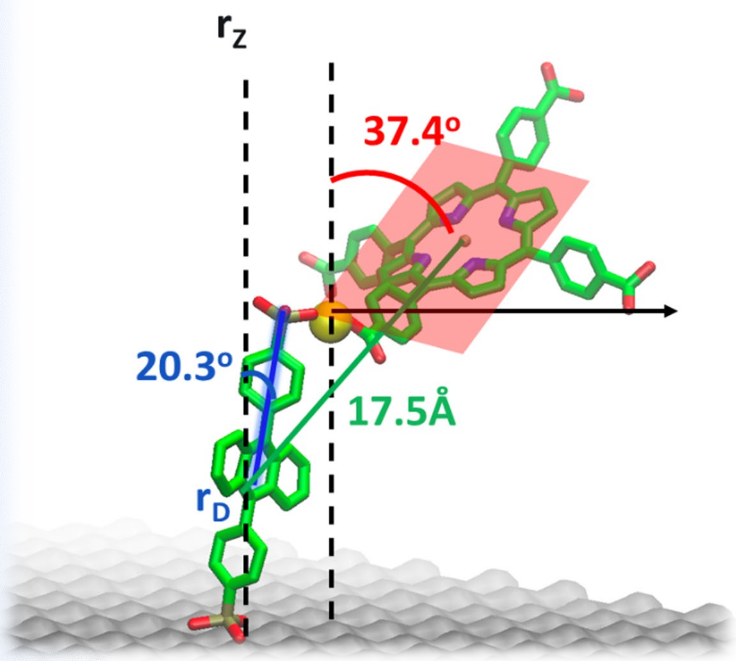
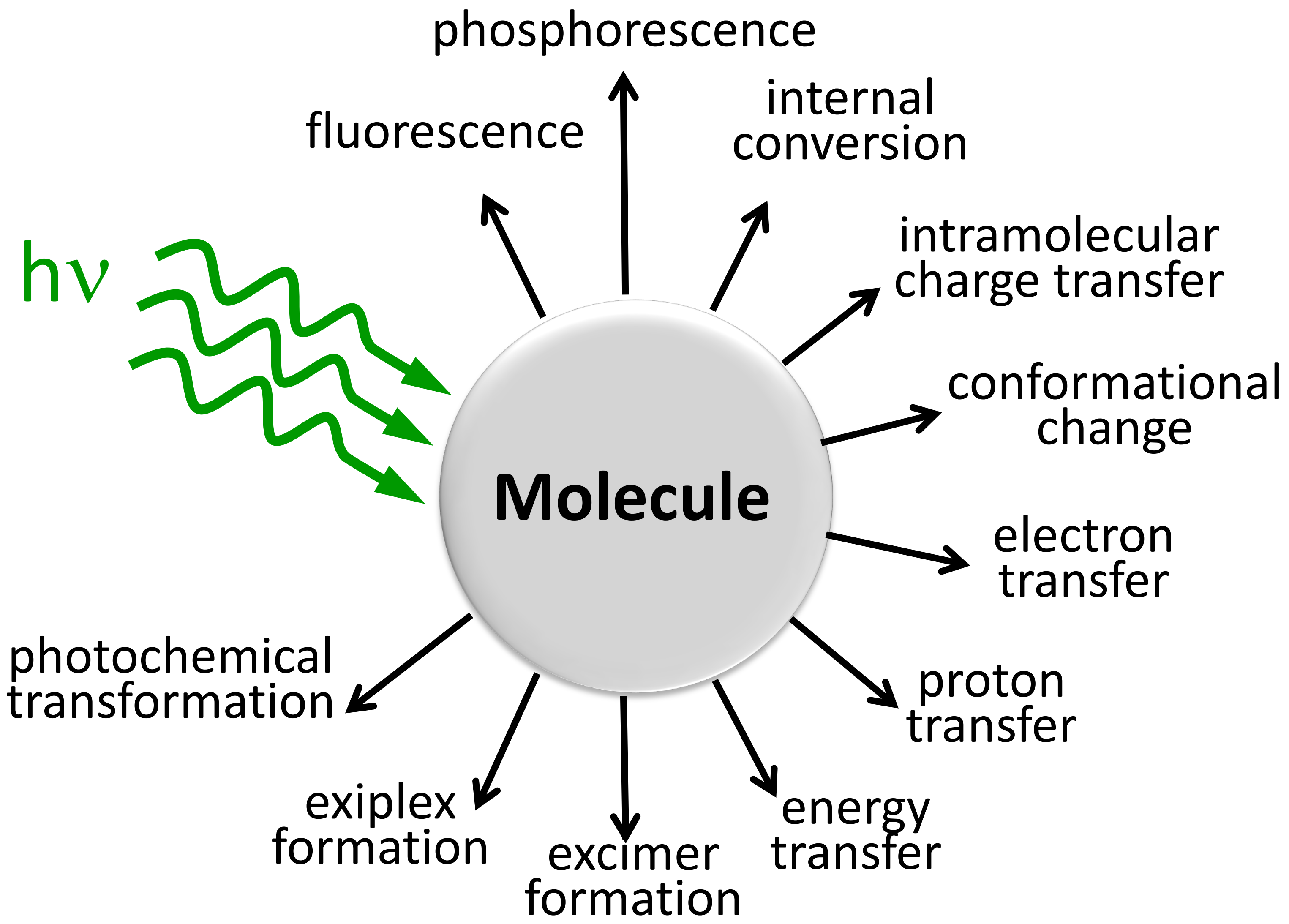
Understanding and Controlling Molecular Excited State Processes Using Metal Oxide Interfaces



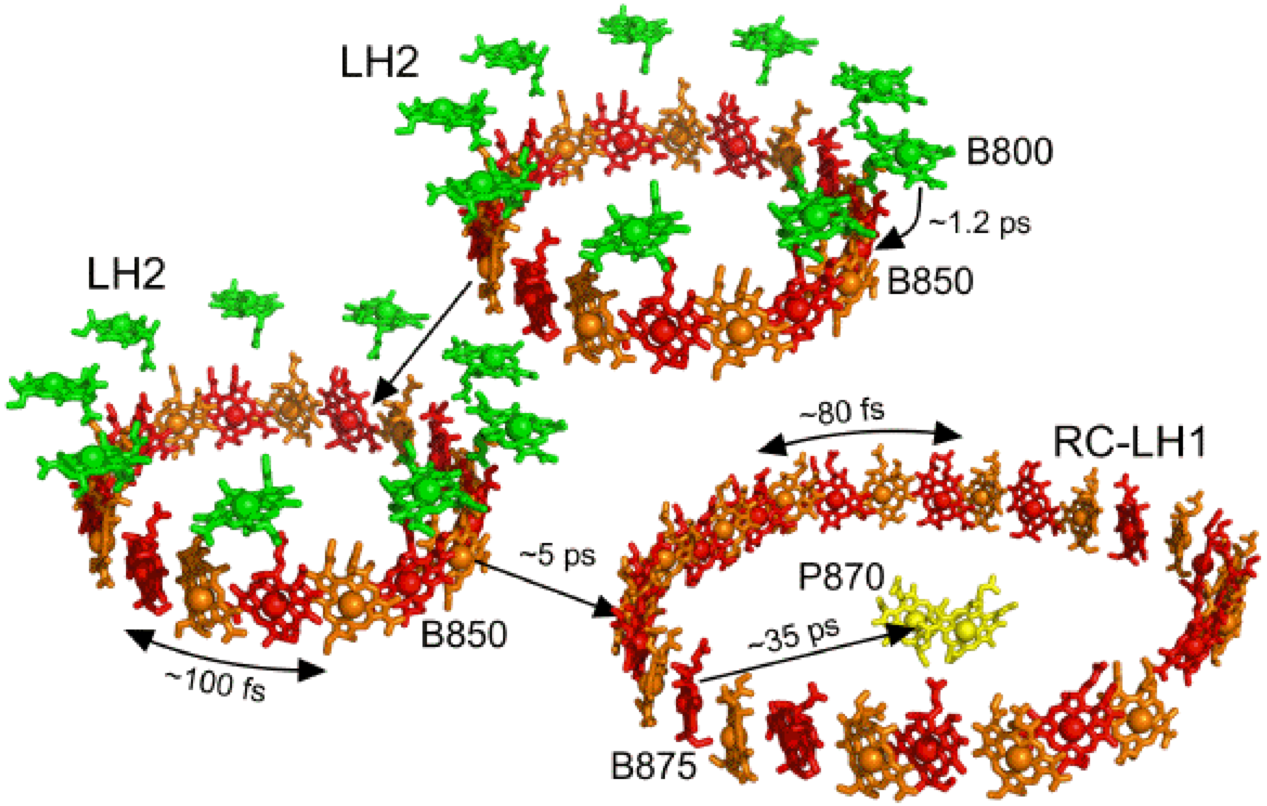
Kenneth Hanson
Department of Chemistry & Biochemistry
Florida State University, Tallahassee, FL, USA

Molecular Photochemistry/Photophysics

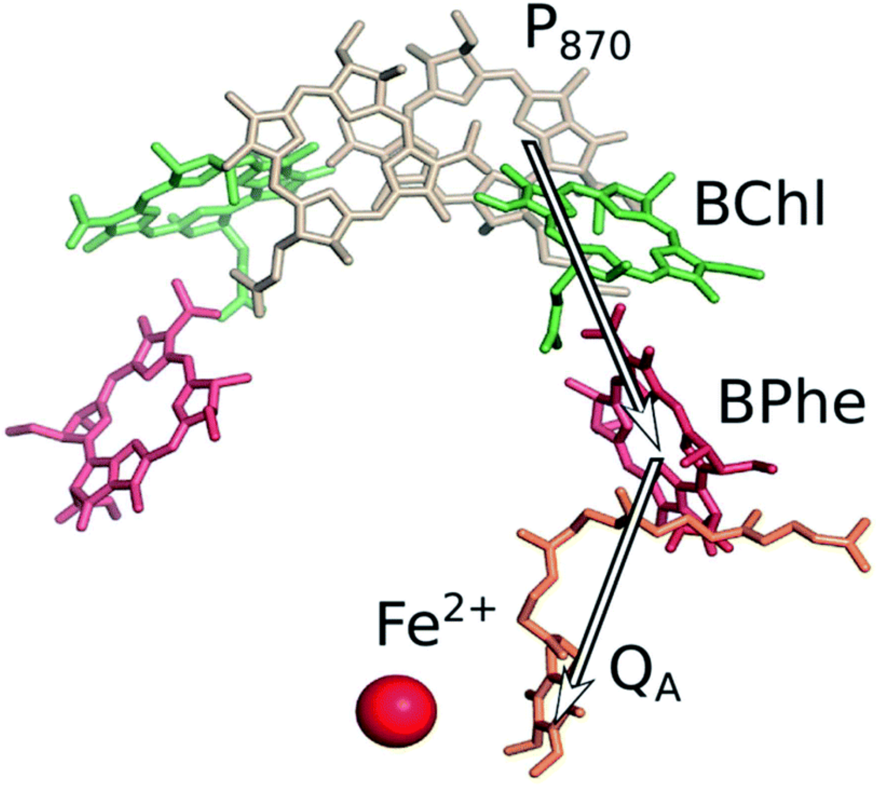


Molecular Photochemistry/Photophysics

Energy Transfer



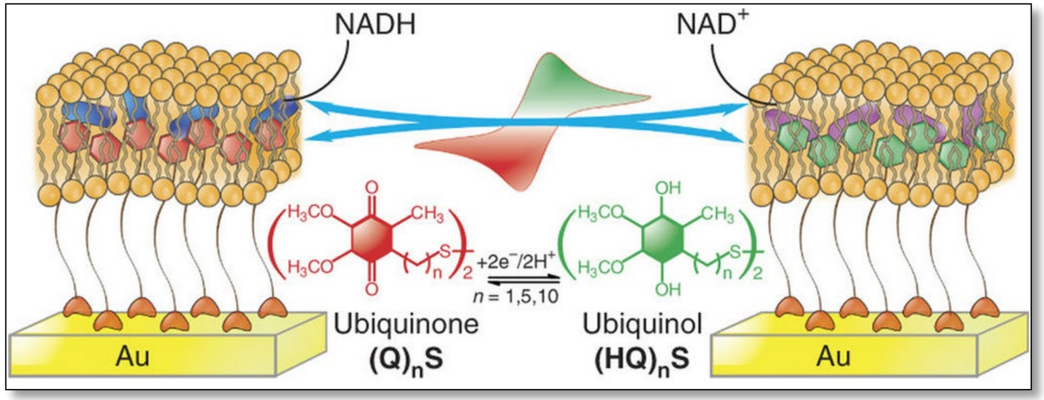
Electron Transfer



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

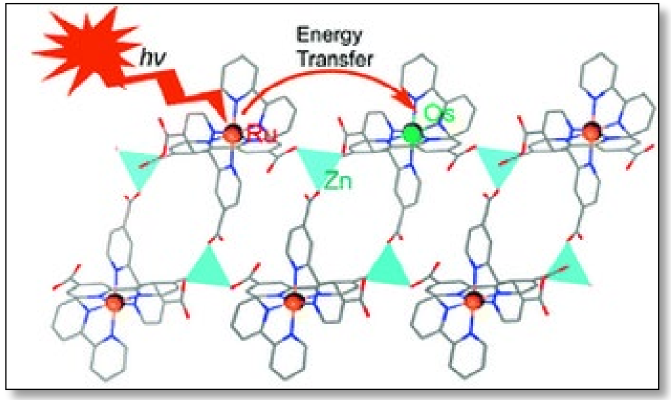
Structural Control: Humans

Phospholipid Bilayers



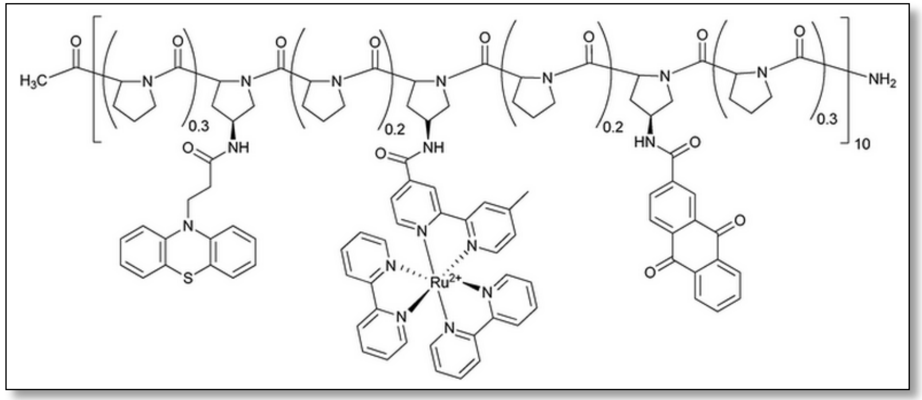
Ma et. al. *Nature Protocols*, **2013**, *8*, 439

Metal Organic Frameworks



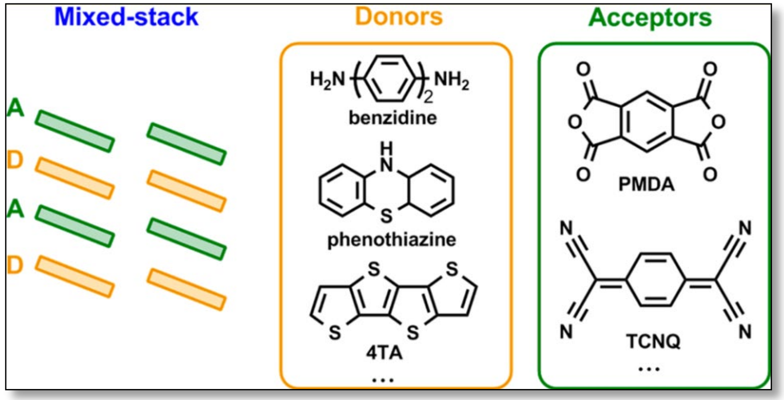
Kent et. al. *J. Am. Chem. Soc.*, **2010**, *132*, 12767

Polypeptides



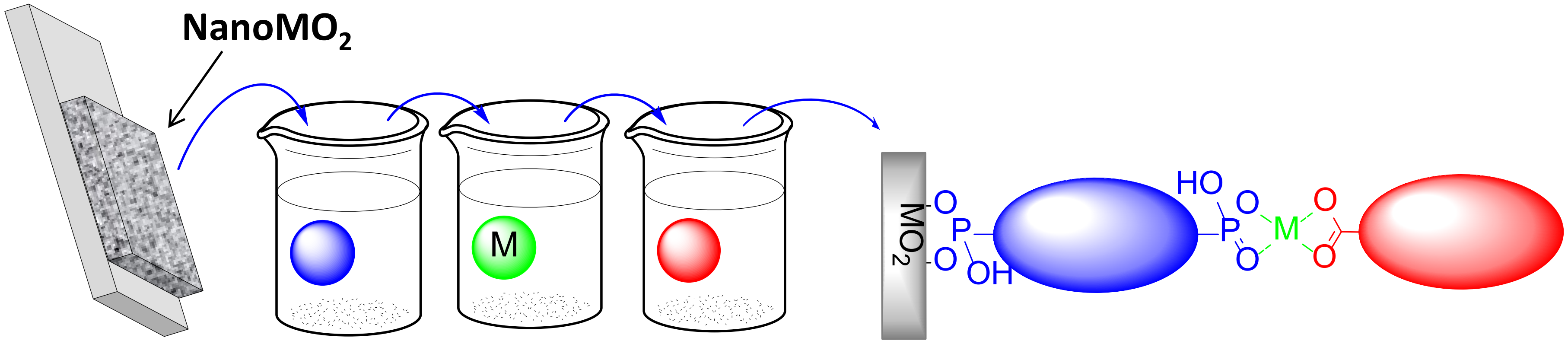
Slate et. al. *J. Am. Chem. Soc.*, **1998**, *120*, 4885

