Molecular Approaches to Solar Energy Conversion

Michael R. Wasielewski

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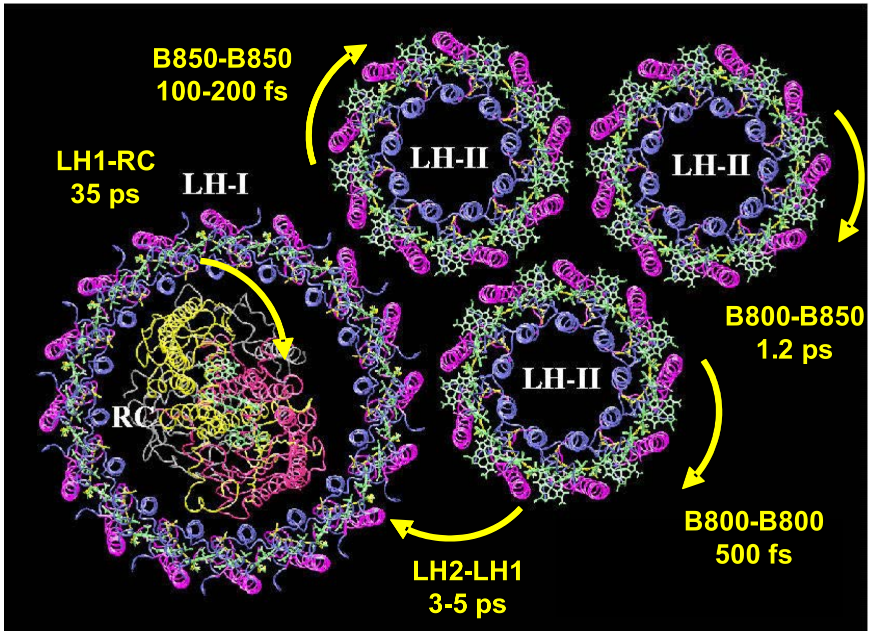
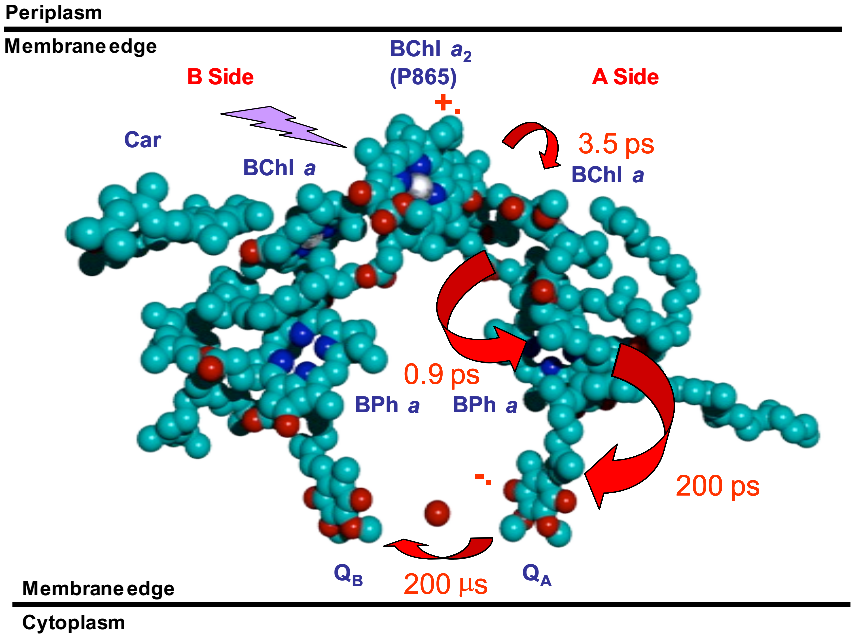
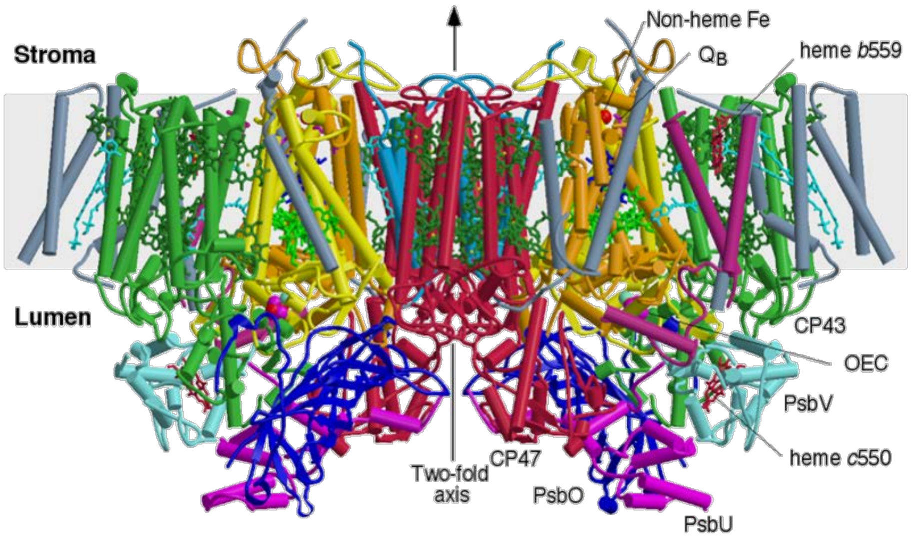
Photosynthesis: Self-assembly Provides Emergent Function







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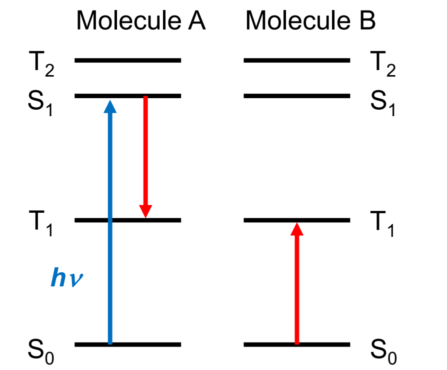
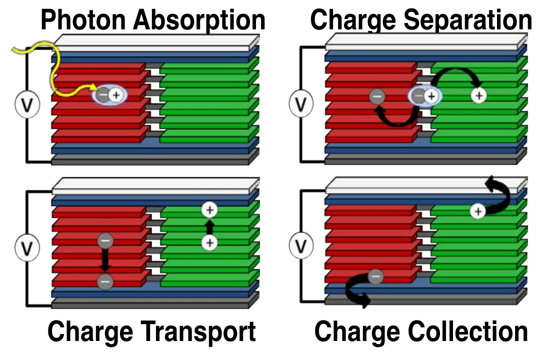
Topics for Discussion

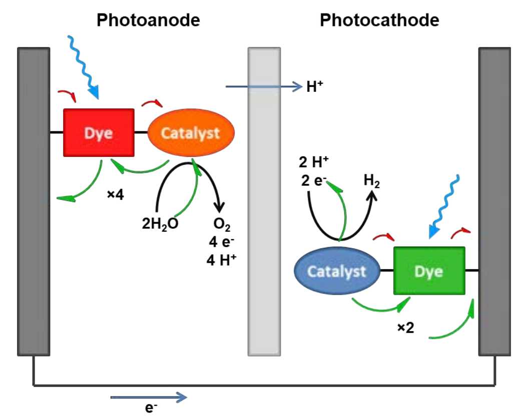
- **Light Harvesting:**
  Singlet fission in molecular materials can generate two excited triplet states from one singlet state that can greatly improve use of the solar spectrum to enhance charge generation yields.



- **Charge Separation and Transport:**
  Self-assembly is used to prepare molecular materials in which photo-generated charge can be transported long distances.



- **Photodriven Catalysis:**
  New photosensitizers that can deliver charge at high potentials to catalysts to carry out energy-demanding reactions.



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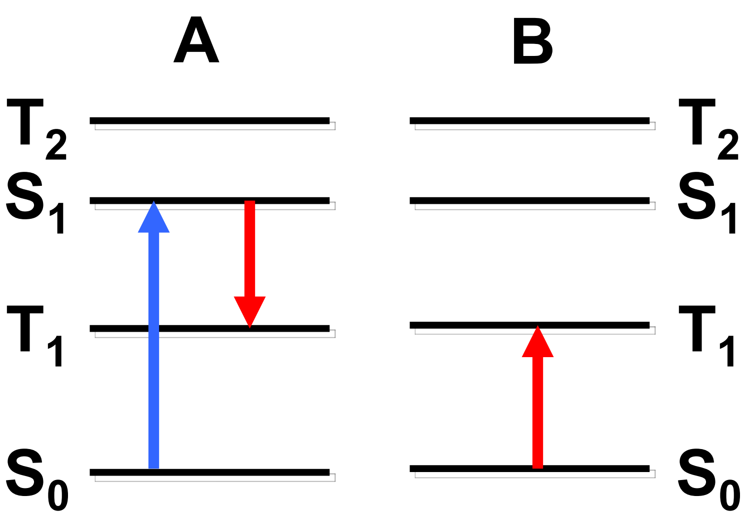
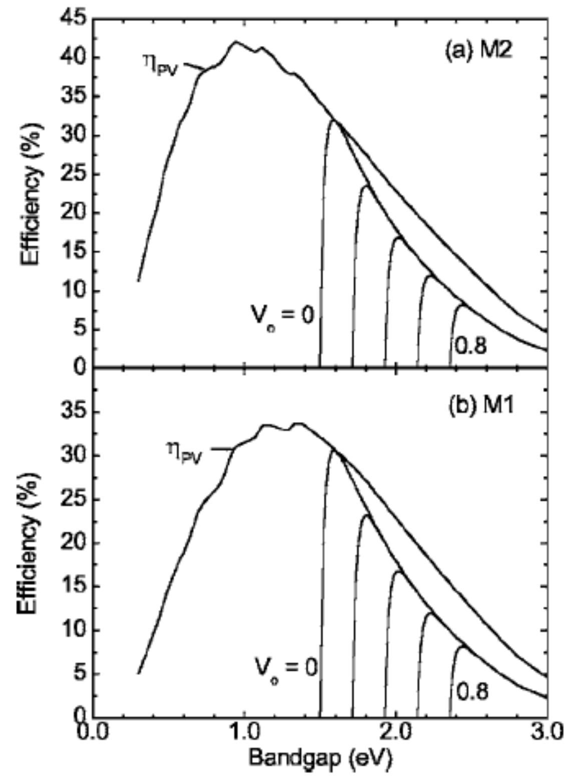
Light Harvesting:
Singlet Exciton Fission (SF)

Originally observed in anthracene and tetracene by Siebrand, Schneider, Swenberg, Pope, and Geacintov: 1965-1969.



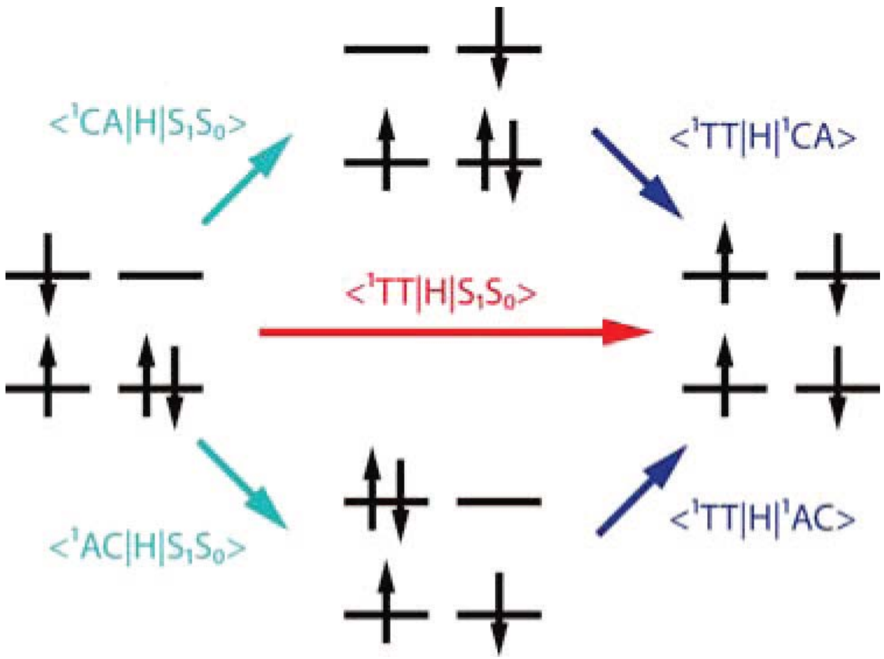
- $E(S_1) > 2E(T_1)$
- $E(T_2) > 2E(T_1)$
- **Optimized Electronic Coupling**
- $k(TT_{sep}) >> k(TT_{annih})$

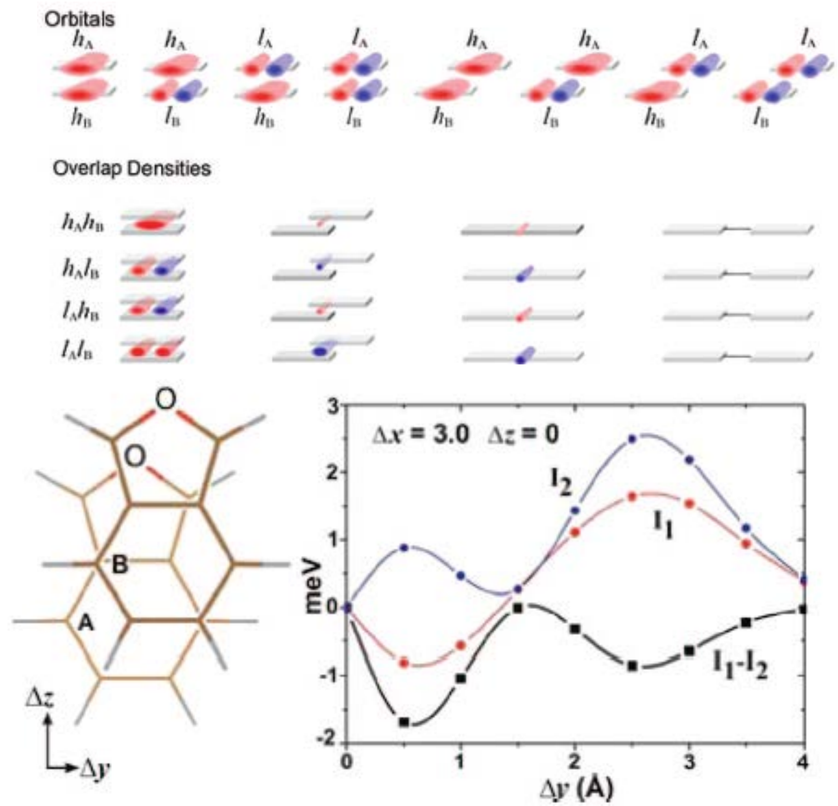


SF can increase the efficiency of solar cells from 33% to 45%

Hanna, M.C.; Nozik, A.J. *J. Appl. Phys.* 2006, *100*, 074510.

Singlet Fission Mechanisms





$$[\ {}^1(S_1S_0) \leftrightarrow CT \leftrightarrow {}^1(T_1T_1)\ ] \rightarrow {}^1(T_1T_1) \rightarrow T_1 + T_1$$

$$\searrow \quad {}^{3,5}(T_1T_1) \quad \nearrow$$

Smith *et al. Chem. Rev.* 2010, *110*, 6891; Greyson *et al. J. Phys. Chem. B* 2010, *114*, 14168; Burdett and Bardeen, *Acc. Chem. Res.* 2013, *46*, 1312; Zimmerman *et al. J. Am. Chem. Soc.* 2011, *133*, 19944; Scholes, G. D. *J. Phys. Chem. A* 2015, *119*, 12699; Kolomeisky et al. *J. Phys. Chem. C* 2014, *118*, 5188.

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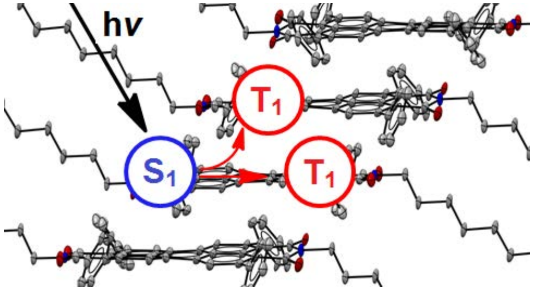
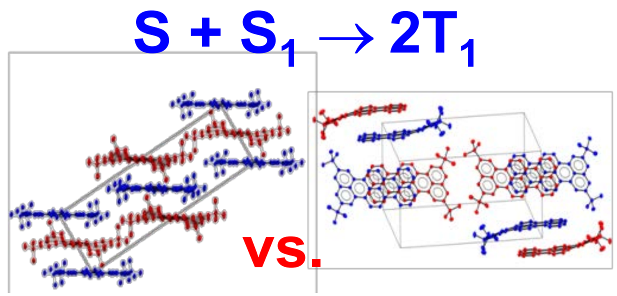
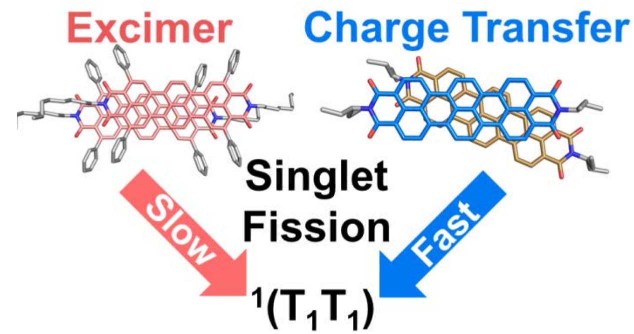
Singlet Fission Mechanisms: Recent Examples



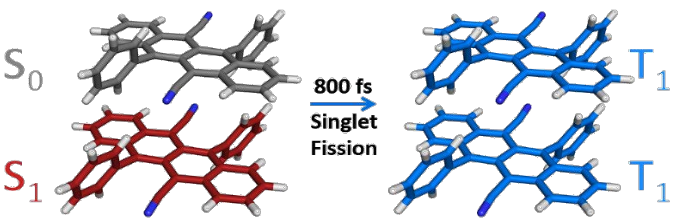
J. Am. Chem. Soc. 135, 14701-14712 (2013).



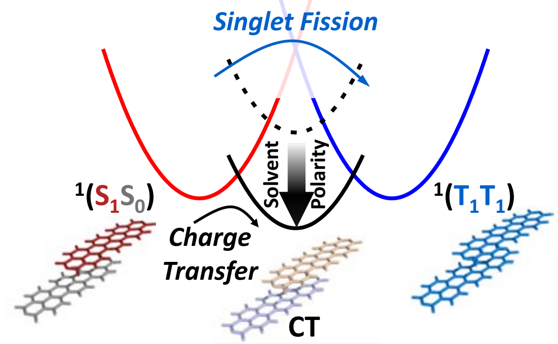
J. Phys. Chem. A 119, 4151-4161 (2015).



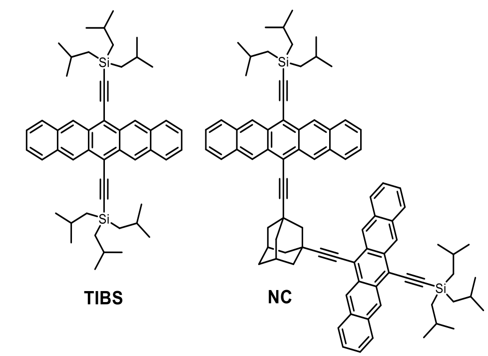
J. Am. Chem. Soc. 139, 663-671 (2017).



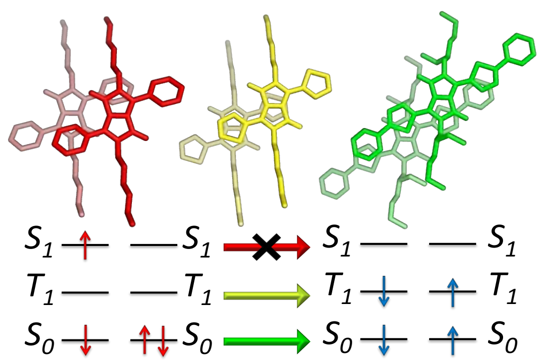
Angew. Chem. Int. Ed. 54, 8679-8683 (2015).



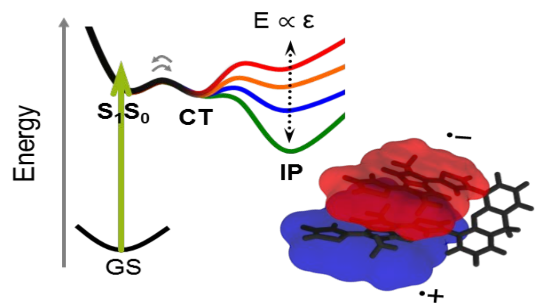
Nat. Chem. 8, 1120-1125 (2016).



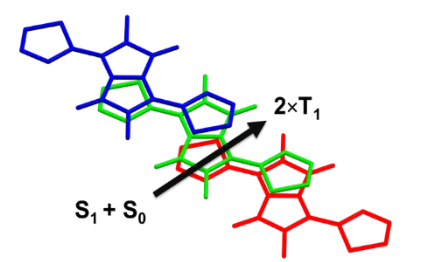
Nat. Comm. 8, 15171 (2017).



J. Phys. Chem B 120, 1357-1366 (2016).



J. Am. Chem. Soc. 138, 11749–11761 (2016).



ChemPhotoChem 2, 223-233 (2018).

