ENERGY AND CHARGE TRANSPORT IN SELF-ASSEMBLING BIO-INSPIRED MATERIALS

Michael R. Wasielewski

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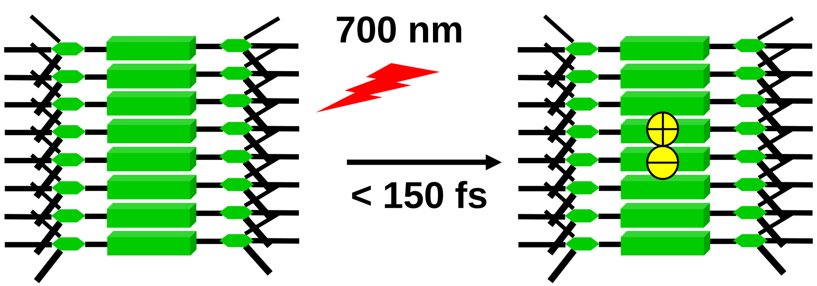
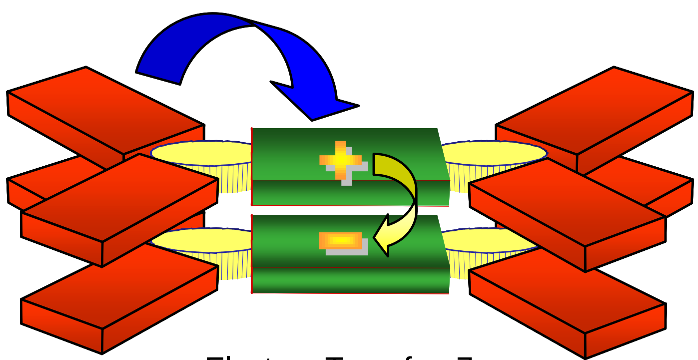
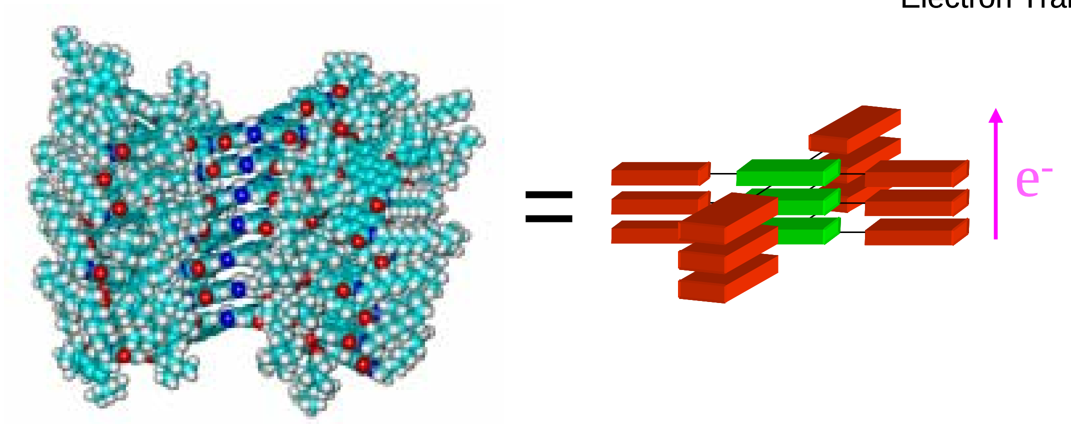