Crystals

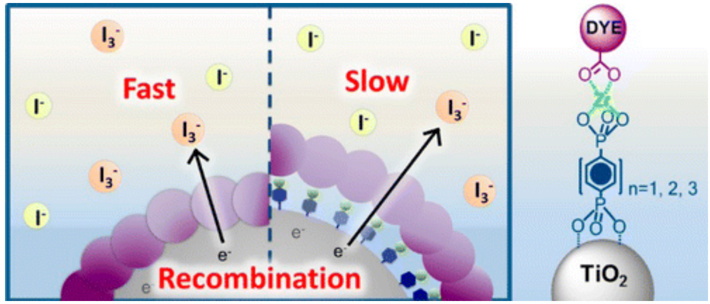


Zhu et. al. *J. Phys. Chem. C*, **2014**, *118*, 14150

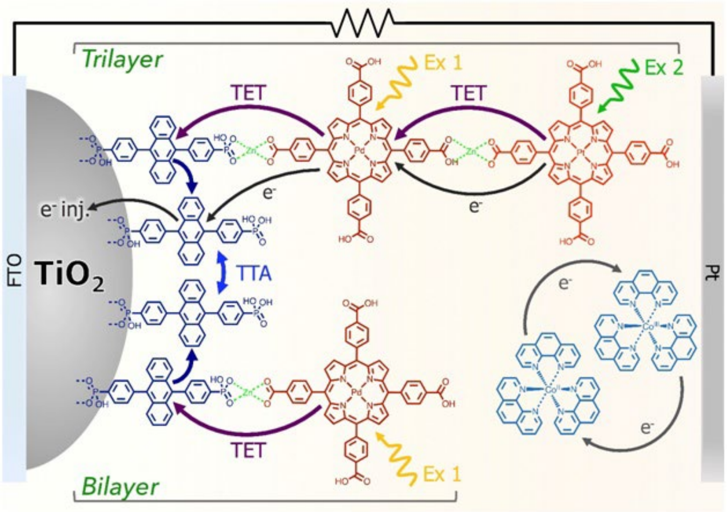
Metal Ion-Linked Multilayer



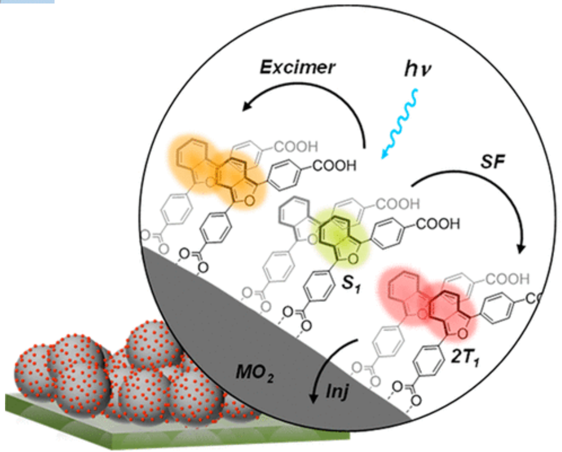
Control e$^-$ Transfer



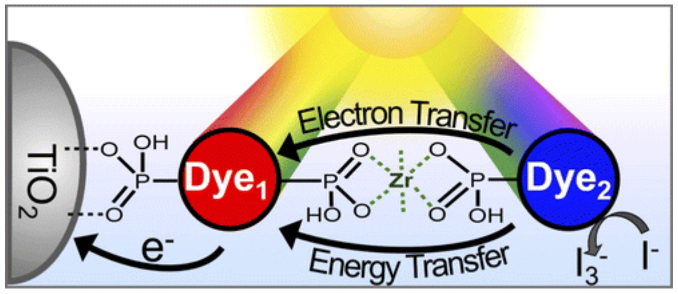
Photon Upconversion



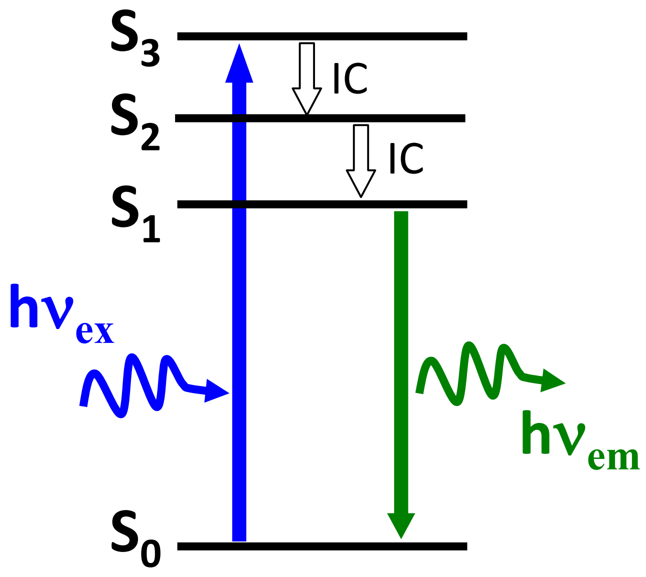
Singlet Fission

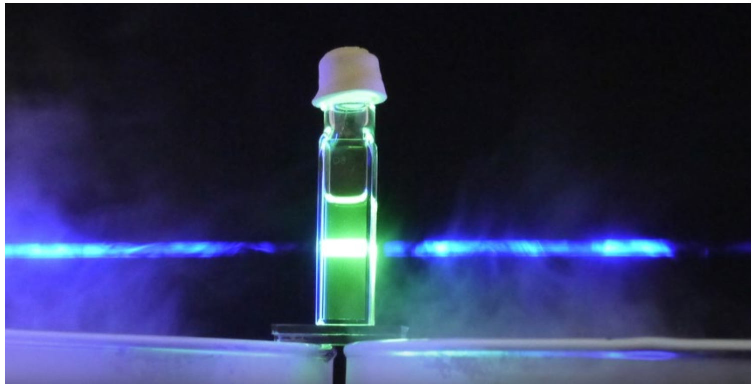


Energy/e$^-$ Cascade

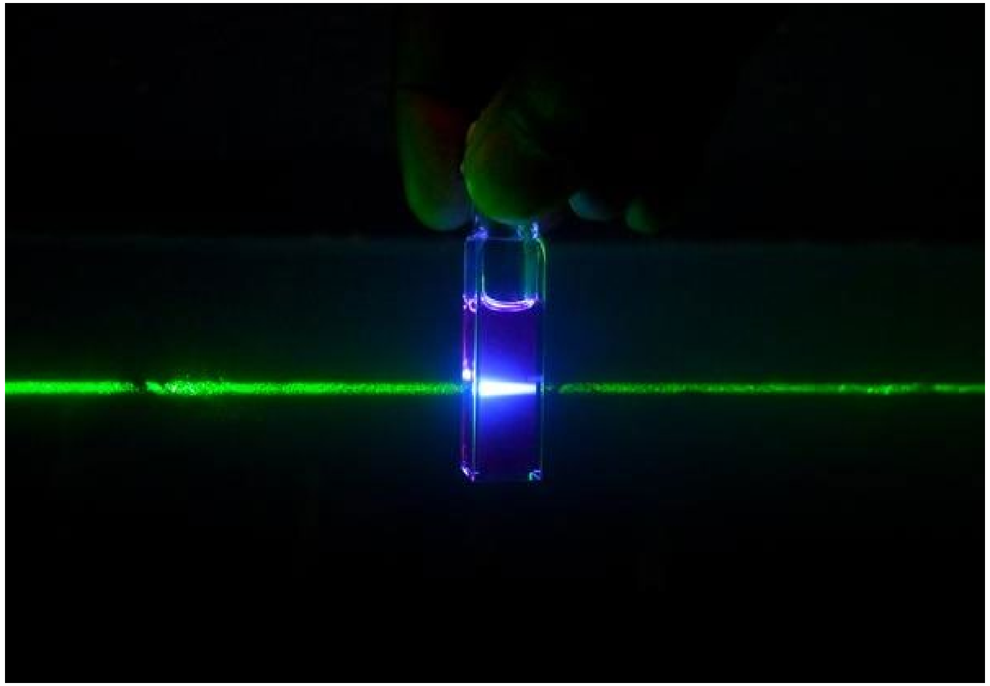


Down Conversion vs. Upconversion



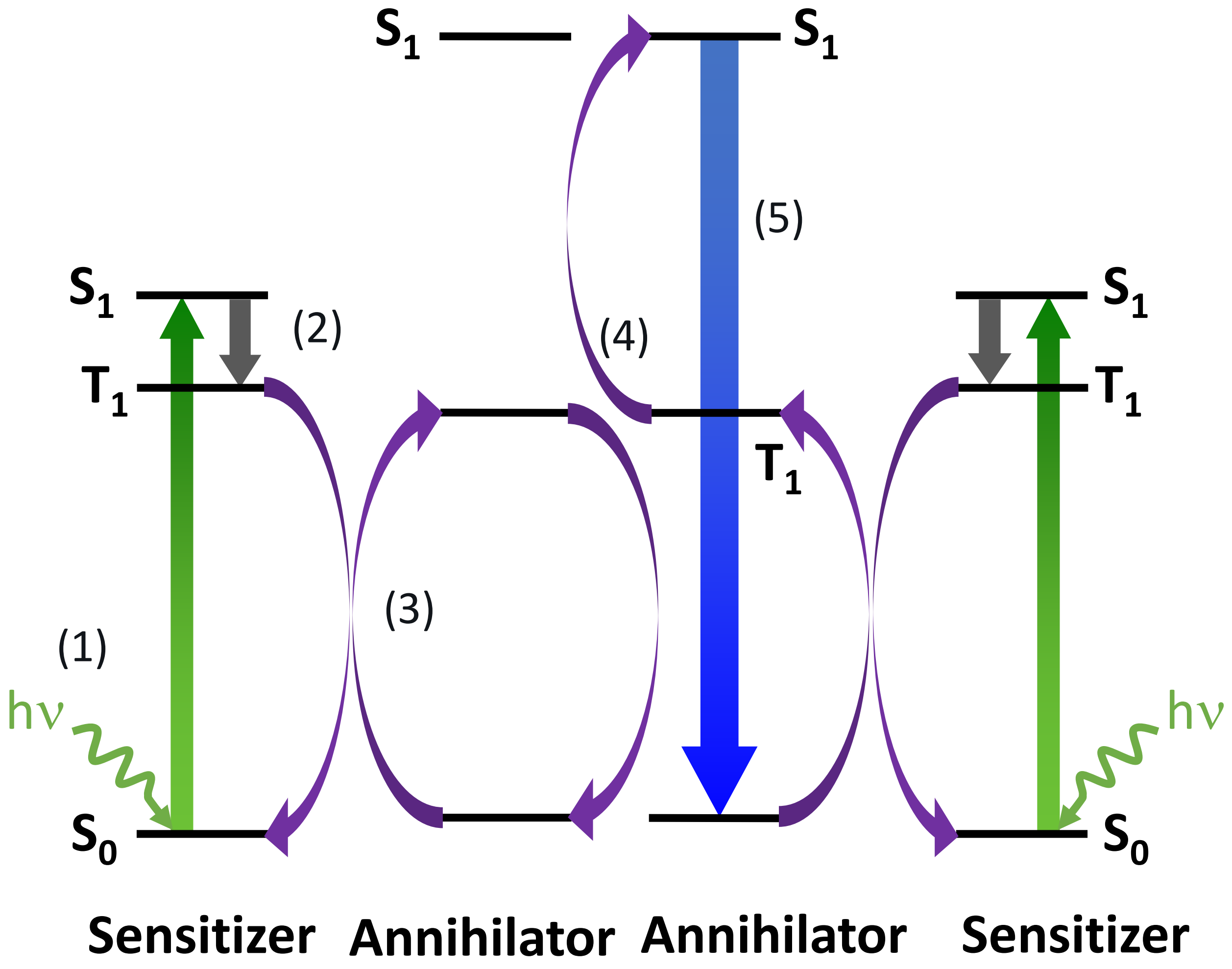


hν → hν



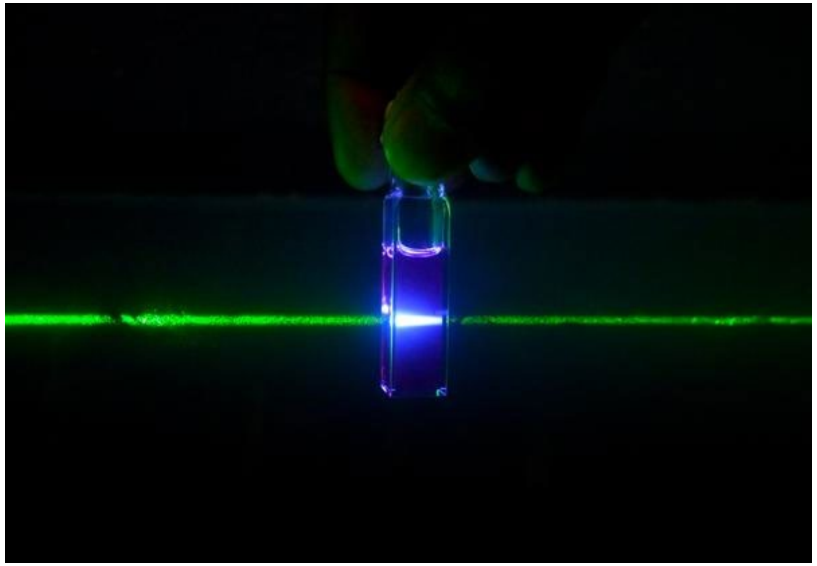
hν → hν

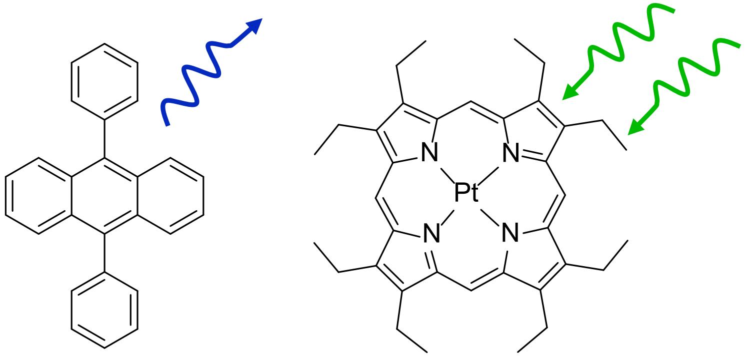
Photon Upconversion

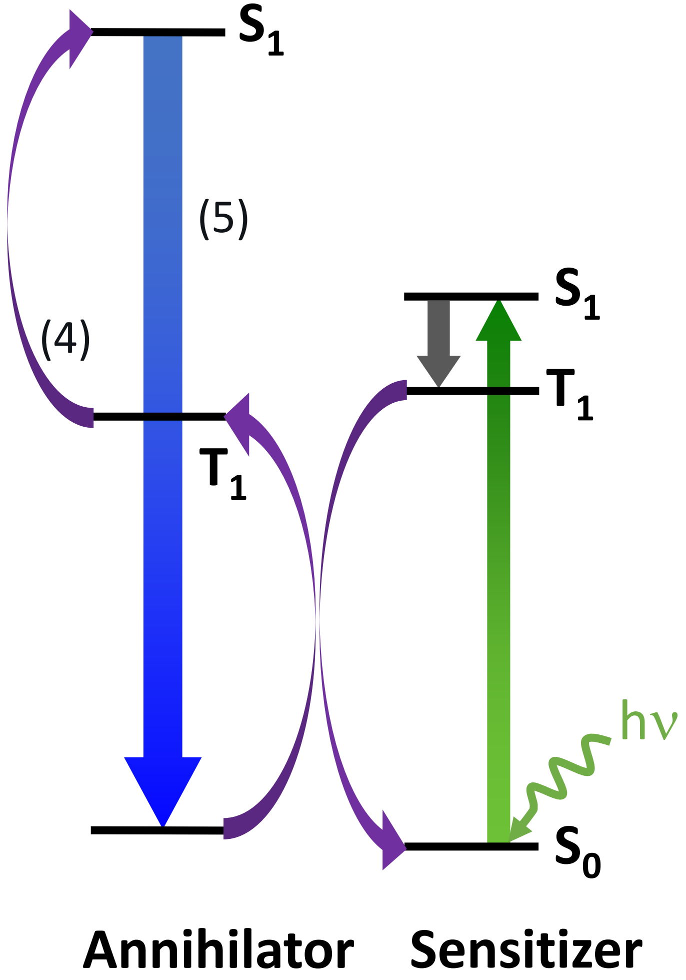


$2\ h\nu \rightarrow h\nu$

Photon Upconversion

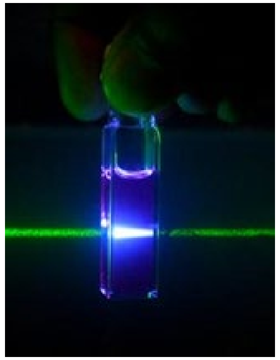






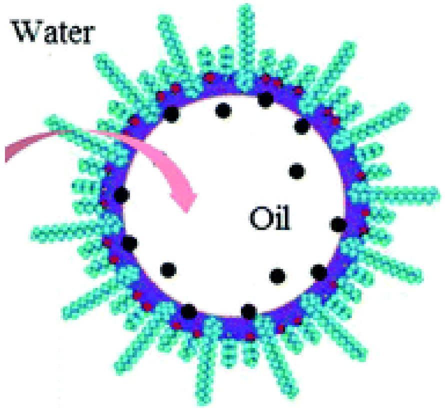
$2\ h\nu \rightarrow h\nu$

Sensitizer-Annihilator Interactions



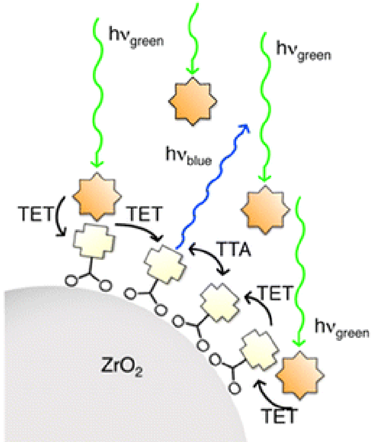
Solution

Chem. Commun., 2004, 2860



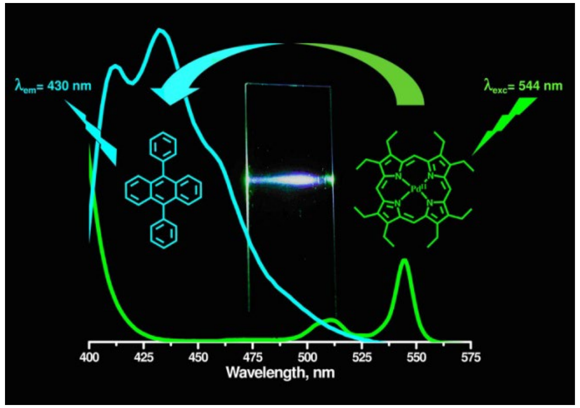
Microemulsion

Photochem. Photobiol. Sci. 2014, 13, 48



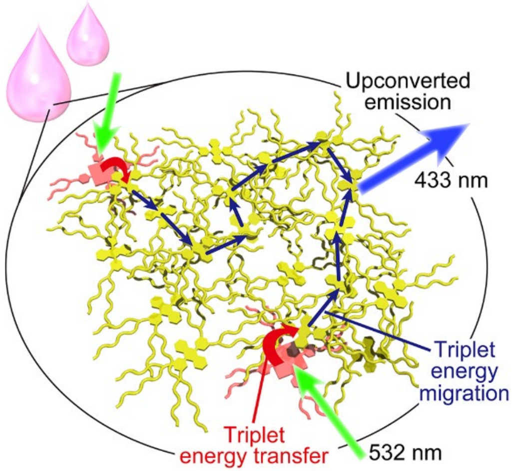
Heterogeneous

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



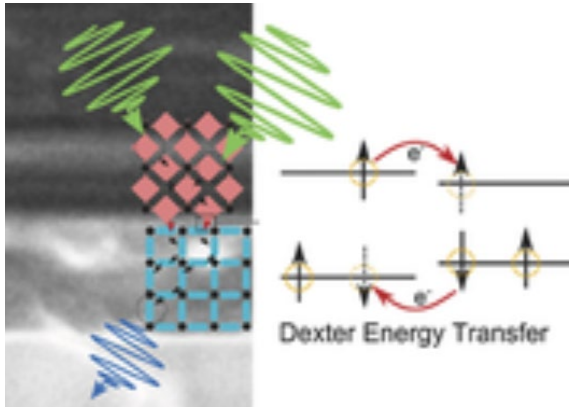
Polymer Films

JACS 2007, 129, 12652



Neat-solvent

JACS 2013, 135, 19056

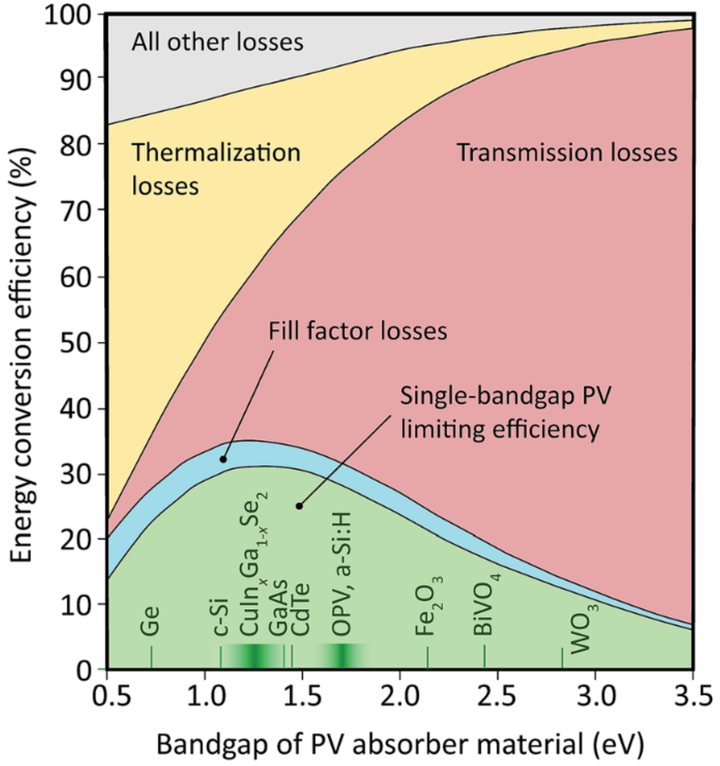


MOF

JACS 2016, 138, 6541

Solar Cell Efficiency

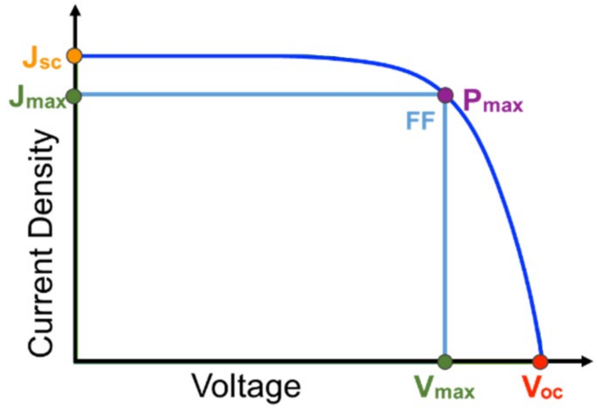
Schulze and Schmidt *Energy Environ. Sci*. **2015**, 8, 103-125



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

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

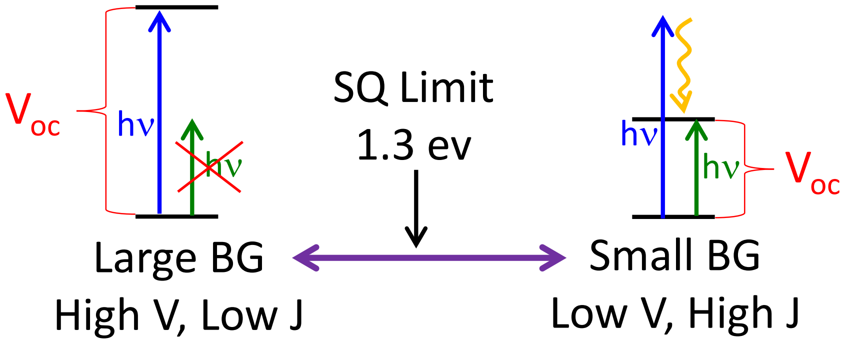
P_{max} = J x V



<u>Max Theoretical Efficiency</u>

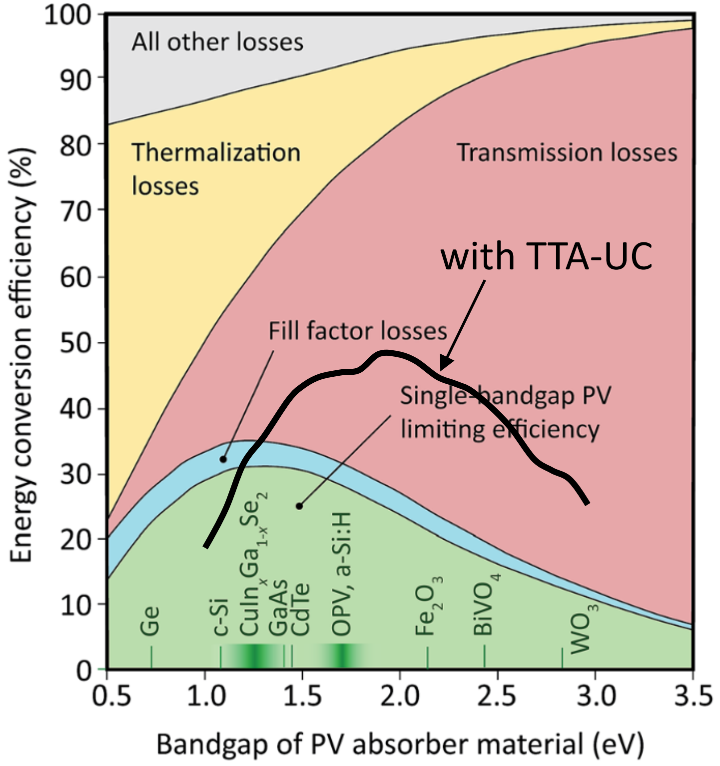
Standard solar cell ~33%

1.3 eV bandgap



Solar Cell Efficiency

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

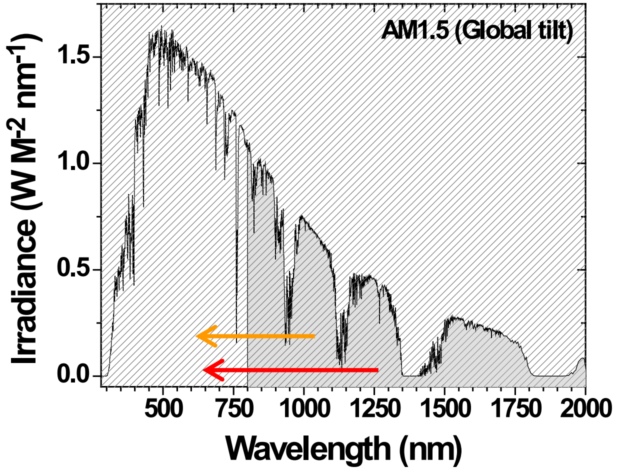


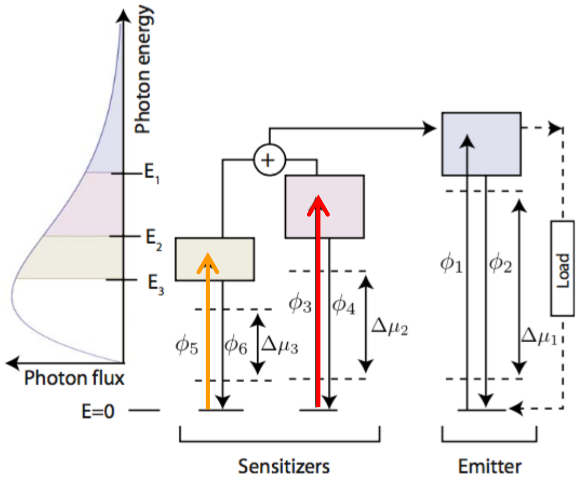
Max Theoretical Efficiency

Standard solar cell ~33%
1.3 eV bandgap

Solar cell with upconversion > 45%
1.76 eV bandgap

Perovskites, OPV, DSSC



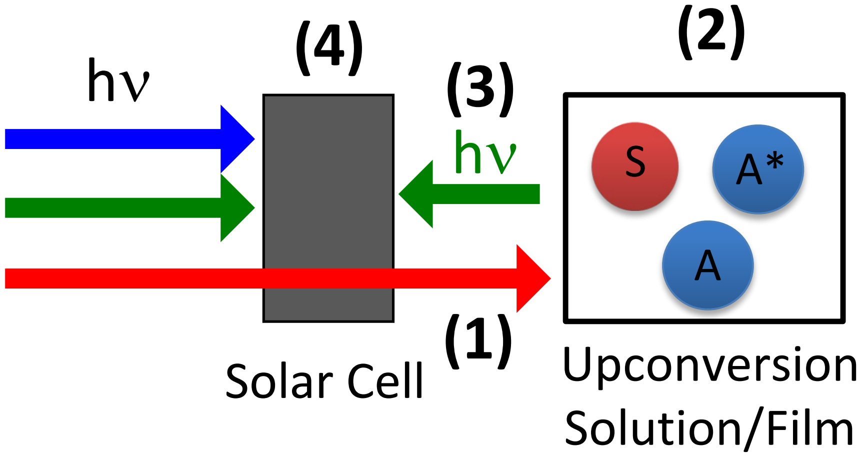


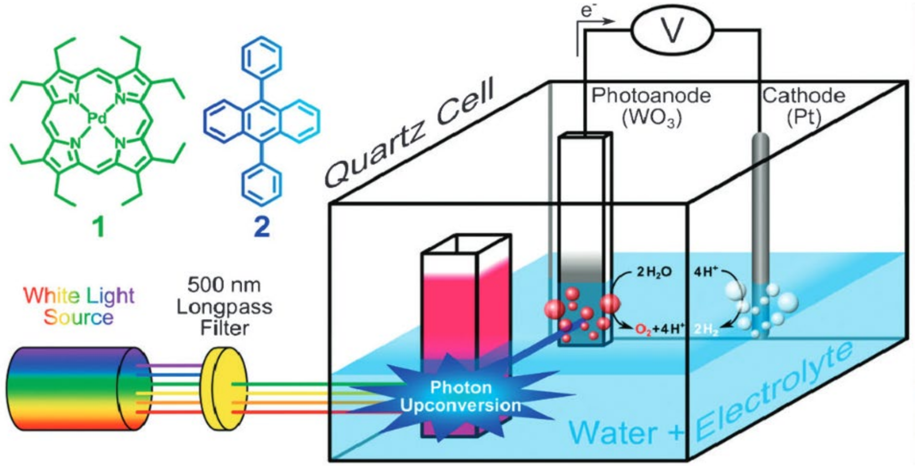
Ekins-Daukes and Schmidt,
Appl. Phys. Lett., **2008** 93, 063507.

Harnessing TTA-UC

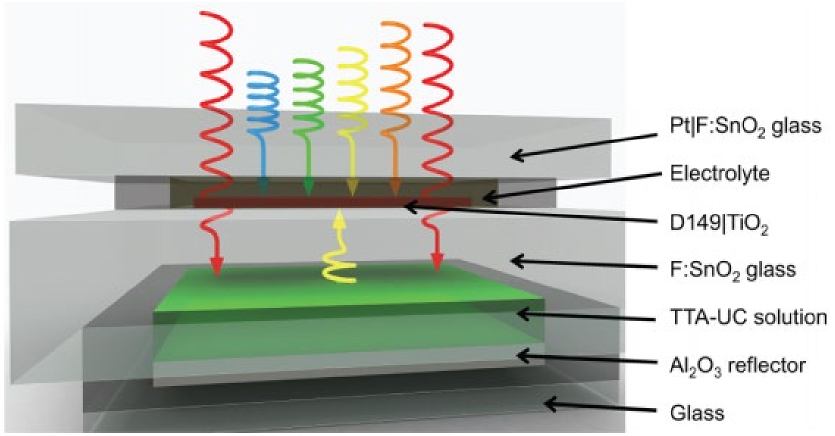
Optical Coupling:

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





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

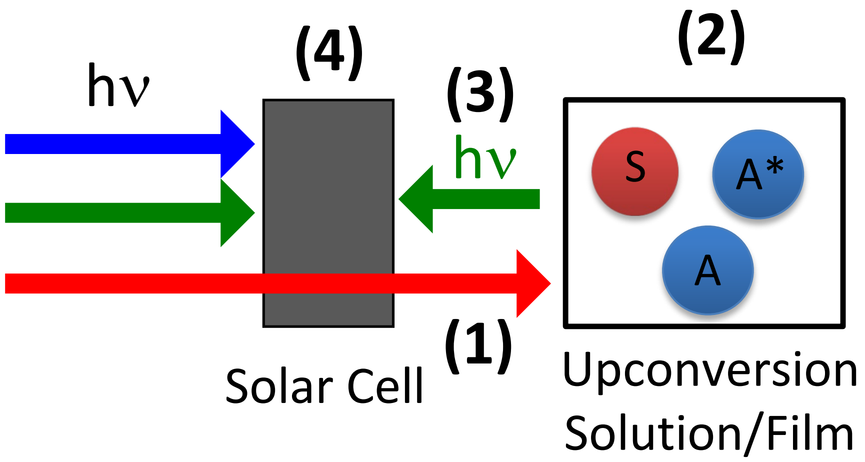


J. Phys. Chem. Lett. **2013**, 4, 2073.

Harnessing TTA-UC

Optical Coupling:

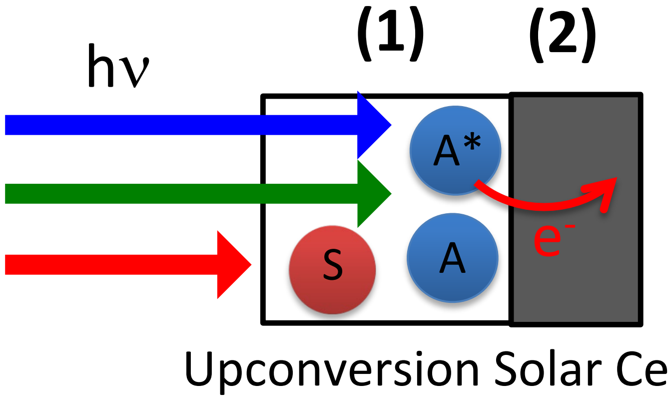
1) Transmission
2) Light absorption and TTA
3) Upconverted emission
4) Absorption by a solar cell



Electronic Coupling:

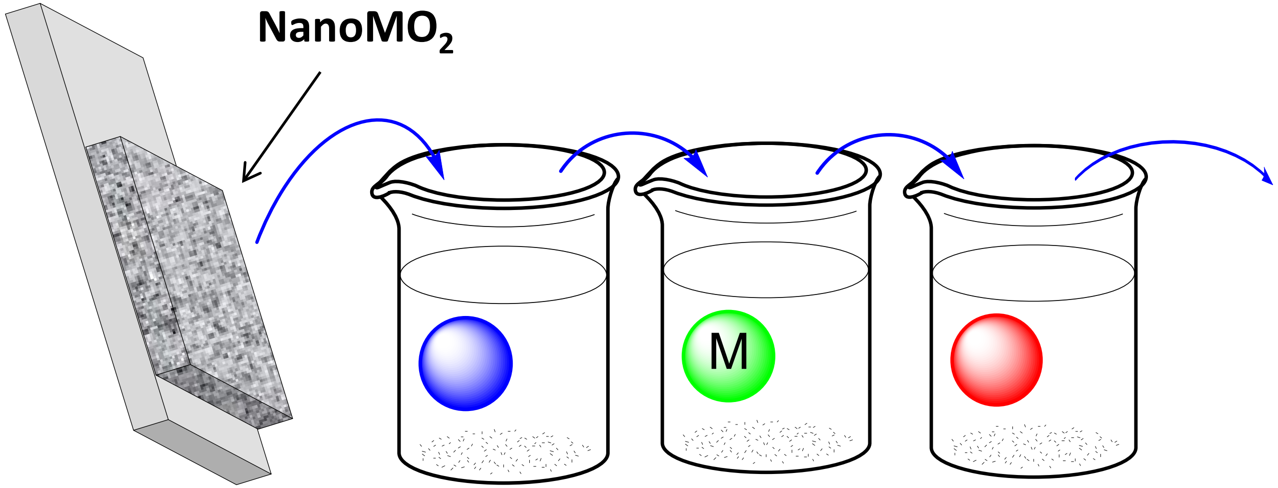
1) Light absorption and TTA
2) Photocurrent Generation

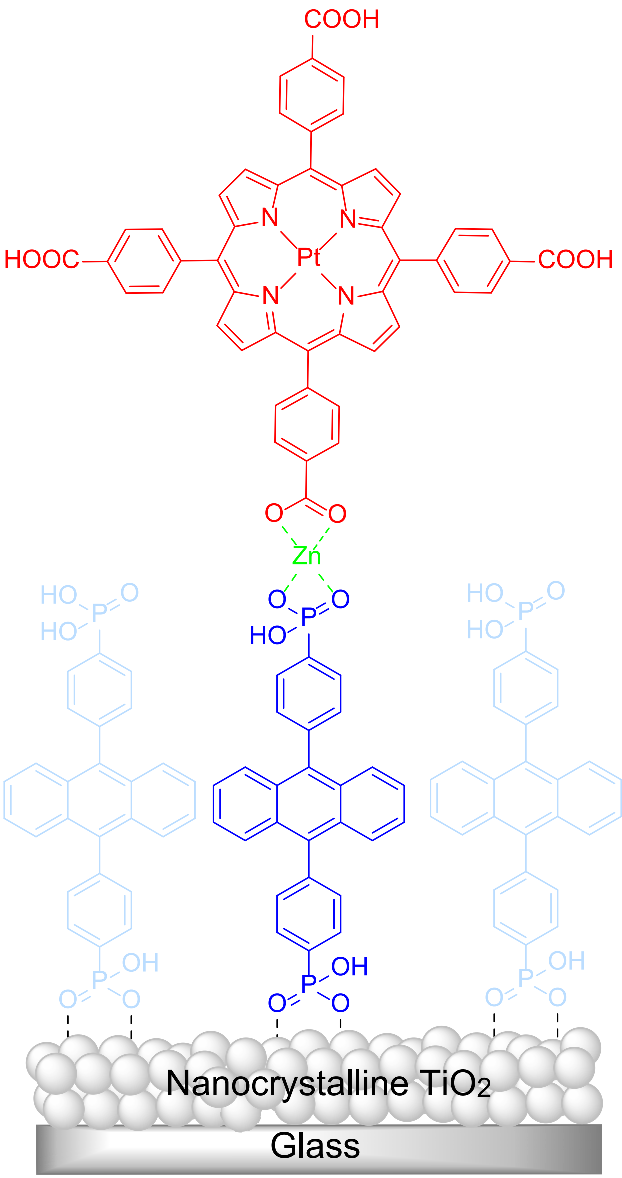
- No isotropic emission
- No self-absorption
- Increase sensitizer concentration



Need A* at a charge separation interface!

Metal Ion-Linked Multilayer

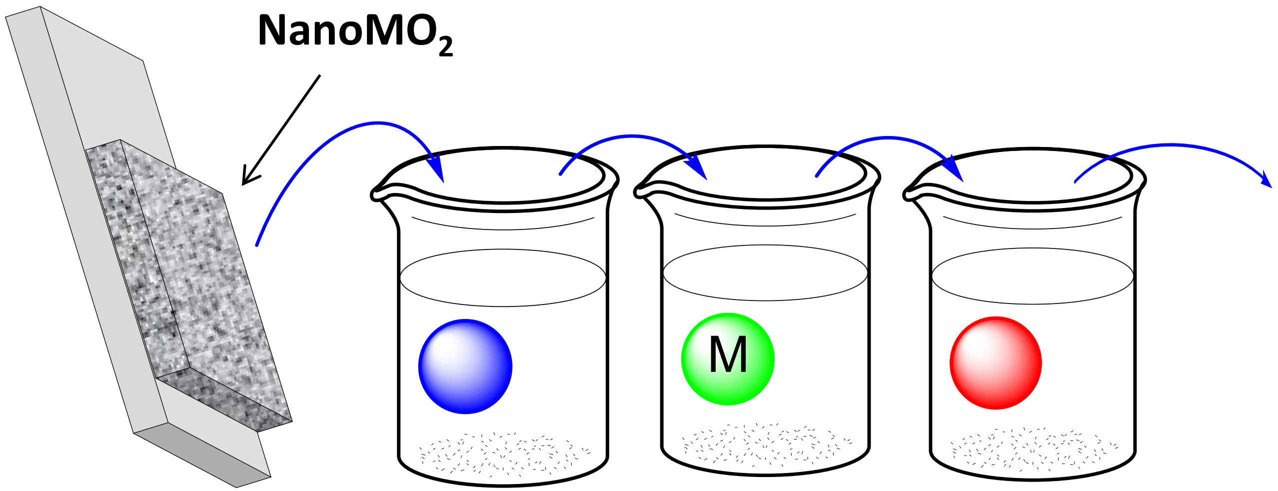


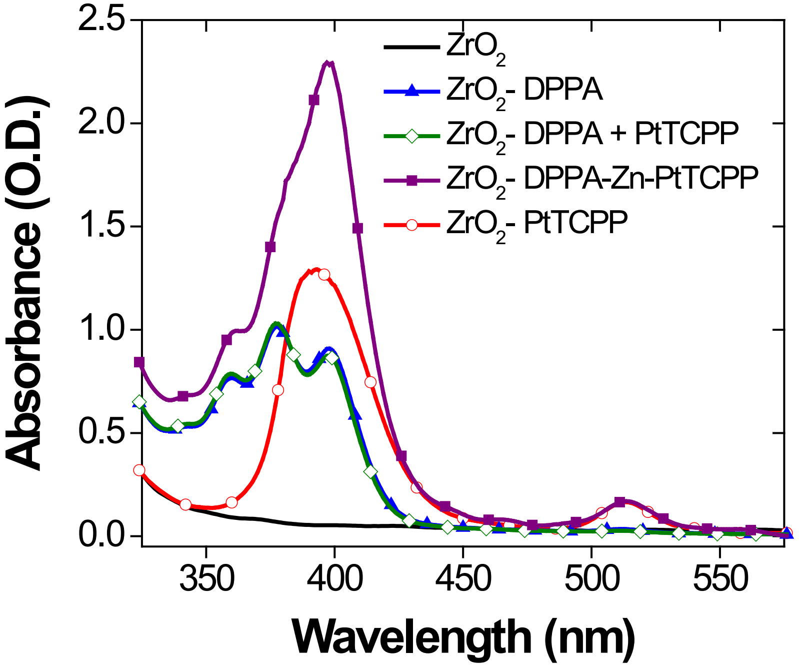


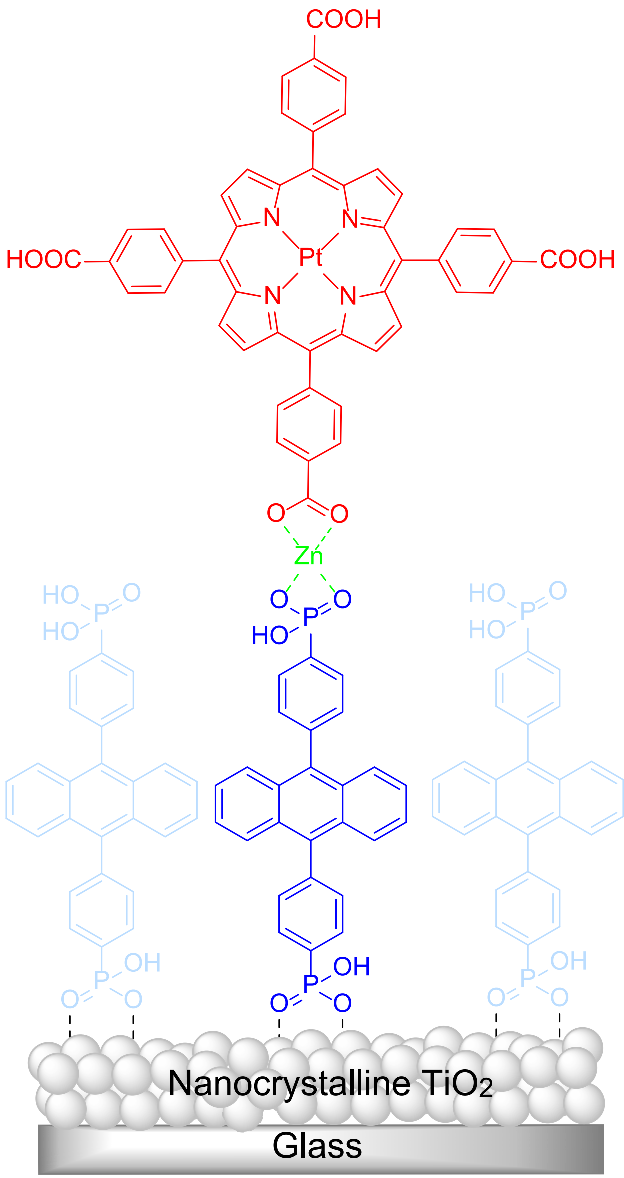
- S and A in proximity
- A-A interactions
- On a charge separation interface
- Easy DSSC integration