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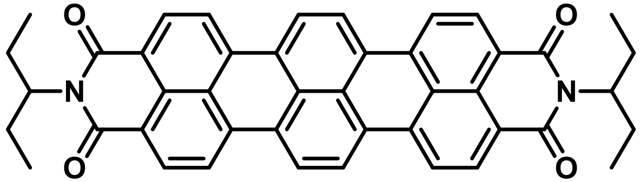
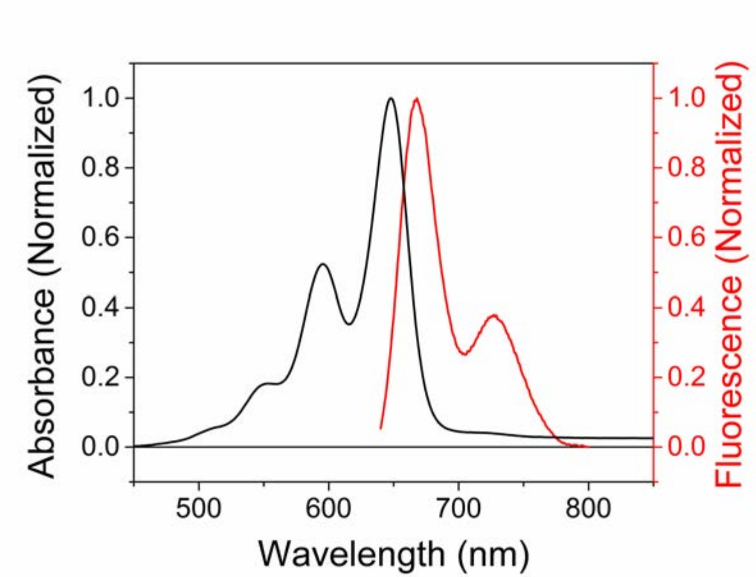
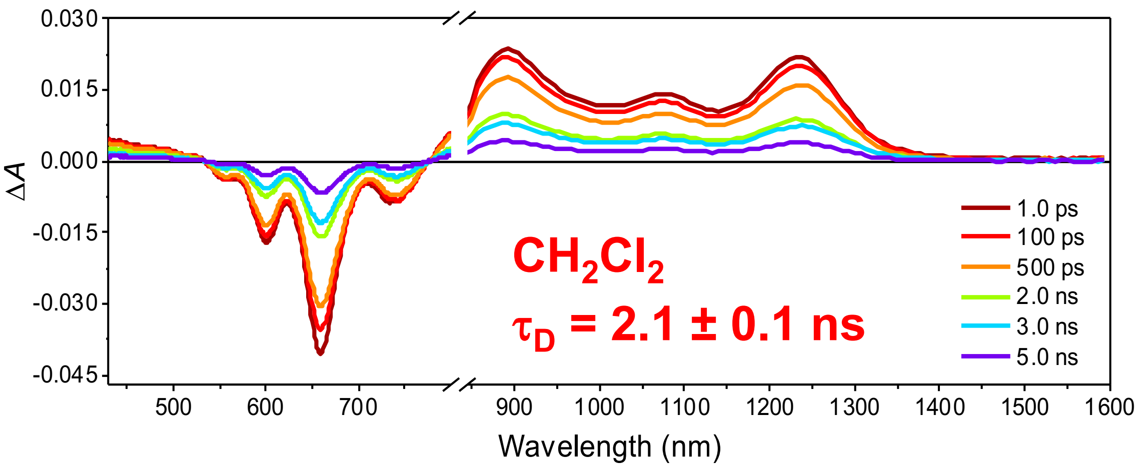
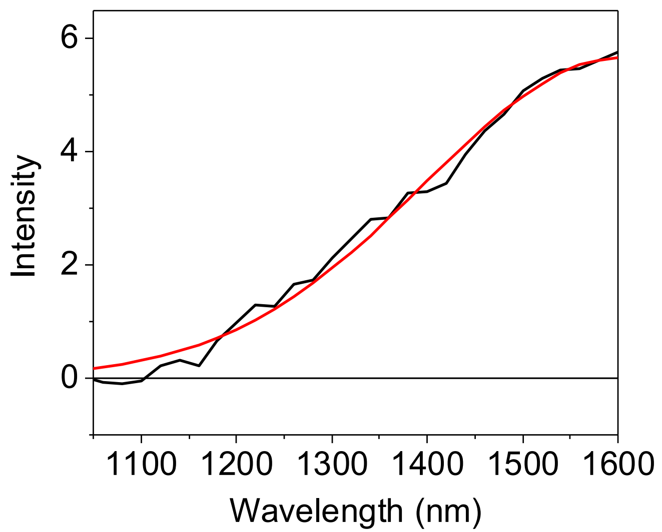
Terrylenediimide (TDI)



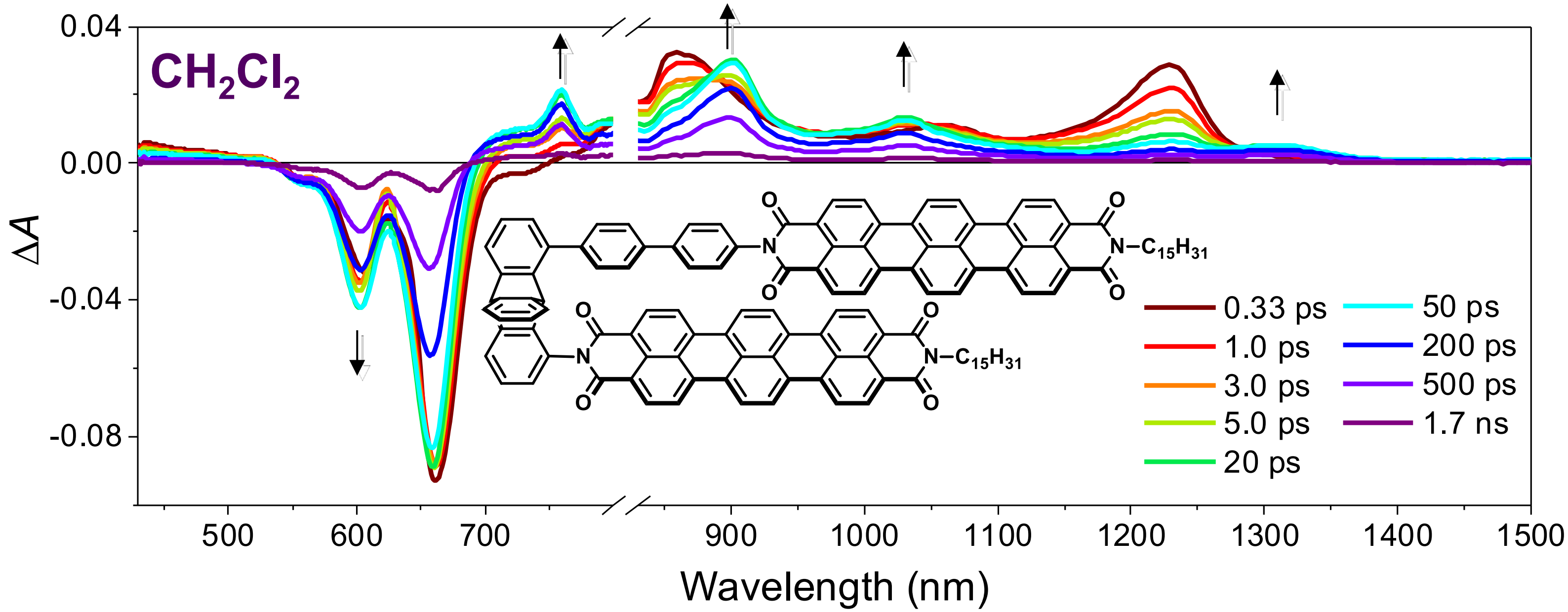


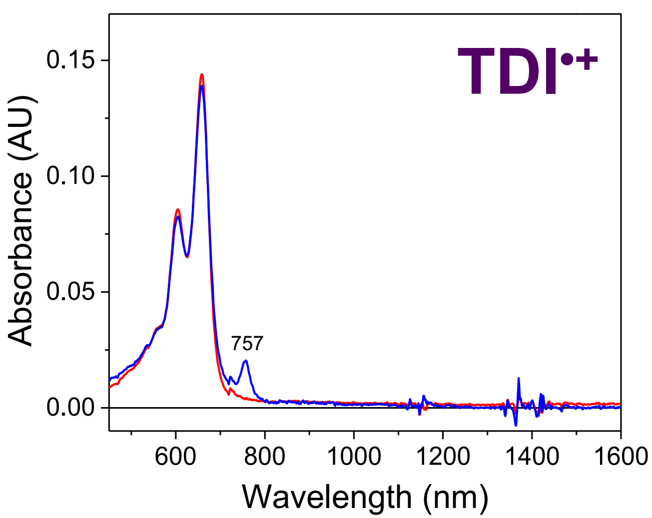
- **Good absorption in the solar spectrum**
  - λ_{max} **= 650nm (93,000 $M^{-1}cm^{-1}$)**
- **$E(S_1) - 2E(T_1) = 0.33$ eV**
  - **$E(S_1) = 1.87$ eV (optical bandgap)**
  - **$E(T_1) = 0.77$ eV (phosphorescence)**
- **High stability**

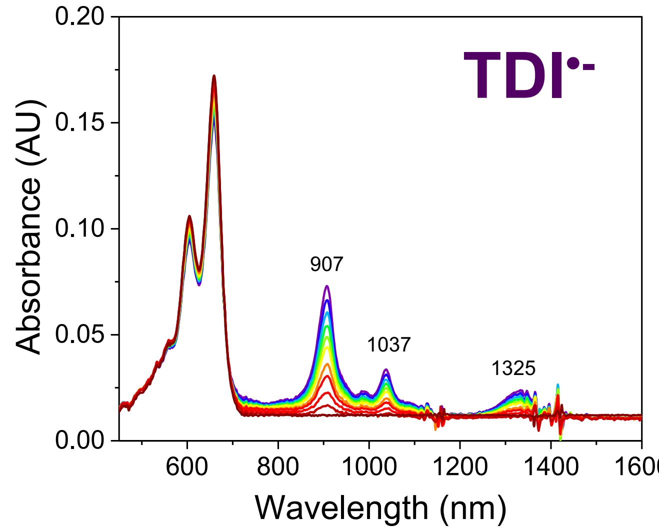




FsTA of the Slip-stacked TDI Dimer with a Biphenyl Offset







E. A. Margulies, C. E. Miller, Y. Wu, L. Ma, G. C. Schatz, R. M. Young and M. R. W., *Nat. Chem.*, **8**, 1120 (2016).

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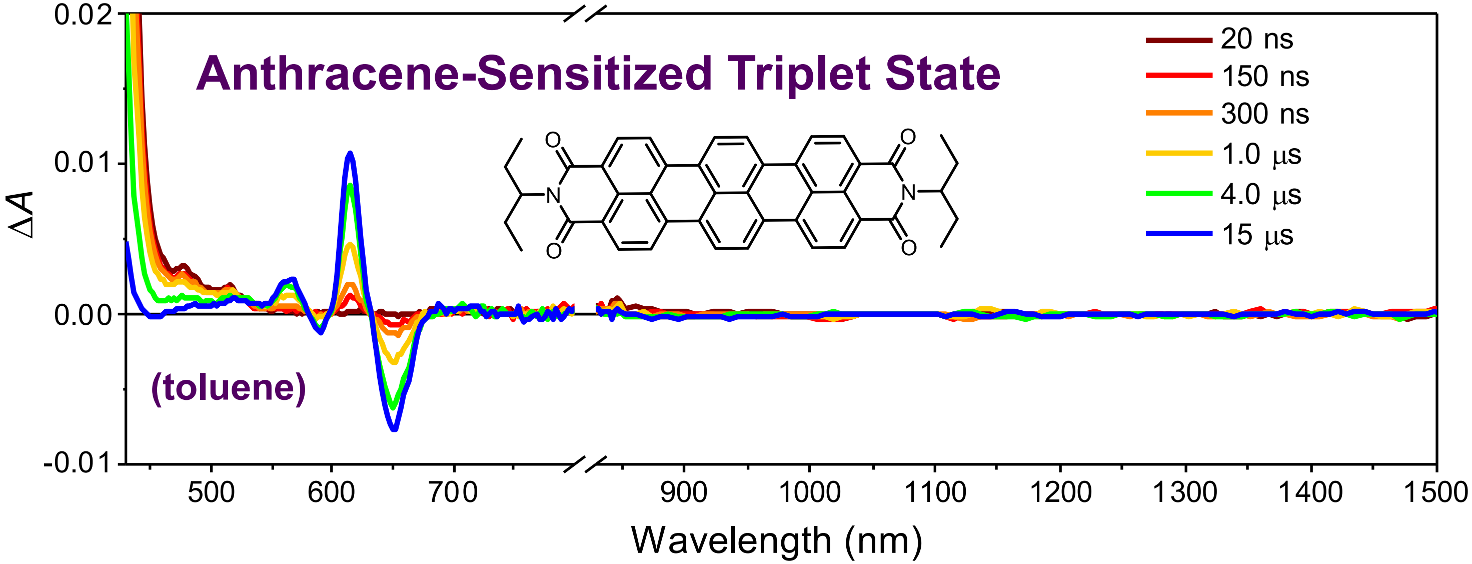
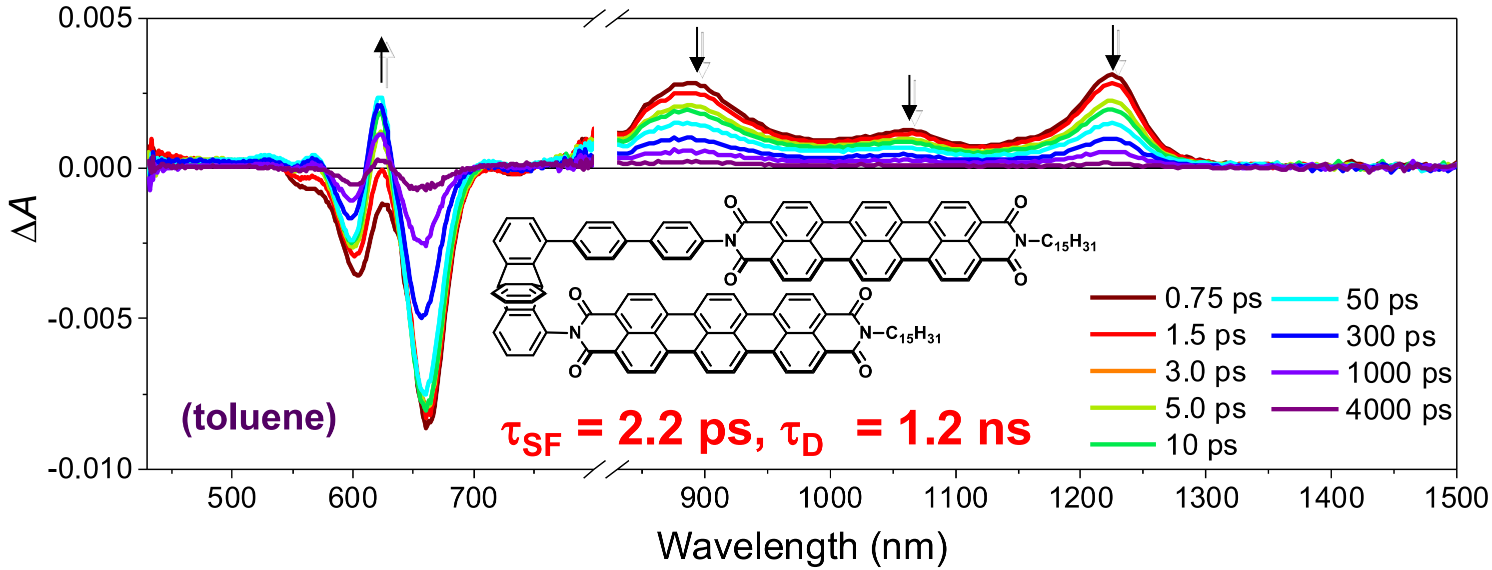
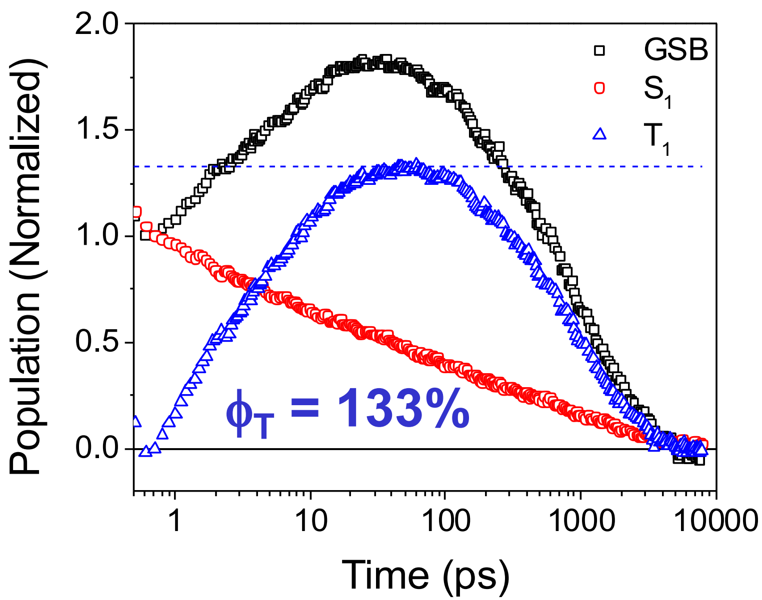
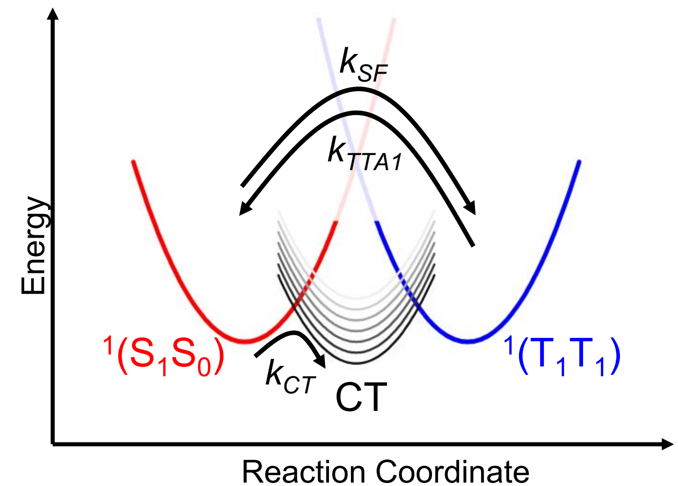




E. A. Margulies, C. E. Miller, Y. Wu, L. Ma, G. C. Schatz, R. M. Young and M. R. W., *Nat. Chem.*, **8**, 1120 (2016).

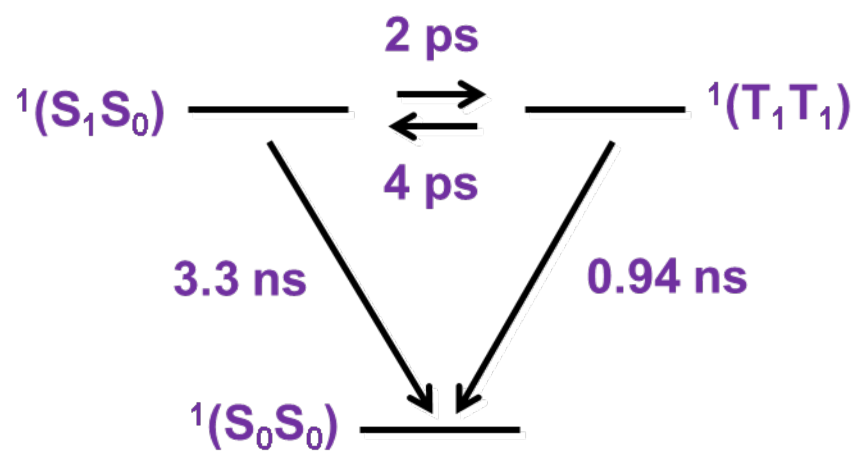
Population Dynamics and Triplet Yield





$$(1/3)\ {}^1(S_1S_0) \rightleftharpoons (2/3)\ {}^1(T_1T_1)$$

$$\frac{N_{TT}}{N_{SS}} = e^{\frac{E_{SS}-E_{TT}}{kT}} = \textbf{18 meV}$$



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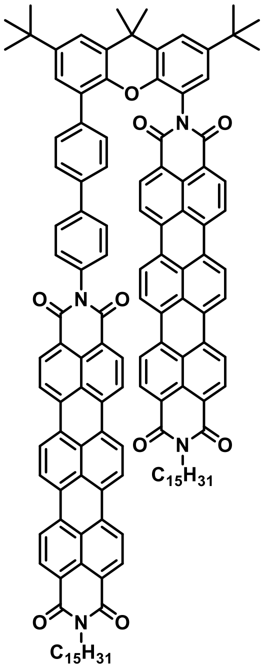
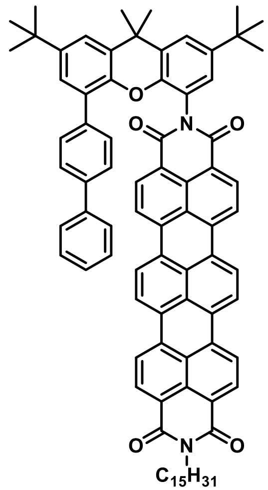
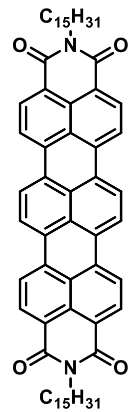
Transient Mid-IR Spectroscopy of a Slip-stacked TDI Dimer



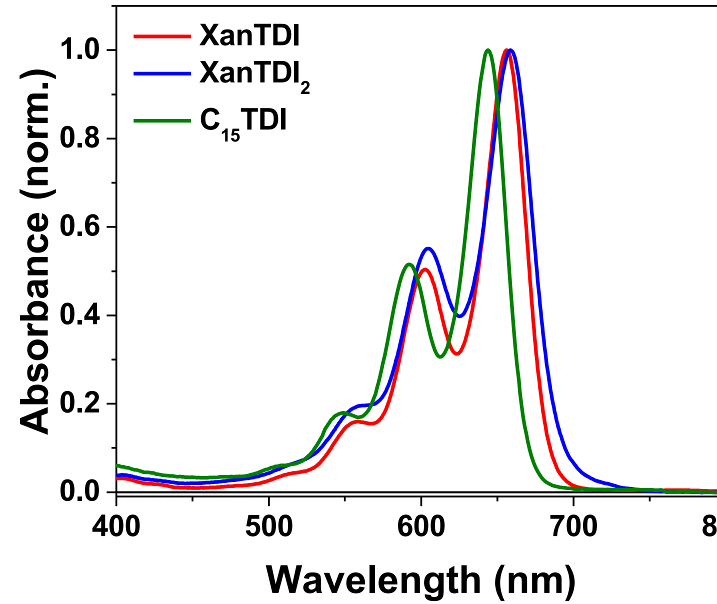
$XanTDI_2$

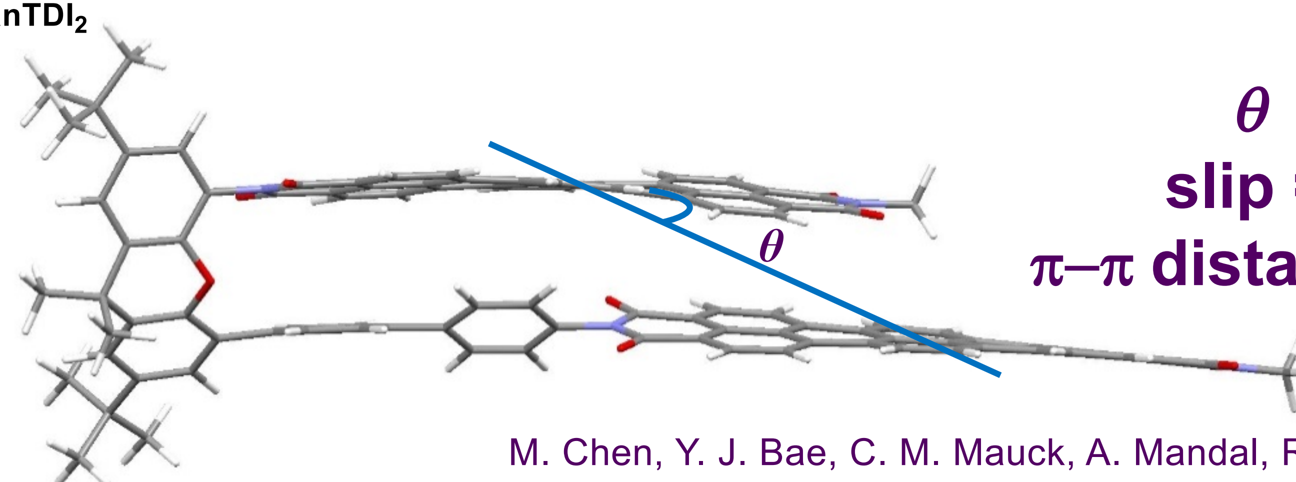


XanTDI



$C_{15}TDI$





θ = 20°
slip = 8.6 Å
π–π distance = 3.5 Å

M. Chen, Y. J. Bae, C. M. Mauck, A. Mandal, R. M. Young, and M. R. Wasielewski, *J. Am. Chem. Soc.* **140**, 9184-9192 (2018).

