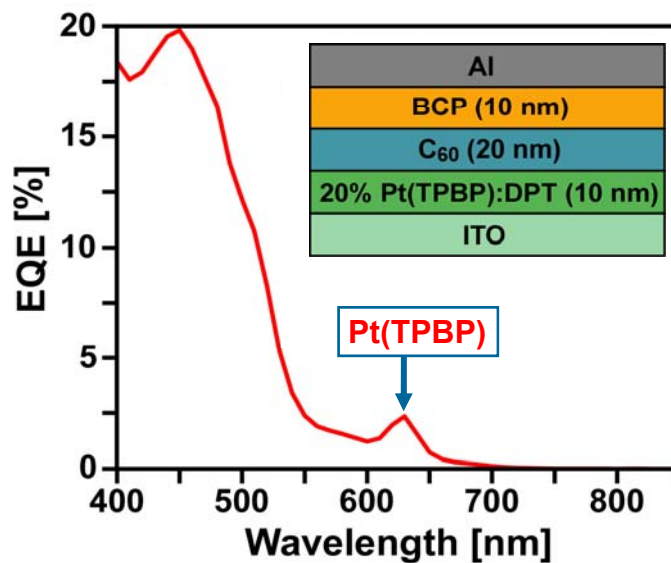
Photoexcitation of DPT



Singlet Energy Transfer

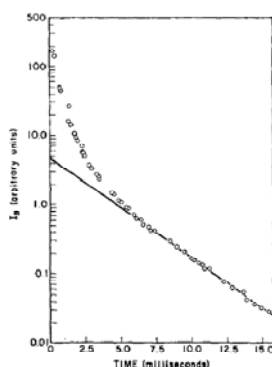


Device Characterization



USC

Singlet Fission

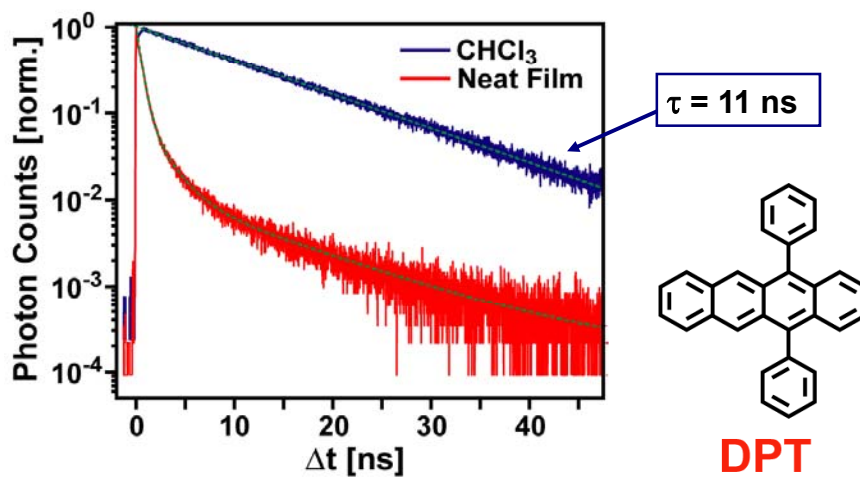


- Pathway to Multiexciton Generation
 - One photon in \rightarrow two excitons out
 - Less photon energy lost to heat
- Has Been Observed in Anthracene, Tetracene, & Pentacene
 - Yield is dependent on morphology
- Fission is Uphill for DPT (0.8 eV \rightarrow 32kT)