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

Metal Ion-Linked Multilayer

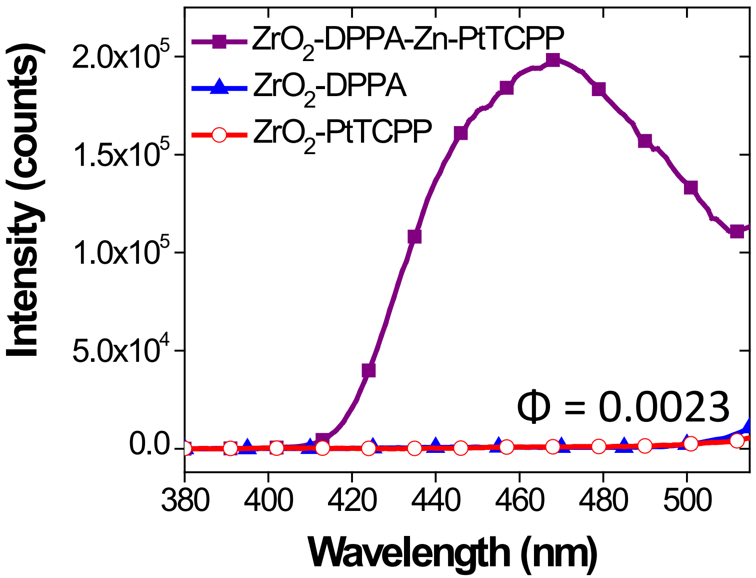


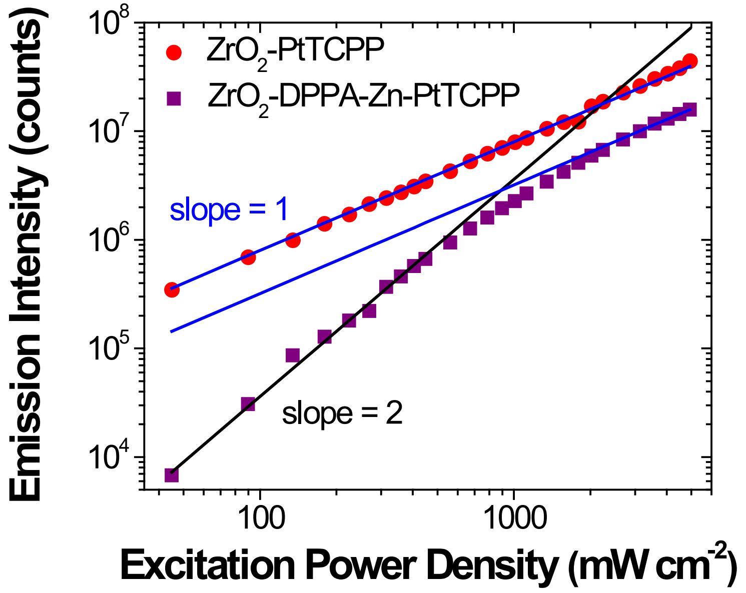


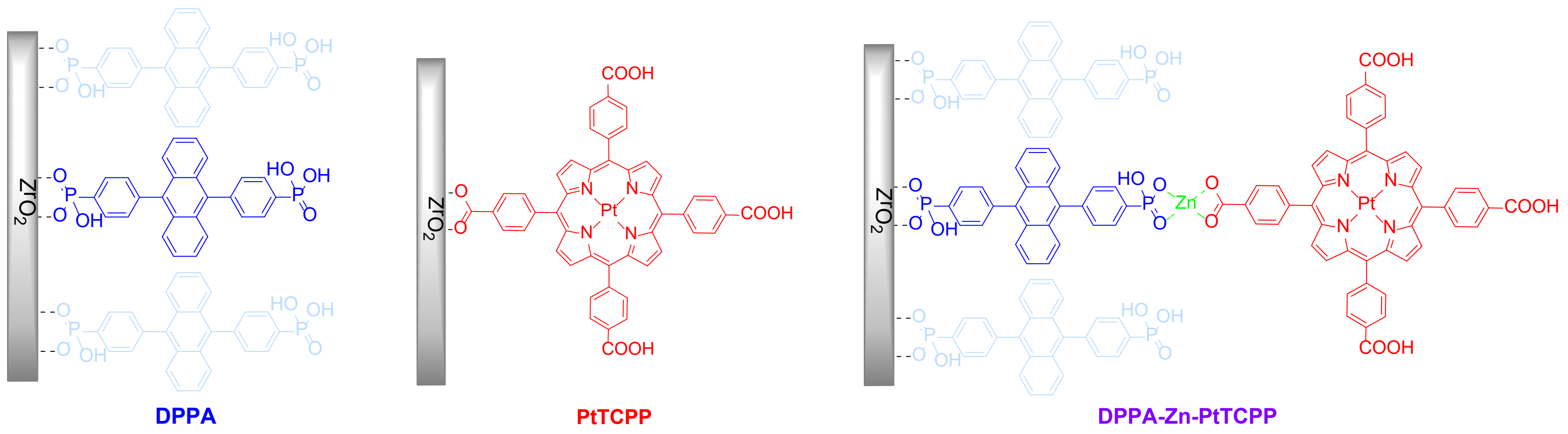


TTA-UC Emission

λ_{ex} = 532 nm (1 W/cm^2)







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

TTA-UC Emission

Weak TTA Limit

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

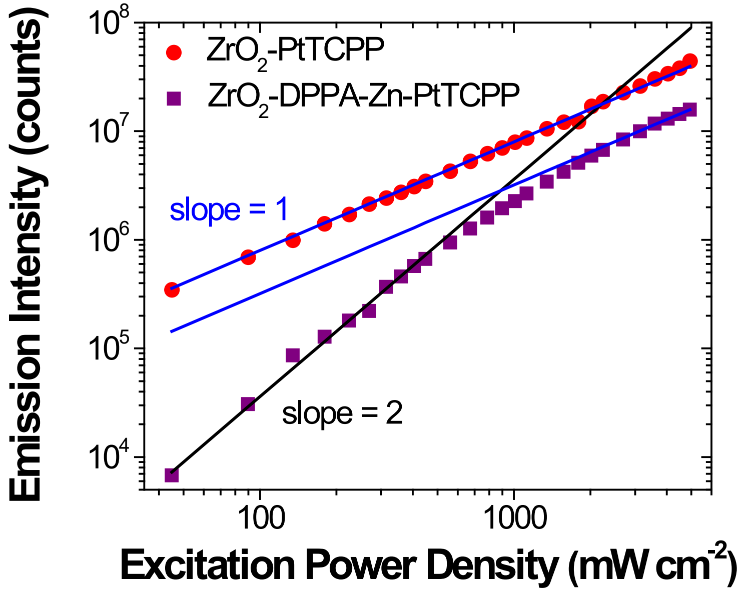
Slope = 2

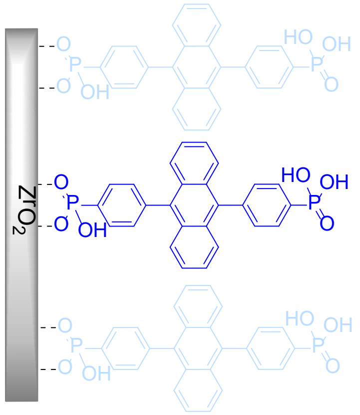
Strong TTA Limit

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

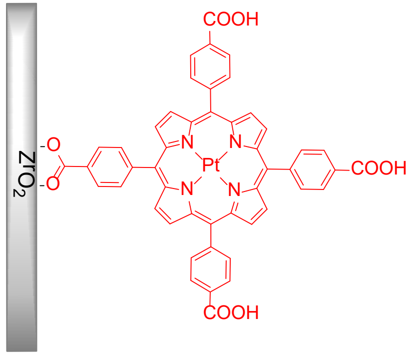
Slope = 1

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

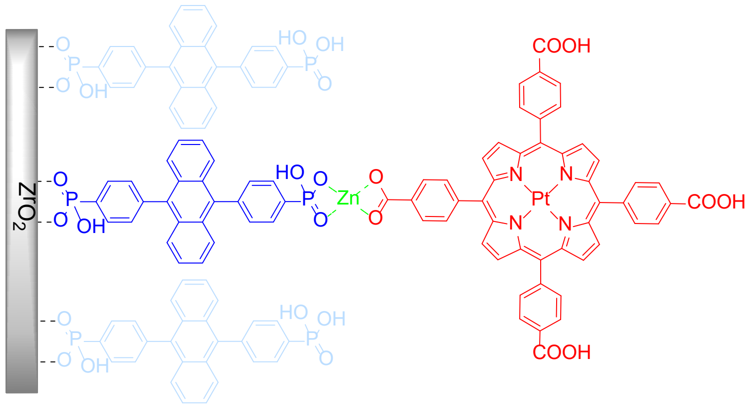




DPPA



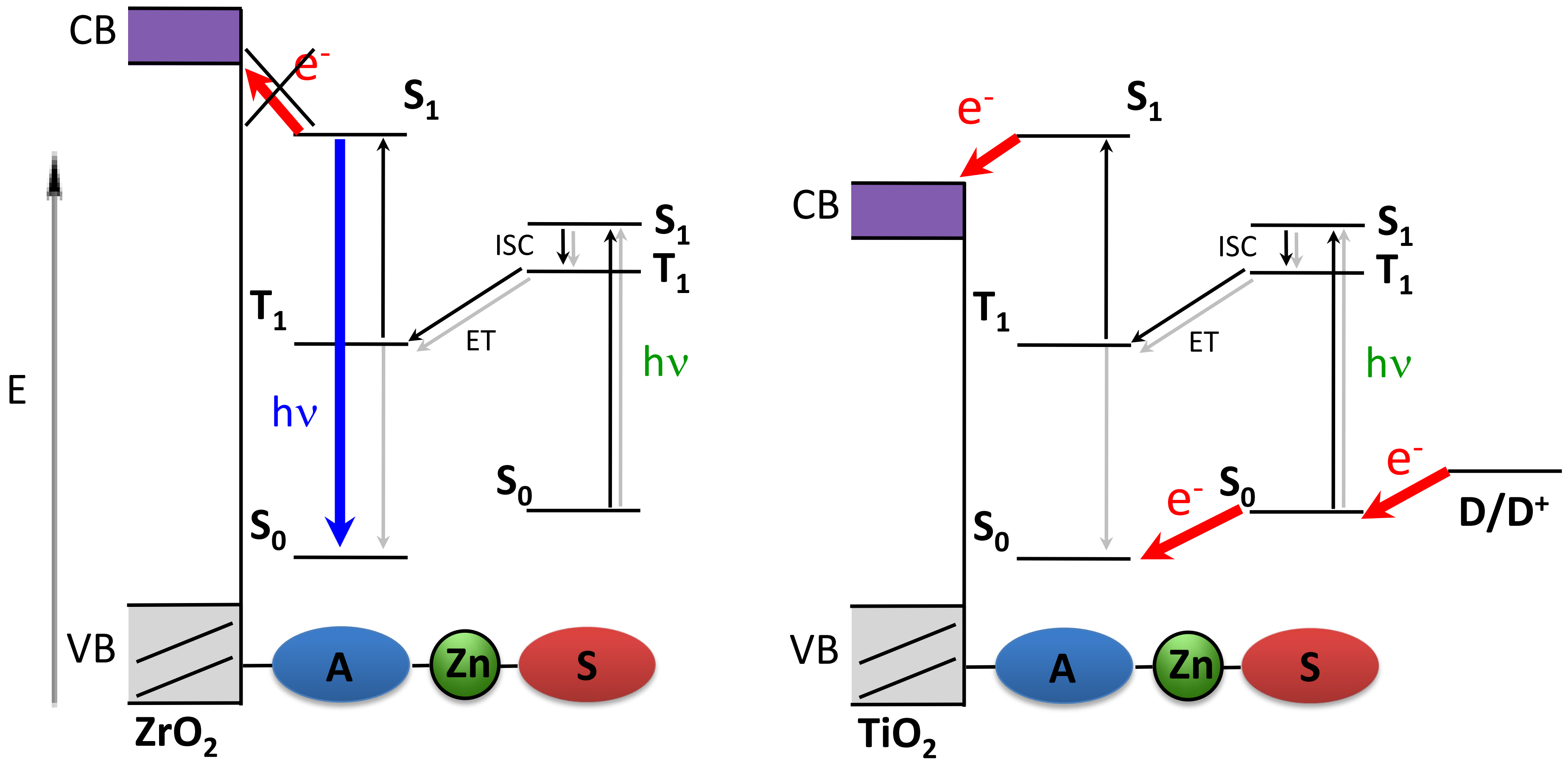
PtTCPP



DPPA-Zn-PtTCPP

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

Mechanism

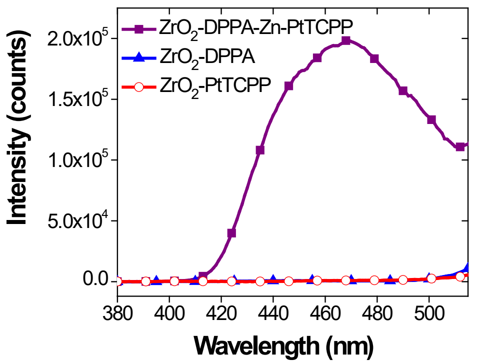


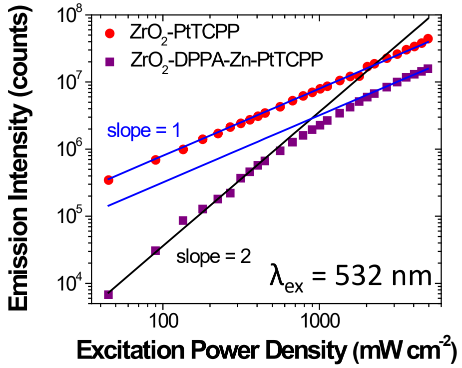
Upconverted Emission!

Photocurrent?

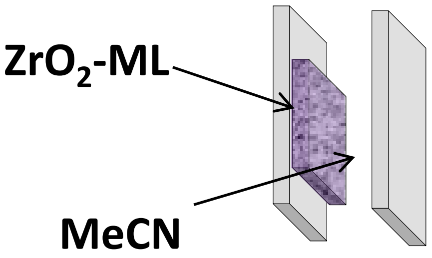
TTA-UC Photocurrent

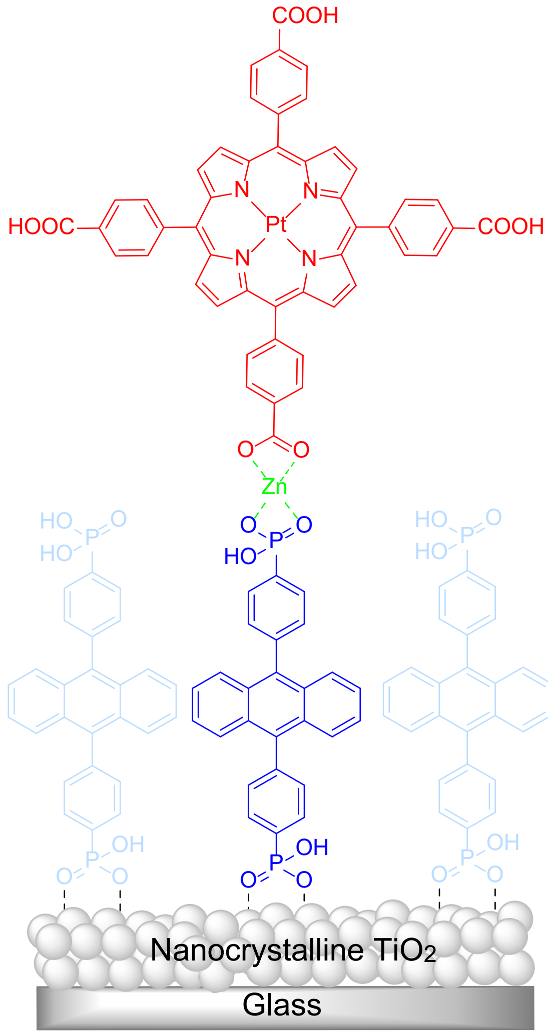
On ZrO_2: Upconverted Emission



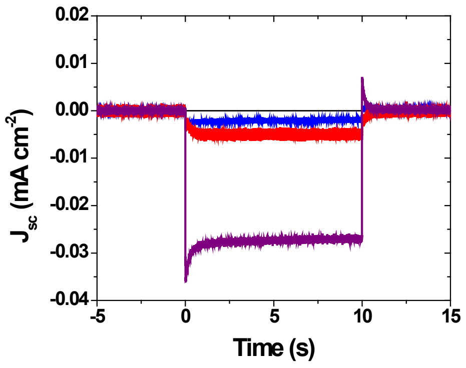


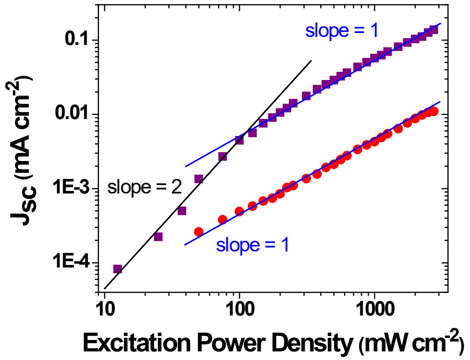
J. Phys. Chem. Lett. **2015**, 6, 4510.

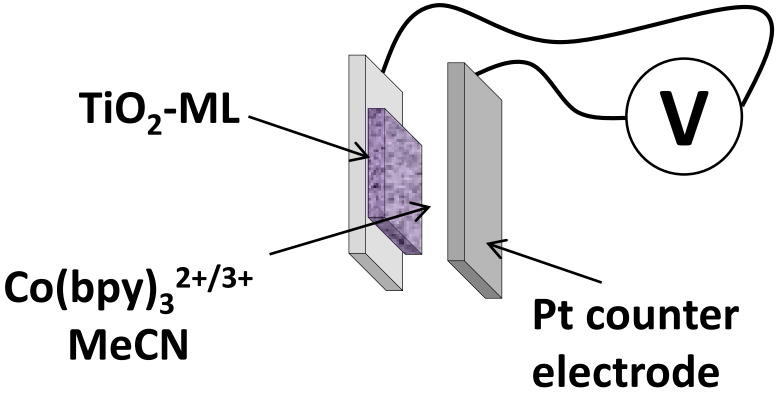




On TiO_2: Upconverted Photocurrent

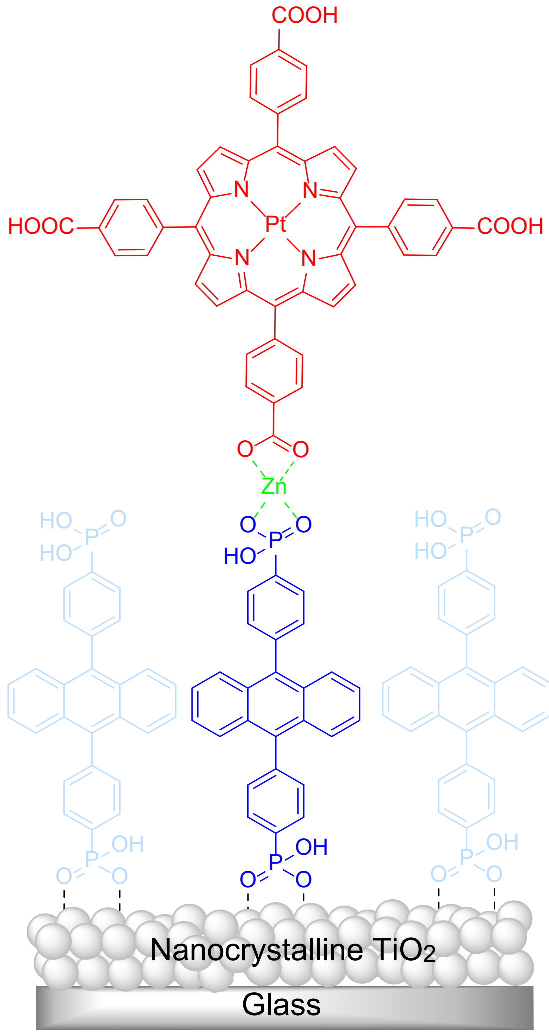




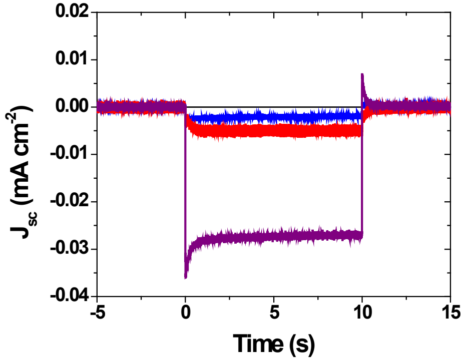


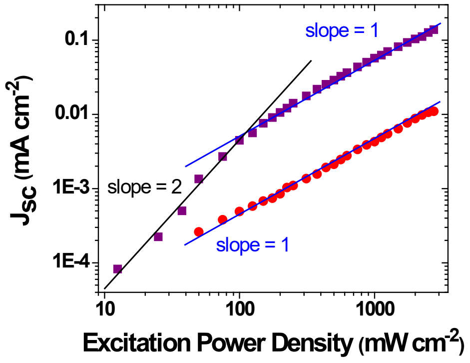
TTA-UC Photocurrent

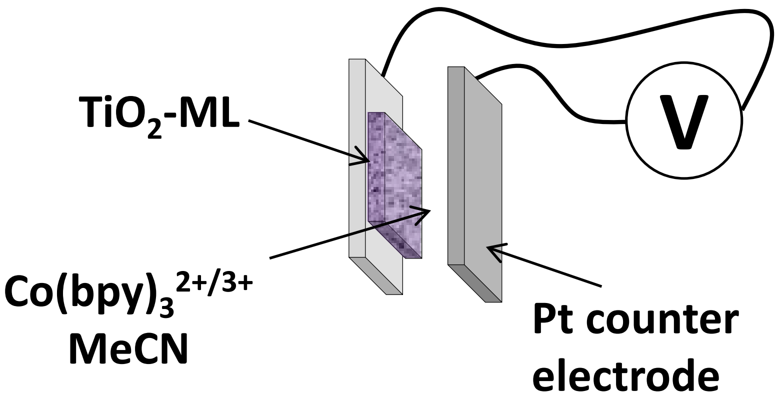
- J_{sc}/V_{oc} greater than the sum of its parts.
- J_{sc}= 0.009 mA/cm^2 *ACS Energy Lett.* **2016**, 1, 3-8.
- Demonstrated an integrated TTA-UC solar cell.
- η = 1.6 x 10^{-5} %



On TiO_2: Upconverted Photocurrent







Hanson Research Group

Side Note: Efficiency

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Researchers pushing limits of solar cells

Kathleen Haughney

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12/02/2015 10:20 am

The Cutting Edge

Tuesday January 12 2016 *reaching 1.4 million monthly*

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The Race for Solar

Light Trapping Innovation Lifts Solar Cell Efficiency To 45 Percent

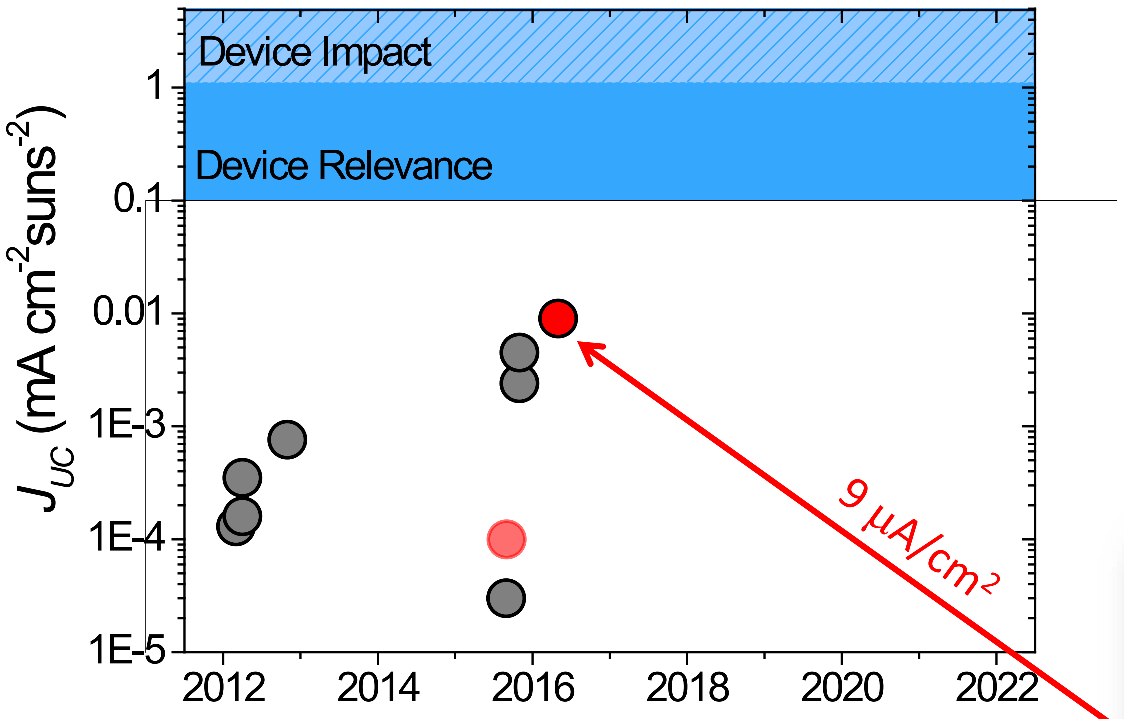
Paul Buckley December 3rd 2015

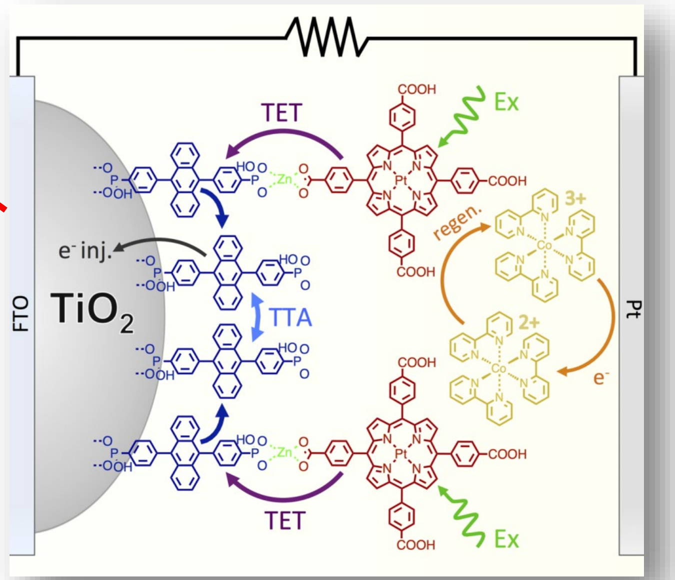
EE Times

$\eta = 1.6 \times 10^{-5}\,\%$

Increasing UC Photocurrent (J_{UC})

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

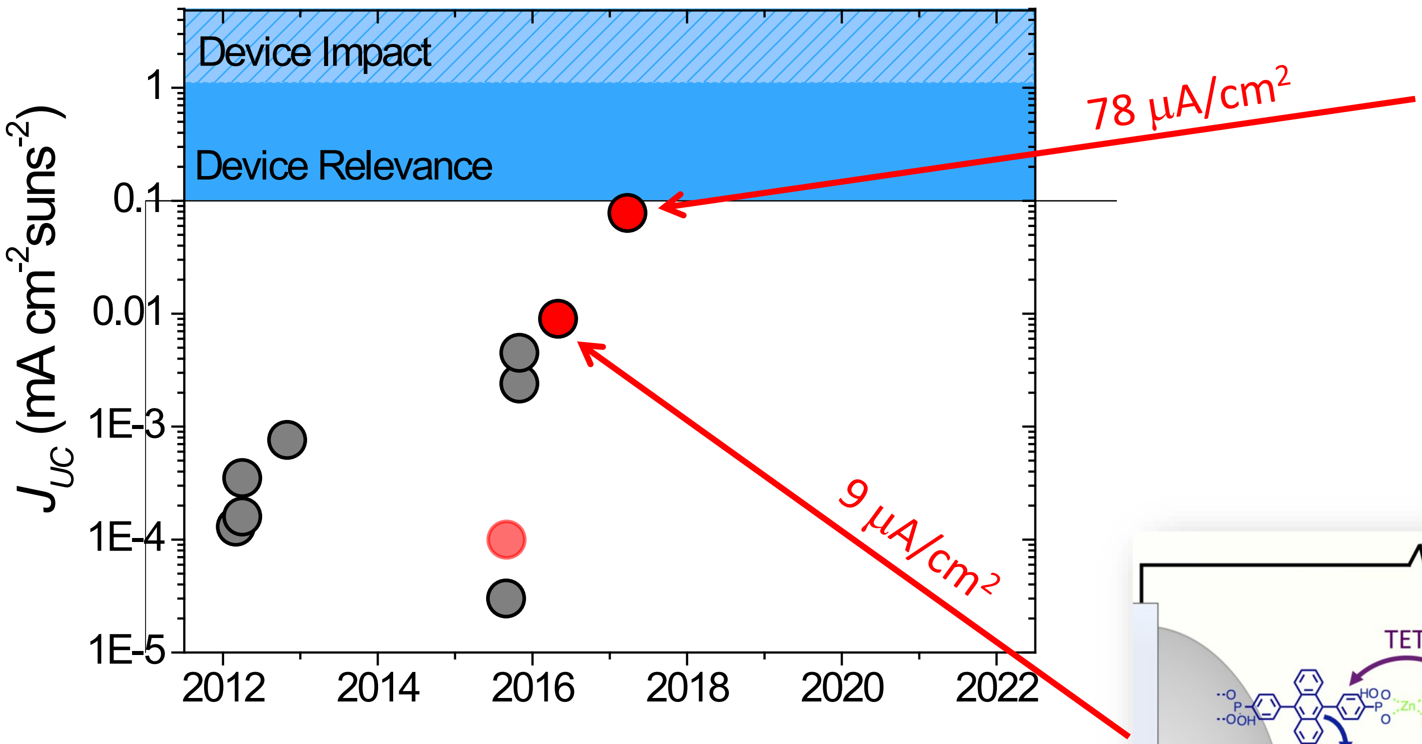


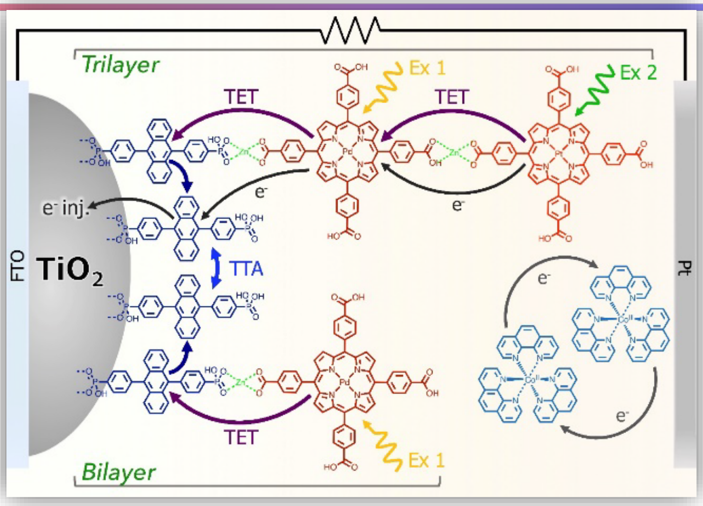


ACS Energy Lett. **2016**, 1, 3-8.

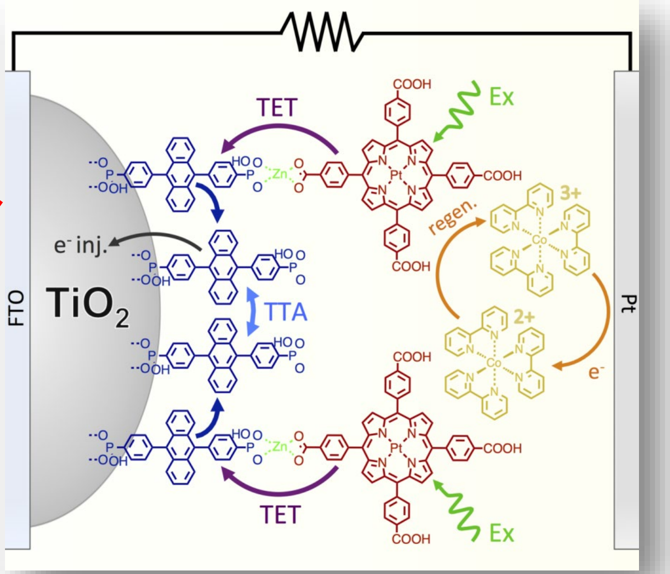
Increasing UC Photocurrent (J_{UC})

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





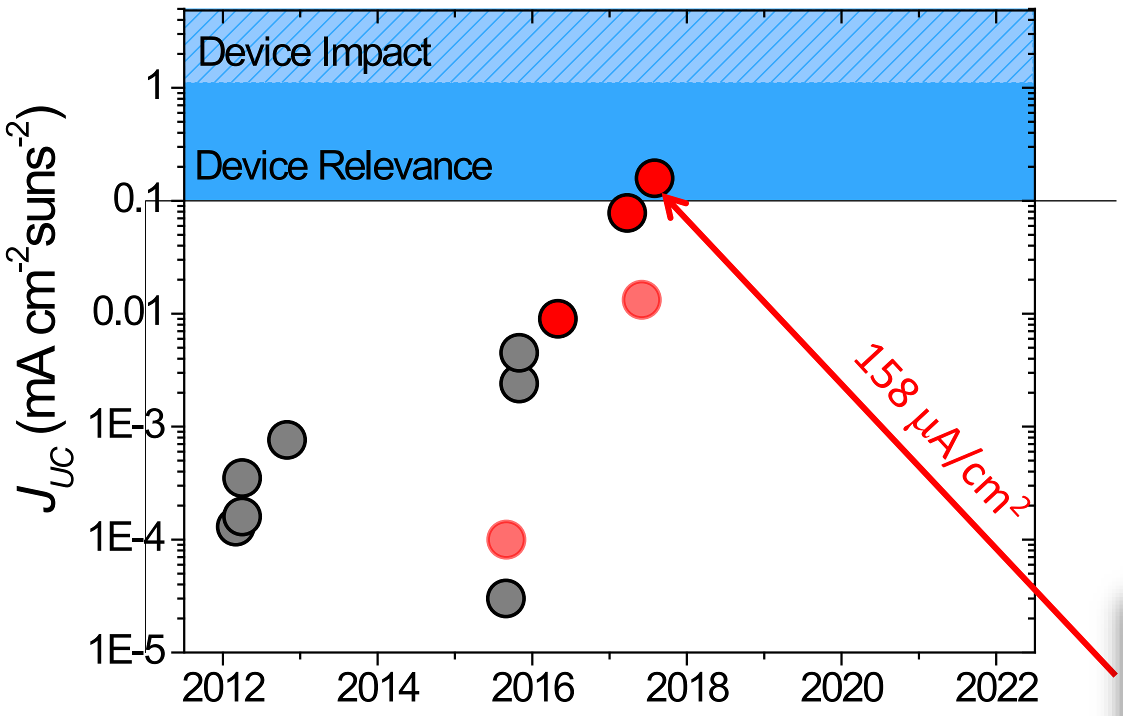
J. Mater. Chem. A, **2017**, 5, 11652-11660.