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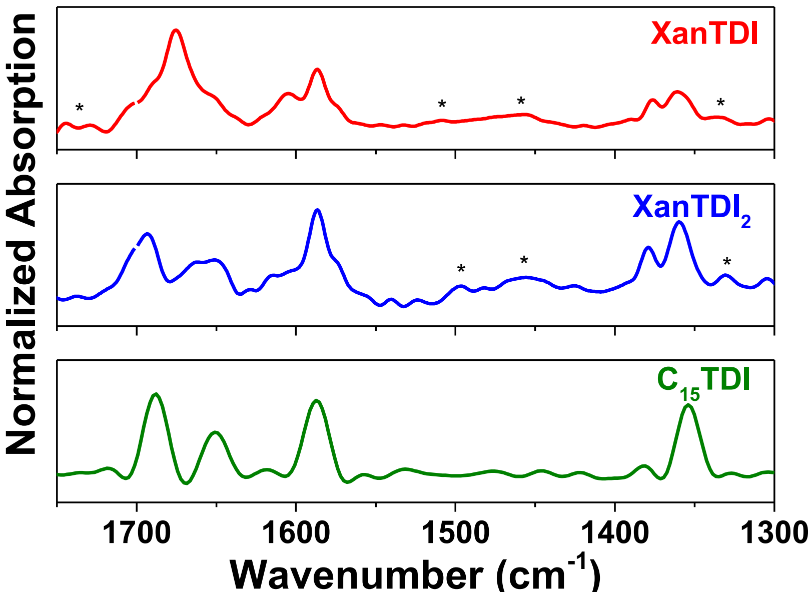
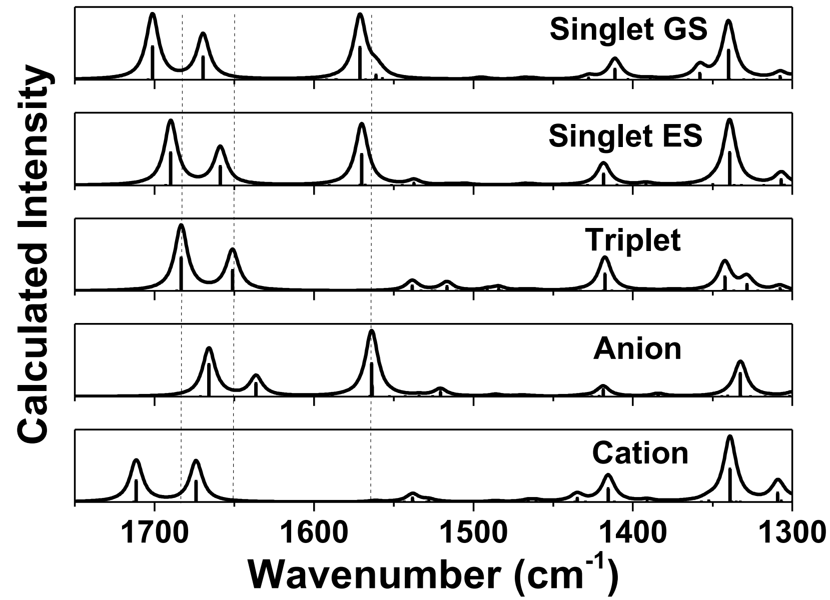
IR Spectra

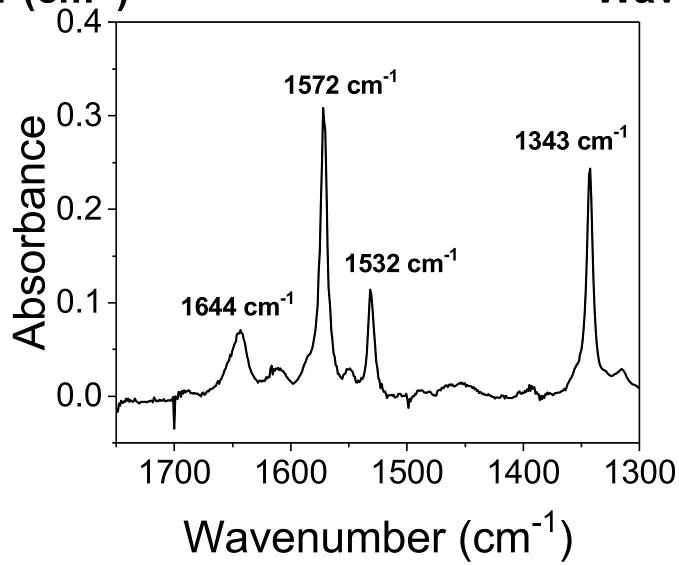
Measured



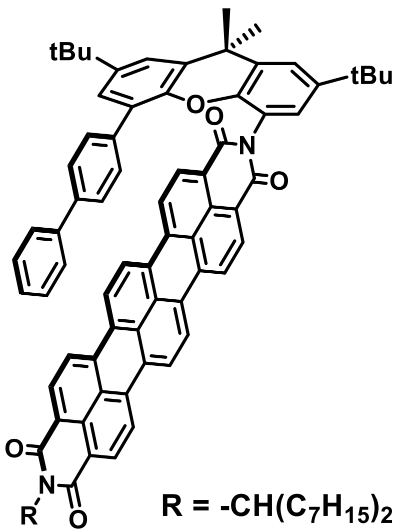
Computed

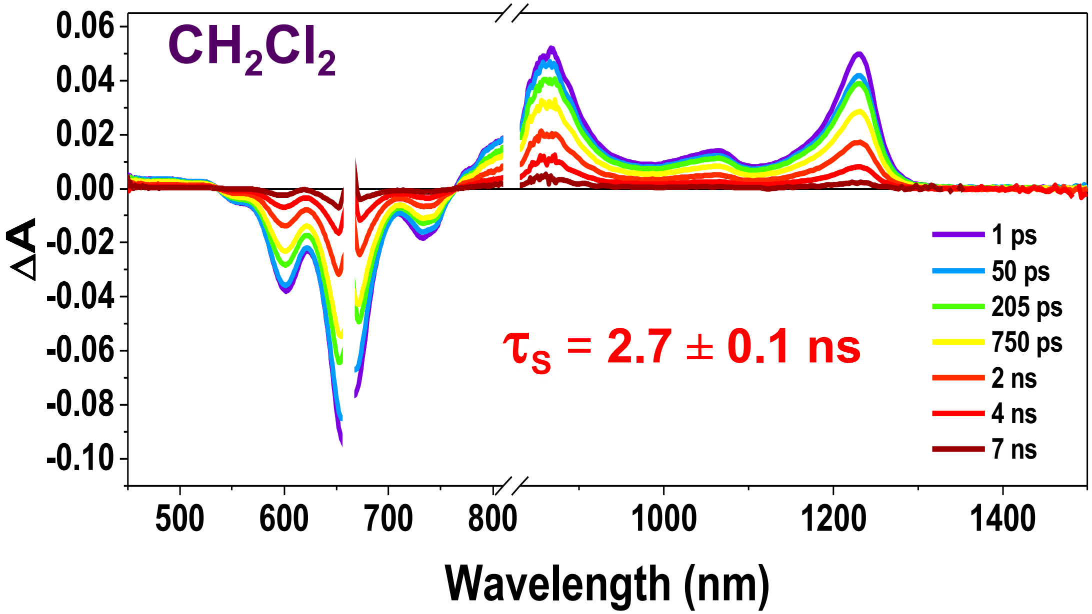


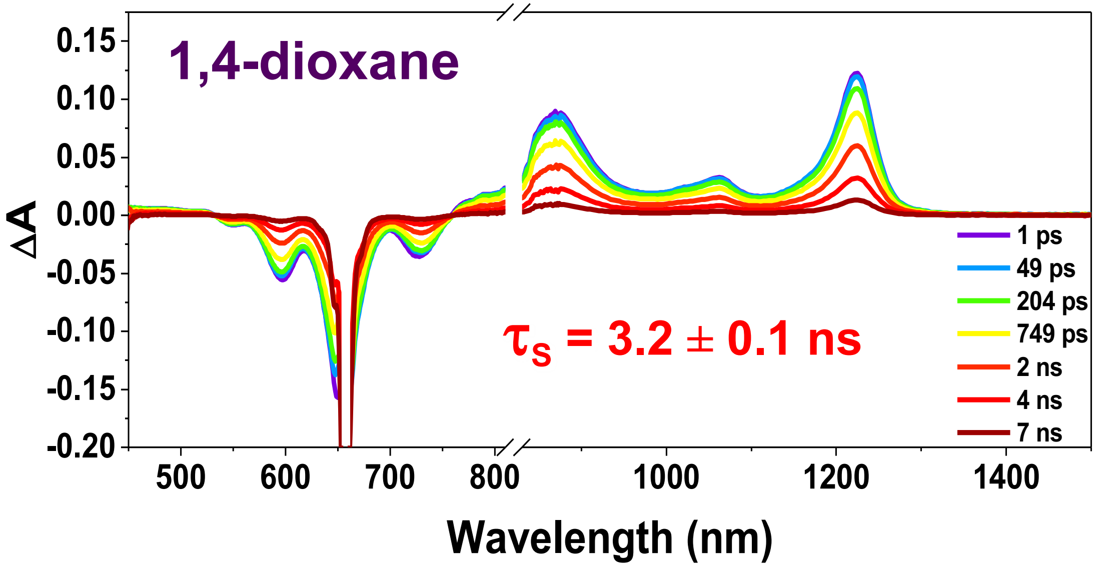
C_{15}TDI Anion In CD_2Cl_2



FsTA and FsIR Data for Xan-TDI







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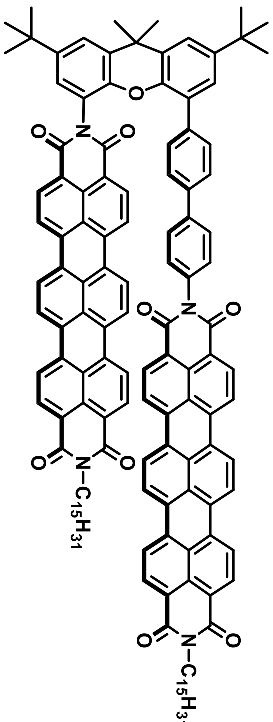
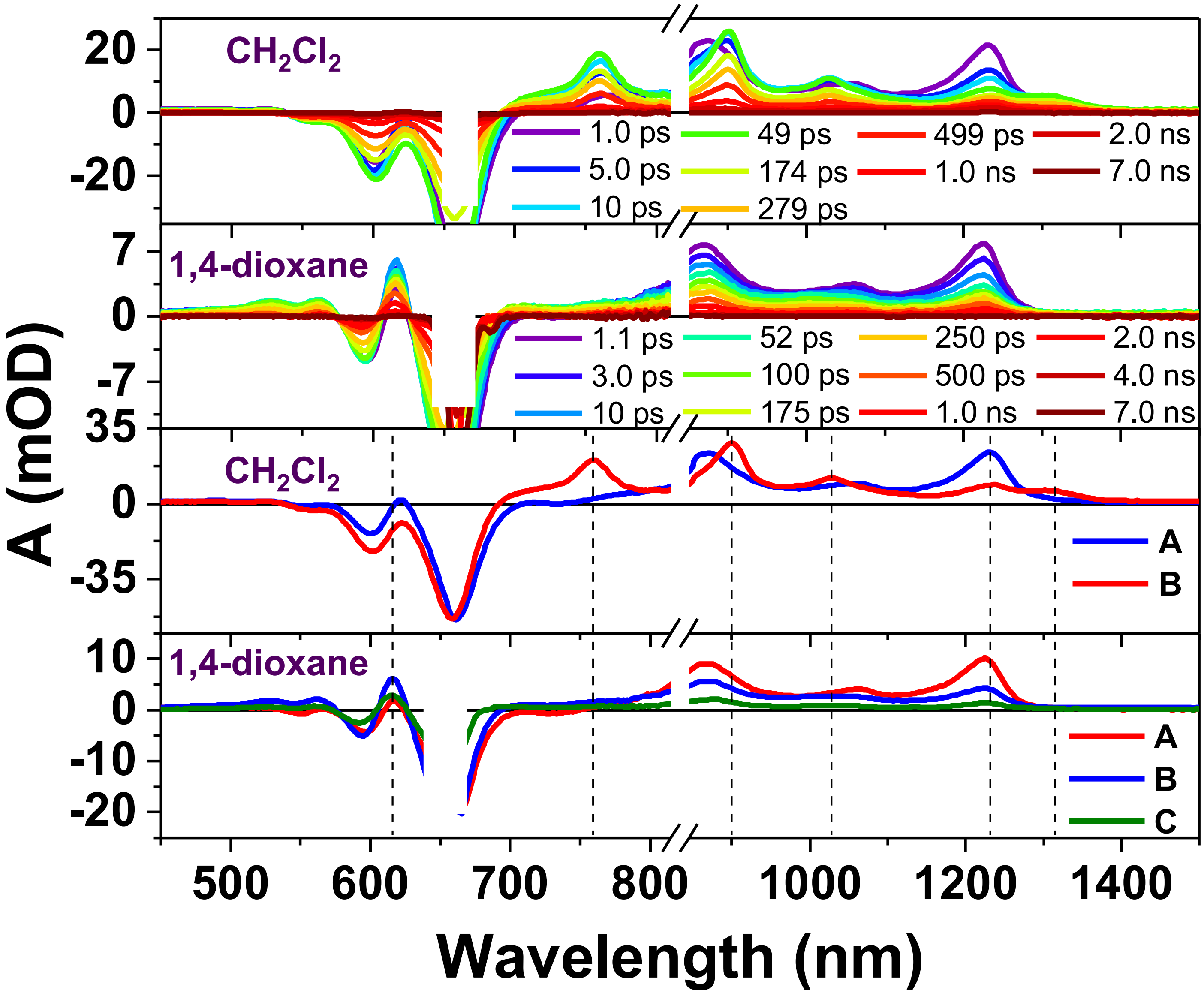
FsTA Data for Xan-TDI_2





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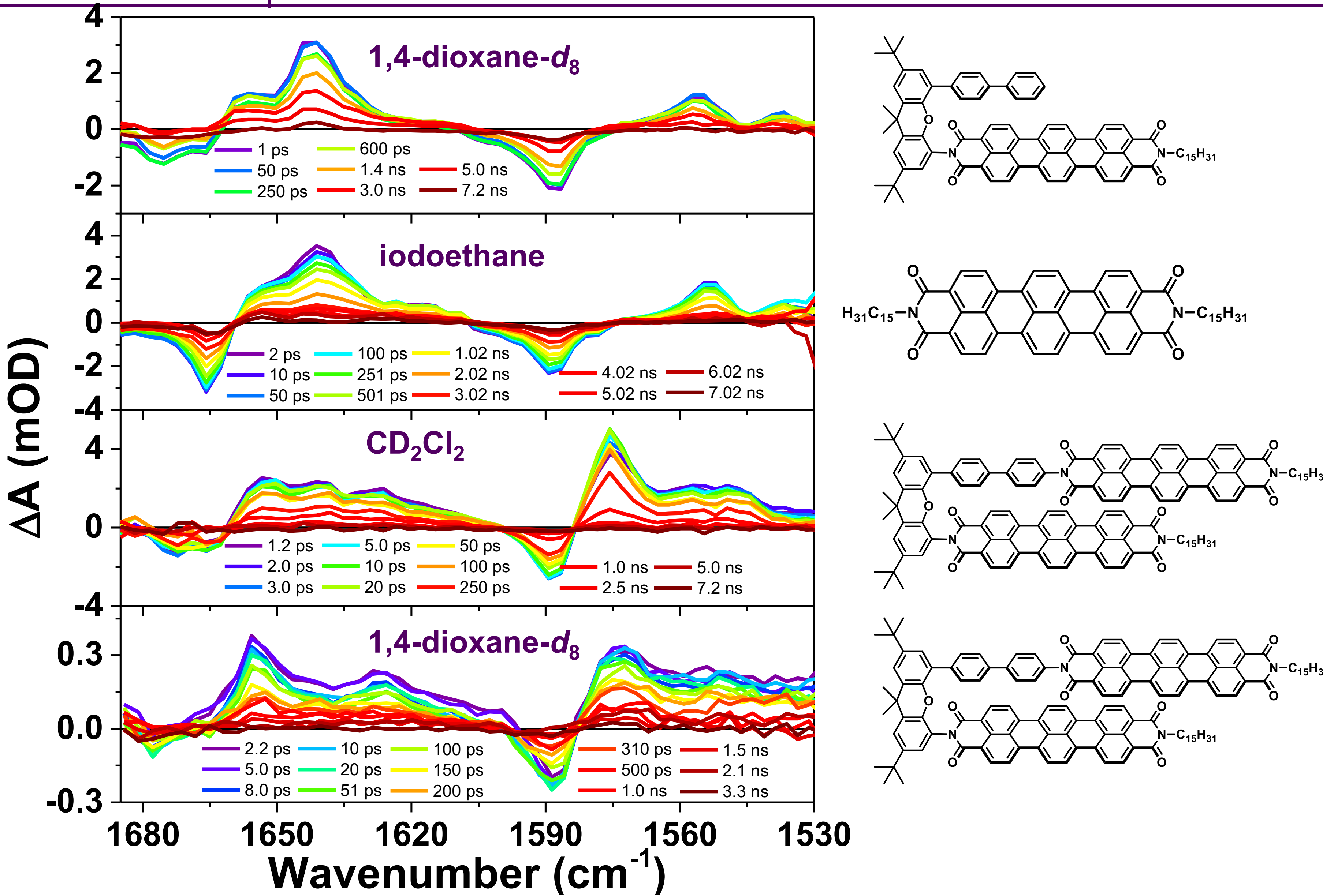
FsIR Data TDI Monomers and Xan-TDI$_2$



