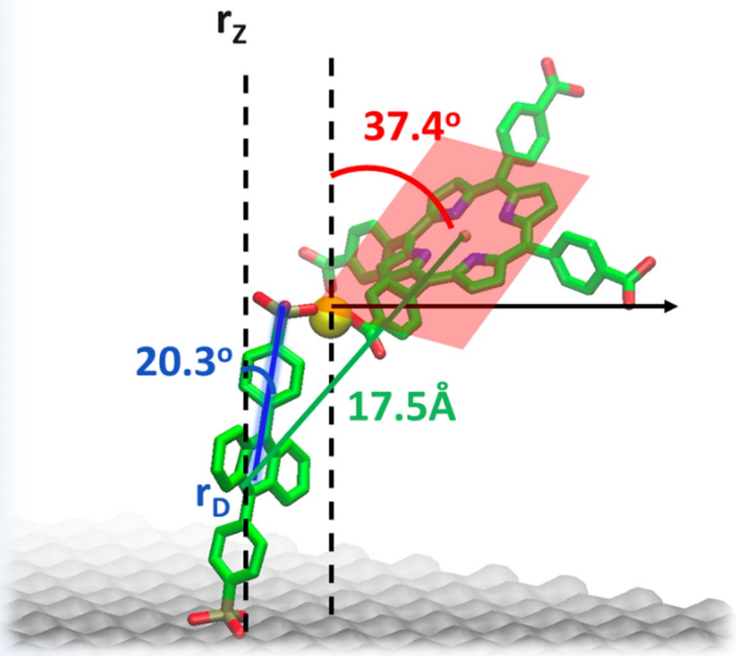
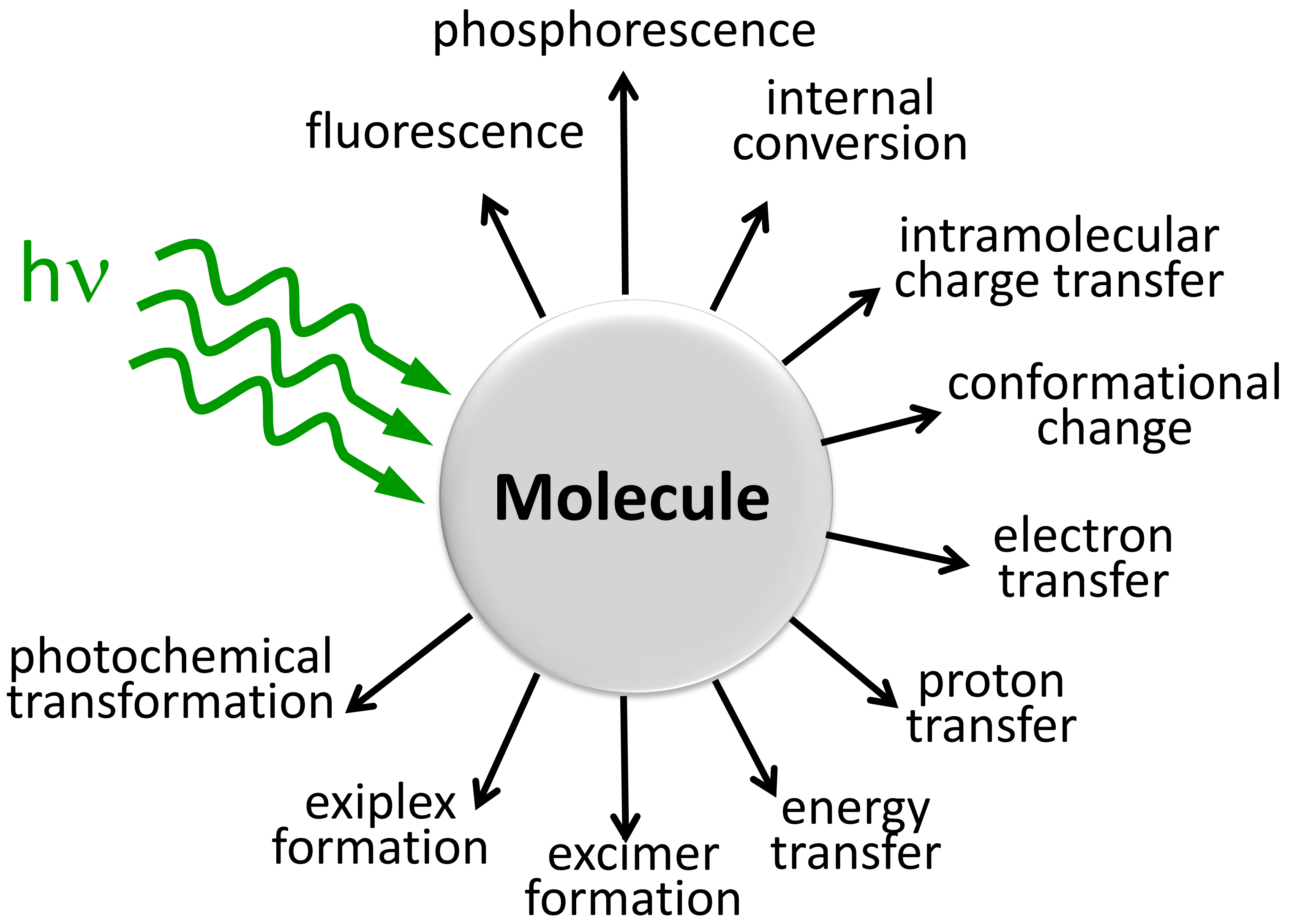
Hanson
Research Group

Understanding and Controlling Molecular Excited State Processes Using Metal Oxide Interfaces



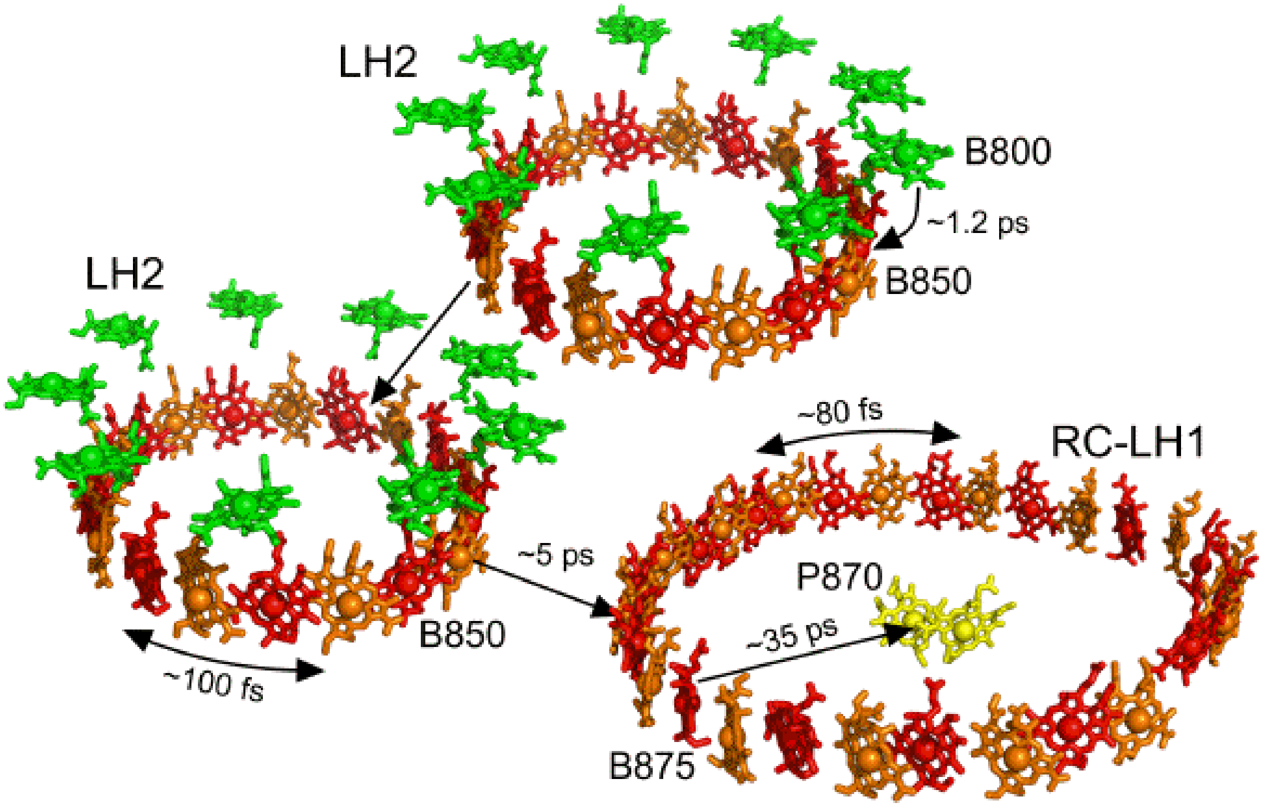
Kenneth Hanson
Department of Chemistry & Biochemistry
Florida State University, Tallahassee, FL, USA

Molecular Photochemistry/Photophysics

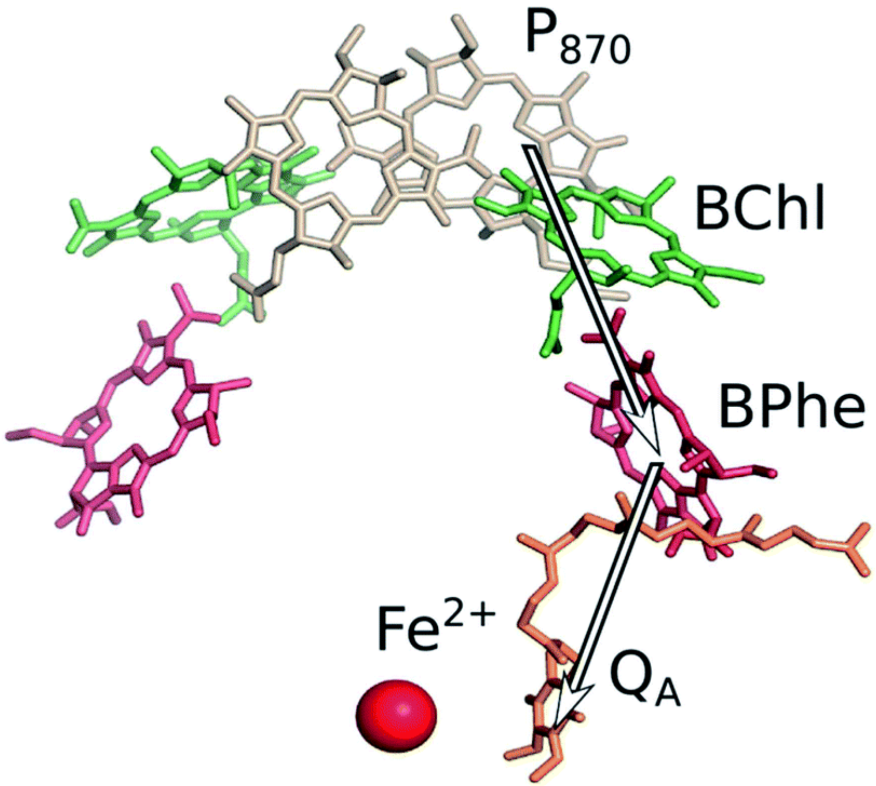


Molecular Photochemistry/Photophysics

Energy Transfer



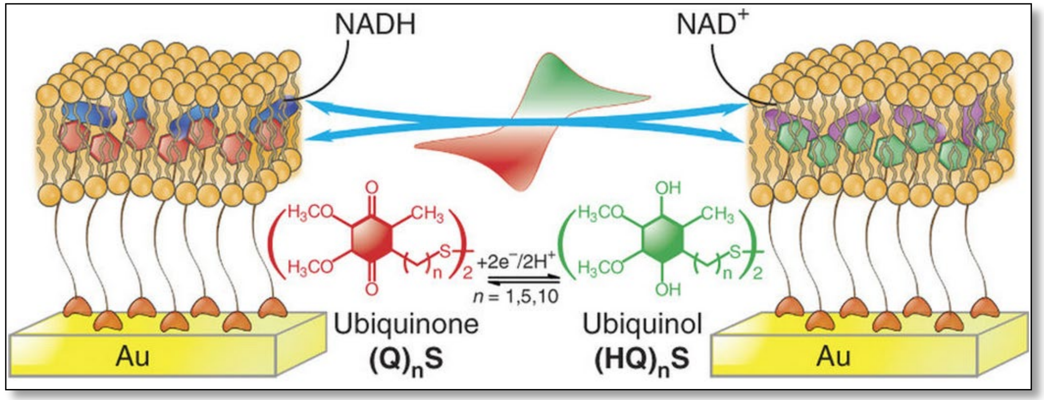
Electron Transfer



Sundström et al. *J. Phys. Chem. B* **1999**, 103, 2327-2346.
Lundholm et al. *RSC Adv.* **2014**, 4, 25502-25509.

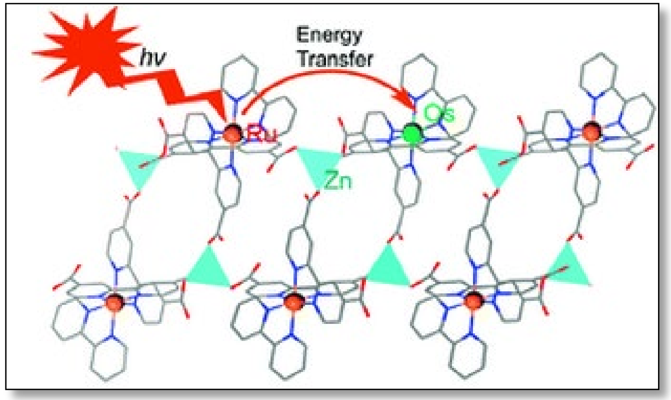
Structural Control: Humans

Phospholipid Bilayers



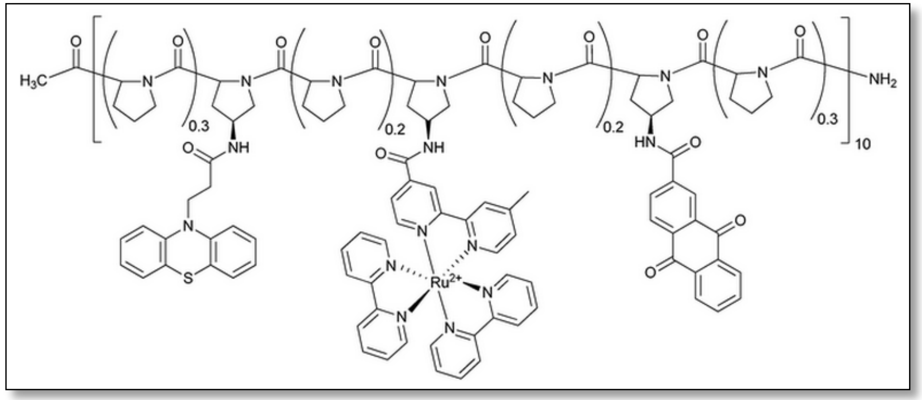
Ma et. al. *Nature Protocols*, **2013**, *8*, 439

Metal Organic Frameworks



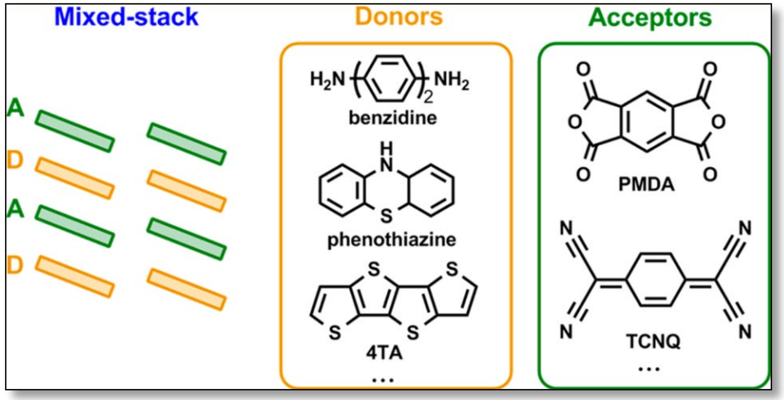
Kent et. al. *J. Am. Chem. Soc.*, **2010**, *132*, 12767

Polypeptides



Slate et. al. *J. Am. Chem. Soc.*, **1998**, *120*, 4885

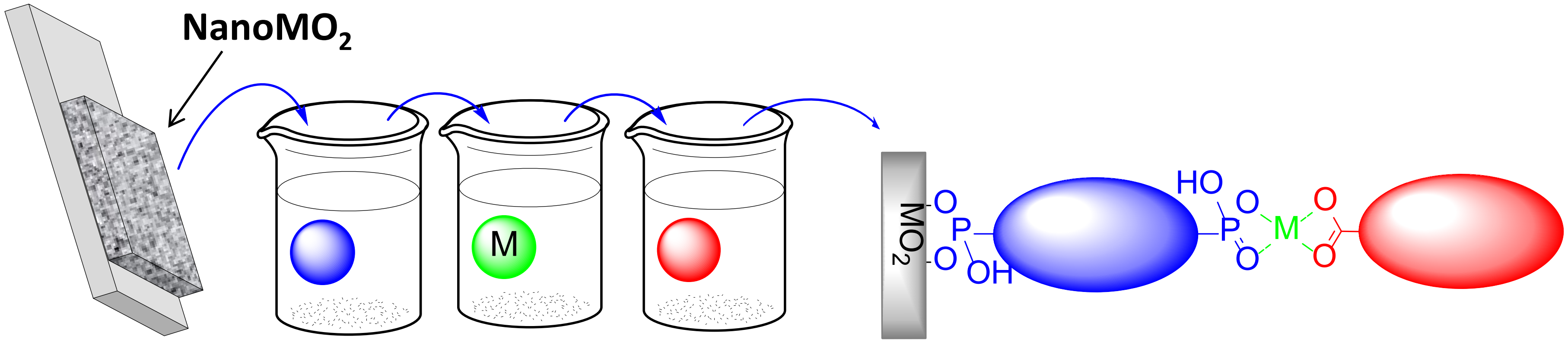
Crystals



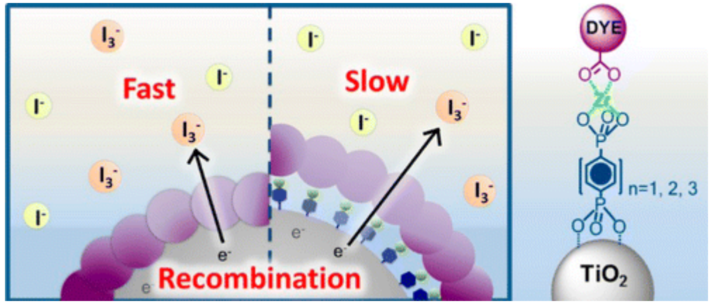
Zhu et. al. *J. Phys. Chem. C*, **2014**, *118*, 14150

Hanson Research Group

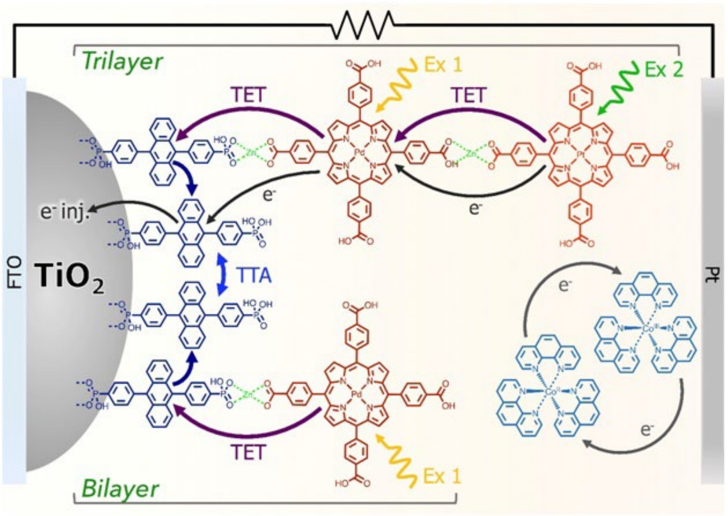
Metal Ion-Linked Multilayer



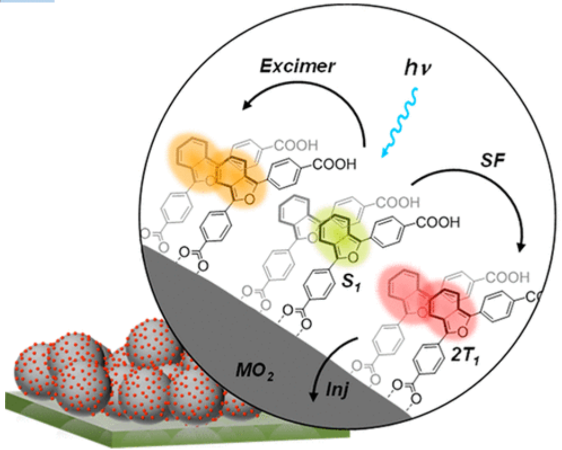
Control e⁻ Transfer



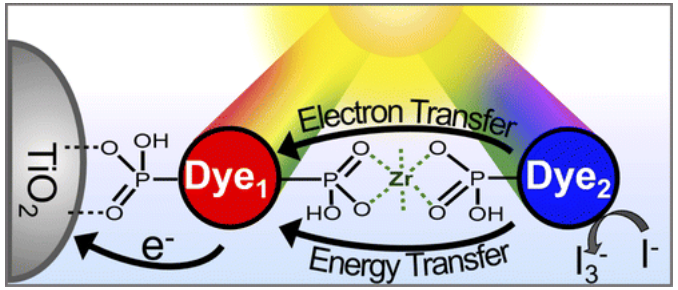
Photon Upconversion



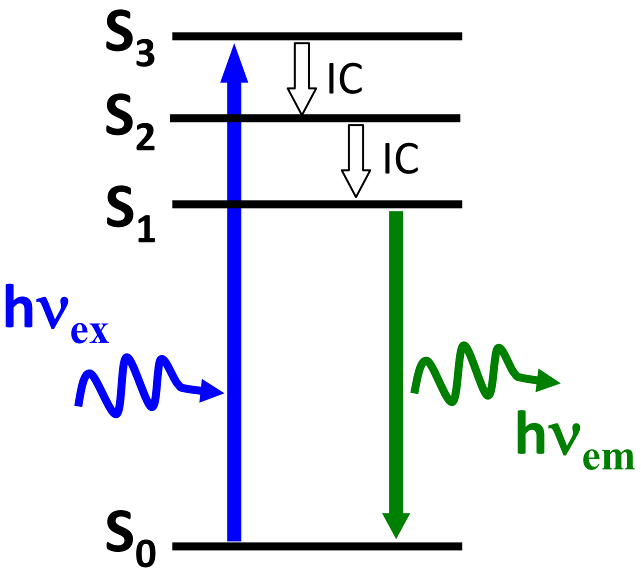
Singlet Fission

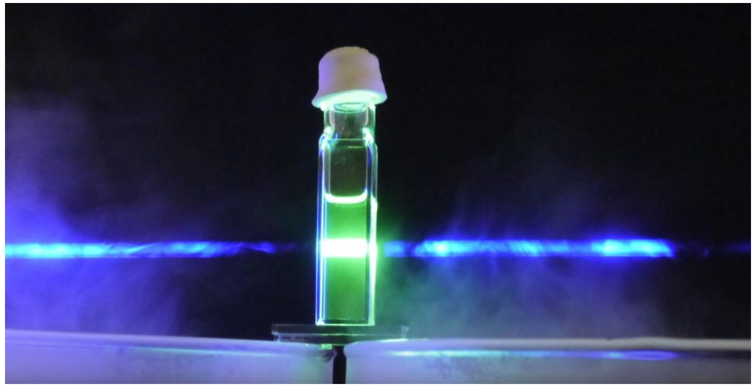


Energy/e⁻ Cascade

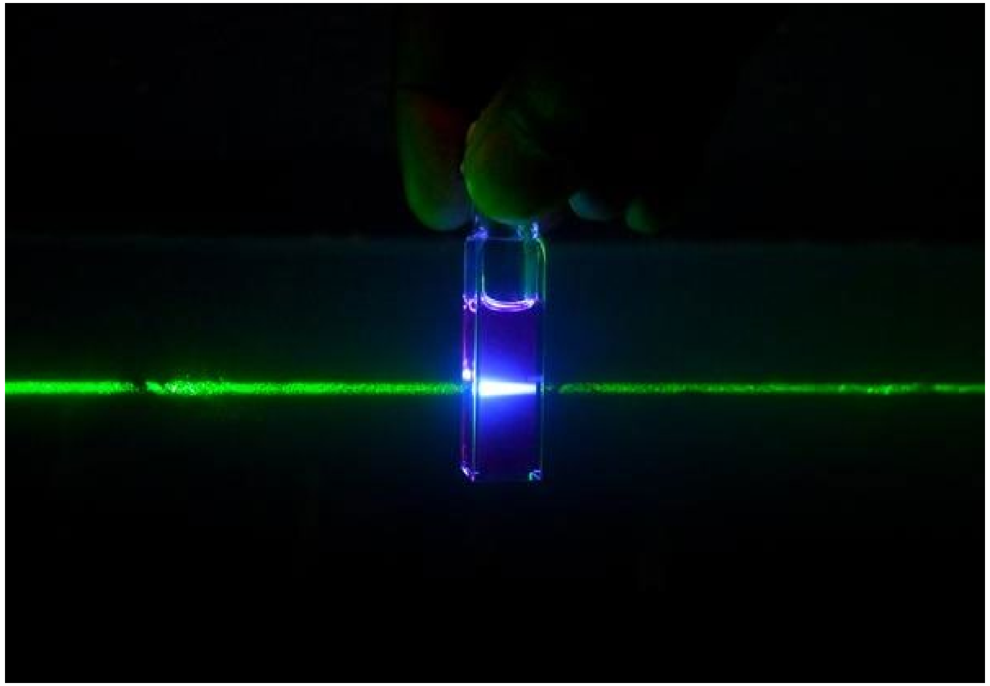


Down Conversion vs. Upconversion



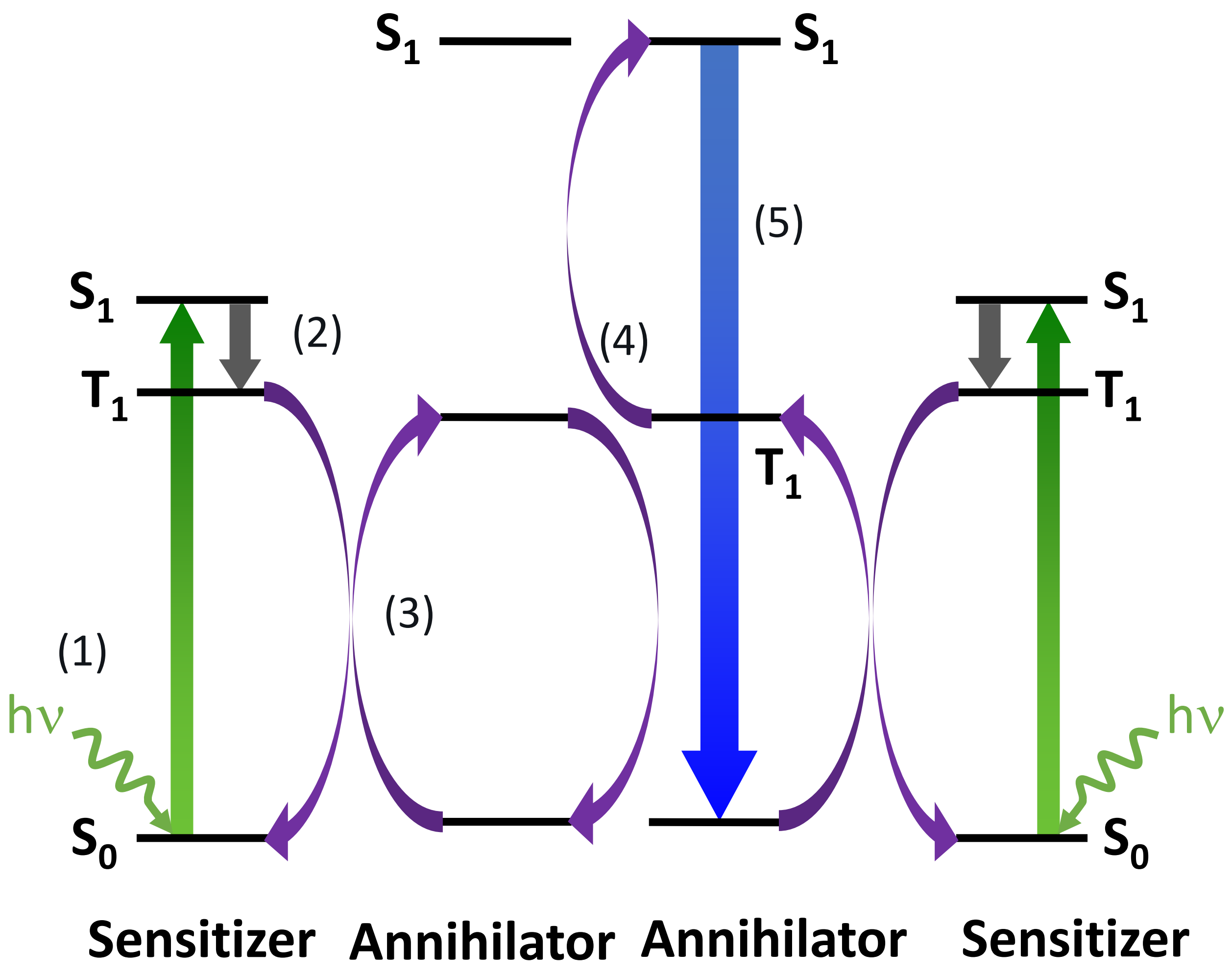


$h\nu \rightarrow h\nu$



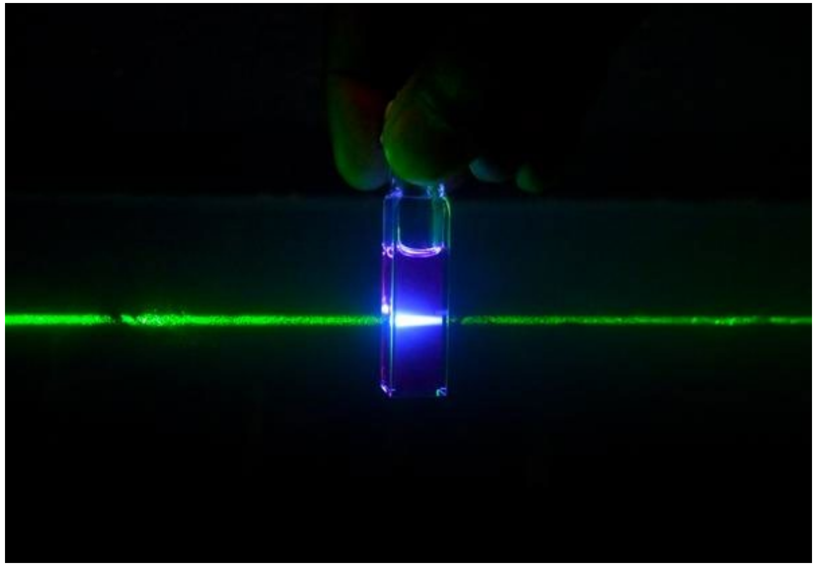
$h\nu \rightarrow h\nu$

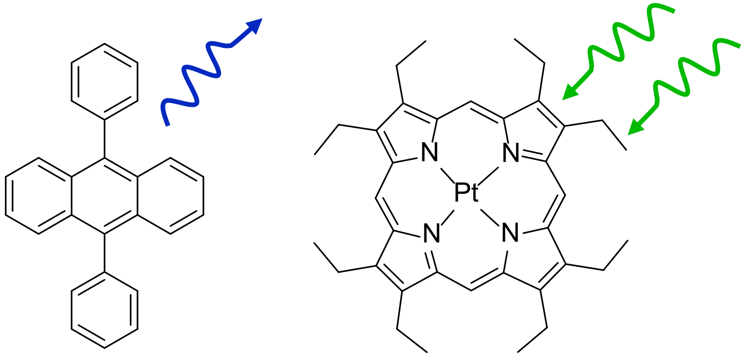
Photon Upconversion

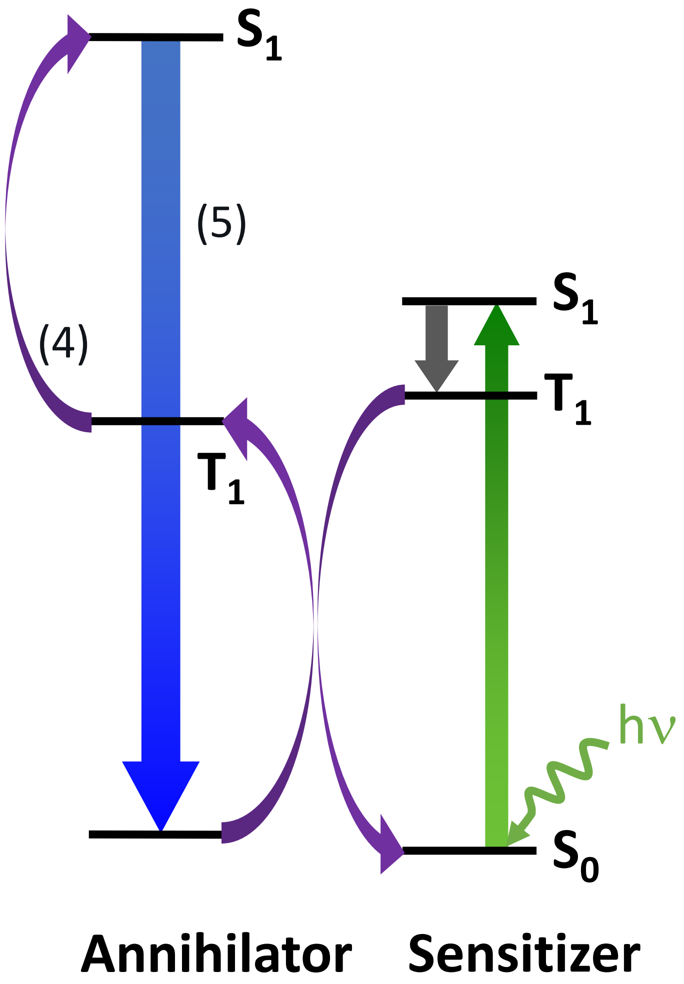


$2\ h\nu \rightarrow h\nu$

Photon Upconversion

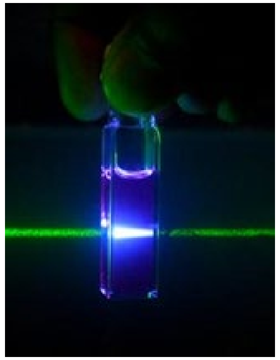






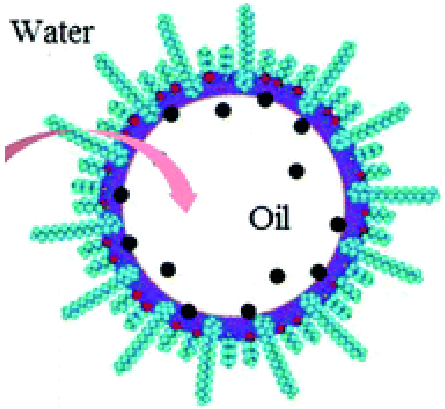
$2\ h\nu \rightarrow h\nu$

Sensitizer-Annihilator Interactions



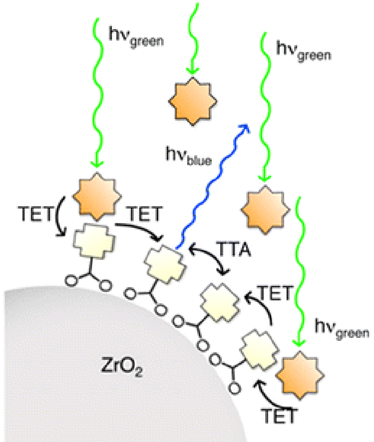
Solution

Chem. Commun., 2004, 2860



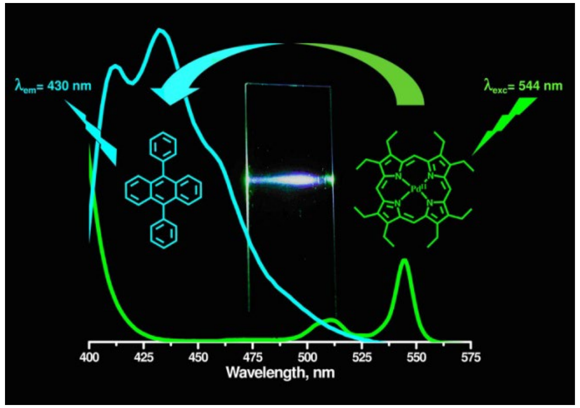
Microemulsion

Photochem. Photobiol. Sci. 2014, 13, 48



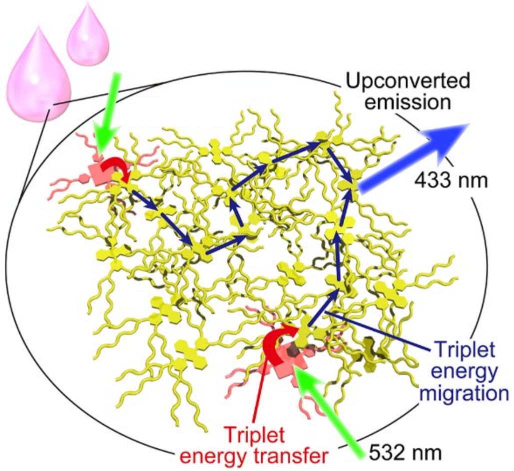
Heterogeneous

J. Phys. Chem. C, 2013, *117*, 14493



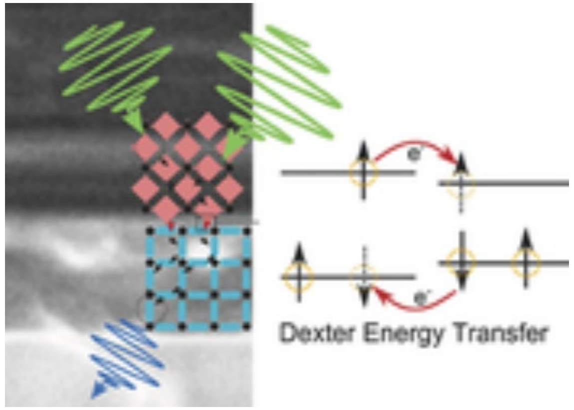
Polymer Films

JACS 2007, 129, 12652



Neat-solvent

JACS 2013, 135, 19056



MOF

JACS 2016, 138, 6541

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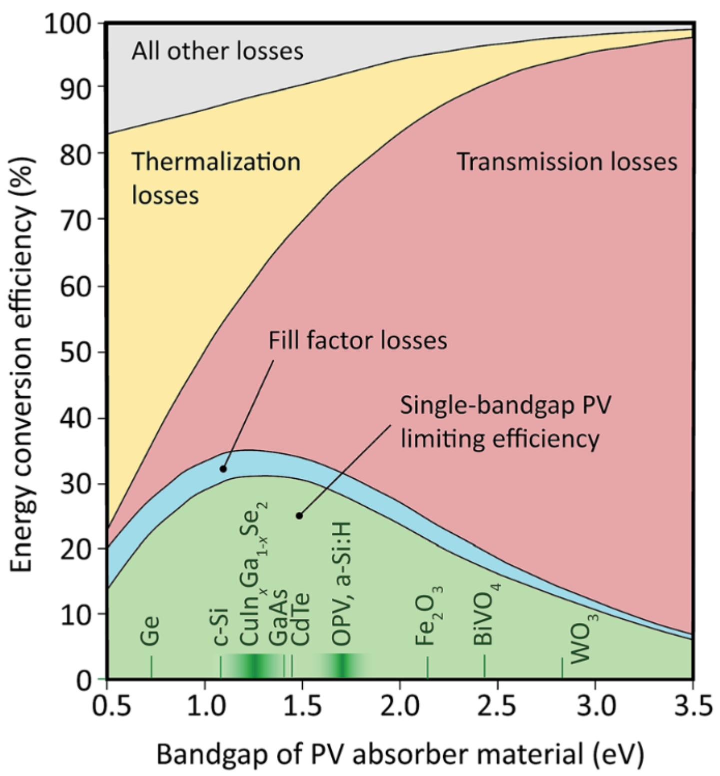
Solar Cell Efficiency