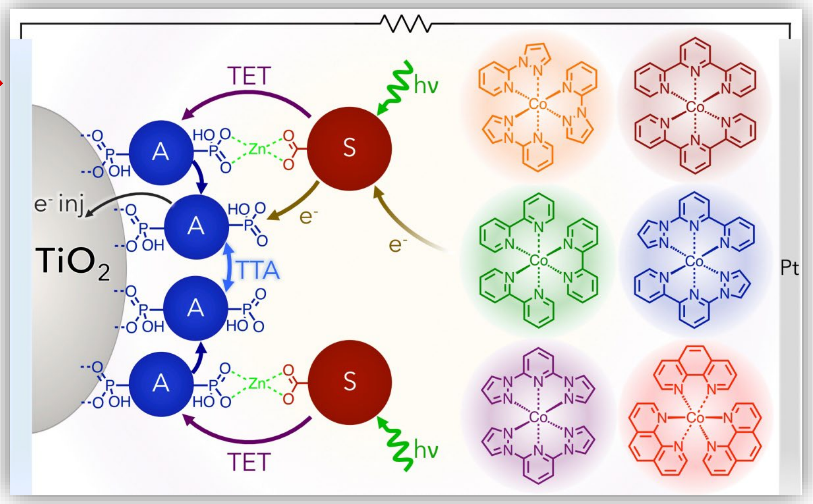


ACS Energy Lett. **2016**, 1, 3-8.

Increasing UC Photocurrent (J_{UC})

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

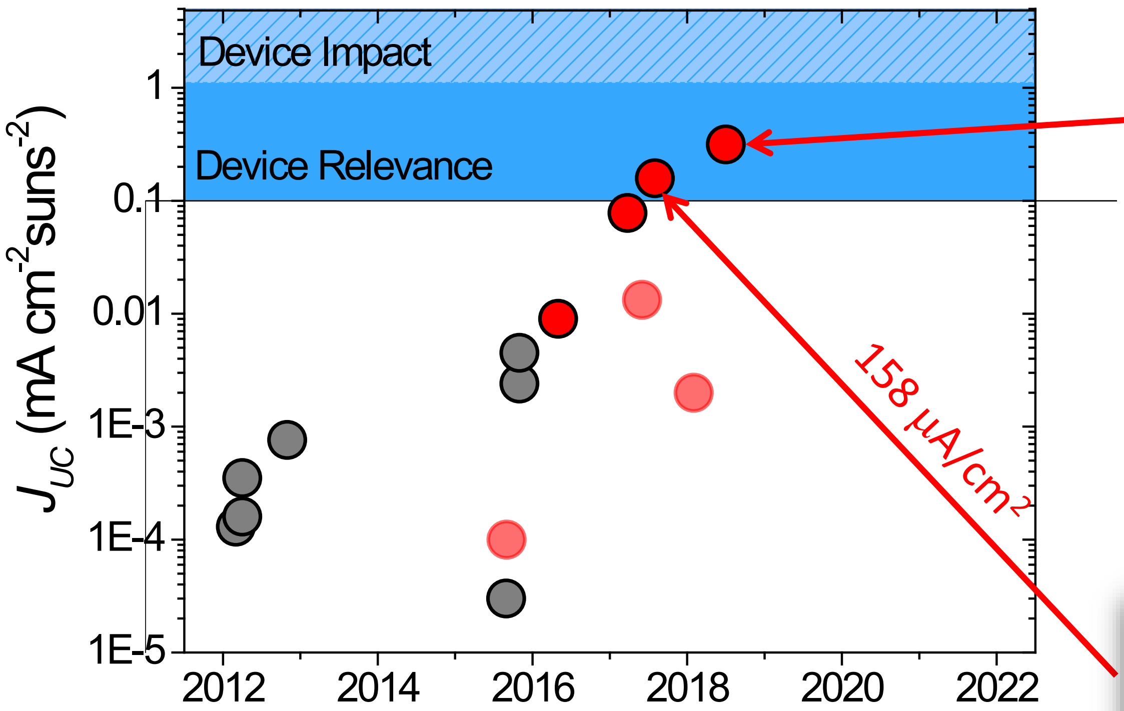




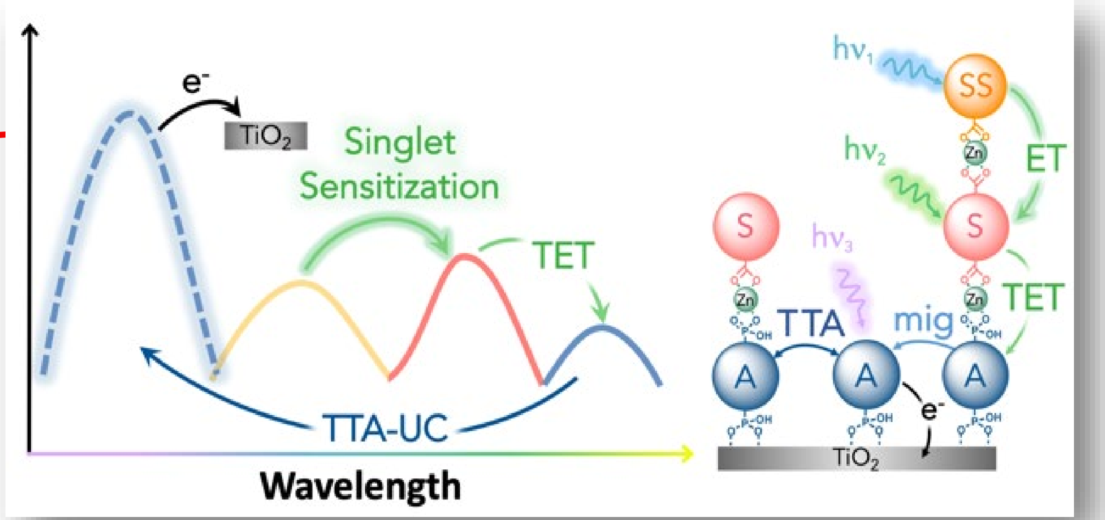
JACS **2017** , 139, 10988.

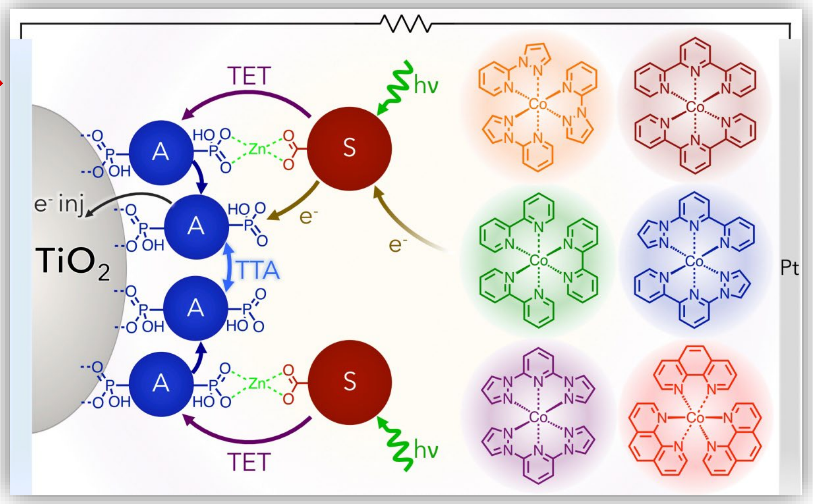
Increasing UC Photocurrent (J_{UC})

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



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

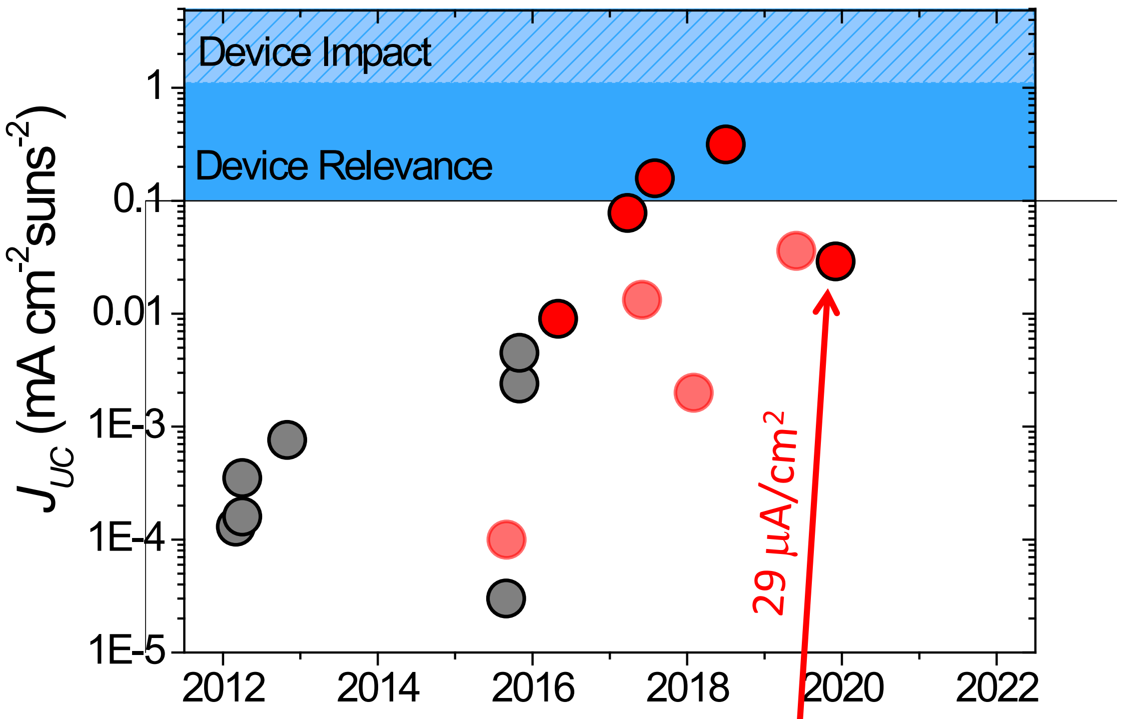


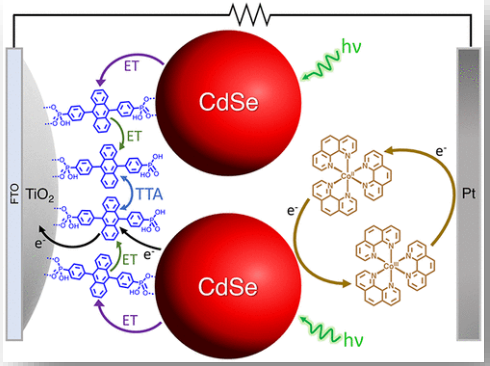


JACS **2017** , 139, 10988.

Increasing UC Photocurrent (J_{UC})

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

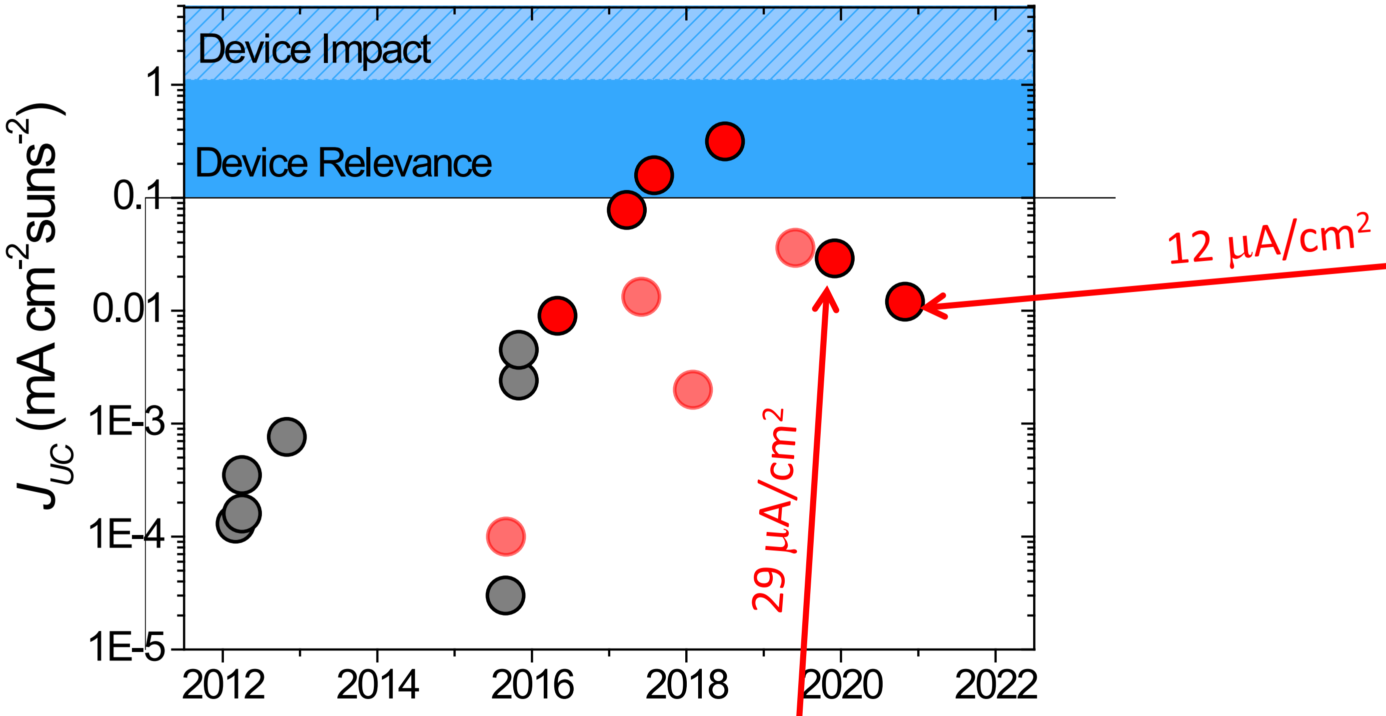




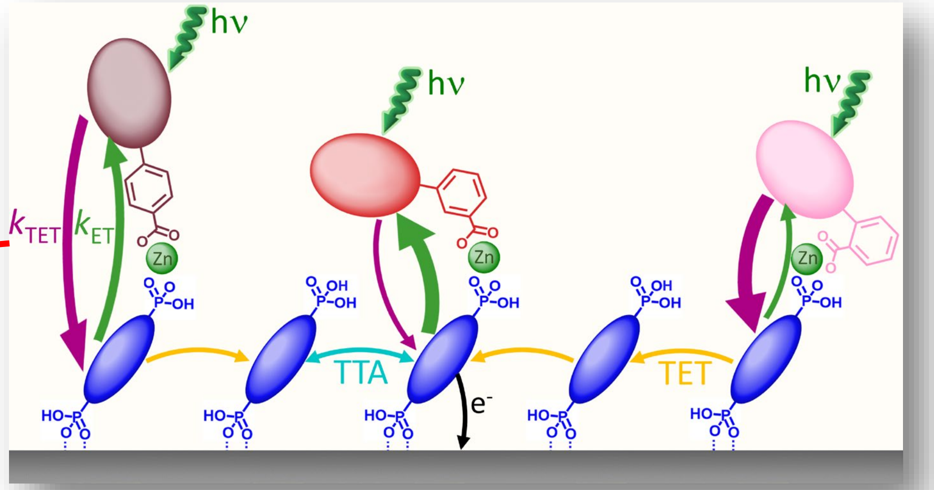
ACS Appl. Energy Mater. **2020**, 3, 29.

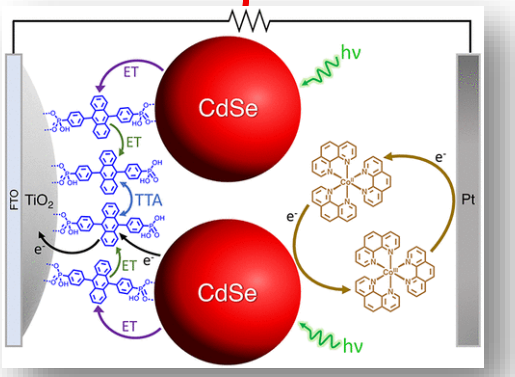
Increasing UC Photocurrent (J_{UC})

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



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

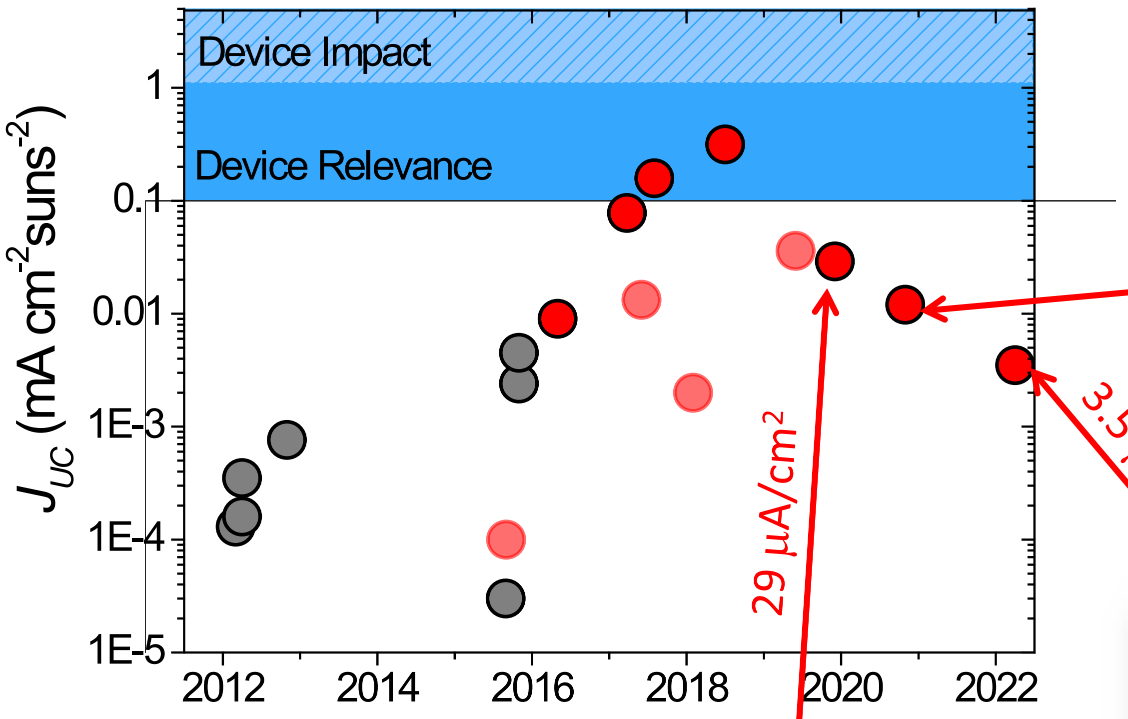




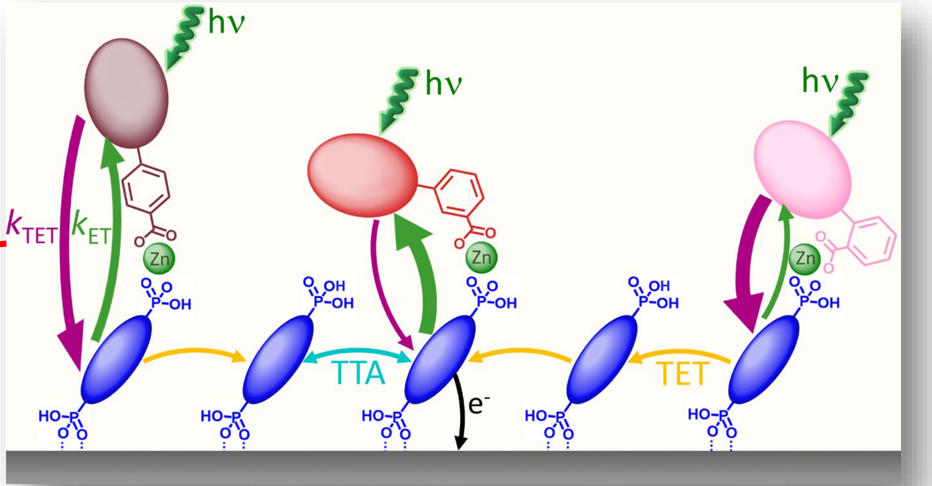
ACS Appl. Energy Mater. **2020**, 3, 29.

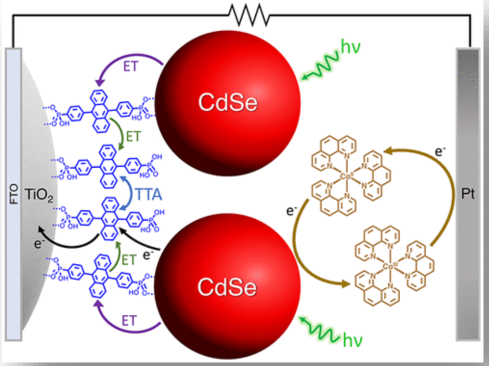
Increasing UC Photocurrent (J_{UC})

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

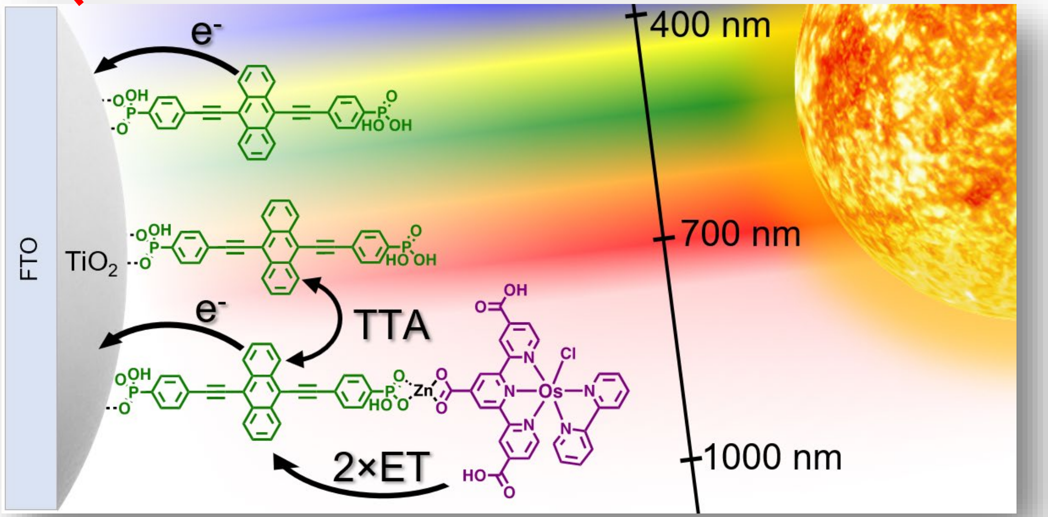


JPC C **2020**, 43, 23597.





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



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

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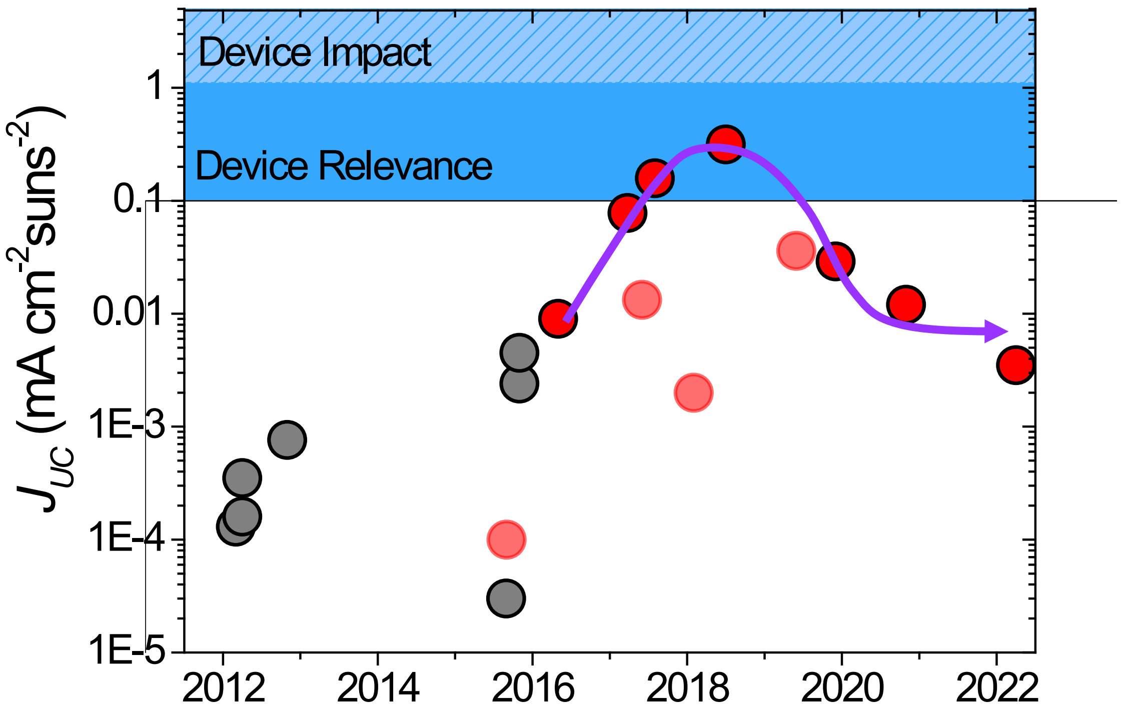
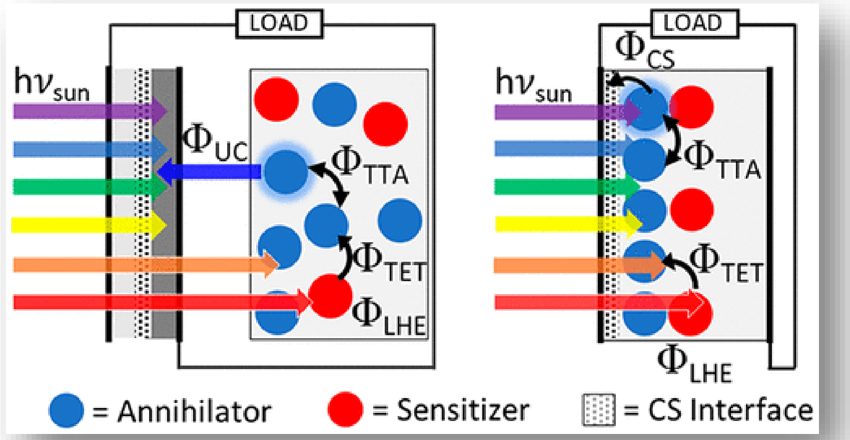
Increasing UC Photocurrent (J_{UC})

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



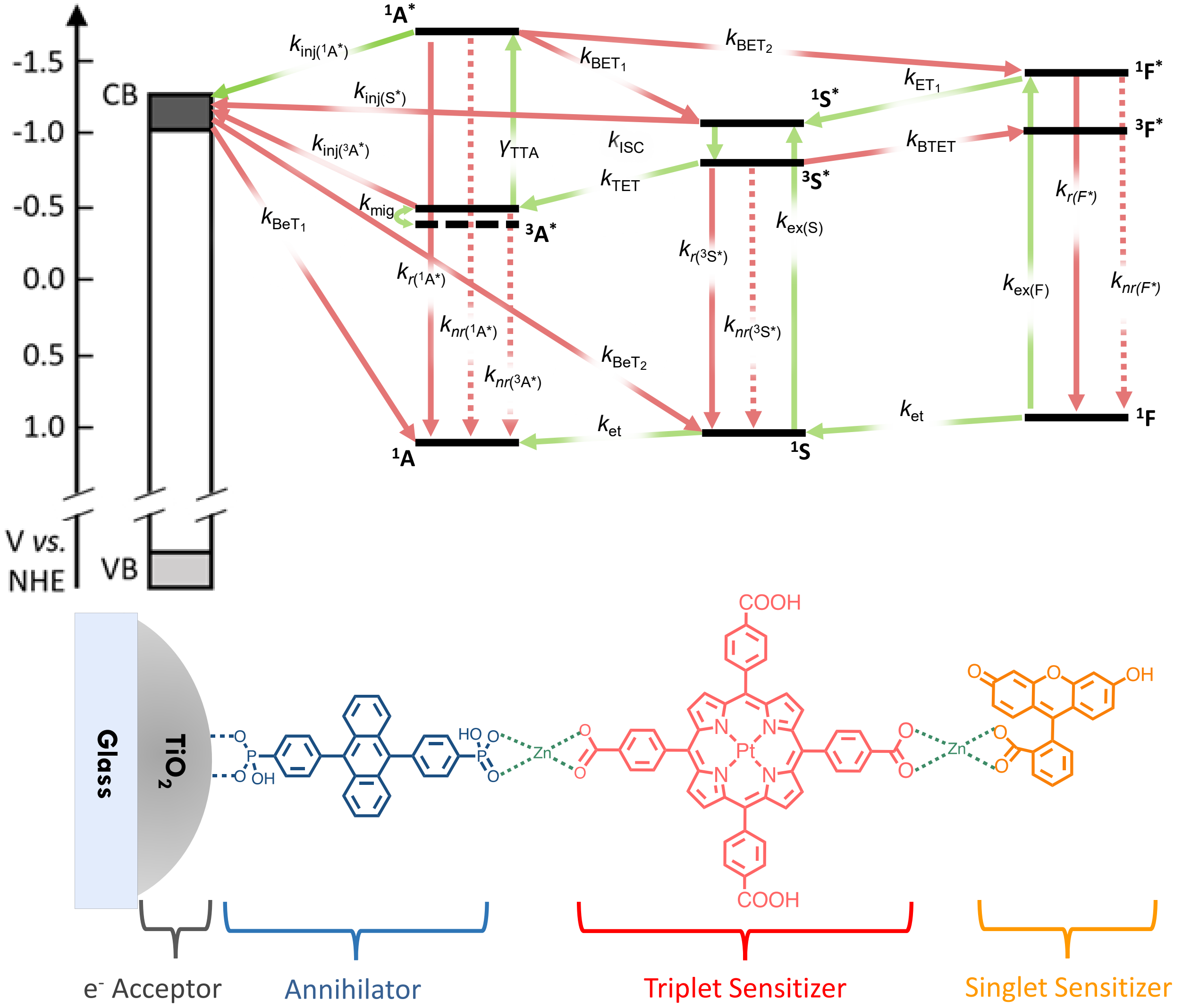
Performance Limitations:



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

Energy and Electron Transfer

Upconversion Trilayer

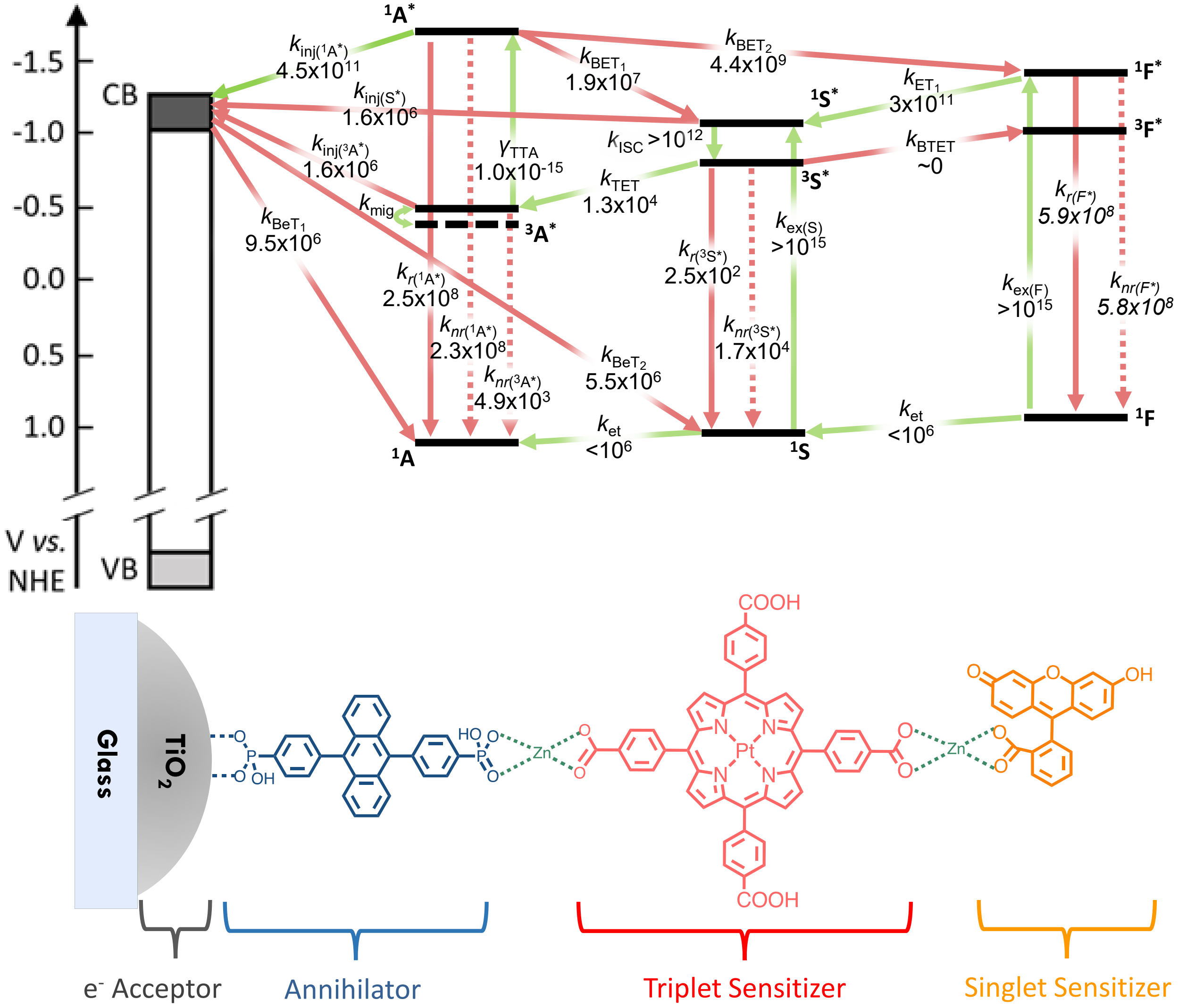


ACS Energy Lett. **2019**, 4, 6, 1458

Hanson Research Group

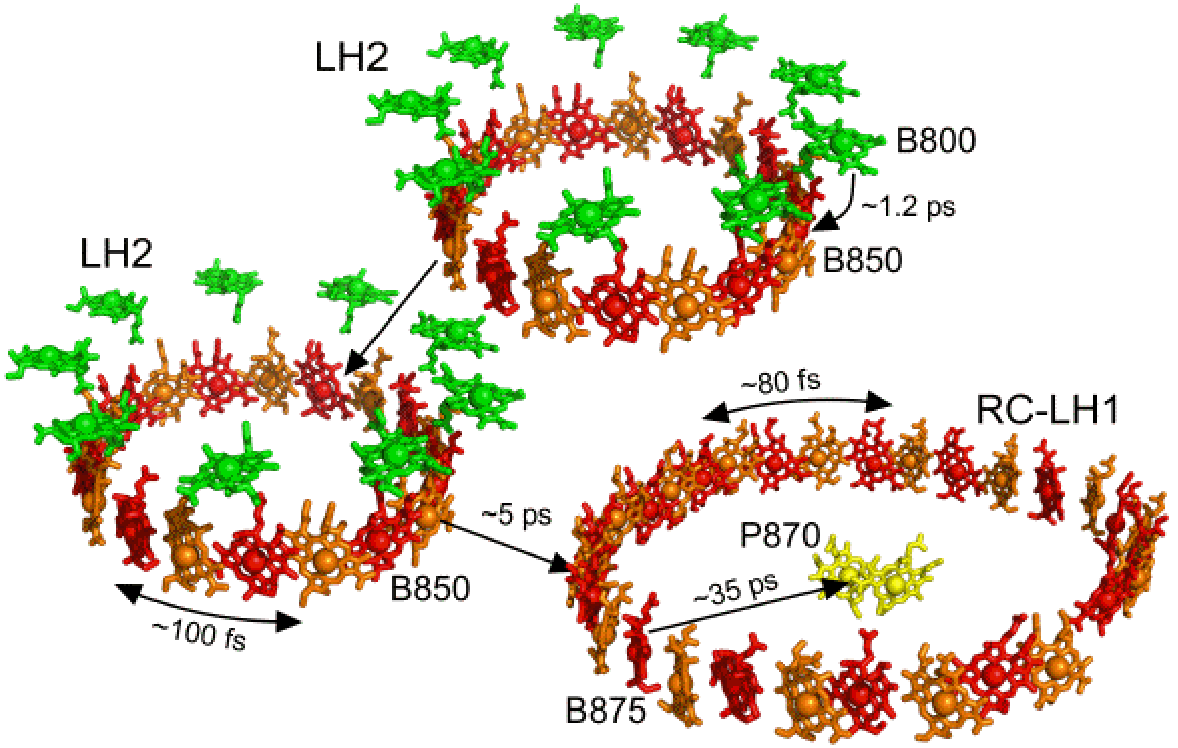
Energy and Electron Transfer

Upconversion Trilayer



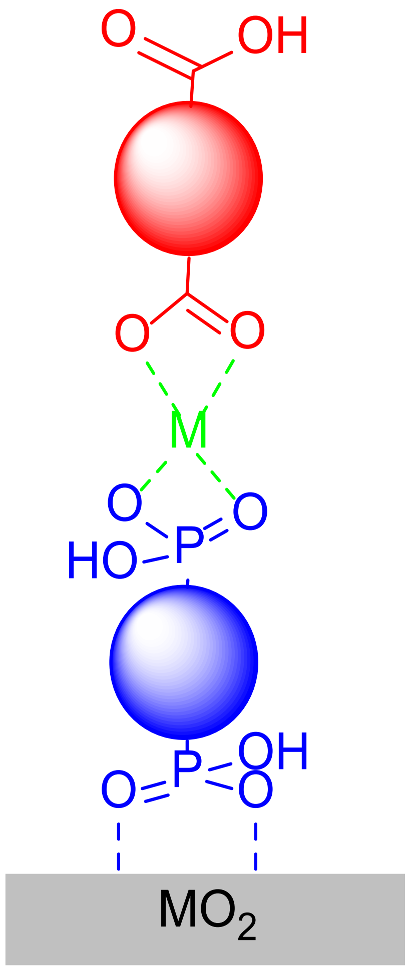
ACS Energy Lett. **2019**, 4, 6, 1458

Photosynthesis

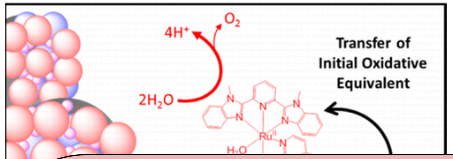


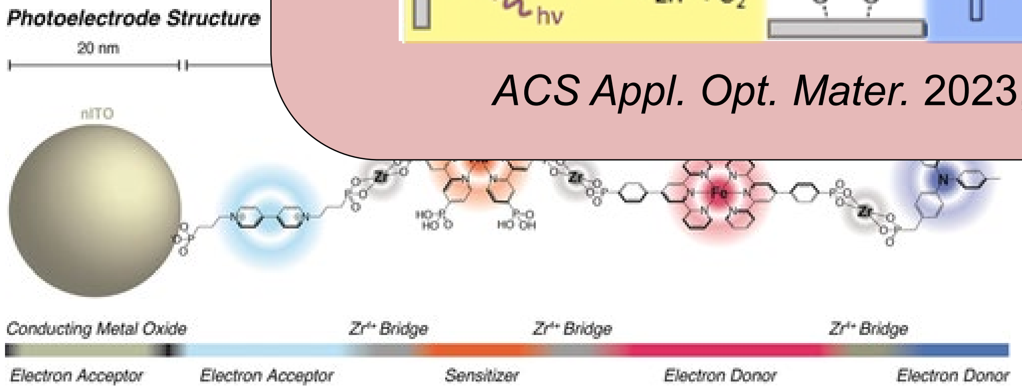
https://doi.org/10.48550/arXiv.1608.06913

Metal Ion Linked Multilayer Structure



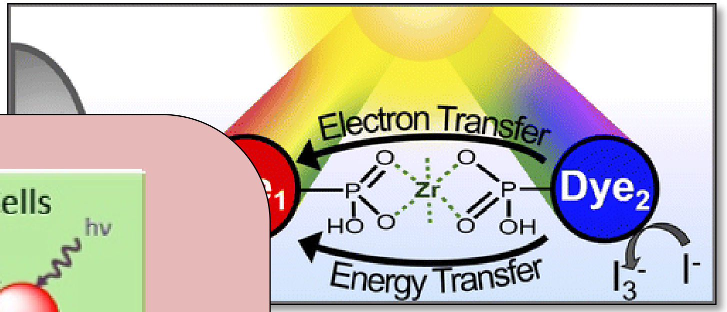
Water Oxidation DSPEC





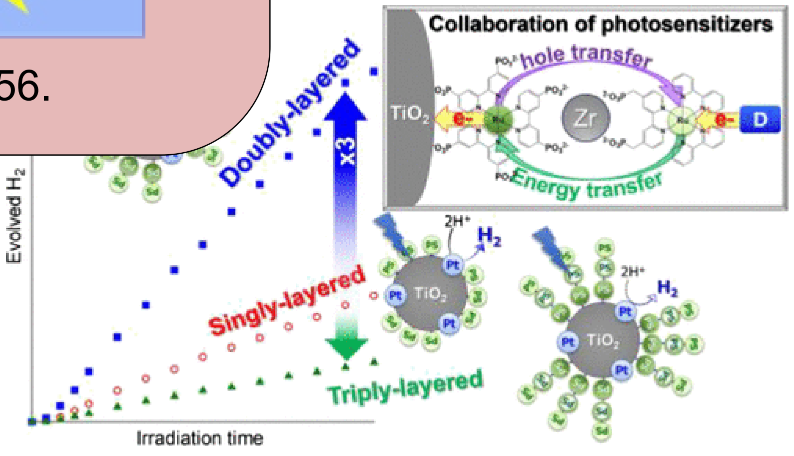
Angew. Chemie. **2018**, 57, 15390.

Energy/Electron Transfer Cascade

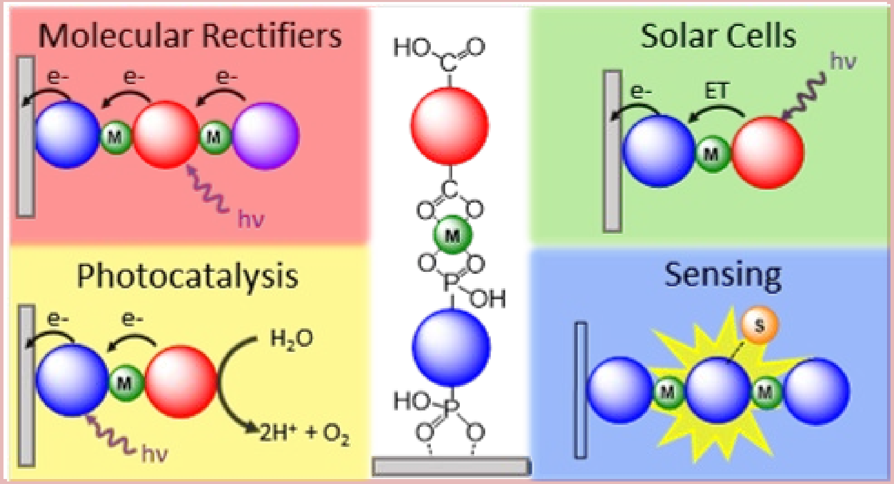


M&I **2016**, 8, 28633

$_2$ Generation



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

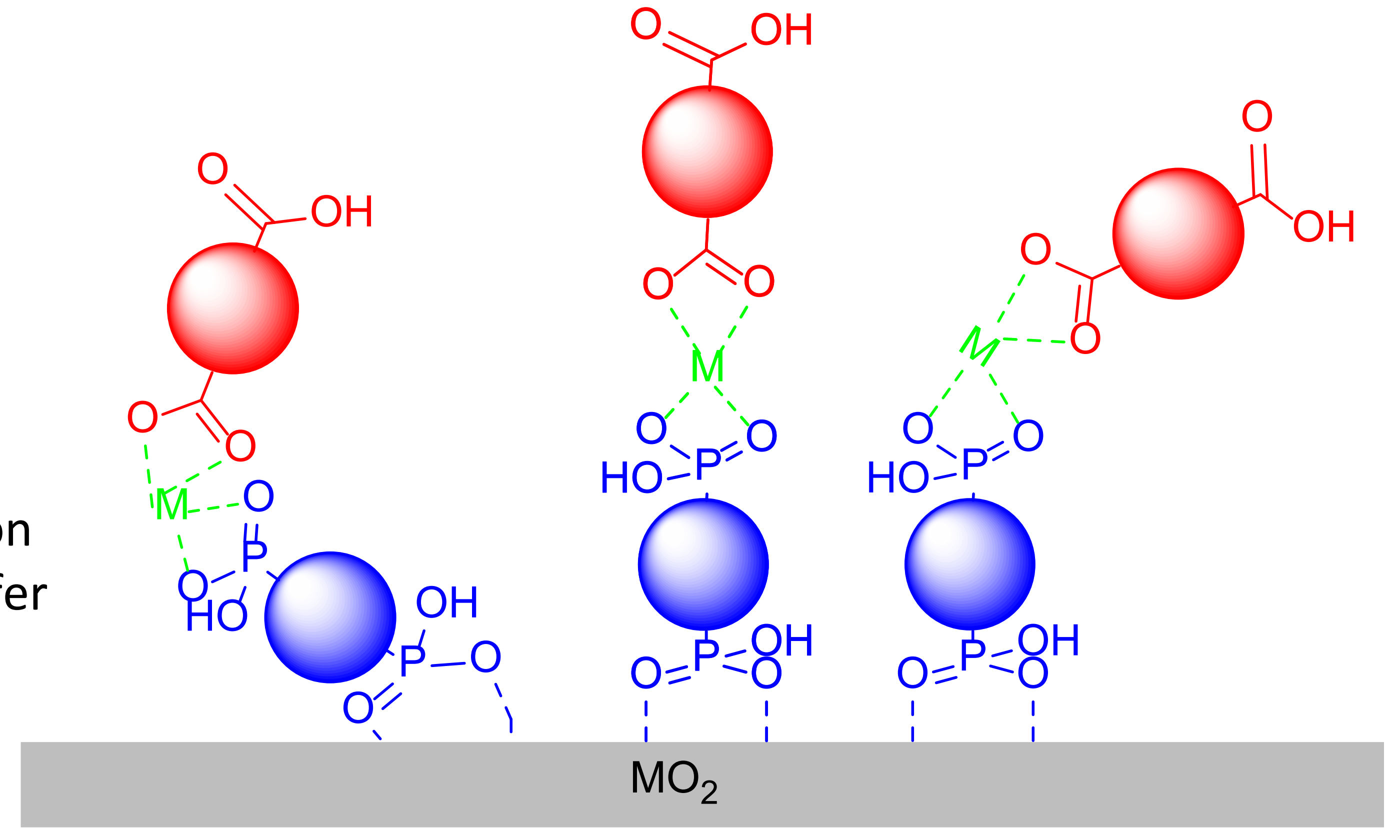


ACS Appl. Opt. Mater. 2023, 1, 1156.

Bilayer Structure

What is known:

- Not co-deposition
- Metal-ion coordination
- Directional E/e⁻ transfer

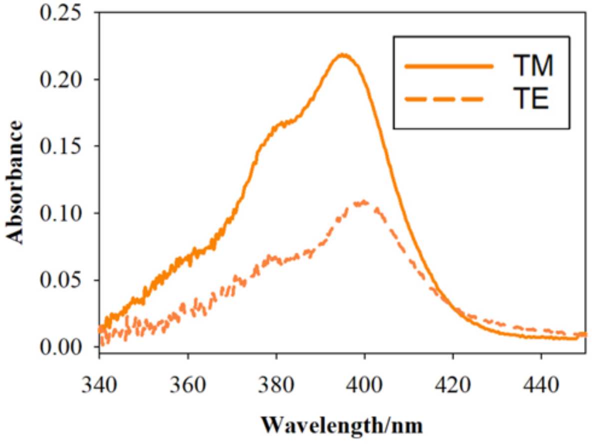


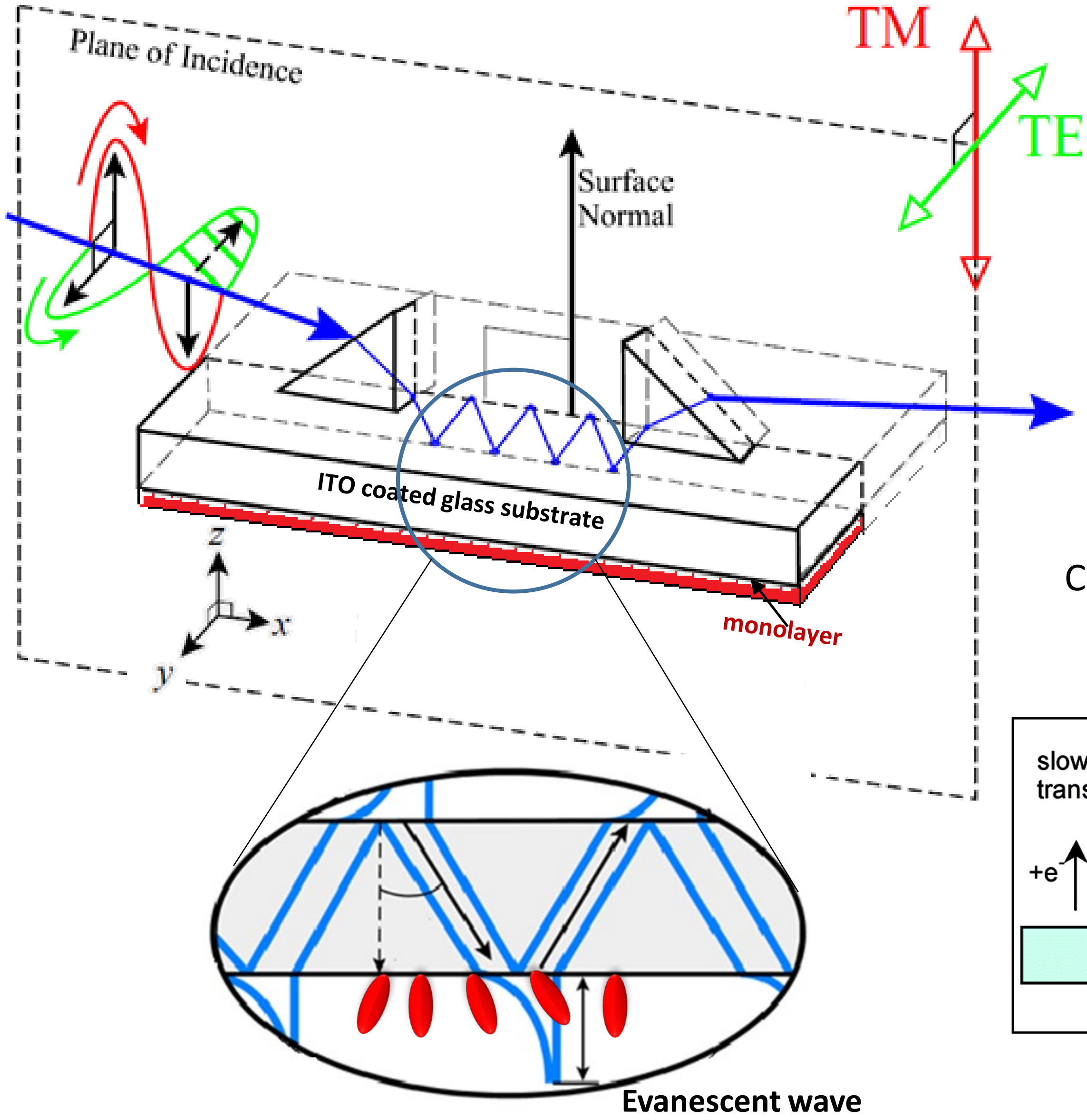
What is not known:

- Surface binding angle
- Relative orientation
- Controllability

Polarized Attenuated Total Reflectance

Prof. Scott Saavedra at UofA:

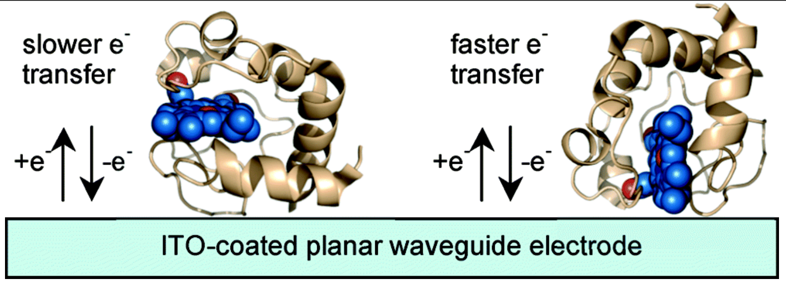




Measure A_{TE} and A_{TM}

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

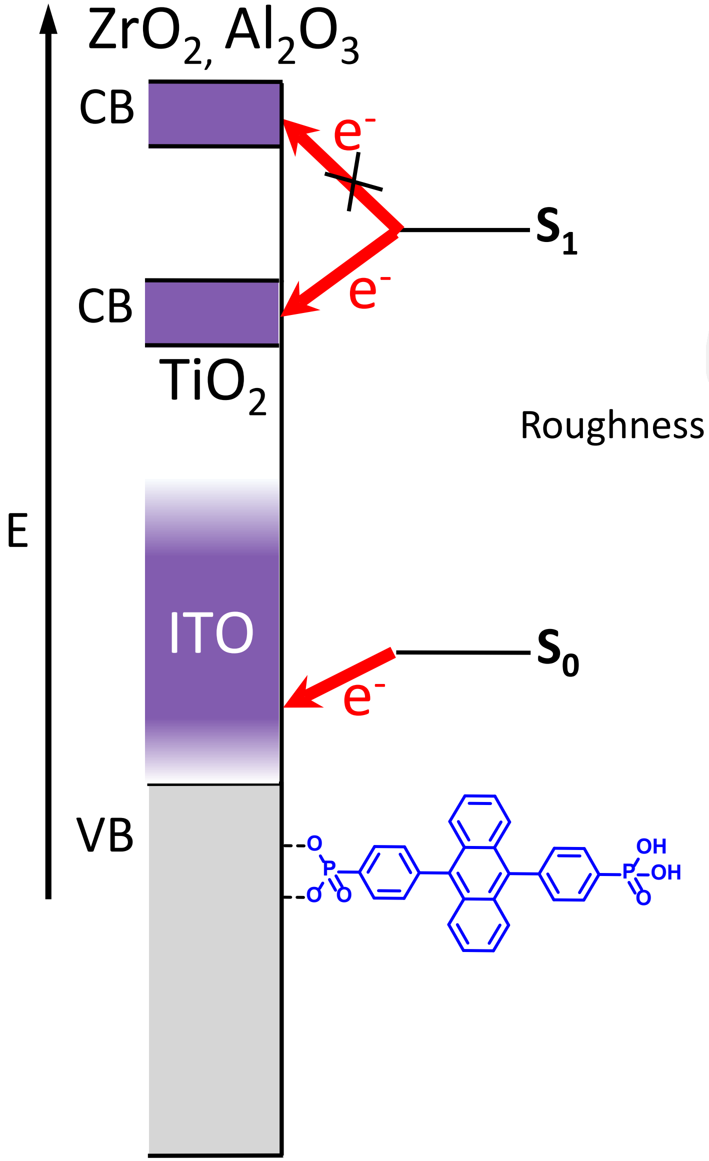
Calculate mean tilt angle θ

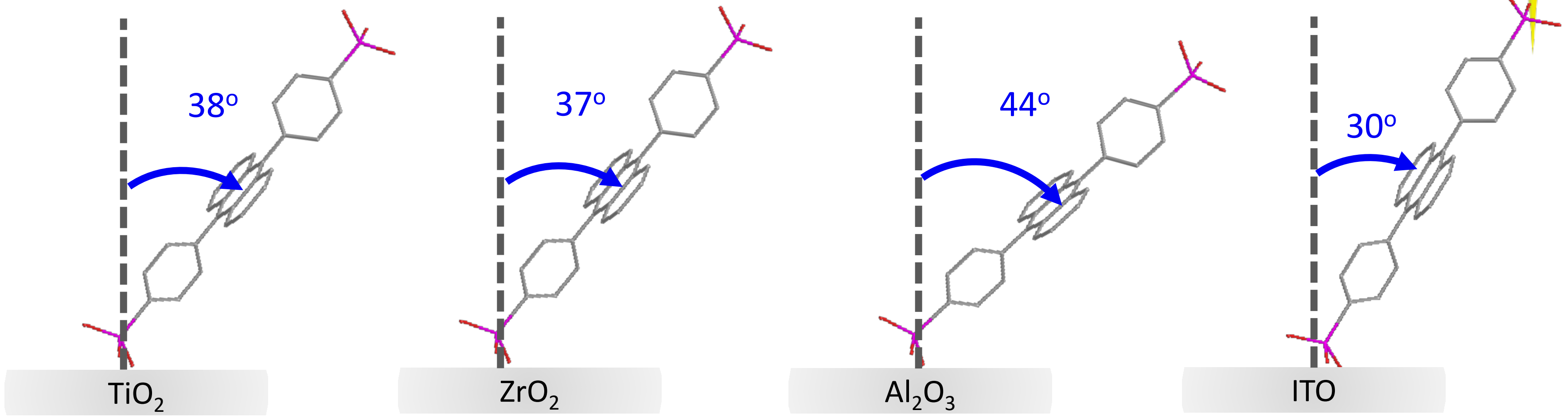


JACS **2008**, 130, 5, 1572

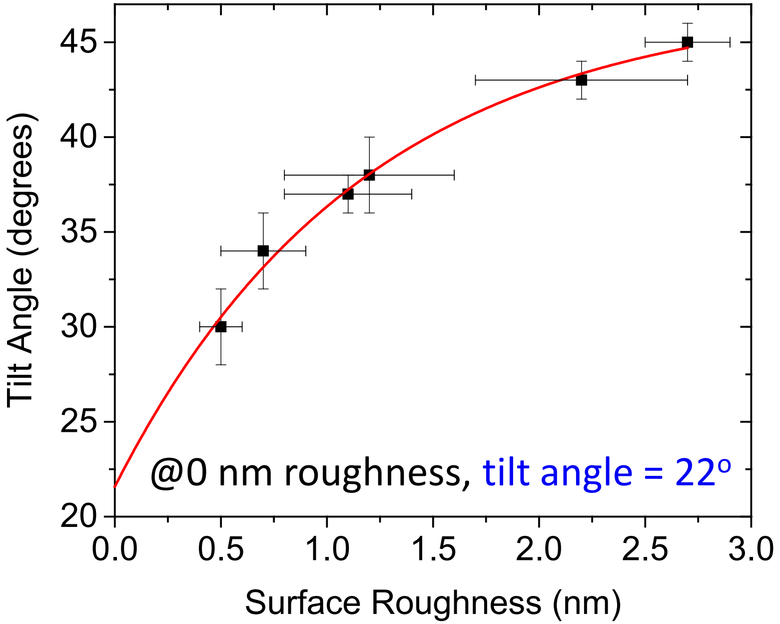
John Thomas Bradshaw , A. PhD. Dissertation, University of Arizona, 2005

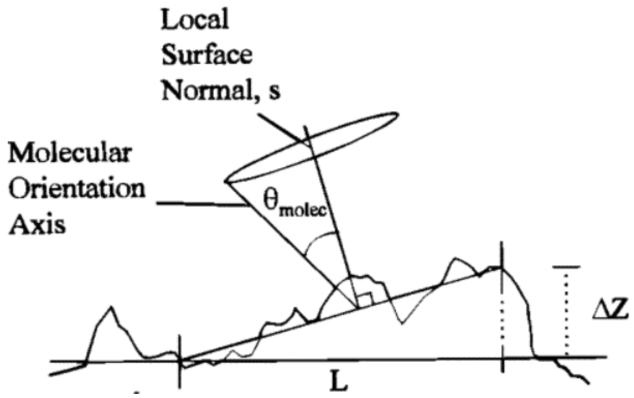
Metal Oxide-Anthracene Structure





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

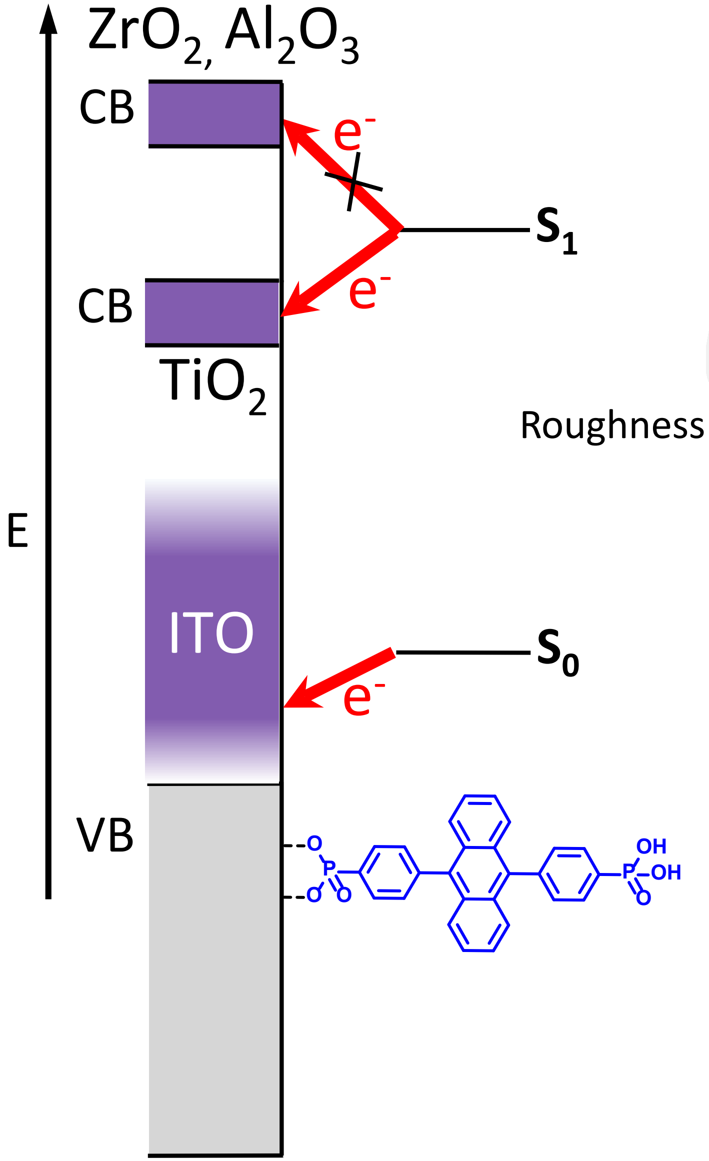


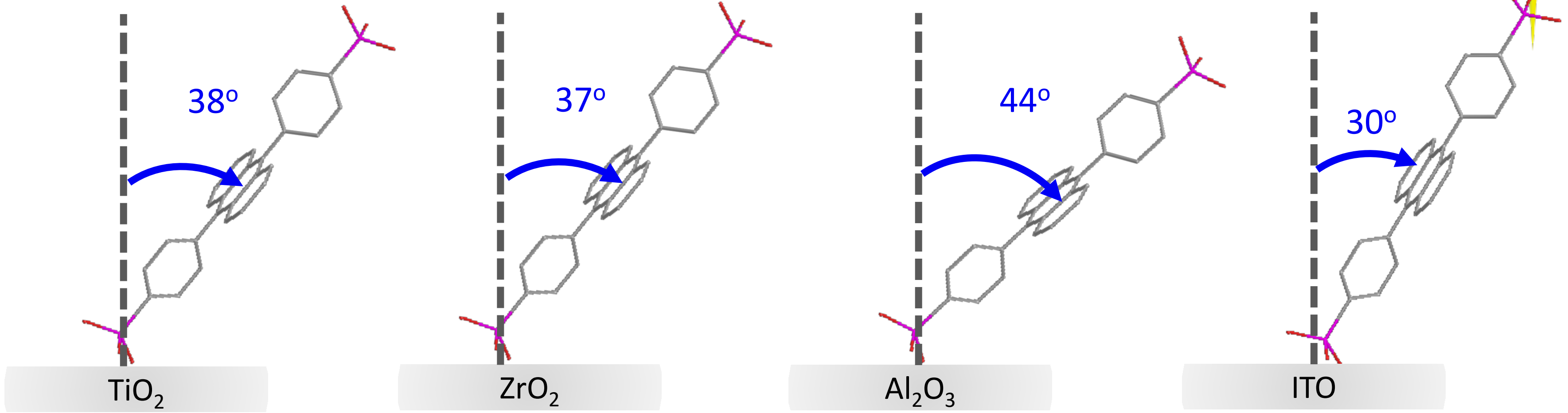


Rowlen et al. *JPC C* **1999**, 103, 1525.