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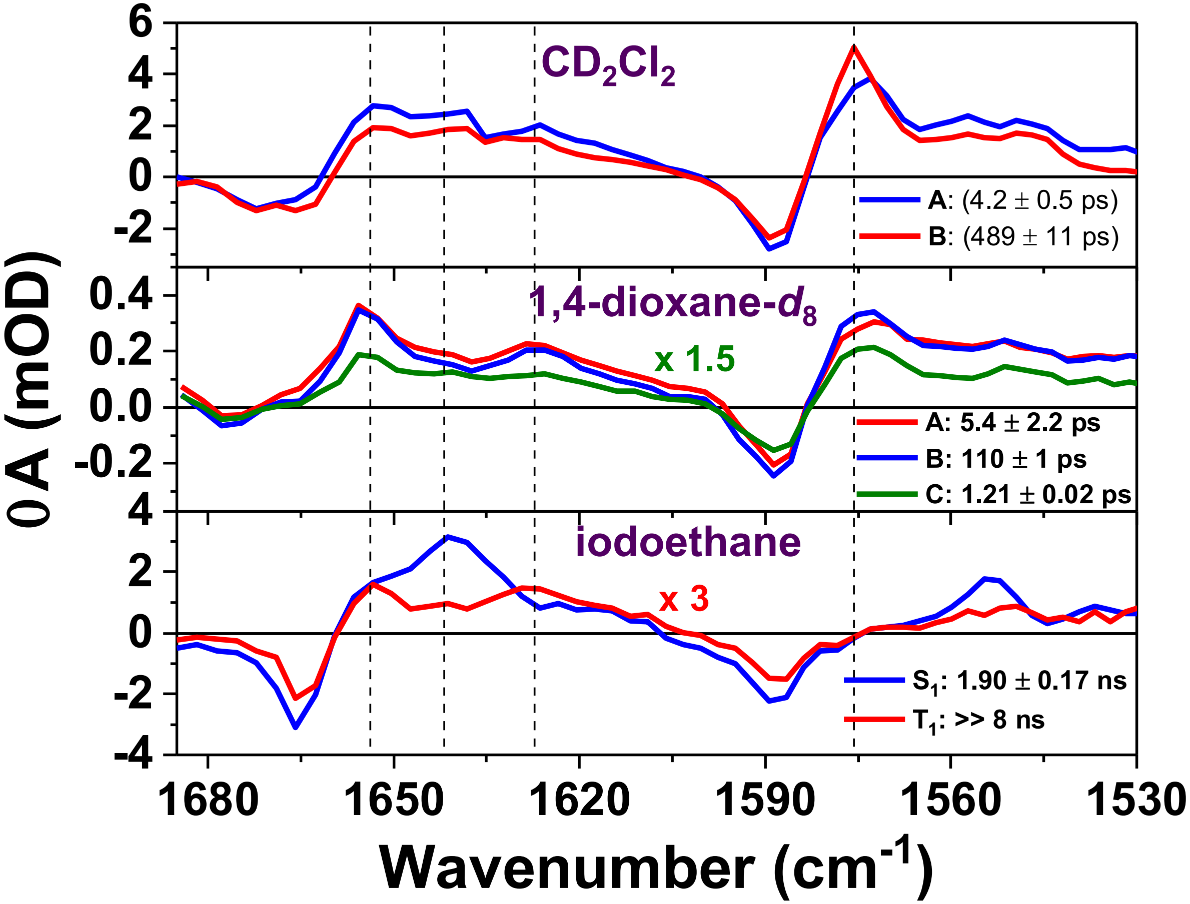
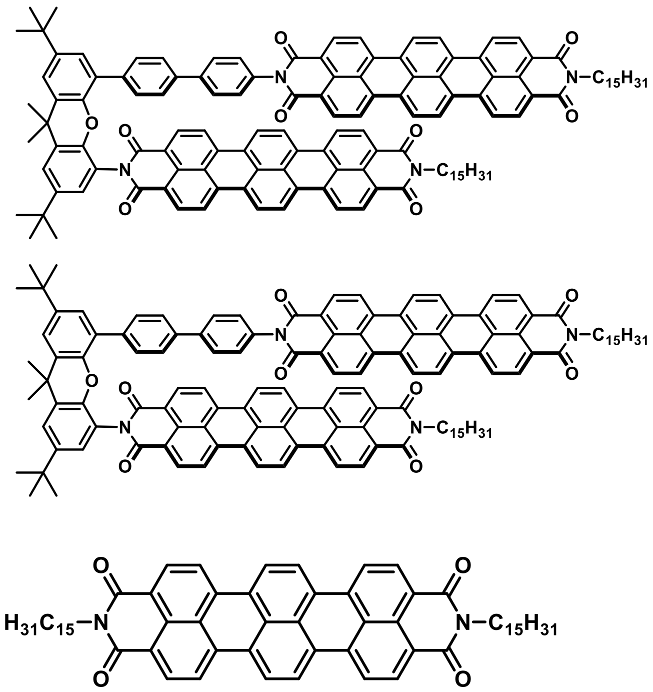
FsIR Data TDI Monomers and Xan-TDI_2





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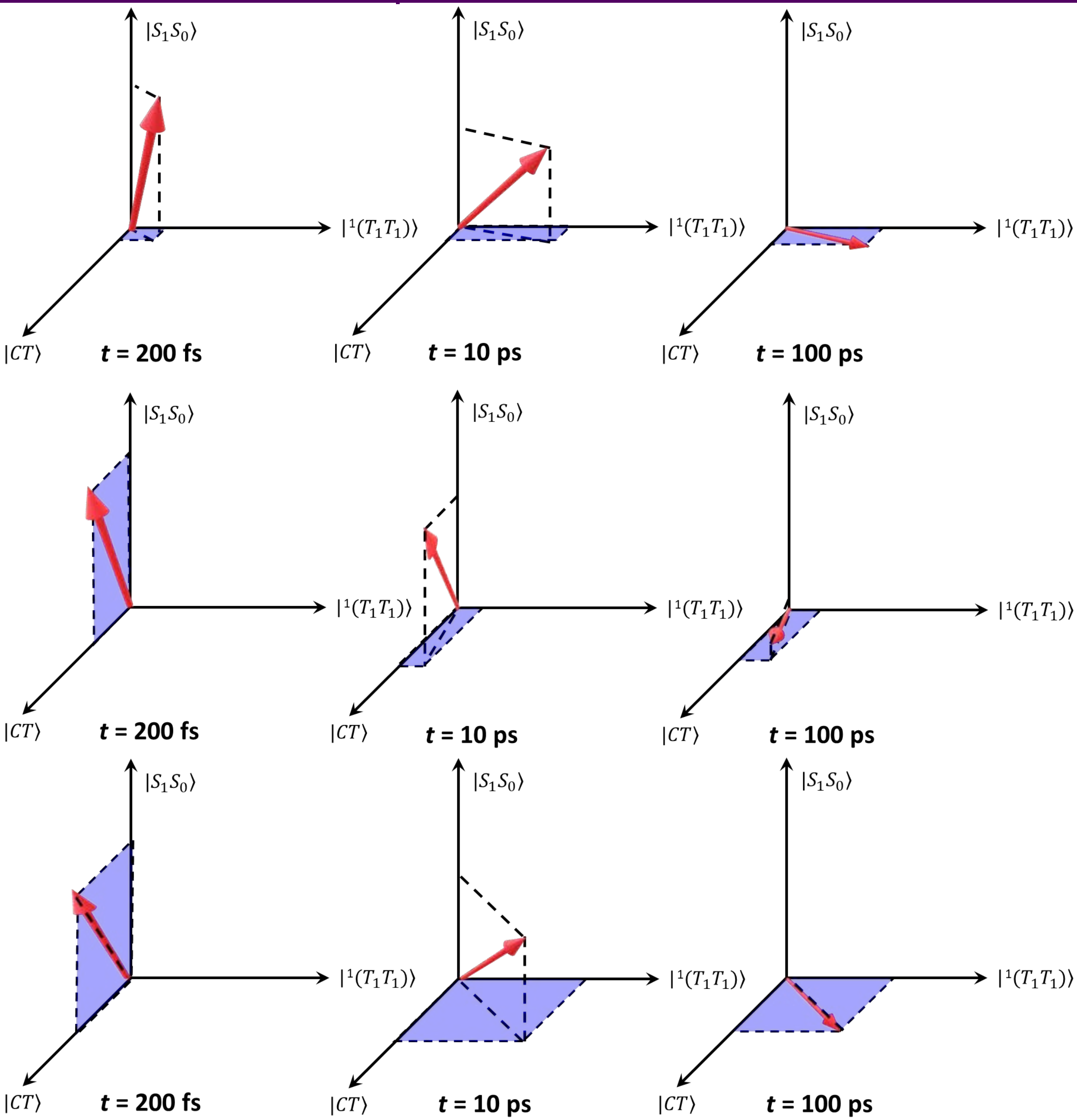
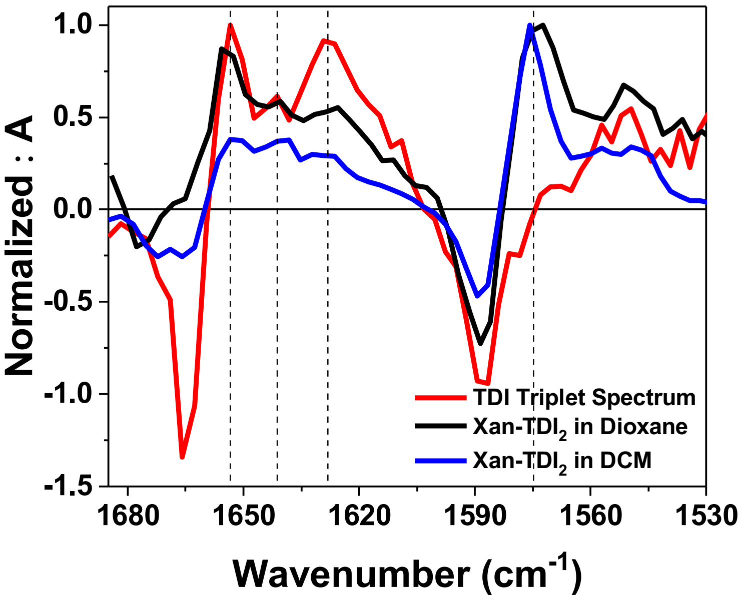
Time Evolution of the Mixed State Population





Summary

- FsIR spectra show that the electronic excited states of the TDI dimer have mixed singlet, triplet and CT character.
- At times < 300 fs, the $^1(S_1S_0)$ state already has significant CT character even in low polarity solvents.
- Nevertheless, the degree of state mixing depends on the solvent polarity, which alters the relative energies of the states and their time evolution.

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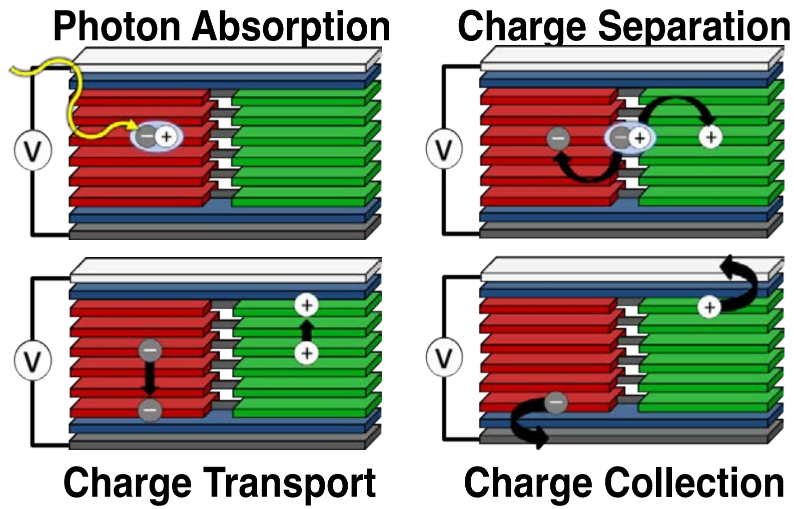
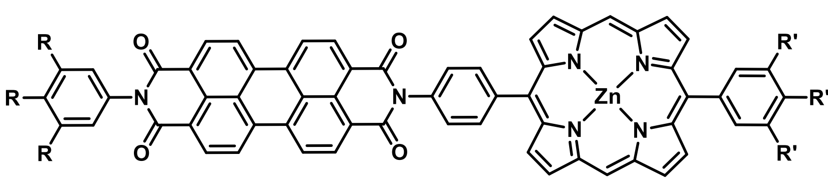
Charge Separation and Transport: Self-Segregating Charge Conduits





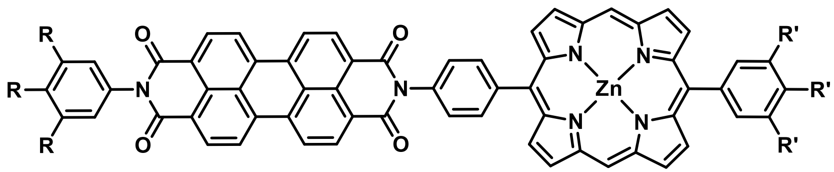
1a: R = C_8H_{17}, R' = $(OCH_2CH_2)_2OCH_3$

1b: R = $C_{20}H_{41}$, R' = $(OCH_2CH_2)_6OCH_3$

J. L. Logsdon, P. E. Hartnett, J. N. Nelson, M. A. Harris, T. J. Marks, MRW, *ACS Appl. Mater. Interfaces* 2017 *9*, 33493.

Route to Ordered Films

Focus on 1a:



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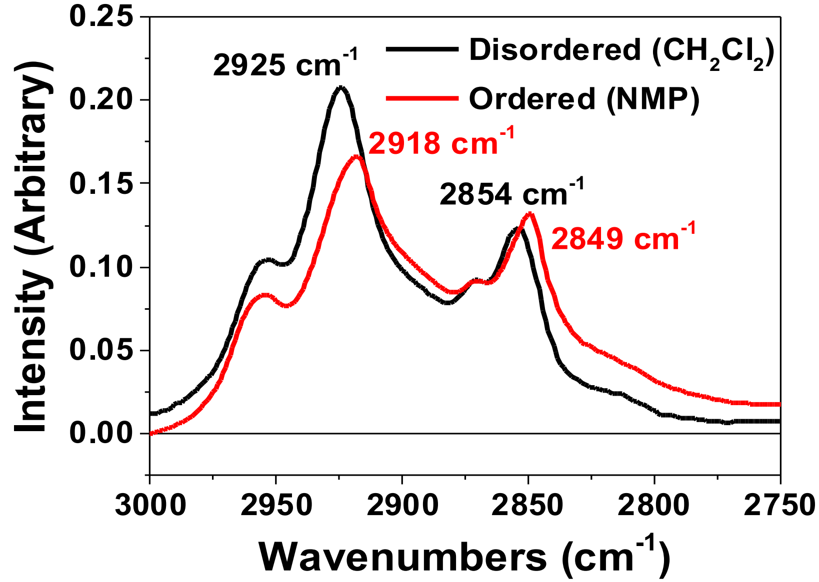

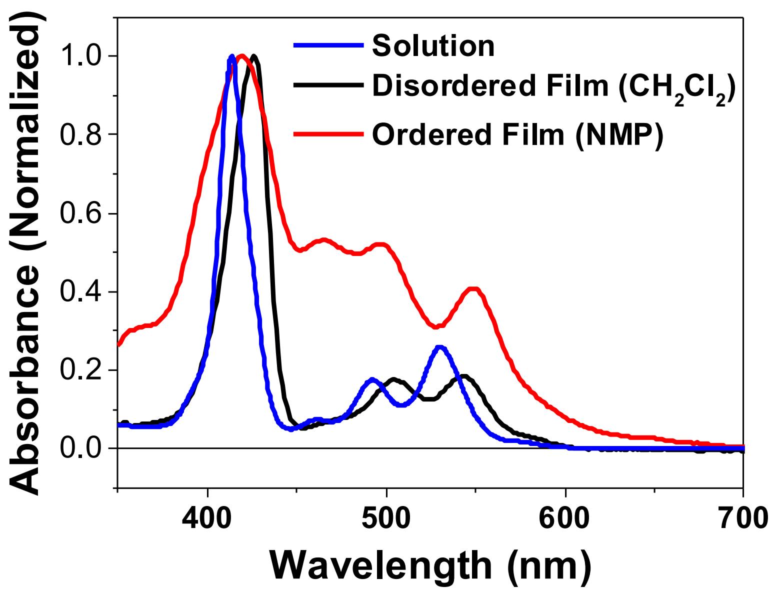

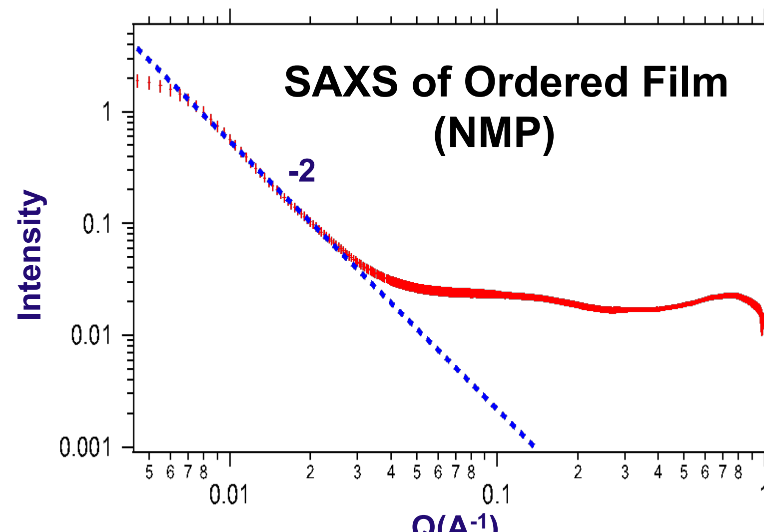

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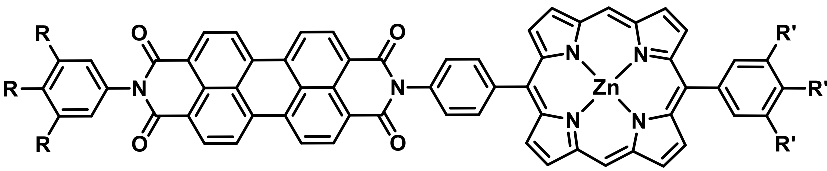
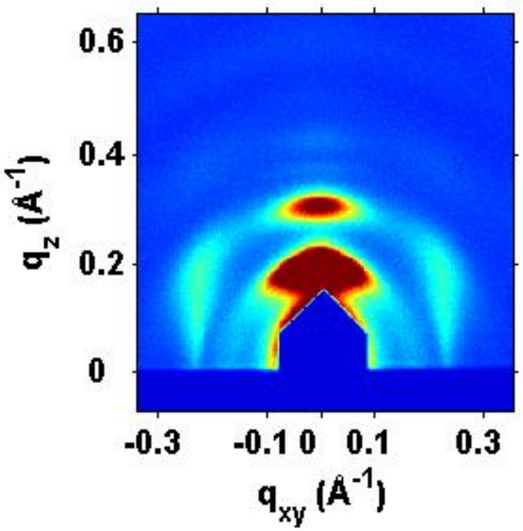
GIWAXS of Ordered Films: Comparing Tails Lengths



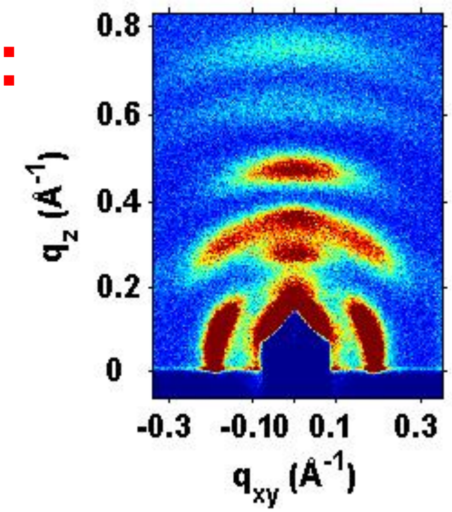
1a: R = C_8H_{17}, R' = $(OCH_2CH_2)_2OCH_3$

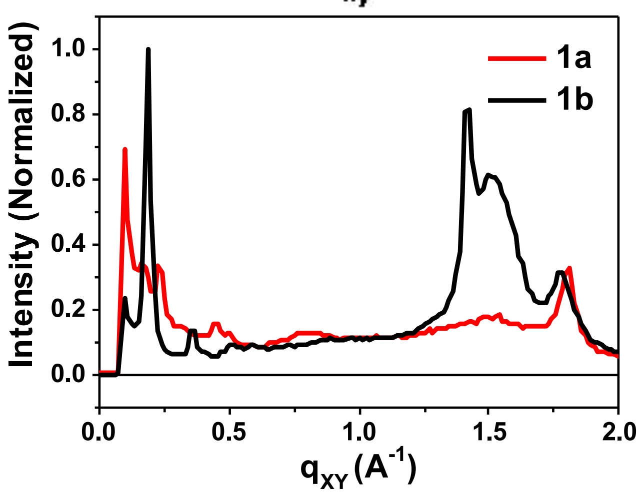
1b: R = $C_{20}H_{41}$, R' = $(OCH_2CH_2)_6OCH_3$

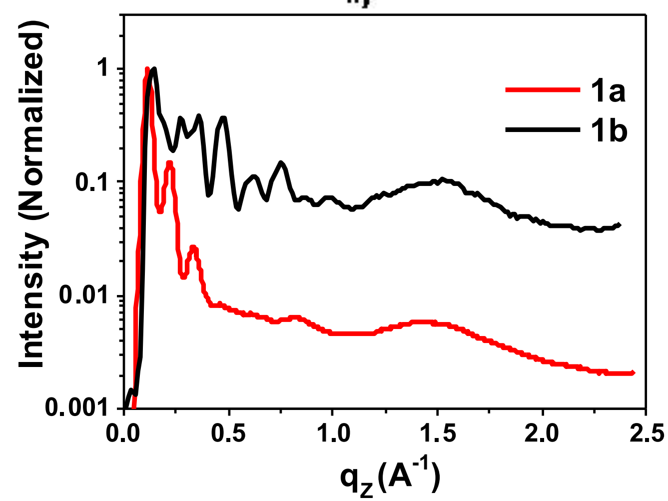
1a:



1b:







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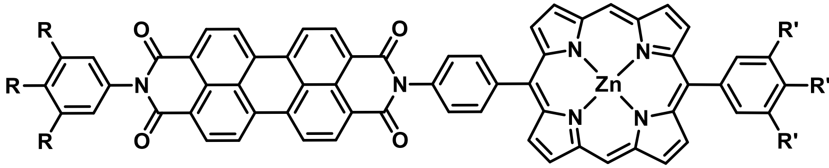
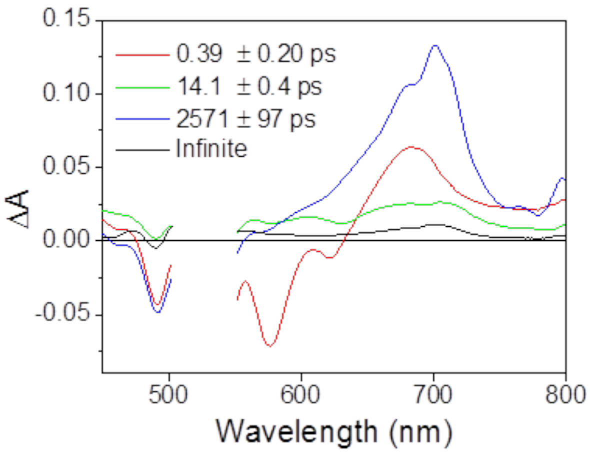
Transient Absorption Spectroscopy and Kinetics



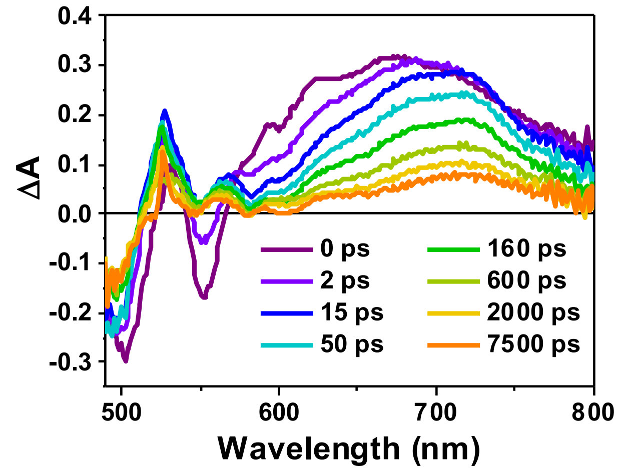
1a: R = C_8H_{17}, R' = $(OCH_2CH_2)_2OCH_3$

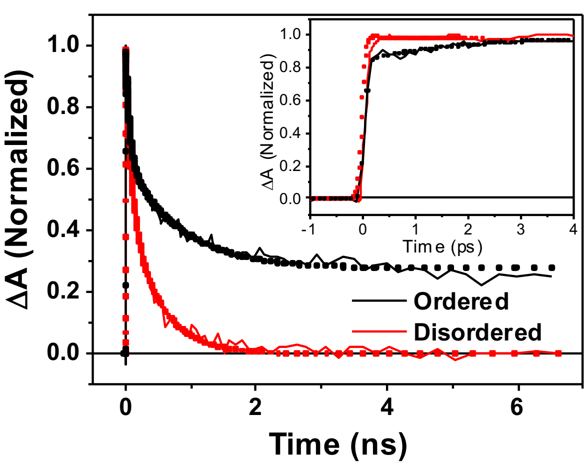
1b: R = $C_{20}H_{41}$, R' = $(OCH_2CH_2)_6OCH_3$

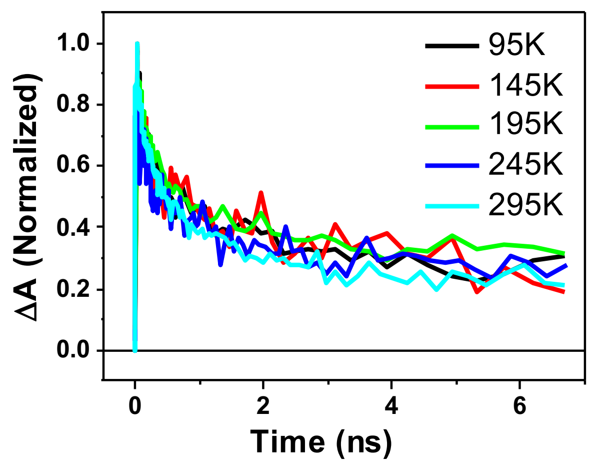
1a in toluene, 525 nm exc.

