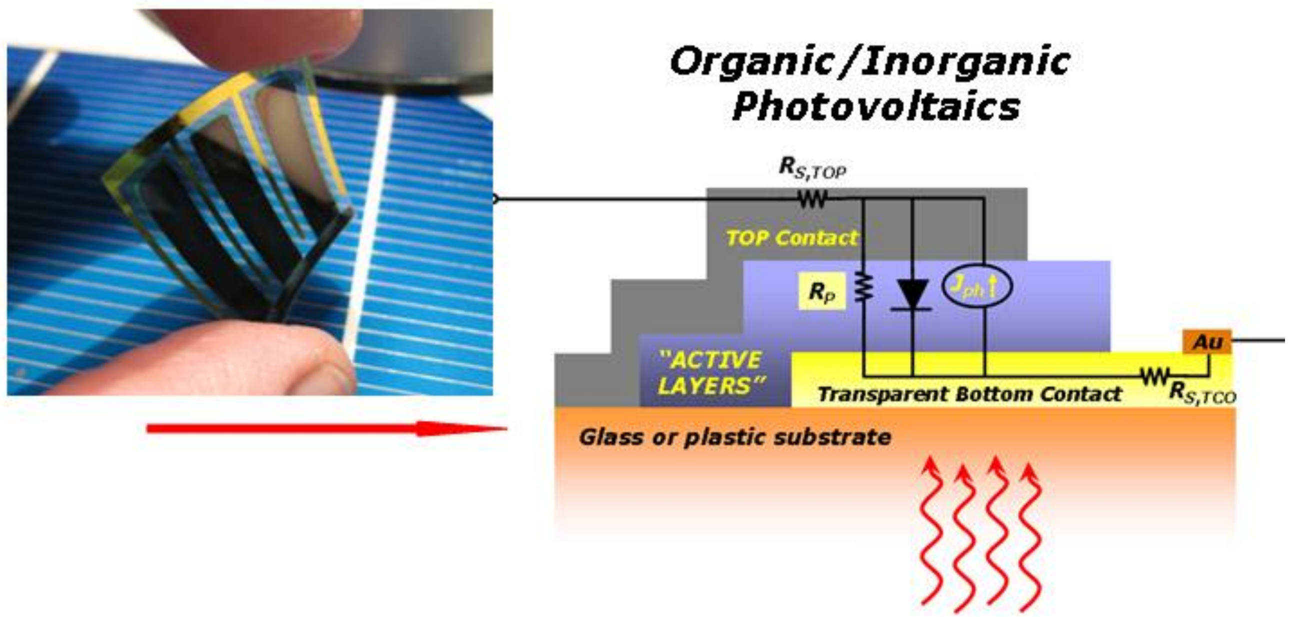
Waveguide spectroscopies to characterize organic thin film/transparent conducting oxide interfaces



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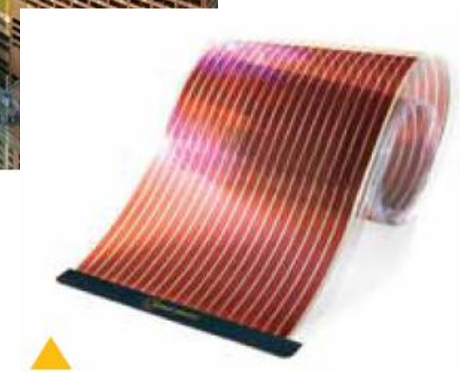
April 19, 2012

Solar Cell Technology

www.konarka.com
Solarmer



<u>Crystalline silicon</u>

- 1950s
- Highest efficiencies
- Expensive to purify materials
- Rigid and heavy modules

<u>Organic Photovolatics (OPV)</u>

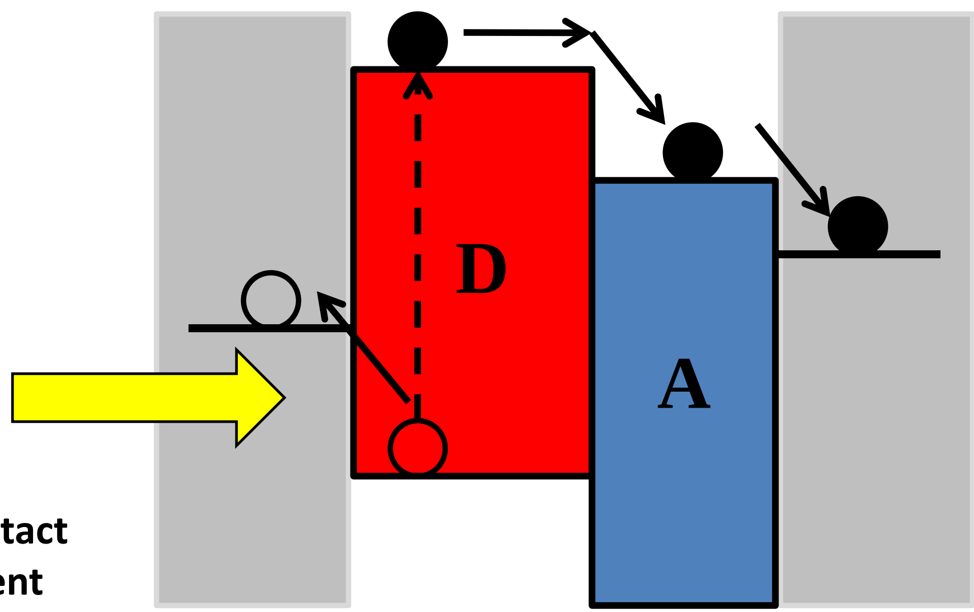
- 2000s
- Lower efficiencies
- Cheap to produce
- Flexible and lightweight materials

DOE funded Energy Frontier Research Center

CIS:SEM

Center for Interface Science: Solar Electric Materials

Light



Metal contact

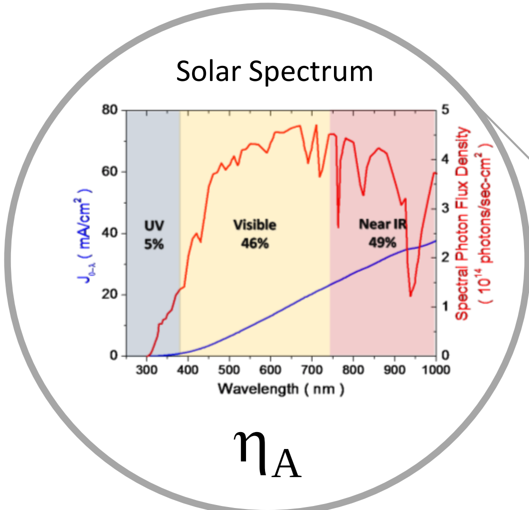
Metal contact (transparent conducting oxide = TCO)