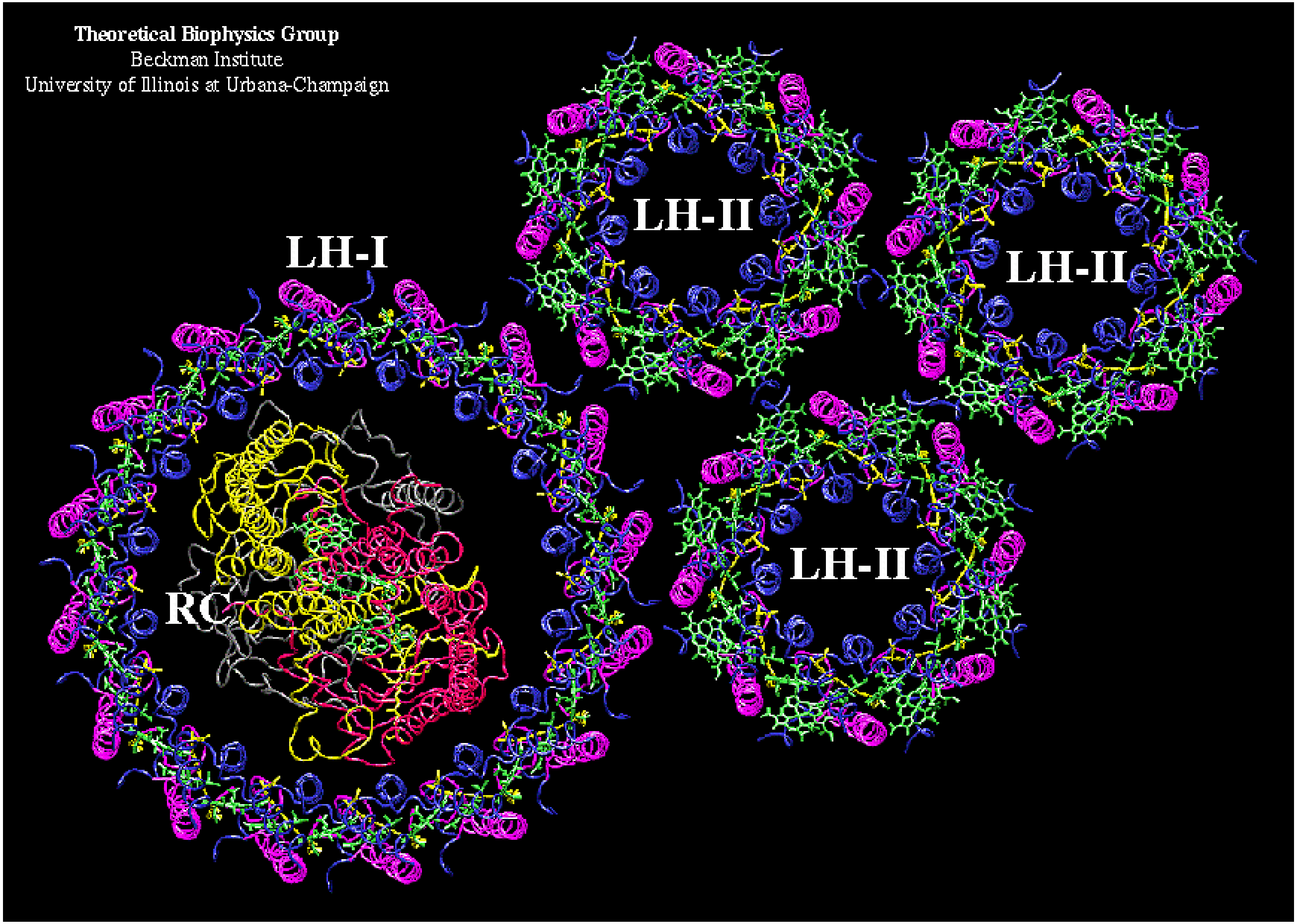
Energy Transfer, 21 ps



Electron Transfer, 7 ps

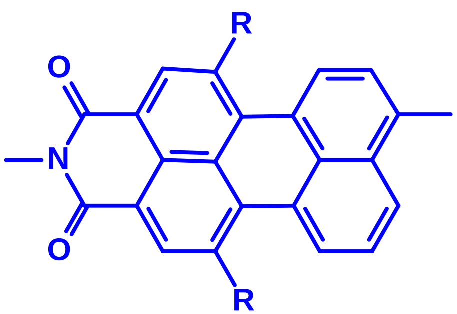


Antenna and Reaction Center Proteins from Photosynthetic Bacteria

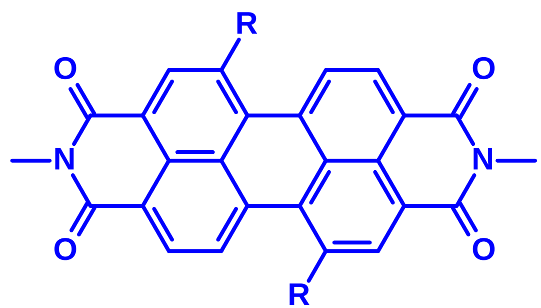


Rylenes Absorbing the Entire Solar Spectrum

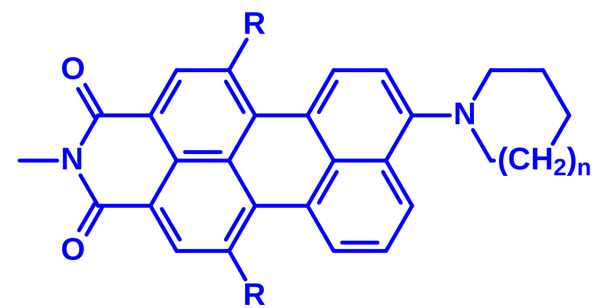
- **Chemically robust, easily oriented due to their rectangular shape**
- **Excellent chromophores as well as electron donors and acceptors**
- **Strong tendency to π stack in a variety of solvents and in the solid**



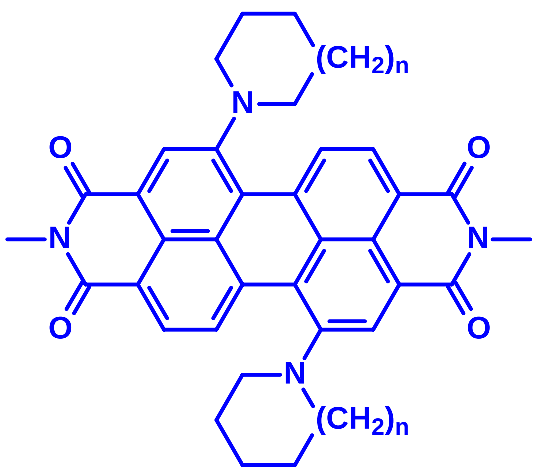
PMI



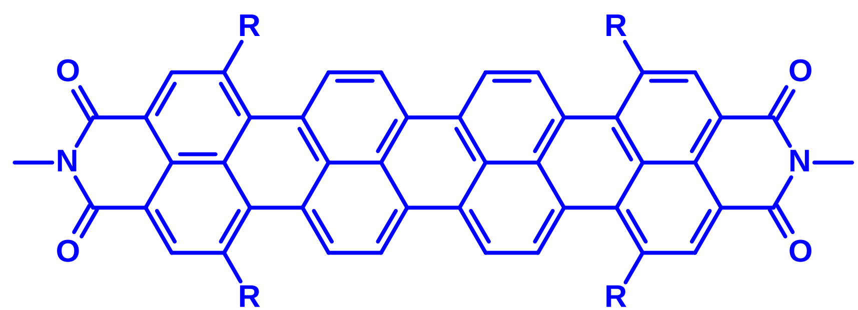
PDI



5PMI (n=0), 6PMI (n=1)