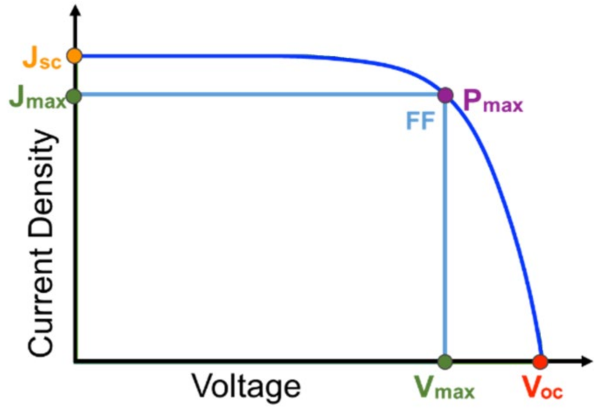
Schulze and Schmidt *Energy Environ. Sci*. **2015**, 8, 103-125



$$ECE(\%) = \frac{P_{max}}{P_{in}} \text{ x } 100$$

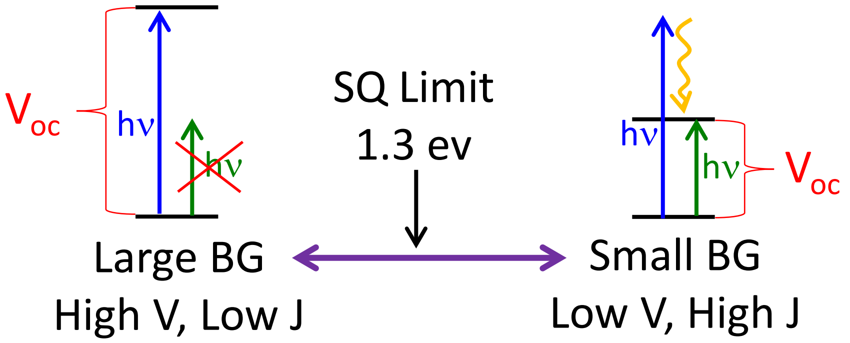
P_{in} = 100 mW/cm^2 (AM1.5)

P_{max} = J x V



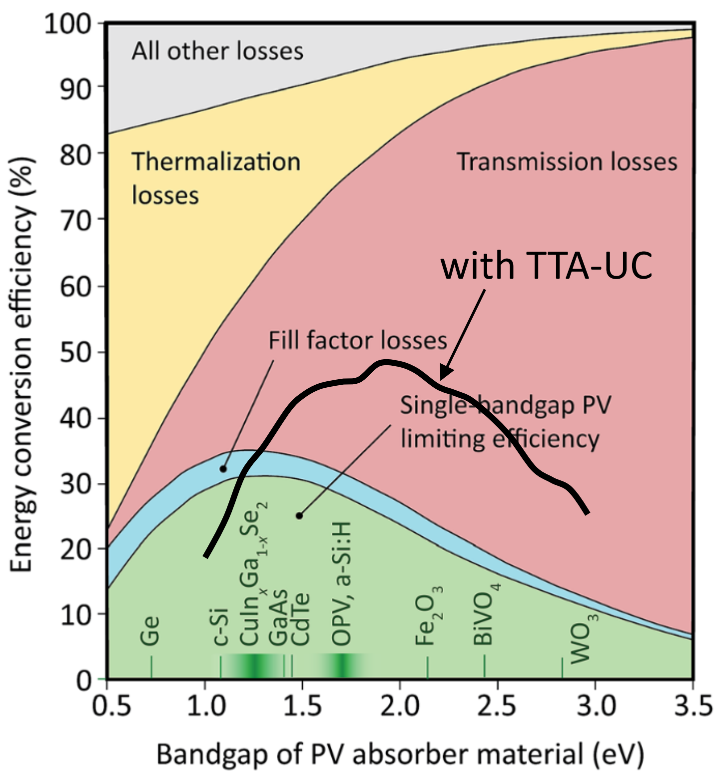
Max Theoretical Efficiency

Standard solar cell ~33%
1.3 eV bandgap

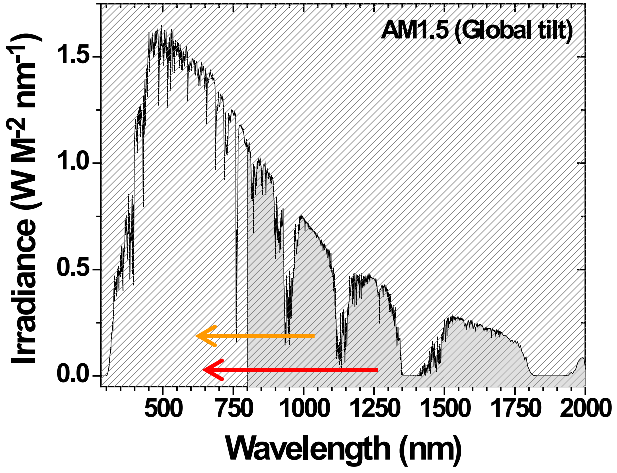


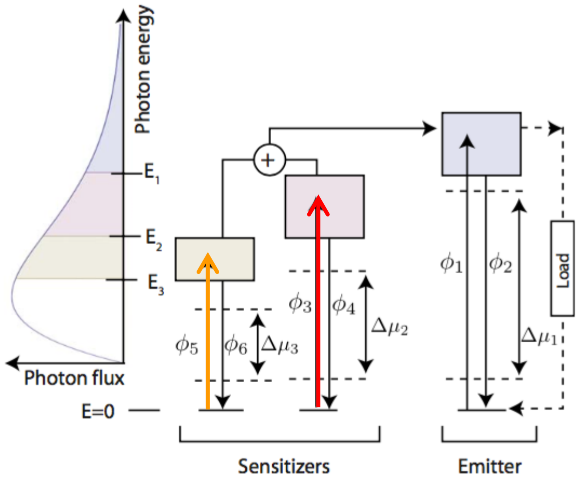
Solar Cell Efficiency

Schulze and Schmidt *Energy Environ. Sci.* **2015**, 8, 103-125



Perovskites, OPV, DSSC





Ekins-Daukes and Schmidt,
Appl. Phys. Lett., **2008** 93, 063507.

Max Theoretical Efficiency

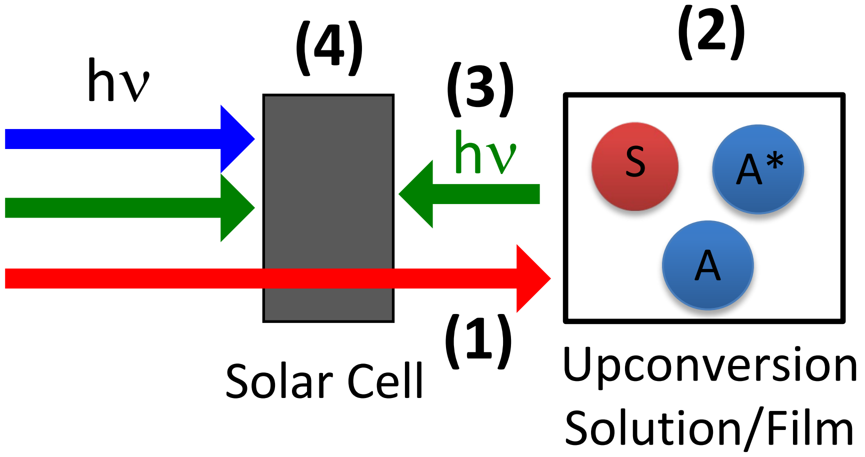
Standard solar cell ~33%
1.3 eV bandgap

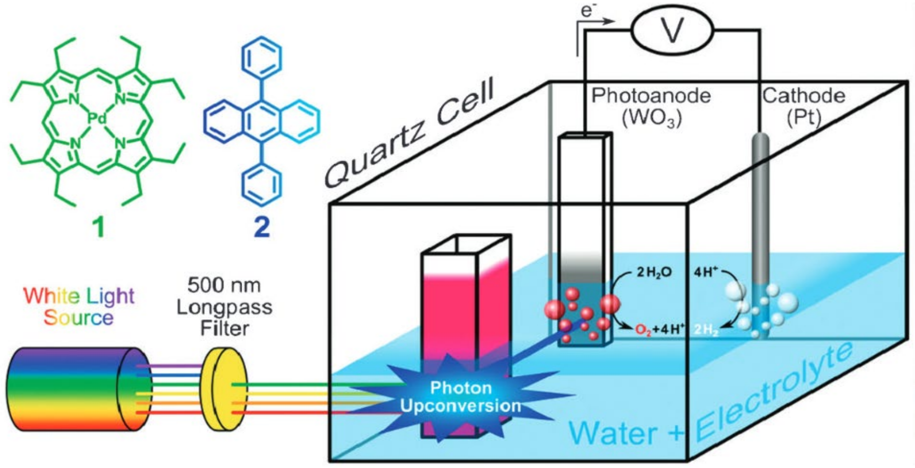
Solar cell with upconversion > 45%
1.76 eV bandgap

Harnessing TTA-UC

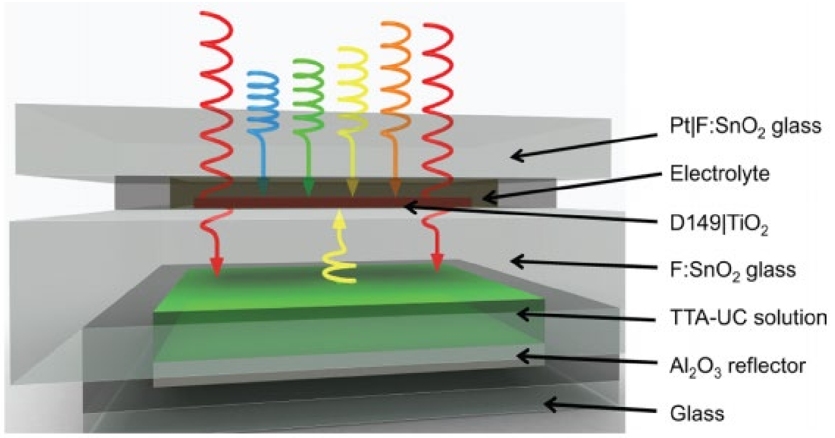
Optical Coupling:

1) Transmission
2) Light absorption and TTA
3) Upconverted emission
4) Absorption by a solar cell





Chem. Commun. **2012**, 48, 209.

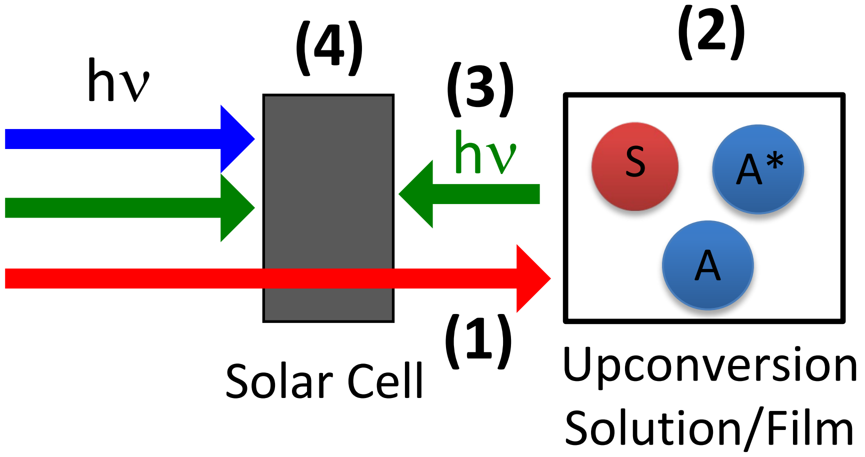


J. Phys. Chem. Lett. **2013**, 4, 2073.

Harnessing TTA-UC

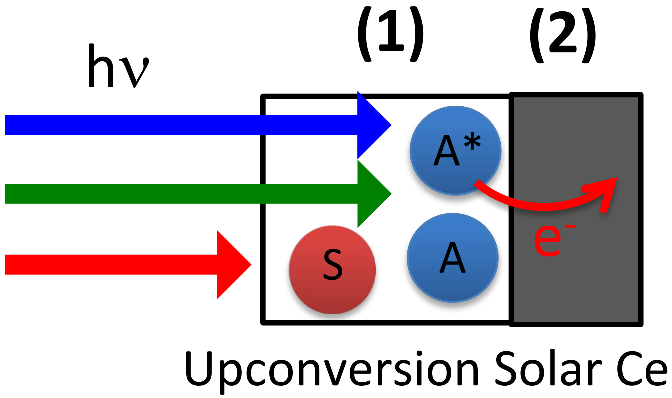
Optical Coupling:

1) Transmission
2) Light absorption and TTA
3) Upconverted emission
4) Absorption by a solar cell



Electronic Coupling:

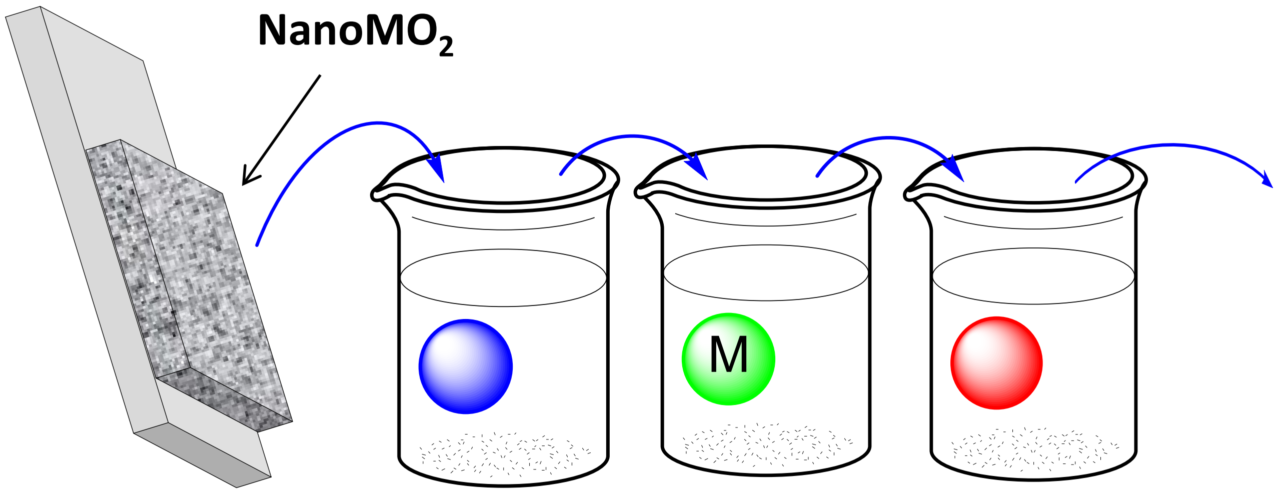
1) Light absorption and TTA
2) Photocurrent Generation

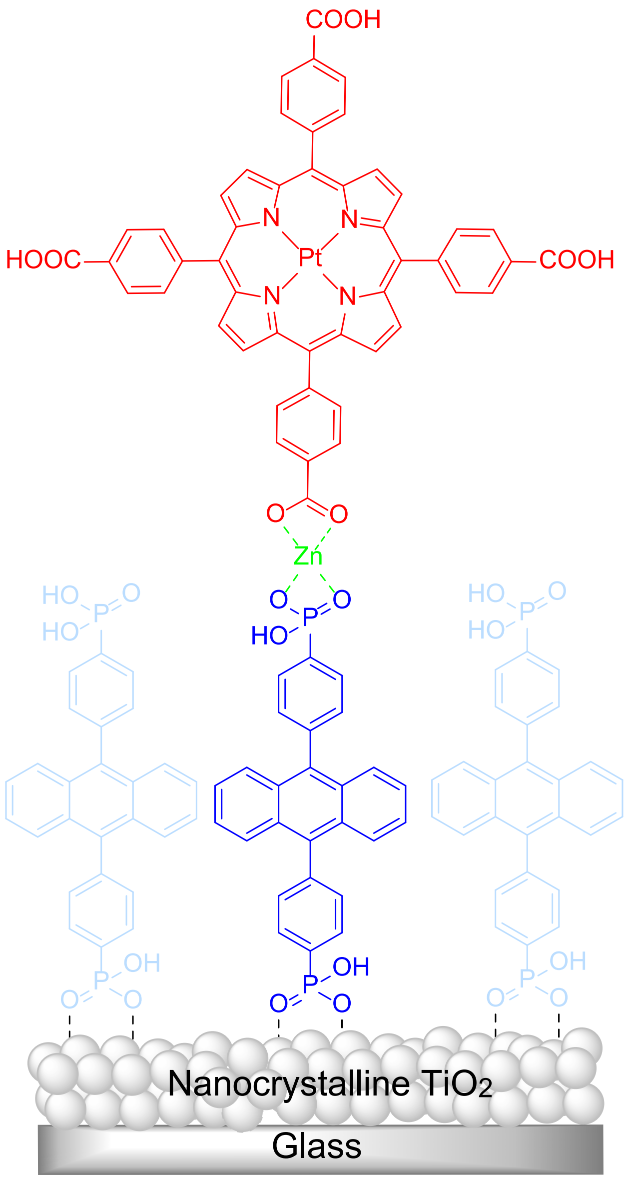


- No isotropic emission
- No self-absorption
- Increase sensitizer concentration

Need A* at a charge separation interface!

Metal Ion-Linked Multilayer





- S and A in proximity
- A-A interactions
- On a charge separation interface
- Easy DSSC integration

Hill et al. *J. Phys. Chem. Lett.* **2015**, 6, 4510.

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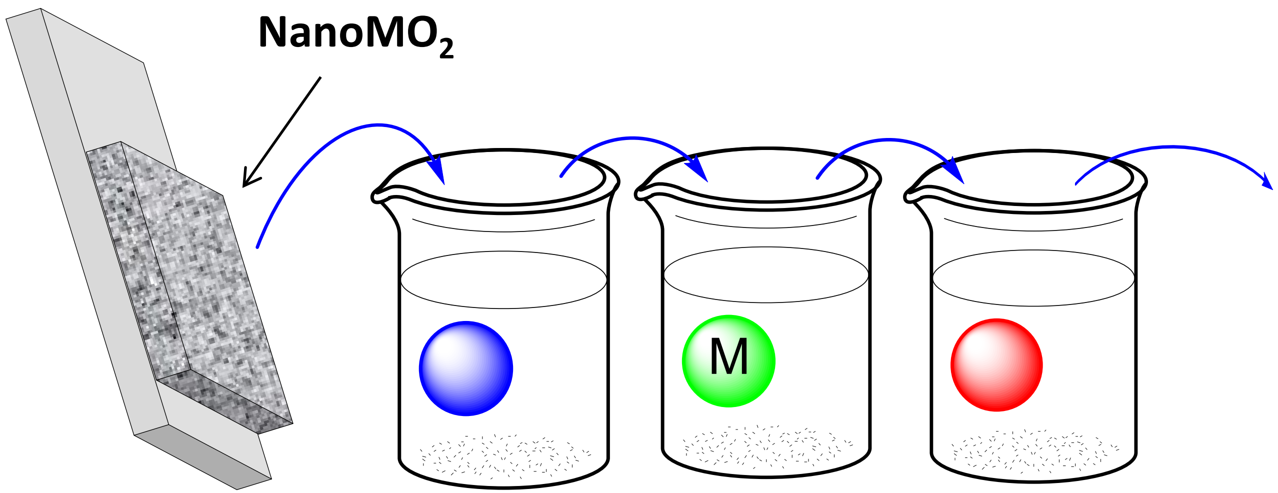
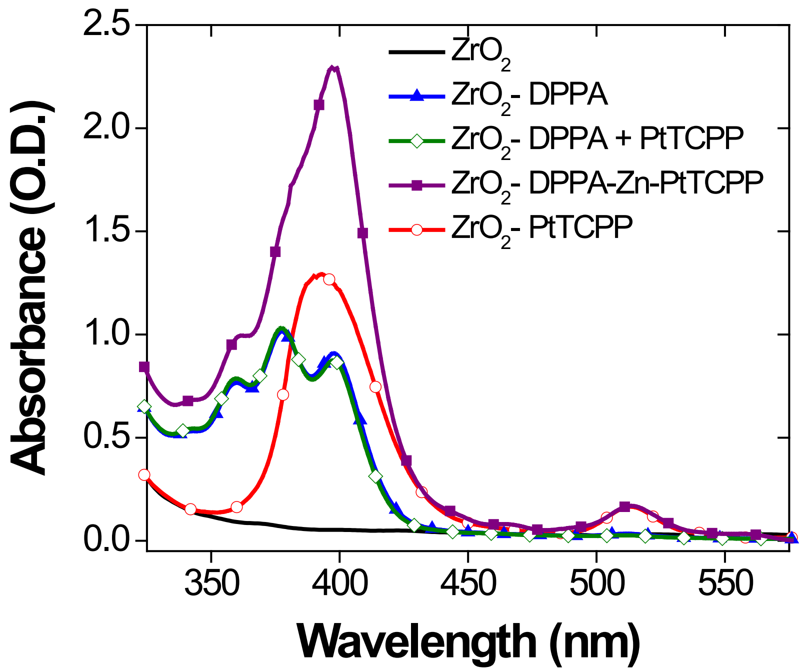
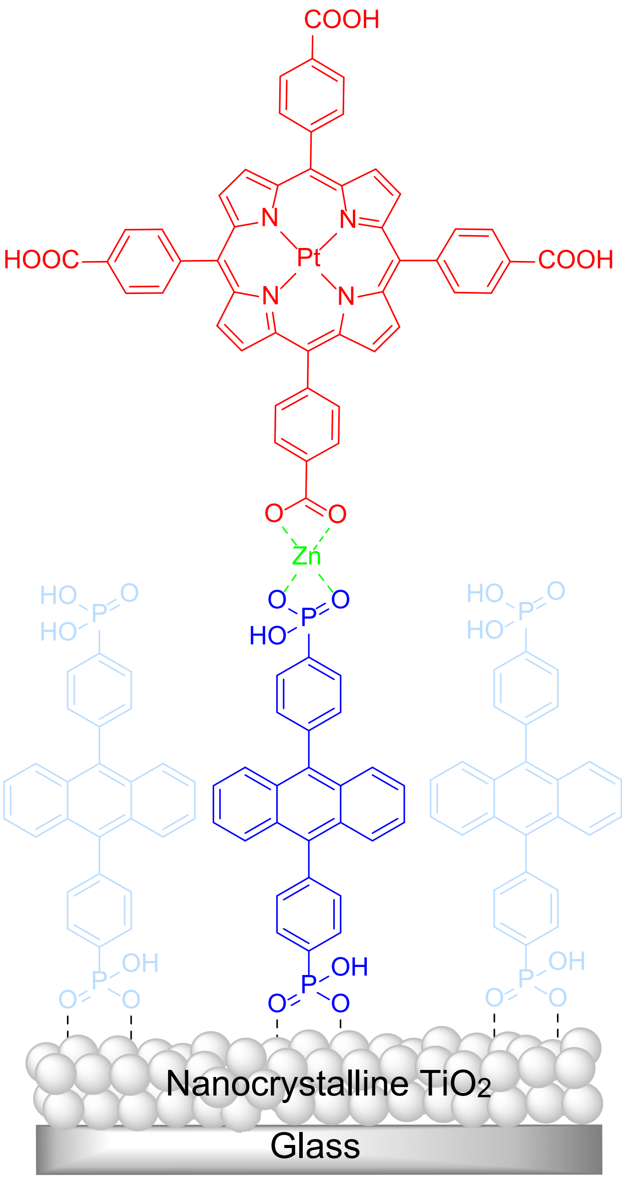
Metal Ion-Linked Multilayer

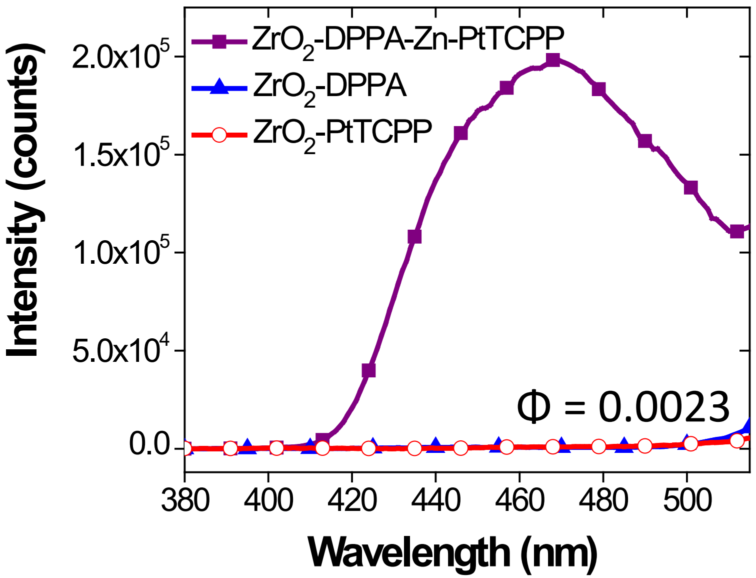


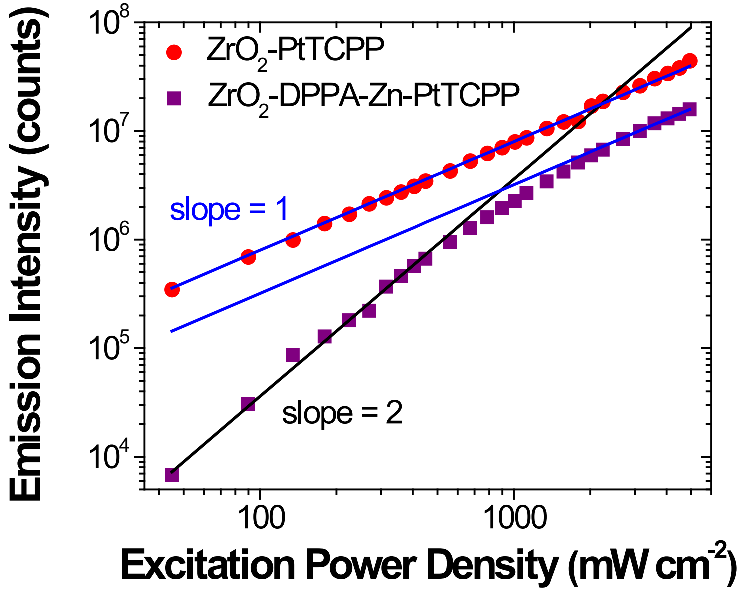


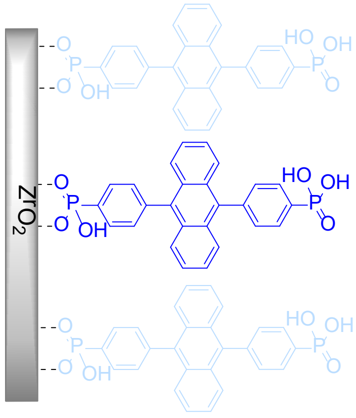


TTA-UC Emission

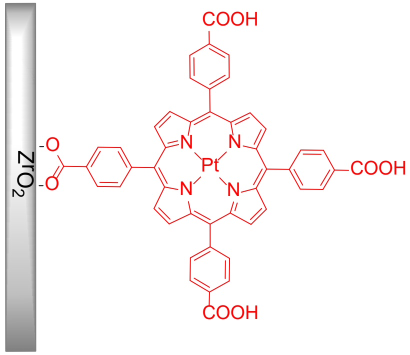
λ_{ex} = 532 nm (1 W/cm^2)



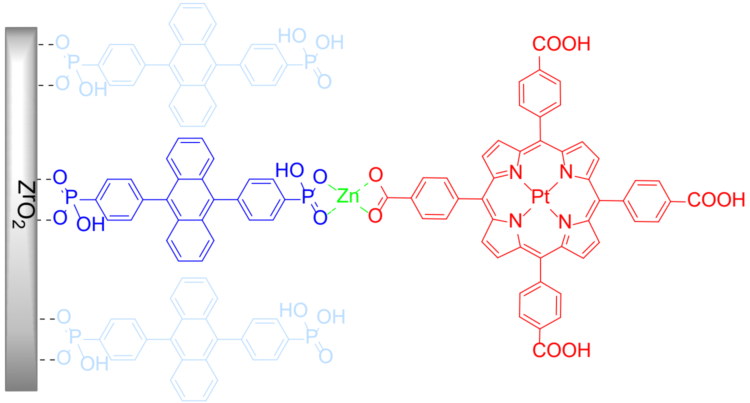




DPPA



PtTCPP



DPPA-Zn-PtTCPP

Hill et al. *J. Phys. Chem. Lett.* **2015**, 6, 4510.

TTA-UC Emission

Weak TTA Limit

$$N_F = \frac{\Phi_F k_{TT}[^3A^*]_0^2}{2k_T}$$

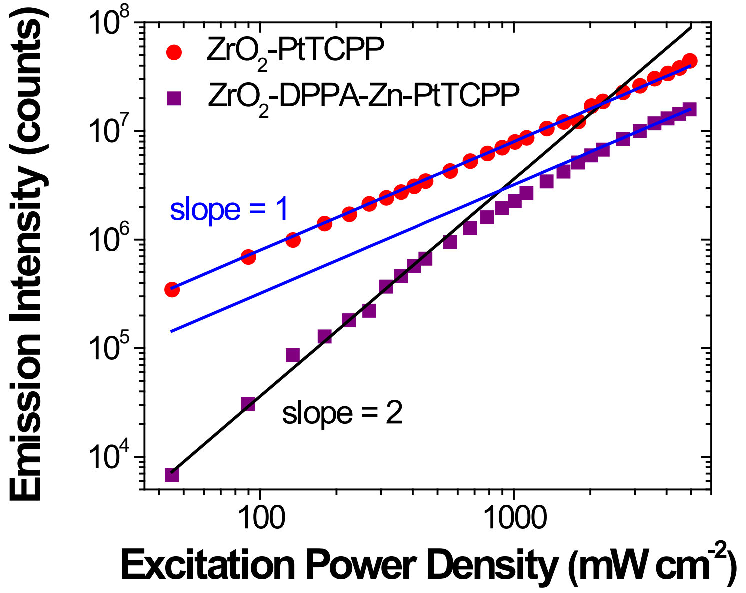
Slope = 2

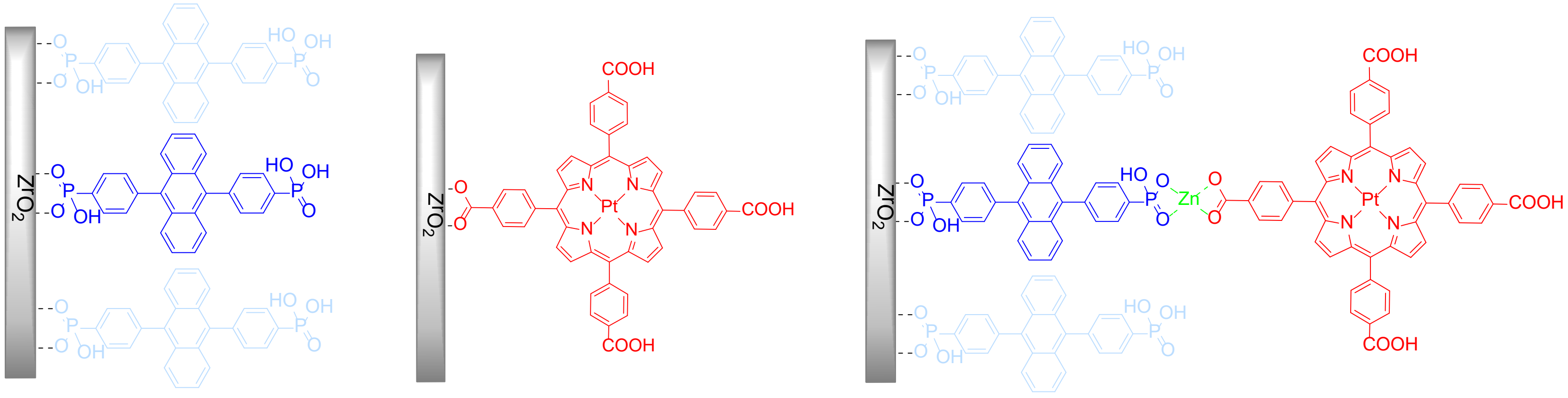
Strong TTA Limit

$$N_F = \Phi_F[^3A^*]_0$$

Slope = 1

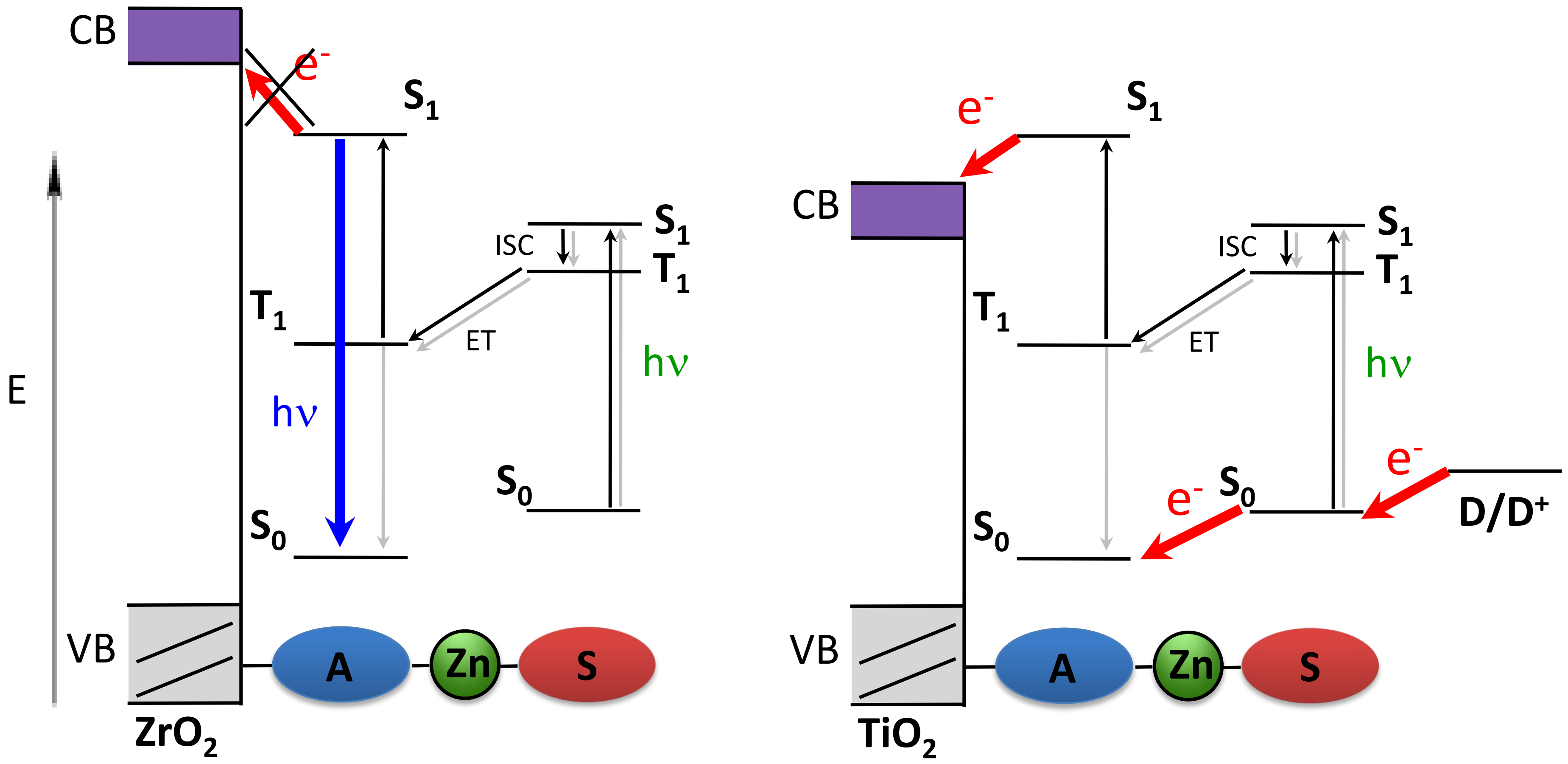
Castellano et al. *J. Phys. Chem. Lett.* **2012**, 3, 299-303.





Hill et al. *J. Phys. Chem. Lett.* **2015**, 6, 4510.

Mechanism



Upconverted Emission!

Photocurrent?