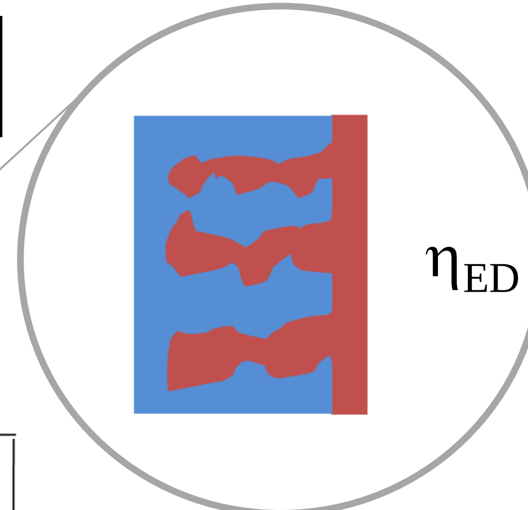
Donor material
- absorbs light & donates electrons

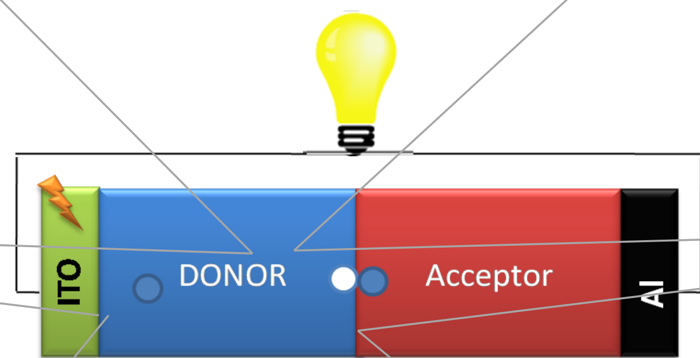
Acceptor material
- accepts electrons

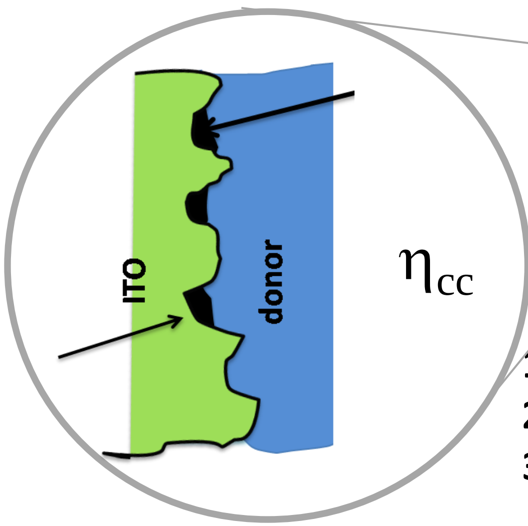
Organic Photovoltaic Efficiency

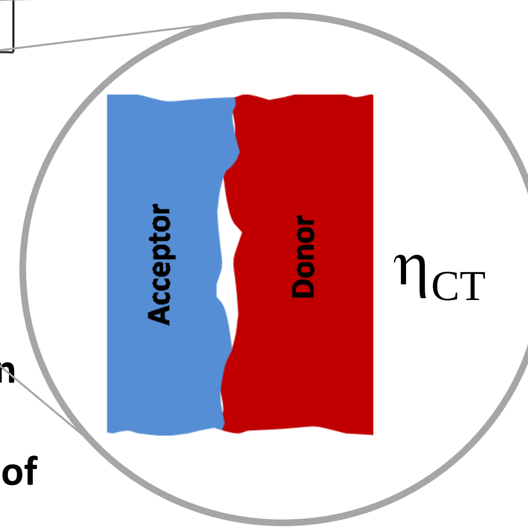
$$\eta_{IQE} = \eta_{A} \times \eta_{ED} \times \eta_{CT} \times \eta_{CC}$$





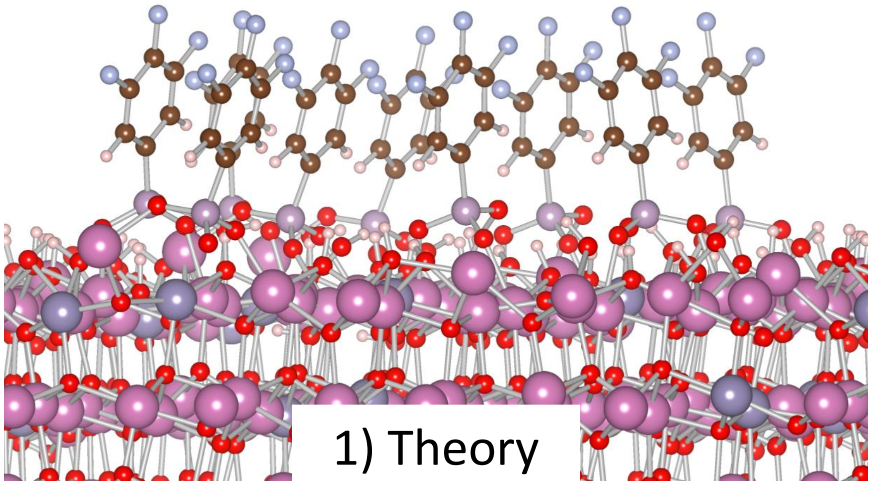






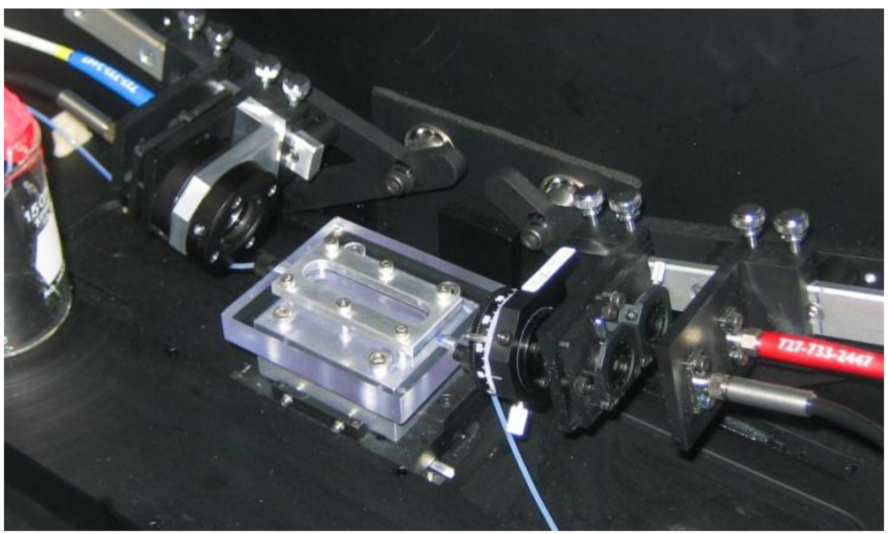
1) **Absorption of a photon → exciton creation**
2) **Exciton diffusion**
3) **Charge transfer (creation of cation radical of donor and anion radical of acceptor)**
4) **Charge collection (in competition with charge recombination)**