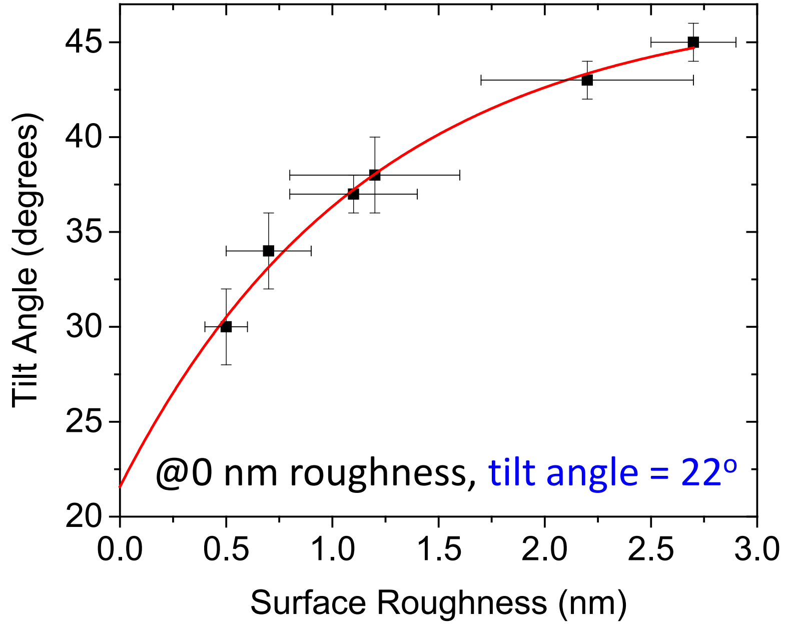
Hanson Research Group

Metal Oxide-Anthracene Structure

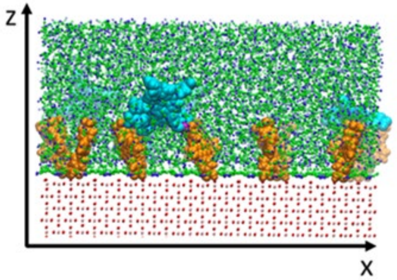


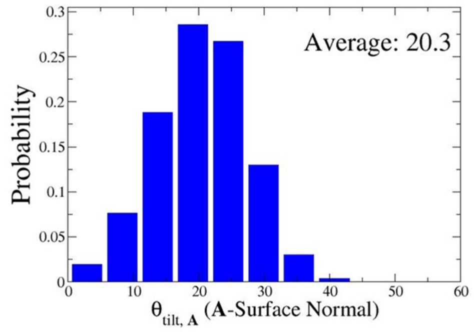


Roughness: 1.2±0.4nm 1.1±0.3nm 2.2±0.5nm 0.5±0.1 nm

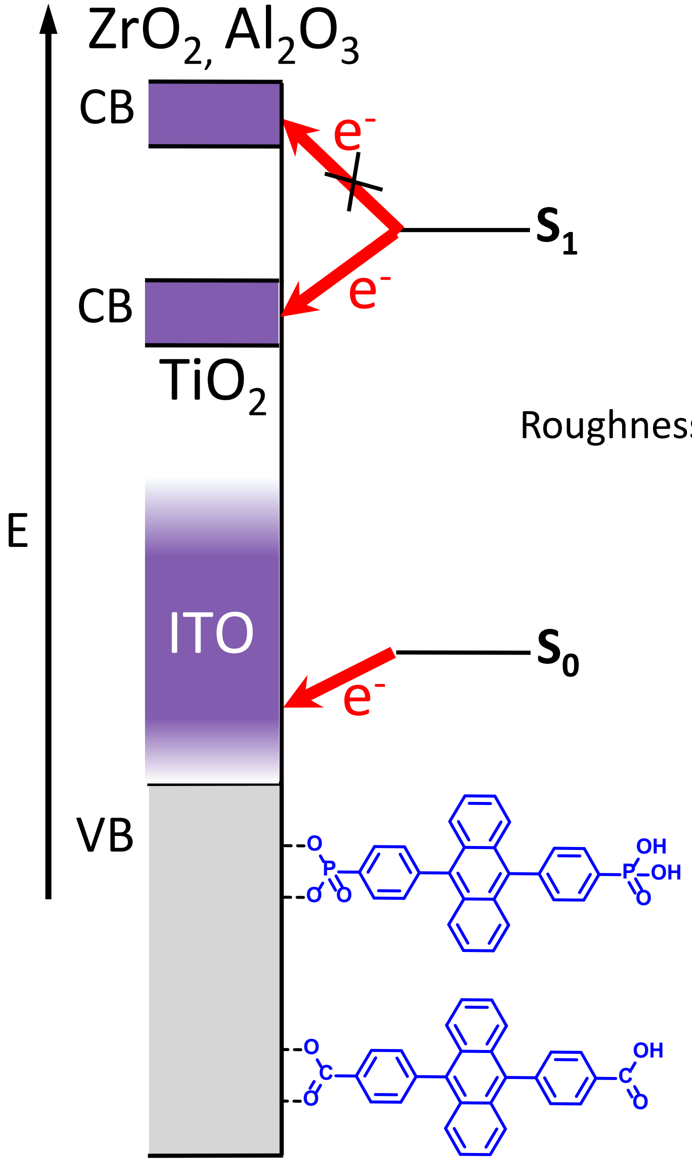


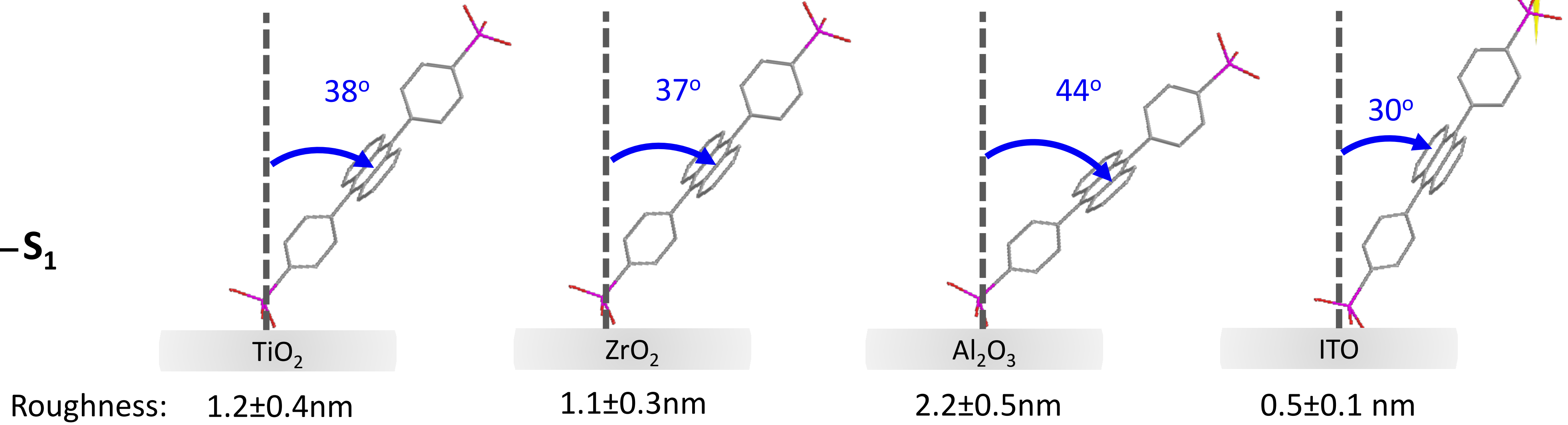
Prof. Wei Yang at FSU:



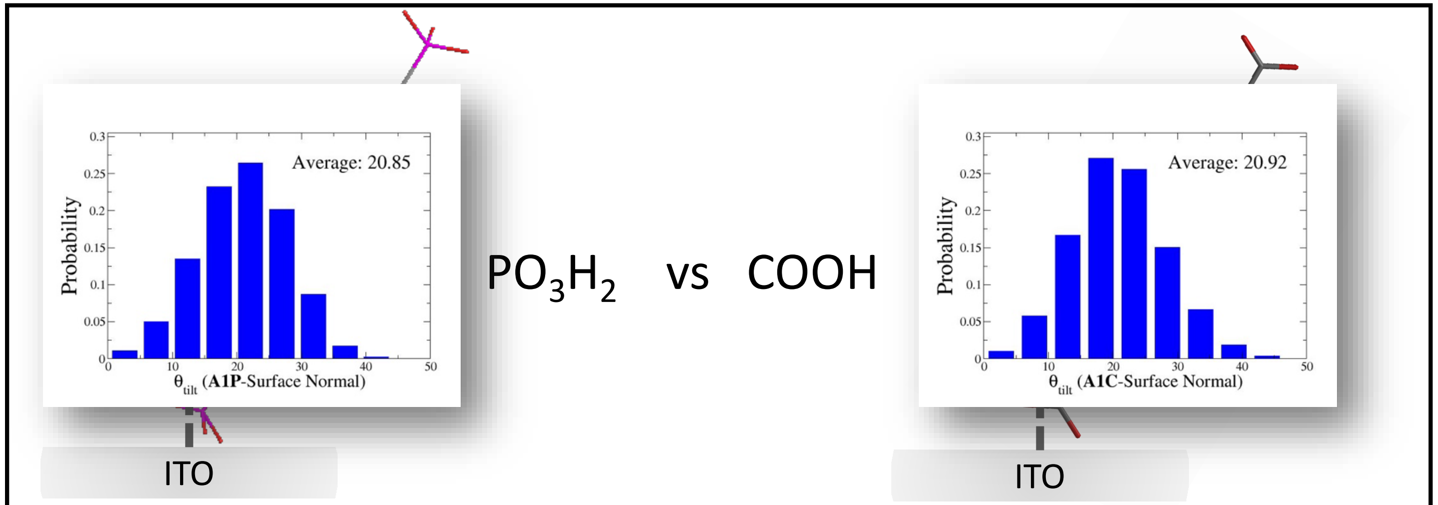


Metal Oxide-Anthracene Structure

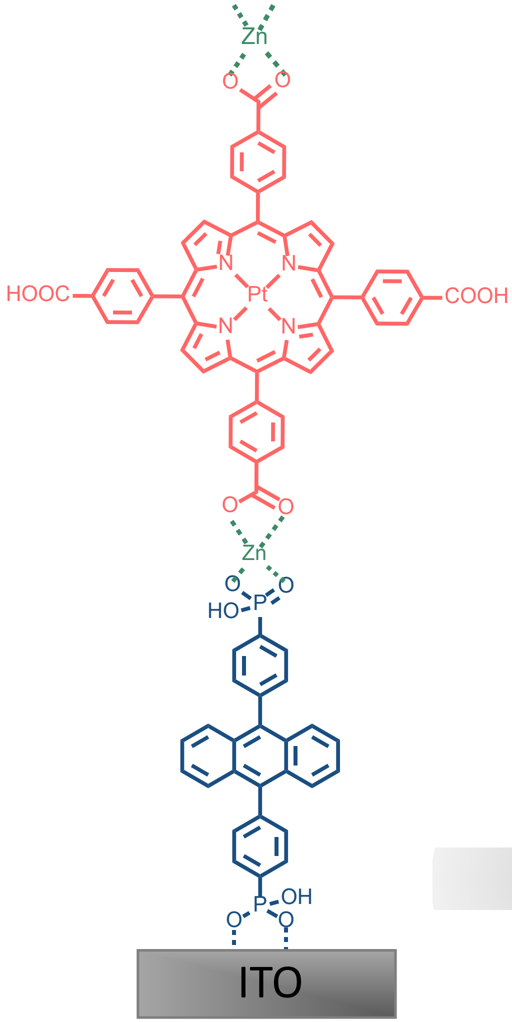


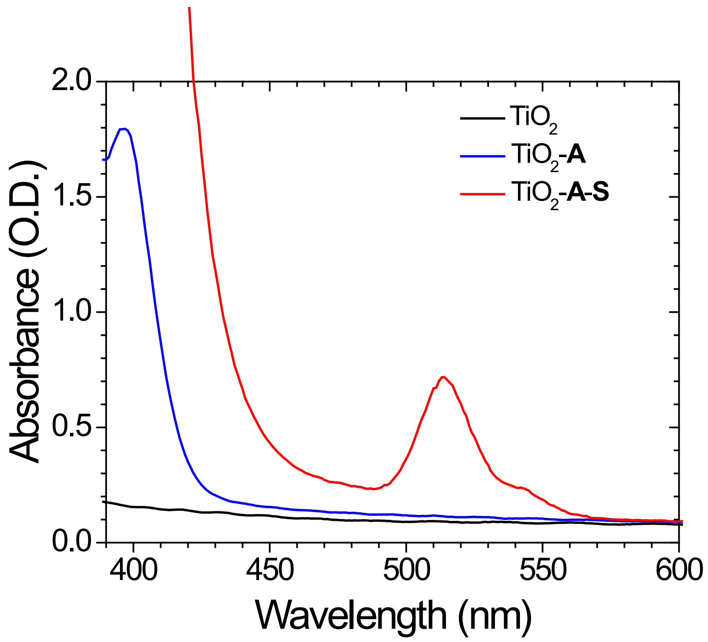


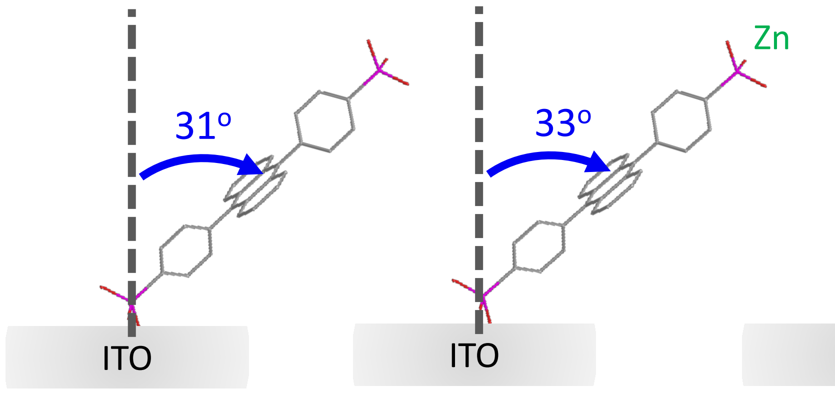
- Similar angle regardless of metal oxide.
- Binding group does not impact angle.
- Orientation dictated by molecular structure/packing.

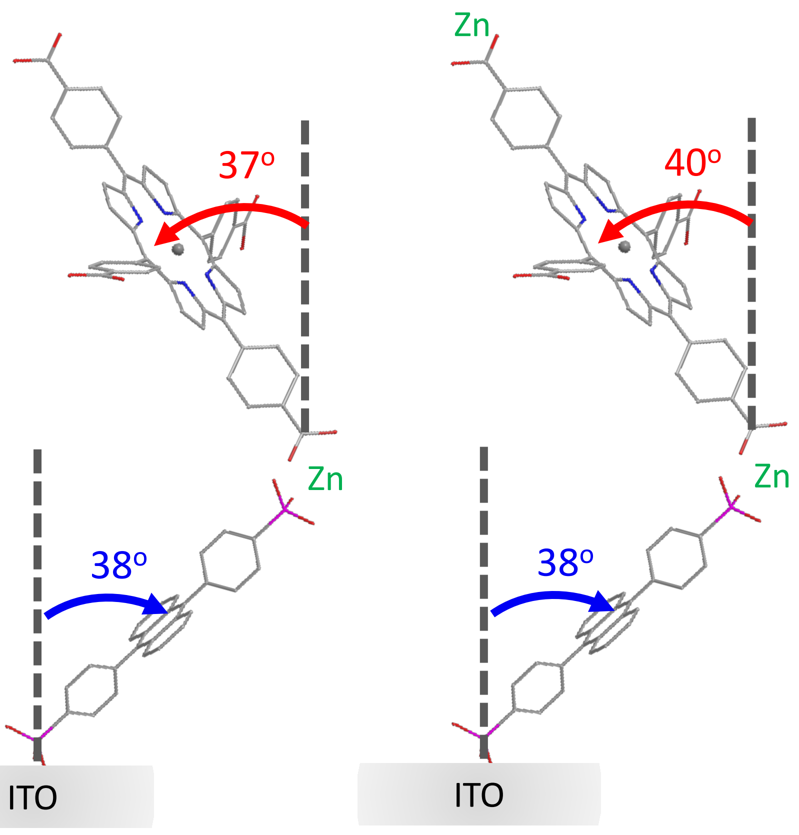


Multilayer Structure

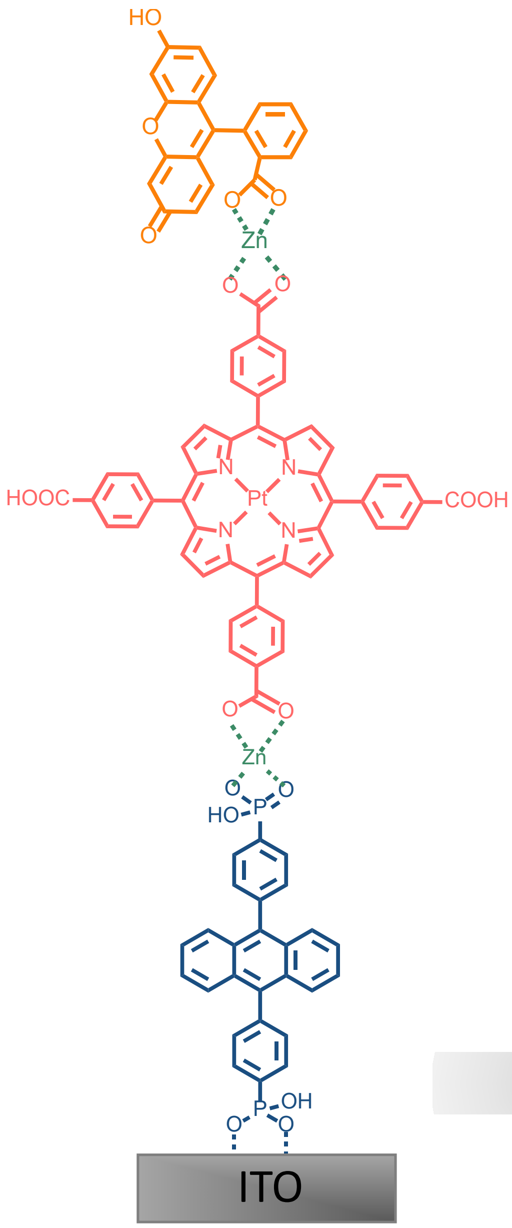


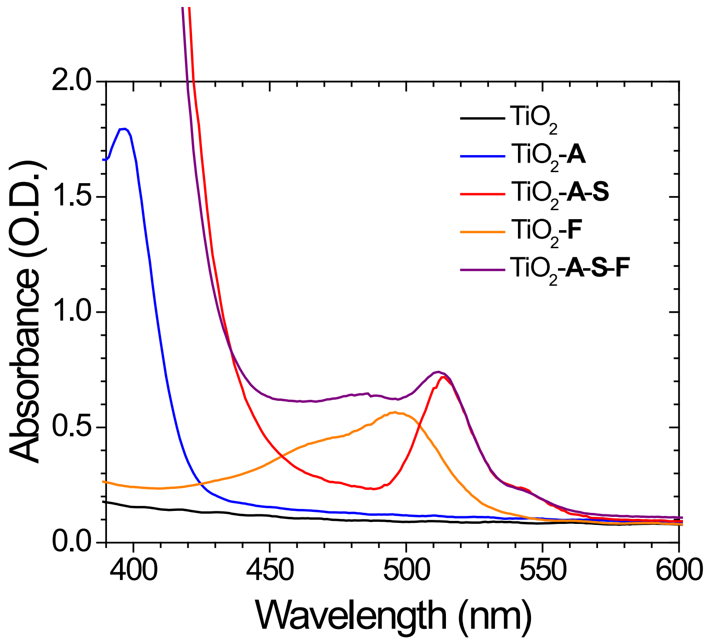




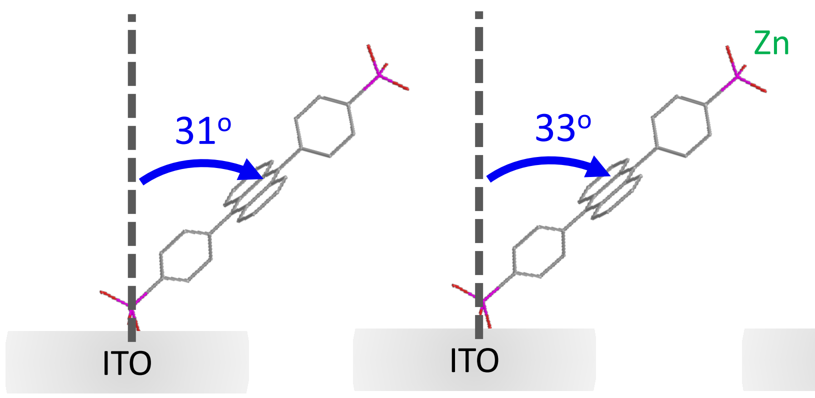
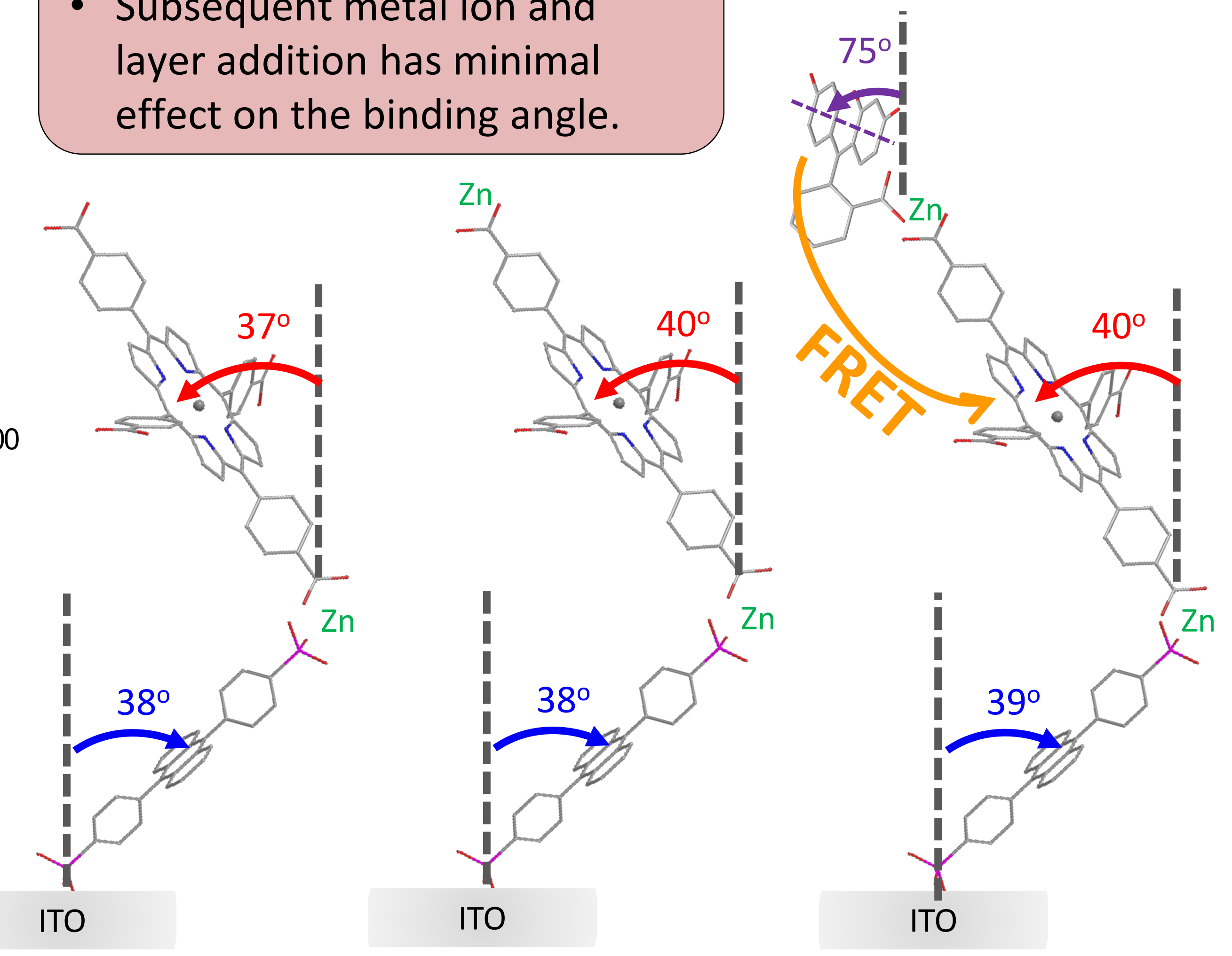


Multilayer Structure

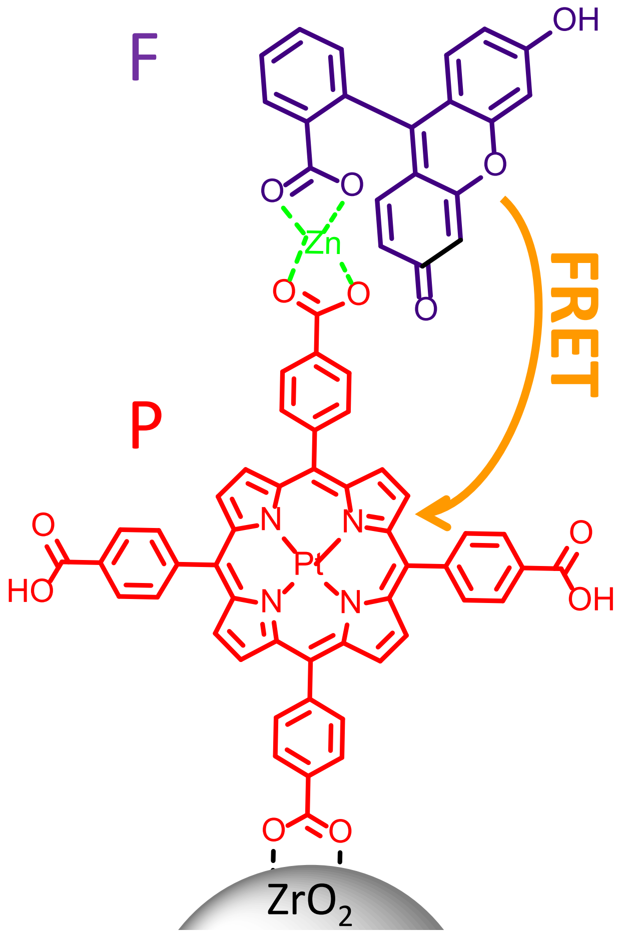


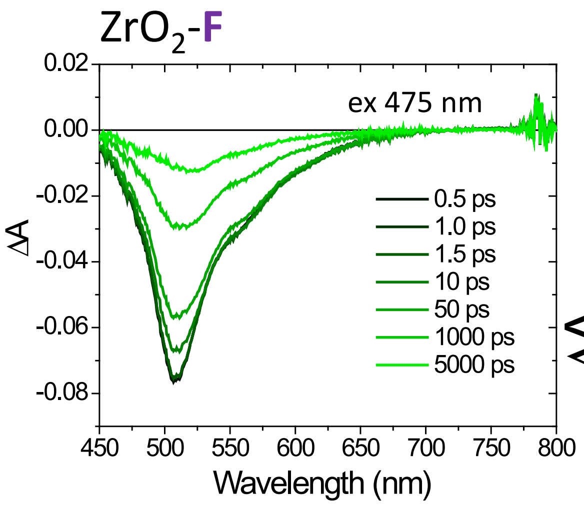


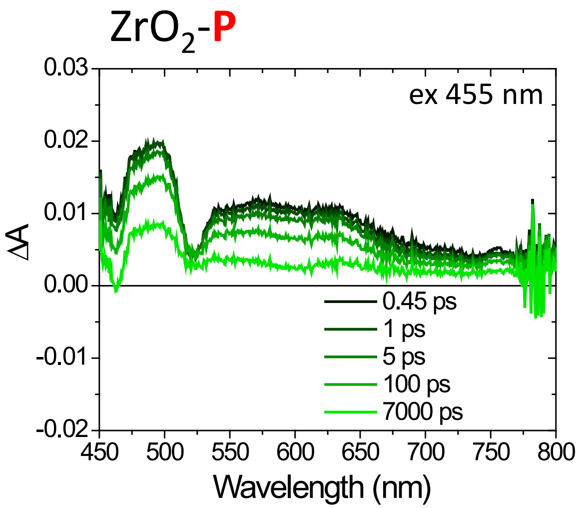
- First multi-chromohore by ATR.
- Subsequent metal ion and layer addition has minimal effect on the binding angle.