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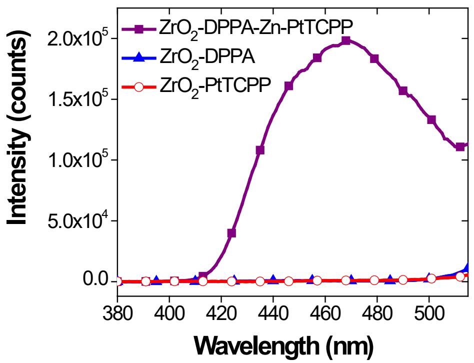
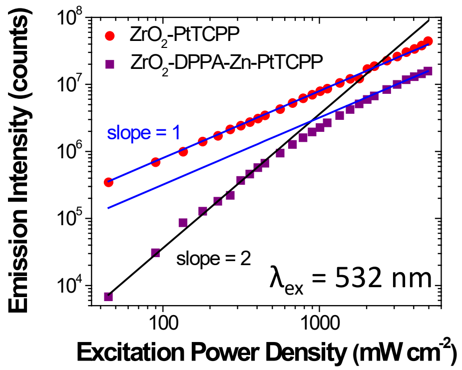
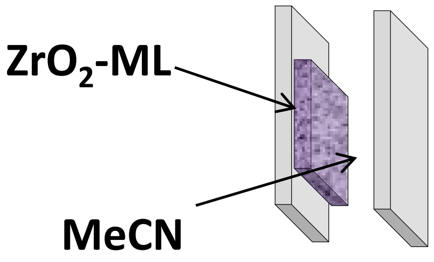
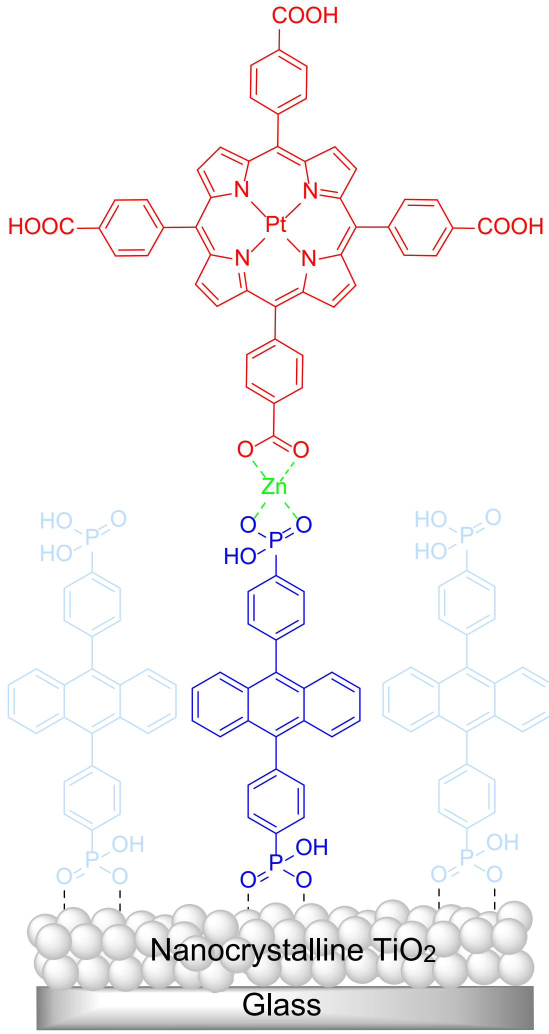
TTA-UC Photocurrent

On ZrO_2: Upconverted Emission



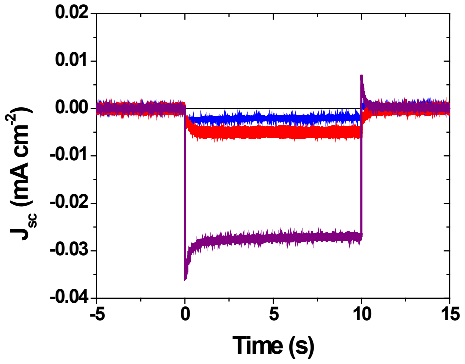


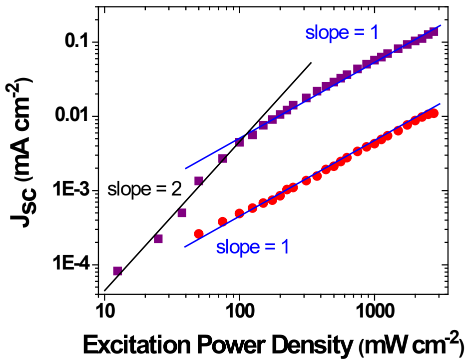


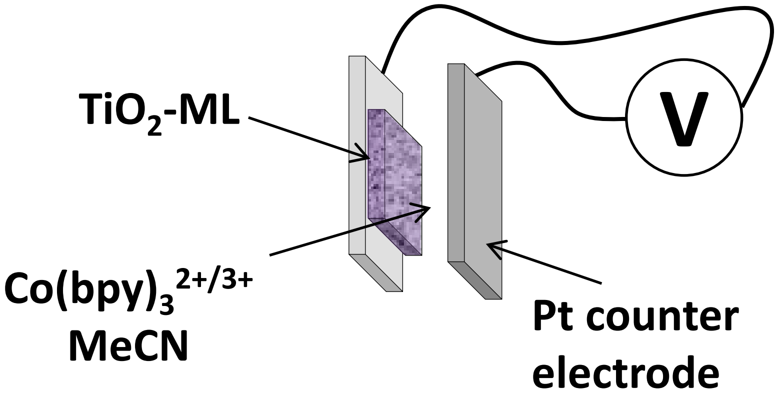


J. Phys. Chem. Lett. **2015**, 6, 4510.

On TiO_2: Upconverted Photocurrent







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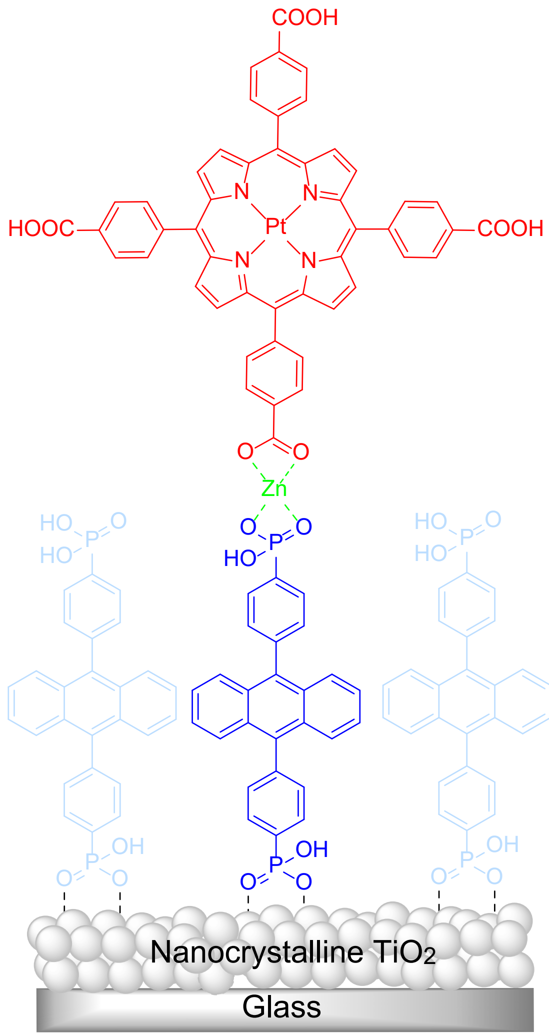
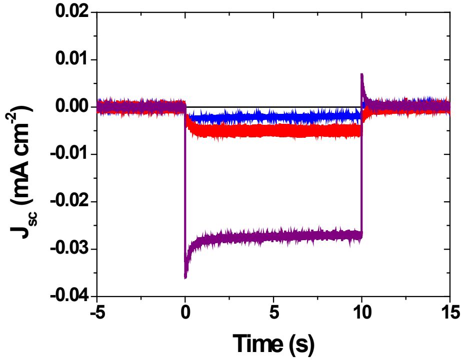
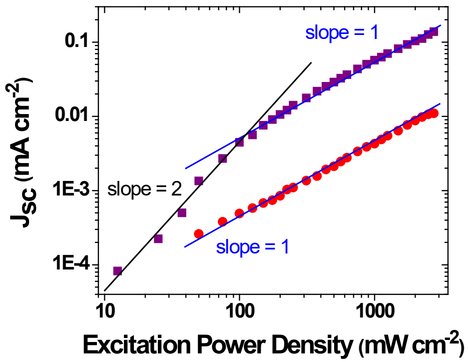
TTA-UC Photocurrent

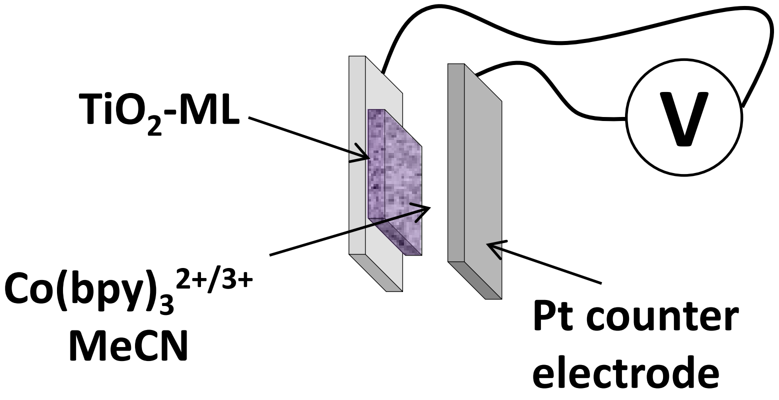
- J_{sc}/V_{oc} greater than the sum of its parts.
- J_{sc}= 0.009 mA/cm^2 *ACS Energy Lett.* **2016**, 1, 3-8.
- Demonstrated an integrated TTA-UC solar cell.
- η = 1.6 x 10^{-5} %



On TiO_2: Upconverted Photocurrent

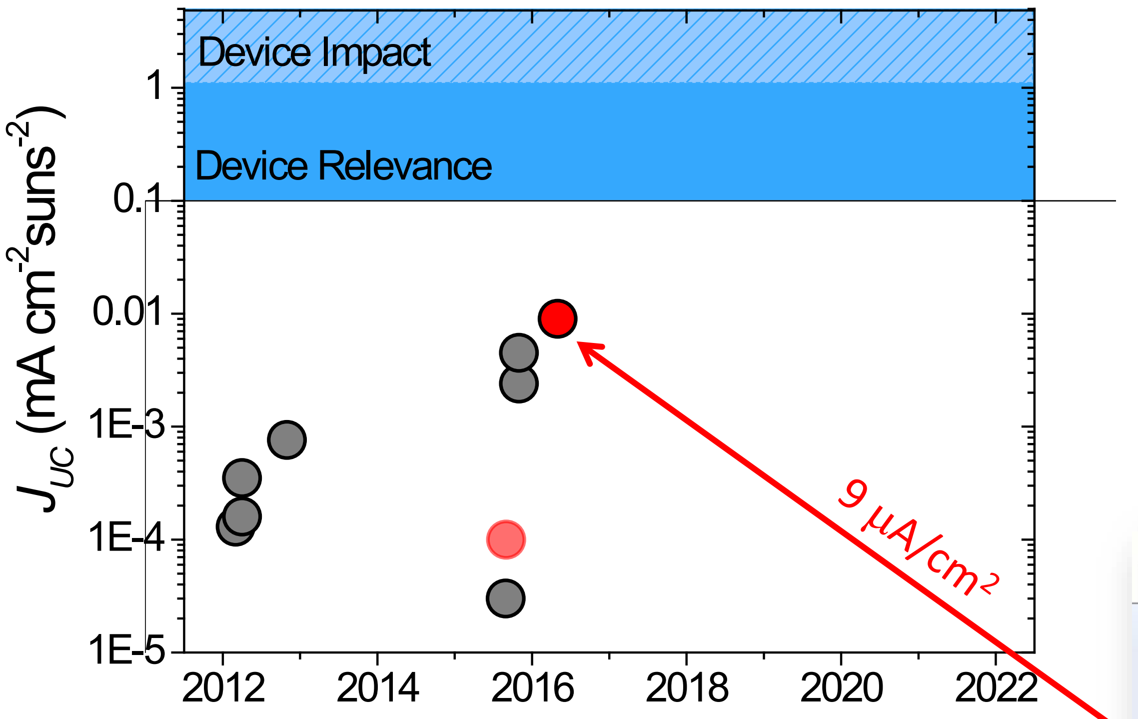


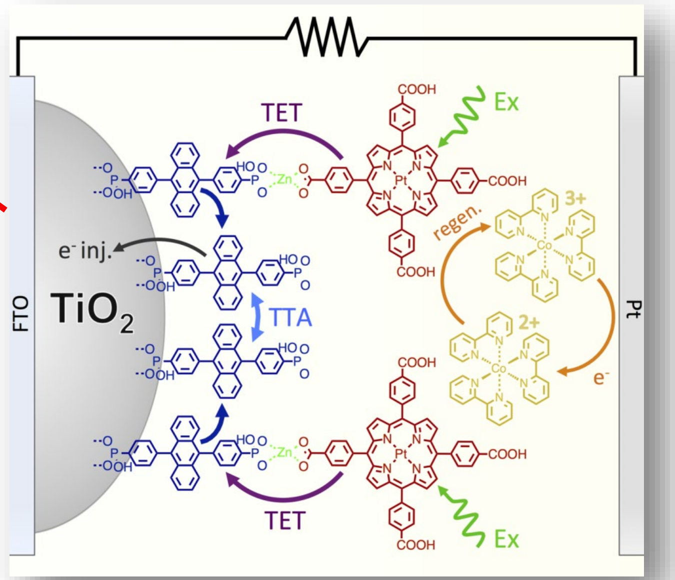




Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810

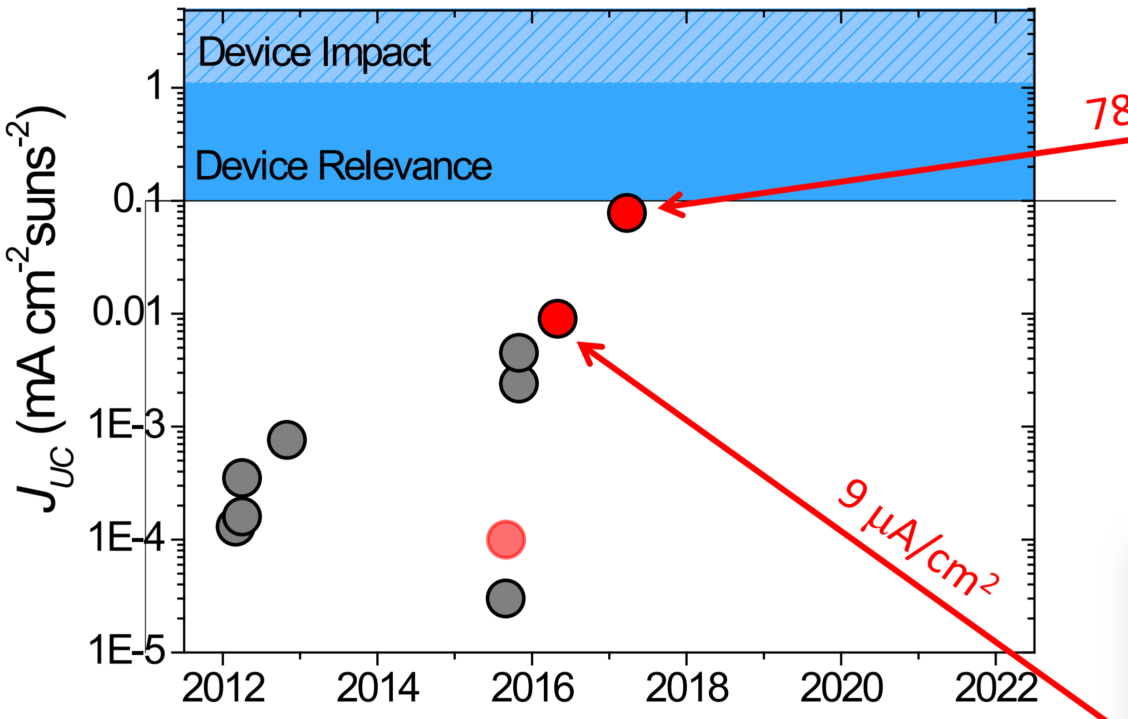


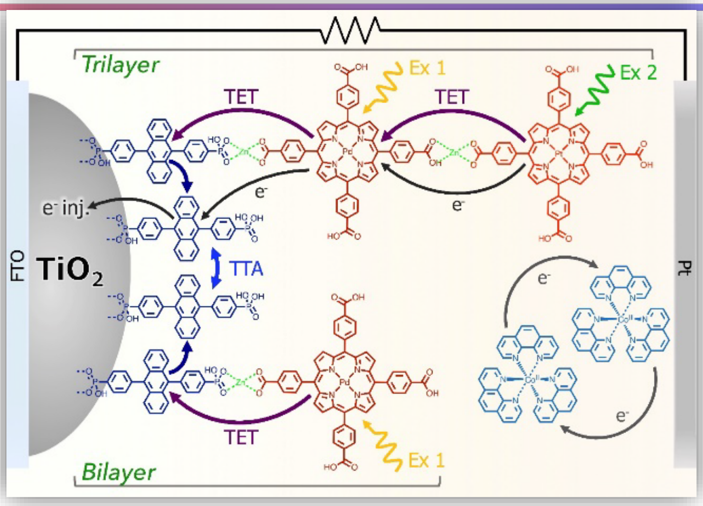


ACS Energy Lett. **2016**, 1, 3-8.

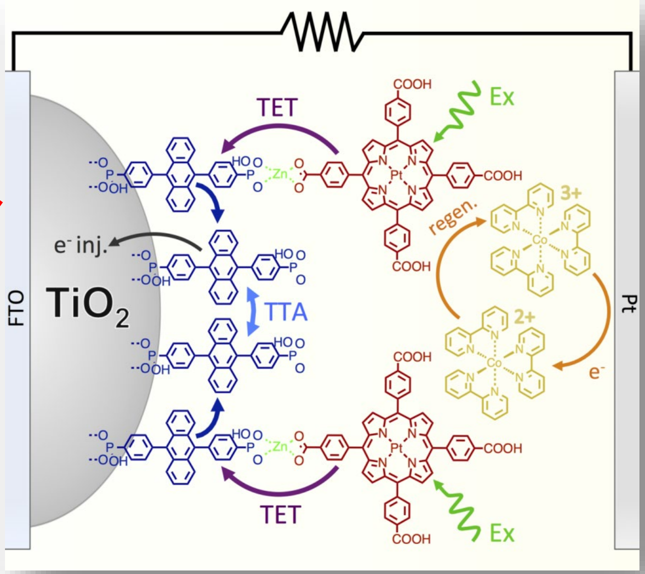
Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810





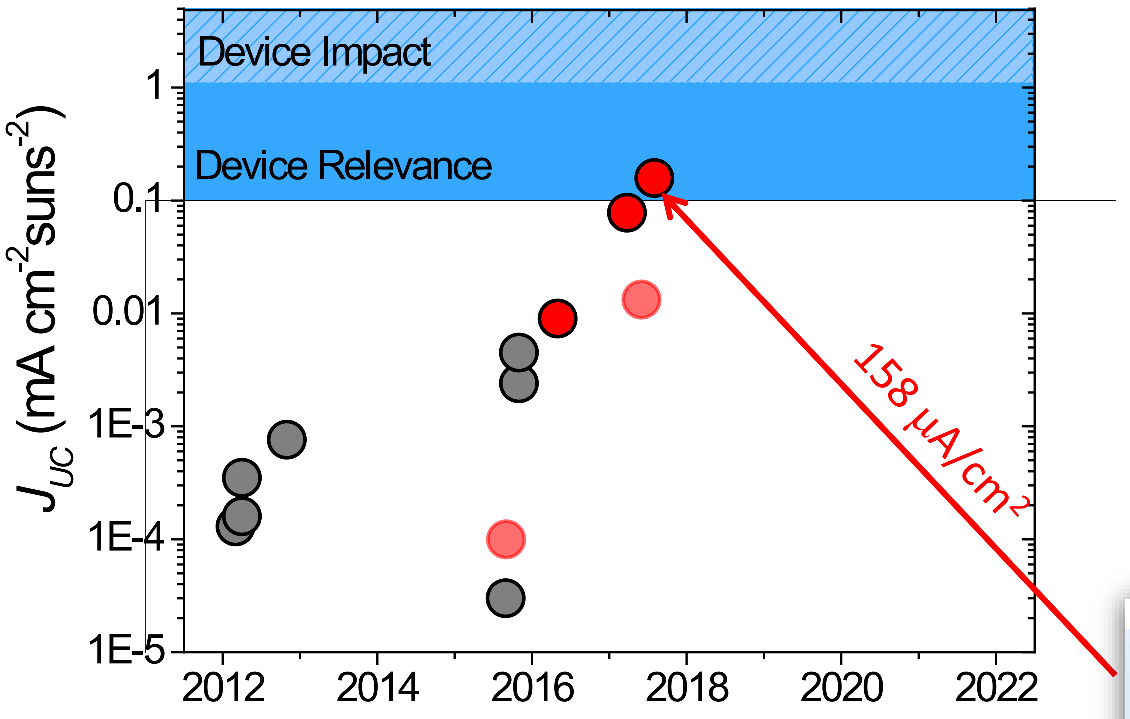
J. Mater. Chem. A, **2017**, 5, 11652-11660.

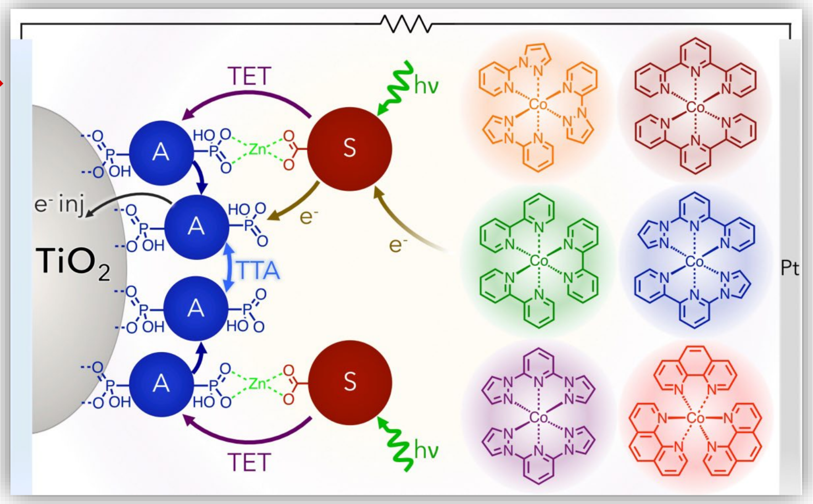


ACS Energy Lett. **2016**, 1, 3-8.

Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810

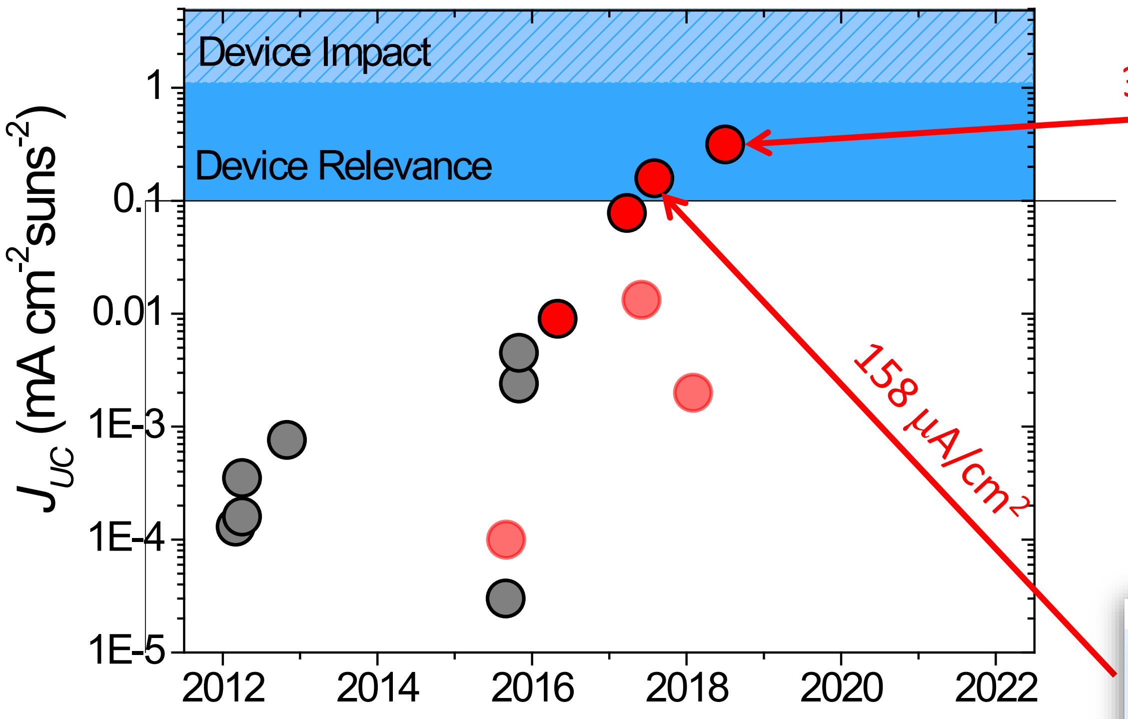




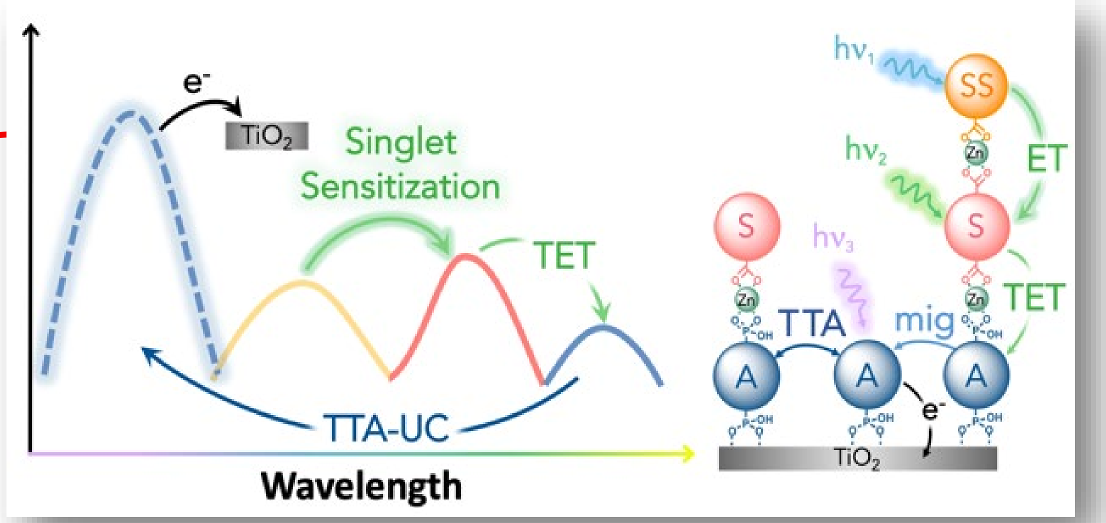
JACS **2017** , 139, 10988.

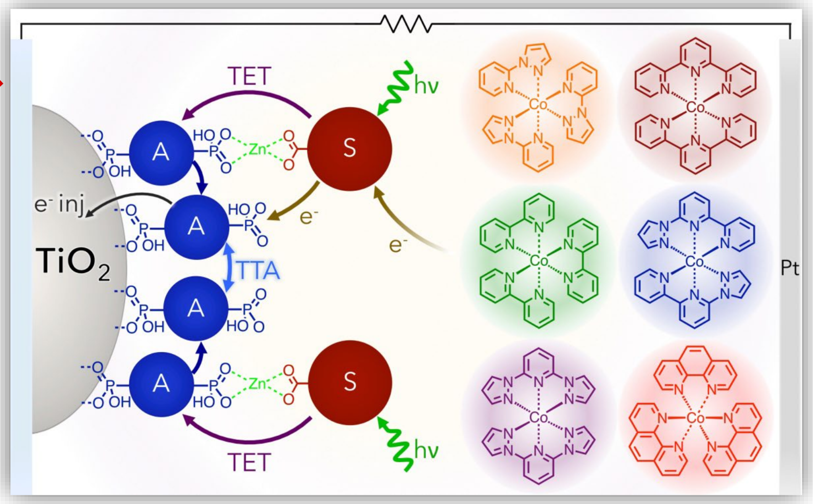
Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810



ACS Energy Lett. **2019**, 4, 1458.

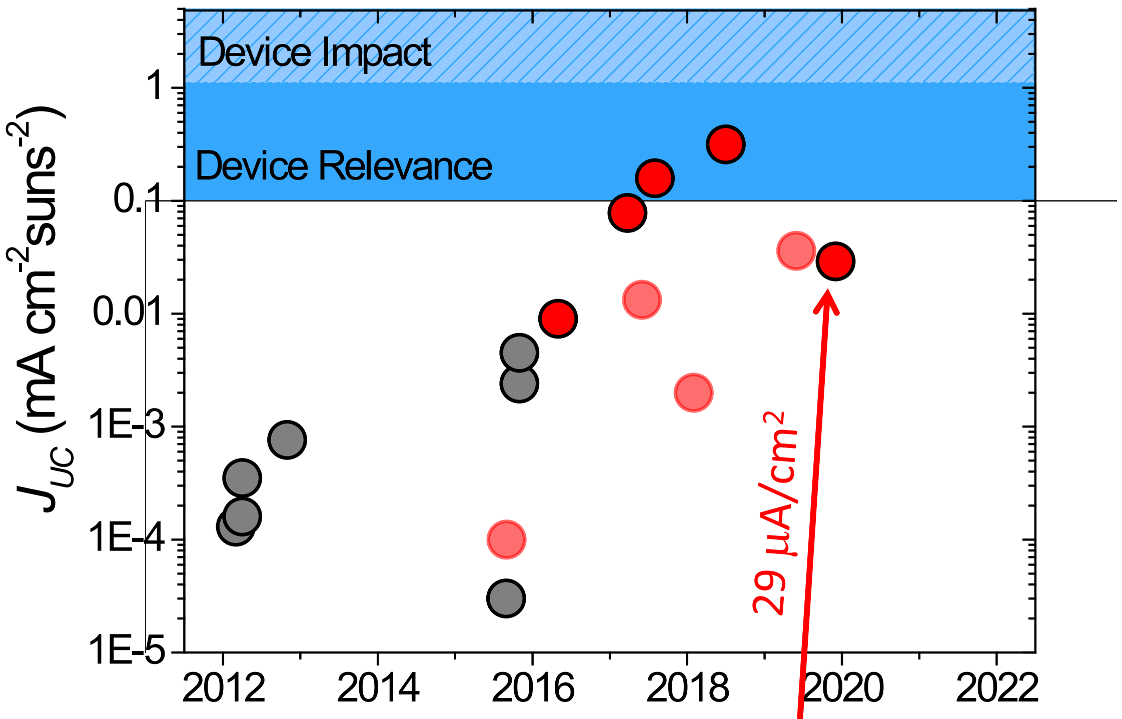


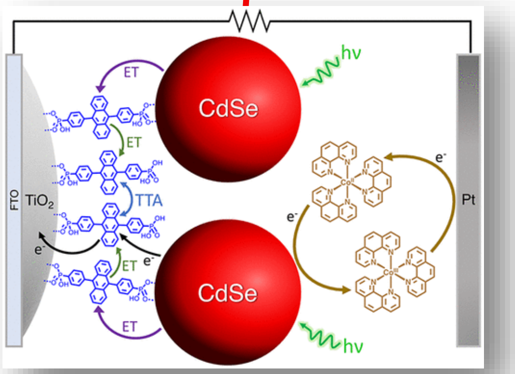


JACS **2017** , 139, 10988.

Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810

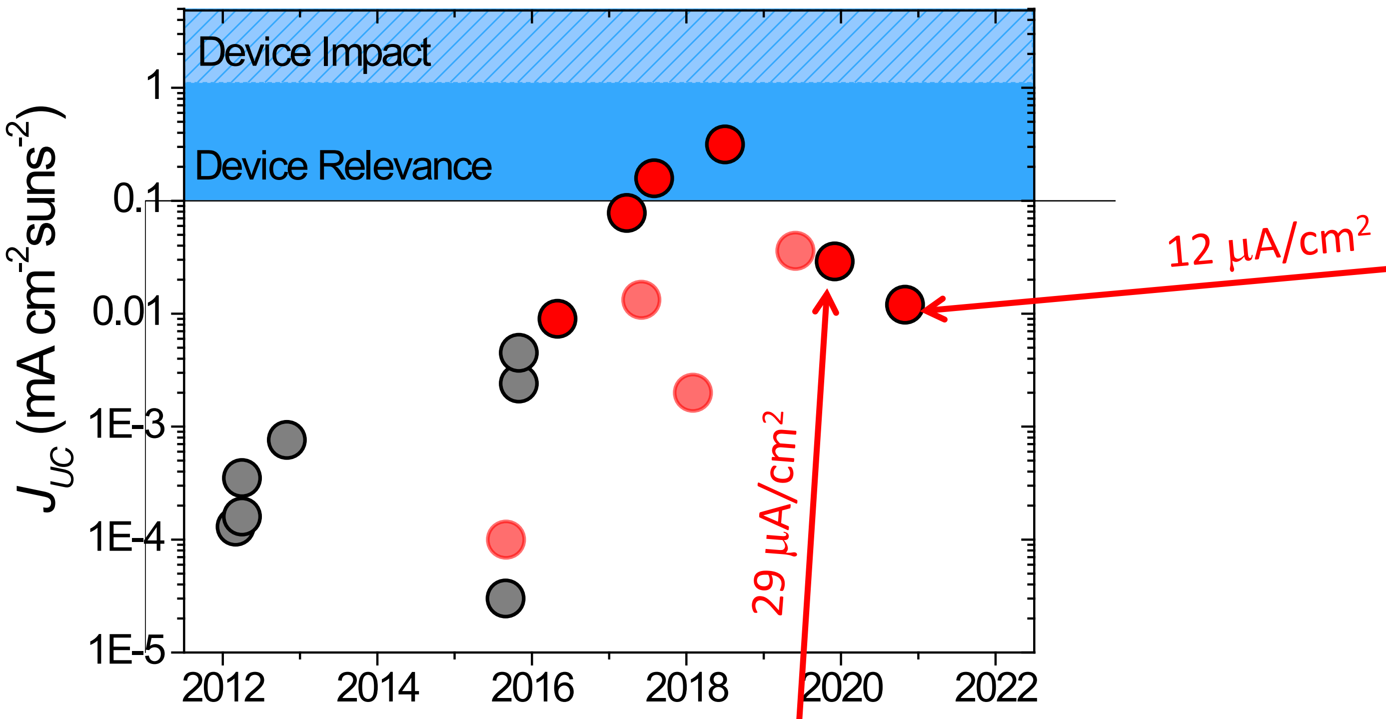




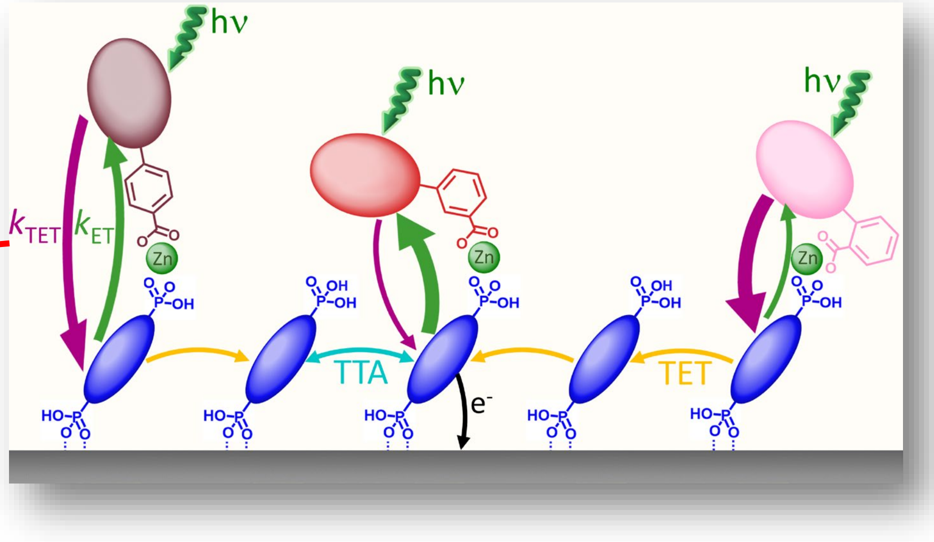
ACS Appl. Energy Mater. **2020**, 3, 29.

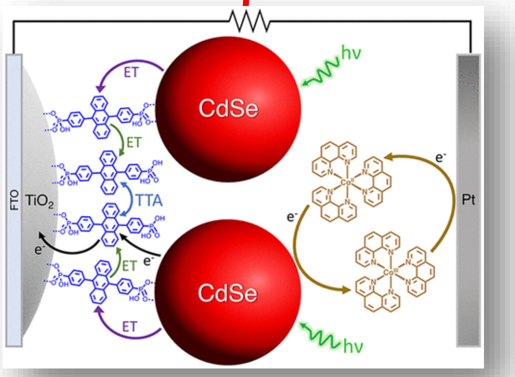
Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810



JPC C **2020**, 43, 23597.



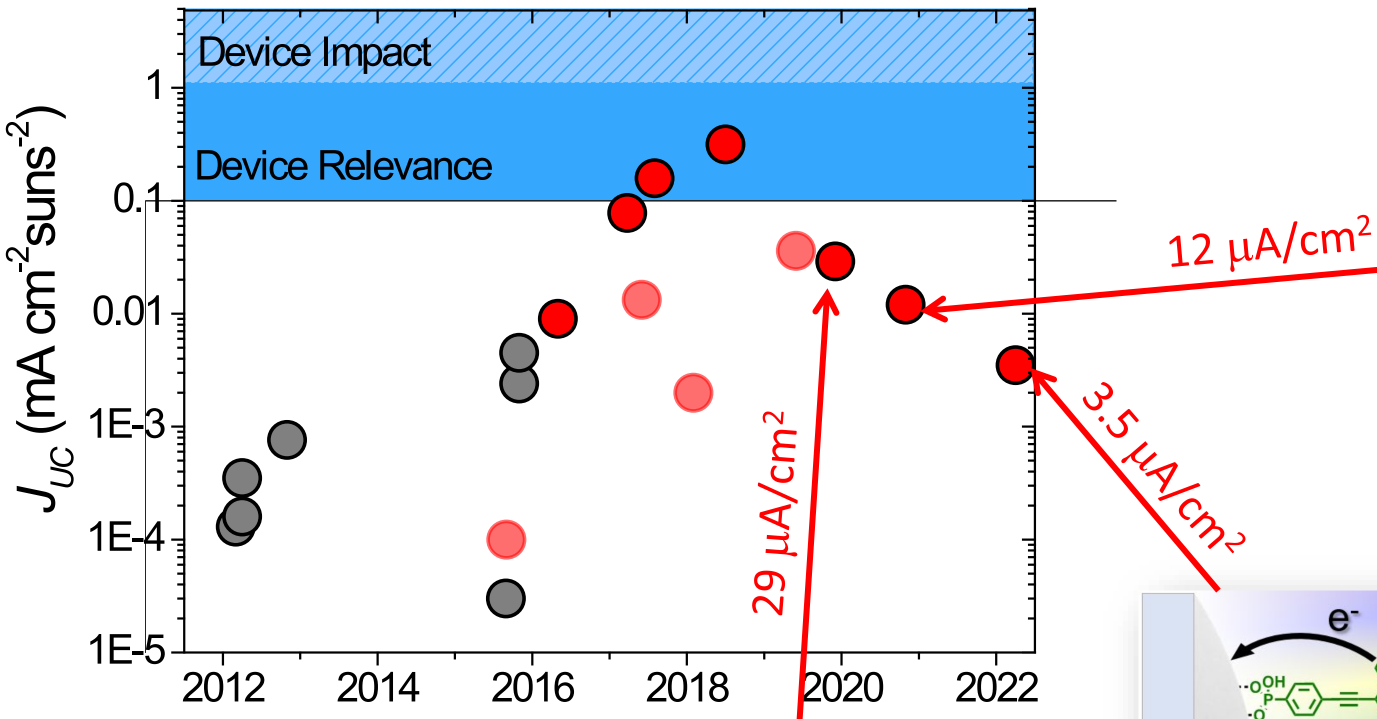


ACS Appl. Energy Mater. **2020**, 3, 29.

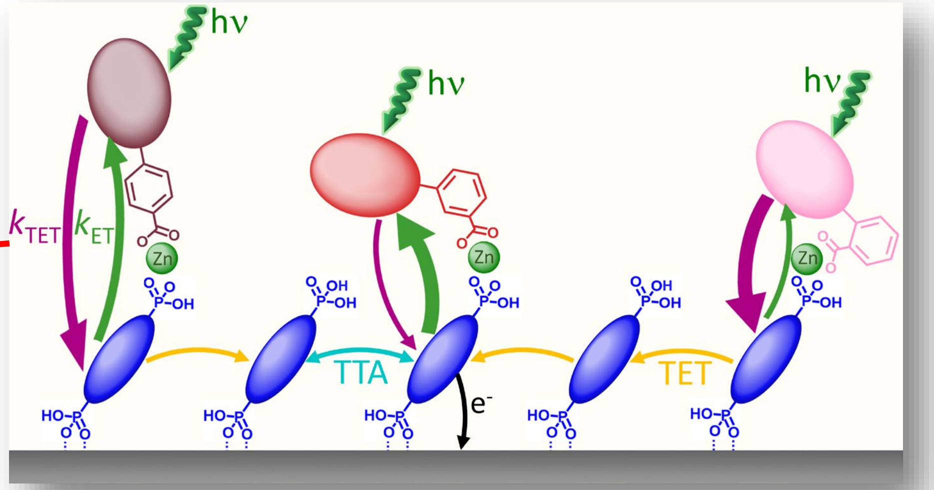
Hanson Research Group

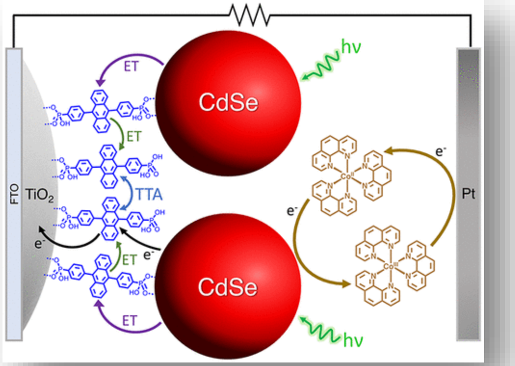
Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810

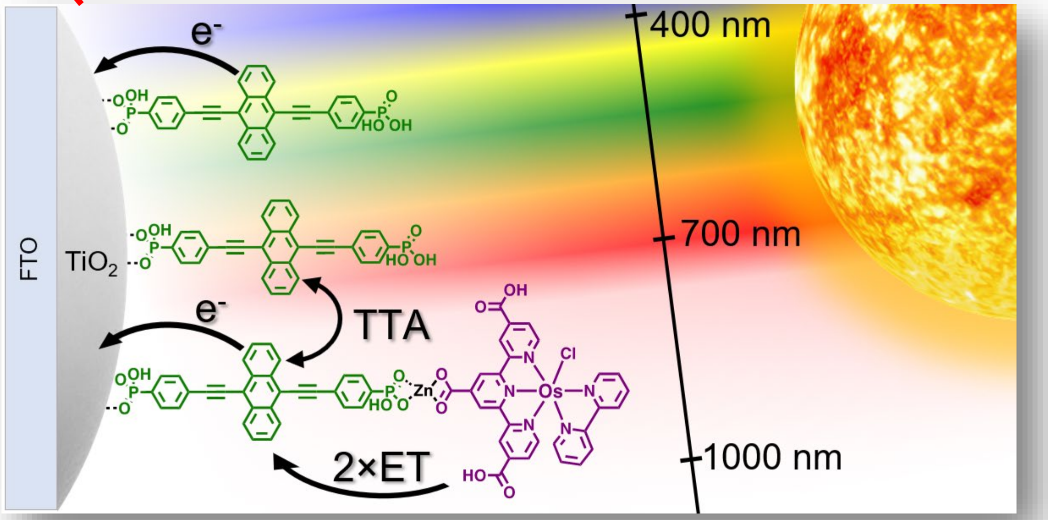


JPC C **2020**, 43, 23597.