Approach to collaborative research

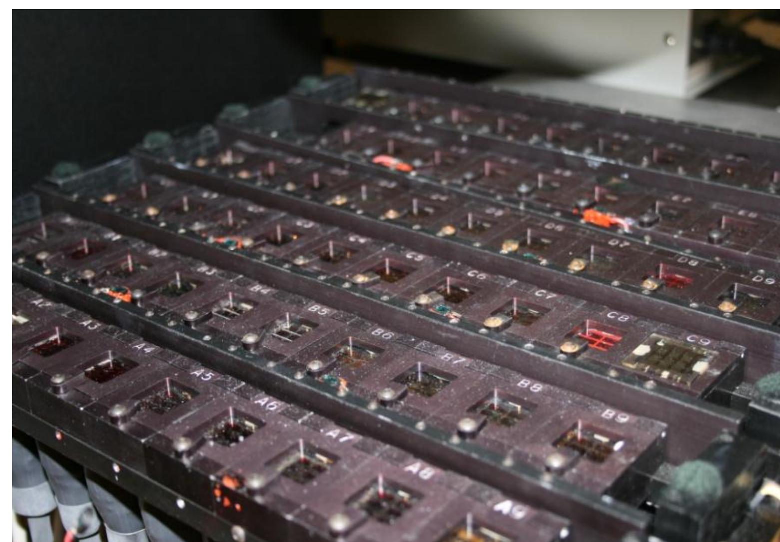


1) Theory

2) Materials



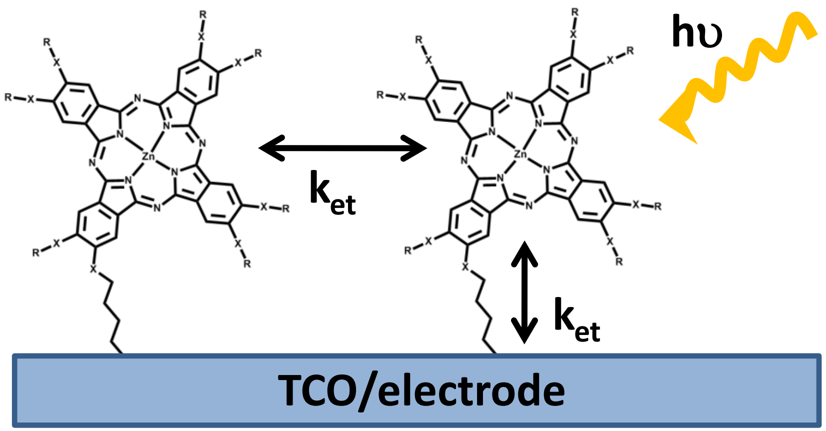
3) Technique Development



4) Applications

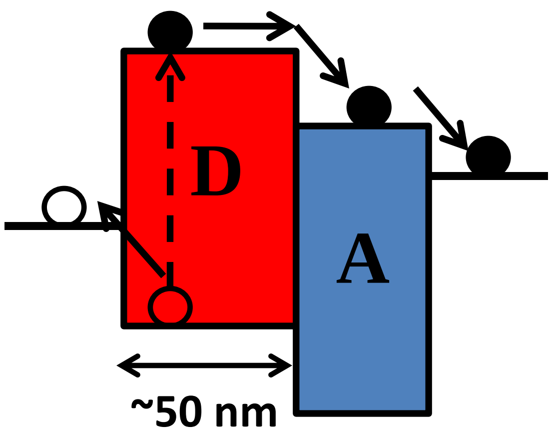
Molecular Hypothesis

The charge collection efficiency is dependent on the rate of charge transfer vs. charge recombination at the organic molecular film/TCO interface



Properties contributing to the rates include:

- Molecular orientation
- Structure/function relationship
- Chemical microenvironment

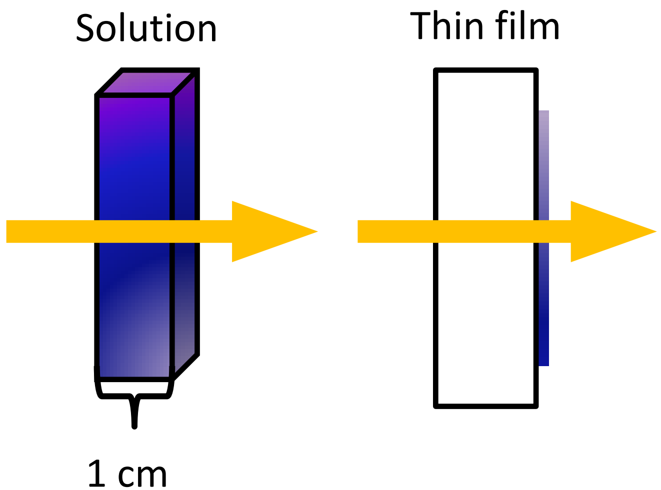


Analytical Challenges

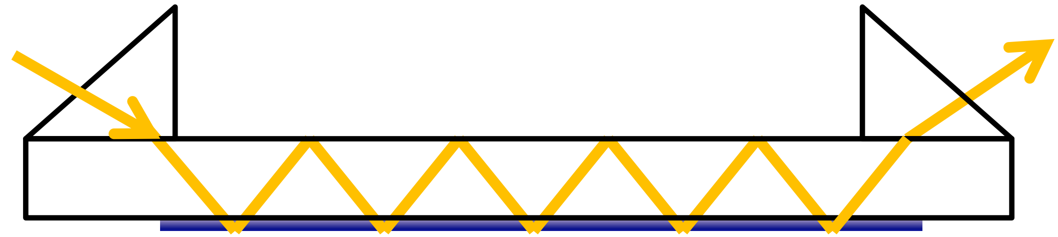
- Sensitivity = few molecules at interface (monolayer/submonolayer)
- Selectivity = molecular populations with different orientations
- Fast reaction kinetics
- In-situ