S. Singh et. al. *J. Chem. Phys.* 42(1) (1965) 330.

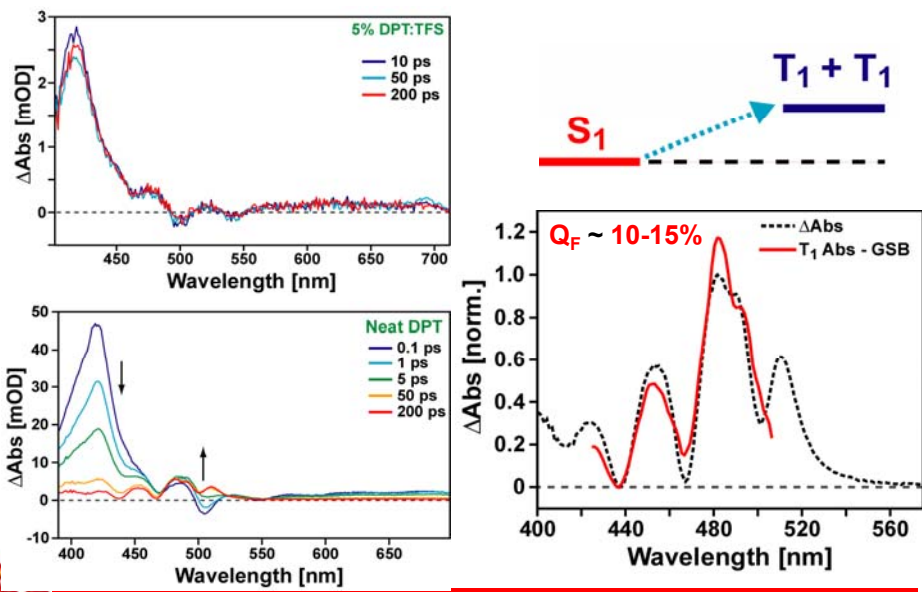
USC

DPT Fluorescence Lifetime Experiments



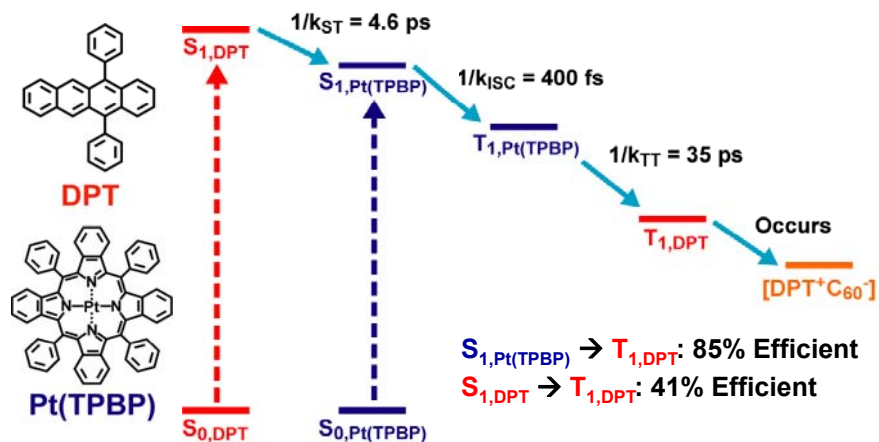
USC

Singlet Fission in DPT



U.L.

Conclusions

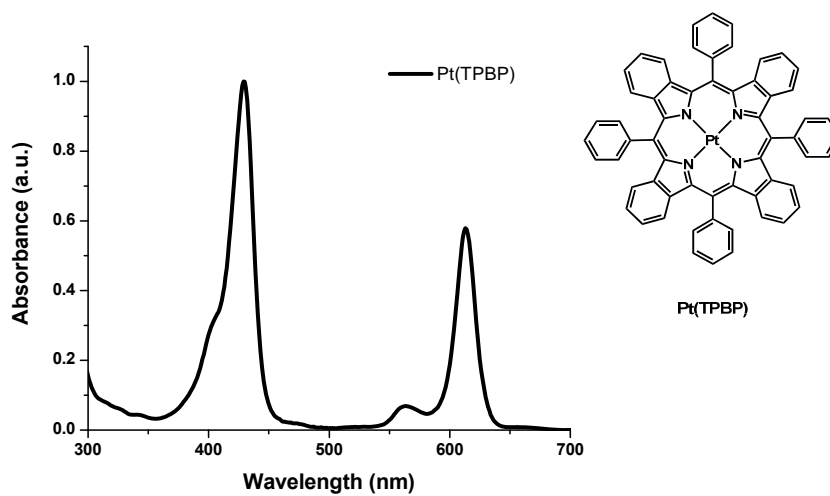


- **Singlet Fission** May Contribute to the Triplet Exciton Yield when Pumping DPT