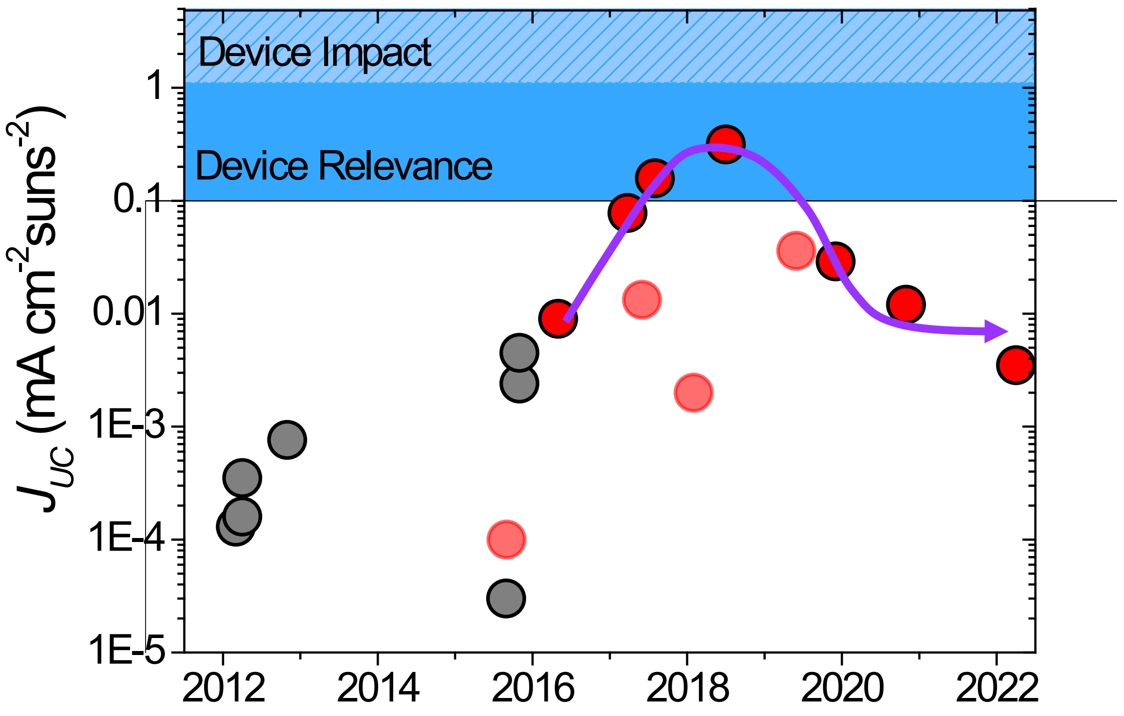
ACS Appl. Energy Mater. **2020**, 3, 29.



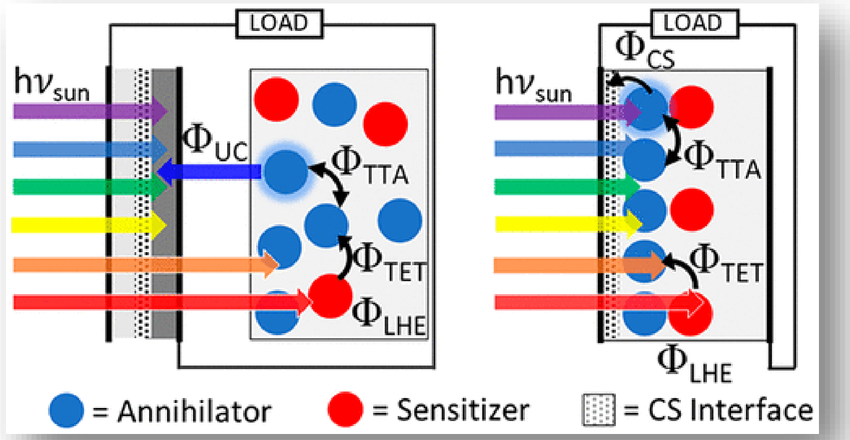
JMC C **2022**, 10, 4947.

Increasing UC Photocurrent (J_{UC})

JPC Lett., **2018**, 9, 5810



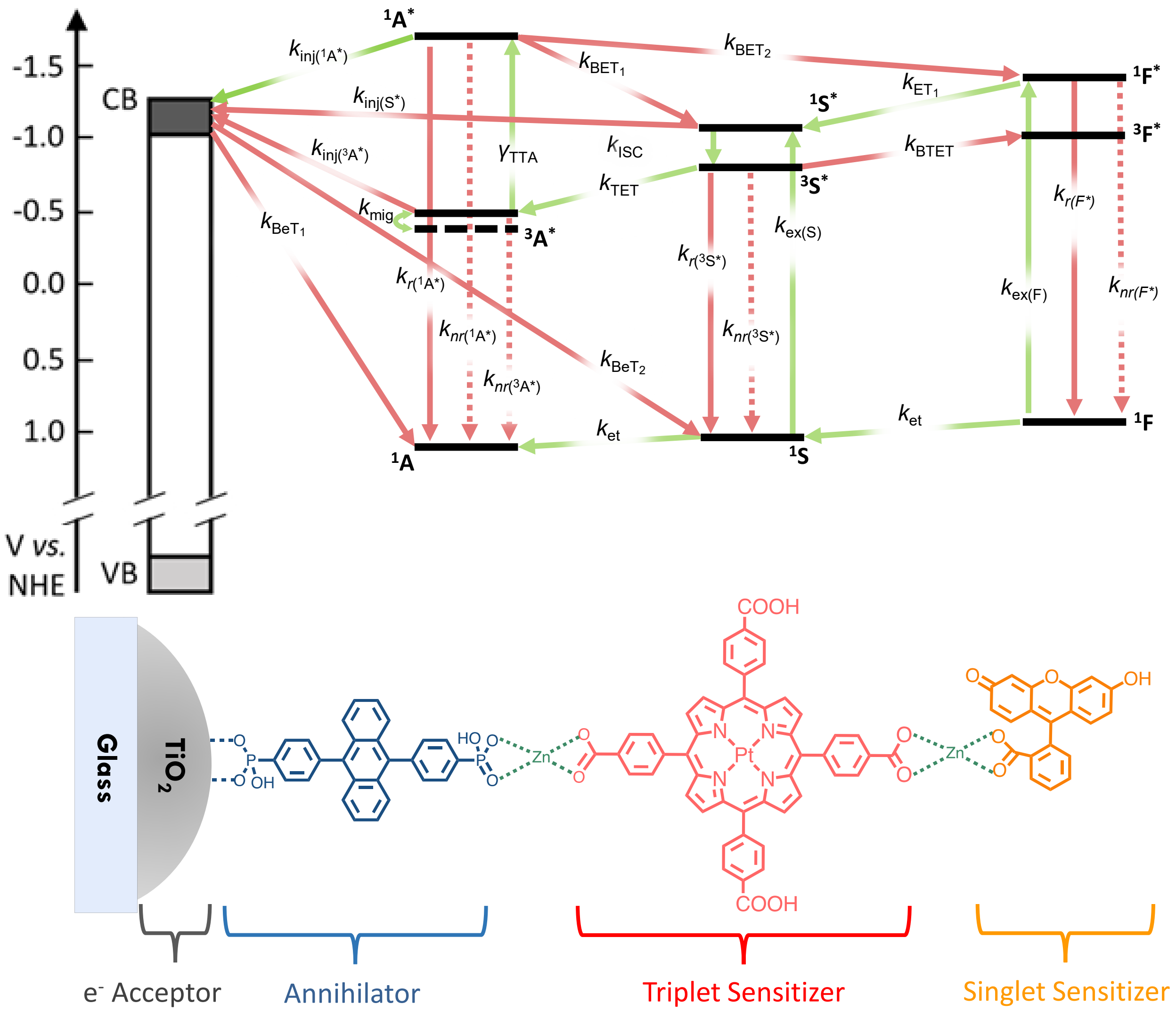
Performance Limitations:



ACS AM&I **2021**, 13, 32601.

Energy and Electron Transfer

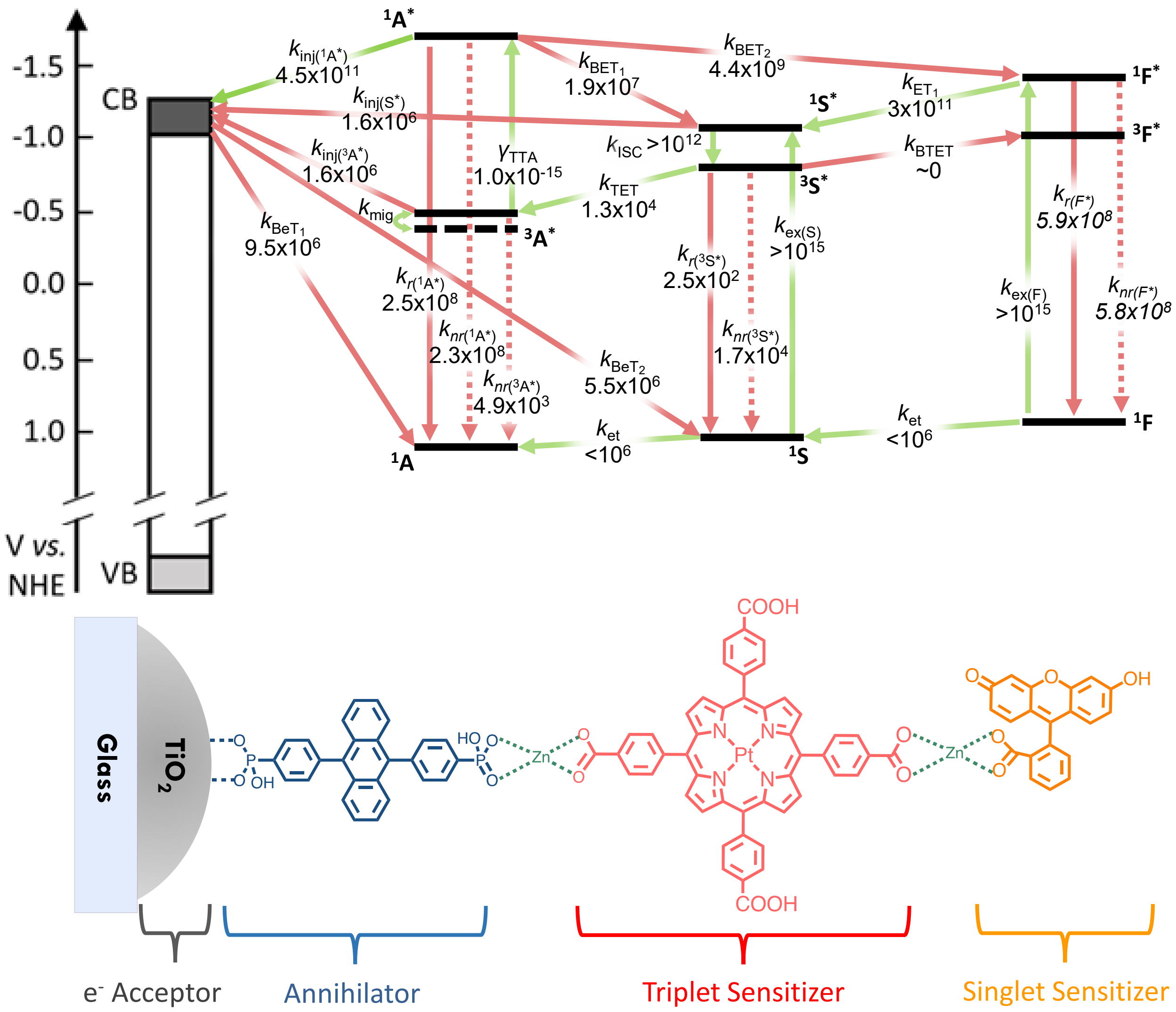
Upconversion Trilayer



ACS Energy Lett. **2019**, 4, 6, 1458

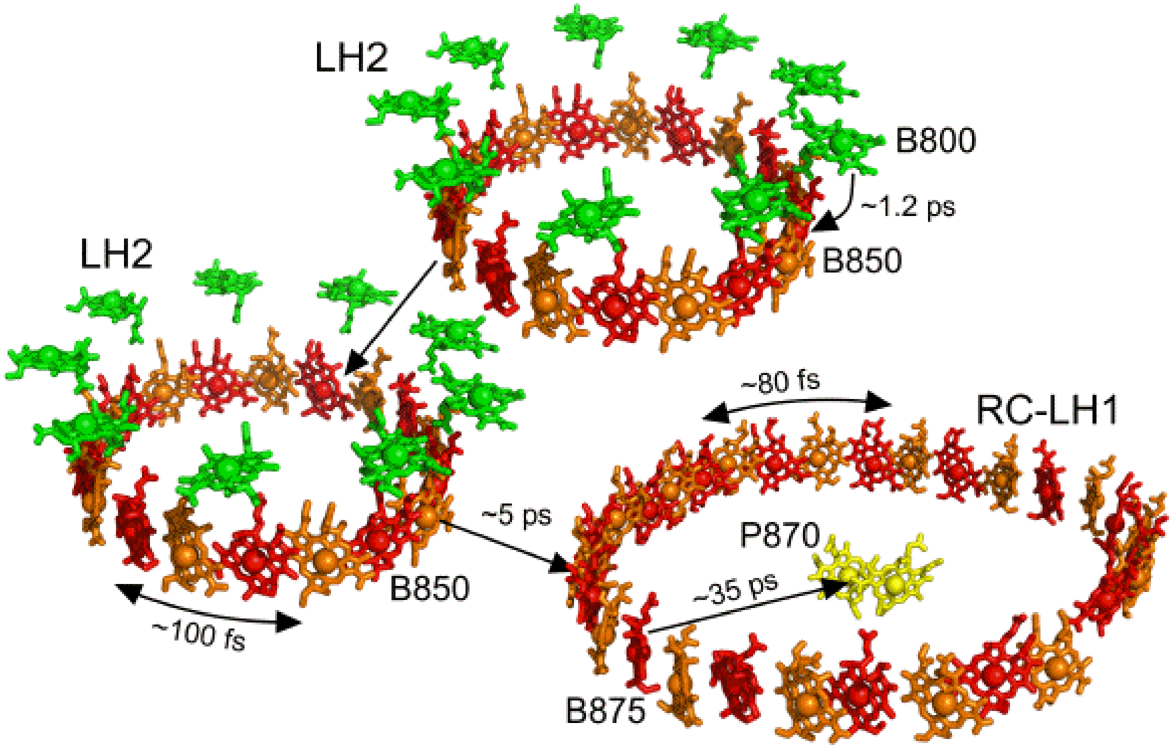
Energy and Electron Transfer

Upconversion Trilayer



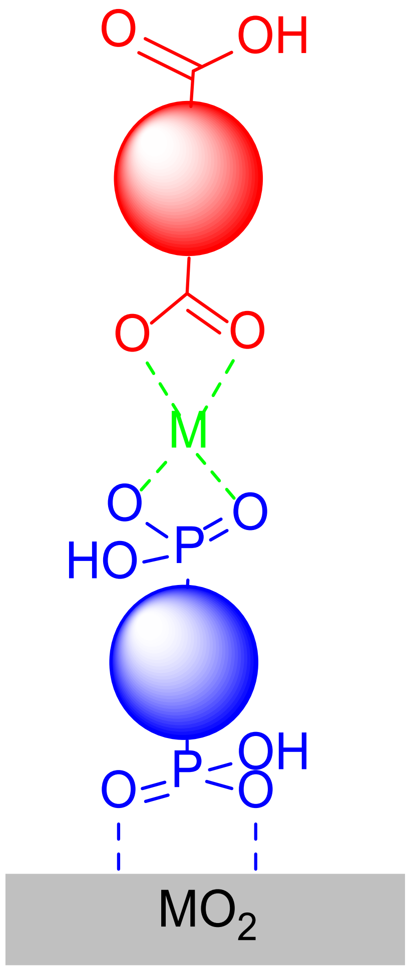
ACS Energy Lett. **2019**, 4, 6, 1458

Photosynthesis

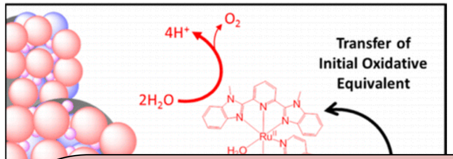


https://doi.org/10.48550/arXiv.1608.06913

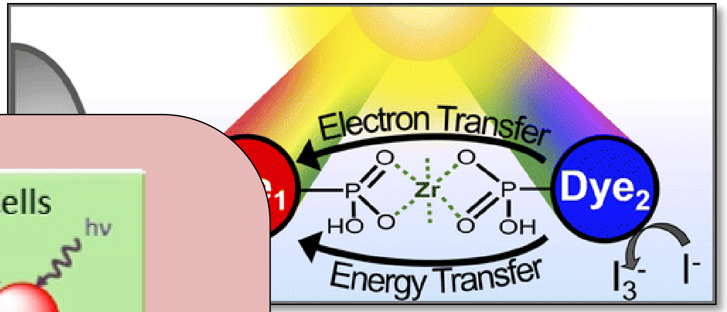
Metal Ion Linked Multilayer Structure



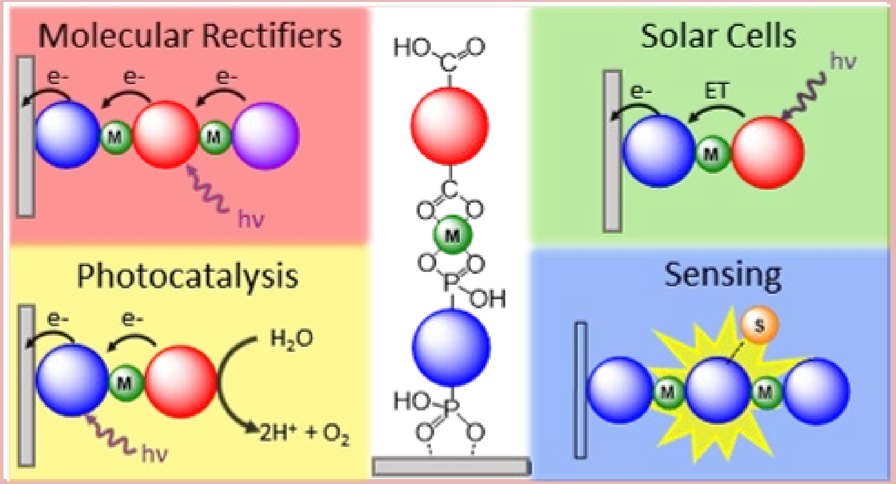
Water Oxidation DSPEC



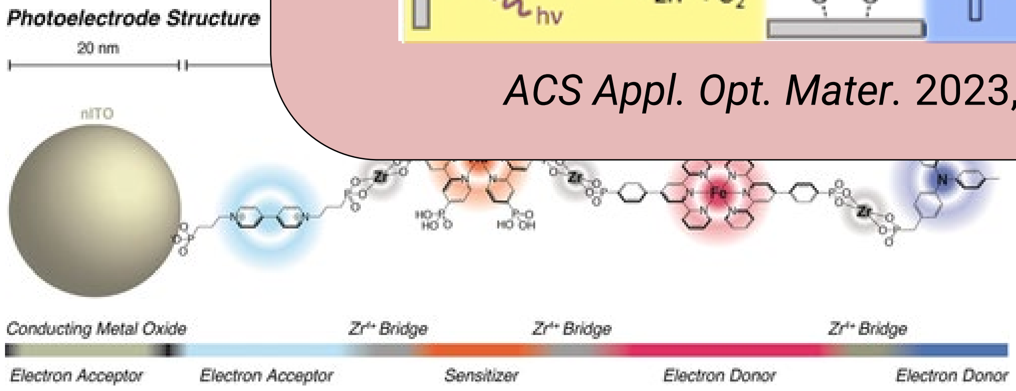
Energy/Electron Transfer Cascade



M&I **2016**, 8, 28633

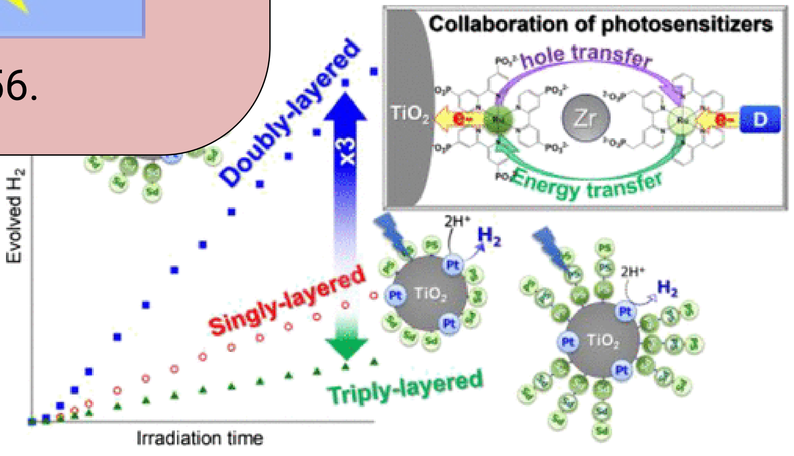


ACS Appl. Opt. Mater. 2023, 1, 1156.



Angew. Chemie. **2018**, 57, 15390.

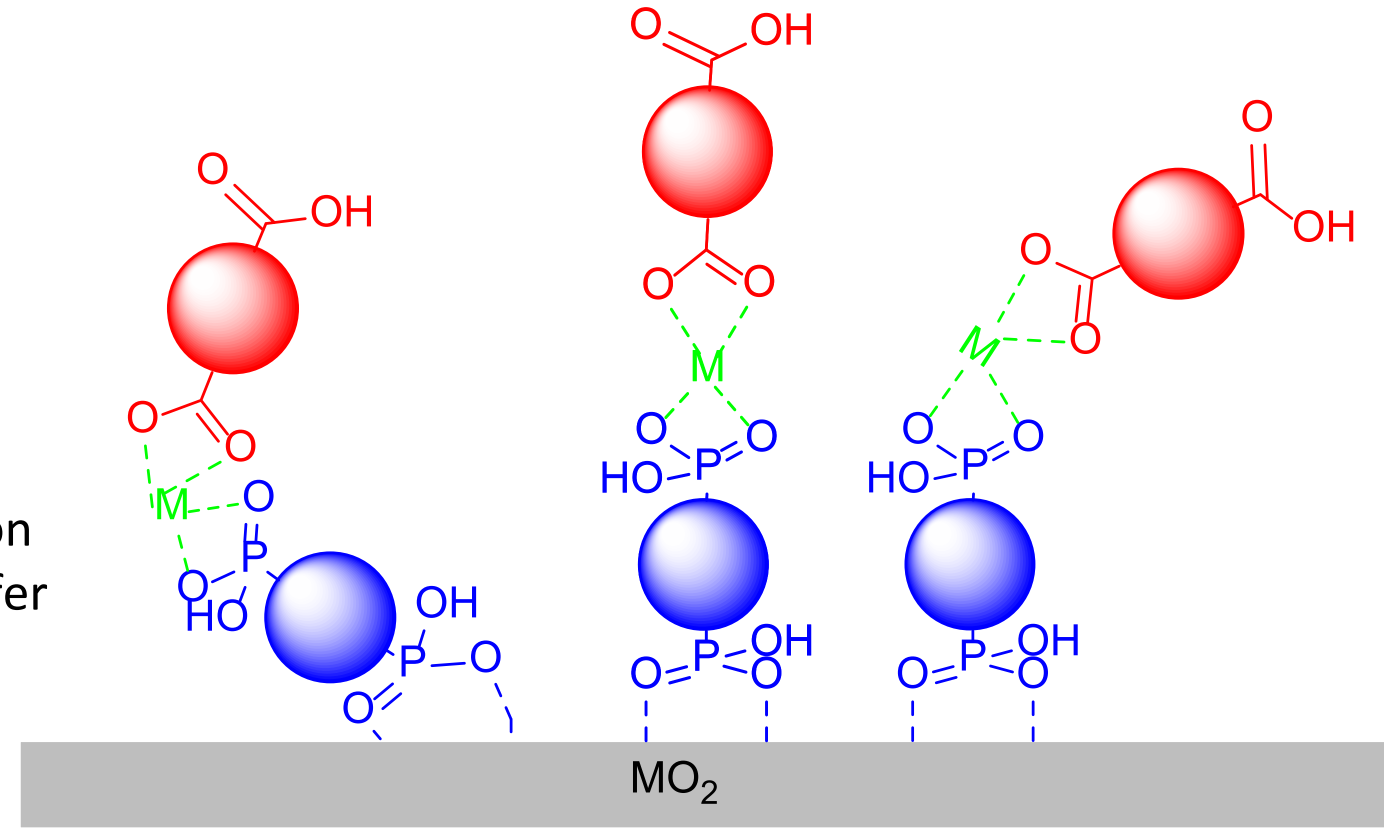
2 Generation



ACS Omega, **2017**, 2, 3901.

Bilayer Structure

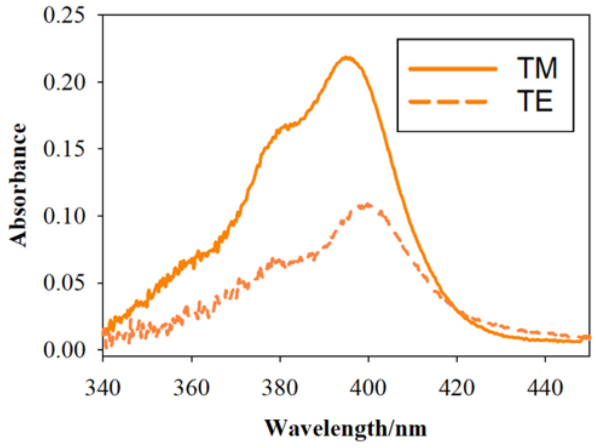
What is known:
- Not co-deposition
- Metal-ion coordination
- Directional E/e⁻ transfer

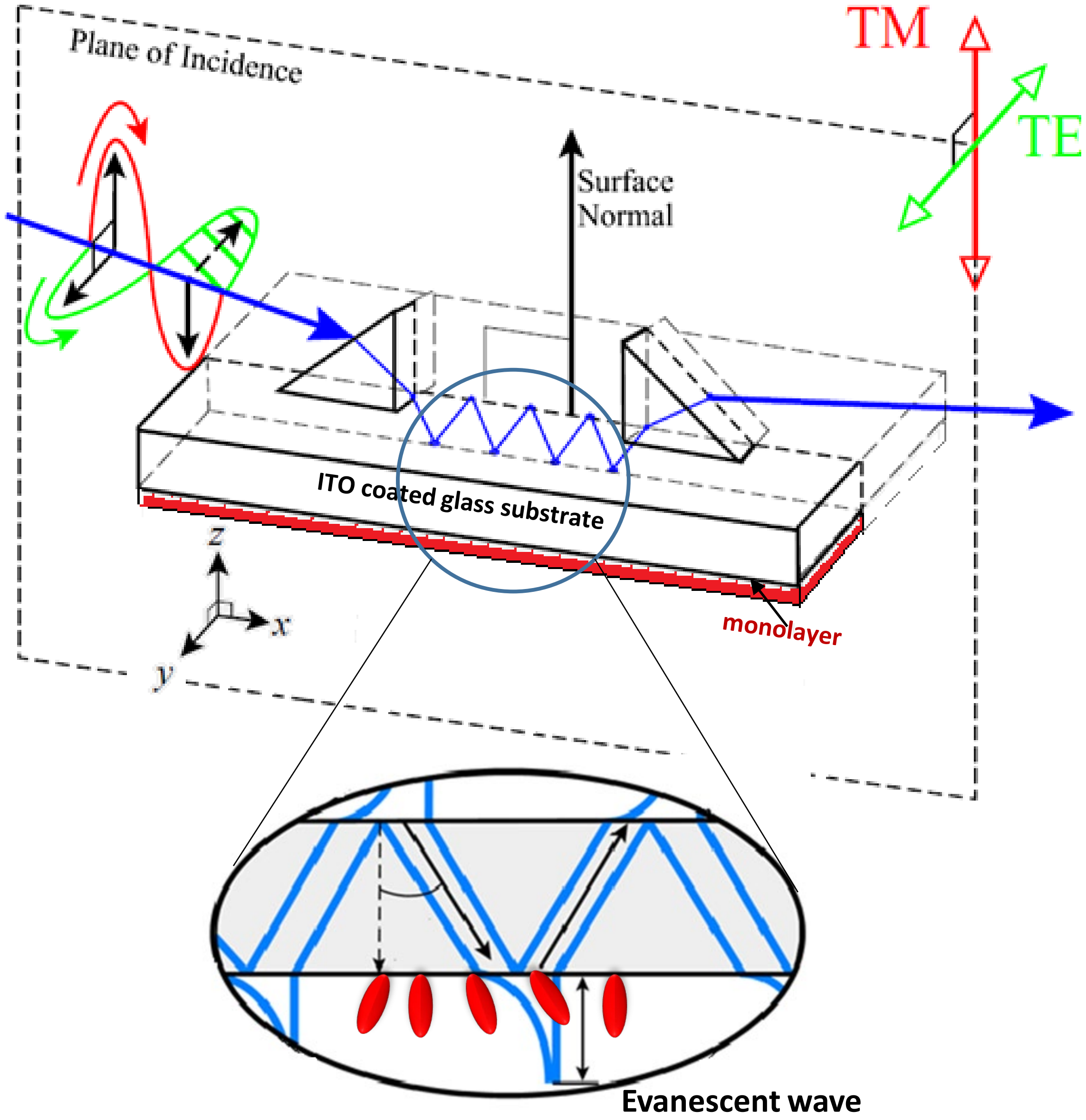


What is not known:
- Surface binding angle
- Relative orientation
- Controllability

Polarized Attenuated Total Reflectance

Prof. Scott Saavedra at UofA





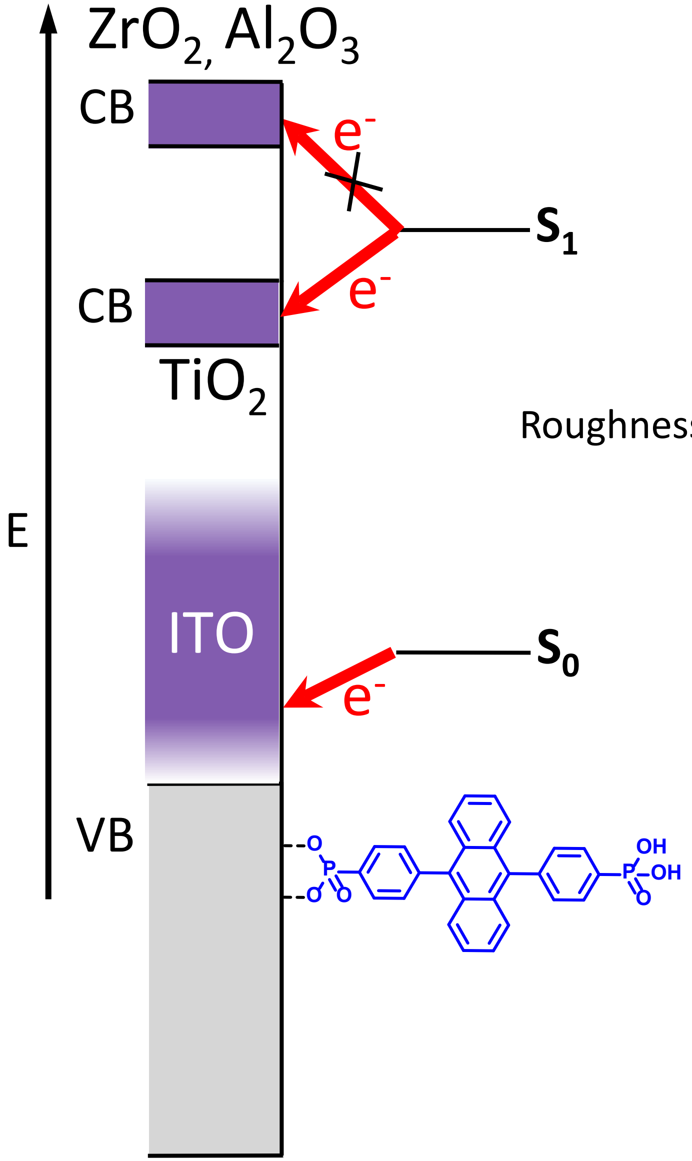
Measure A_{TE} and A_{TM}

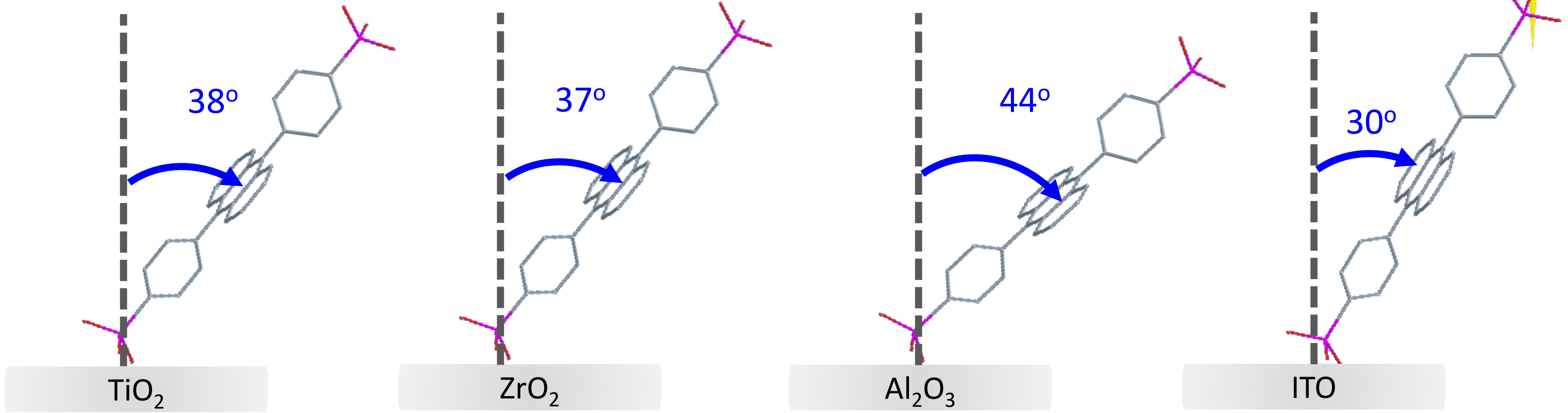
Dichroic ratio $\rho = \frac{A_{TE}}{A_{TM}}$

Calculate mean tilt angle θ

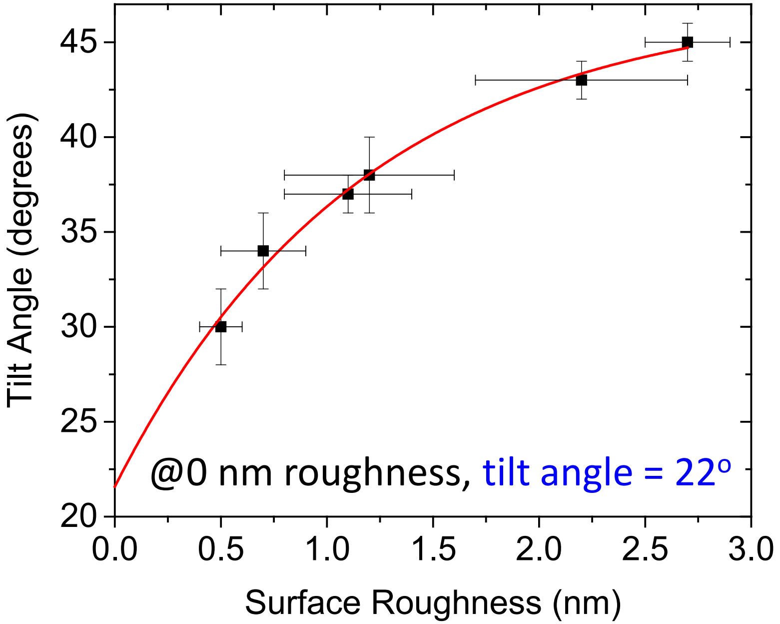
John Thomas Bradshaw , A. PhD. Dissertation, University of Arizona, 2005

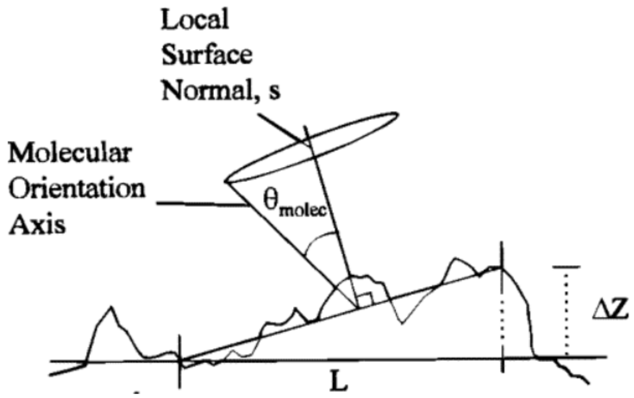
Metal Oxide-Anthracene Structure





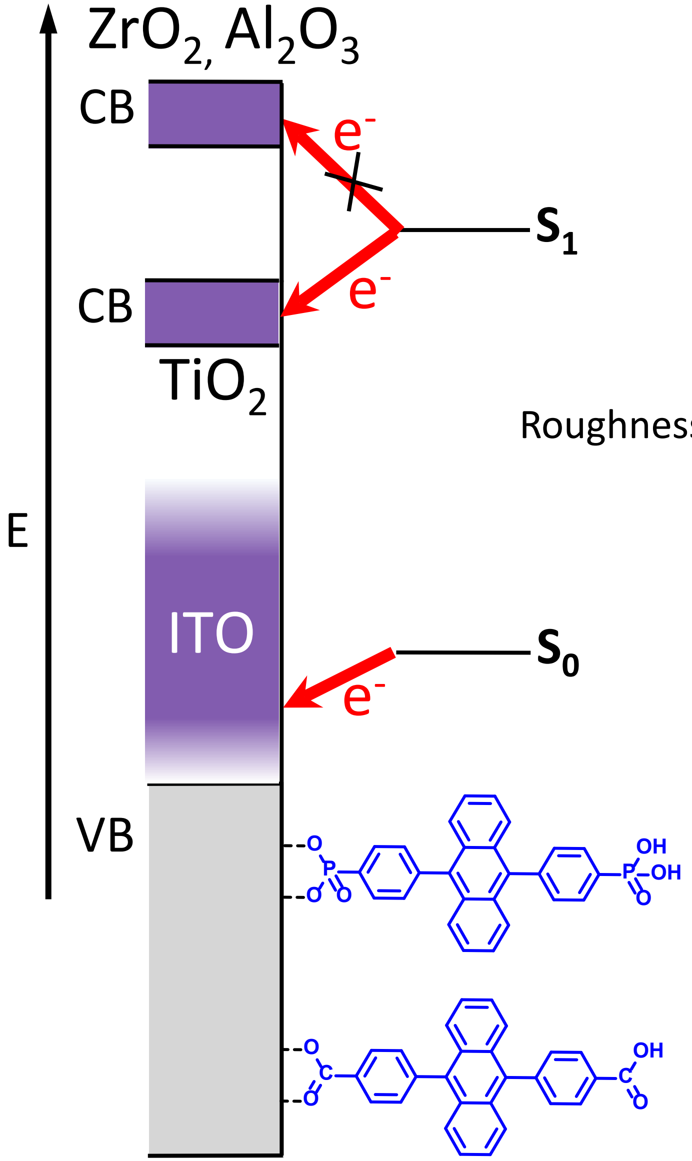
Roughness: 1.2±0.4nm 1.1±0.3nm 2.2±0.5nm 0.5±0.1 nm

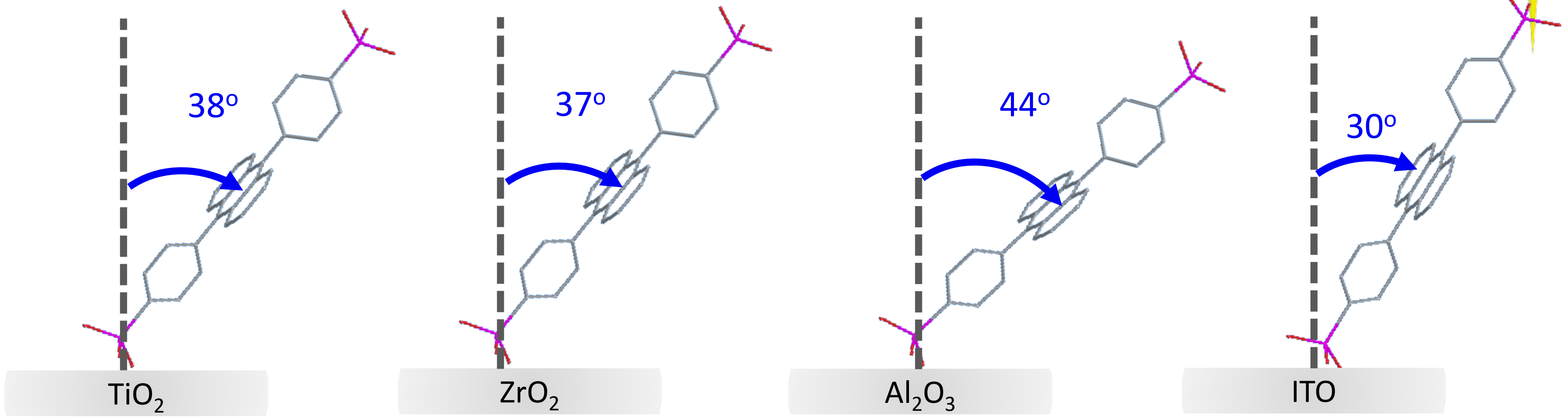




Rowlen et al. *JPC C* **1999**, 103, 1525.