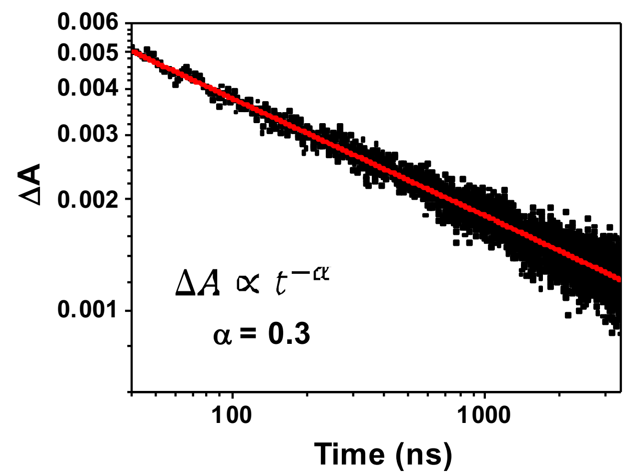


1a ordered film (NMP), 525 nm exc.









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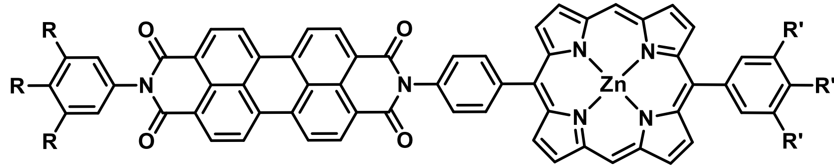
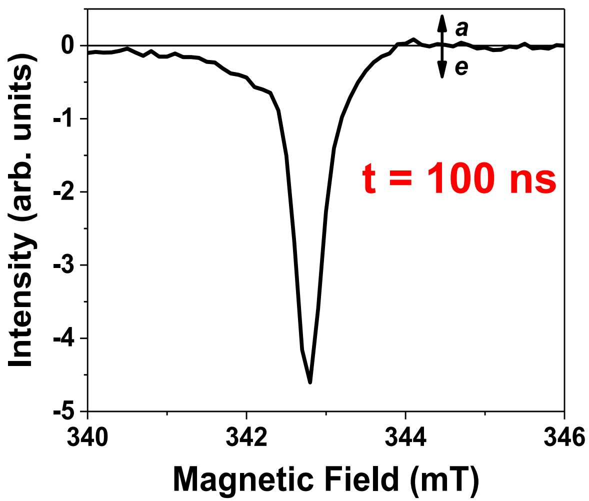
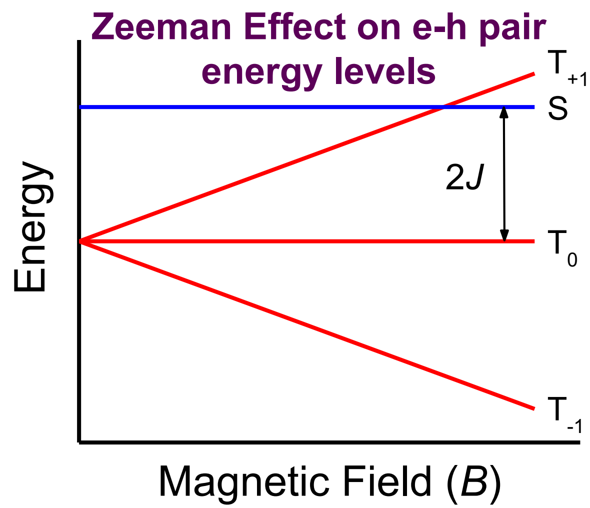
Probing the CT State using TREPR and TR-Microwave Conductivity

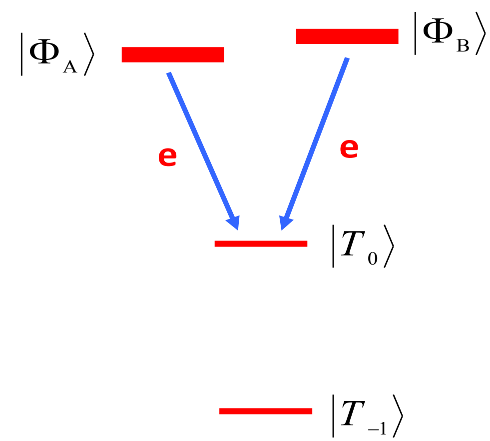


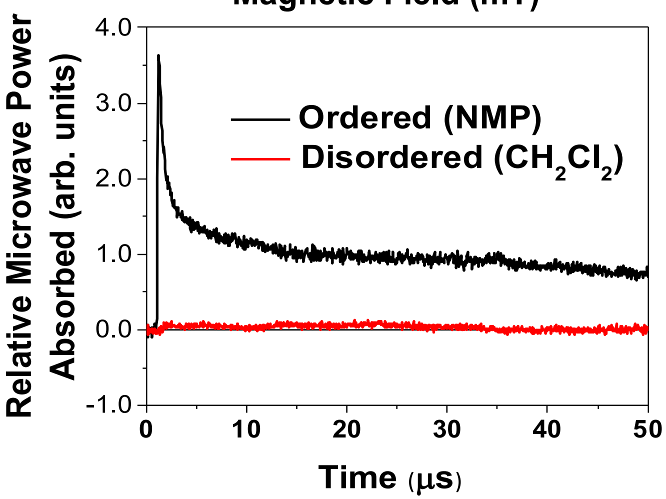
1a: R = C_8H_{17}, R' = $(OCH_2CH_2)_2OCH_3$

1b: R = $C_{20}H_{41}$, R' = $(OCH_2CH_2)_6OCH_3$







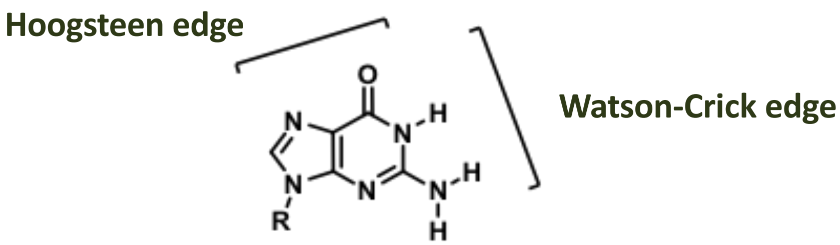


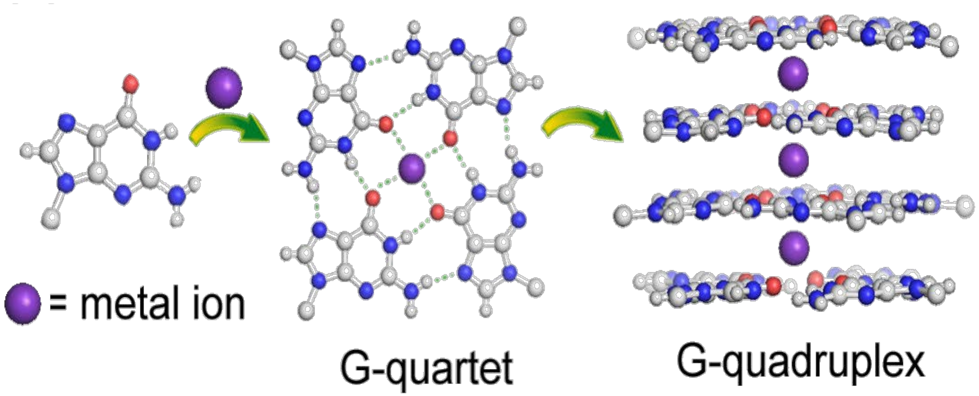
Free carrier yield in ordered films of 1a-b.

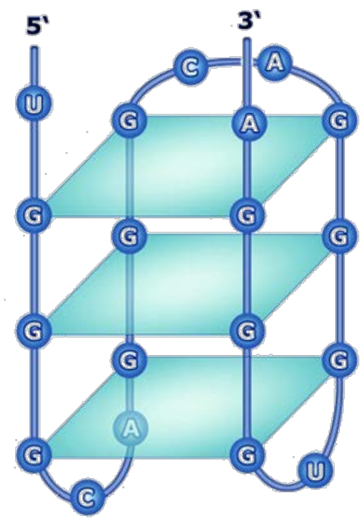
Molecule	FC Yield (%)
1a	30 ± 3
1b	27 ± 3

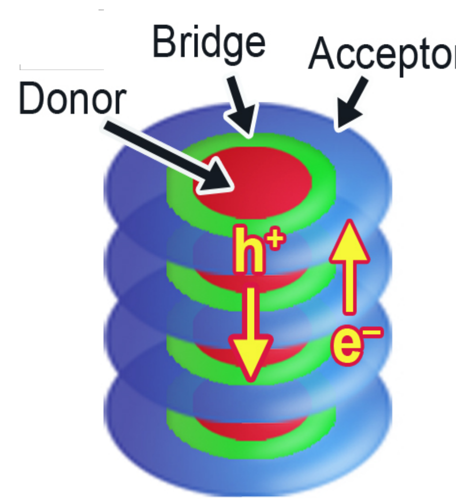
A Bio-inspired Approach

Functional G-Quadruplexes:









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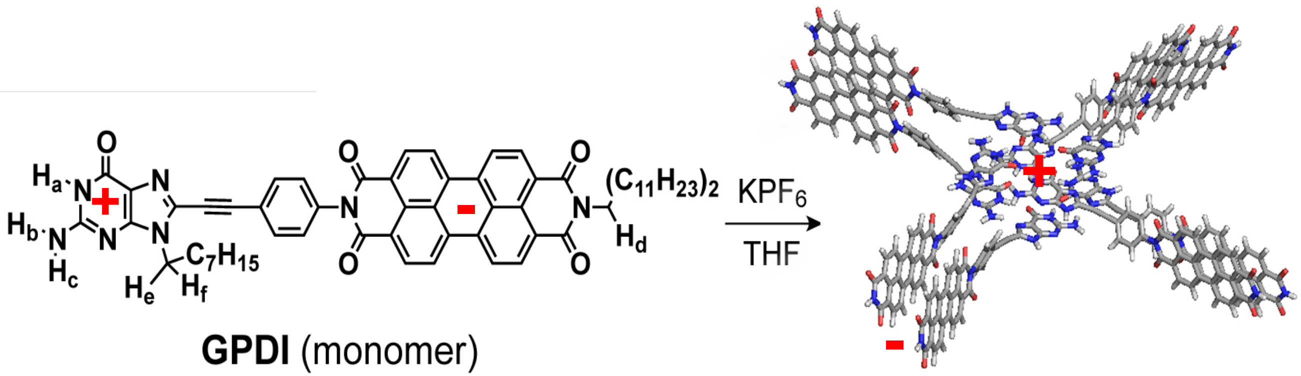
Functional G-Quadruplexes



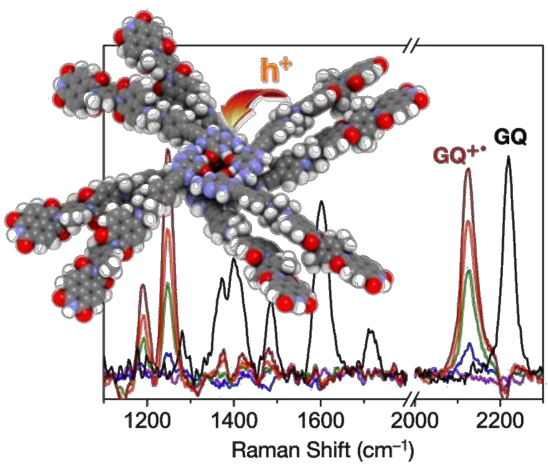
GPDI (monomer)

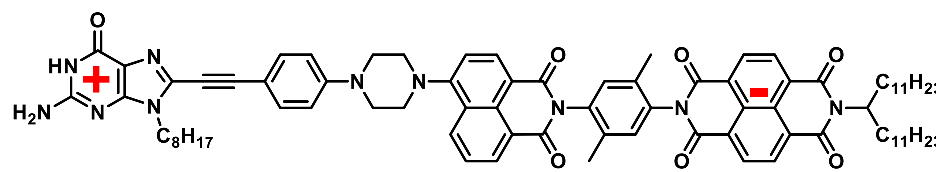
GPDI quadruplex (C_4 8mer)

τ_{CR} = 10 ps

τ_{CR} = 1 ns

Y.-L. Wu, K. E. Brown, and MRW, *J. Am. Chem. Soc.* 135, 13322-13325 (2013).





Rapid hole hopping in the GQF core

Y.-L. Wu, K. E. Brown, D. M. Gardner, S. M. Dyar and MRW, *J. Am. Chem. Soc.* 137, 3981-3990 (2015).

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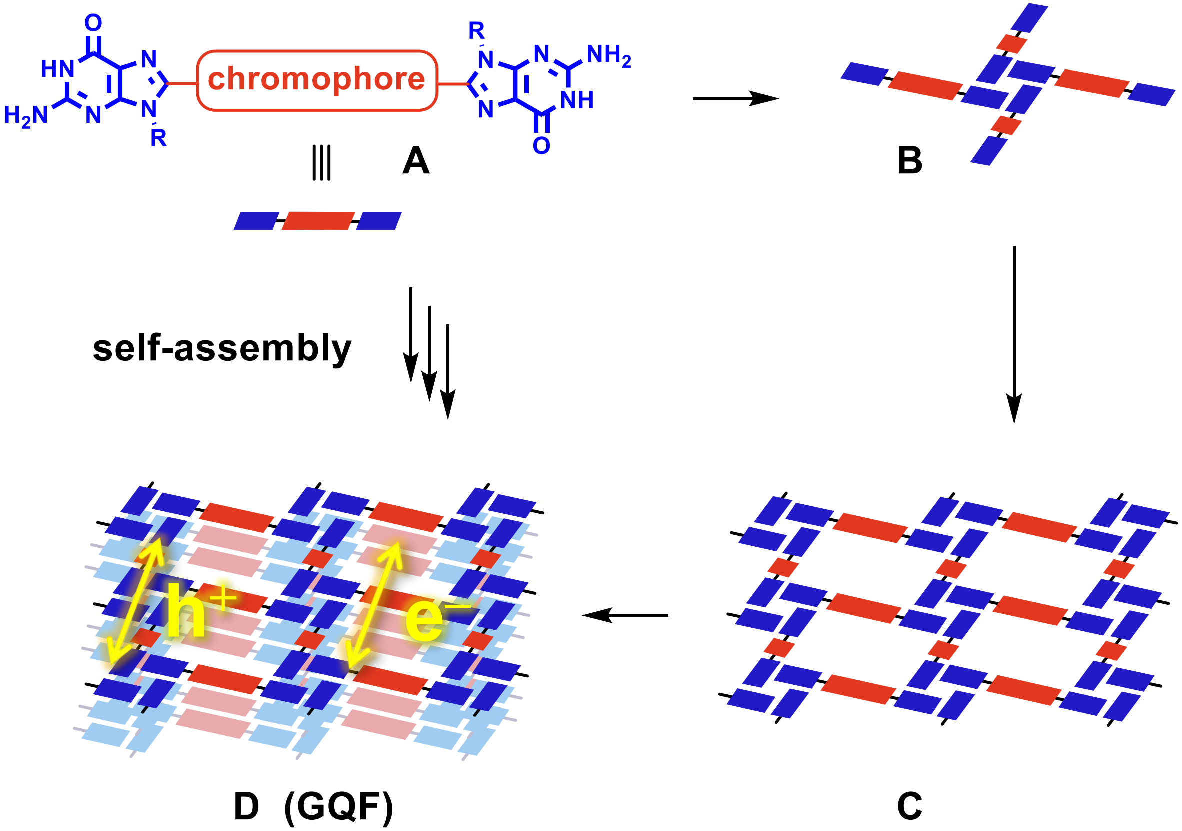
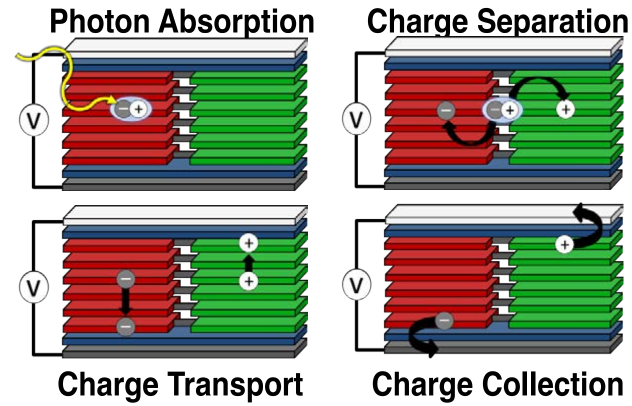
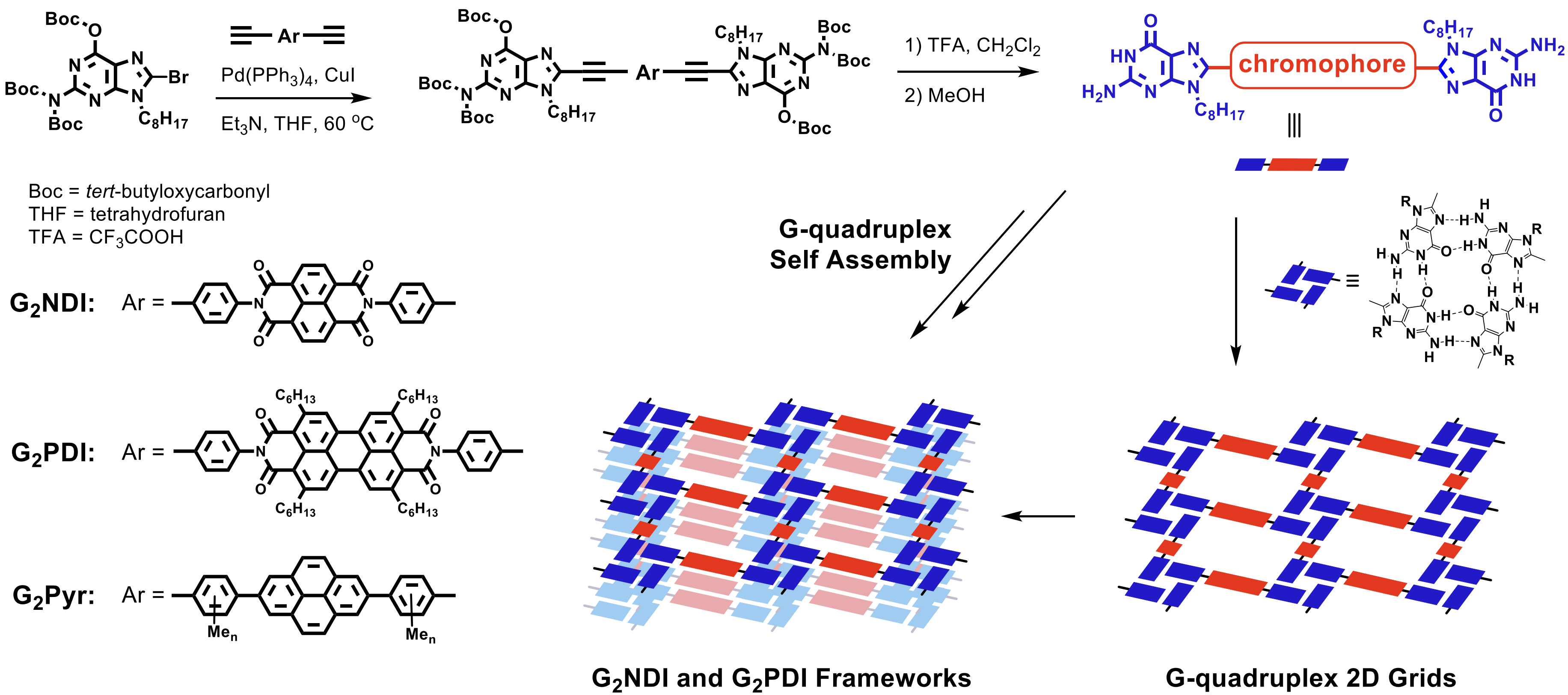
G-Quadruplex Frameworks (GQFs)





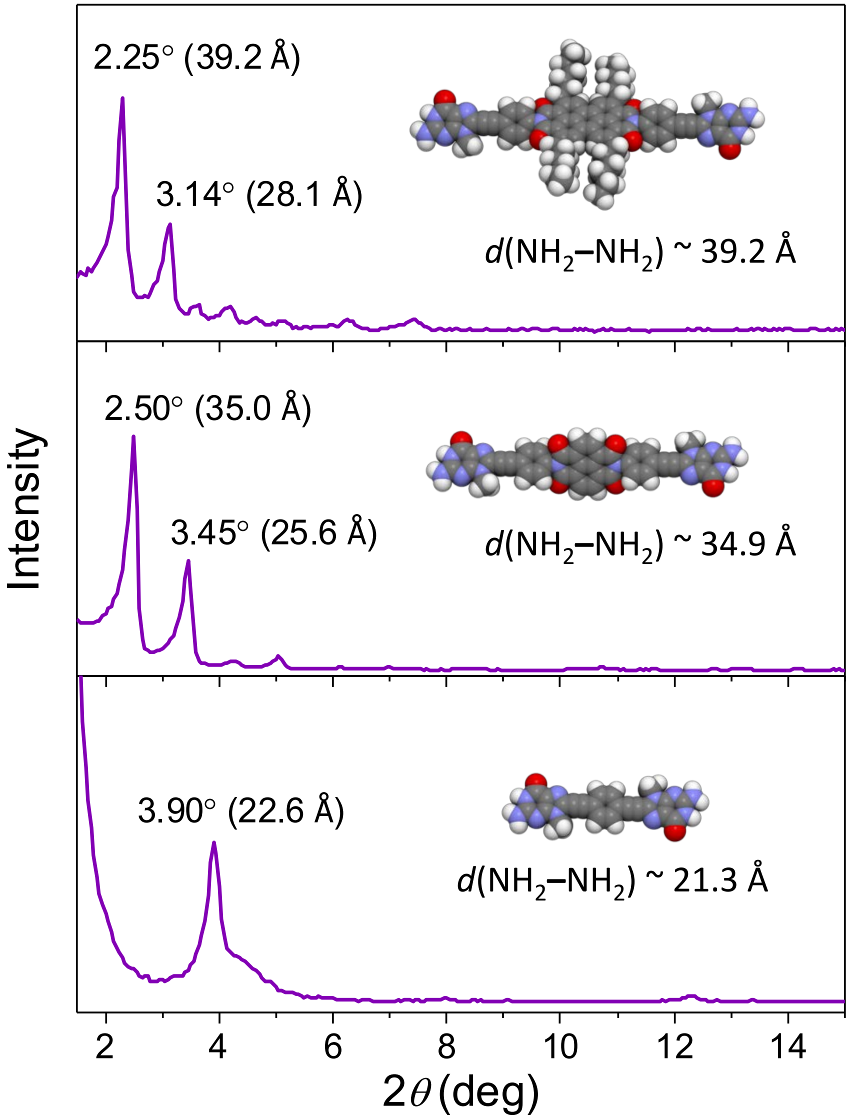
Y.-L. Wu, N. E. Horwitz, K.-S. Chen, D. A. Gomez-Gualdron, N. S. Luu, L. Ma, T. C. Wang, M. C. Hersam, J. T. Hupp, O. K. Farha, R. Q. Snurr. and M. R. Wasielewski, *Nat. Chem.* 9, 466-472 (2017).