USC

Pt(TPBP) Absorption Enhancement

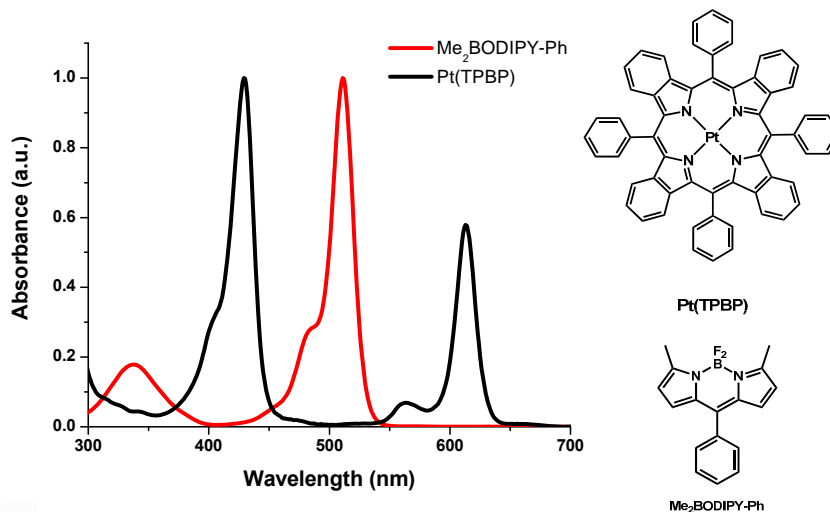
Can we compensate for the low 450–550 nm absorption intramolecularly?



USC

Pt(TPBP) Absorption Enhancement

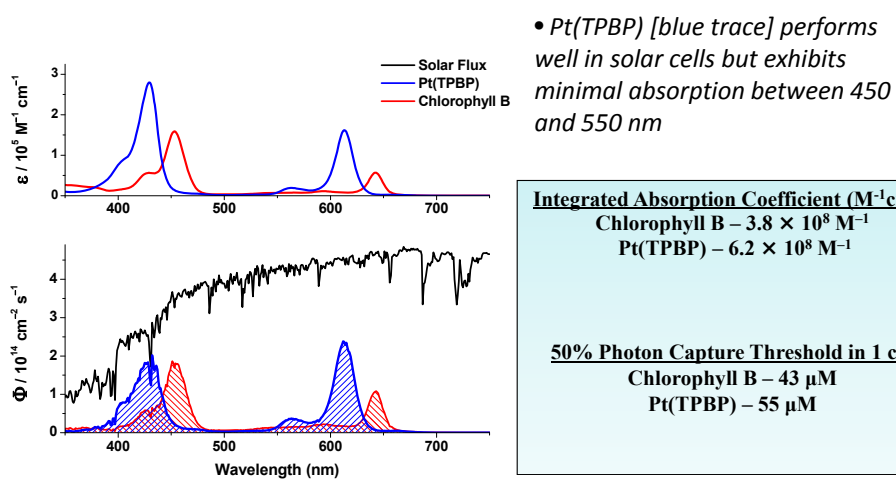
A multichromophoric approach using BODIPY antennae:



USC

Collecting Solar Energy

Covering the visible spectrum with broad, intense absorbers

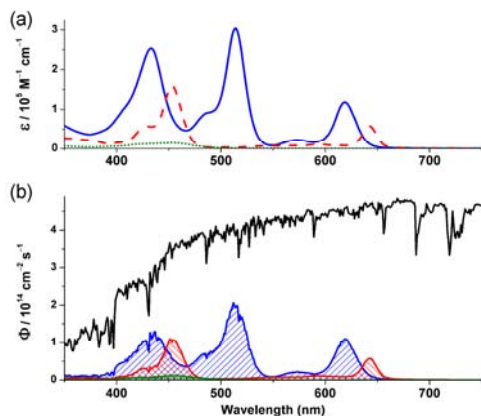


Rate of photon absorption ($2 \mu\text{M sol'n}$)

USC

Collecting Solar Energy

Covering the visible spectrum with broad, intense absorbers



- Pt(TPBP) + 4 BDP: blue trace
- Chlorophyll B: red trace
- Ru(bpy)₃²⁺: green trace

Integrated Absorption Coefficient (M⁻¹cm⁻¹)

Chlorophyll B – 3.8 × 10⁸ M⁻¹
 Pt(TPBP) – 6.2 × 10⁸ M⁻¹
 Pt(TPBP)/BDP – 11.0 × 10⁸ M⁻¹
 Ru(bpy)₃²⁺ – 0.7 × 10⁸ M⁻¹