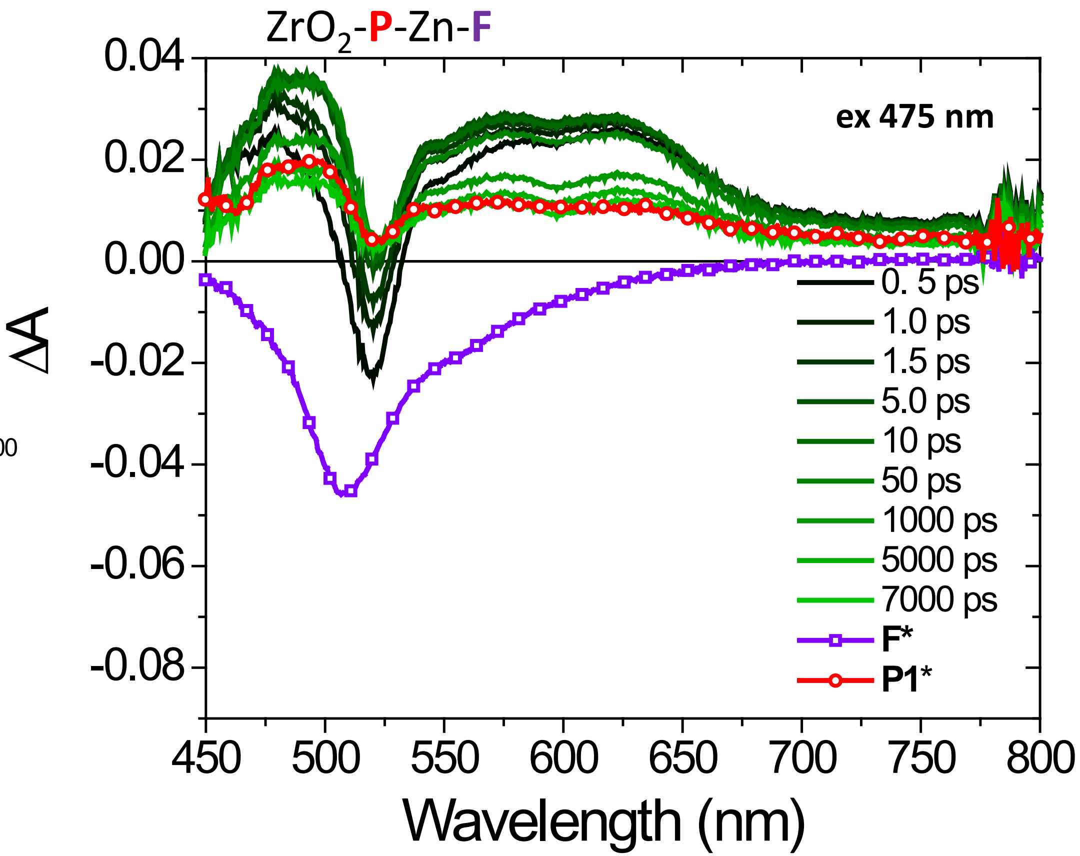



Structure and Energy Transfer





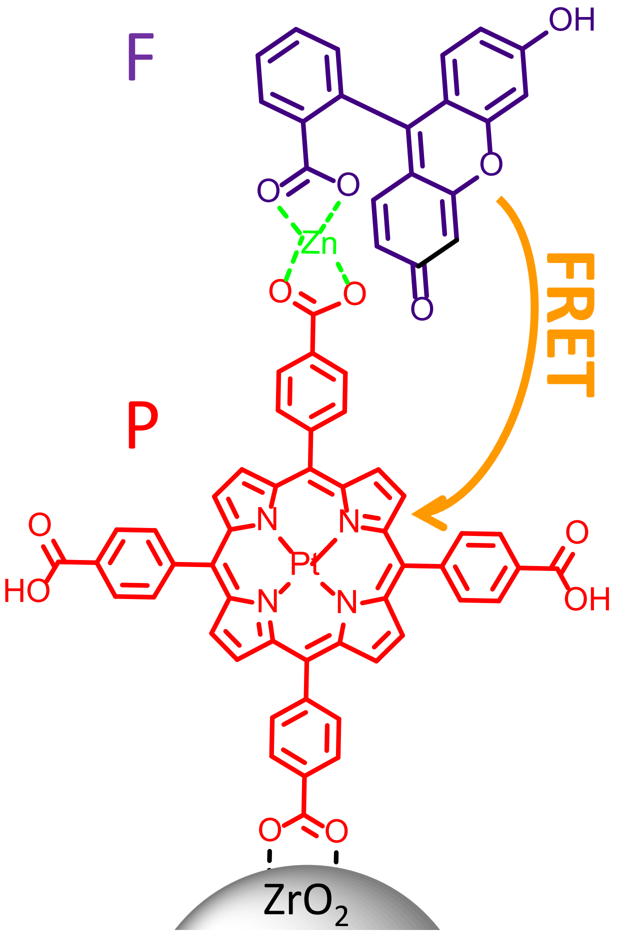




$$k_{ET} = \frac{1}{\tau_{bilayer}} - \frac{1}{\tau_P}$$

$k_{ET} = 3\times10^{11}\ s^{-1}$
$\Phi_{FRET} \approx 100\%$

Structure and Energy Transfer



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

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

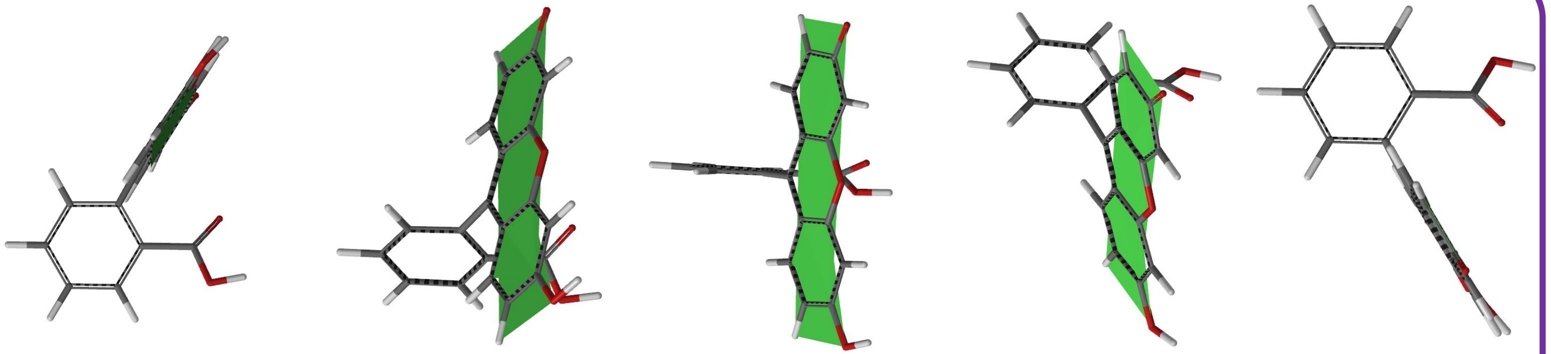
ϕ_D = fluorescence QY of F

n = refractive index

J = overlap integral

κ^2 = orientation factor

r = distance between F and P



$\Phi_{\text{FRET(calc)}}$ = >99% | >99% | >99% | >99% | >99%

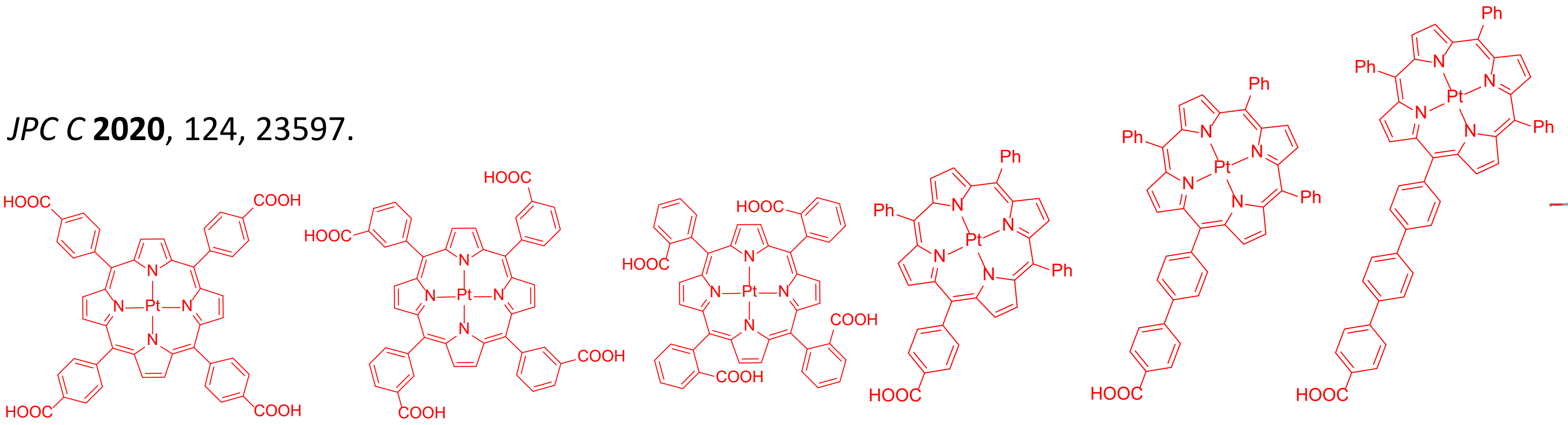
$$k_{ET} = \frac{1}{\tau_{bilayer}} - \frac{1}{\tau_P}$$

$k_{\text{ET}} = 3\times10^{11}\ s^{-1}$

$\Phi_{\text{FRET}} \approx 100\%$

Moving Forward: Controlling Energy Transfer

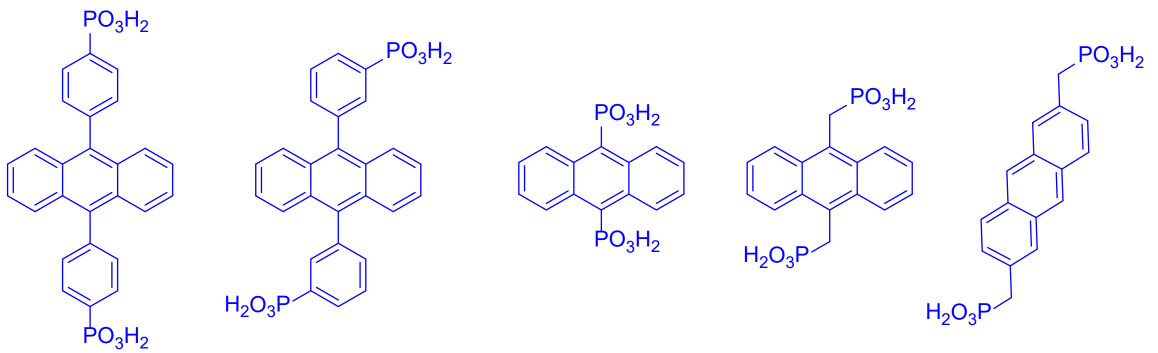
JPC C **2020**, 124, 23597.

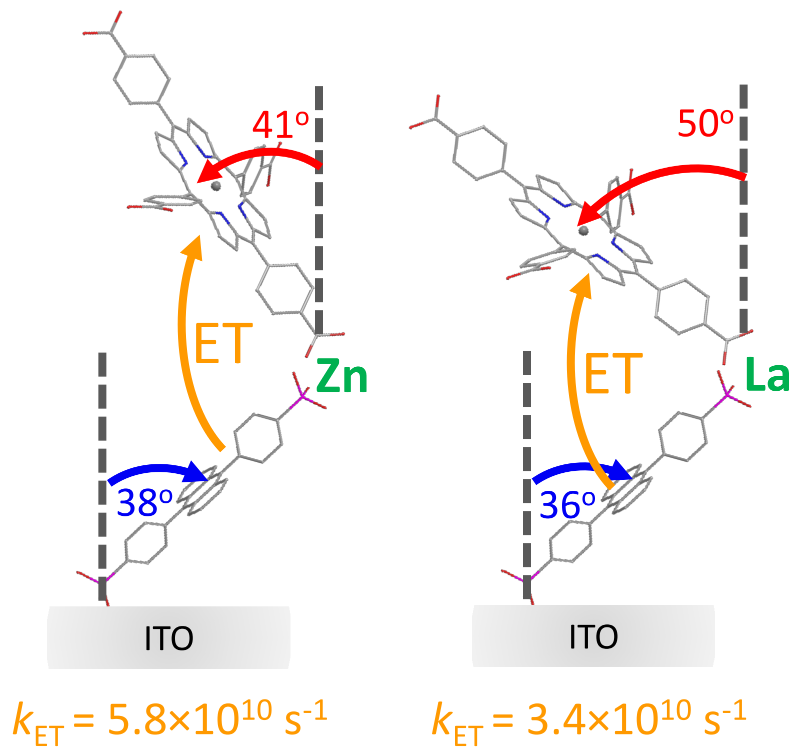


JPC C **2018**, 122, 9835.
Langmuir **2017**, 33, 9609.

Cd^{II} Cu^{II} Fe^{II} La^{III} Mn^{II} Sn^{IV} Zr^{IV} Zn^{II}

JPE **2017**, 8, 022004.
PCCP **2018**, 20, 20513.

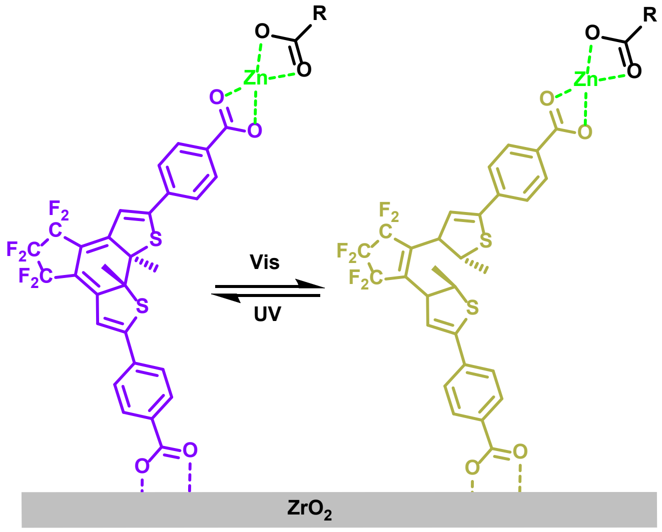


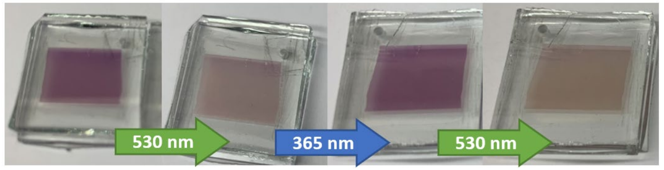


MO_2

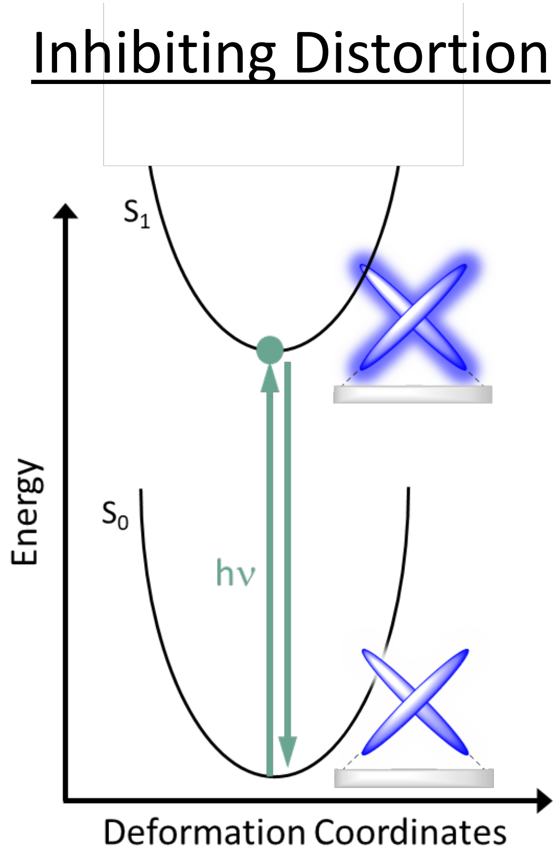
Moving Forward: Controlling Structure

Molecular Switches



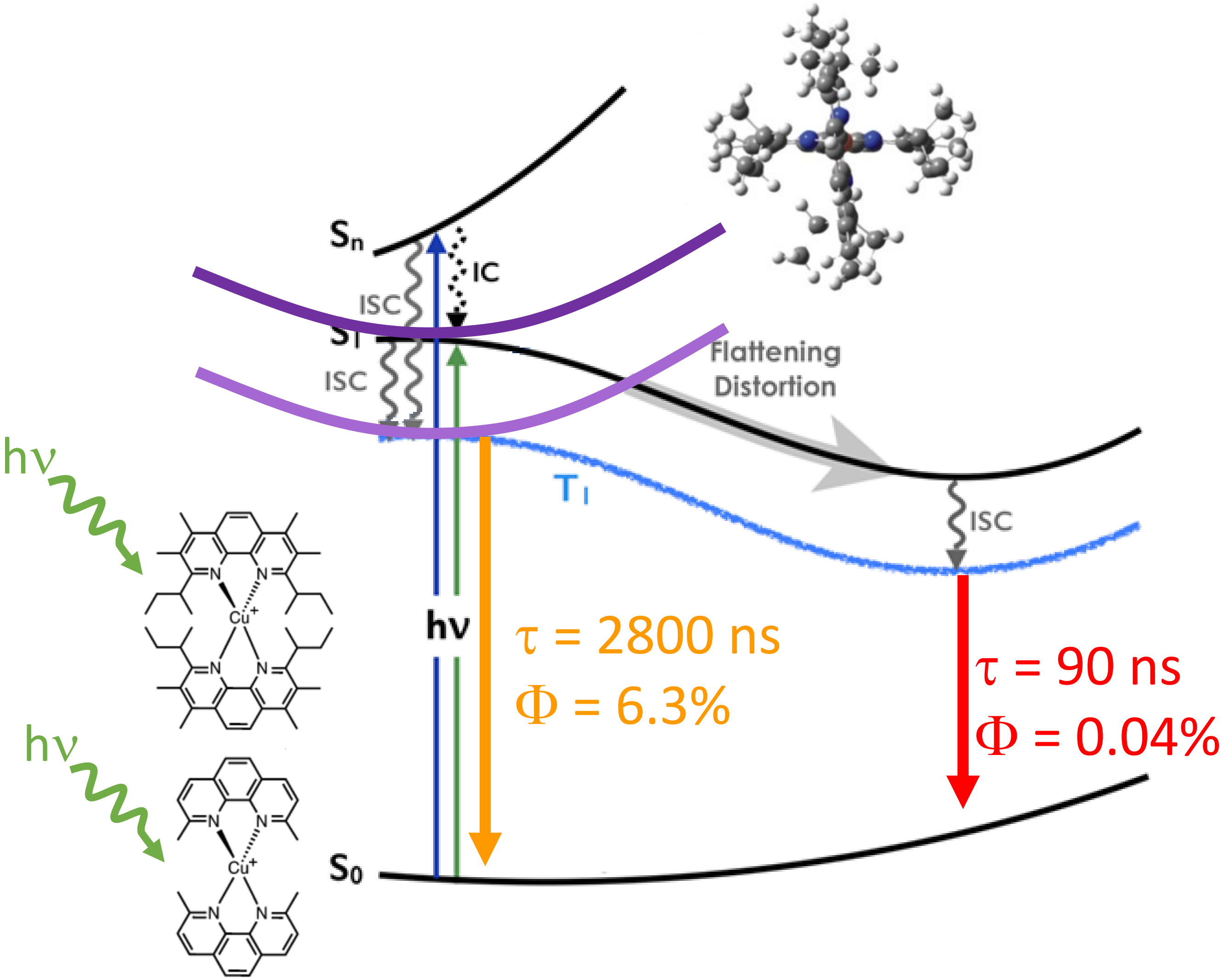


Inhibiting Distortion

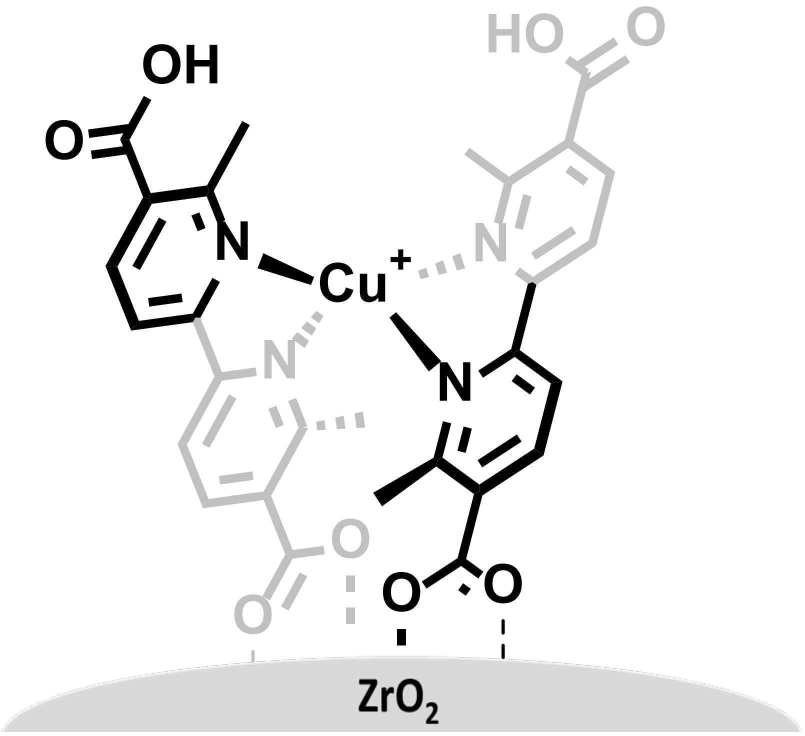


Inhibiting Distortion

Steric Bulk



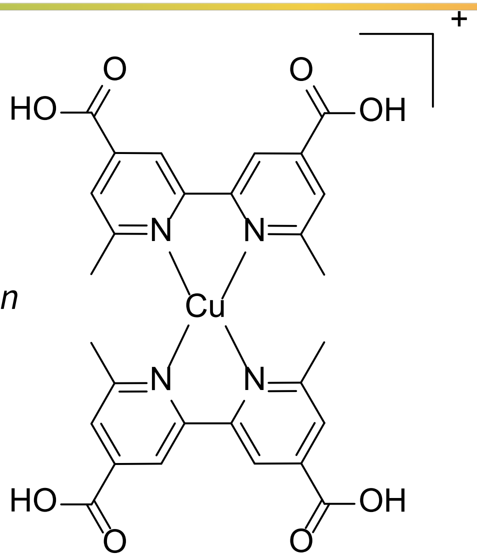
Strategic Surface Binding

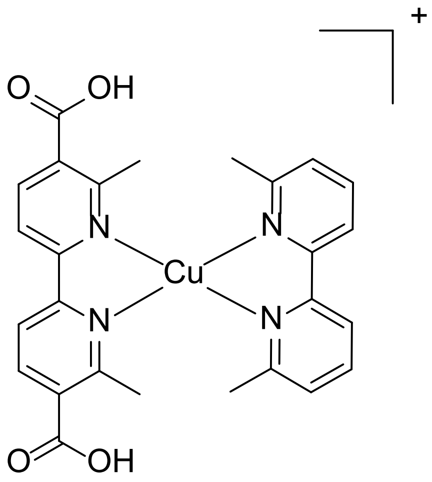


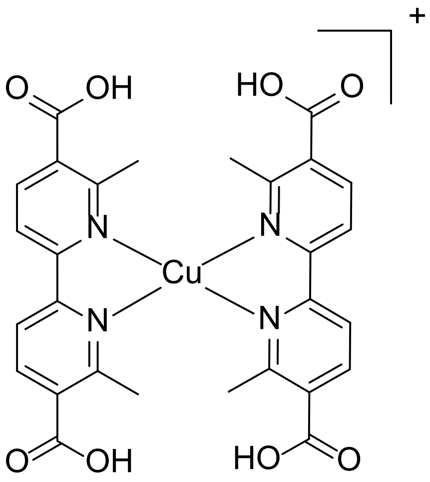
J. Phys. Chem. A **2015**, 119, 13, 3181–3193

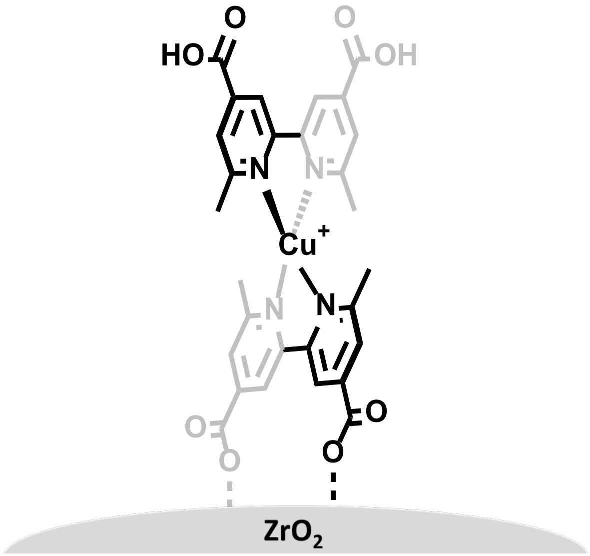
Strategic Surface Binding

Constable et al. *Dalton Trans.* **2009**, 6634









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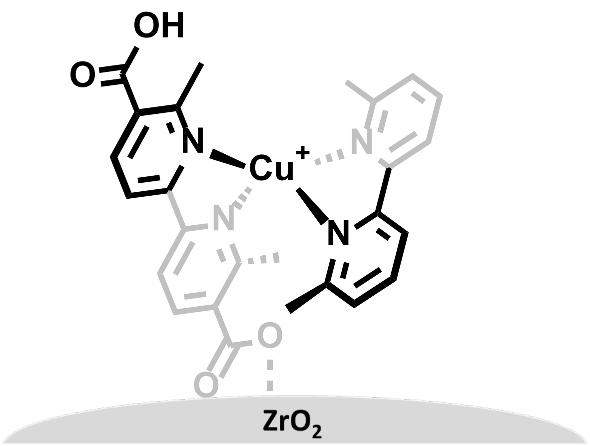

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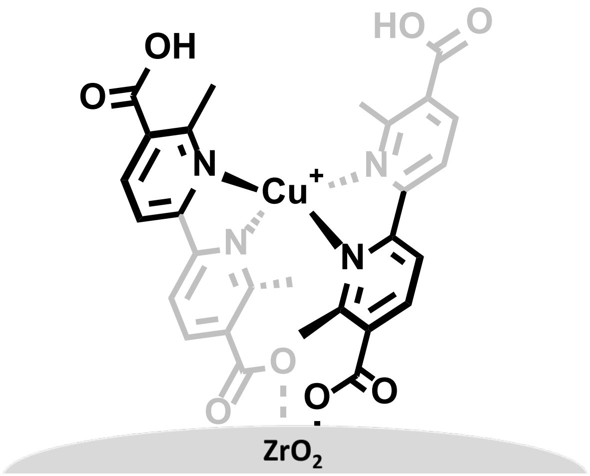
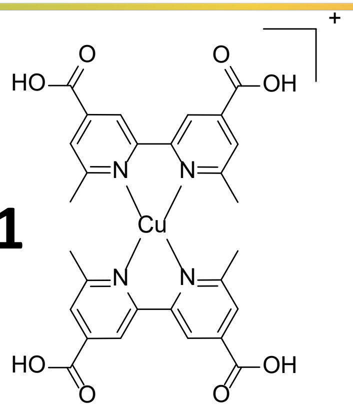


3

Transient Absorption

1



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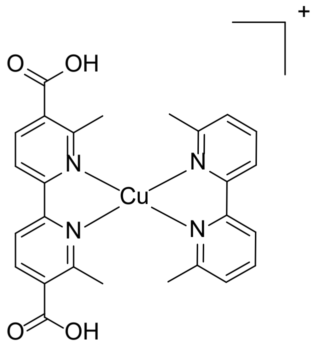

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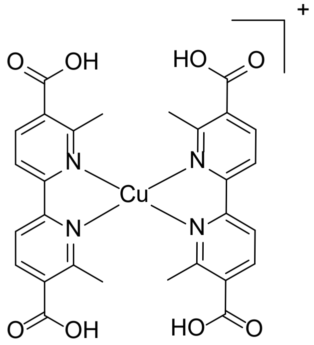
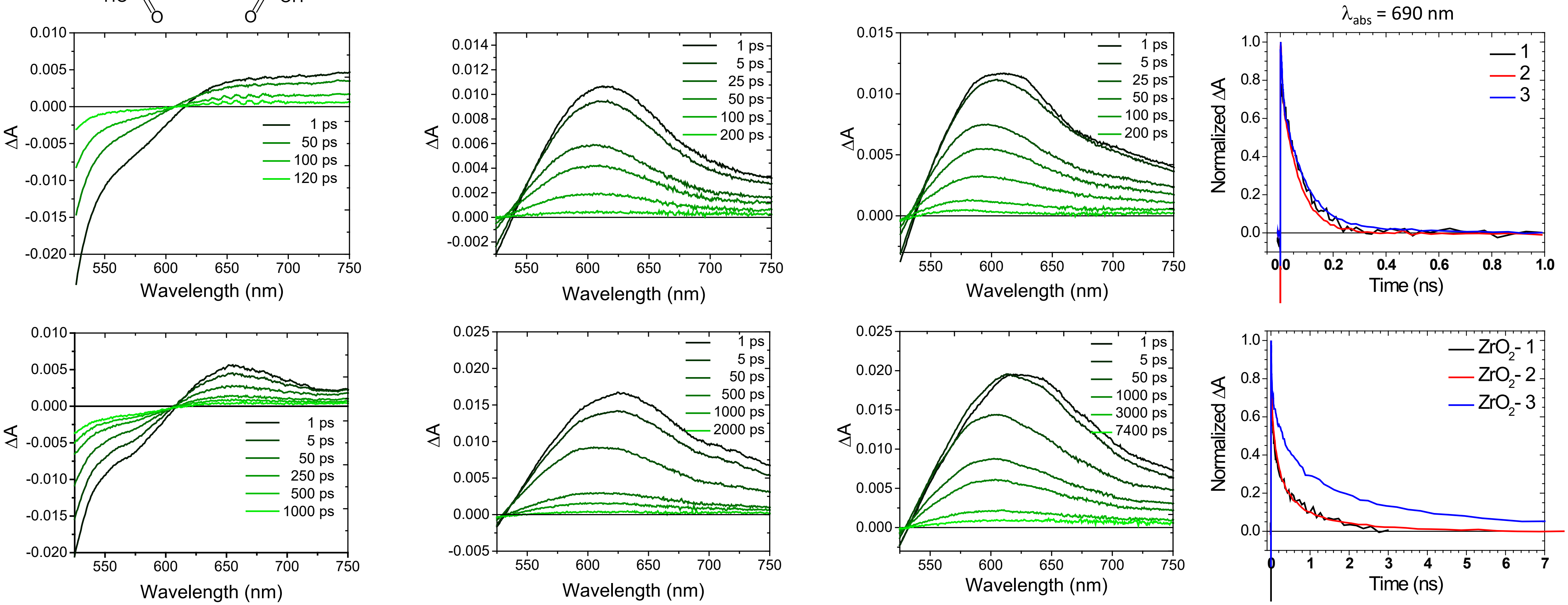