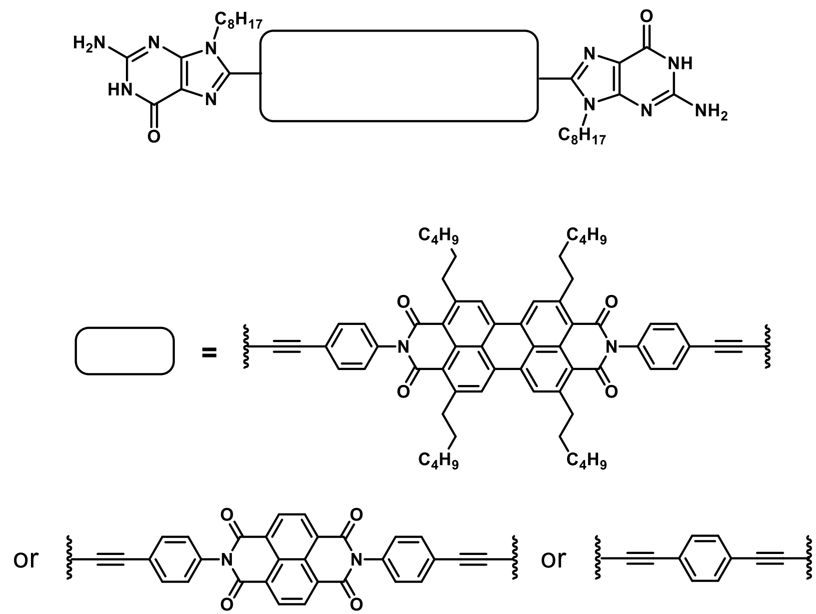
Synthesis of GQFs

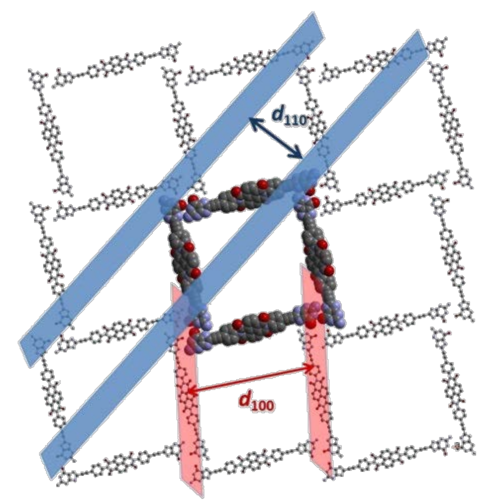


Y.-L. Wu, N. E. Horwitz, K.-S. Chen, D. A. Gomez-Gualdron, N. S. Luu, L. Ma, T. C. Wang, M. C. Hersam, J. T. Hupp, O. K. Farha, R. Q. Snurr. and M. R. Wasielewski, *Nat. Chem.* 9, 466-472 (2017).

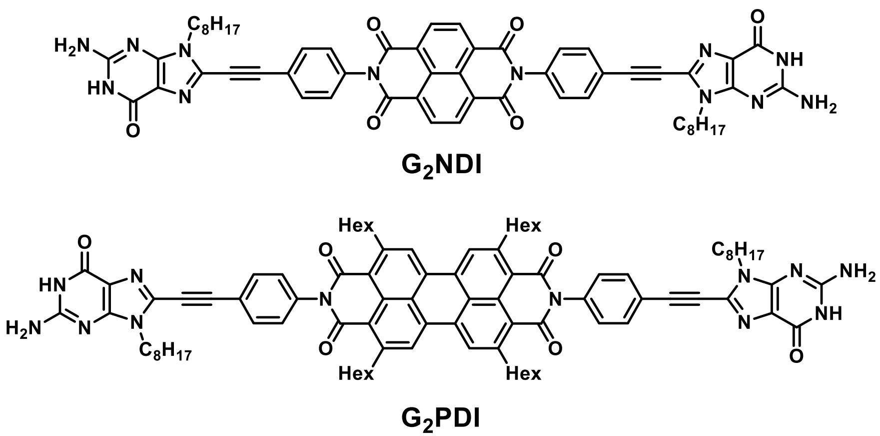
Crystalline GQF: Strong PXRD

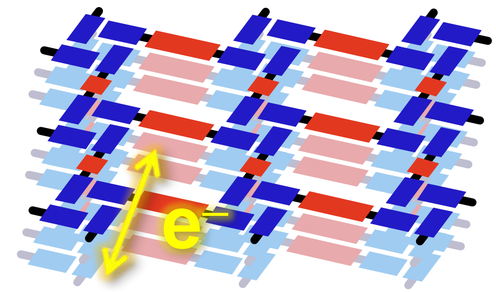


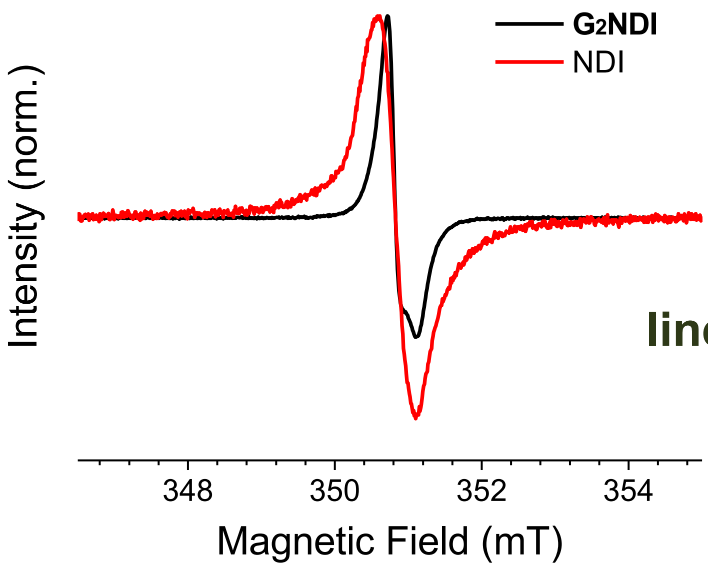




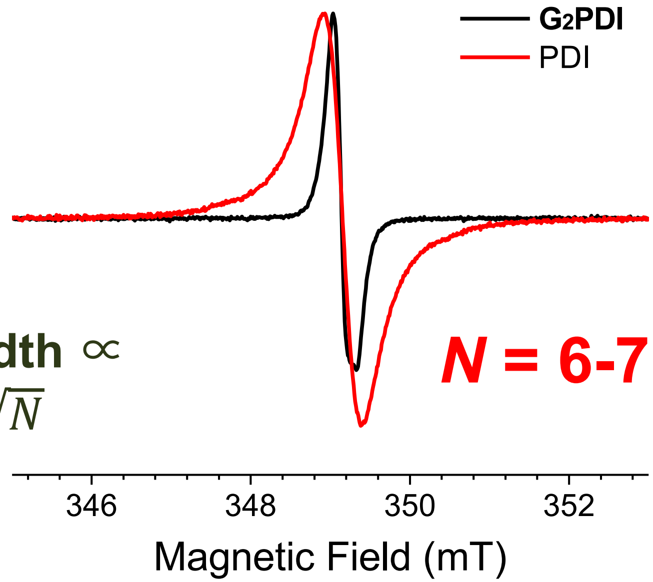
Facile Electron Movement in a GQF







linewidth ∝ $1/\sqrt{N}$



N = 6-7

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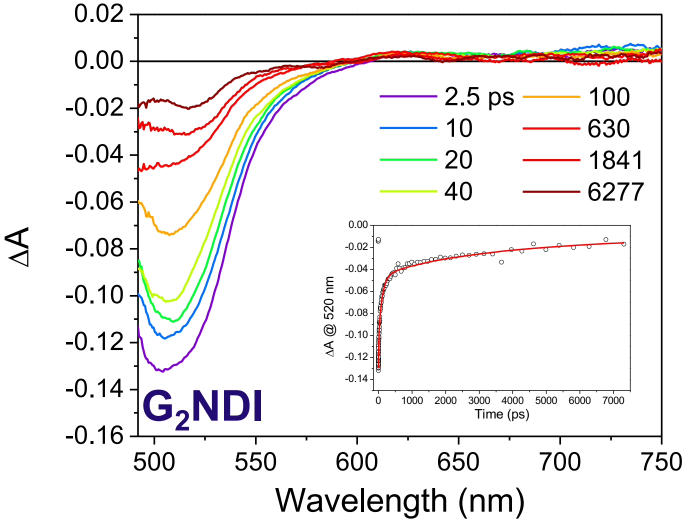
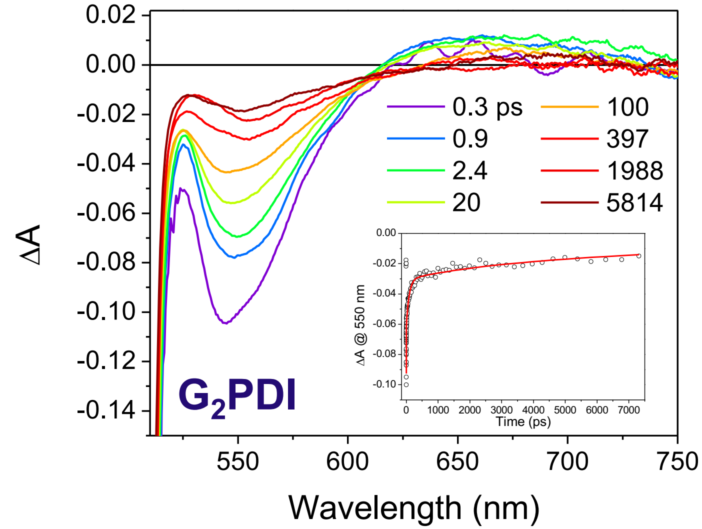
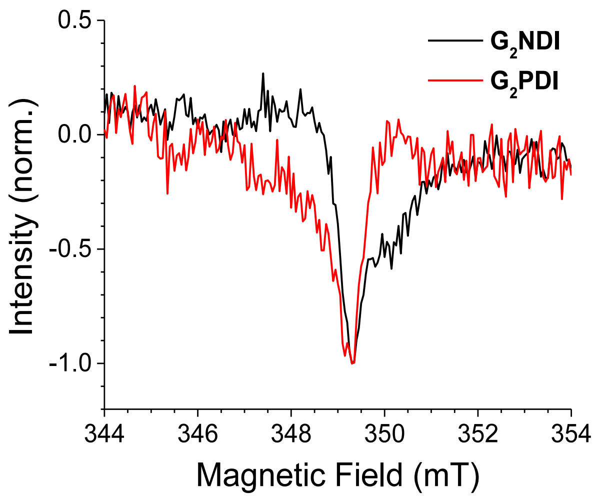
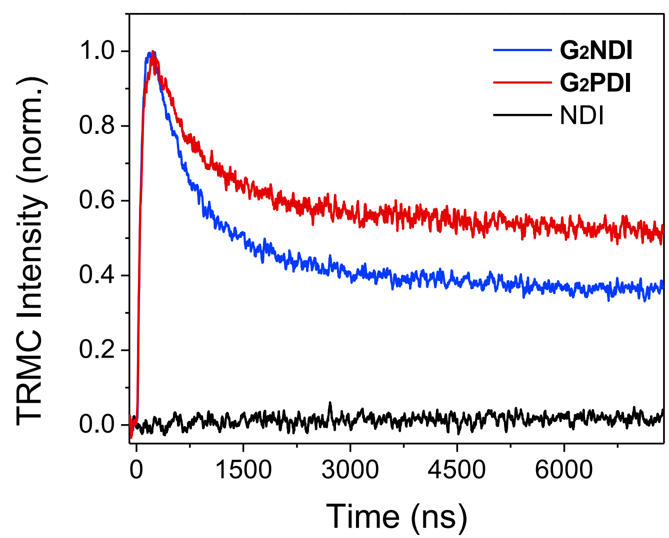
Long-lived and Mobile Charge Carriers in a GQF









Summary

- Ordered thin solid films of self-segregating ZnP-PDI molecules display charge conduit behavior resulting in independent charge carriers that persist for > 10 μs.
- G-quadruplex frameworks assemble into ordered structures in which ultrafast photo-driven charge separation results in independent charge carriers that also persist for > 10 μs.

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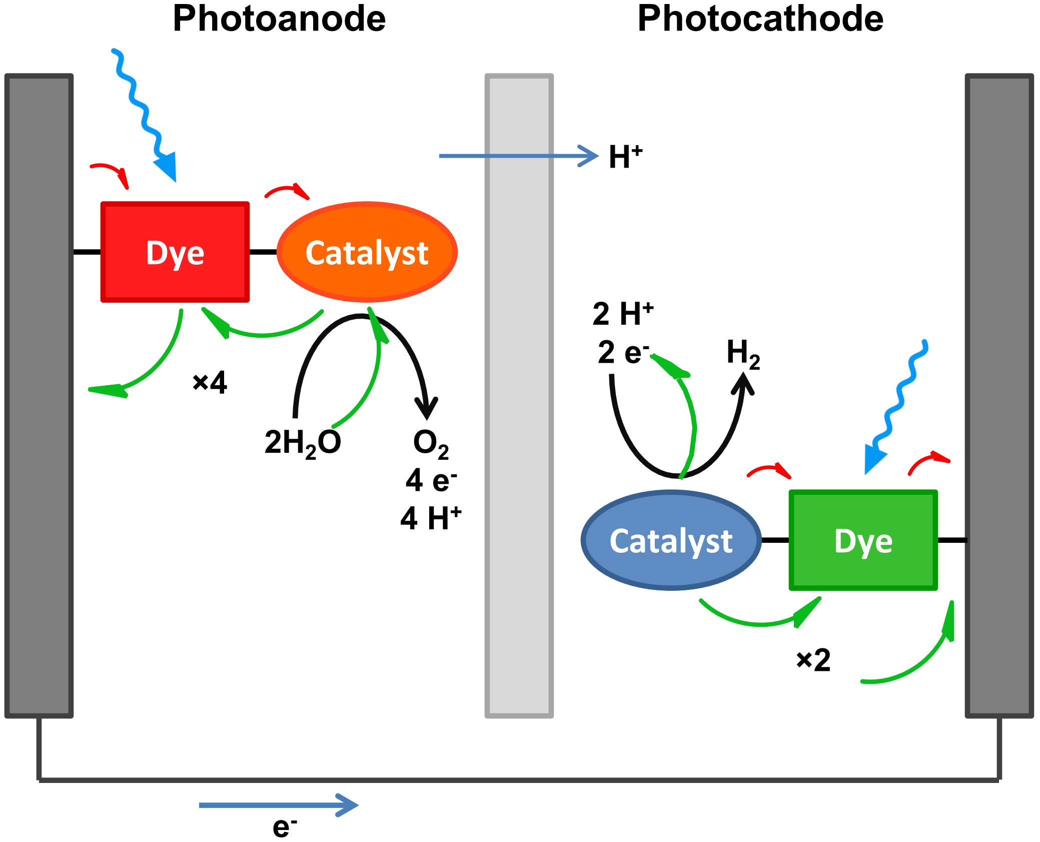
Photodriven Catalysis: Photosensitizers for Energy Demanding Reactions

Solar Fuels

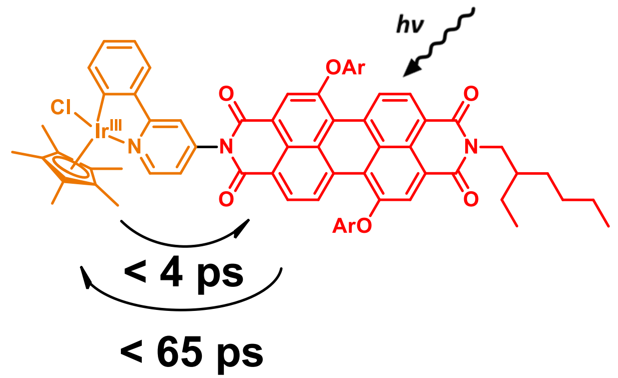
Image from SOFI
http://www.solar-fuels.org/research-applications/

Molecular Approach to Photoelectrochemical Cells

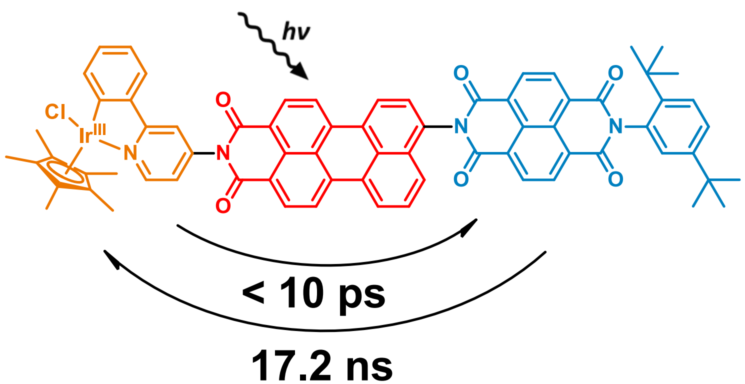


Overall Strategy

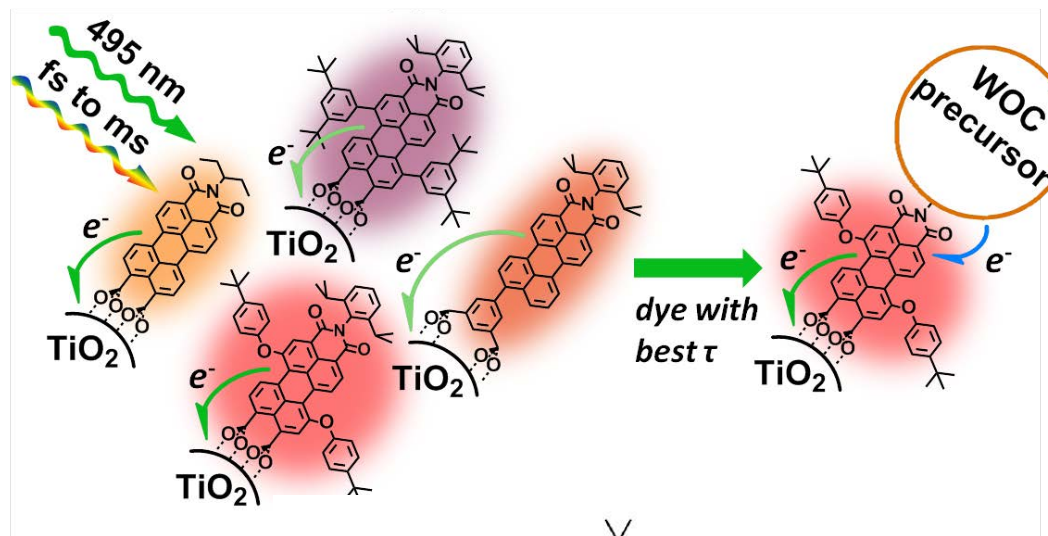
Use time-resolved spectroscopy to probe photo-initiated multi-step catalytic mechanisms: *One step at a time*

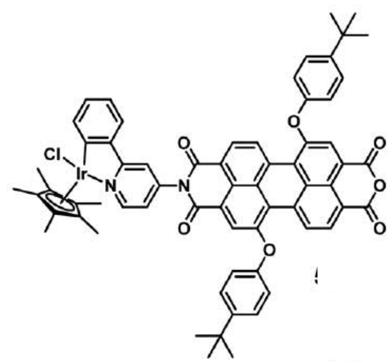


Vagnini, M. T. *et al. Proc. Natl. Acad. Sci.* 2012, *109*, 15651-15656.