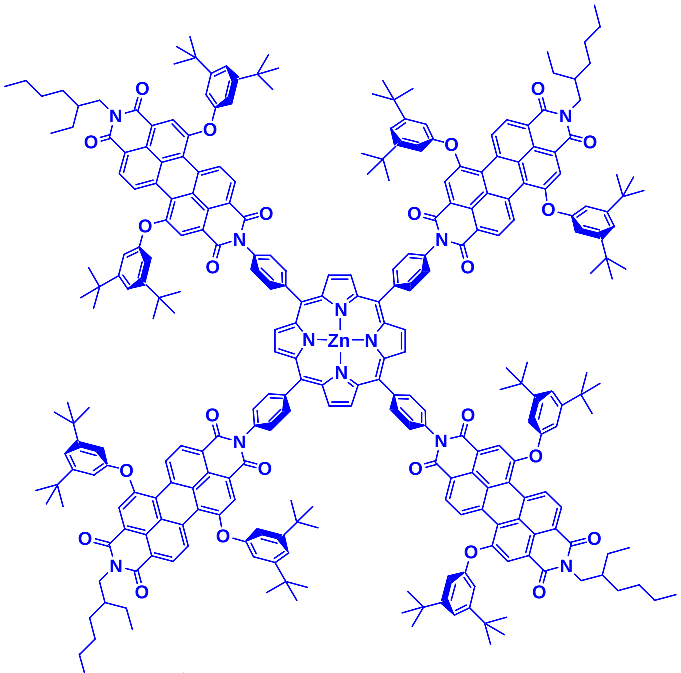
5PDI (n=0), 6PDI (n=1)

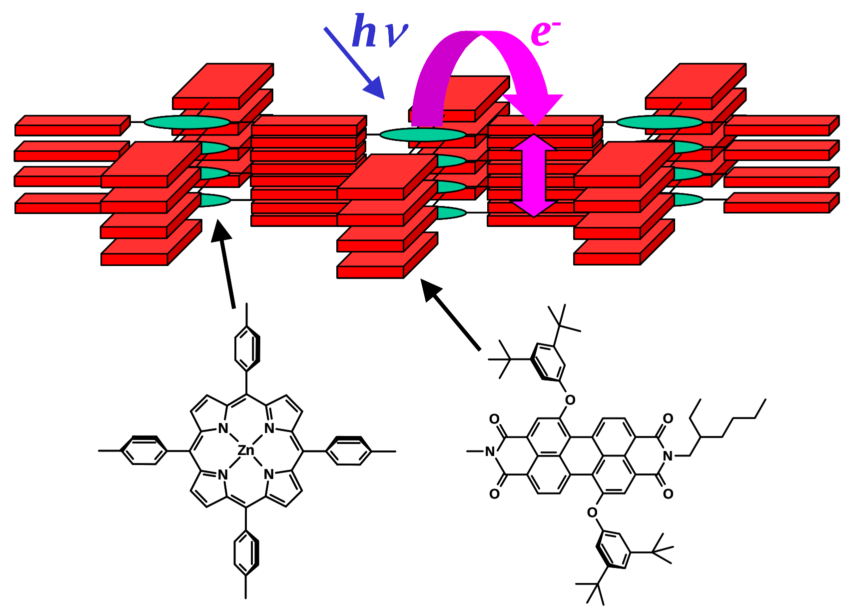


QDI

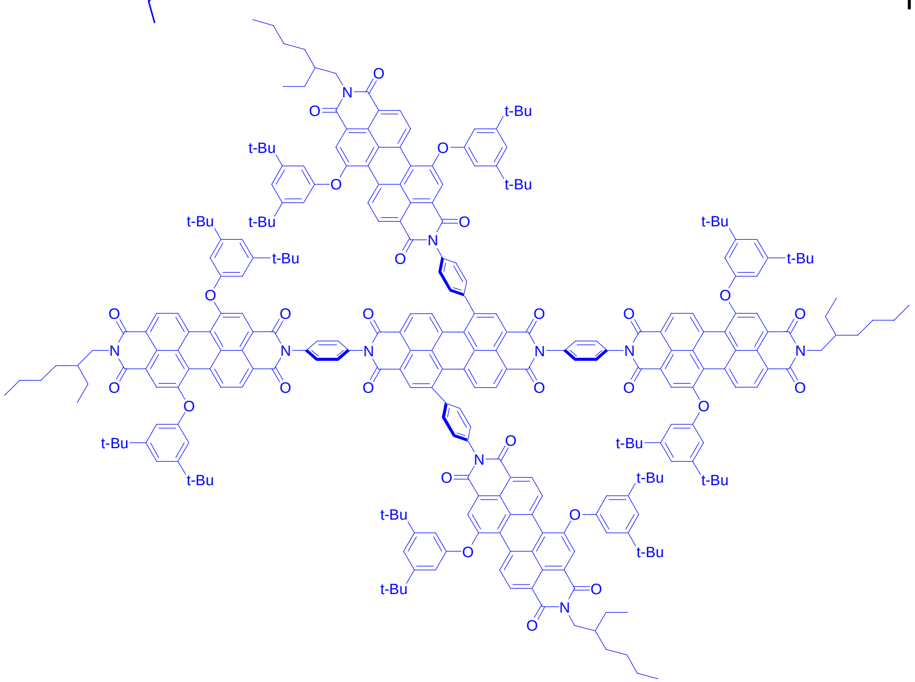
R = 3,5-di-t-butylphenoxy

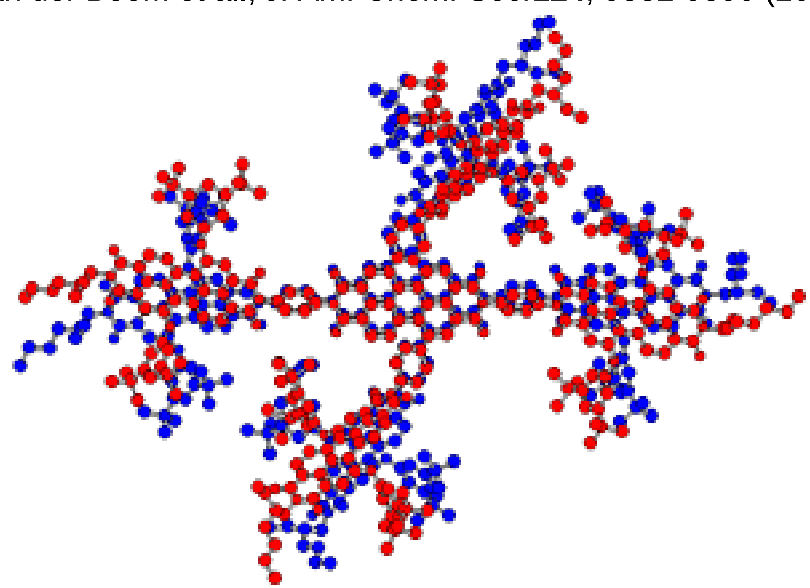
Self-Assembled PDI Arrays for Electron and Energy Transfer