In MeOH

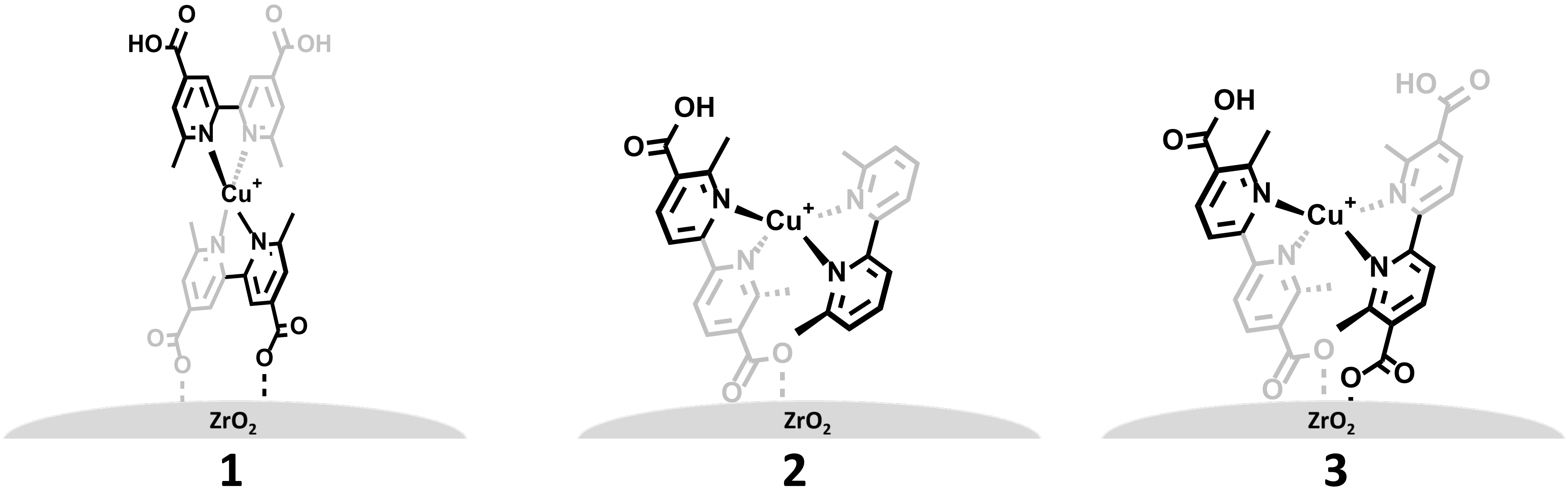
λ_{ex} = 500 nm

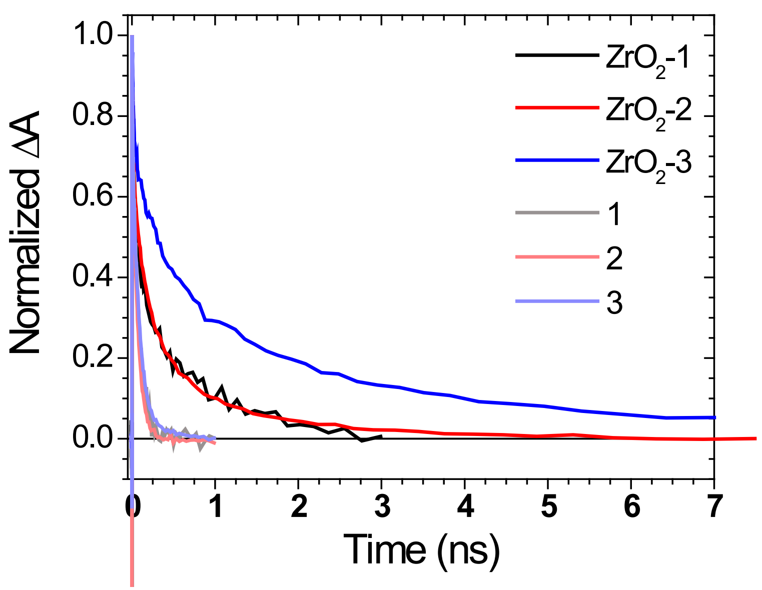
On ZrO_2 in MeOH

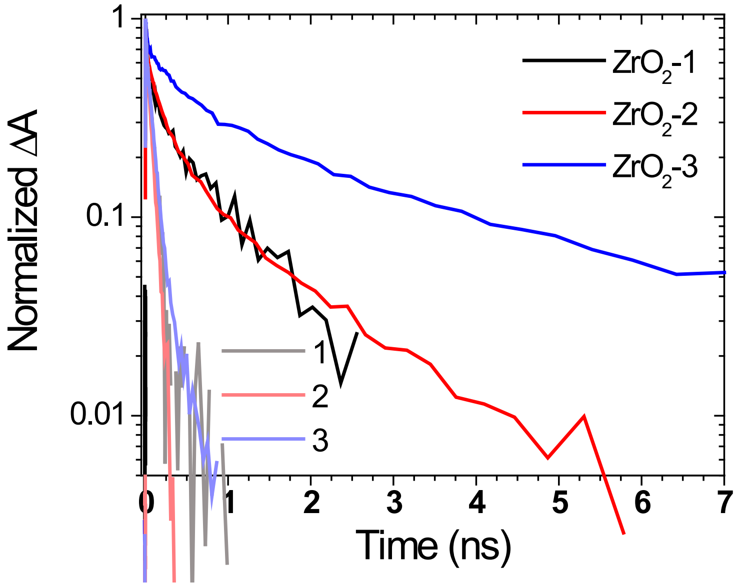
λ_{ex} = 500 nm



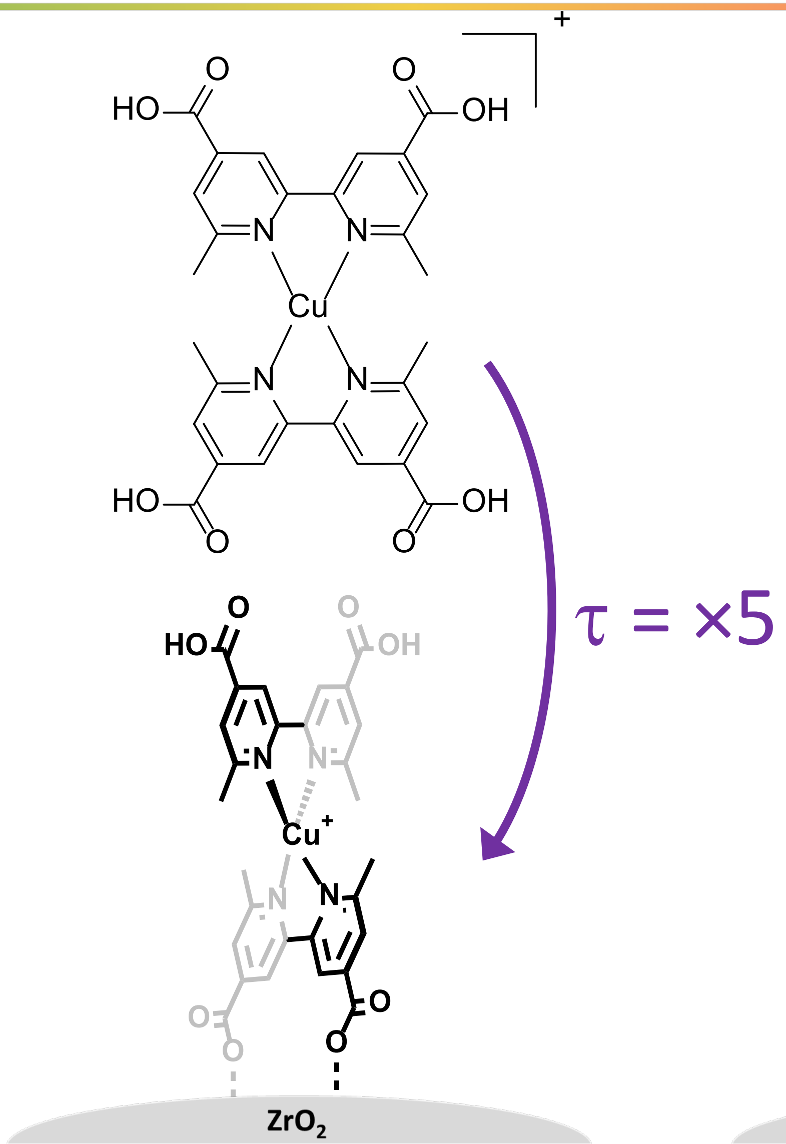
Decay Kinetics







Strategic Surface Binding



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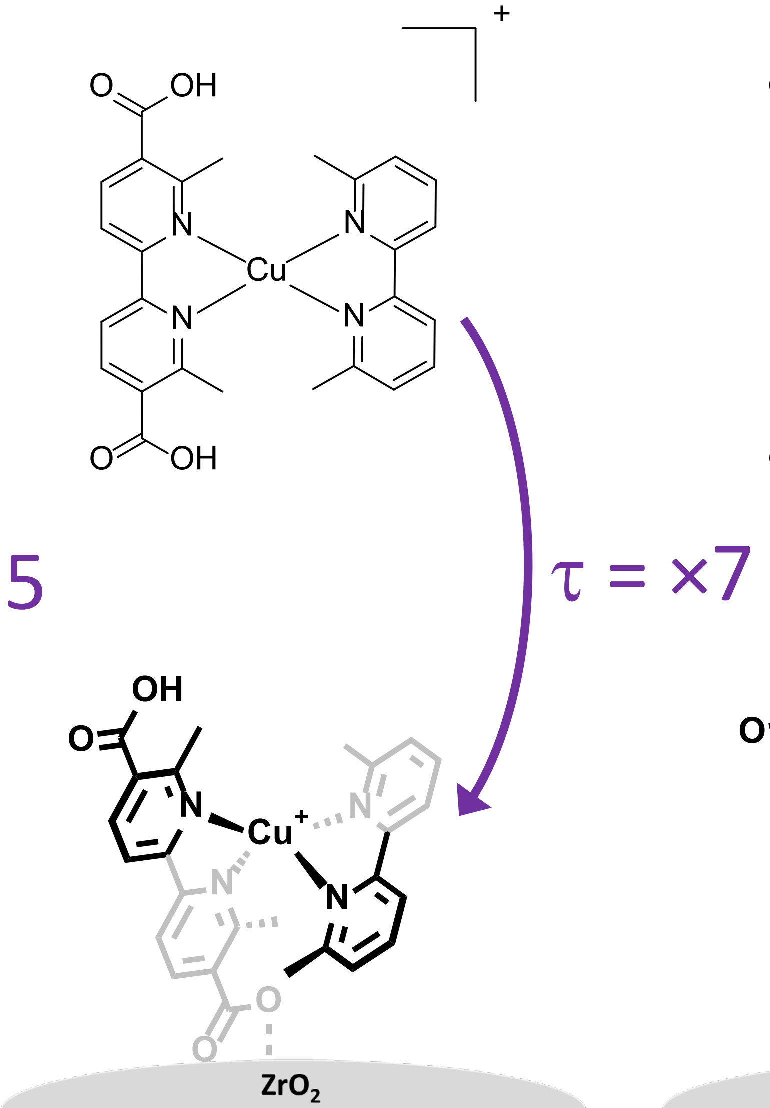

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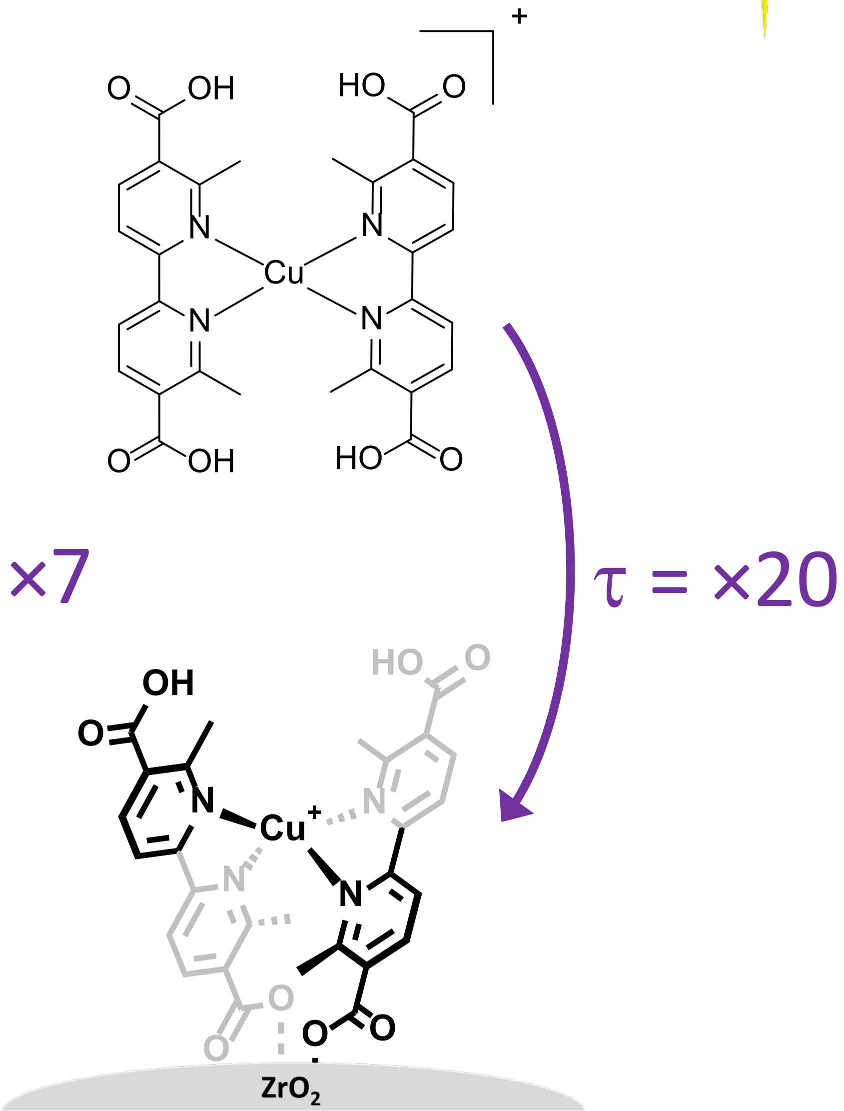
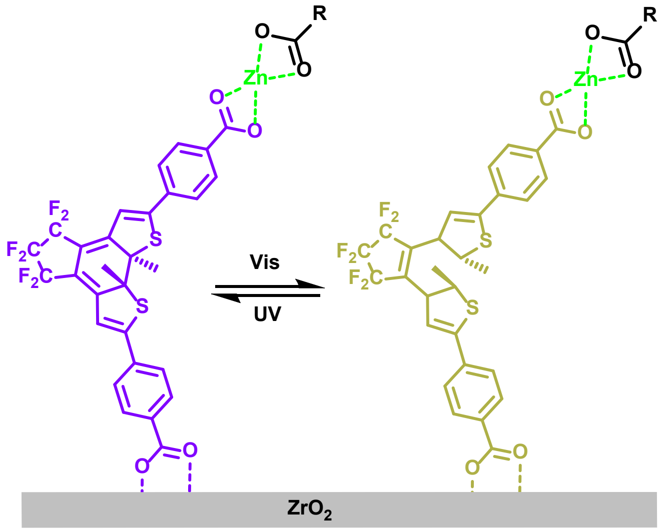
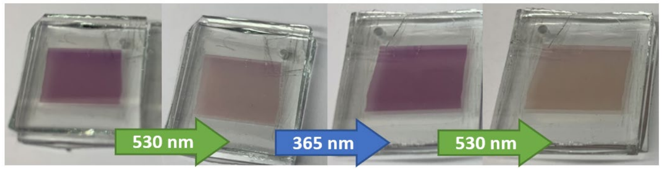


3

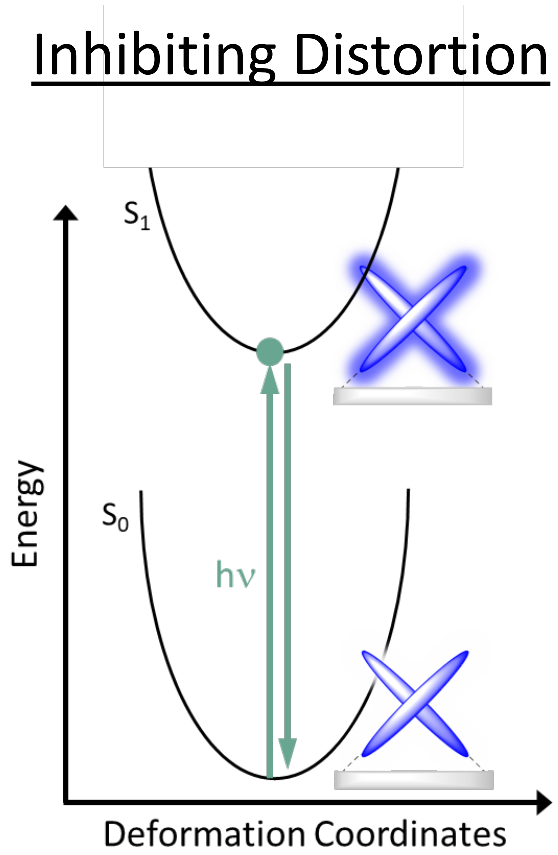
Moving Forward: Controlling Structure

Molecular Switches

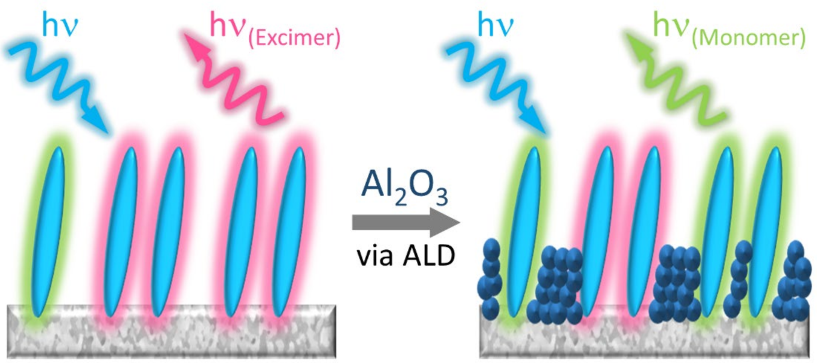




Inhibiting Distortion

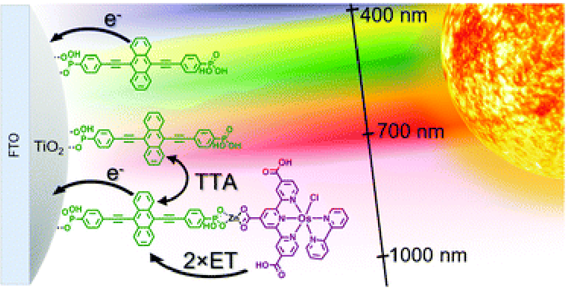


Atomic Layer Deposition

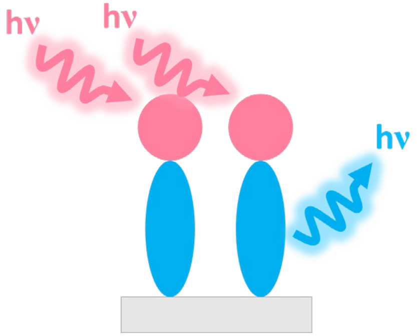


Controlling Intermolecular Interactions

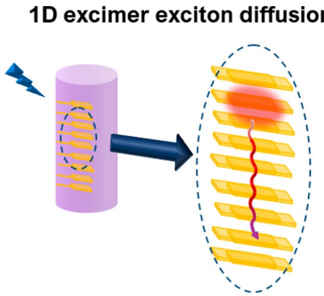
Up-Conversion



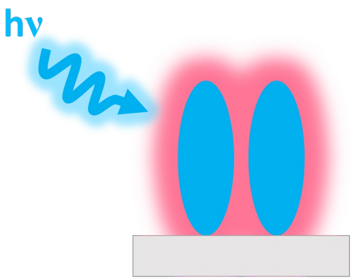
Beery, D. et al. *J. Mater. Chem. C.* **2022**.



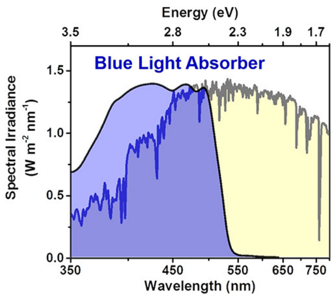
Excimer Emission

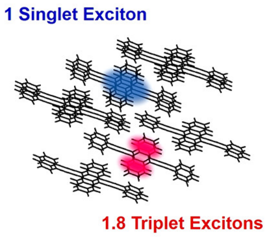


Myong, M. S., et al. *J. Phys. Chem. C.* **2021**.

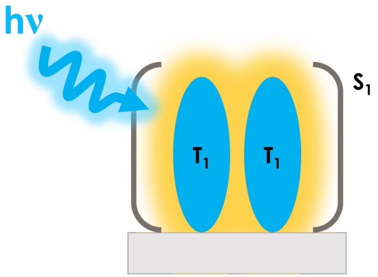


Singlet Fission

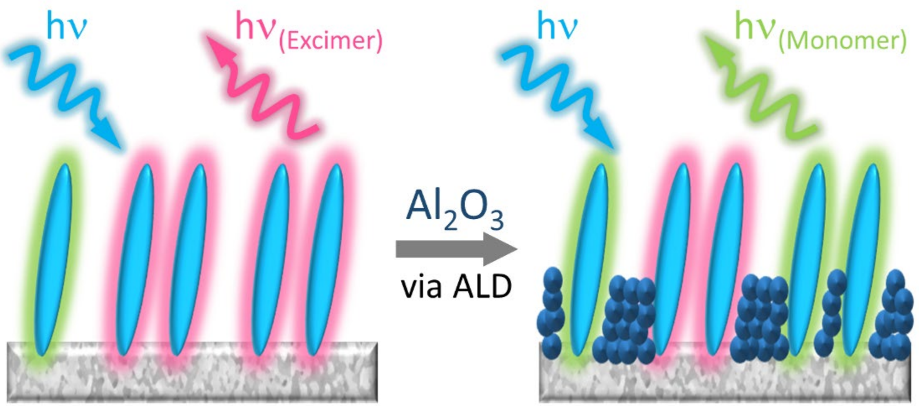




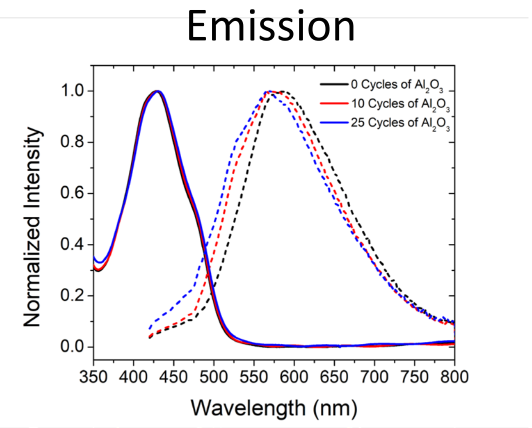
Bae, Y. J., et al. *J. Am. Chem. Soc.* **2018**.

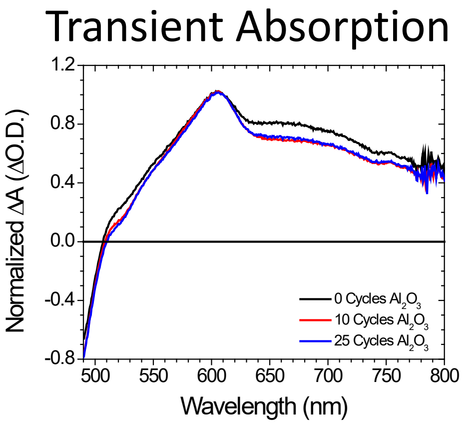


Atomic Layer Deposition



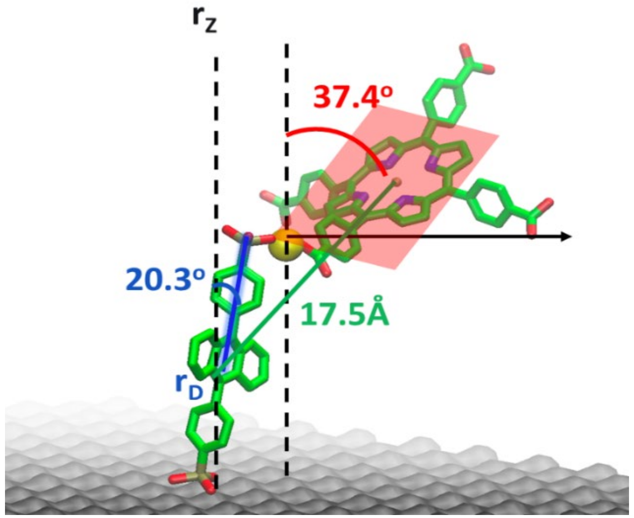
Knorr et. al. *Molecules* **2023**, 28, 4835.

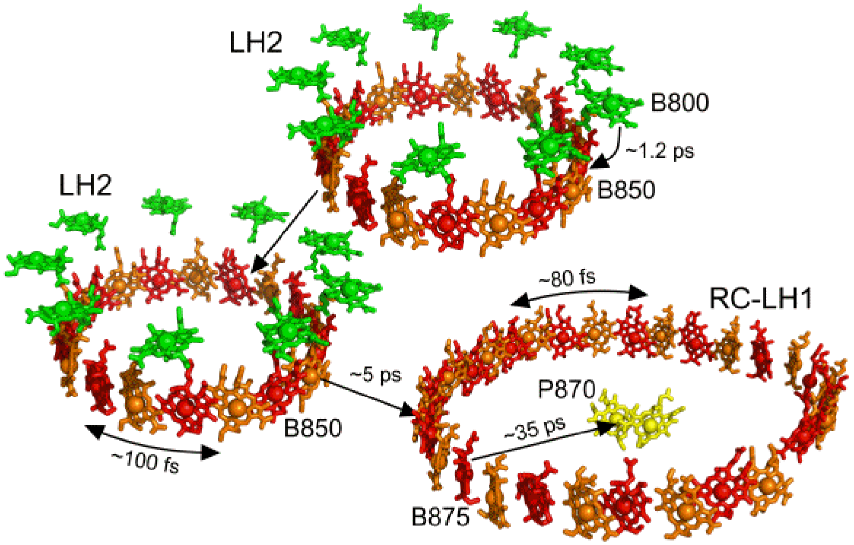




Conclusions

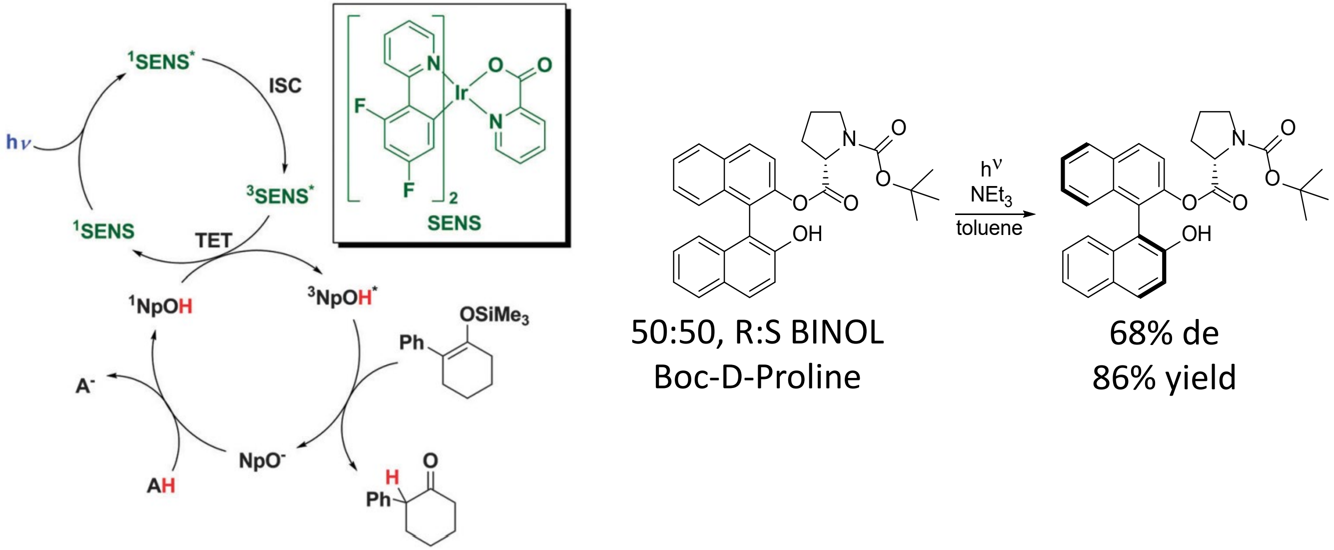
- TTA-UC Emission
  - On ZrO_2: Blue to green upconversion
  - Quadratic to Linear Behavior
- TTA-UC Solar Cell
  - Improvements with component selection
  - J_{UC} up to 315 μA/cm^2
  - Structure matters
- Determine Structure (polarized ATR)
  - 1st layer orientation is MO_x independent
  - 2nd layer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



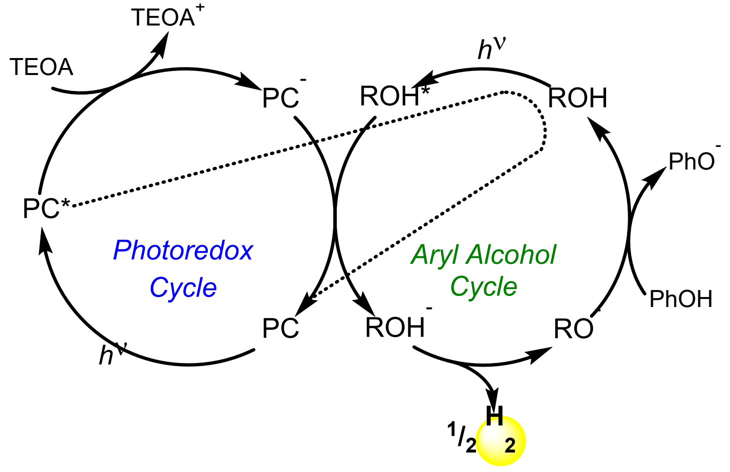


Other Projects

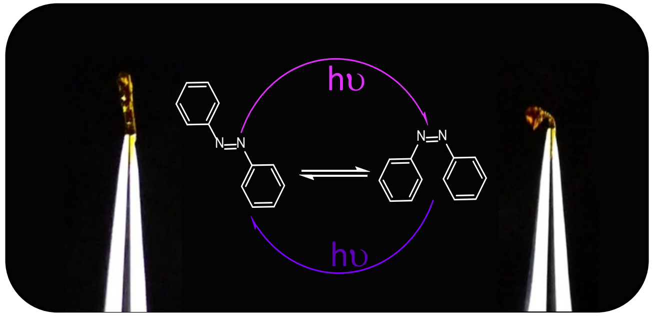
ES Proton Transfer Catalysis/Enrichment

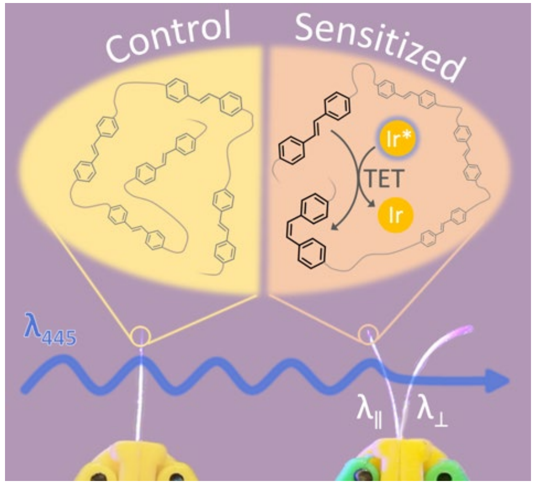


H_2 Generation Z-Scheme

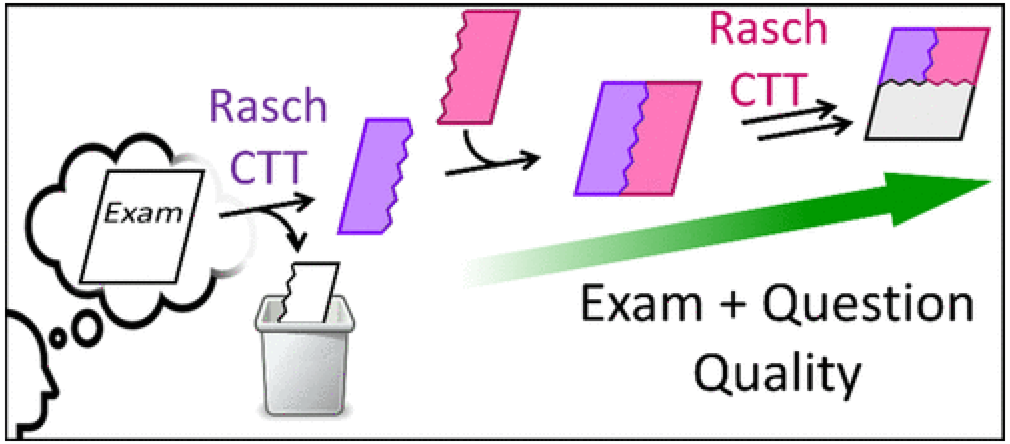


Photomechanical Polymers





Using IRT and CCT to Analyze Exams



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Not Pictured Contributors

- Dr. Sean Hill
- Dr. Tristan Dilbeck
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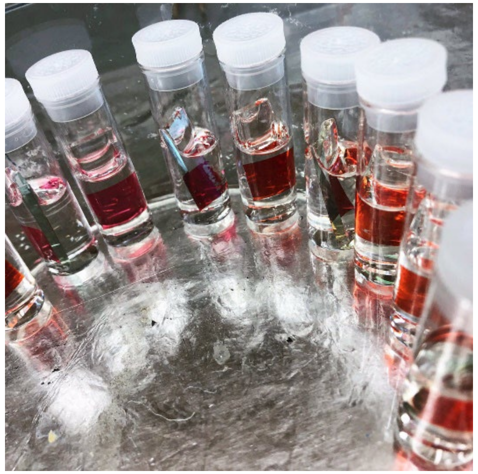
- Cory Ruchlin (McGill)
- Jonathan Wheeler (NCSU)
- Cody Basquill (FSU)
- Ethan Lambert (FSU)
- Dominic Willadsen (REU)

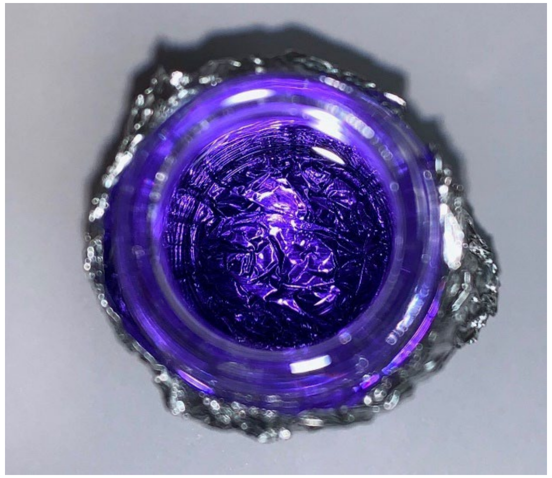
Collaborators

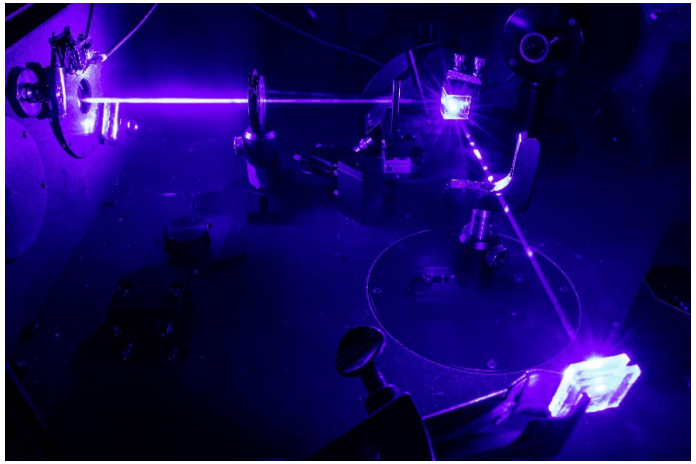
- Dr. Raaj Winfred
- Dr. Wei Yang
- Dr. Scott Saavedra

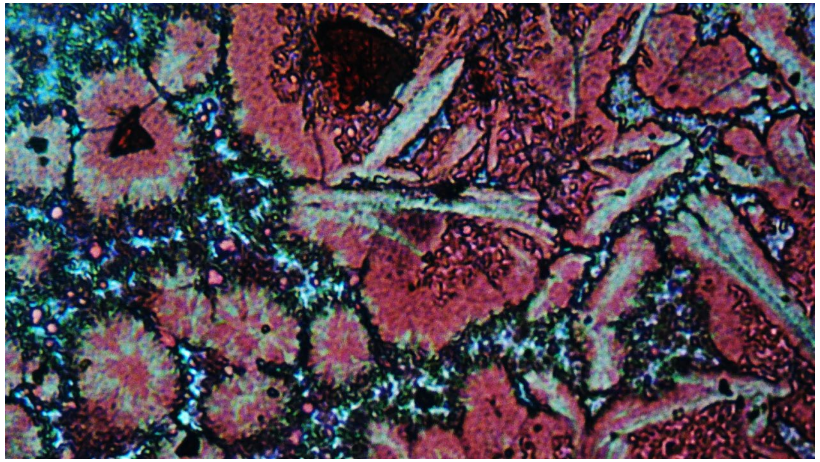
Hanson
Research Group

Questions?









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