Optical changes in weakly absorbing films

Transmission geometry

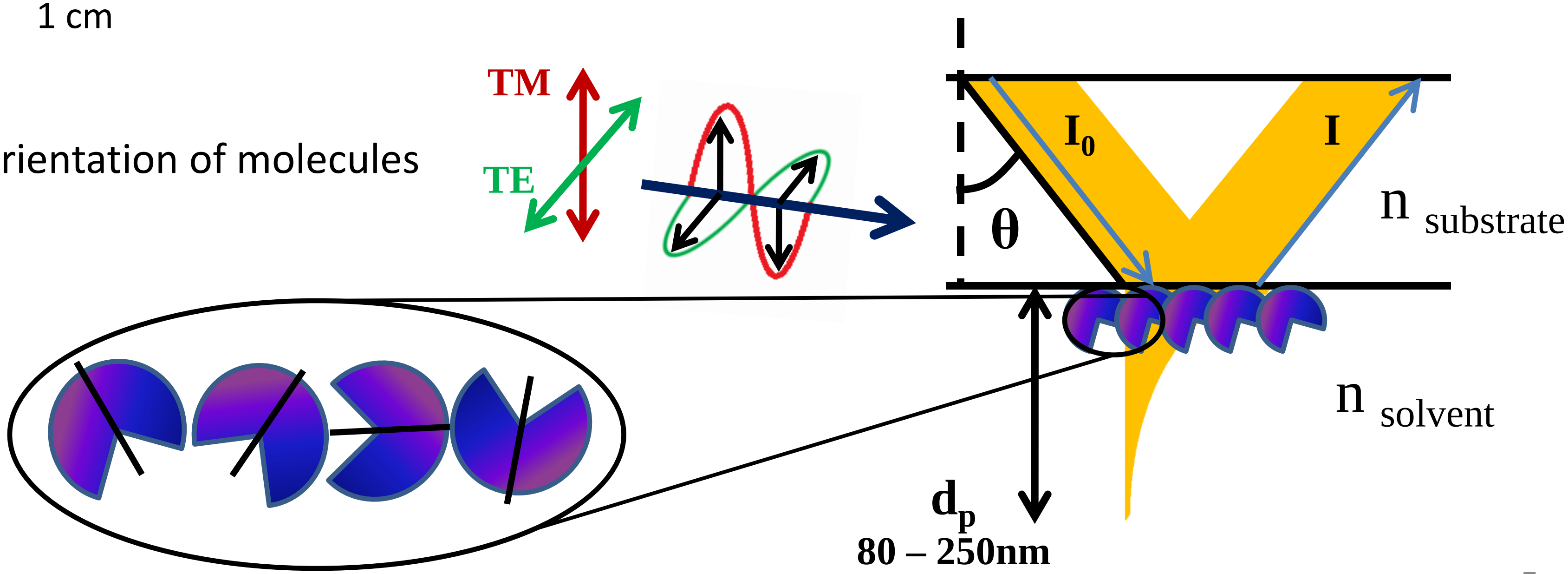


Attenuated Total Reflectance (ATR)

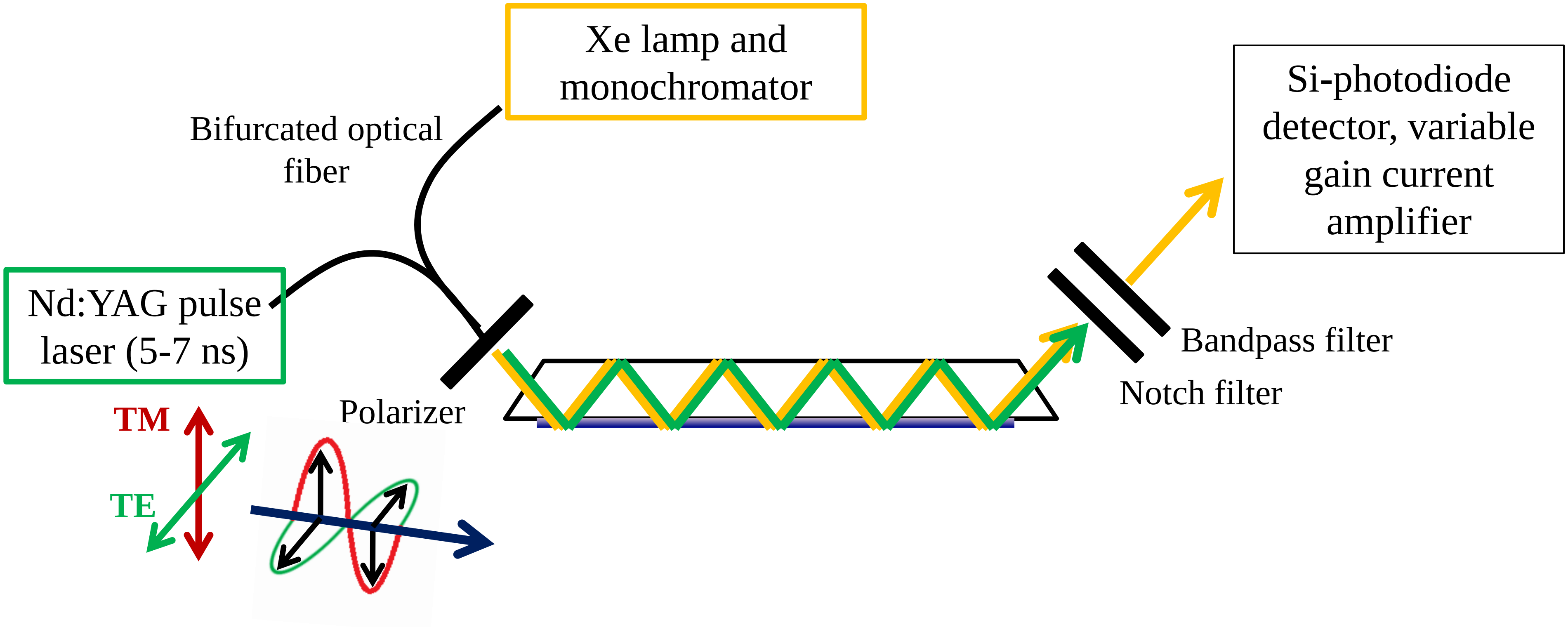


Relative sensitivity increases by 10-100x with ATR geometry vs. Transmission geometry

Orientation of molecules



Transient ATR Spectroscopy

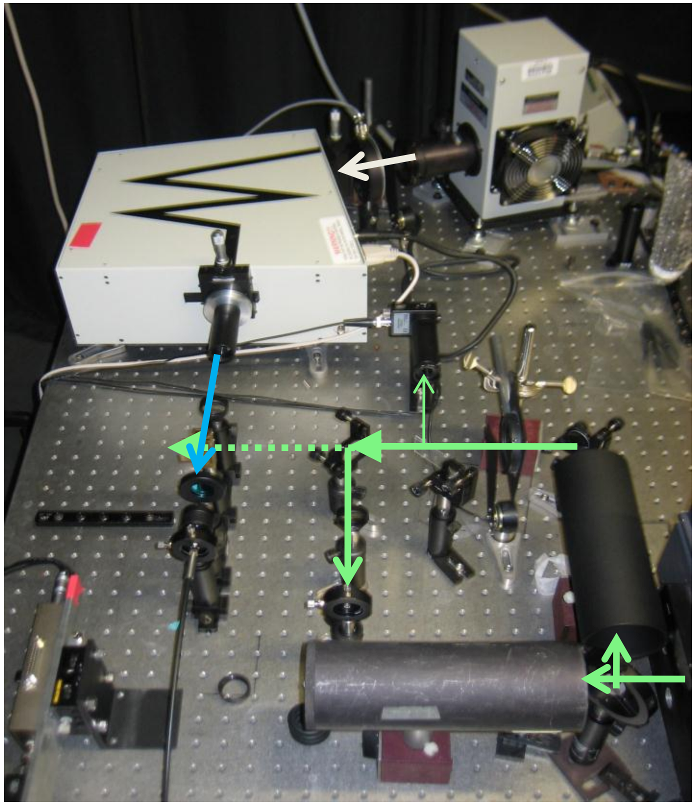


Advantages to this geometry:

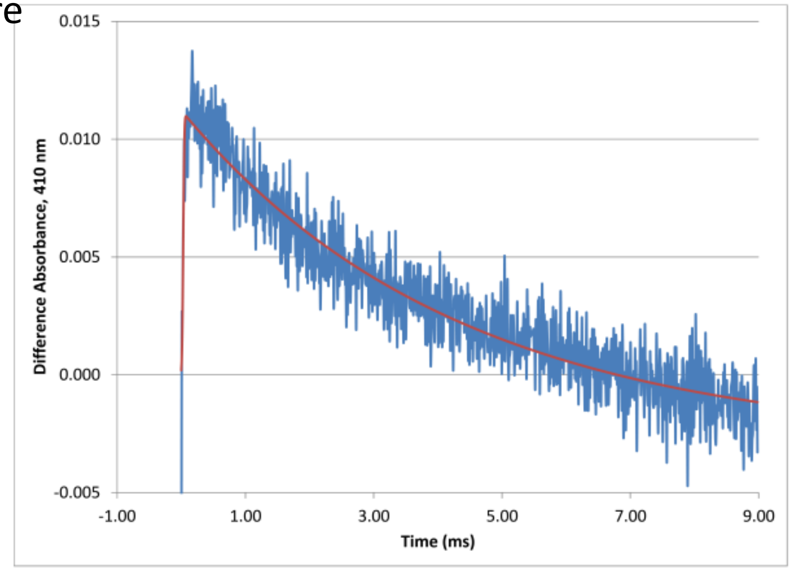
1) Collinear coupling = nearly identical interaction with film
2) Lower intensity pump beam needed = minimizes photodegradation/bleaching
3) Polarization of both beams = relationship between molecular orientation and reaction kinetics

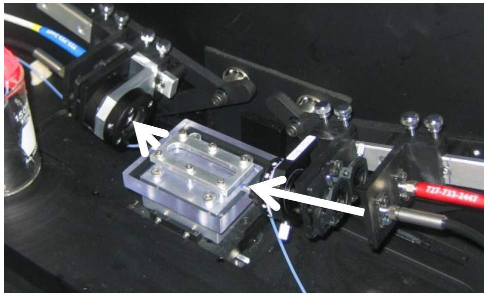
Simon, A.M. et al. *Anal. Chem.*, **2011**, *83,* 5762–5766

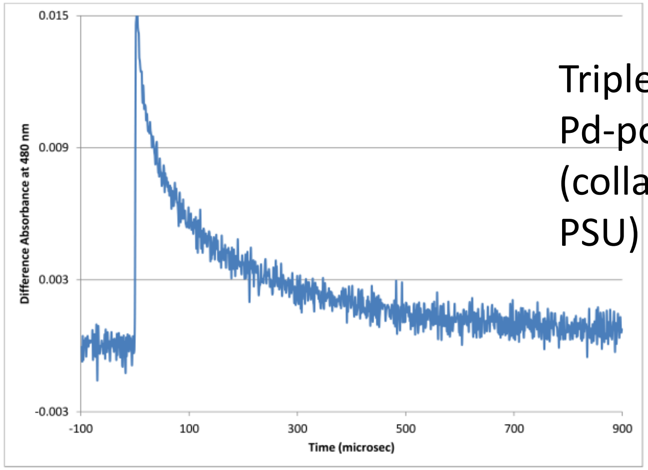
Transient ATR Spectroscopy



Benchmarked with bacteriorhodopsin in planar membranes: Γ = 2 pmol/cm^2 = ca. 0.01 ML of retinal chromophore



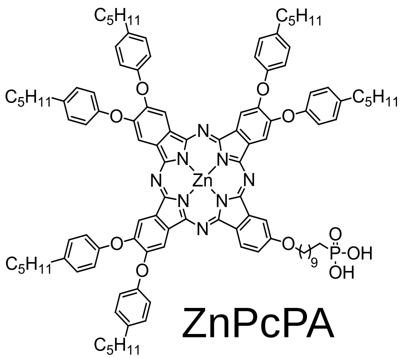




Triplet decay of self-assembled Pd-porphyrin films (collaboration with T. Mallouk, PSU)

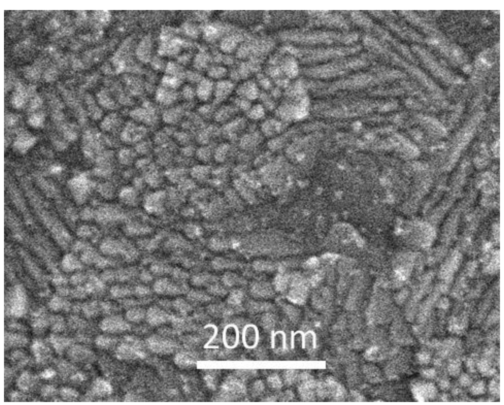
Simon, A.M. et al. *Anal. Chem.*, **2011**, *83*, 5762–5766

ZnPcPA Monolayers: Probing Relationships Between Molecular Orientation/Aggregation and k_{ET}

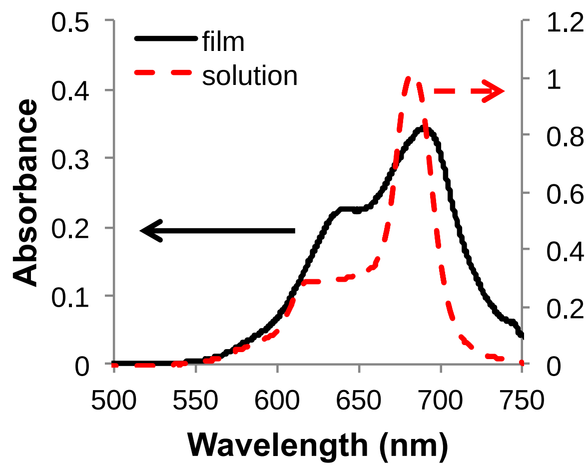


ZnPcPA

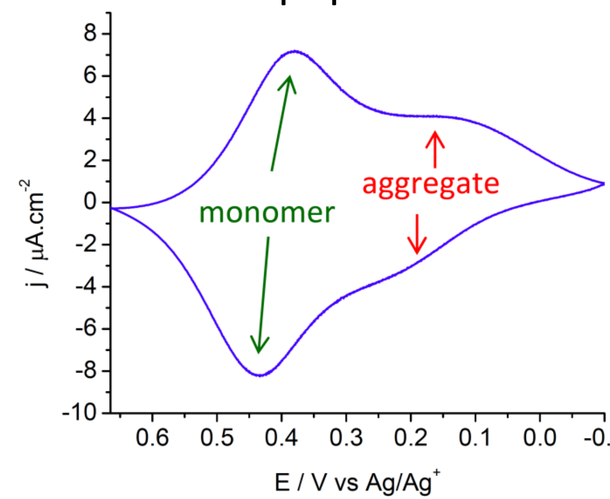
polycrystalline surface of unmodified ITO