50% Photon Capture Threshold in 1 cm

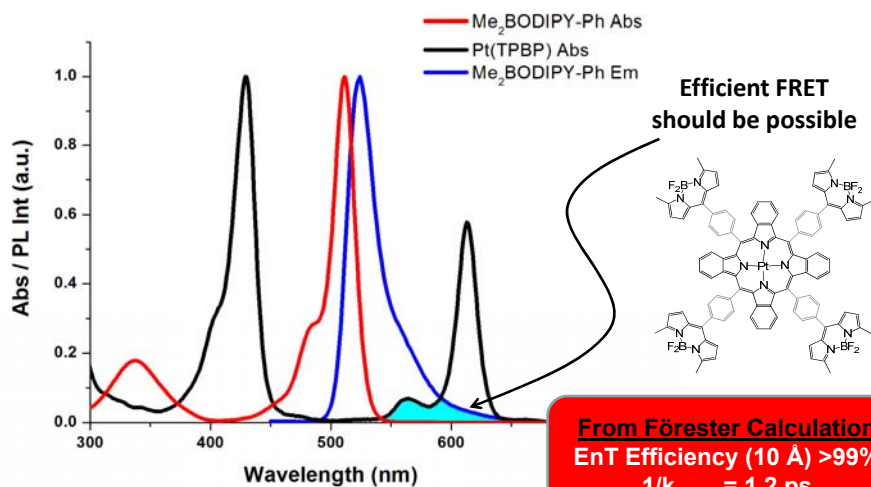
Chlorophyll B – 43 μM
 Pt(TPBP) – 55 μM
 Pt(TPBP)/BPD – 12 μM
 Ru(bpy)₃²⁺ – 1000 μM

Rate of photon absorption (2 μM sol'n)

USC

Pt(TPBP) Absorption Enhancement

A multichromophoric approach using BODIPY antennae:



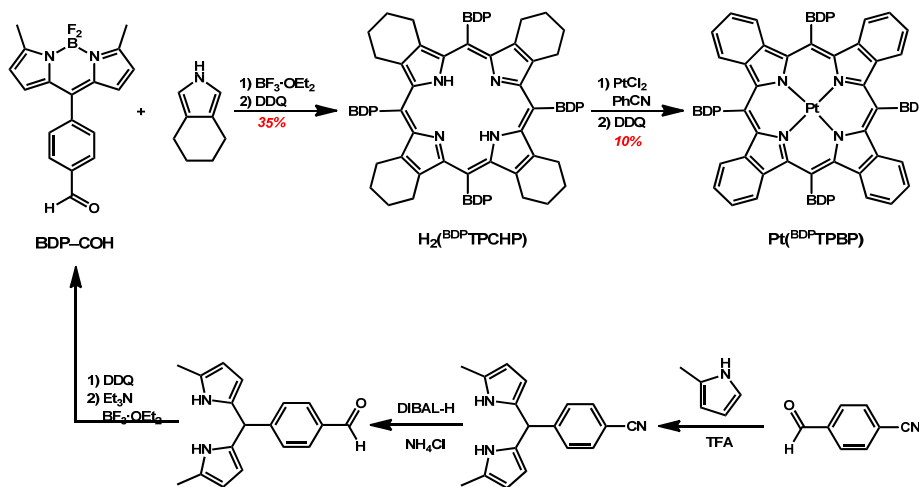
Efficient FRET should be possible

From Förster Calculation
 EnT Efficiency (10 Å) >99%
 1/k_{FRET} = 1.2 ps

USC

Synthetic Strategy

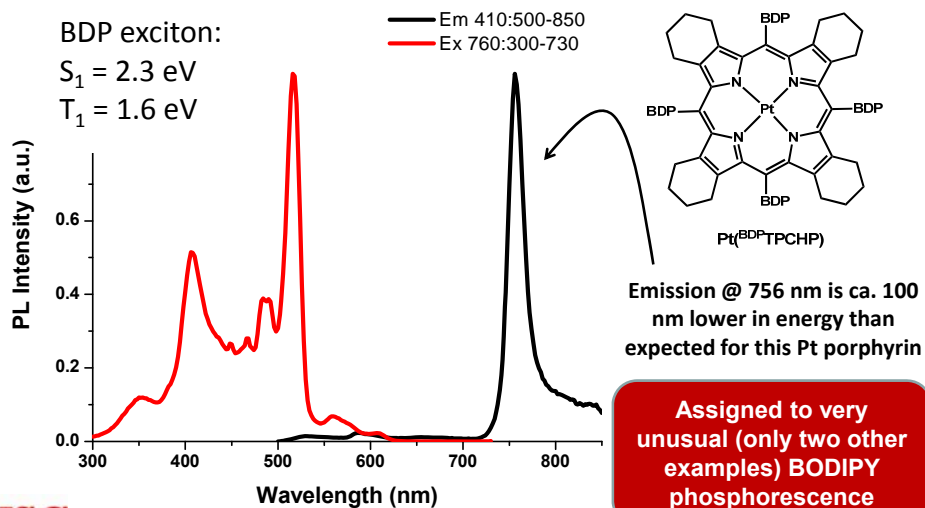
Synthesis had some hiccups at first, but we can obtain pure material...



USC

BODIPY Phosphorescence

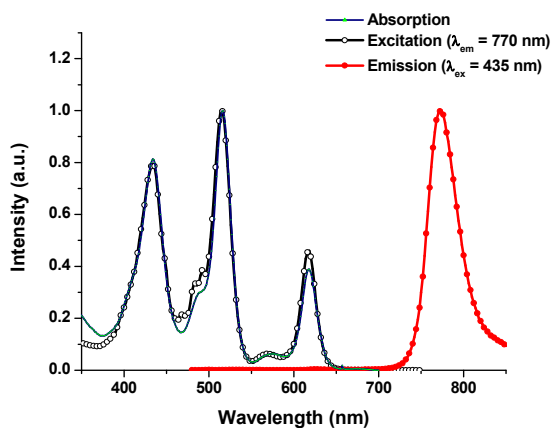
Low-temperature PL of the platinum cyclohexenoporphyrin intermediate $\text{Pt}(\text{BDPTPCHP})$ showed an unexpected low-energy emission:



USC

Pt(BDP)TPBP Photophysics

For the oxidized product, a single phosphorescent emission is observed irrespective of solvent:

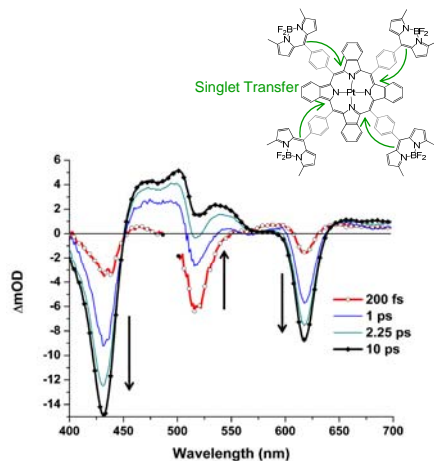


Nonradiative rates are very medium-dependent:

Solvent	Φ	τ
Toluene	0.26	67 μ s
2-MeTHF	0.14	36 μ s
Cyclohexane	0.13	33 μ s
DCM	0.006	< 1 μ s
PMMA (0.5 wt %)	0.17	95 μ s
2-MeTHF (77 K)	N/A	92 μ s

Emission (764 nm @ 77K) is very close in energy to BODIPY triplet – is 3 BDP involved?

Transient Absorption (1 BDP \rightarrow 1 Por)

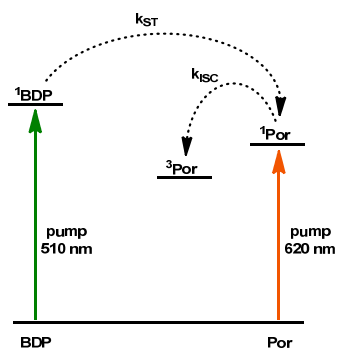


Upon irradiation of BODIPY (510 nm), a bleach immediately appears and recovers with growth of the benzoporphyrin triplet