Metal Oxide-Anthracene Structure

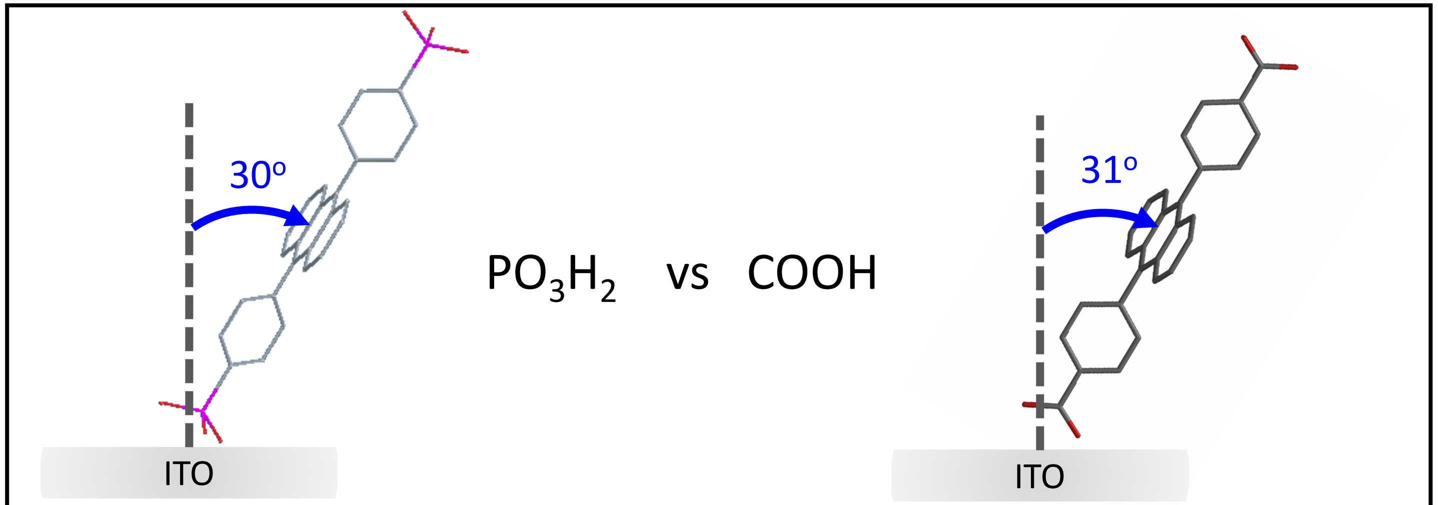




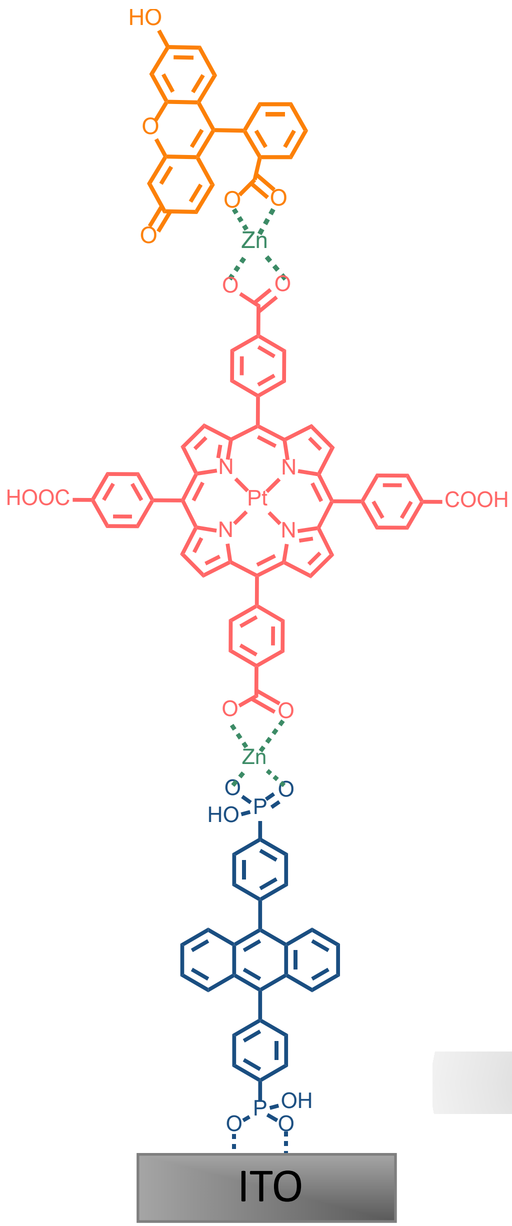
Roughness:	1.2±0.4nm	1.1±0.3nm	2.2±0.5nm	0.5±0.1 nm

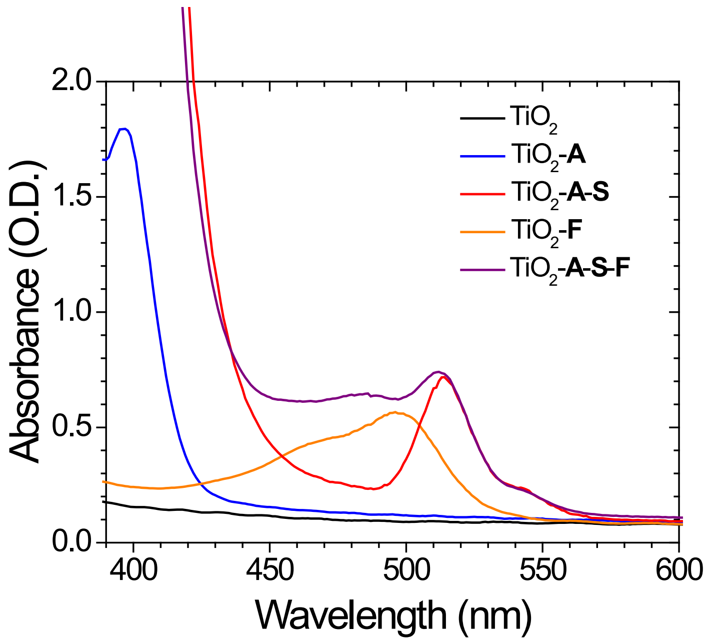
- Similar angle regardless of metal oxide.
- Binding group does not change the angle.

JPC C **2023**, 127, 2705

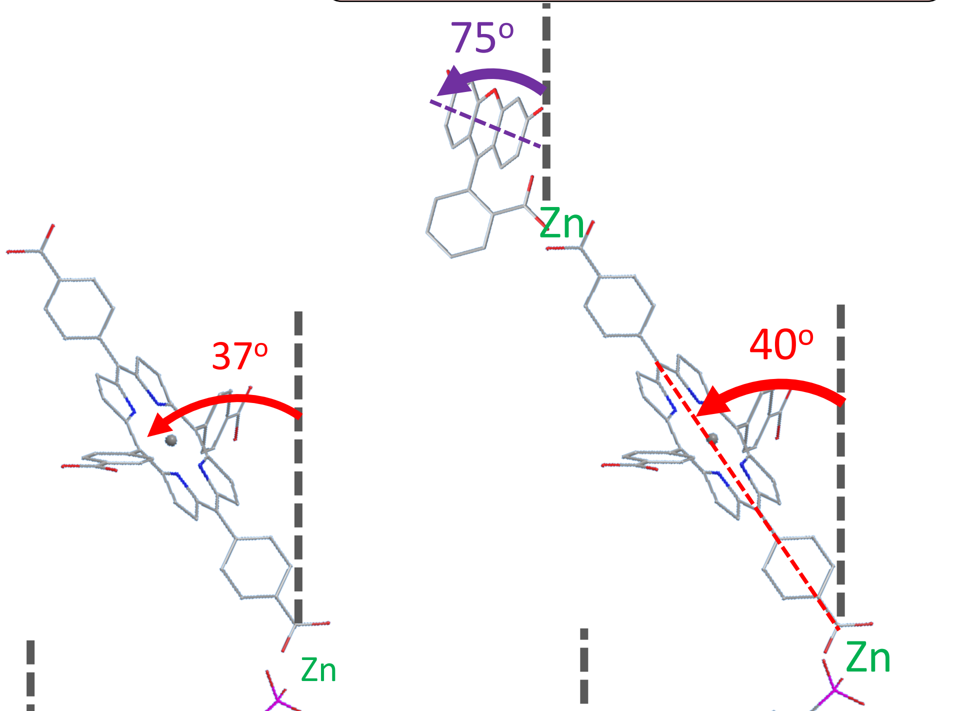


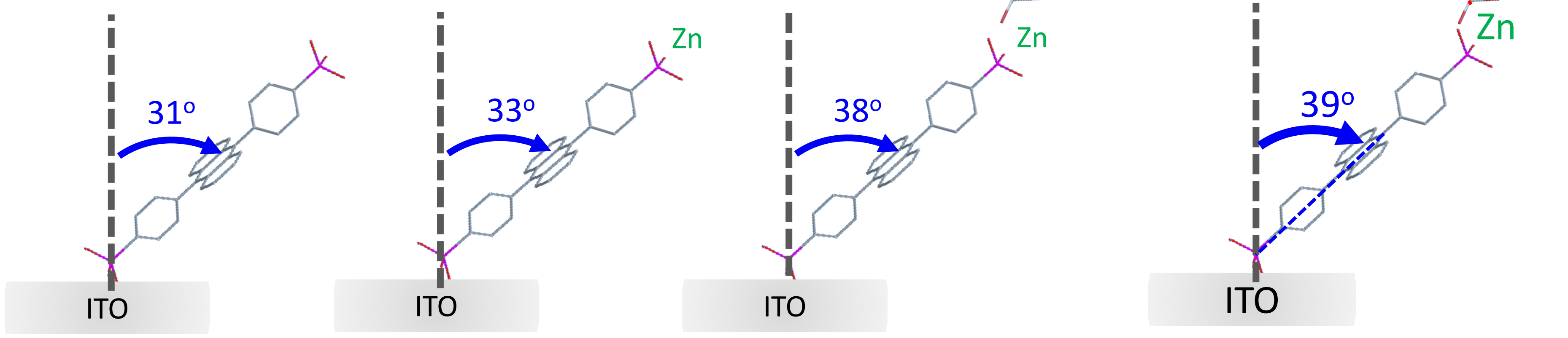
Multilayer Structure





One possible structure.

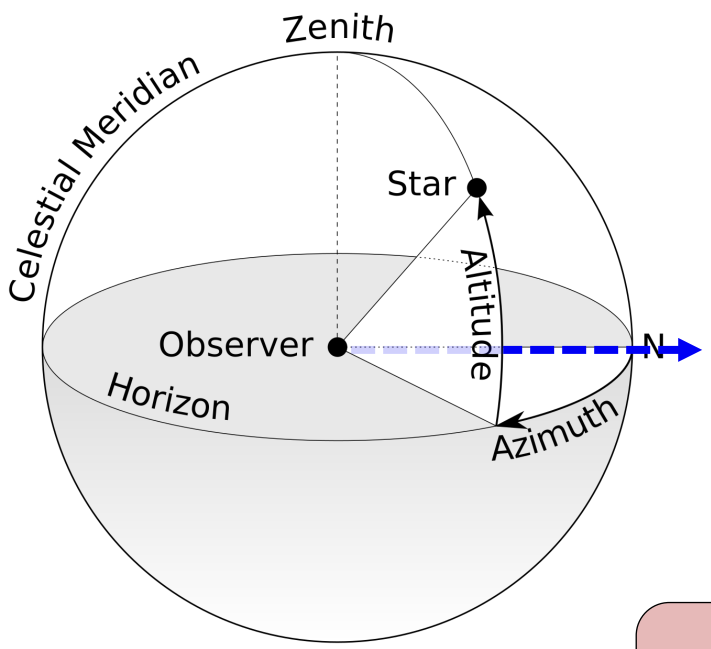




Langmuir **2023**, 39, 10670.

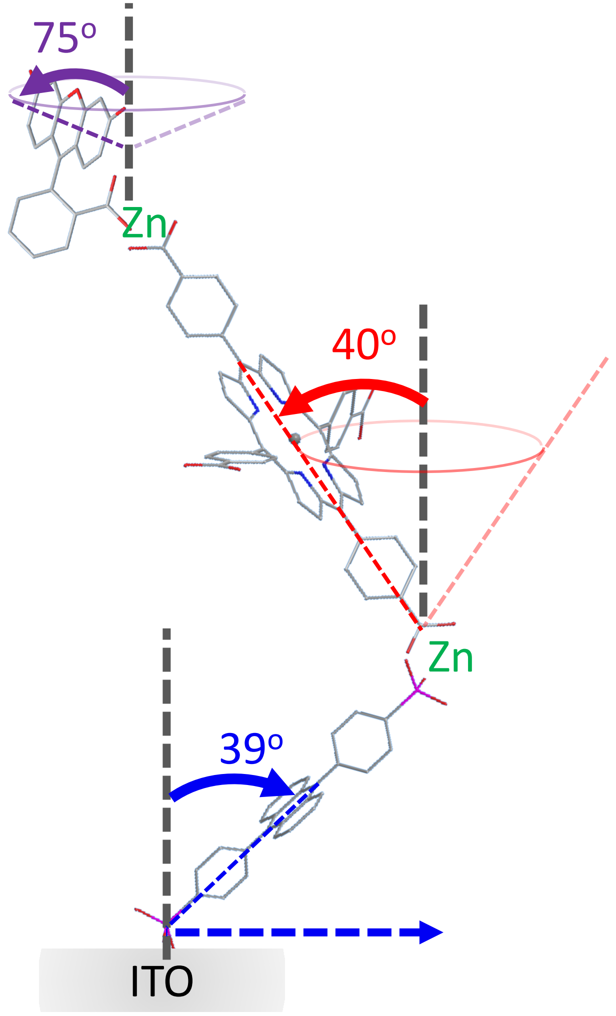
Multilayer Structure

Azimuthal Angle



Is the angular measurement in a spherical coordinate system which represents the horizontal angle from a frame of reference (usually North).

Can determine structure if we know the angle between the chromophores!

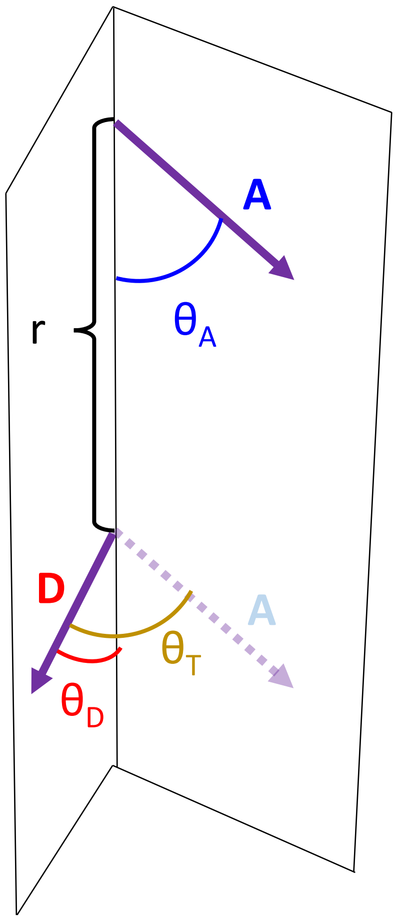


FRET and Structure

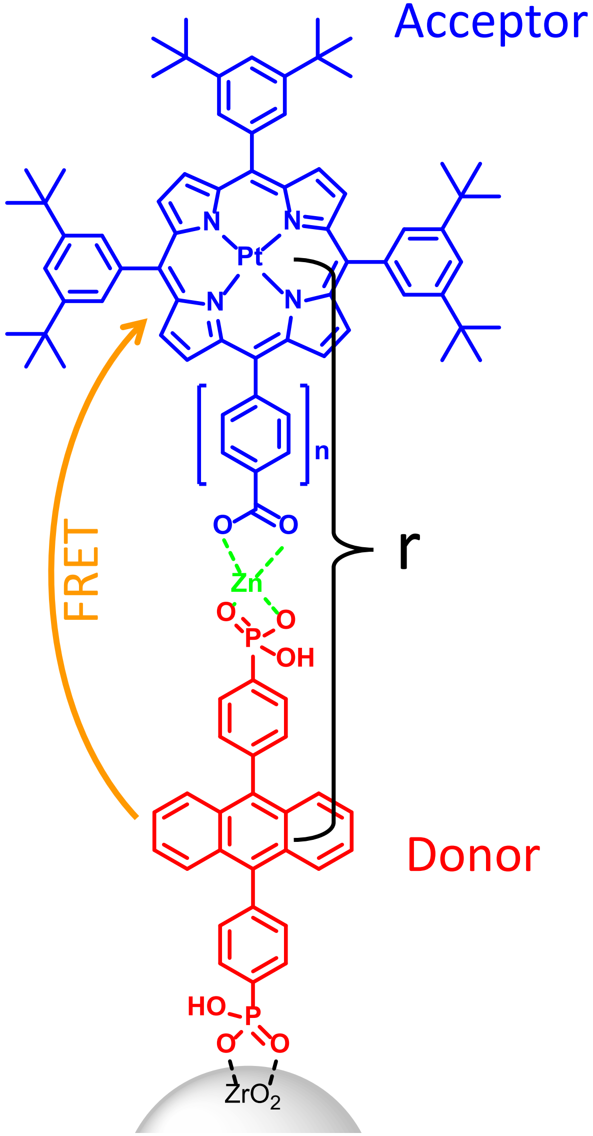
$$E = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6}$$

$$R_0 = 9780\,[J\,\phi_D\,n^{-4}\,\kappa^2]^{1/6}$$

J = overlap integral
ϕ_D = fluorescence QY of D
n= refractive index
κ^2= orientation factor
r = distance

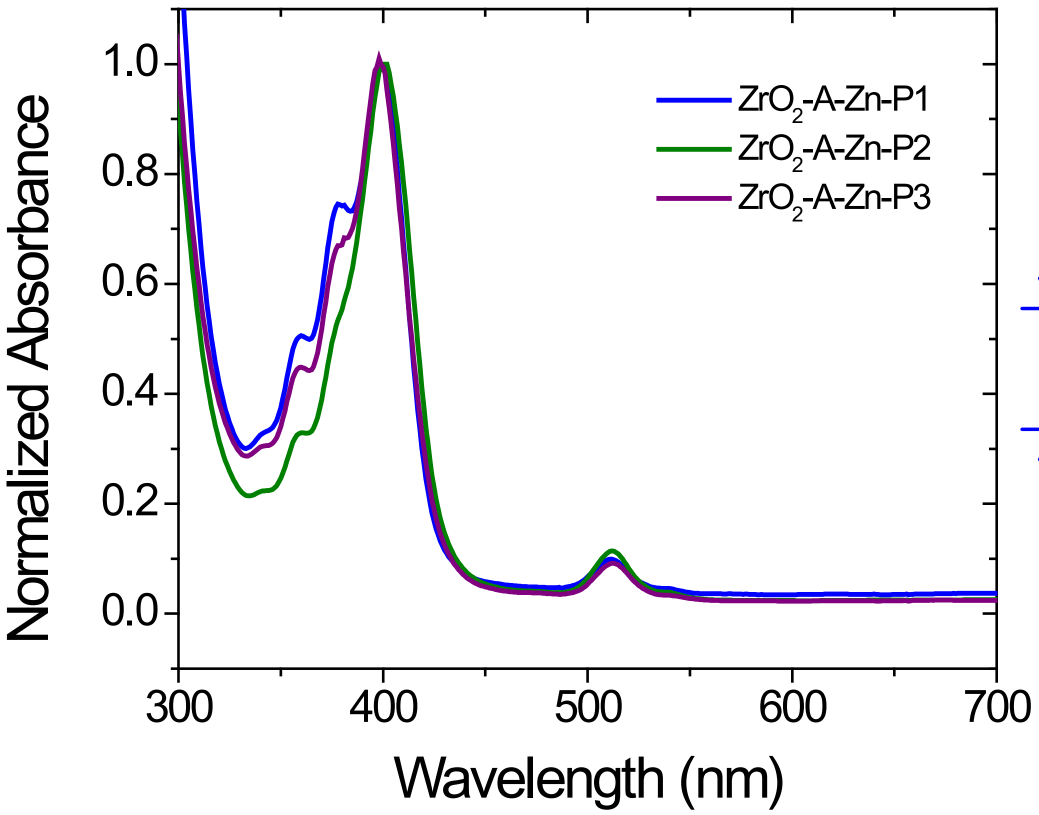


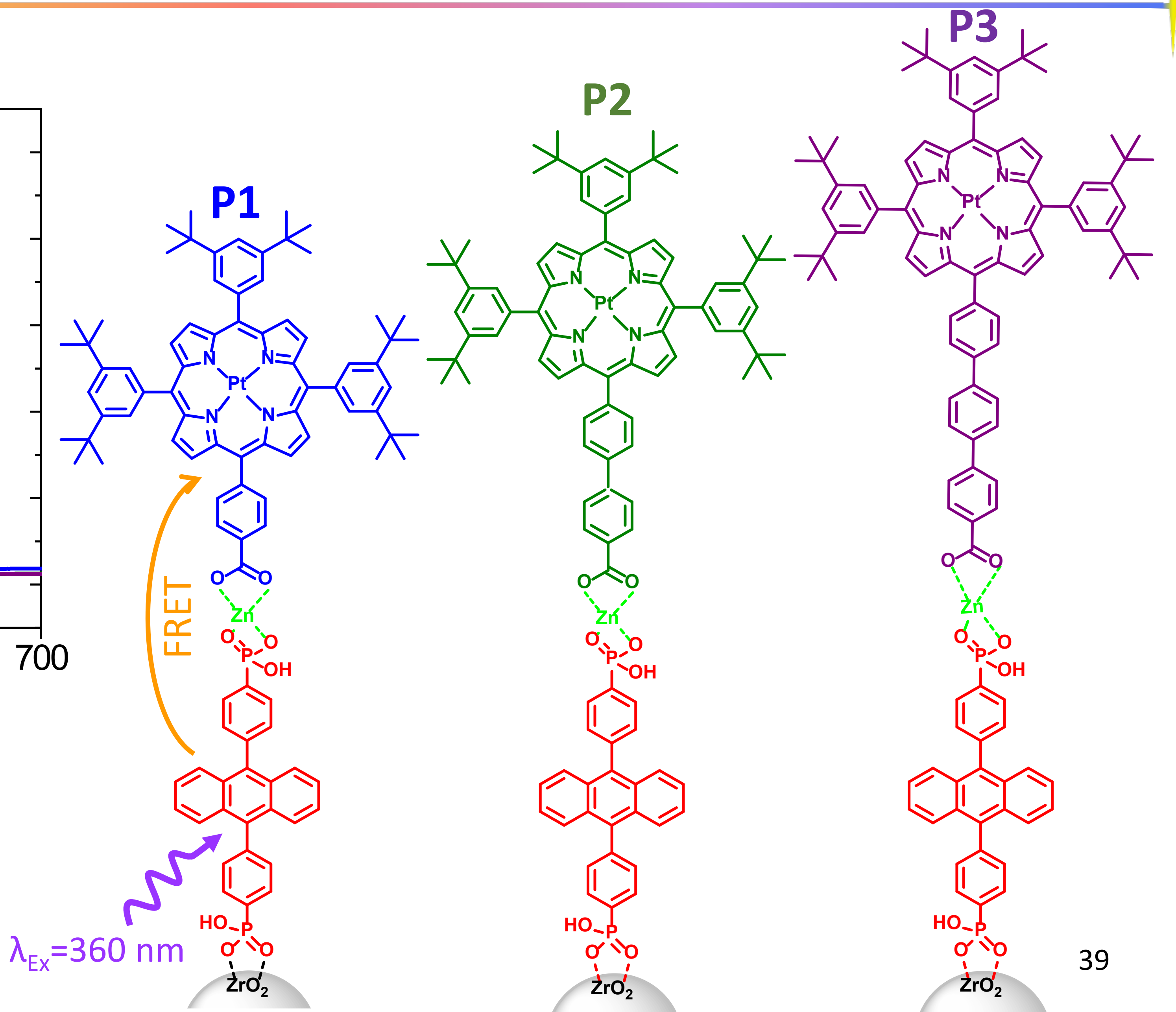
$\kappa^2 = (\cos \theta_T - 3 \cos \theta_D \cos \theta_A)^2$



Lakowicz, J.R. *Principles of Fluorescence Spectroscopy*, 3rd ed; Springer Science: New York **2006**

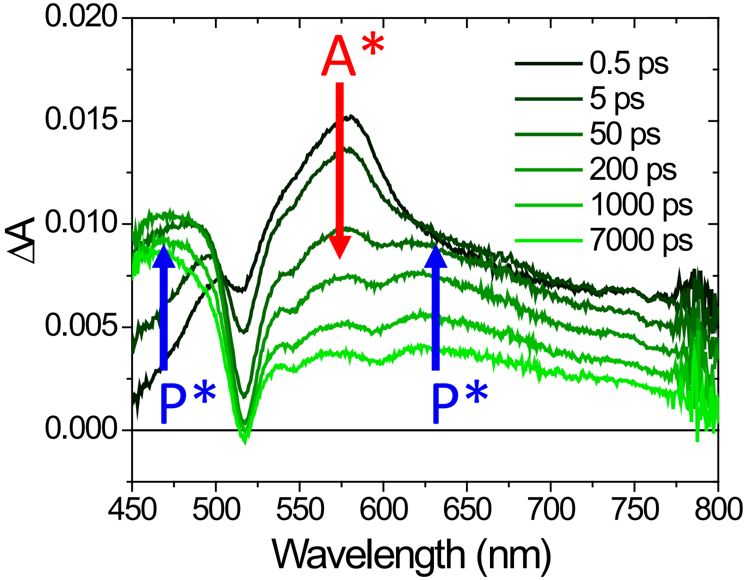
FRET and Relative Orientation





FRET and Relative Orientation

Transient Absorption



Sample	τ (ps)	Φ_{FRET}
ZrO_2-**A**-**Zn**-**P1**	38	99%
ZrO_2-**A**-**Zn**-**P2**	41	99%
ZrO_2-**A**-**Zn**-**P3**	175	97%

P2

$$E = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6}$$

$$R_0 = 9780\,[J\,\phi_D\,n^{-4}\,\kappa^2]^{1/6}$$

J = overlap integral

ϕ_D = fluorescence QY of D

n= refractive index

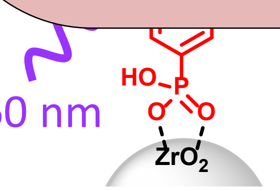
κ^2= orientation factor

r = distance

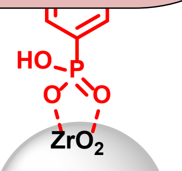
J, Φ_D, and n are known/the same.

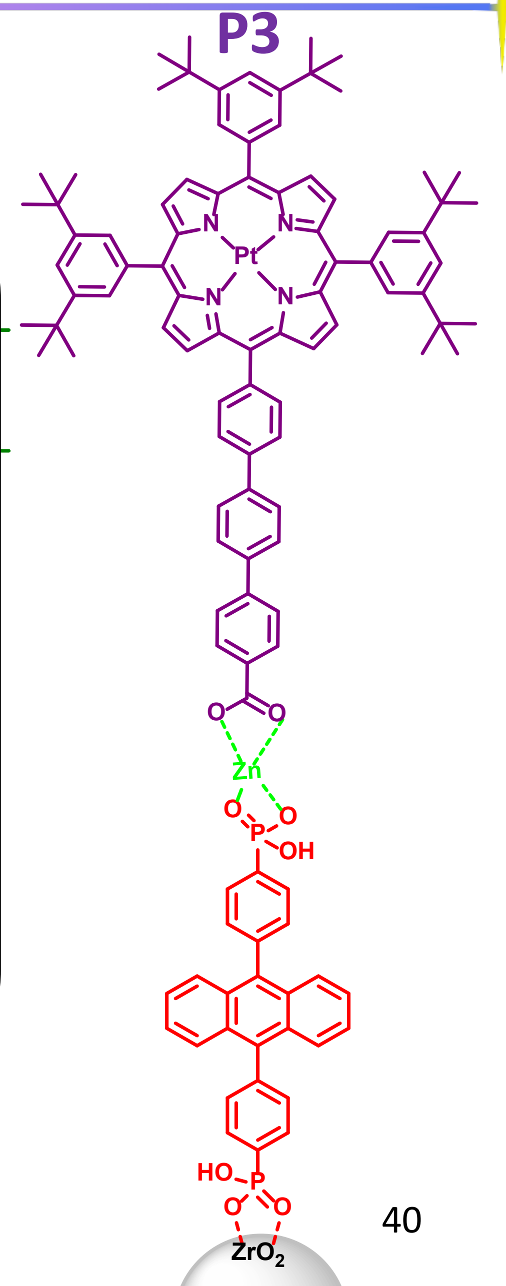
Use change in r/E to find κ^2.

(assumes constant κ^2 for P1-3)

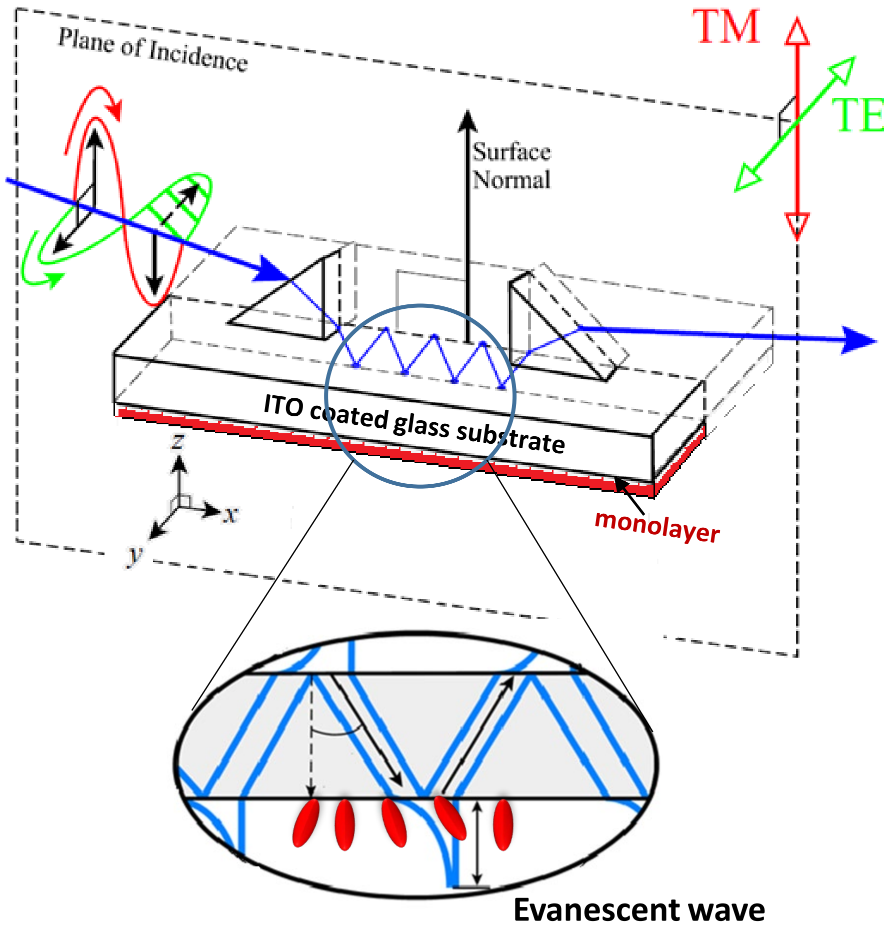


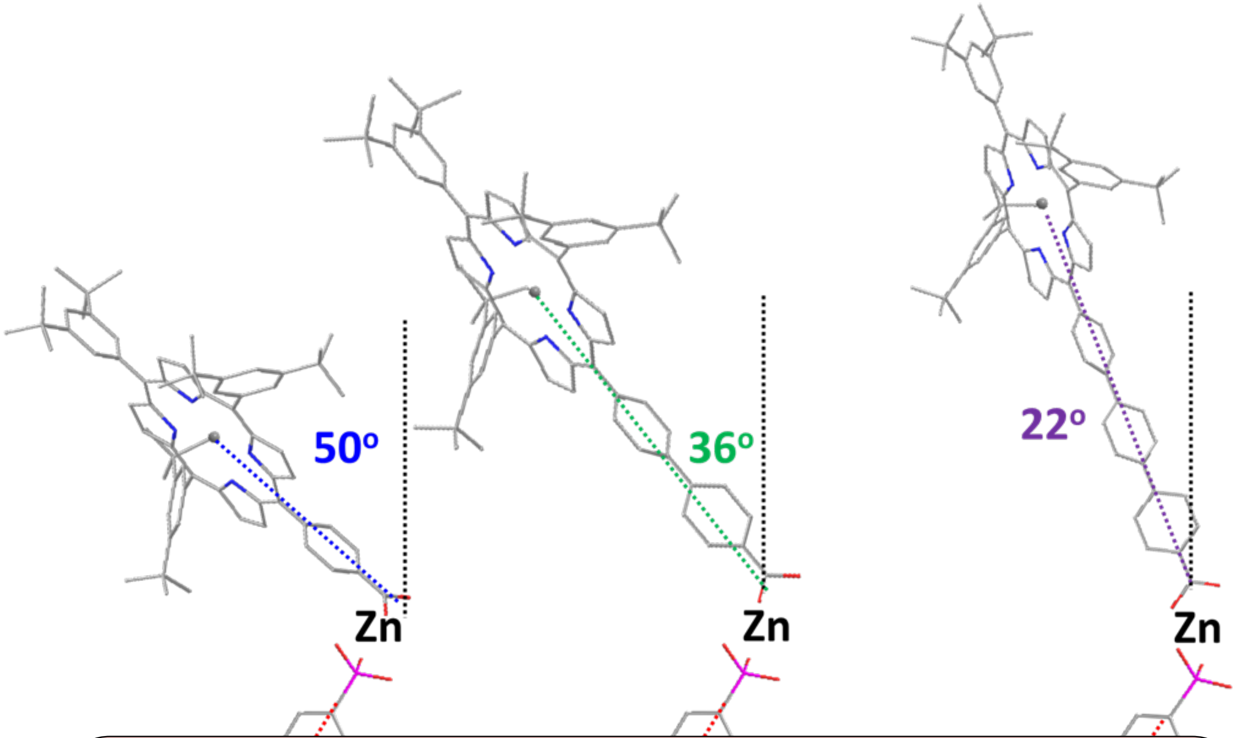
λ_{Ex}=360 nm





Polarized ATR



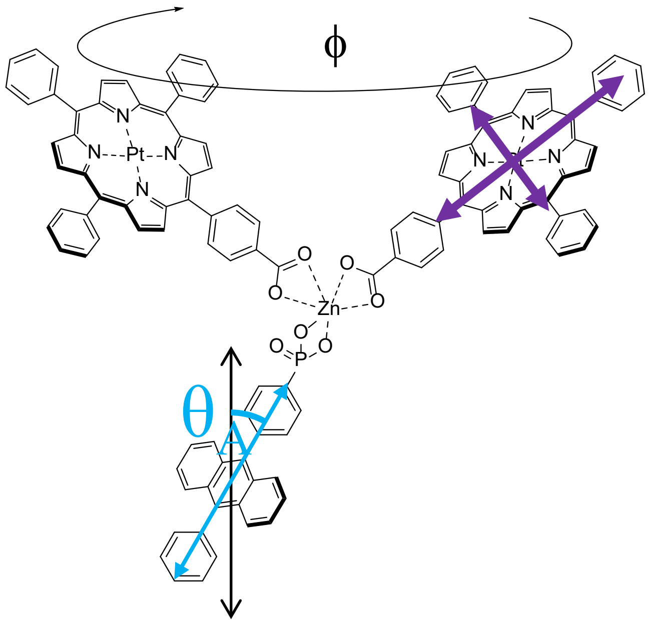


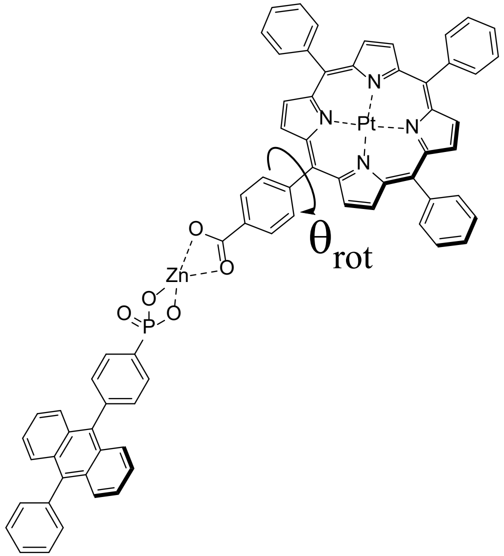
Both κ² and r are changing.

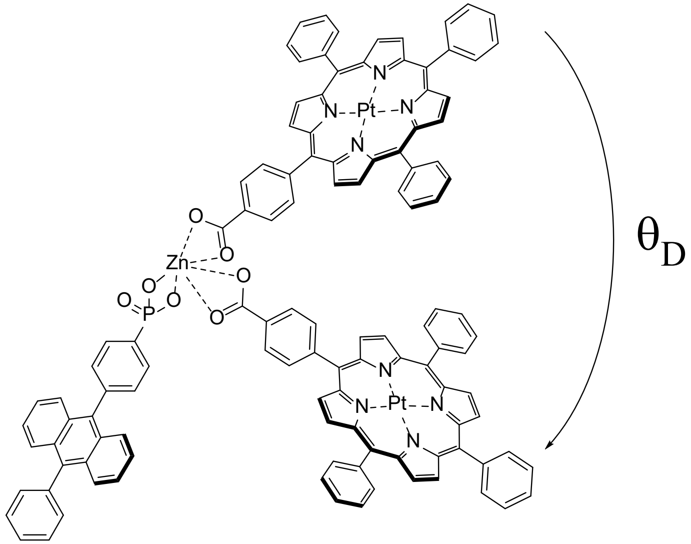
This method will not work.