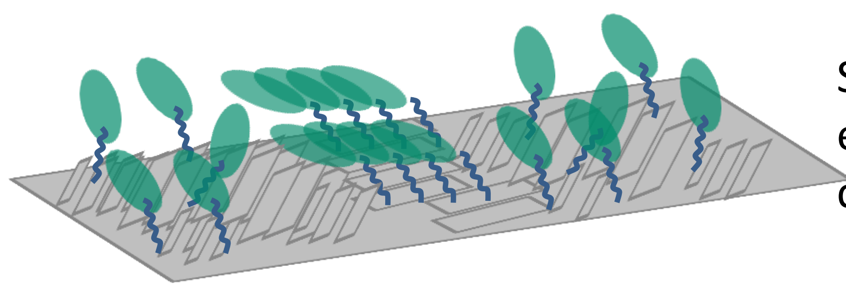


Dissolved vs monolayer spectra show presence of adsorbed aggregates



Electrochemically distinct monomer and aggregate subpopulations





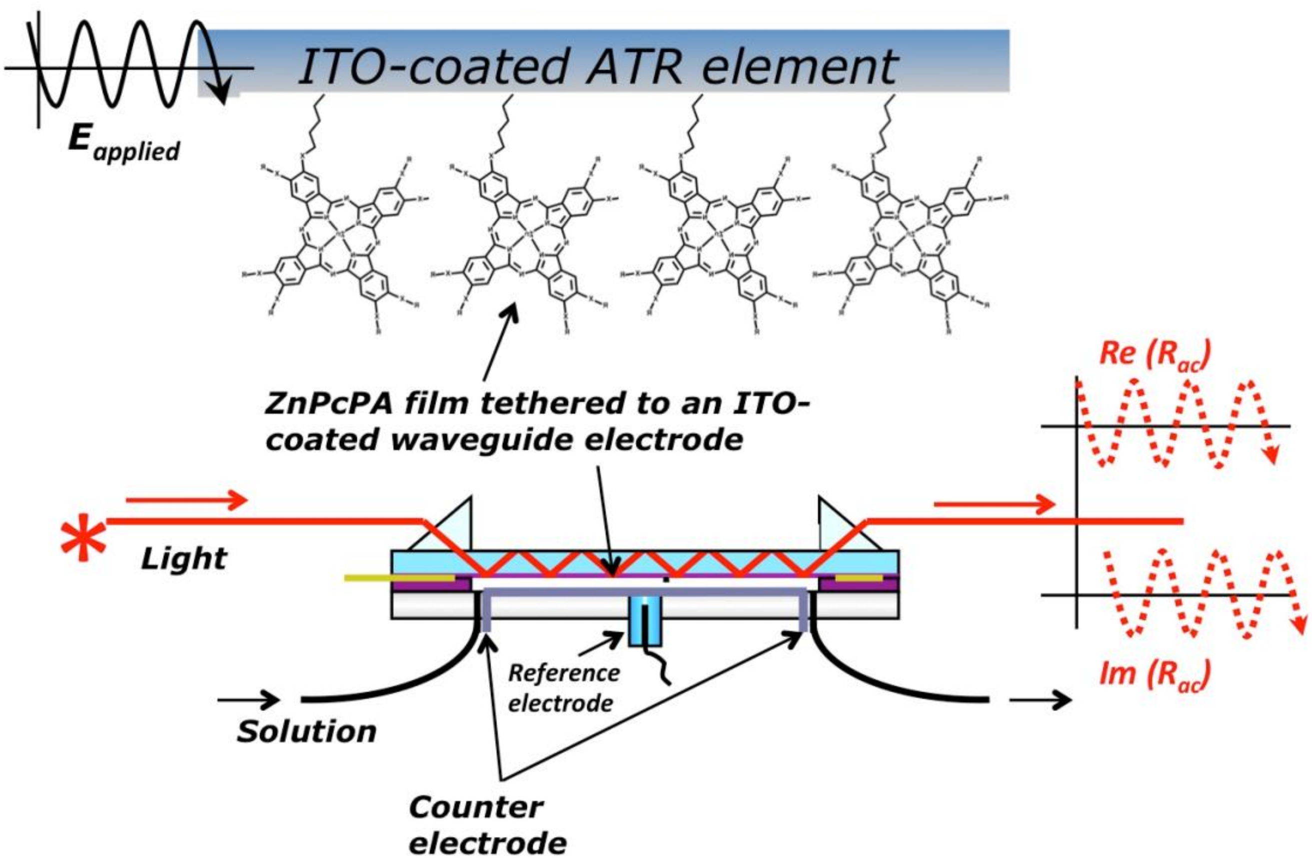
Spectroscopic and electroactive surface coverage = 1.2 ML

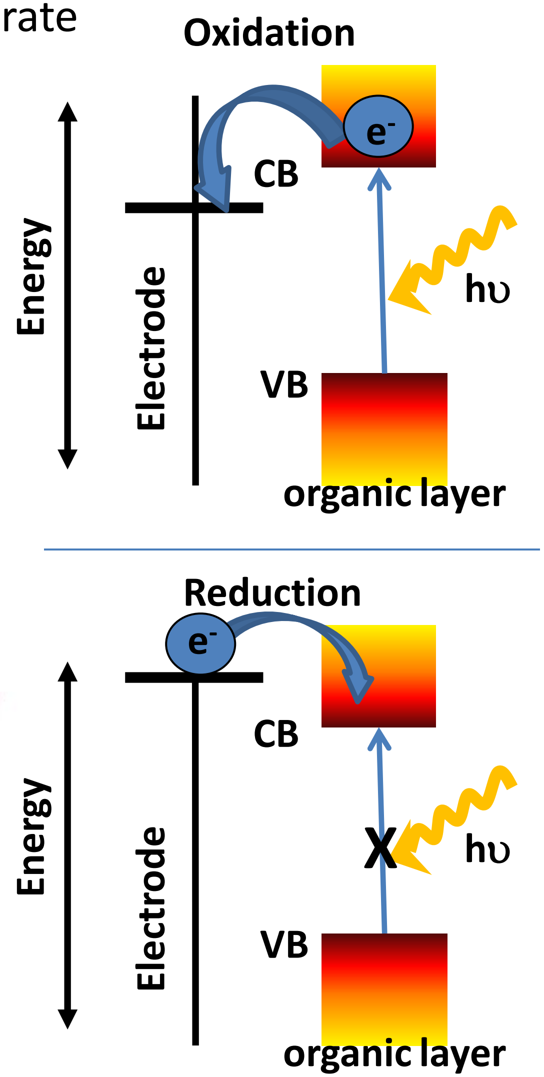
Lin, H. et al. *J Phys Chem Lett.*, **2012**, *3,* 1154–1158

Spectroelectrochemistry in ATR geometry

Potential-controlled experiment: spectroscopically observe the redox behavior of the thin film

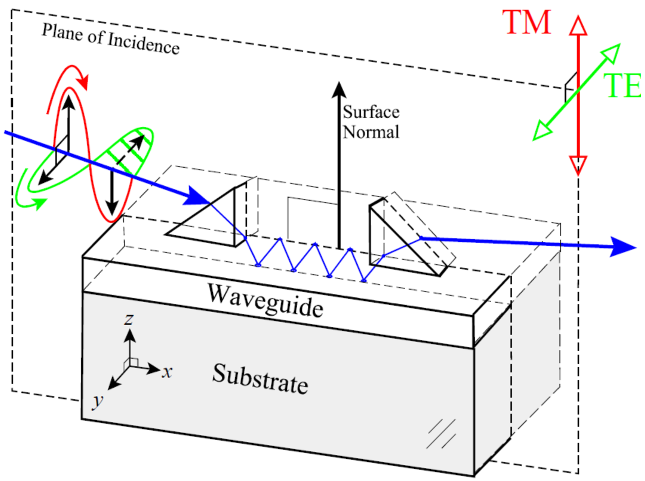
Potential-modulated experiment: measure the charge transfer rate