Singlet Energy Transfer

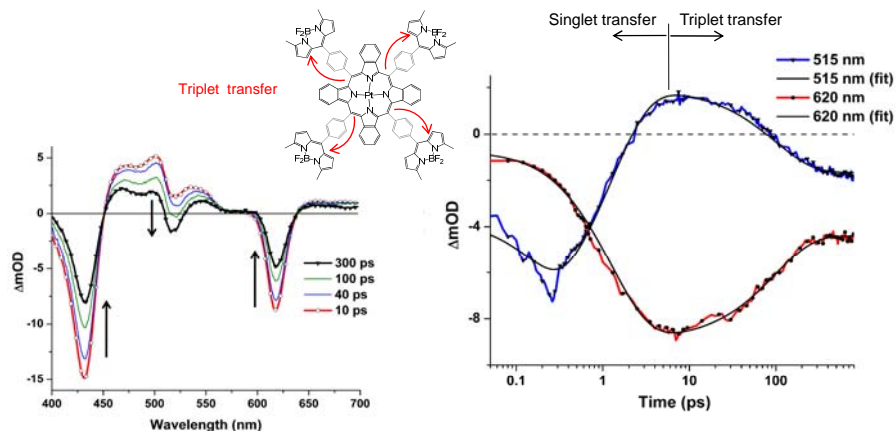
$$k_{ST}^{-1} = 1.29 \pm 0.11 \text{ ps}$$

$$k_{FRET}^{-1} (\text{pred.}) = 1.2 \text{ ps}$$



Singlet transfer here is 4x faster than intermolecular: DPT-PtTPBP.

Transient Absorption ($^3\text{Por} \rightarrow ^3\text{BDP}$)



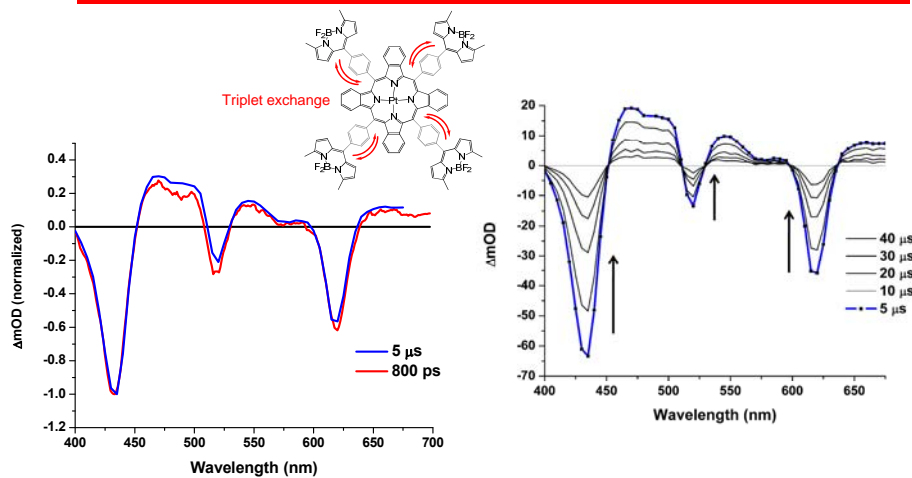
Triplet energy transfer ($k_{\text{TT}}^{-1} = 99.6 \pm 7.1$ ps)

This redistribution of energy is made possible by the different singlet-triplet gaps of porphyrin and BODIPY.
 S_1-T_1 : BDP = 0.7 eV, PtTPBP = 0.3 eV

Triplet transfer is ca 3x slower than for intermolecular: DPT-PtTPBP

USC

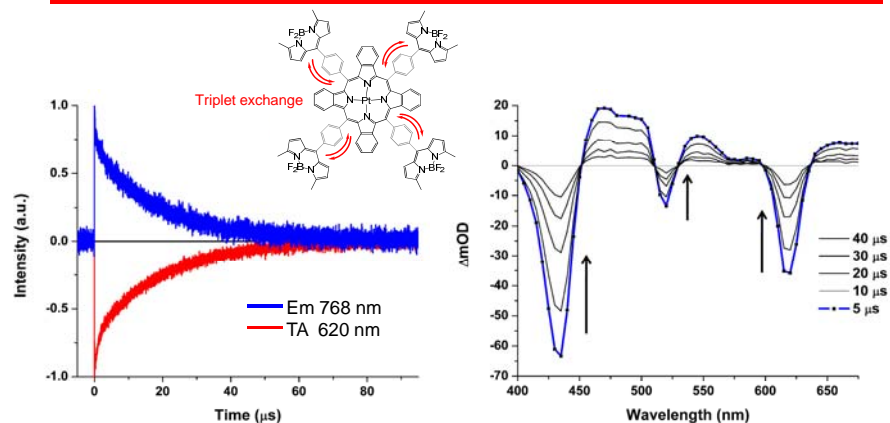
Nanosecond Transient Absorption



The transient absorption profile remains constant from the pico- to microsecond regime:

USC

Nanosecond Transient Absorption

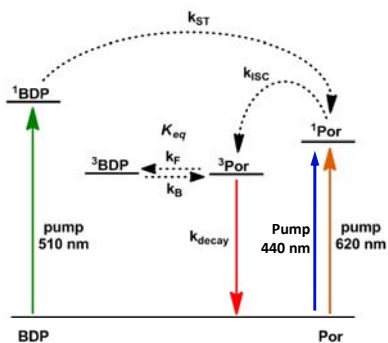


The microsecond TA decay matches the phosphorescence decay

USC

Energy Transfer in the Ensemble

A concerted view of the multichromophoric system:



Measured rate constants and energy levels for Pt(BDP)TPBP

k_{ST} (${}^1\text{BDP} \rightarrow {}^1\text{Por}$)	$7.8 \times 10^{11} \text{ s}^{-1}$
k_{ISC} (Por)	$2.5 \times 10^{12} \text{ s}^{-1}$
k_F (${}^3\text{Por} \rightarrow {}^3\text{BDP}$)	$1.0 \times 10^{10} \text{ s}^{-1}$
k_B (${}^3\text{BDP} \rightarrow {}^3\text{Por}$)	$1.6 \times 10^{10} \text{ s}^{-1}$
$k_{\text{decay}} = k_r + k_{nr}$	$1.5 \times 10^5 \text{ s}^{-1}$
$K_{eq} = k_F/k_B$	0.61
$E({}^3\text{BDP})$	758 nm
$E({}^3\text{Por})$	764 nm

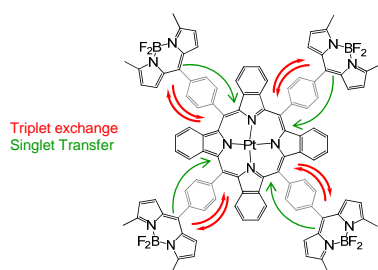
Energy absorbed across the visible is efficiently funneled into an equilibrated state containing roughly isoenergetic BODIPY and porphyrin triplets

k_{TT} (${}^3\text{BDP} \rightarrow {}^3\text{Por}$) is consistent with predictions from Balzani's work for triplet superexchange across a single phenylene linker ($1.1 \times 10^{10} \text{ s}^{-1}$)

USC

Energy Redistribution in a Core-Shell System

These findings show that energy can be efficiently funneled and redistributed in core-shell chromophores by triplet management



Measured rate constants and energy levels for Pt(BDP)TPBP

$k_{ST} (^1BDP \rightarrow ^1Por)$	$7.8 \times 10^{11} s^{-1}$
$k_{ISC} (Por)$	$2.5 \times 10^{12} s^{-1}$
$k_f (^3Por \rightarrow ^3BDP)$	$1.0 \times 10^{10} s^{-1}$
$k_B (^3BDP \rightarrow ^3Por)$	$1.6 \times 10^{10} s^{-1}$
$k_{decay} = k_r + k_{nr}$	$1.5 \times 10^5 s^{-1}$
$K_{eq} = k_f/k_B$	0.61
$E(^3BDP)$	758 nm
$E(^3Por)$	764 nm

Lowering the shell chromophore energy or raising the core energy will shift the equilibrium to localize ALL of the excitons on the periphery.

Por-Por excimer formed in neat thin films, limits exciton diffusion

USC

Acknowledgements

- People:
Cody Schlenker, Patrick Erwin, Slava Diev
Matt Whited, Sean Roberts, Steve Bradforth, Eric McAnally
Department of Chemistry
University of Southern California

Steve Forrest, Jeramy Zimmerman, Richard Lunt, Eric Yu
Department of Physics and Electrical Engineering
University of Michigan

Alec Durrell, Harry Gray
Department of Chemistry
California Institute of Technology
- Funding:
 - Global Photonic Energy Corporation
 - DoE (Energy Frontier Research Centers, USC + UM)
 - King Abdulla University of Science and Technology
 - NSF: SOLAR program

USC