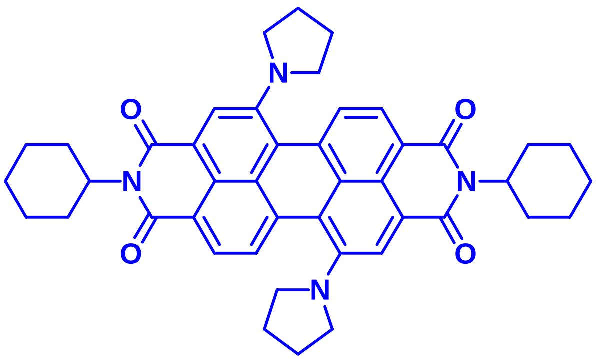
T. van der Boom et al., *J. Am. Chem. Soc.* **124**, 9582-9590 (2002).





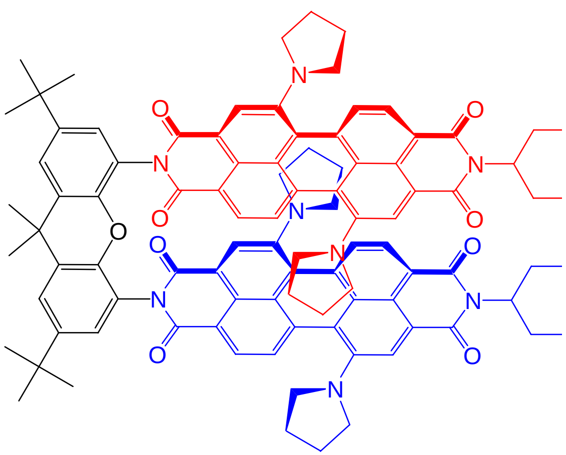
M. J. Ahrens et al., *J. Am. Chem. Soc*. **126**, 8284-8294 (2004).

Symmetry-Breaking in the Excited State Leads to Quantitative Charge Separation in Dimers of 5PDI, a Green Chlorophyll *a* Mimic

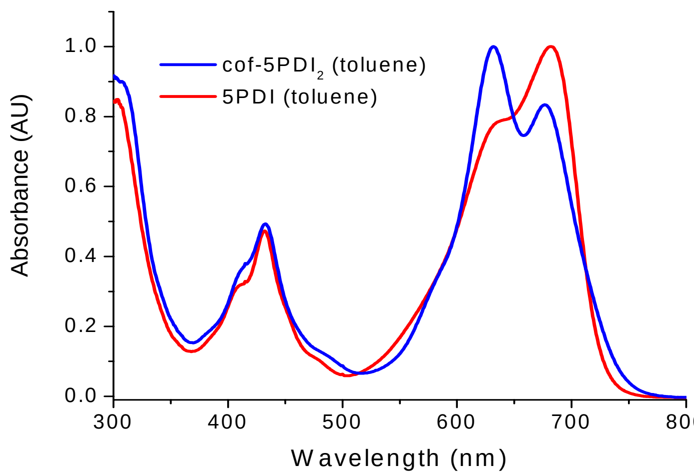


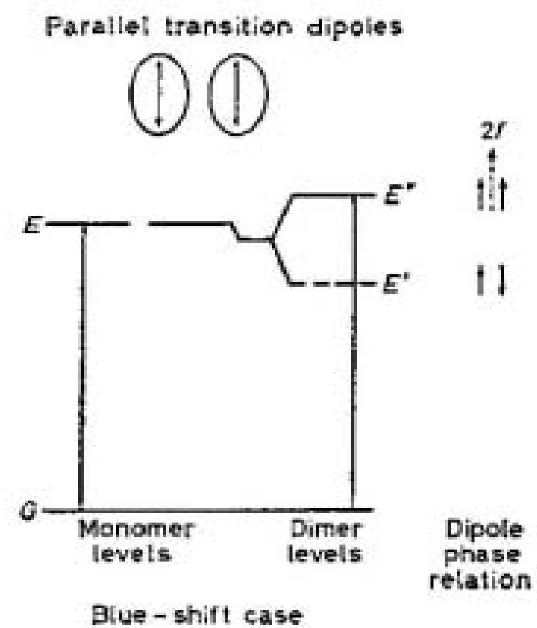
5PDI

- **Strong absorber of 600-800 nm light.**
- **E_{OX} = 0.68 V and E_{RED} = -0.76 V vs. SCE**
- **The π-stacked cofacial chromophores undergo symmetry breaking in the excited state leading to quantitative charge separation.**