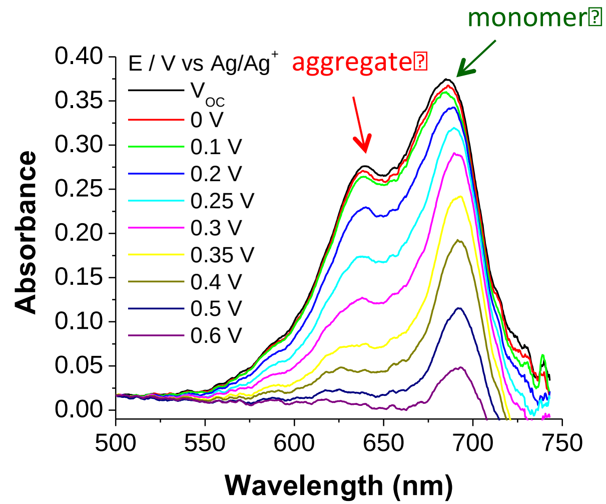


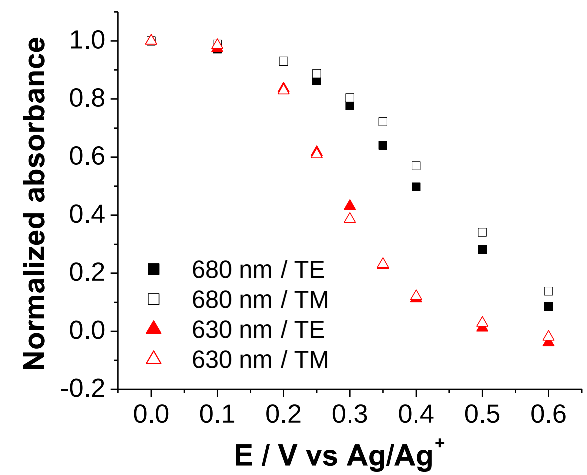


1) Identify midpoint potential
2) Wavelength of light

Waveguide Spectroelectrochemistry and Molecular Orientation Studies

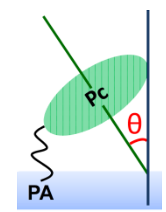




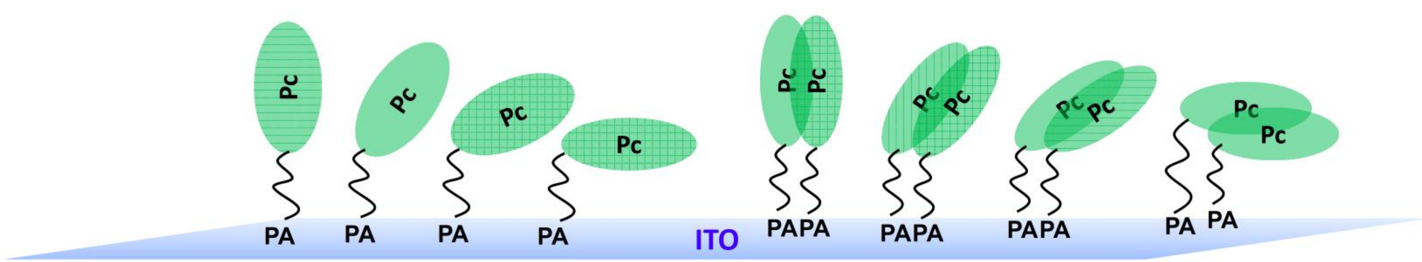


Mean tilt angle of Pc molecular planes determined using both

- polarized waveguide ATR
  - $\theta_{monomer}$ = 33˚ ± 1˚
  - $\theta_{aggregate}$ = 58˚ ± 0.7˚
- NEXAFS: $\theta_{entire\ film}$ = 52˚ ± 1˚

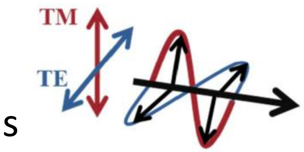


Distribution of molecular orientations

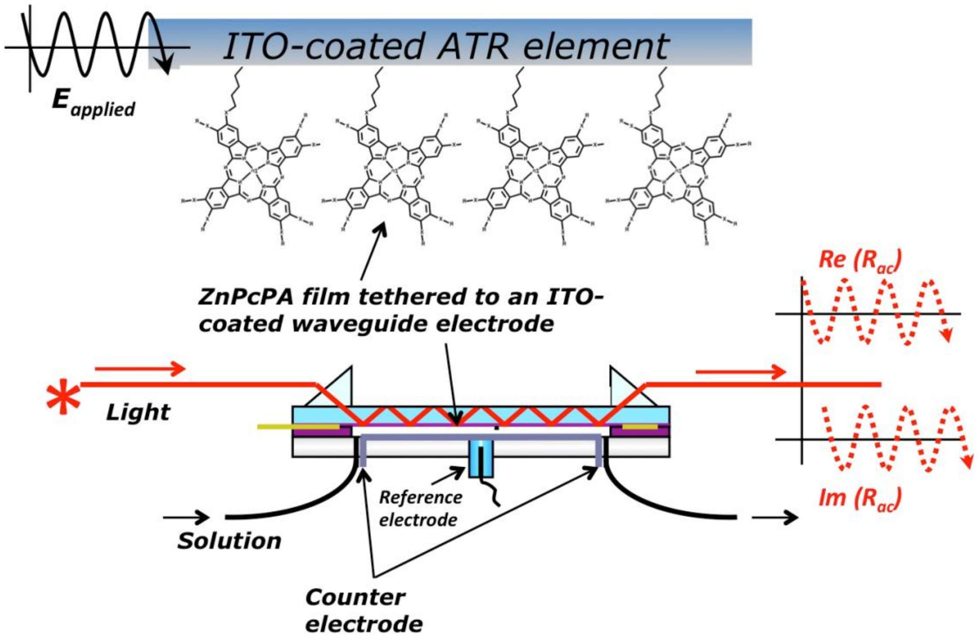


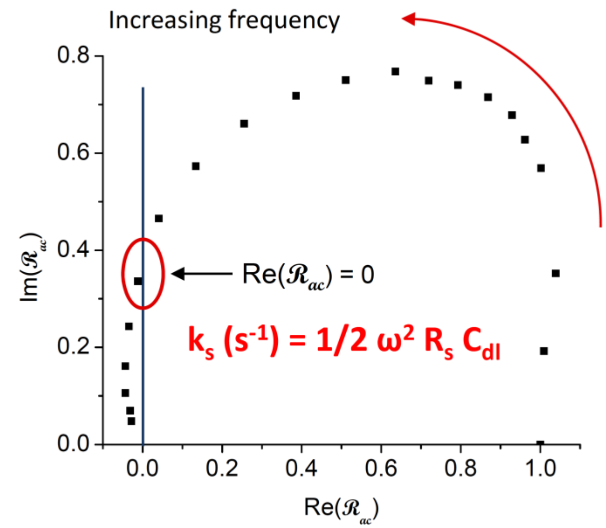
Lin, H. et al. *J Phys Chem Lett.*, **2012**, *3,* 1154–1158