Also, this is only one possible orientation!

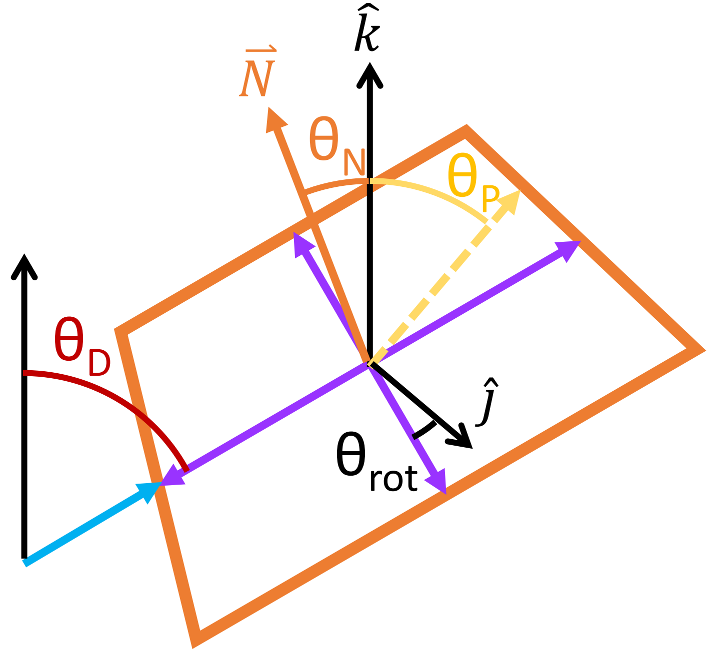
Porphyrin Orientation







Cory Ruchlin, McGill
Former FSU UG



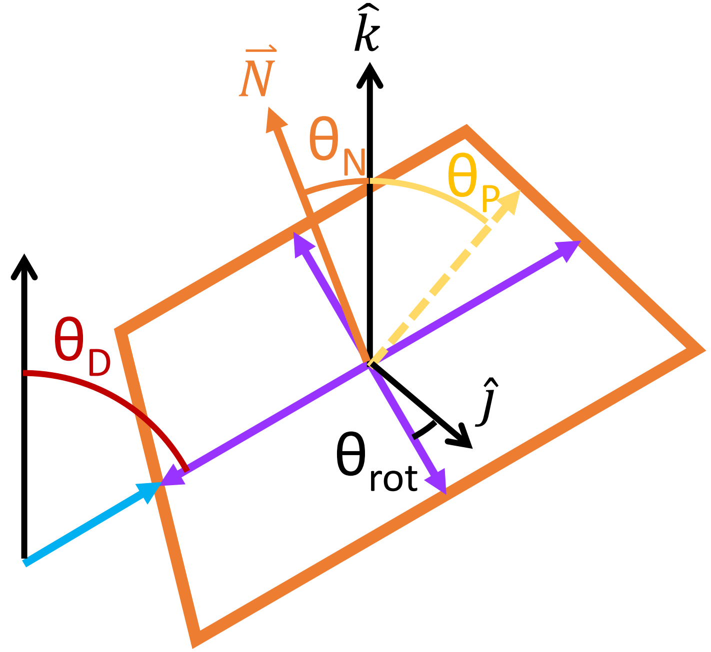
Porphyrin Orientation

$$\mu_{1x} = \sin\theta_D \cos\varphi$$
$$\mu_{1y} = \sin\theta_D \sin\varphi$$
$$\mu_{1z} = \cos\theta_D$$
$$\mu_{2x} = -\sin\theta_{rot}\cos\theta_D\cos\varphi - \cos\theta_{rot}\sin\varphi$$
$$\mu_{2y} = \cos\theta_{rot}\cos\varphi - \sin\theta_{rot}\cos\theta_D\sin\varphi$$
$$\mu_{2z} = \sin\theta_{rot}\sin\theta_D$$

$$\vec{N} = \widehat{\mu_1} \times \widehat{\mu_2}$$
$$\vec{N} \cdot \hat{k} = \sin\theta_P$$

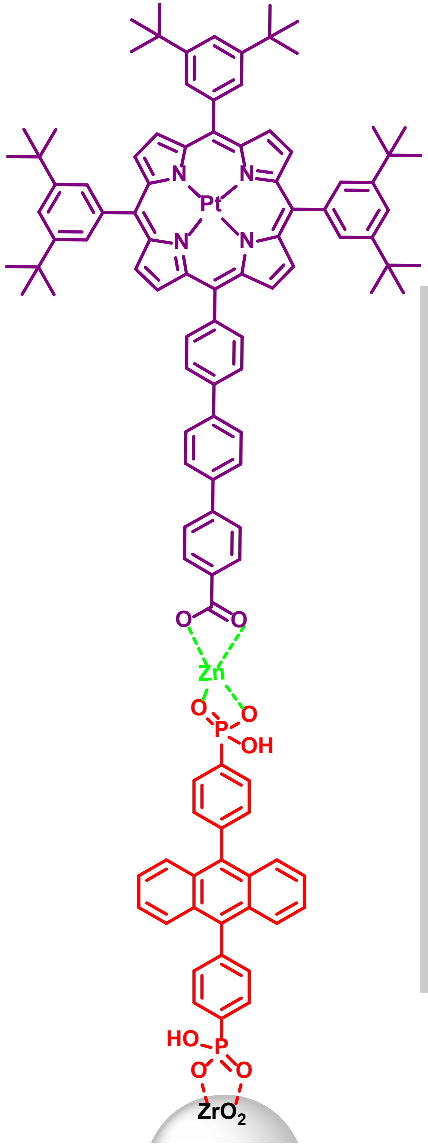
$$\alpha = \frac{\arccos(\vec{r_A} \cdot \vec{r_{DA}})}{l_A \|\vec{r_{DA}}\|}$$
$$\beta_1 = \frac{\arccos(\widehat{\mu_1} \cdot \vec{r_{DA}})}{\|\vec{r_{DA}}\|}$$
$$\beta_2 = \frac{\arccos(\widehat{\mu_2} \cdot \vec{r_{DA}})}{\|\vec{r_{DA}}\|}$$
$$\gamma_1 = \frac{\arccos(\widehat{\mu_1} \cdot \vec{r_A})}{\|\vec{r_A}\|}$$
$$\gamma_2 = \frac{\arccos(\widehat{\mu_2} \cdot \vec{r_A})}{\|\vec{r_A}\|}$$

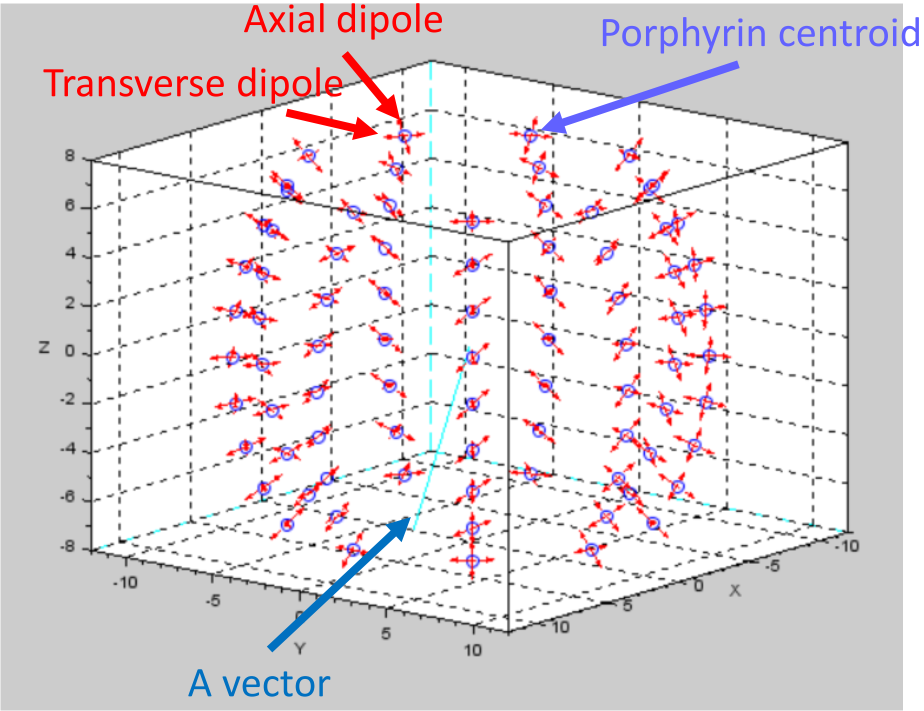
Cory Ruchlin, McGill
Former FSU UG



$$\kappa_i^2 = (\cos\gamma_i - 3\cos\alpha\cos\beta_i)^2$$
$$\langle\kappa^2\rangle = \frac{\kappa_1^2 + \kappa_2^2}{2}$$

Porphyrin Orientation

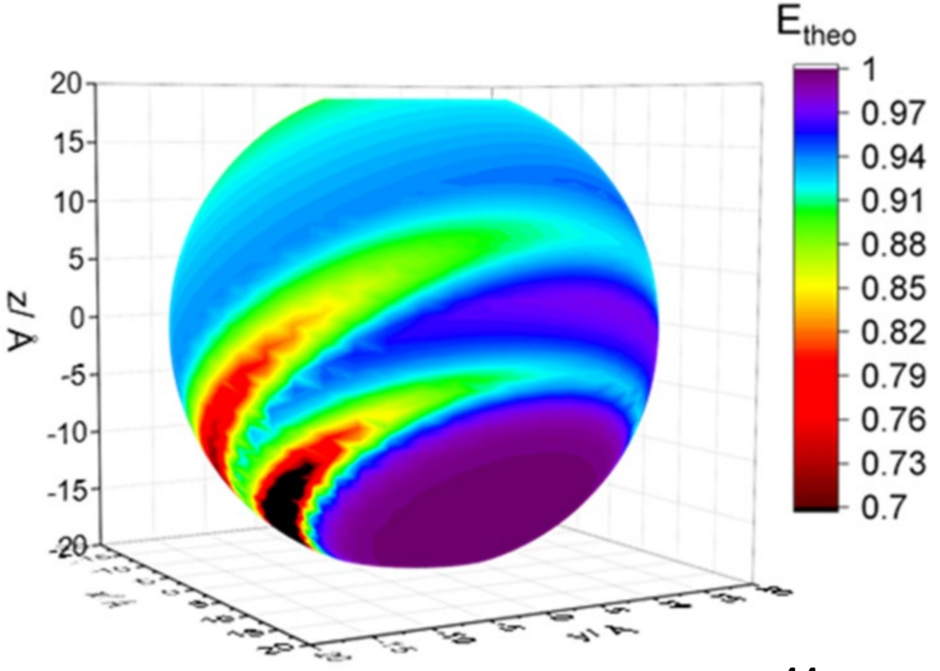




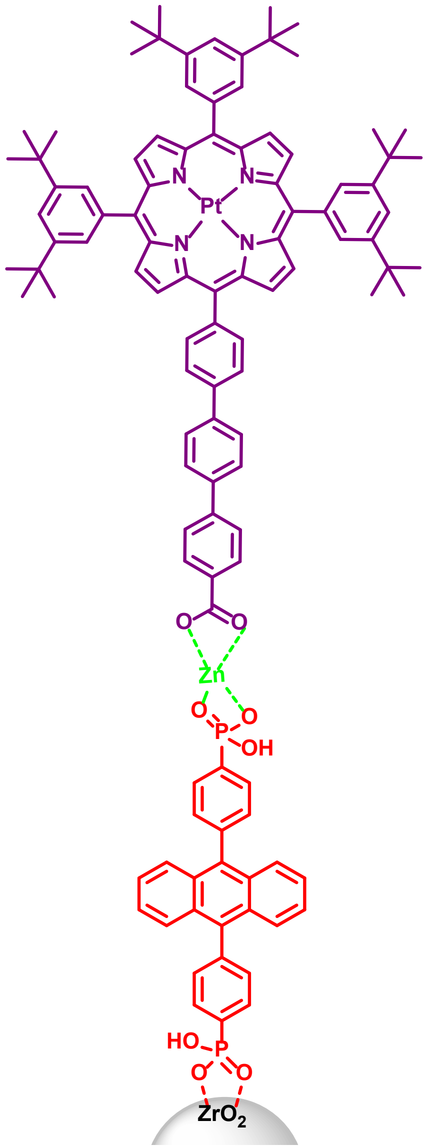
Theoretical FRET Efficiency

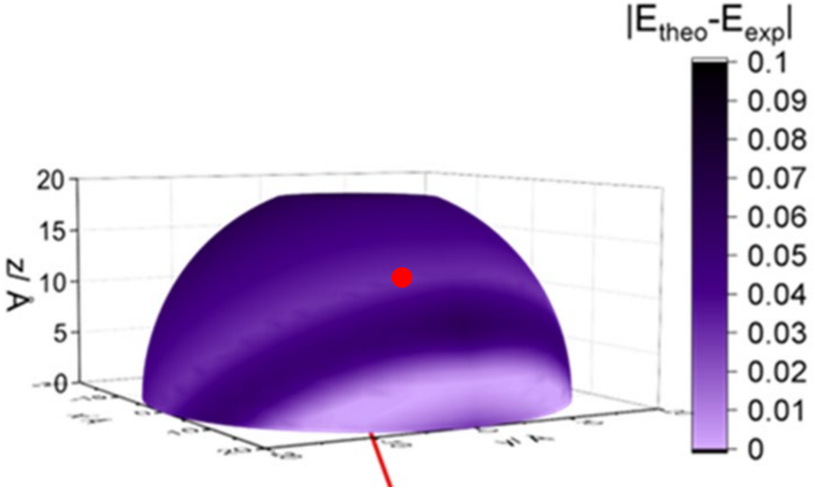
$$E_{theo} = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6}$$

$$R_0 = 9780\ [J\ \phi_D\ n^{-4}\ \kappa^2]^{1/6}$$



Porphyrin Orientation

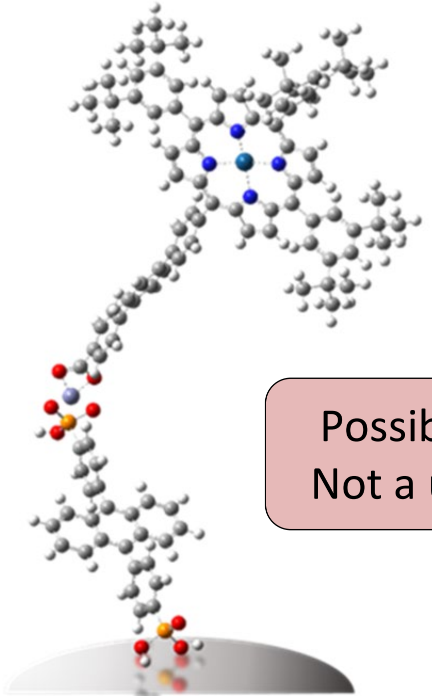




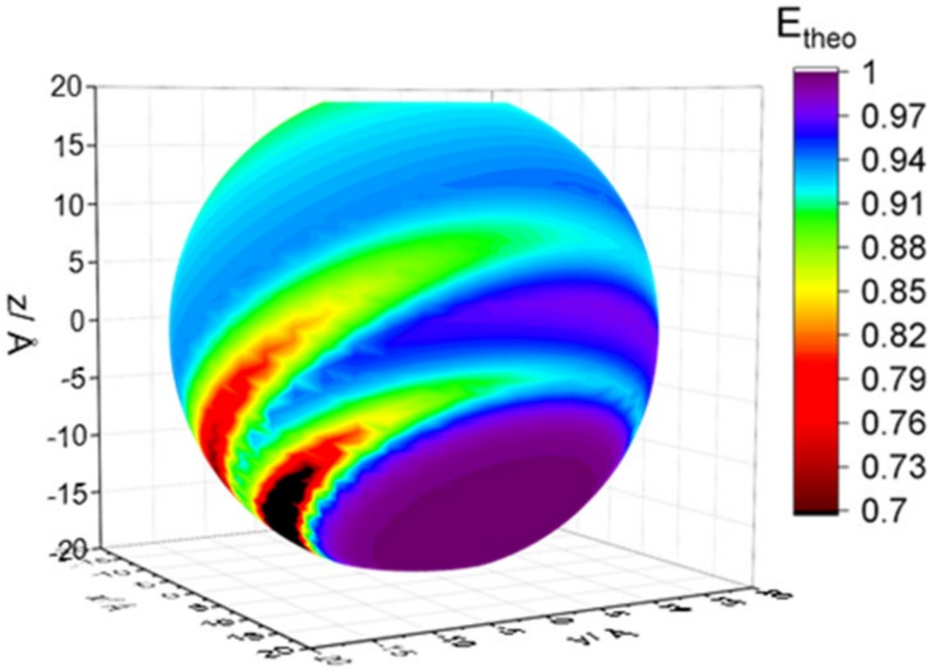
Theoretical FRET Efficiency

$$E_{theo} = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6}$$

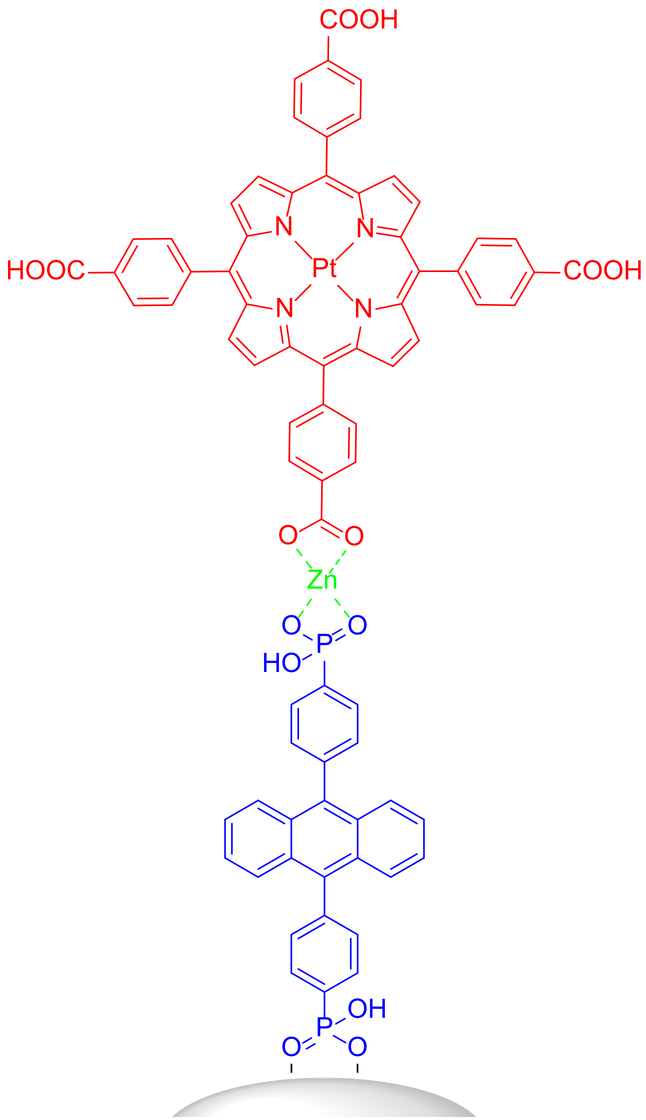
$$R_0 = 9780\ [J\ \phi_D\ n^{-4}\ \kappa^2]^{1/6}$$



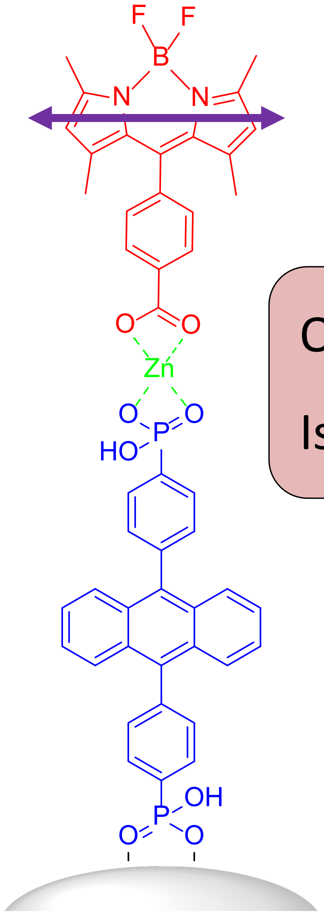
Possible orientation.
Not a unique answer.



~~Porphyrin~~ Orientation



Old Bilayer

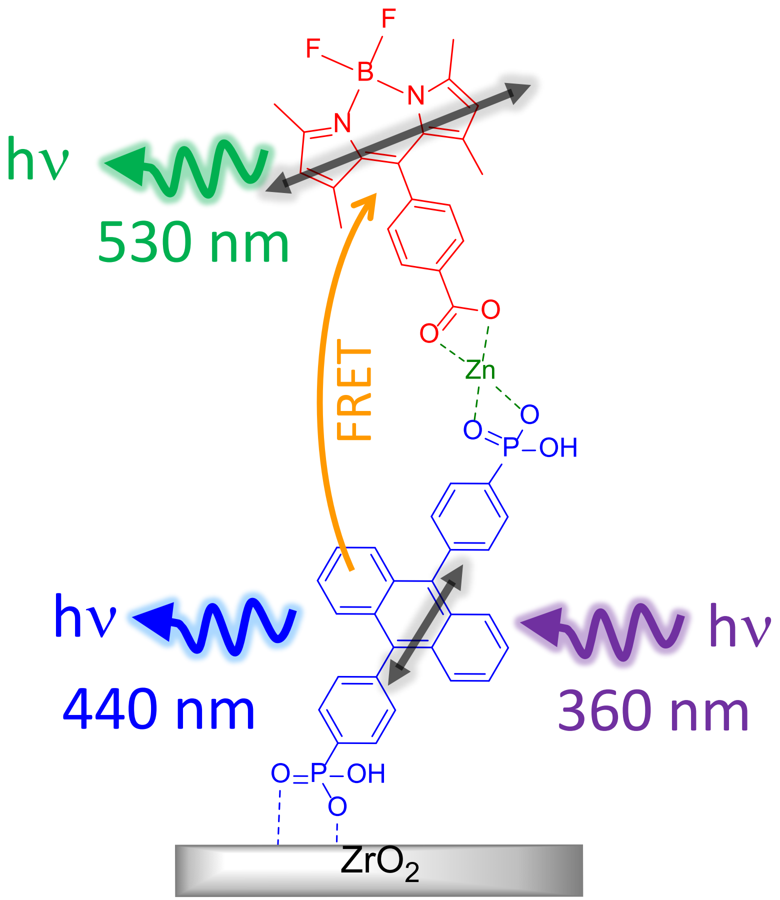


New Bilayer

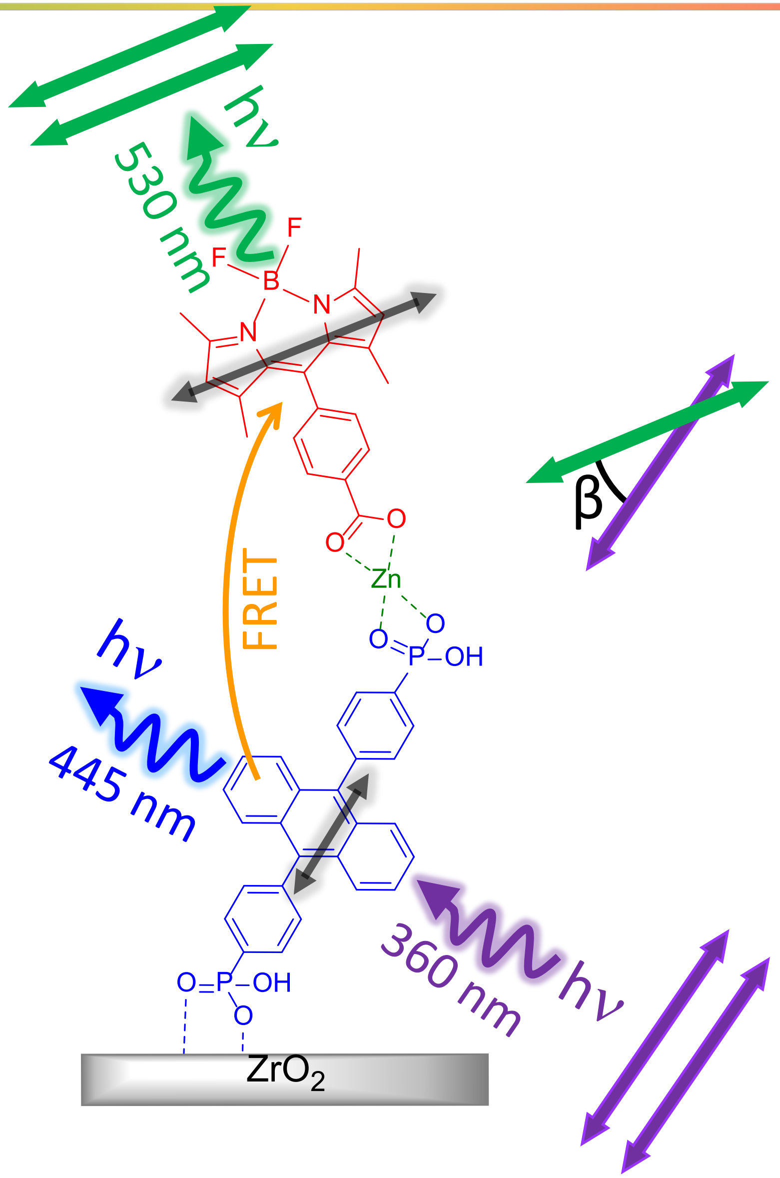
One transition dipole moment.

Is a fluorescent FRET acceptor.

Emission Anisotropy



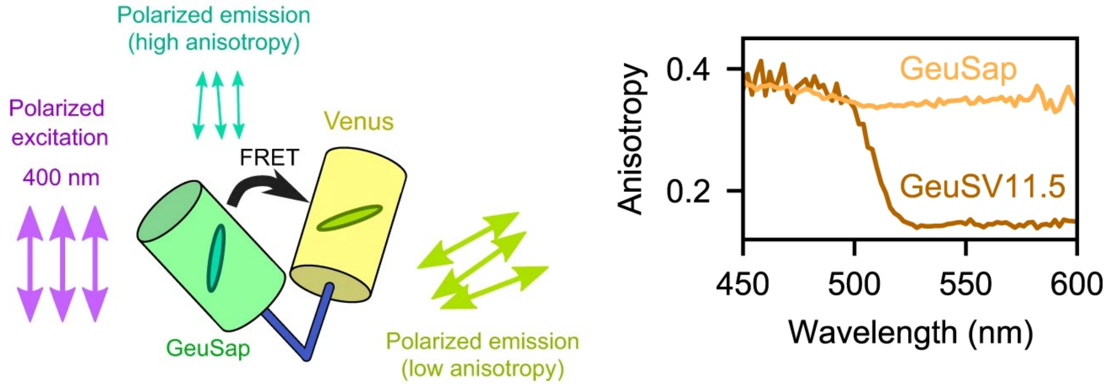
Emission Anisotropy

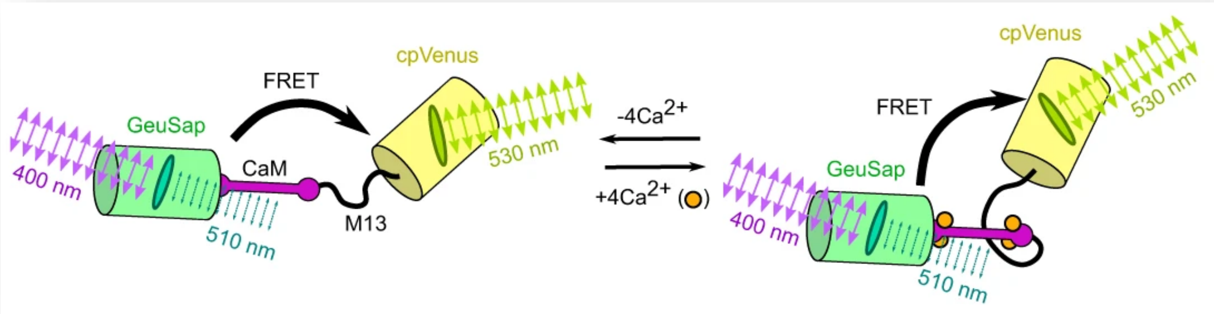


Quantification of FRET-induced angular displacement by monitoring sensitized acceptor anisotropy using a dim fluorescent donor

Danai Laskaratou[1], Guillermo Solís Fernández[2], Quinten Coucke[2], Eduard Fron[2,3], Susana Rocha[2], Johan Hofkens[2], Jelle Hendrix[2,4] & Hideaki Mizuno[1]

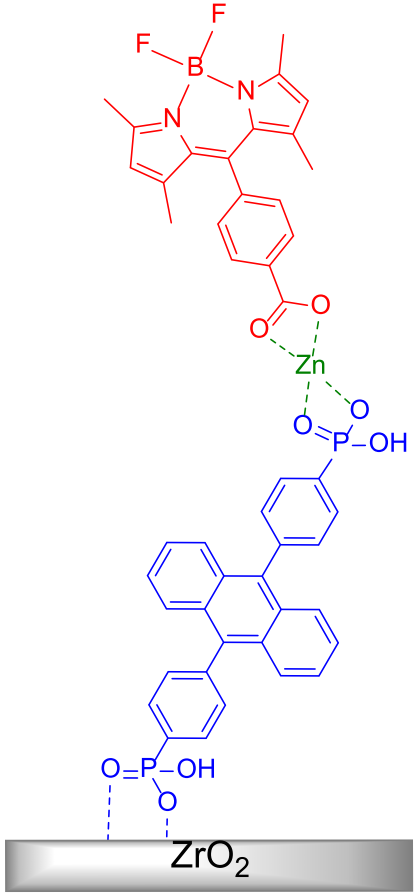
Nat. Commun. **2021**, *12*, 2541.