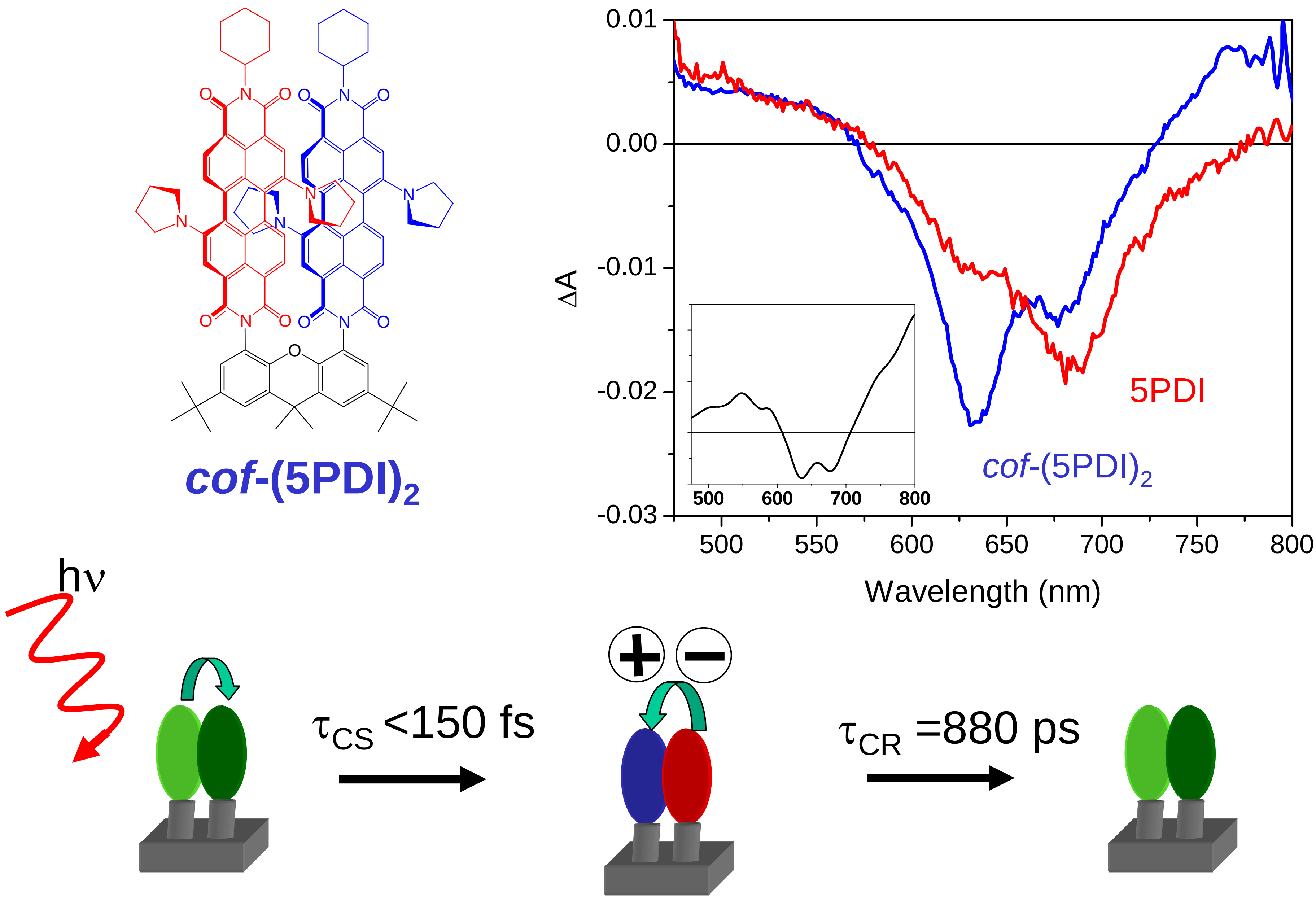


***cof*-(5PDI)$_2$**



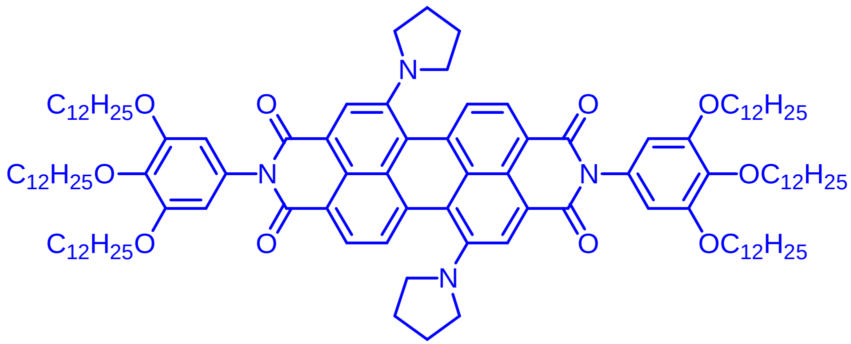


J. M. Giaimo et al., *J. Am. Chem. Soc*. **124**, 8530-8531 (2002).

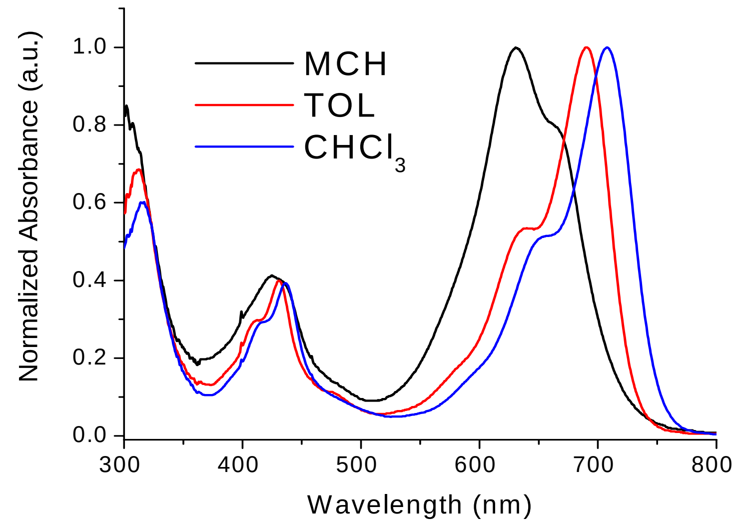


cof-(5PDI)$_2$
0.01
0.00
-0.01
-0.02
-0.03
ΔA
500
550
600
650
700
750
800
Wavelength (nm)
5PDI
cof-(5PDI)$_2$
hν
τ_{CS} <150 fs
τ_{CR} =880 ps