Vagnini, M. T. *et al. Chem. Sci.* 2013, *4*, 3863-3873.





Lindquist, R. J.; Phelan, B. T.; Reynal, A.; Margulies, E. A.; Shoer, L. E.; Durrant, J. R.; Wasielewski, M. R., *J. Mater. Chem. A* 2016, *4*, 2880.

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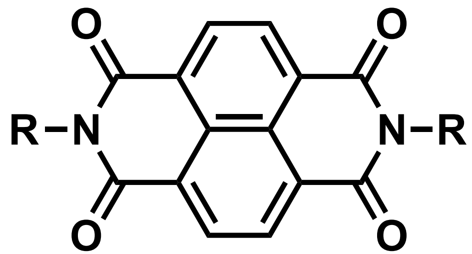
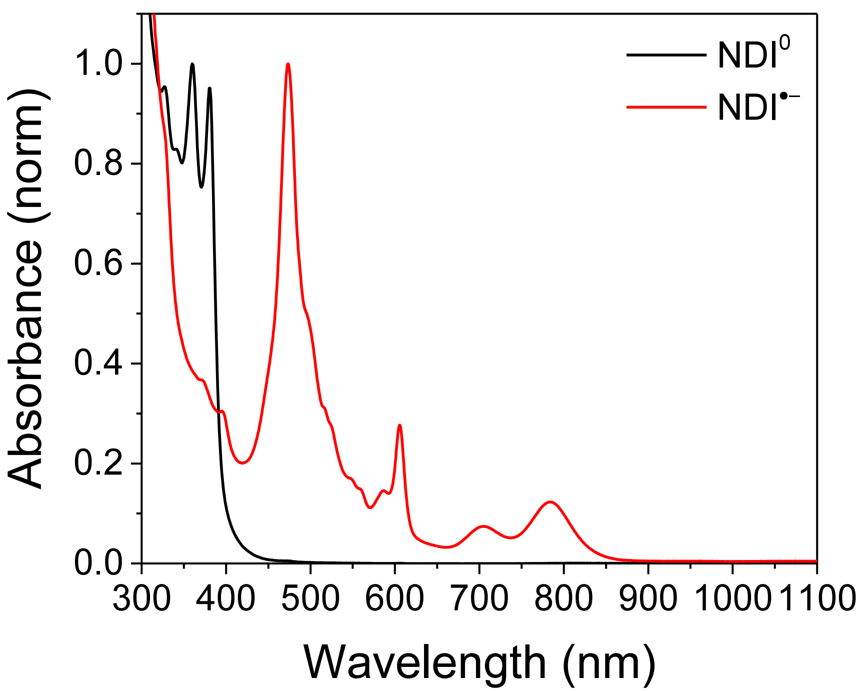
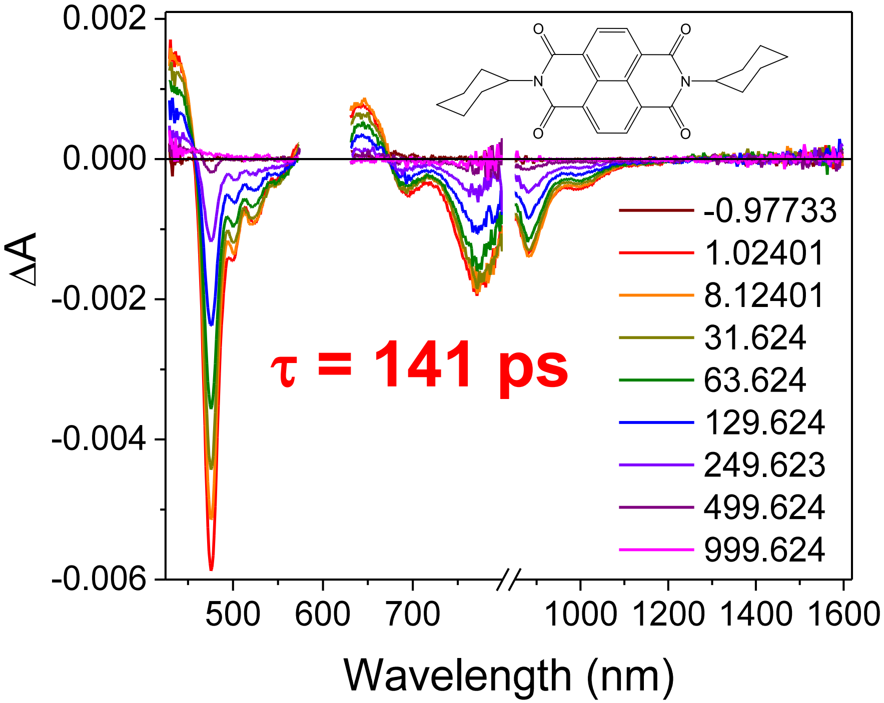
Photoexcited NDI anions are Super-reductants

Reduced at –0.48, –0.99 V vs SCE
$^*NDI^{1-}$ has –2.08 V reducing power
$^*NDI^{2-}$ has –3.07 V reducing power



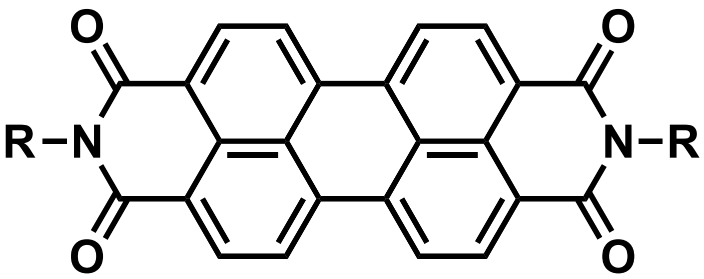


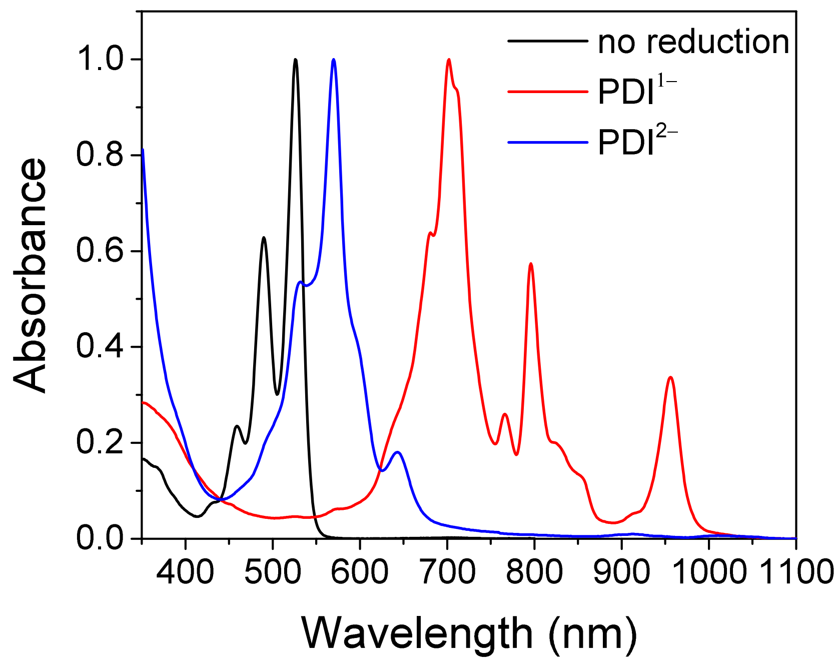


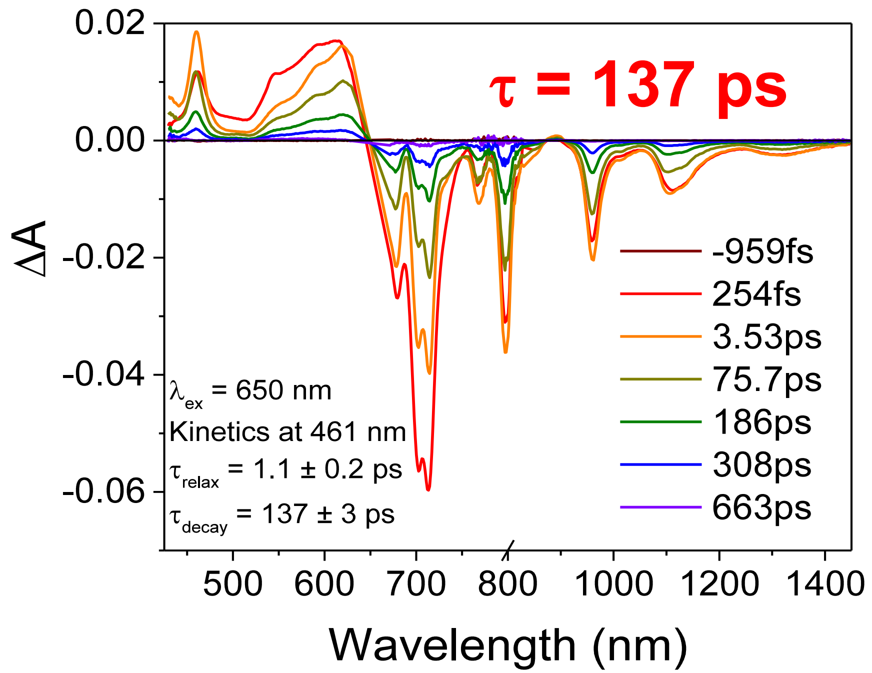
D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas and MRW, *J. Phys. Chem. A*, 2000, 104, 6545-6551.

Photoexcited PDI anions are Super-reductants

Reduced at –0.43, –0.73 V vs SCE
$^*PDI^{1-}$ has –1.73 V reducing power
$^*PDI^{2-}$ has –2.45 V reducing power





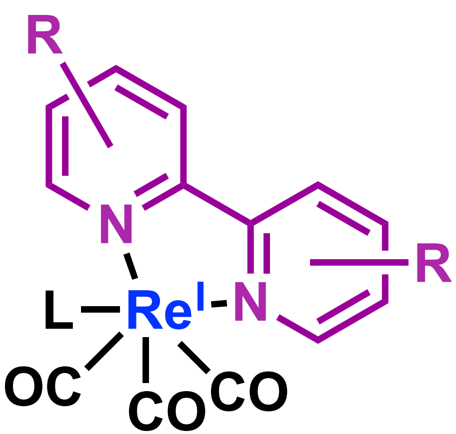


D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas and M. R. Wasielewski, *J. Phys. Chem. A*, 2000, 104, 6545-6551.

Photoexcited Radical Anions as Super-reductants

Strategy:

- Couple photoexcited radical anions with hard to reduce catalysts.
- Use multi-step electron transfer to increase the lifetime of the reduced catalyst intermediates.



Re(R_2-bpy)$(CO)_3$L:

- bpy ligand reduced at –(1.2-1.35) V vs SCE and Re center reduced at –(1.5-1.65) V vs SCE (varies depending on R)
- Binds CO_2 very poorly after one electron reduction
- Binds CO_2 very well (and catalysis initiated) after second reduction and loss of L

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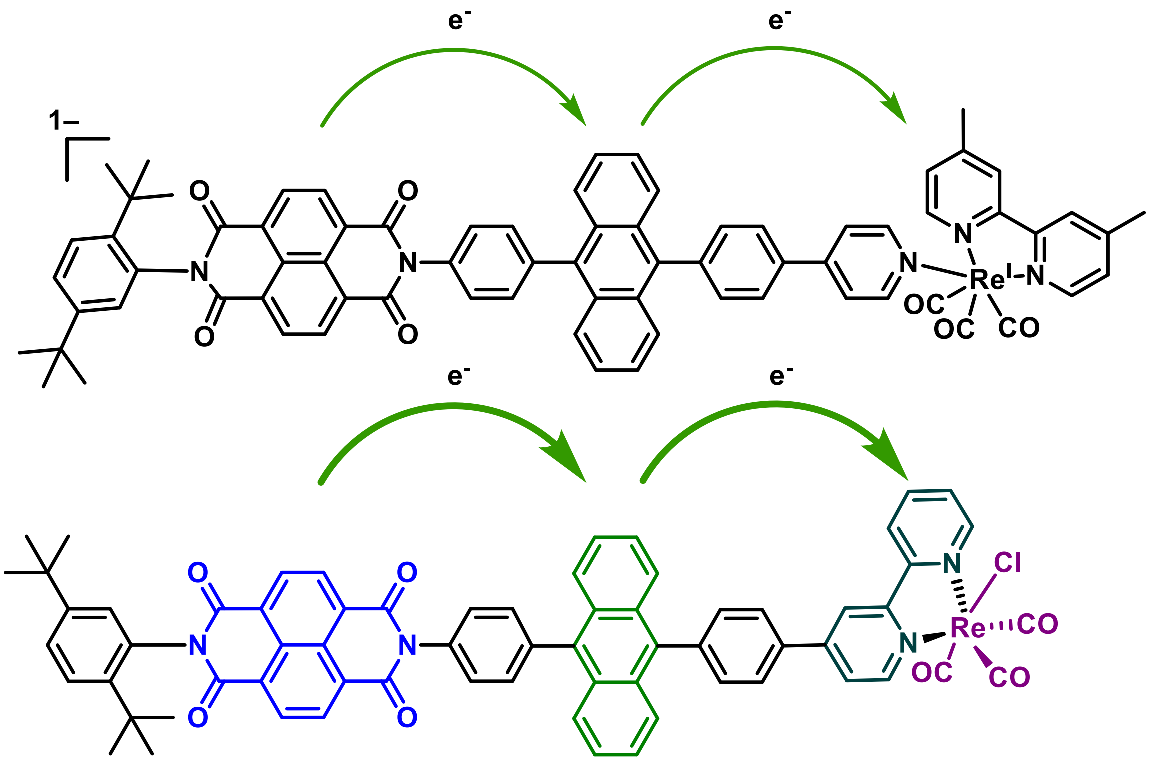
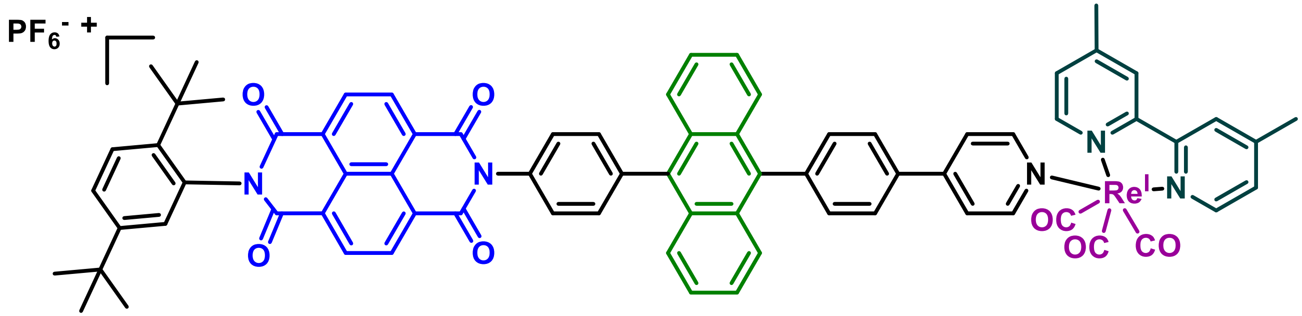
Photoexcited Radical Anions as Super-reductants

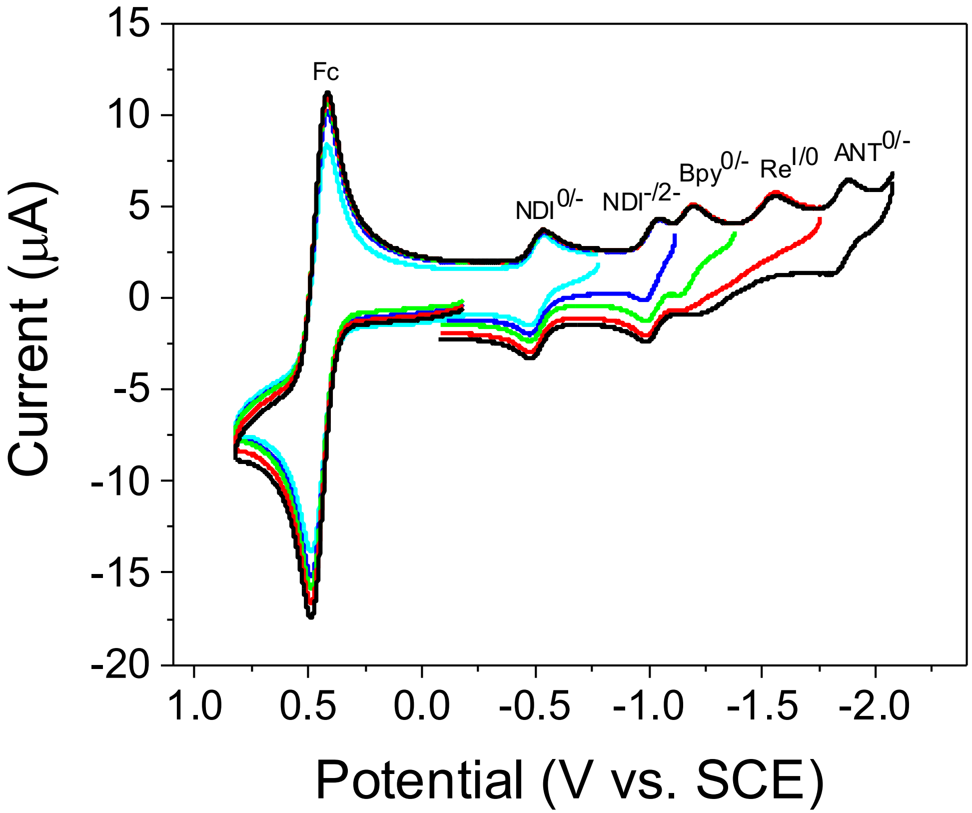
- Use a triad to enhance the charge shift lifetimes.
- Diffusive encounter with CO_2 should be more facile.
- Longer charge shift lifetimes allow the study of intermediates, charge accumulation, and catalysis.



J. F. Martinez, N. T. La Porte, C. M. Mauck, and MRW, *Faraday Discuss.* 198, 235-249 (2017).

Electrochemistry of the Re Complex





NDI: -0.51 V, -1.01 V

DPA: -1.85 V

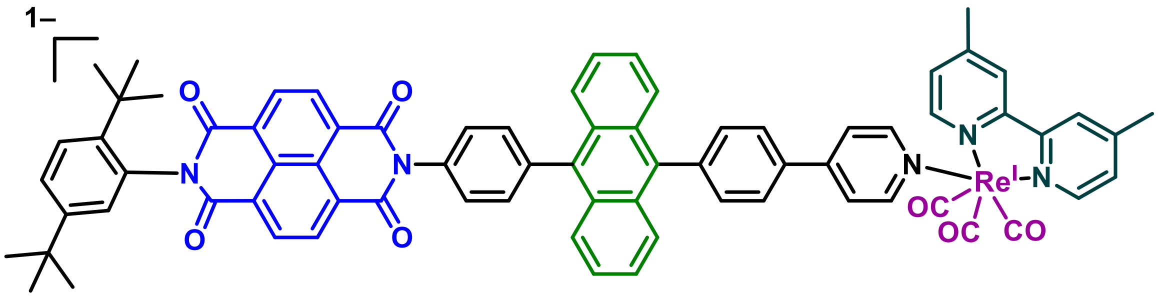
Bpy: -1.20 V

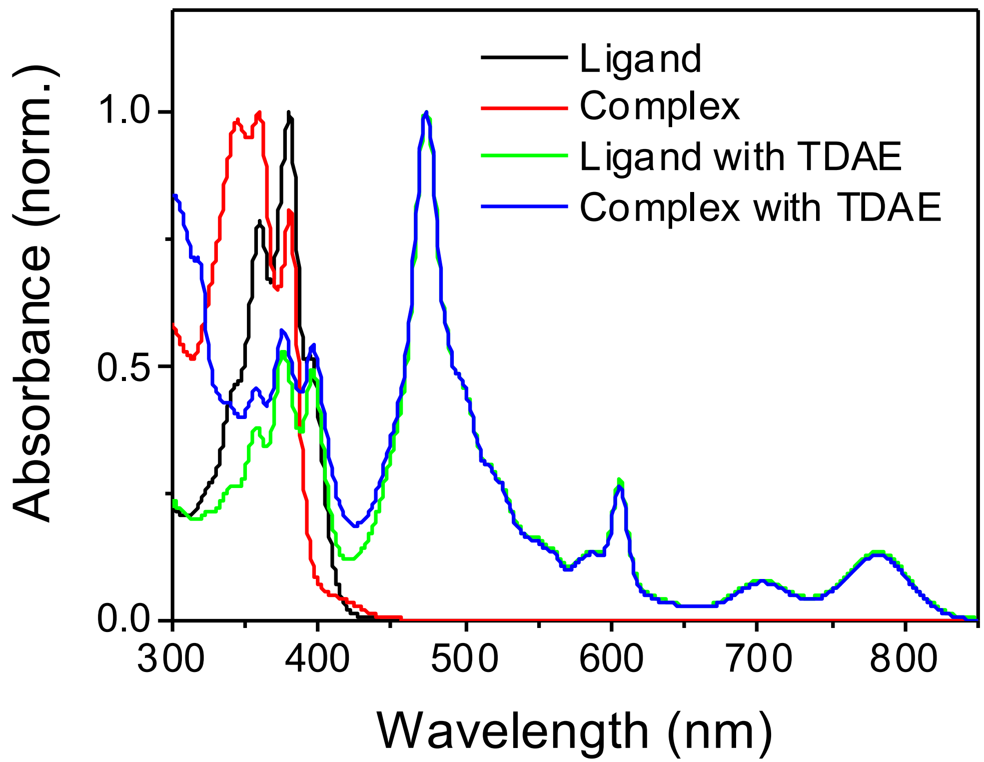
Re: -1.55 V

Excited State Reduction

Potential of *NDI•– : -2.11 V

Excitation Window

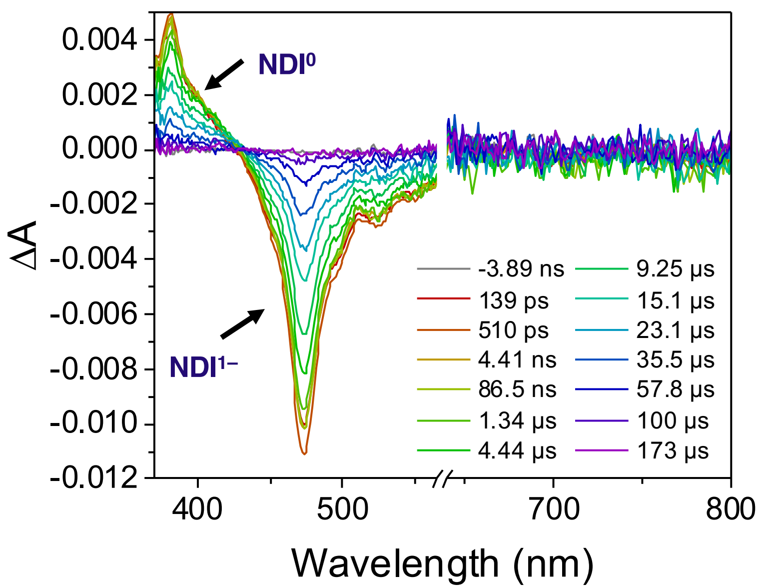


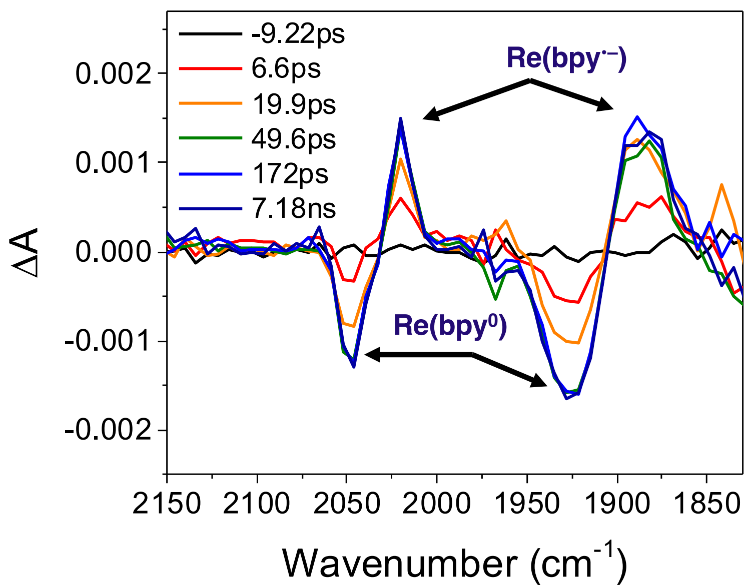


NDI•- can be selectively excited at 450-850 nm.