Correlating Orientation and Charge Transfer Rate Constants by PM-ATR



Using different polarizations and wavelengths, differently oriented subpopulations of molecules are probed





	Monomer		Aggregate	
	680 nm		630 nm	
$k_s (s^{-1})$ by CV	1.7 ± 0.2		2.4 ± 0.1	
Polarization	TE	TM	TE	TM
$k_s\ (s^{-1}) \times 10^2$	2.0 ± 0.6	1.7 ± 0.5	21 ± 5	7 ± 2

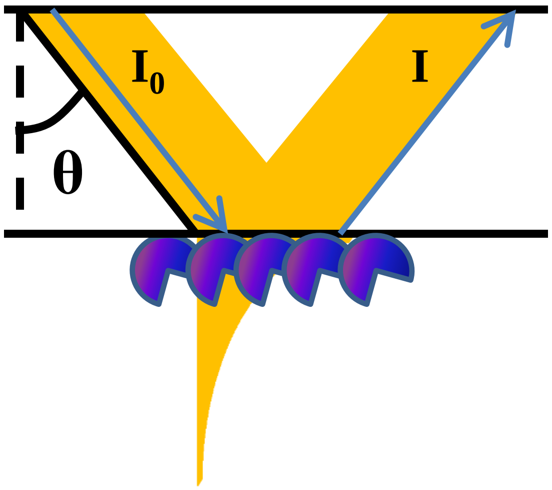
Impact: Resolution of orientation-dependent charge transfer rates

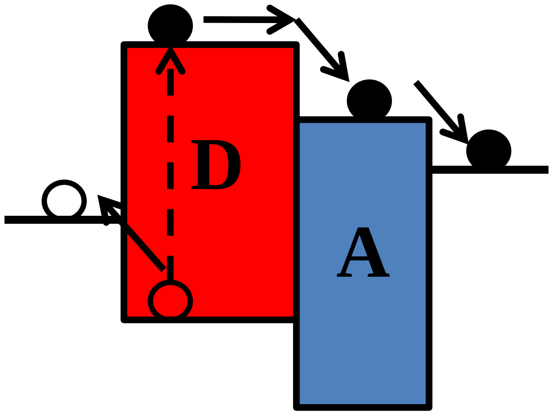
Lin, H. et al. *J Phys Chem Lett.*, **2012**, *3,* 1154–1158

Take home message

- Waveguide spectroscopies combined with transient absorption and electrochemical potential modulation are uniquely addressing the **fundamental questions** about charge transfer/recombination kinetics at the molecular film/TCO interface

- Continuous development of these techniques coupled with the feedback loop framework of the CIS:SEM will help provide answers for basic chemistry questions





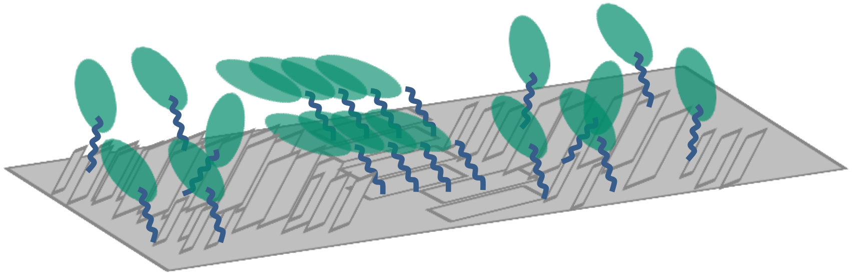
Future directions

Faster timescales

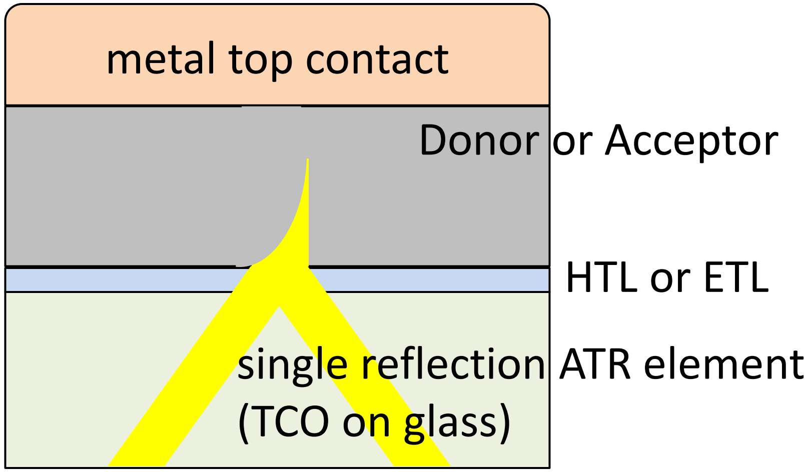
New facility combines Helios/Eos with range of 50 ps to 500 ms

Needs to be configured for ATR geometry and benchmarked

Implement and assess strategies to control orientation, compare to $Pc(PA)_4$



Variable-angle ATR in a diode to monitor concentration-distance profiles of charge carrier generation



Acknowledgements

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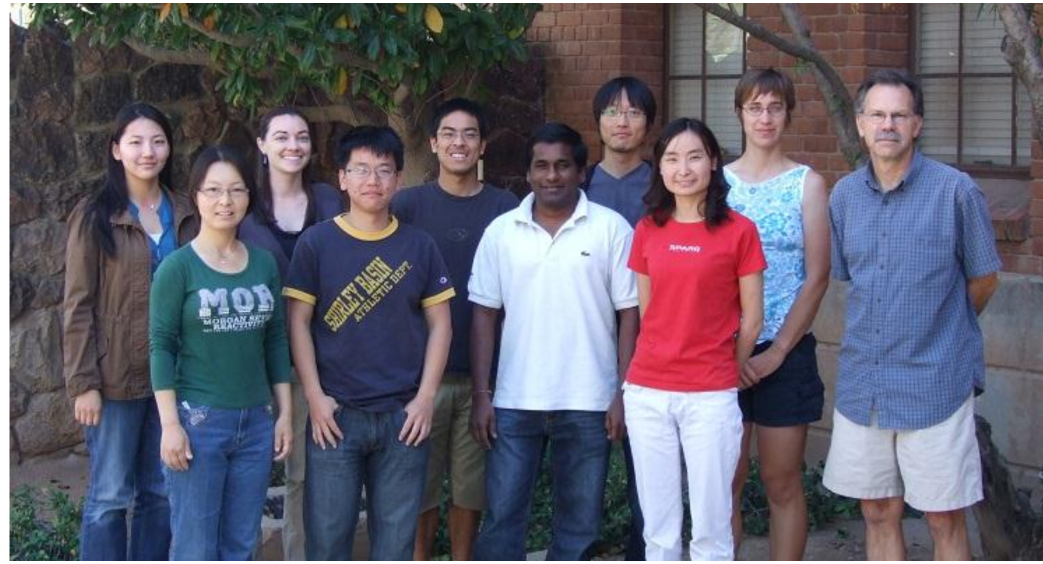

US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center (CIS:SEM)

Poster #36 & Poster #52