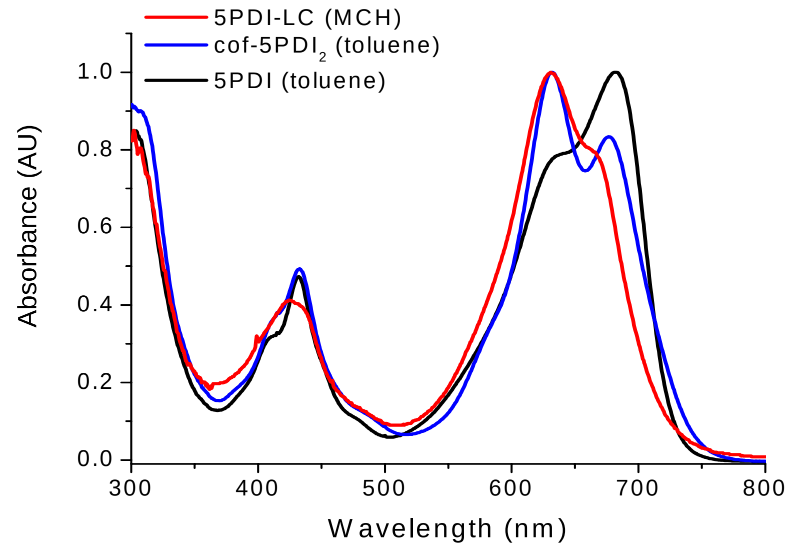
Symmetry-Breaking in the Excited State Leads to Quantitative Charge Separation in Self-Assembled 5PDI Oligomers

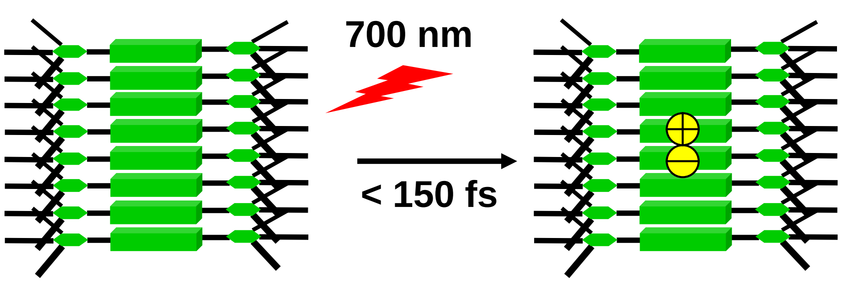


5PDI-LC



- **5PDI self-assembles into cofacial stacks.**
- **Stacks form larger ordered bundles.**
- **Strong absorber of 600-800 nm light.**
- **E_{OX} = 0.68 V and E_{RED} = -0.76 V vs. SCE**
- **The π-stacked cofacial chromophores undergo symmetry breaking in the excited state leading to quantitative charge separation.**



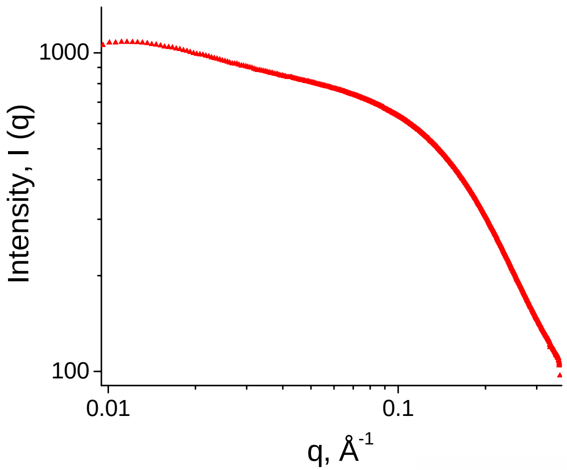


Michael Fuller

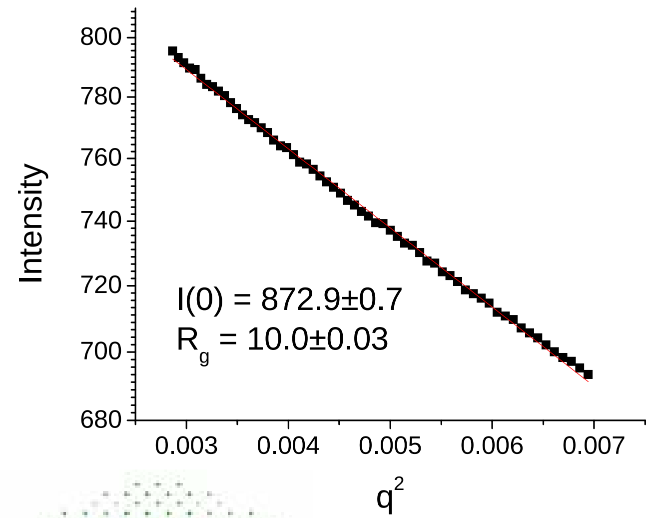
Small-Angle X-ray Scattering Studies in Solution