Femtosecond Transient Absorption in the Vis/NIR and mid-IR

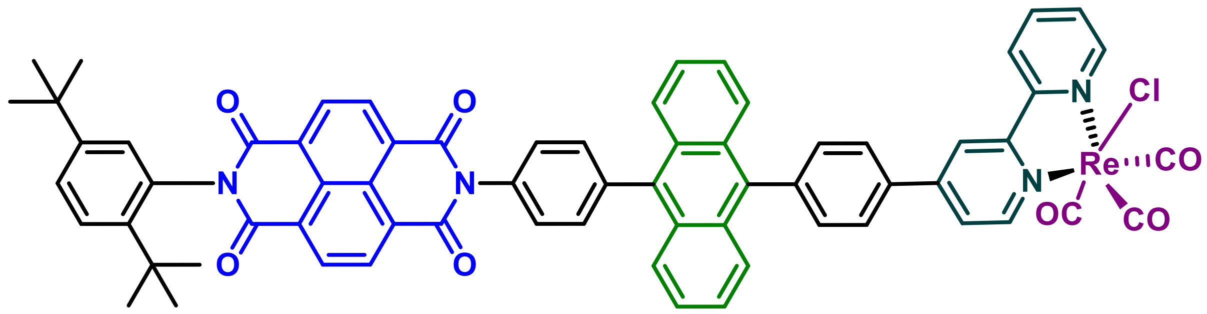
τ_{CS1} = 21 ps τ_{CS2} < 4 ps

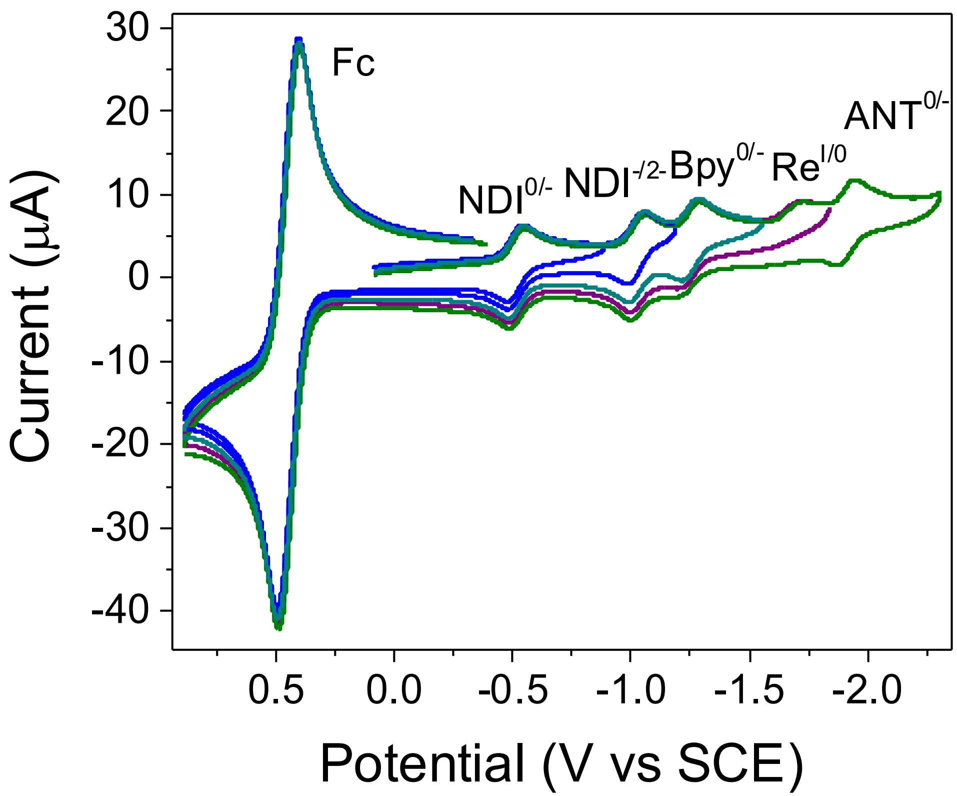




Long reverse charge shift lifetime τ_{RCS} = 43.4 ± 1.2 μs

Electrochemistry of the Re Complex





NDI: -0.52 V, -1.04 V

DPA: -1.85 V

Bpy: -1.30 V

Re: -1.50 V

Excited State Reduction

Potential of $^*NDI^{\bullet-}$: -2.12 V

Light-driven Reduction of a Re-based CO_2 Reduction Catalyst

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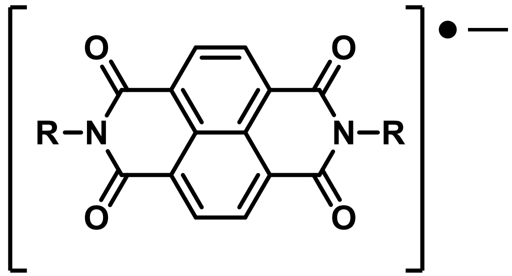
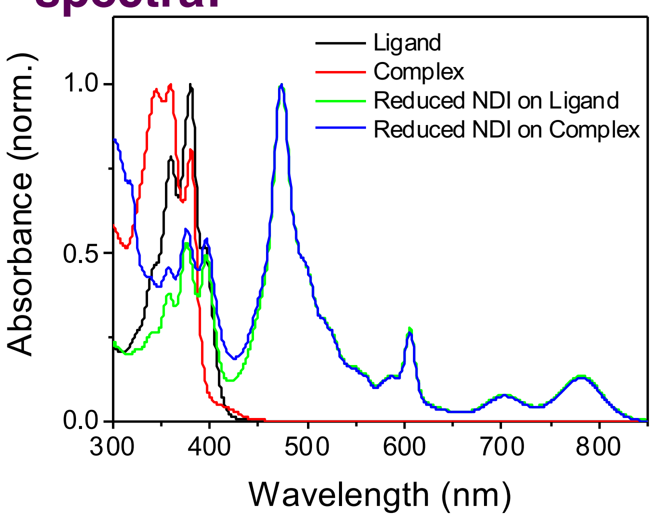
NDI Radical Anion:



Reduction of the non-innocent bpy ligand:

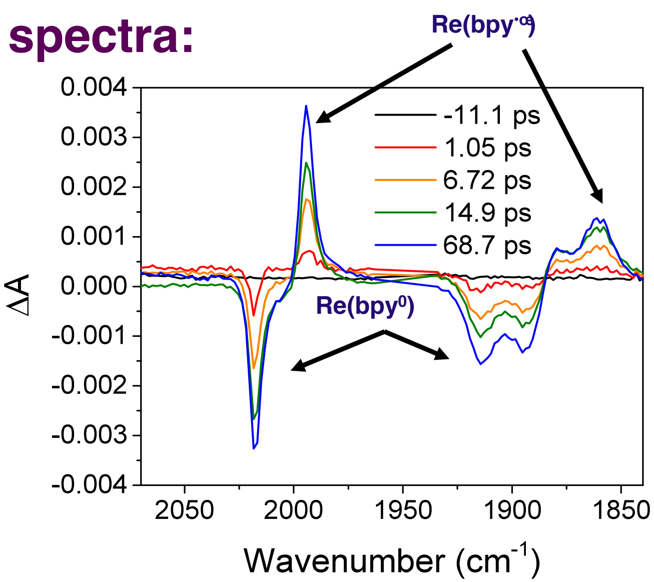
NDI is reversibly reduced at –0.48 V vs SCE
The excited NDI radical anion has –2.12 V of reducing potential using near-infrared light at 800 nm.

Ground state spectra:



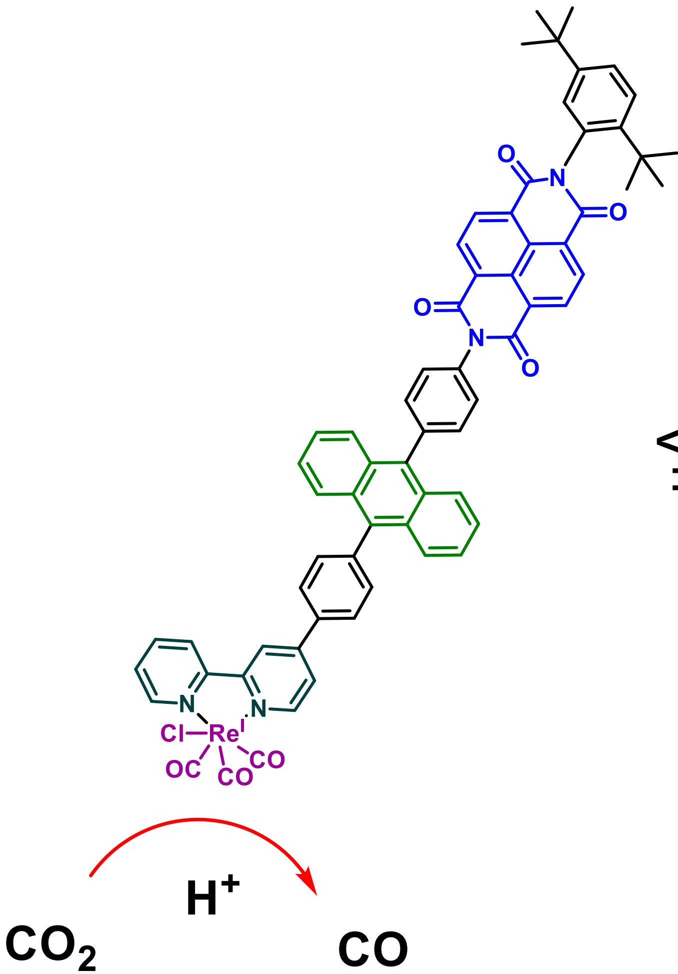
Femtosecond IR spectra:

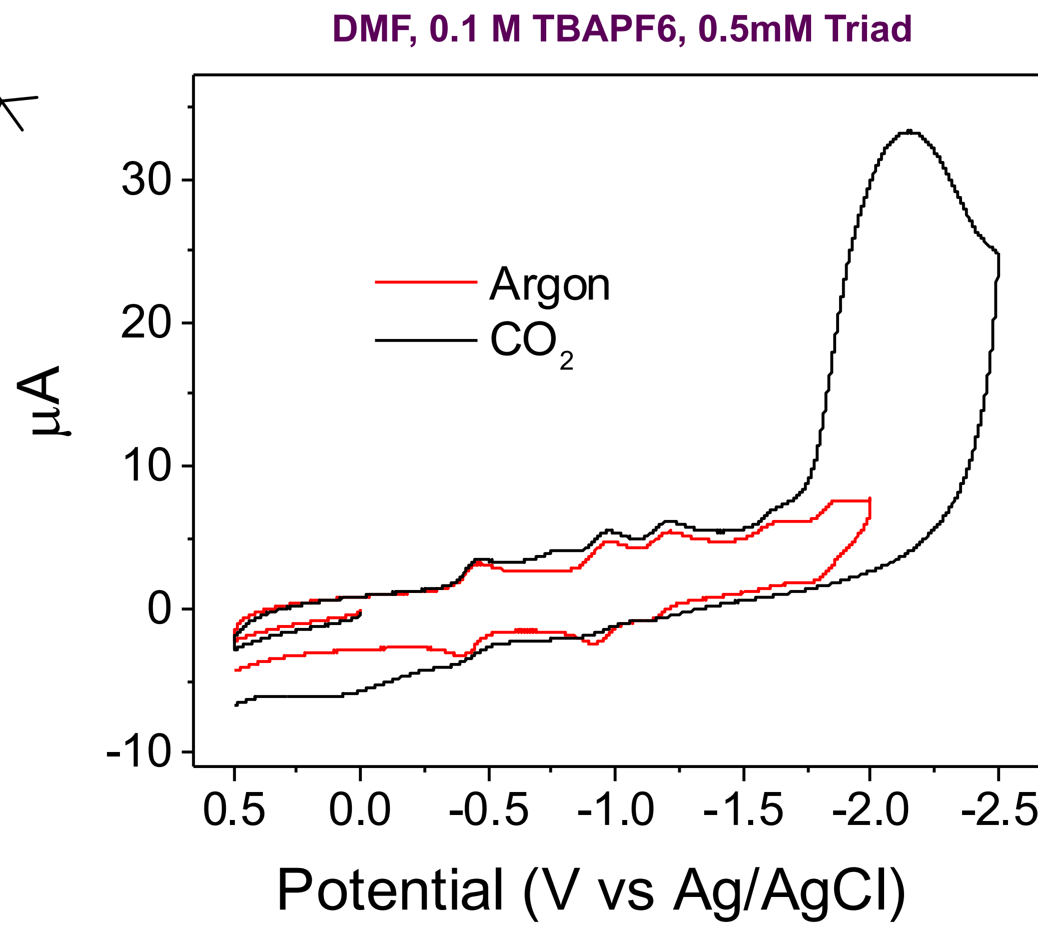
τ_{CS} = 5 ps



τ_{RCS} = 24.4 ns

Electrocatalytic CO_2 Reduction





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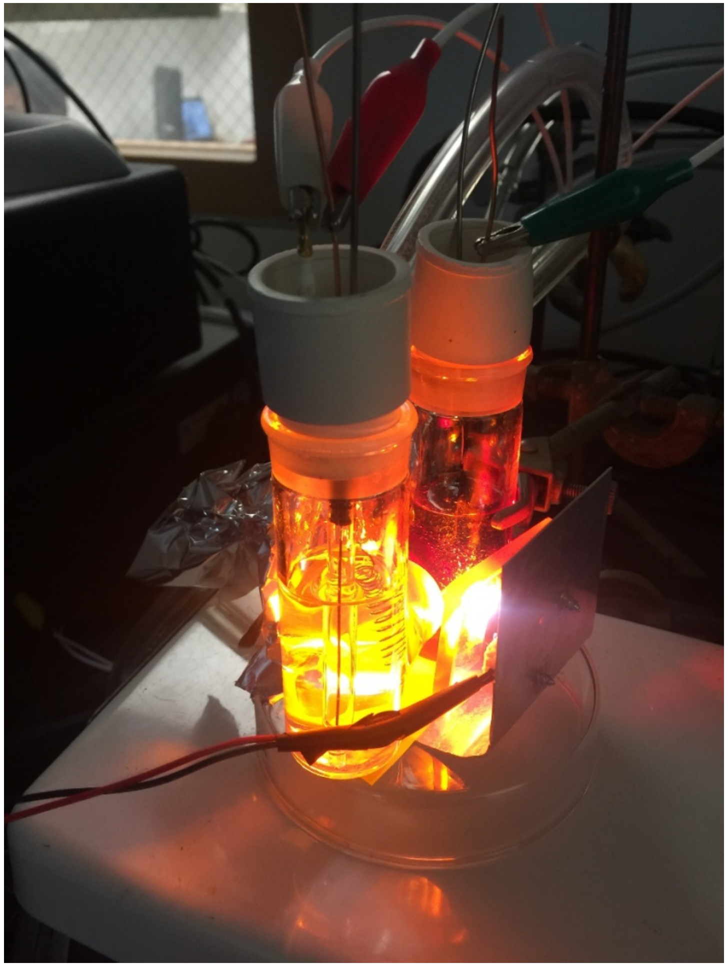
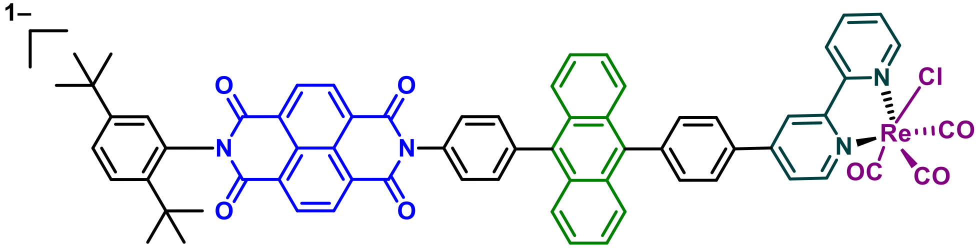
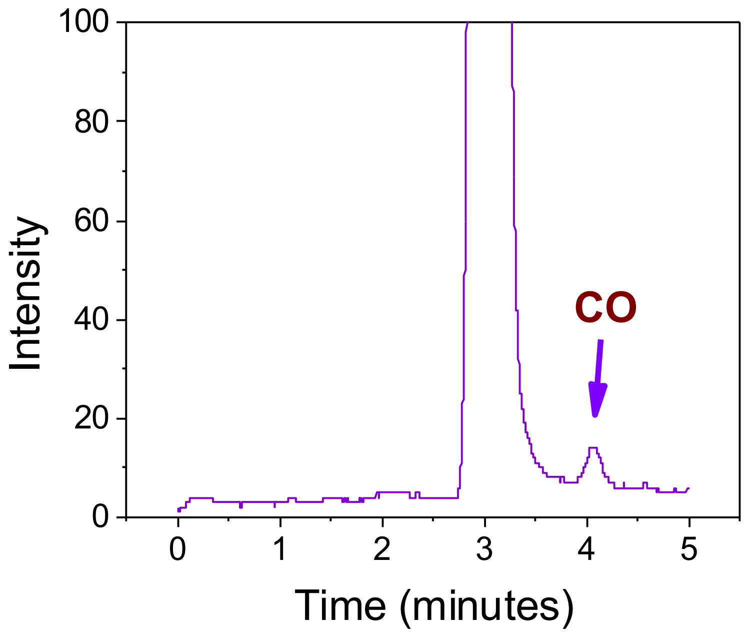
Bulk Photoelectrolysis



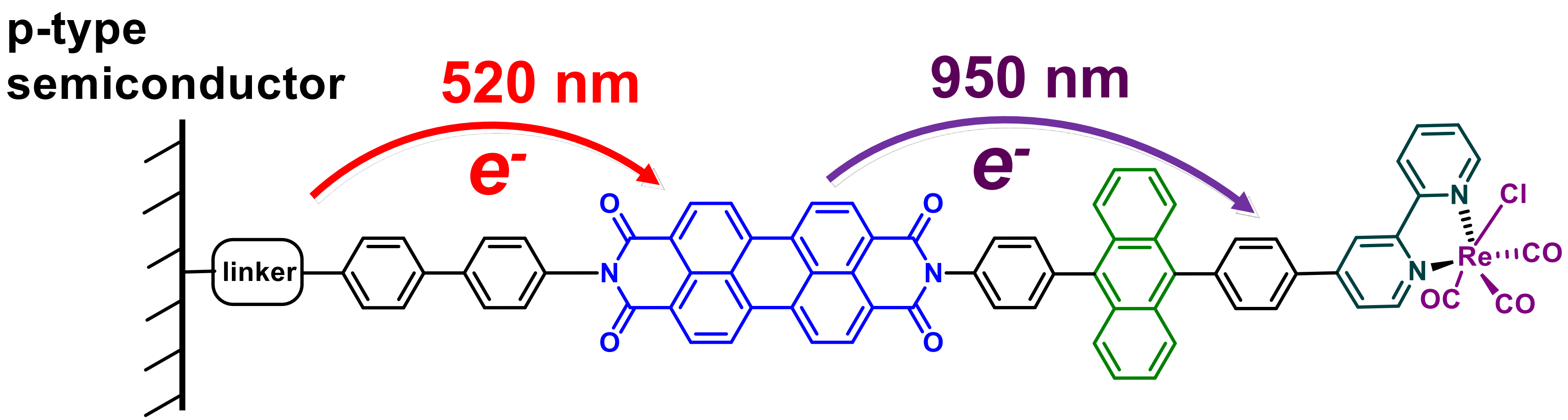




-0.6V vs. SCE applied potential, 0.1 M TBAPF6, 0.1 M MeOH, 0.1mM Triad. λ >520nm

Light-driven Super-Reductants for CO_2 Reduction

The next step:



Use two electron transfer steps that take advantage of both visible and near-infrared photons.

Summary

- Arylene diimide radical anions can be reversibly reduced at mild potentials to radical anions.

- Arylene diimide radical anions absorb in the visible and near-IR spectral regions.

- Excited states of the radical anions are powerful reductants that can drive energy-demanding reactions such as CO_2 reduction catalysts.

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