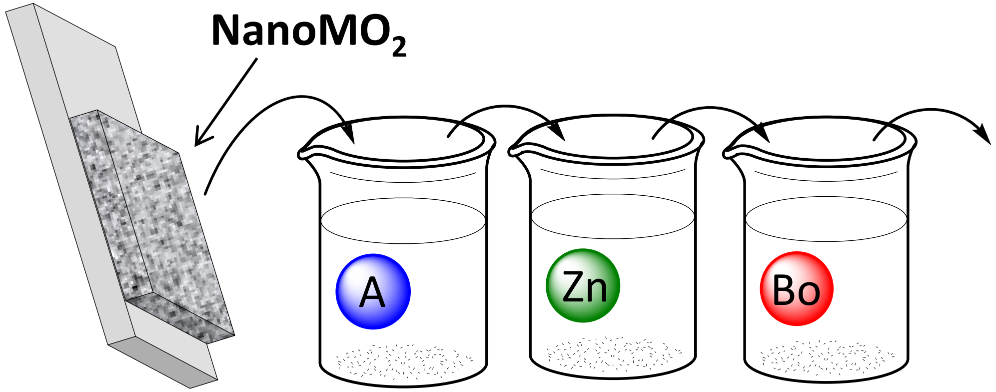


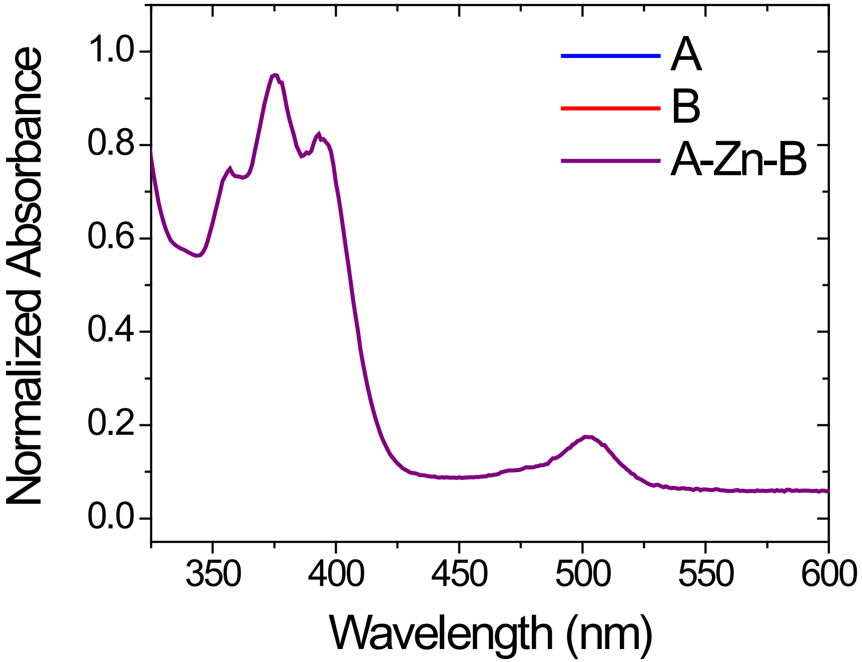
Hanson Research Group

Emission Anisotropy

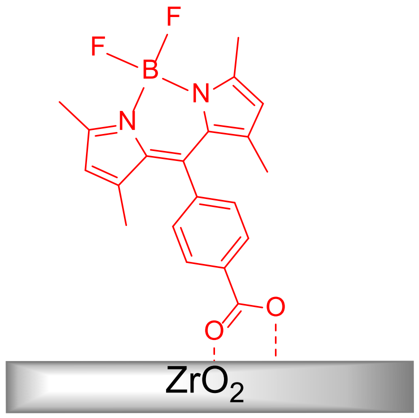


ZrO$_2$-A-Zn-B

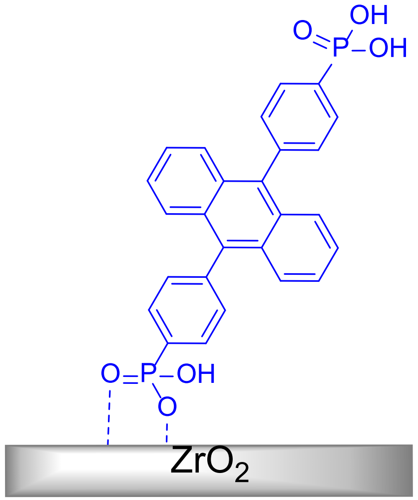




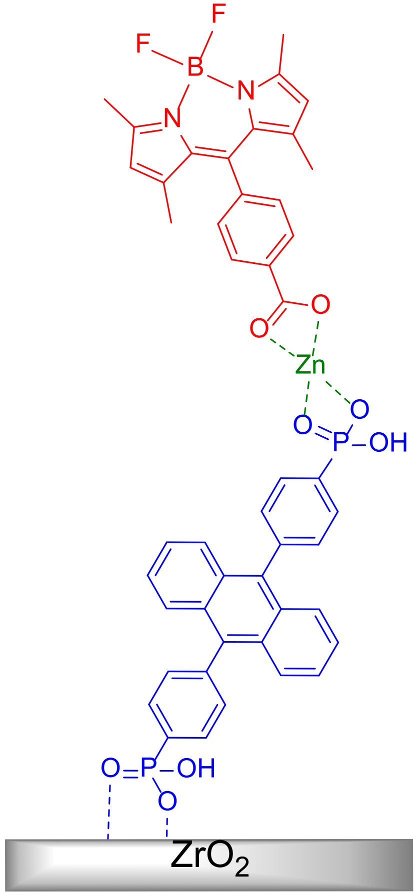
Emission Anisotropy



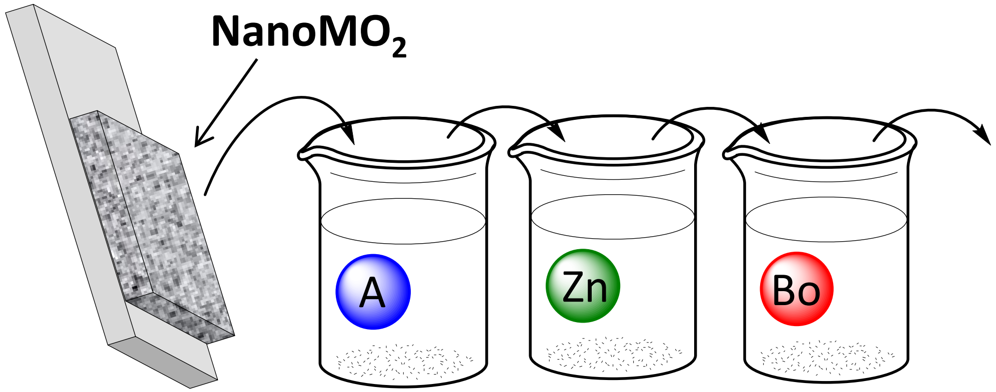
ZrO$_2$-B

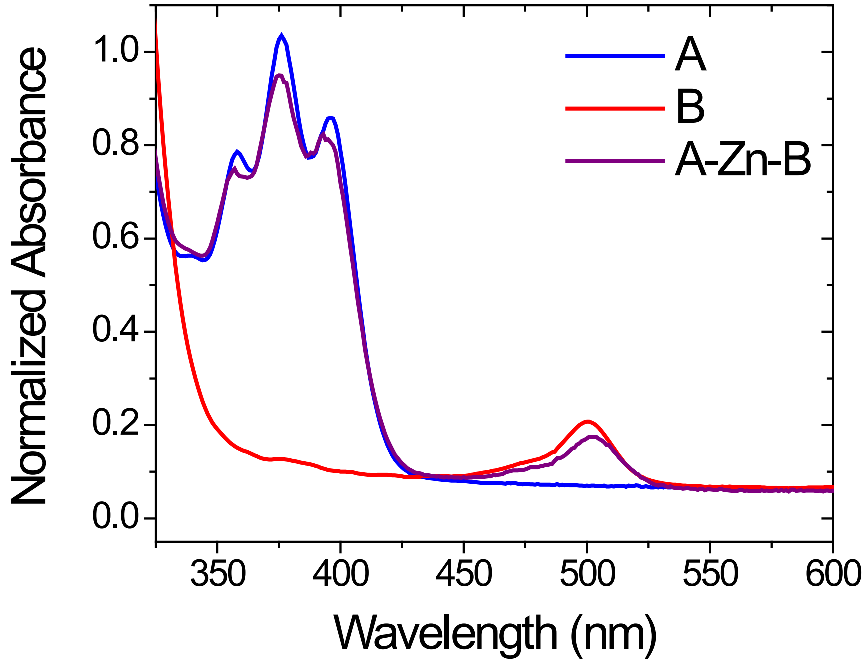


ZrO$_2$-A

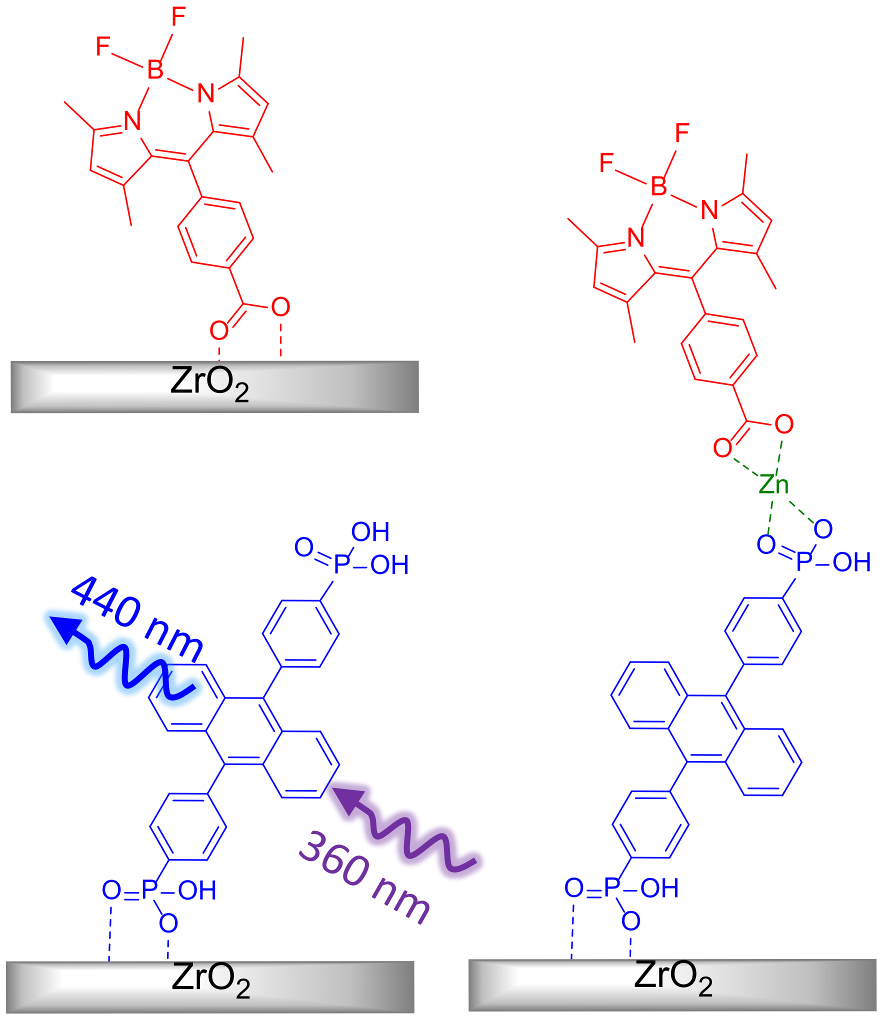


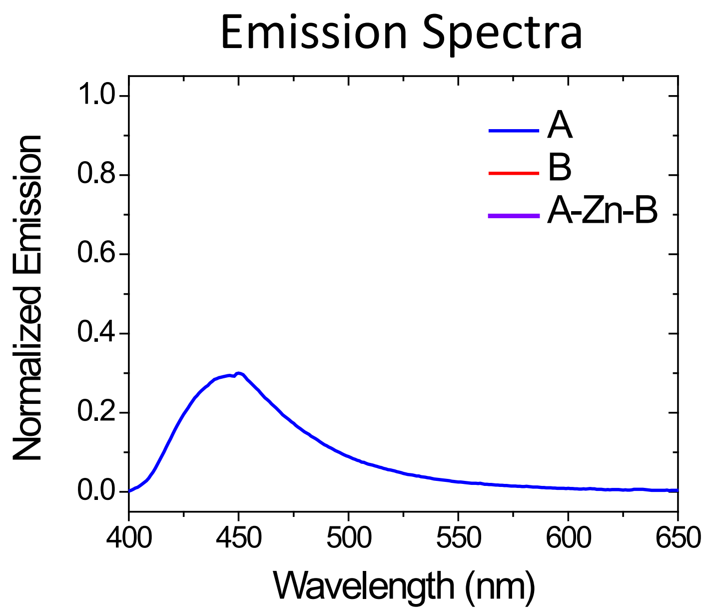
ZrO$_2$-A-Zn-B





Emission Anisotropy





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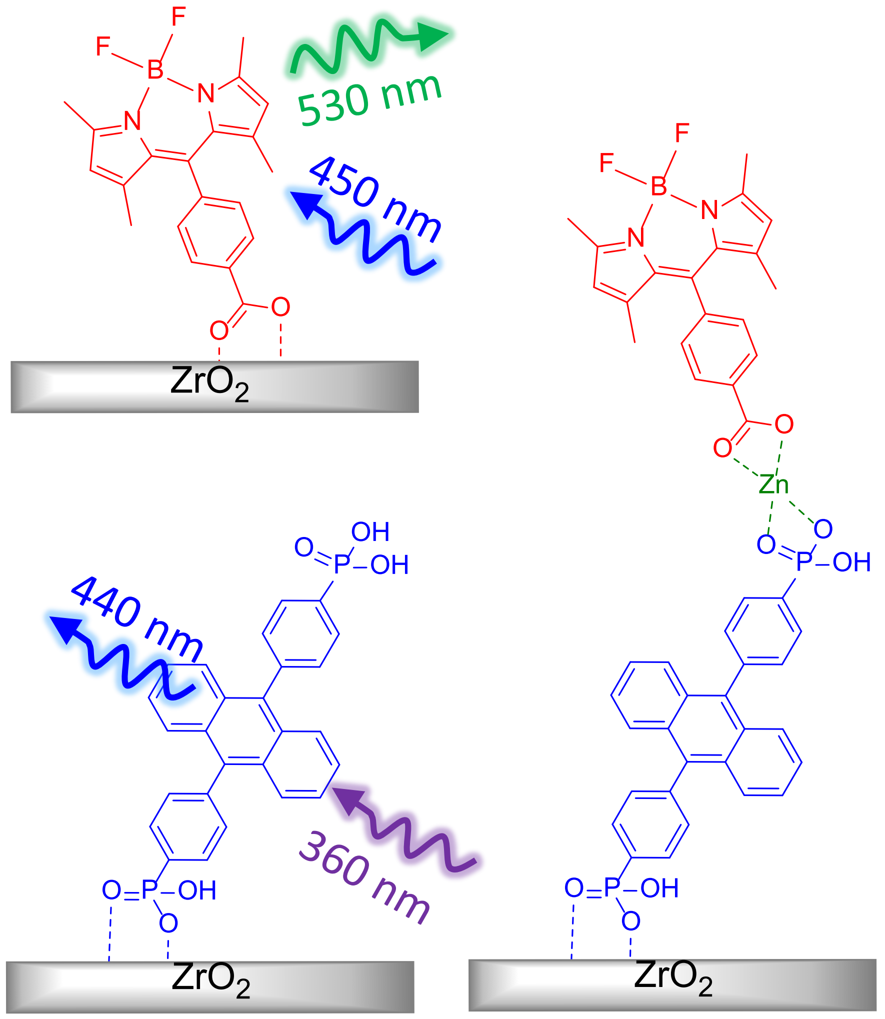
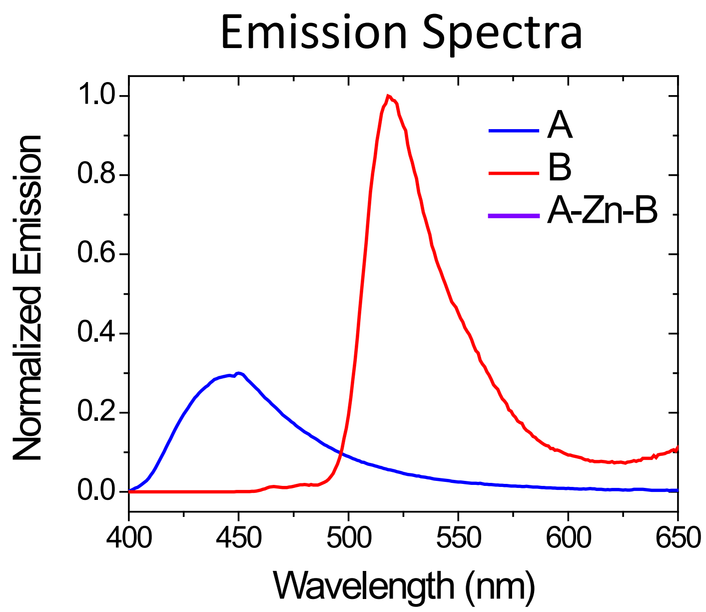
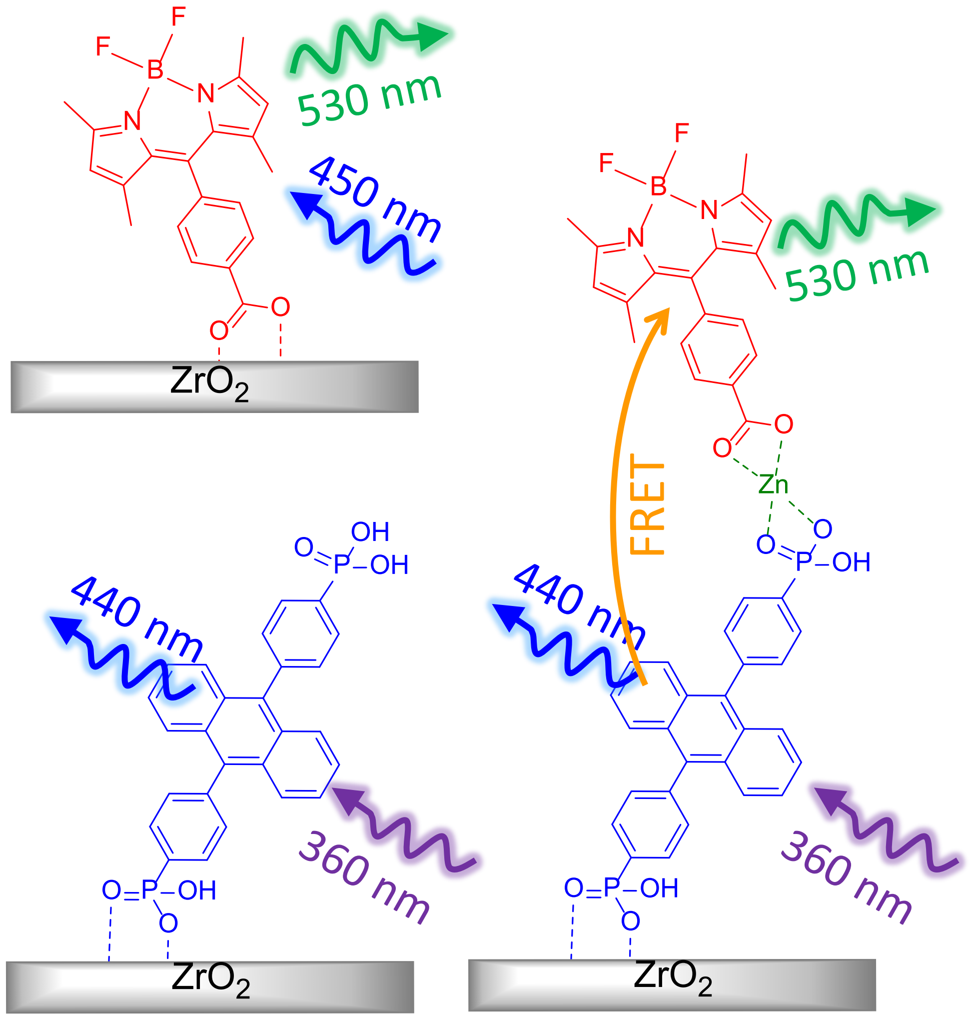
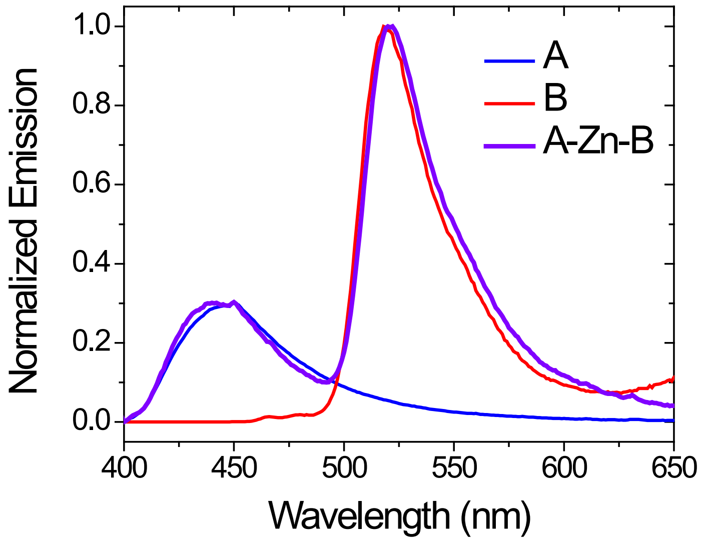




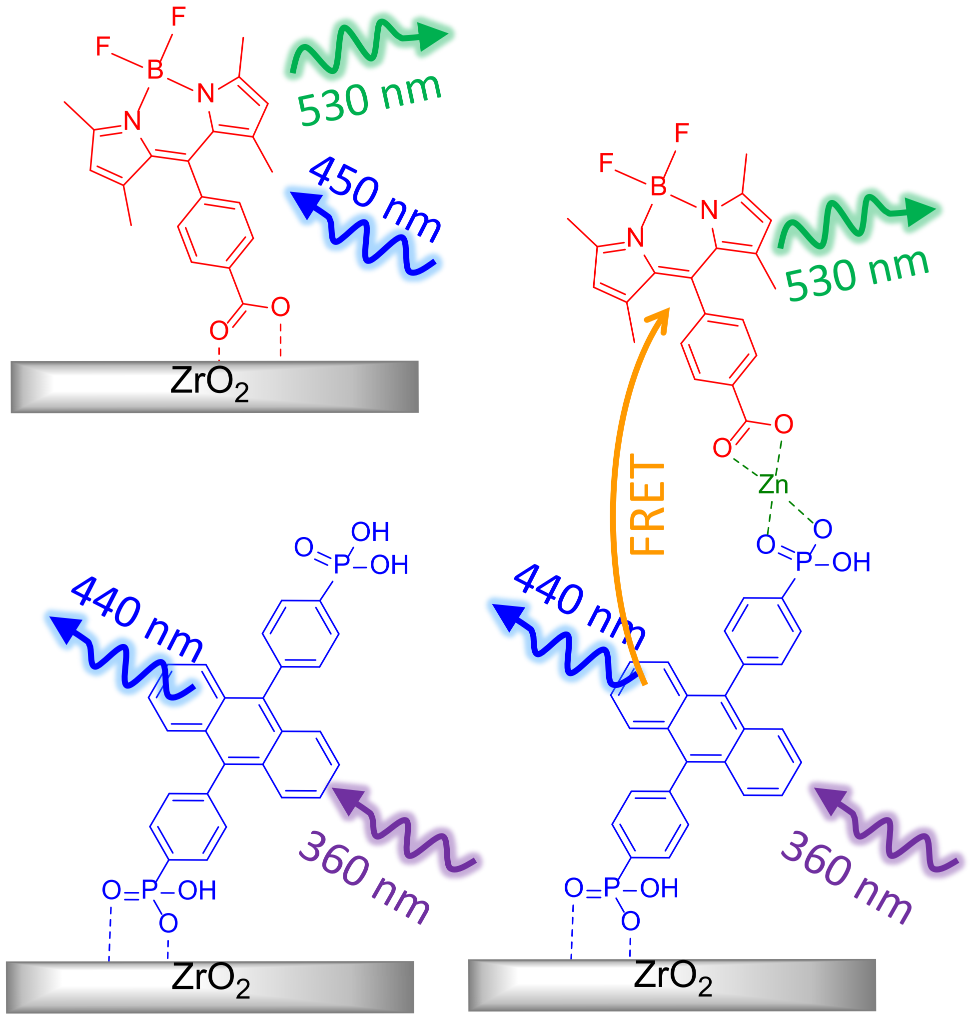
Emission Anisotropy



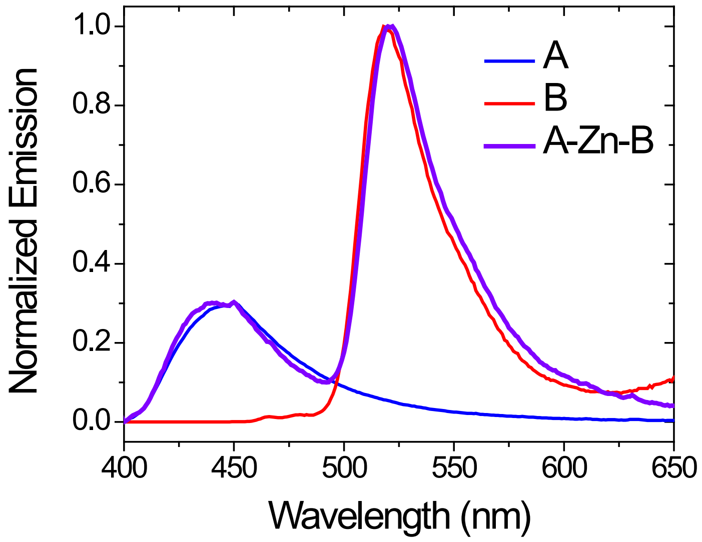
Emission Spectra



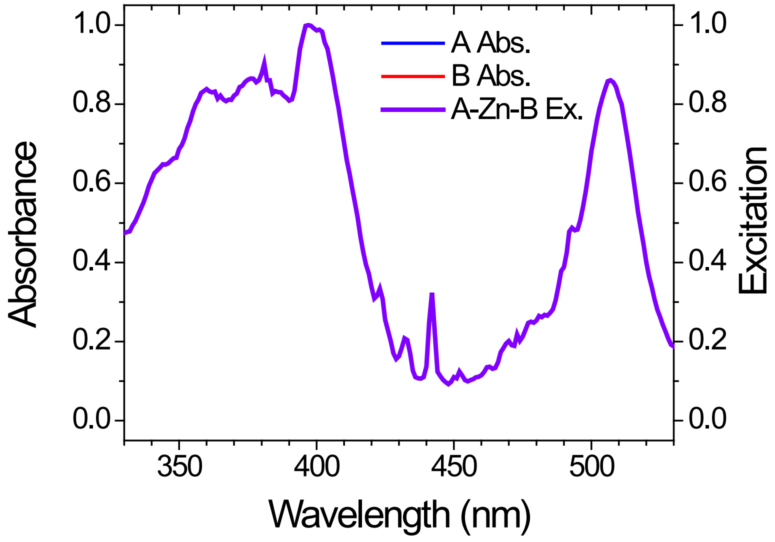
Emission Anisotropy



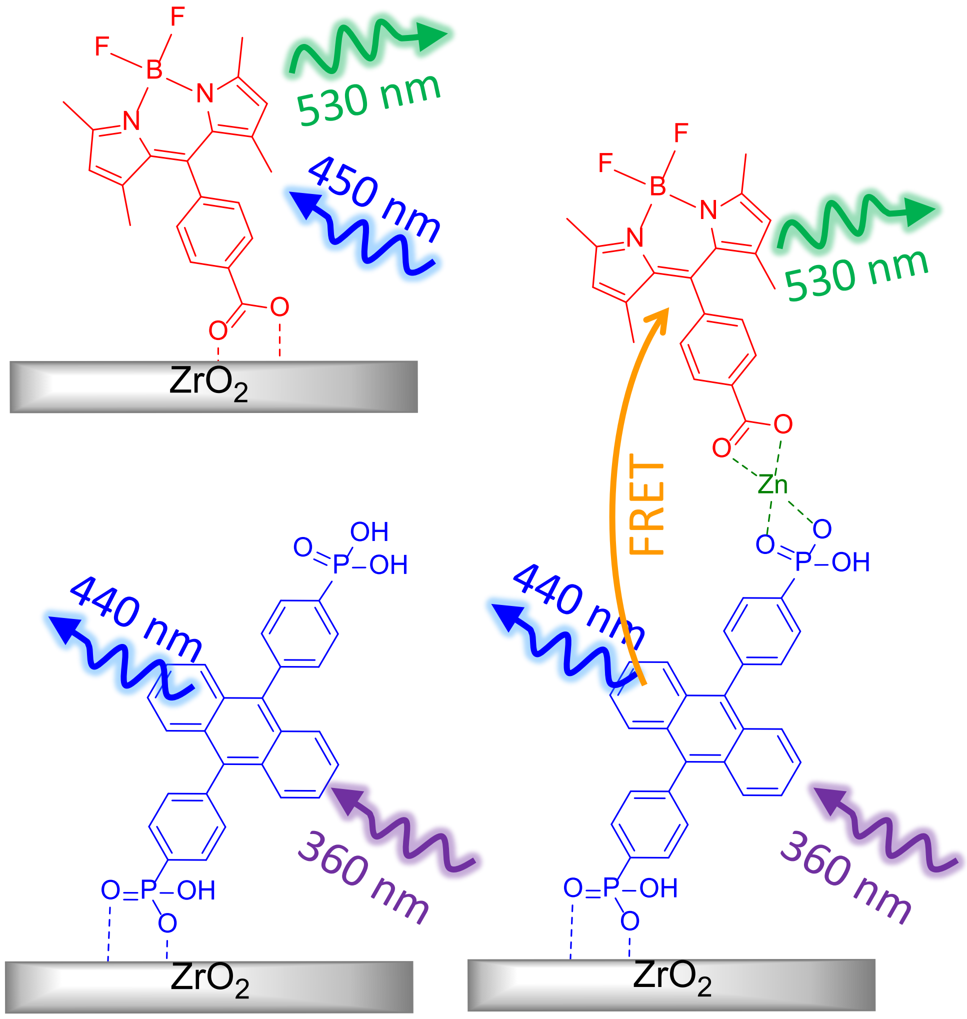
Emission Spectra



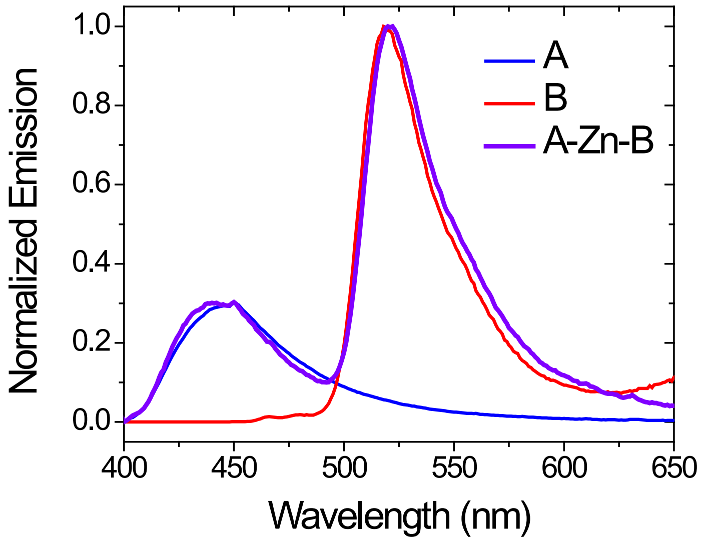
Excitation Spectra (575 nm emission)



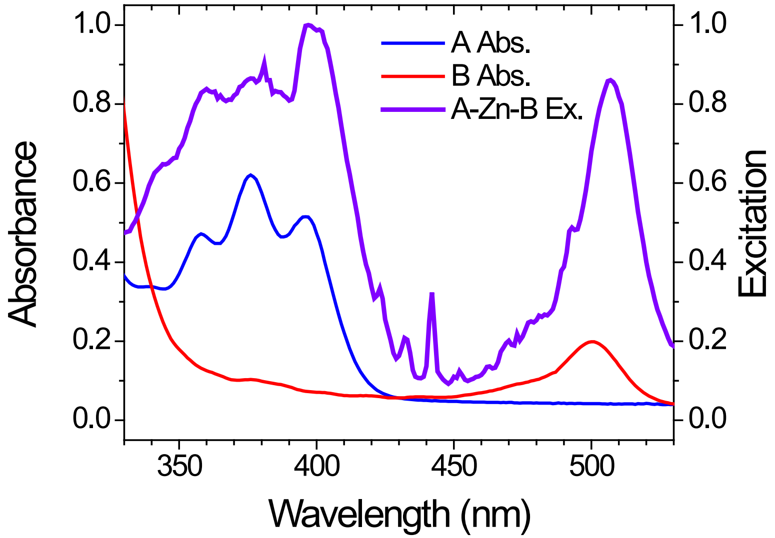
Emission Anisotropy



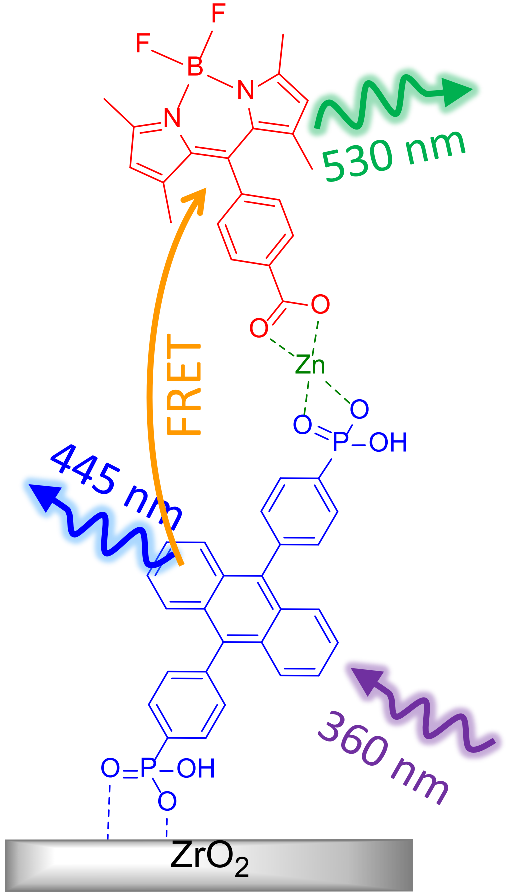
Emission Spectra

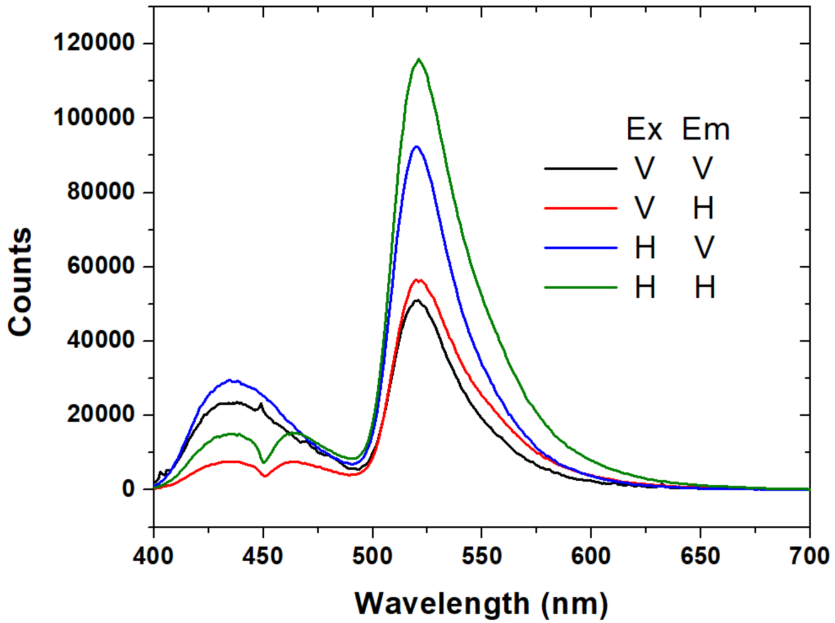


Excitation Spectra (575 nm emission)



Emission Anisotropy





$G = I_{HV}/I_{HH}$

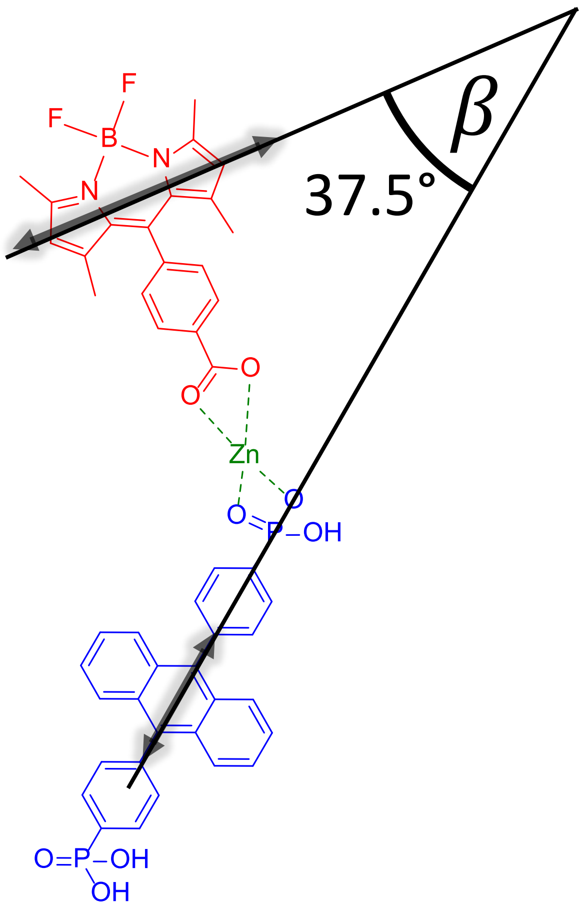
$$r = \frac{I_{VV} - G * I_{VH}}{I_{VV} + 2 * G * I_{VH}}$$

$$r = r_o \left(\frac{1}{1 + \tau/\theta}\right)$$

$$r_o = 0.4 \left(\frac{3\cos^2(\beta) - 1}{2}\right)$$

$\beta = 37.5°$

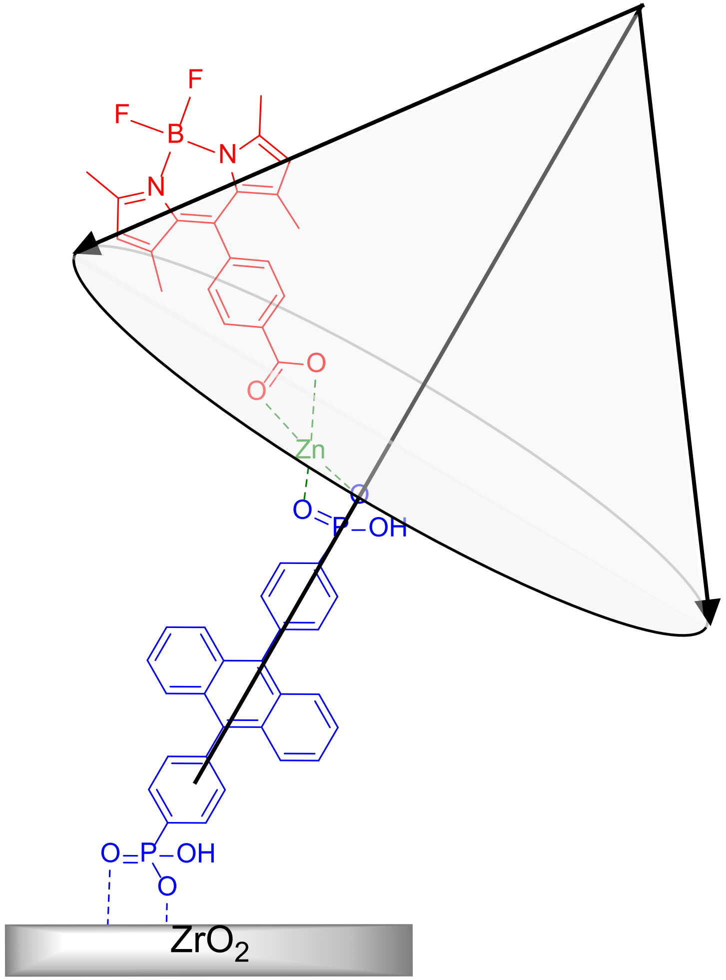
Bilayer Structure



β = 37.5°

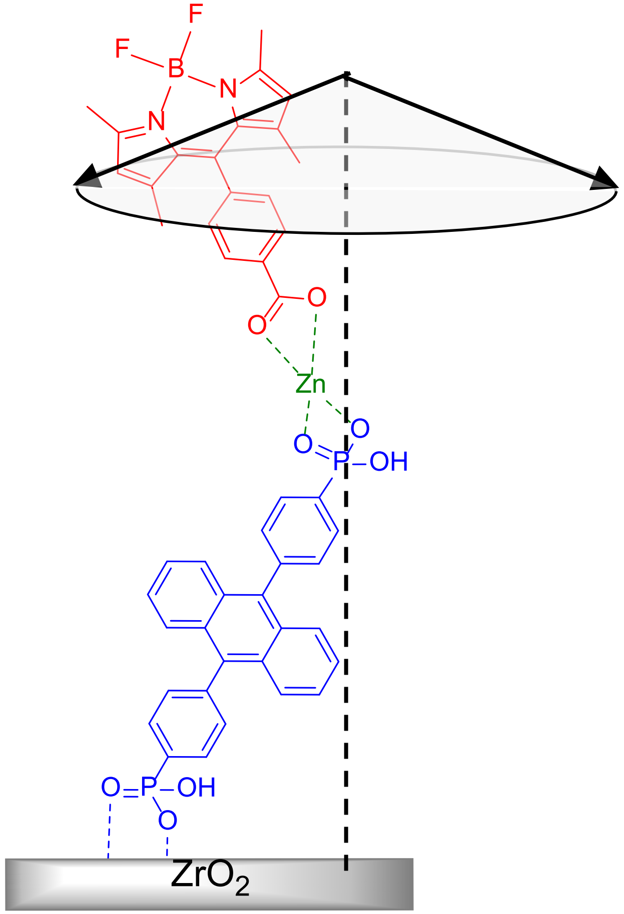
Bilayer Structure

Emission Anisotropy		Polarized ATR		The Average Structure



β = 37.5°

+



Θ = ?

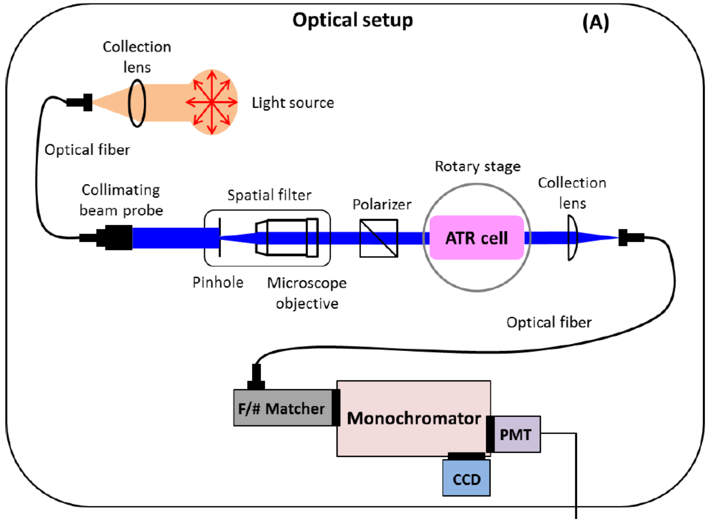
=

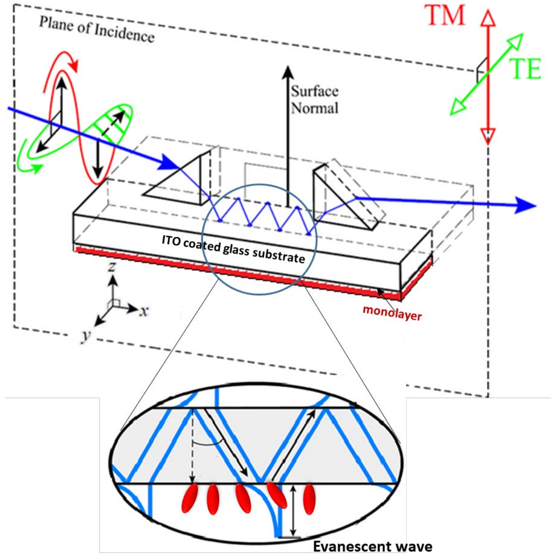
?