Advanced Photon Source, Argonne National Laboratory

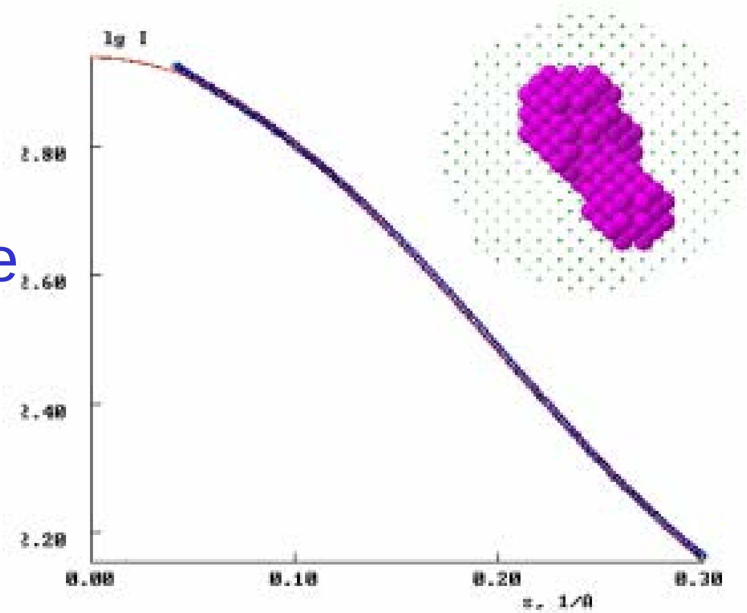
Scattering Intensity



Guinier Plot

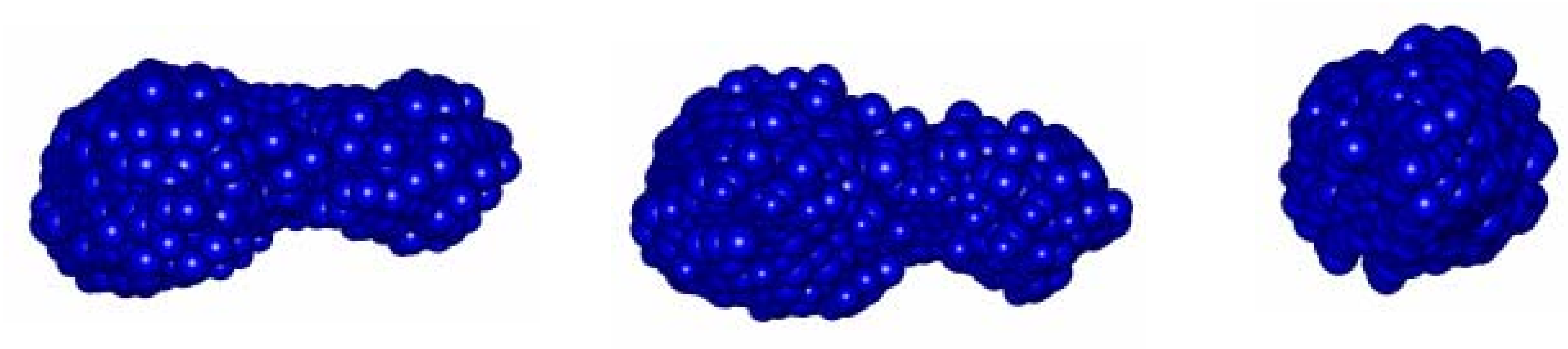


Simulated Annealing Reconstruction of the Aggregate Shape



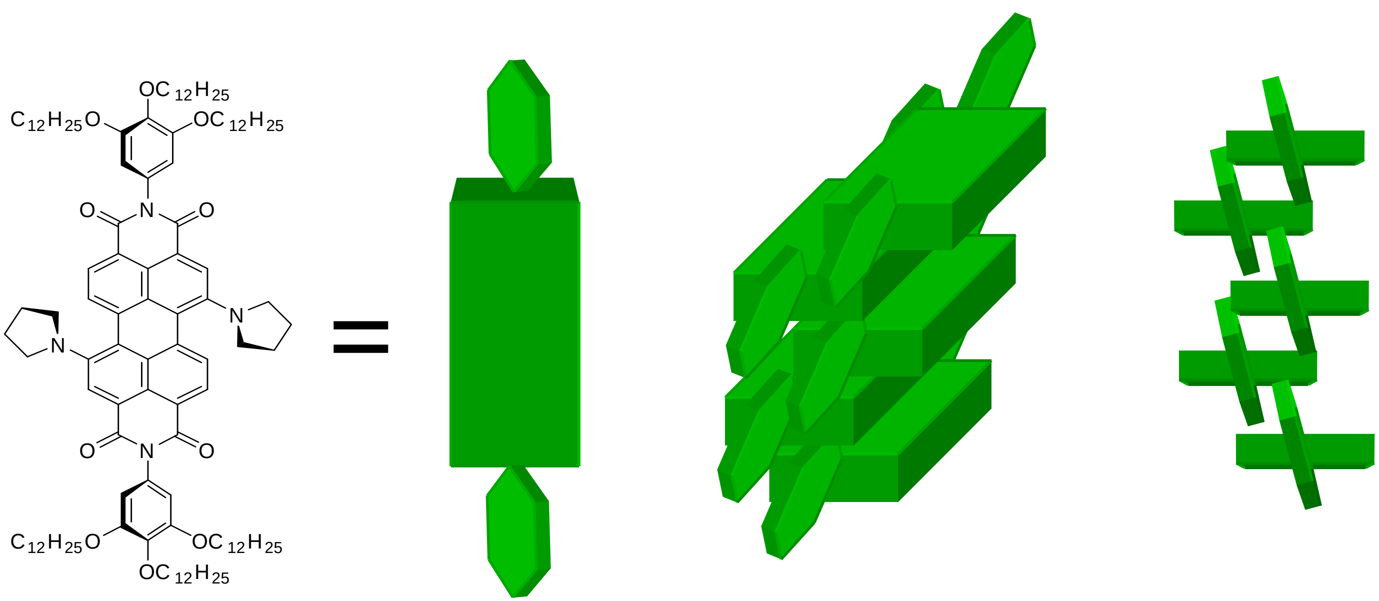
Boris Rybtchinski

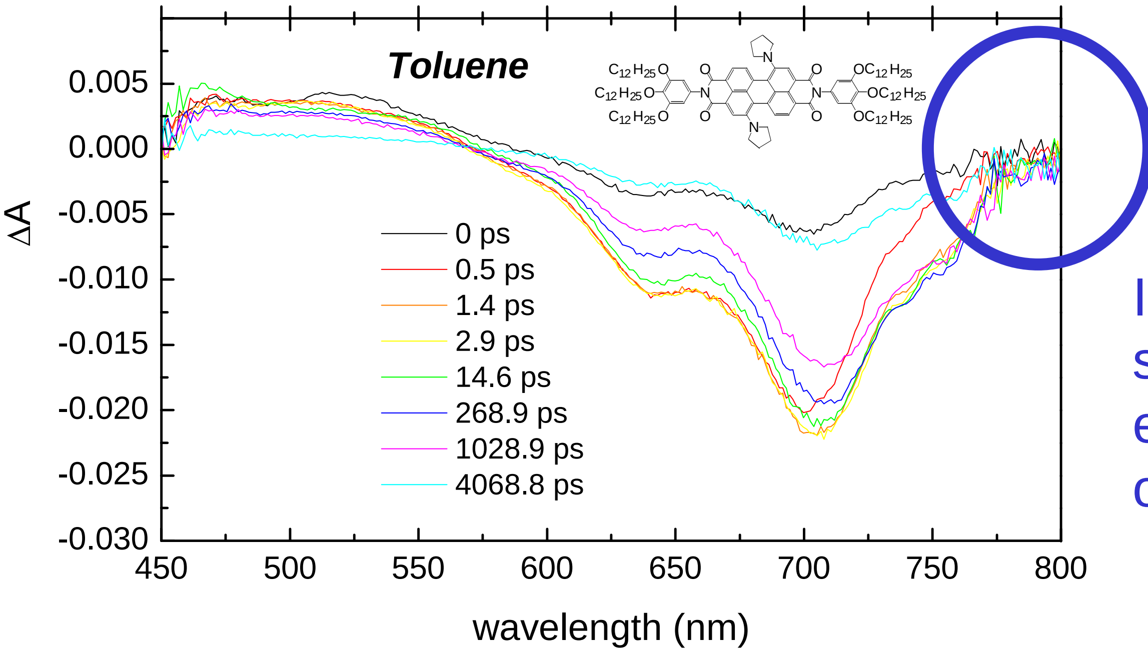
5PDI-LC Aggregate Structure in Solution (10^{-4} M)