Polarized Attenuated Total Reflectance

Prof. Scott Saavedra at UofA:

Retired Summer 2023



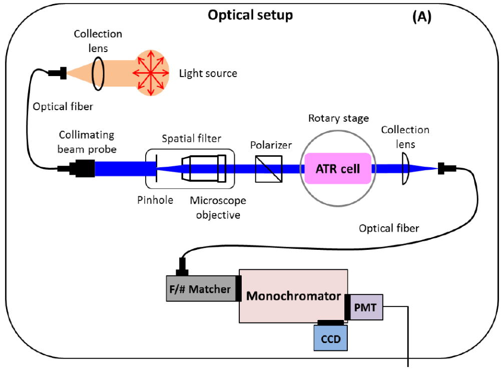


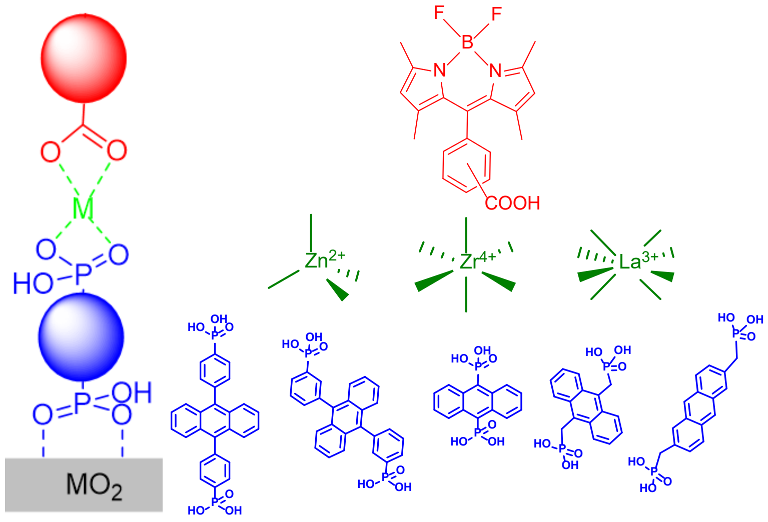
DMR-EPM-2327754

FSU Spectroscopy User Facility

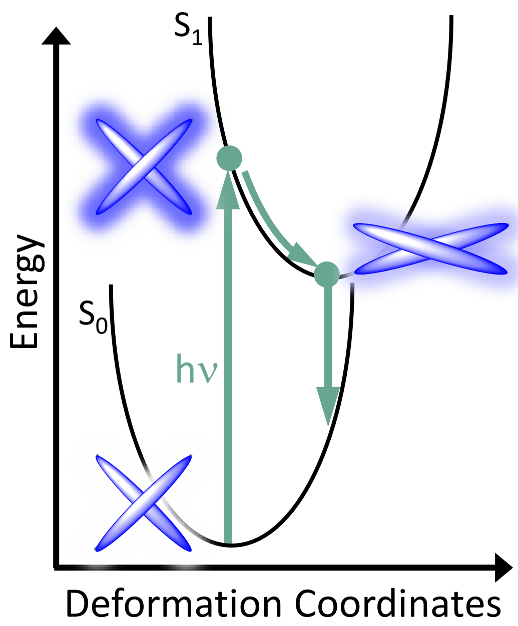
Ongoing/Future Work

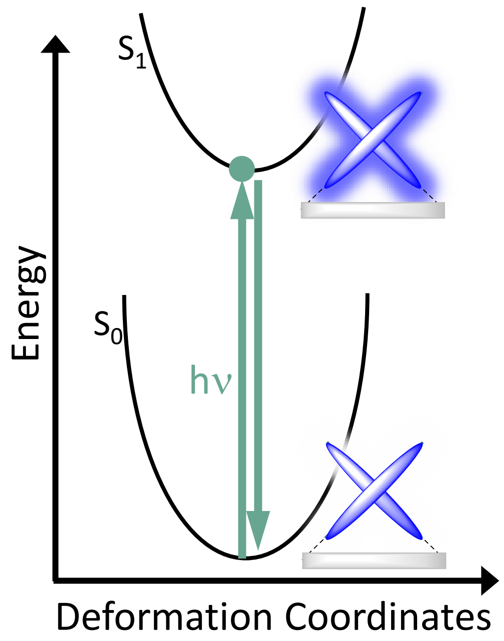
Anisotropy/Polarized ATR



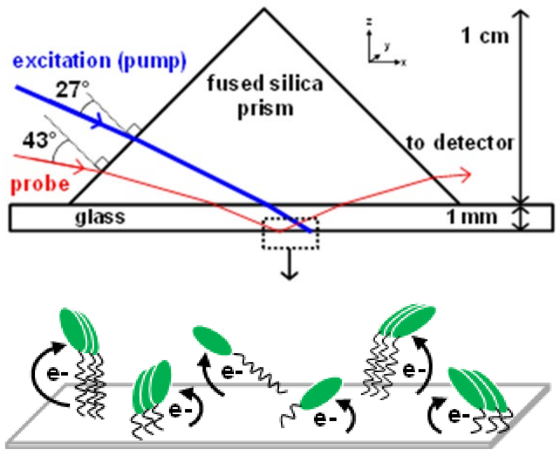


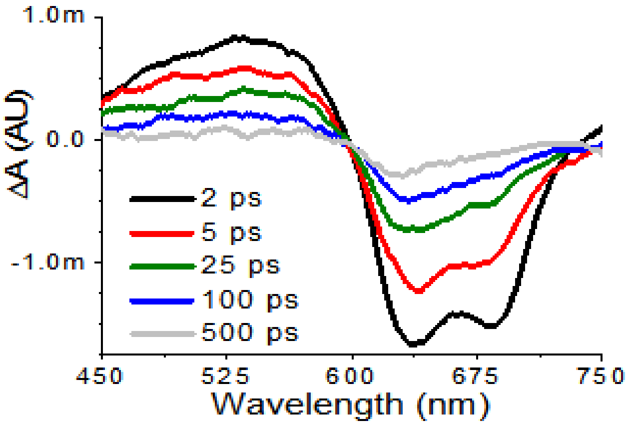
Inhibiting Distortion





Ultrafast Transient Polarized ATR

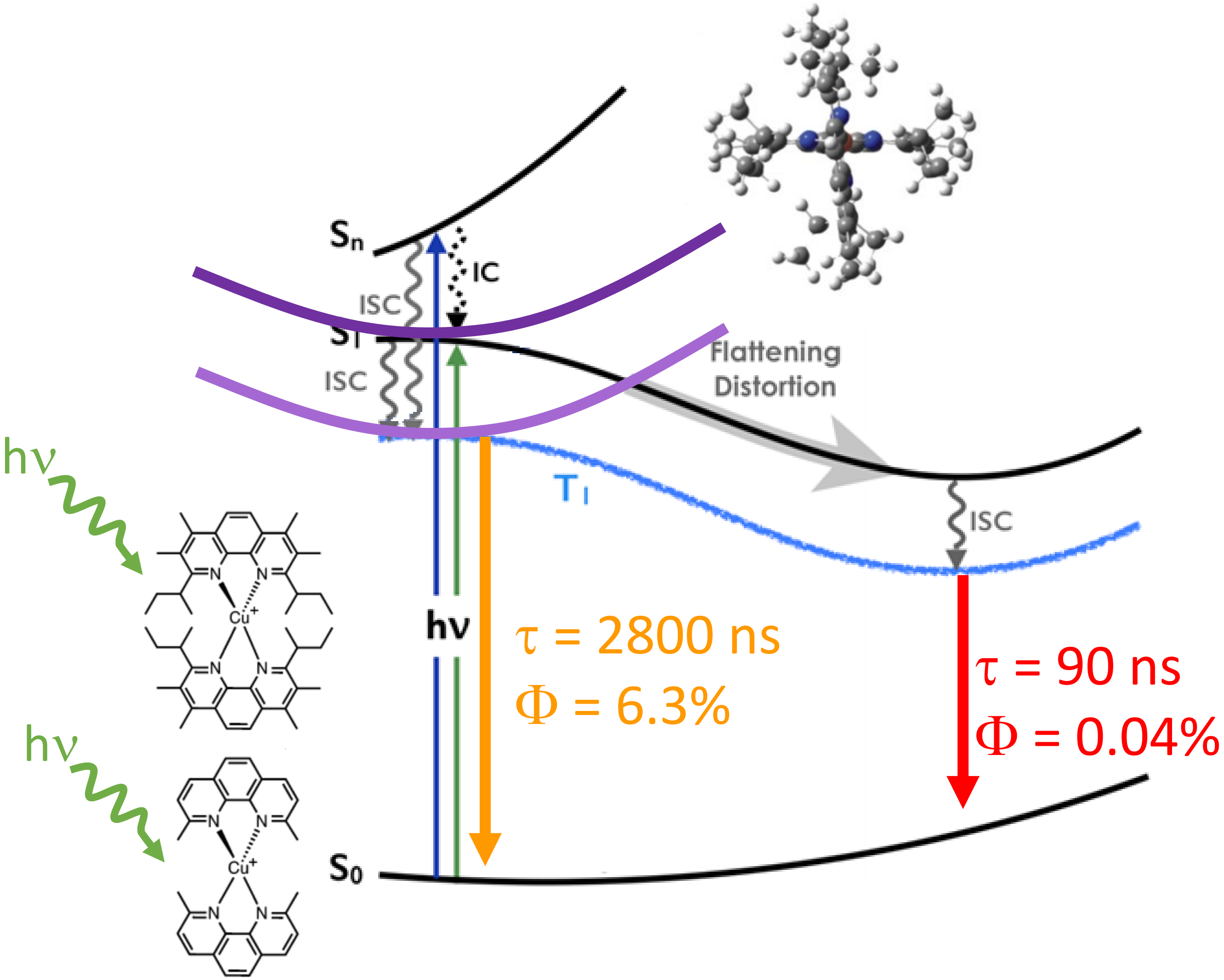




Saavedra (unpublished)

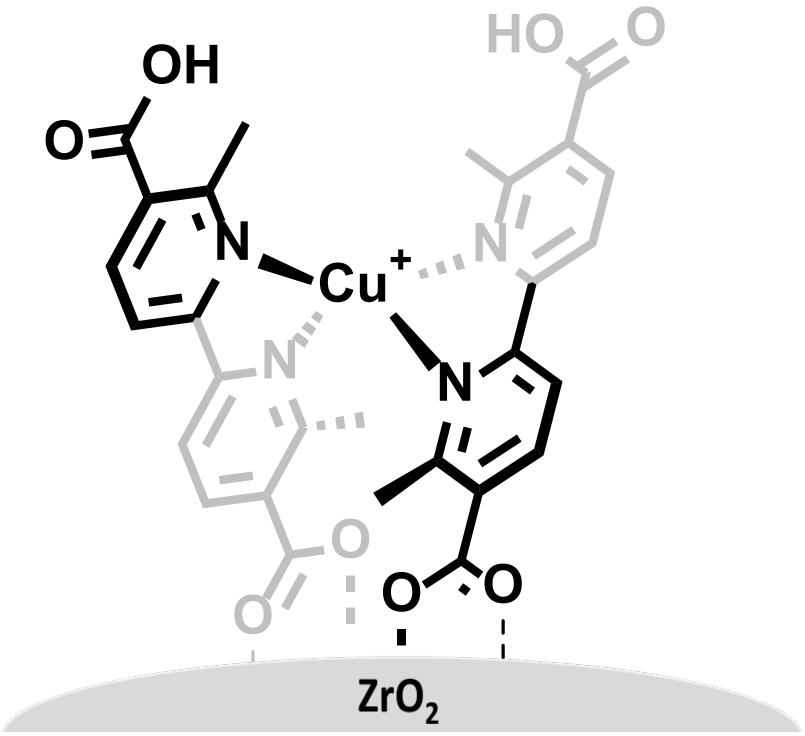
Inhibiting Distortion

Steric Bulk

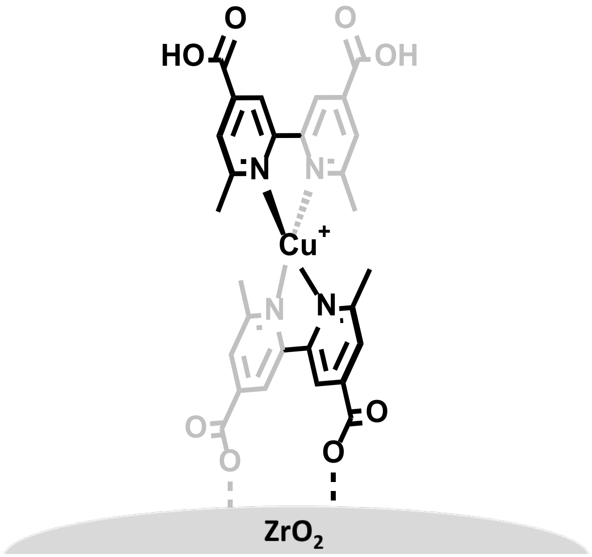


J. Phys. Chem. A **2015**, 119, 13, 3181−3193

Strategic Surface Binding



Decay Kinetics



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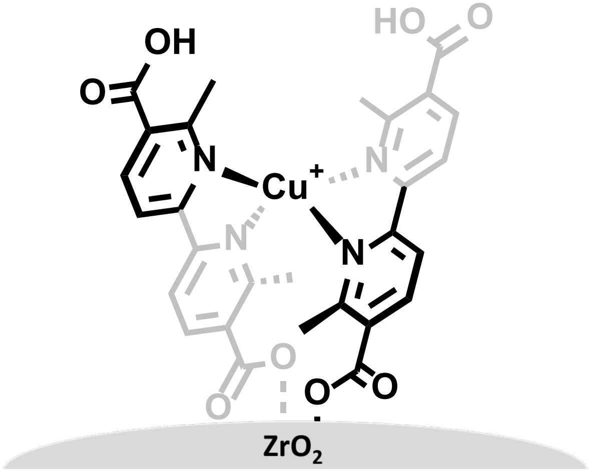

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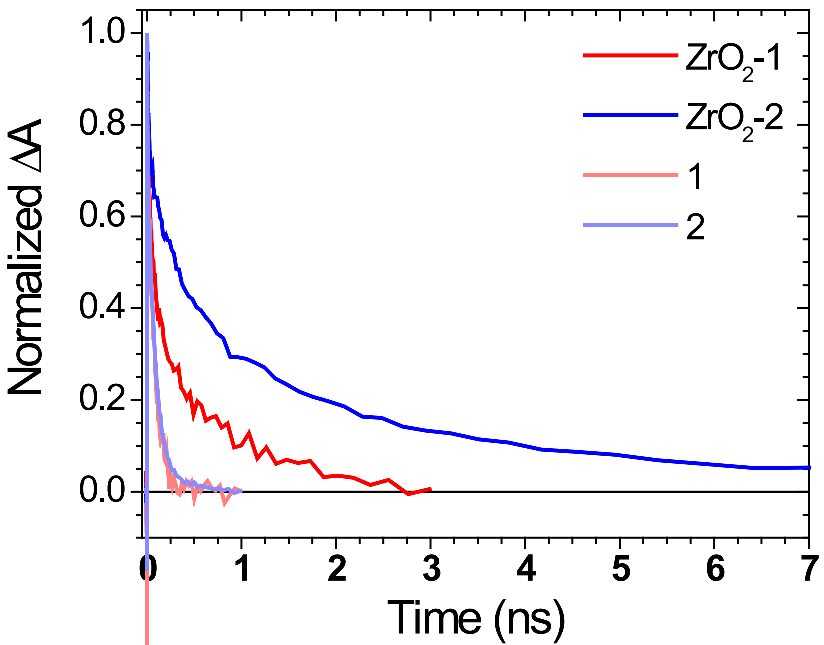
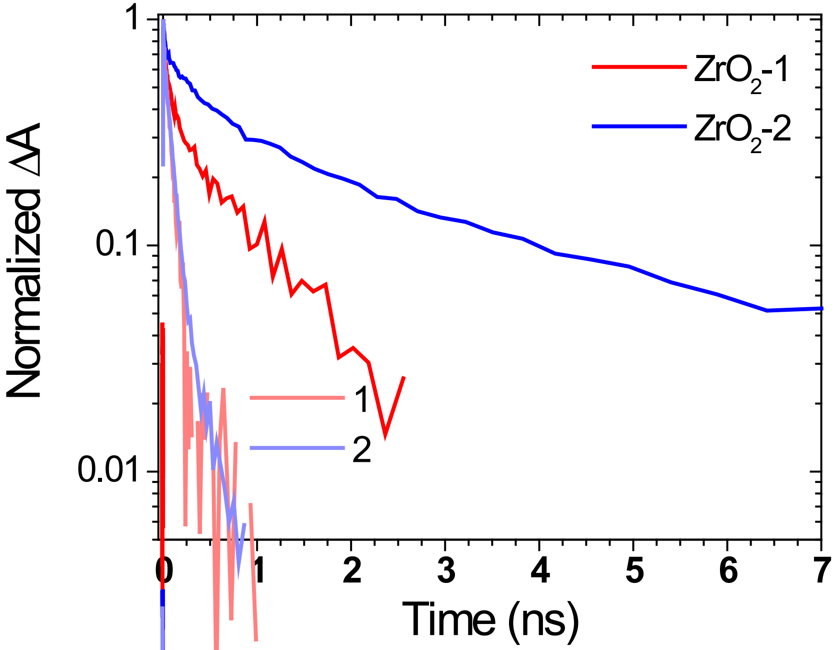
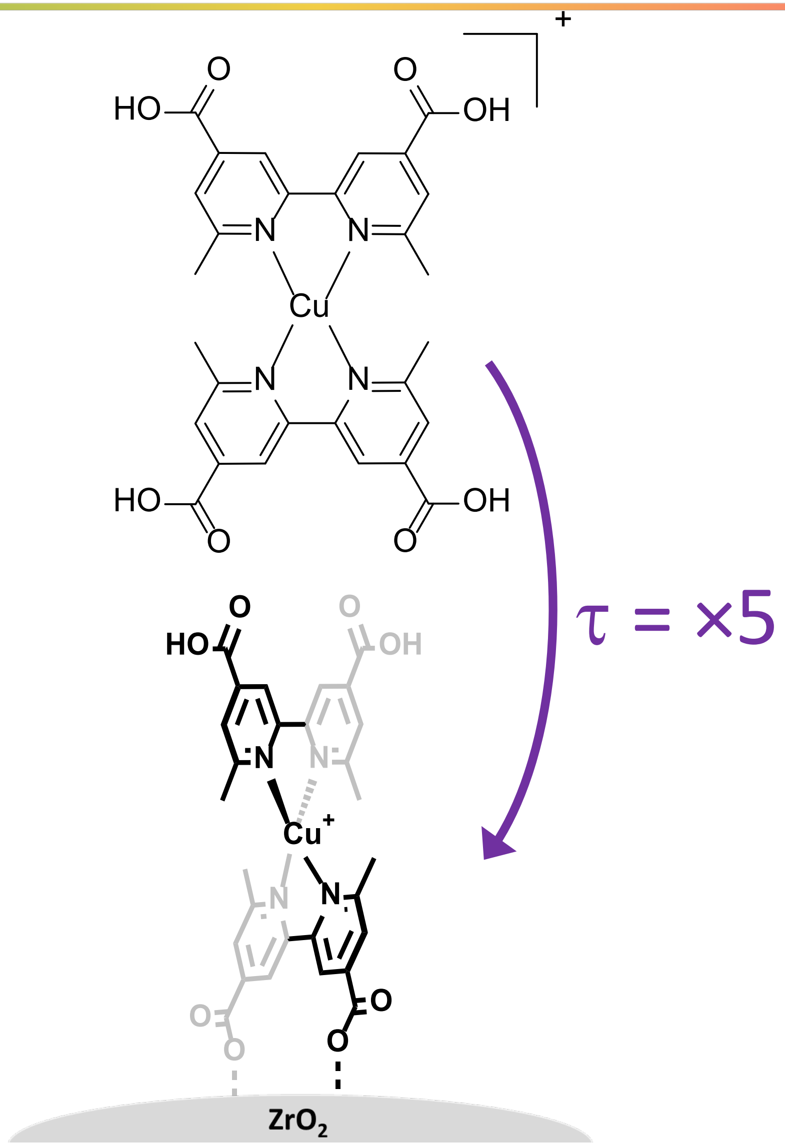




Strategic Surface Binding



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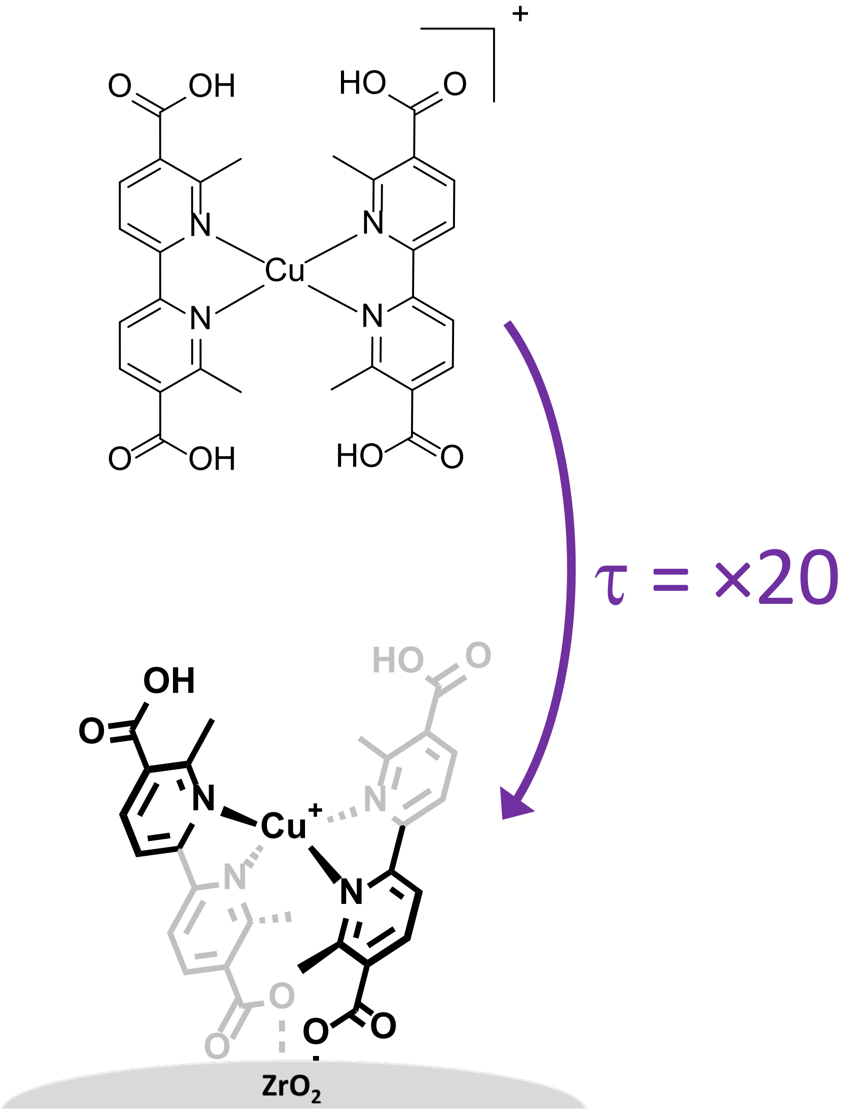
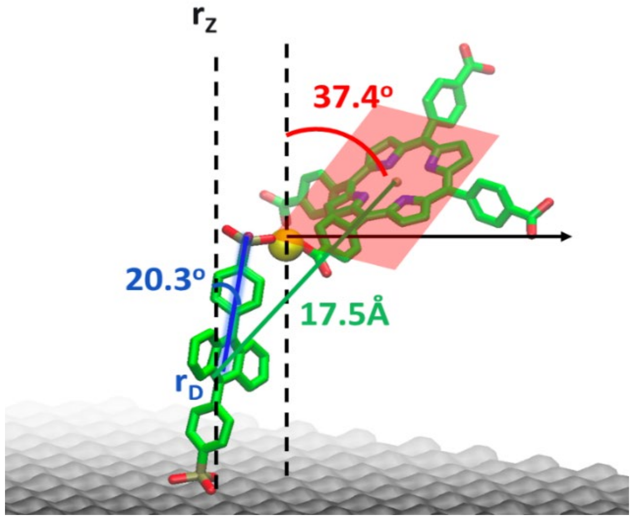
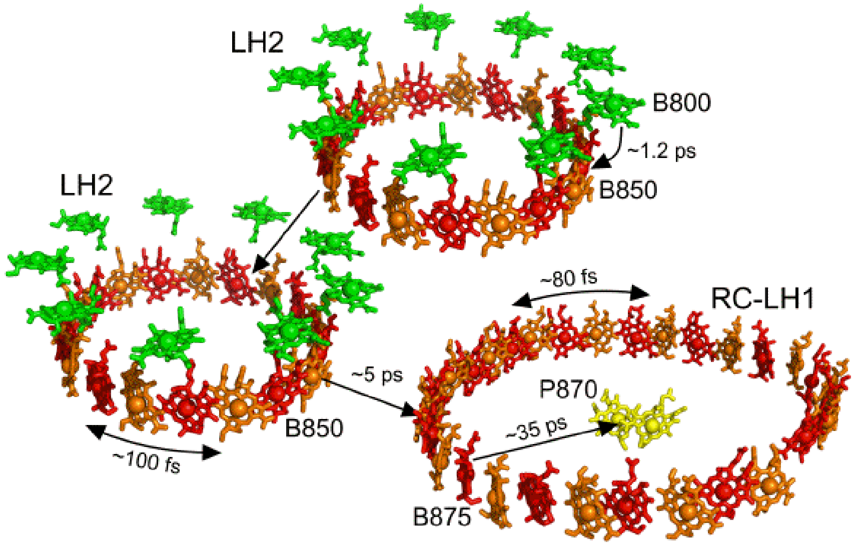


3

Conclusions

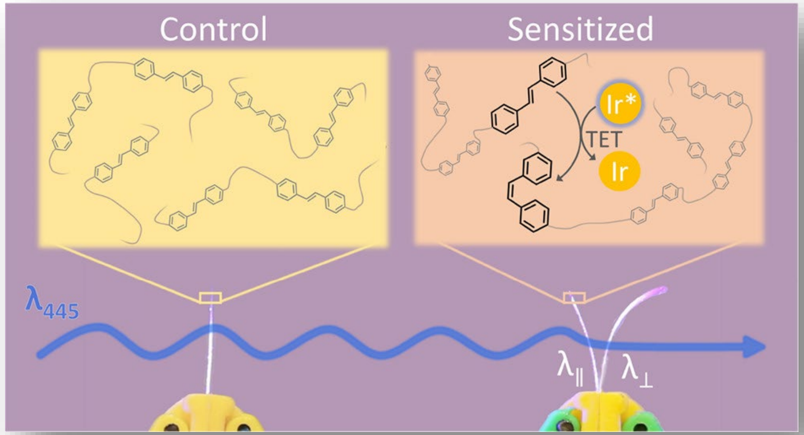
- TTA-UC Emission
  - On ZrO_2: Blue to green upconversion
  - Quadratic to Linear Behavior
- TTA-UC Solar Cell
  - Improvements with component selection
  - J_{UC} up to 315 μA/cm^2
  - Structure matters
- Determine Structure (polarized ATR)
  - 1st layer orientation is MO_x independent
  - 2nd layer dependent on metal and binding group
  - Reasonable agreement between ATR and Theory (MM)
- Efforts to Control Structure are Underway





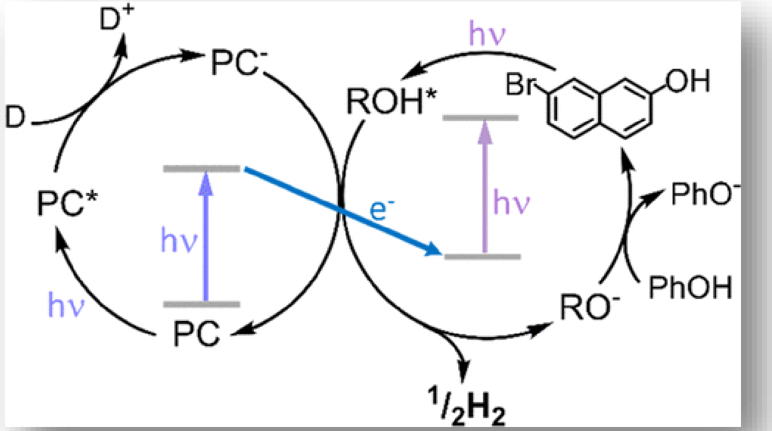
Other Research Efforts

Photomechanical Polymers



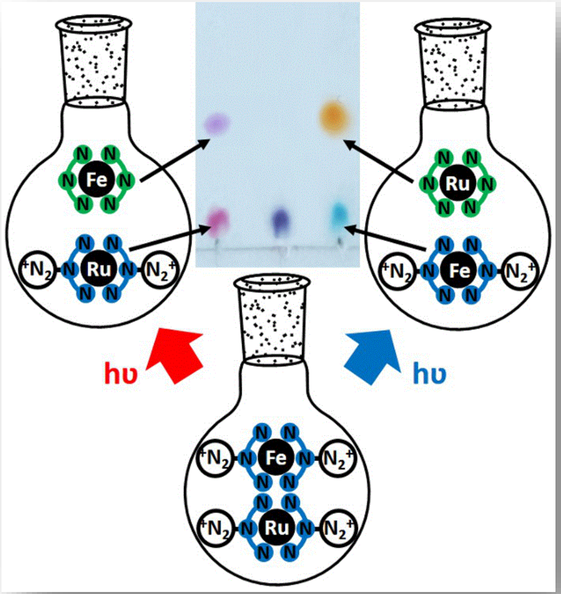
ACS Appl. Polym. Mater. **2022**, 4,4081

Z-Scheme H_2 Generation



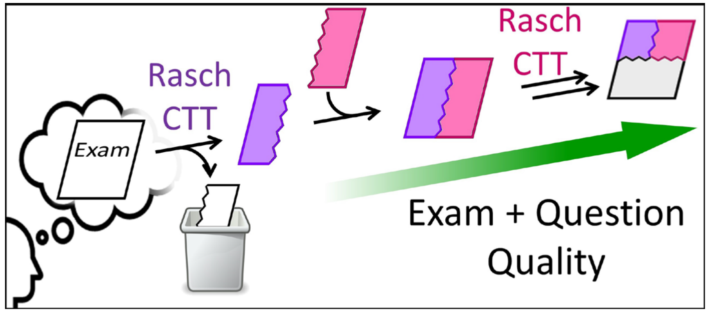
J. Am. Chem. Soc. **2022**, 144, 21568

Photochemical Separations

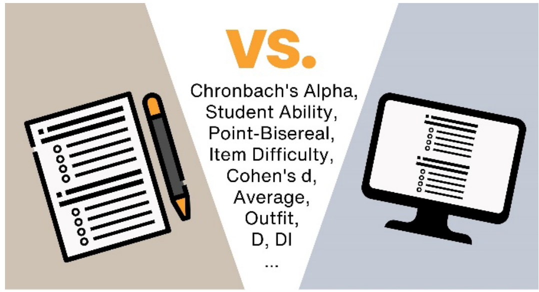


Chem. Commun. **2018**, 54, 7507

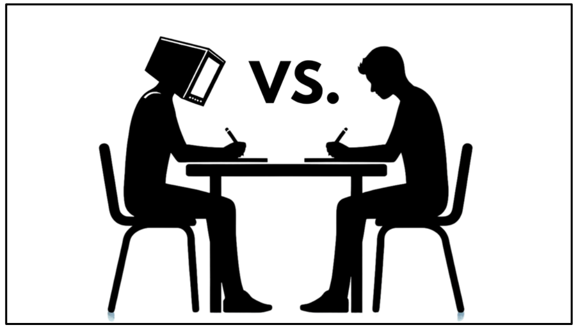
Chem. Ed. Research



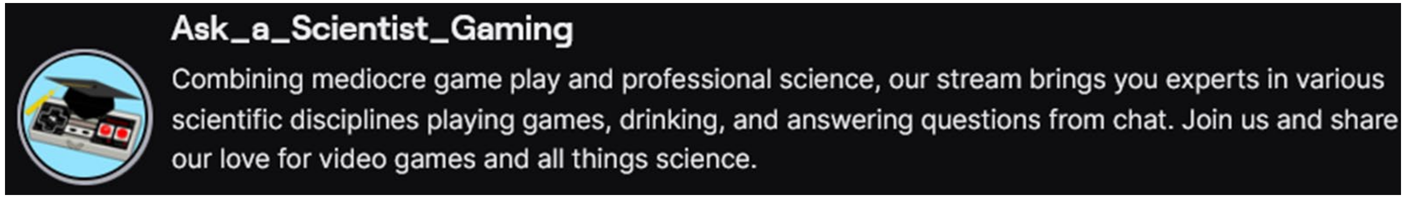
J. Chem. Educ. **2021**, 98, 5, 1529.



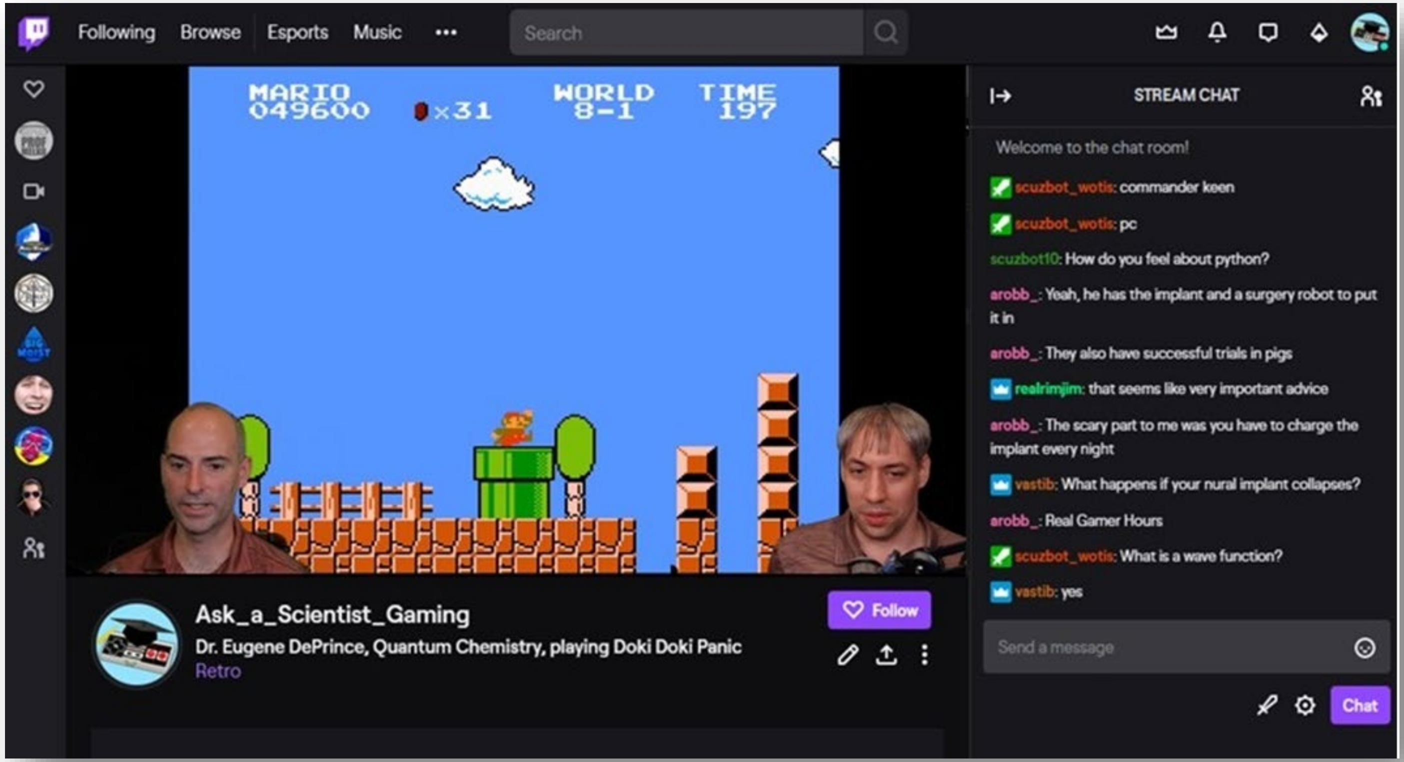
J. Chem. Educ. **2023**, 9, 3454.



J. Chem. Educ. **2024**, ASAP.

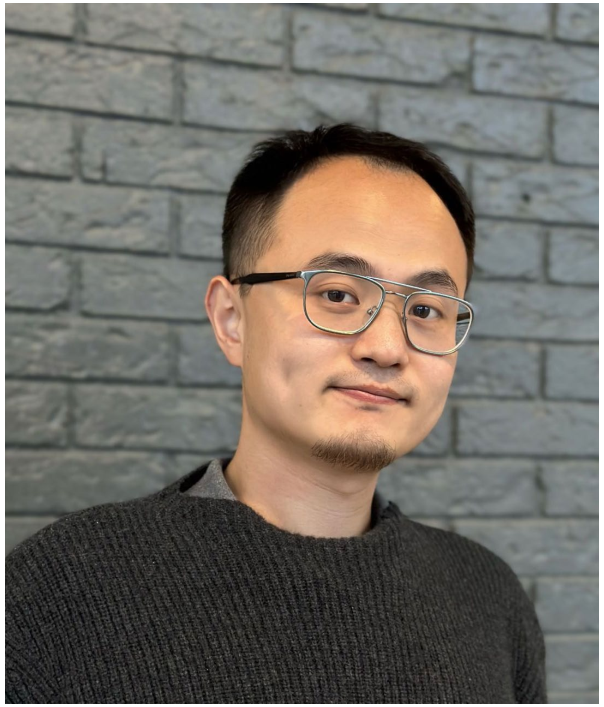


Every other Wed. 8-11 pm ET



Ask_a_Scientist_Gaming on Twitch.tv

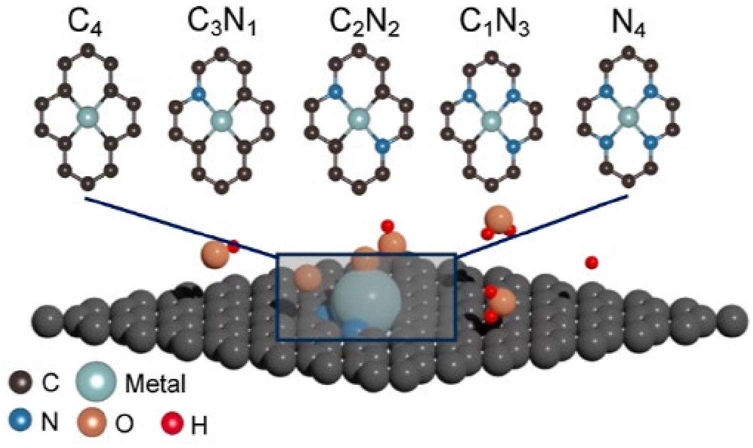
Wed. July 3rd, 8-11 pm ET

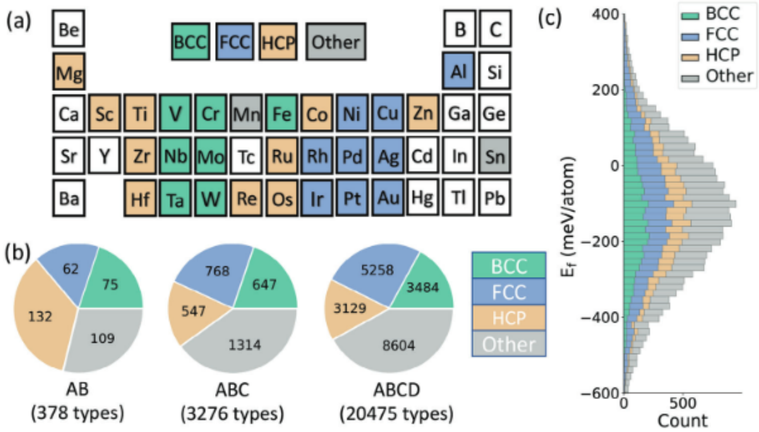


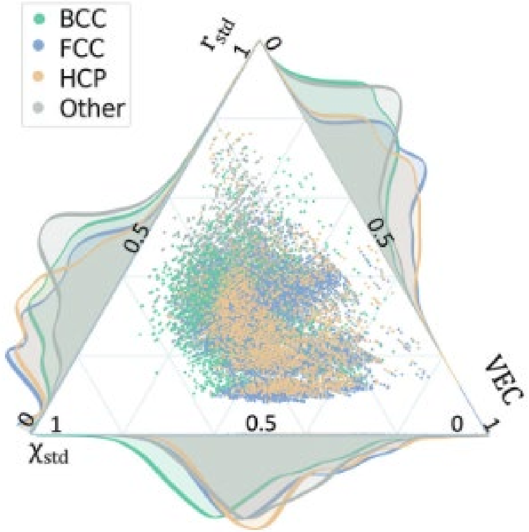
Games: Double Dragon
Contra
Super Mario Bros.
NARC

Guest:
Prof. Bin Ouyang
(Chemistry & Biochemistry)

Expertise:
Computational chemistry
Machine learning
Energy storage materials







Hanson Research Group

Acknowledgements

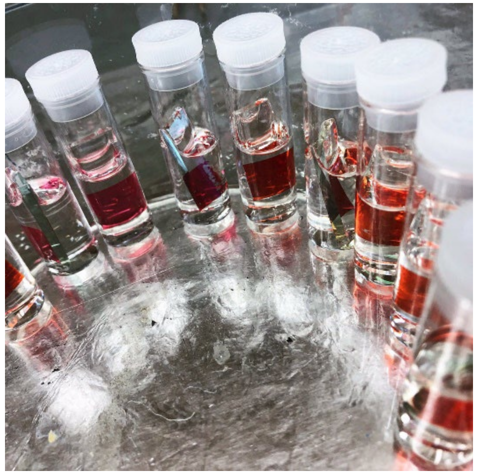
Not Pictured Contributors

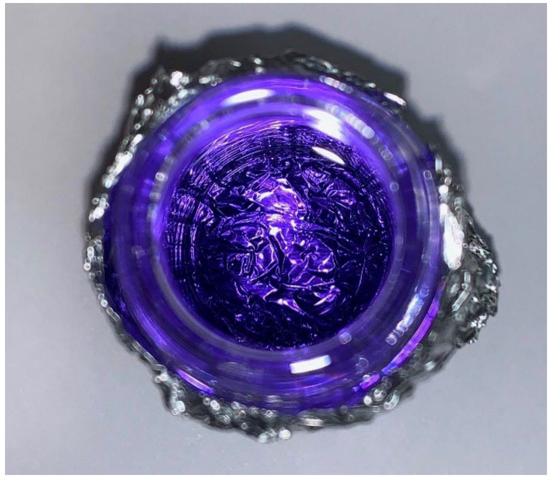
- Dr. Ashley Arcidiacono (Uchicago, Postdoc)
- Dr. Suli Ayad (TCC, Prof.)
- Cory Ruchlin (McGill, Grad)
- Sarah Lindbom
- Luke Jodoin

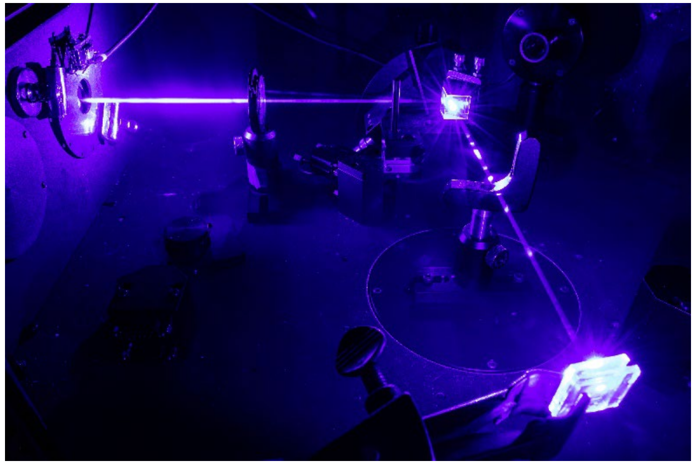
Collaborators

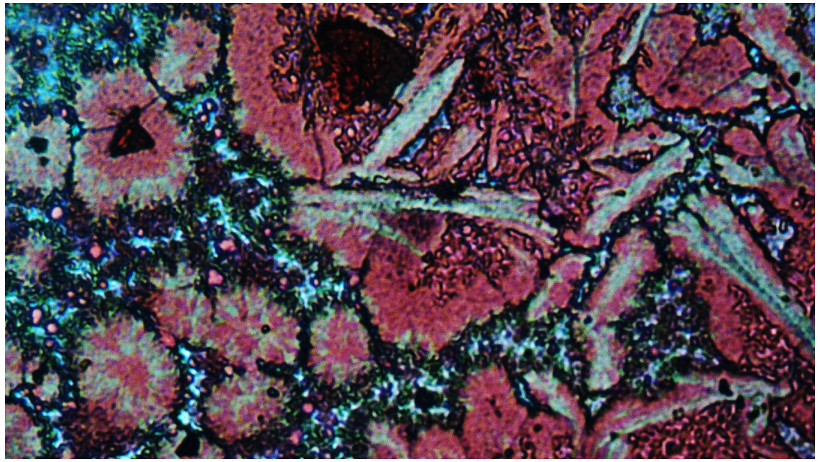
- Dr. Raaj Winfred (FSU)
- Dr. Igor Alabugin (FSU)
- Nikolas R. Dos Santos (FSU)
- Dr. Scott Saavedra (UA)
- Dr. Brooke Massani (UA)
- Dr. Bünyemin Çoşut (Gebze Tech)

Questions?









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