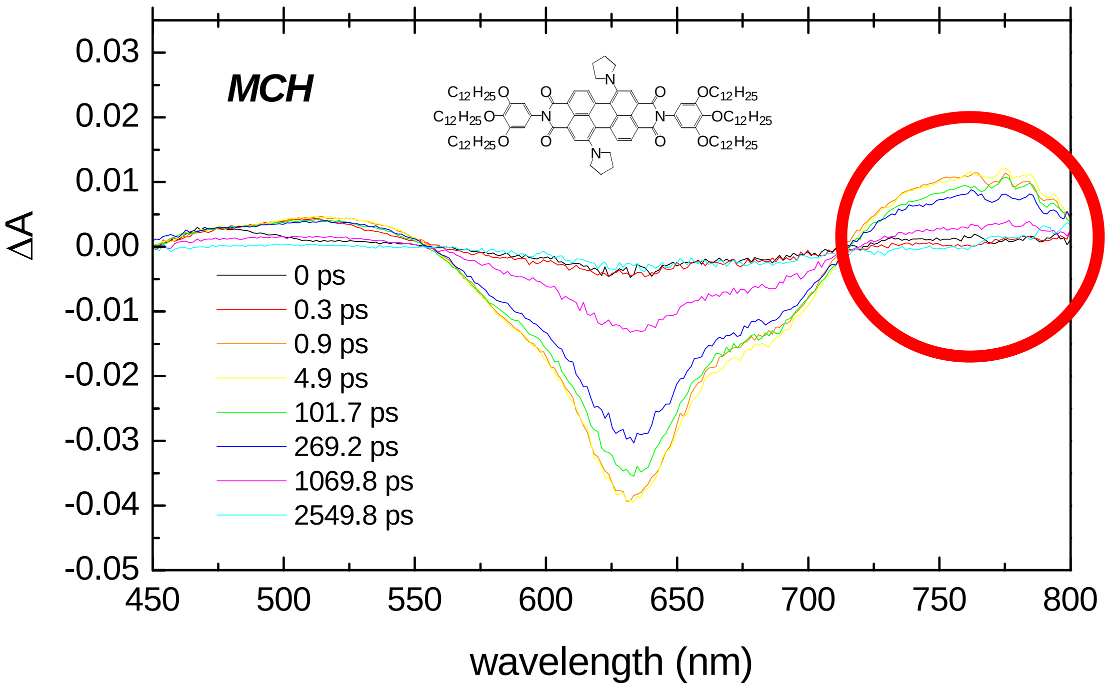
x y z

3.6 x 2.0 x 1.8 nm



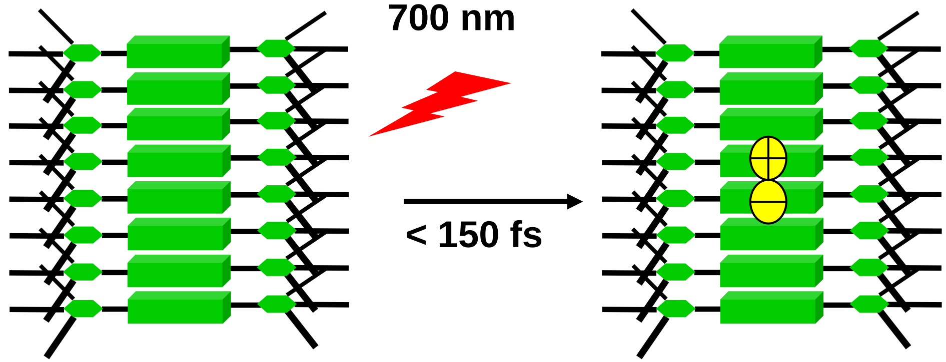


In TOL, $\Delta A = 0$ at λ >740 nm suggests that photoinduced electron transfer does not occur

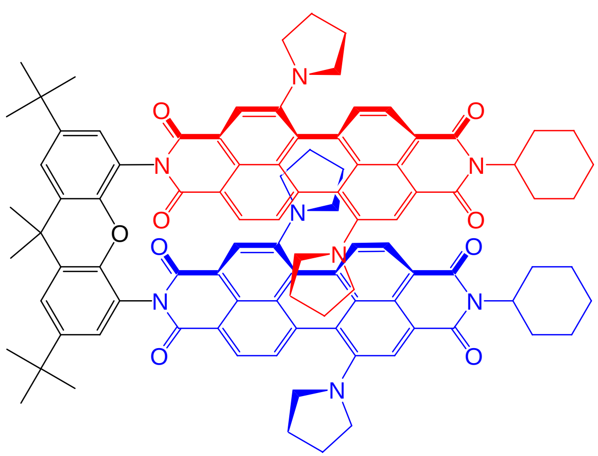


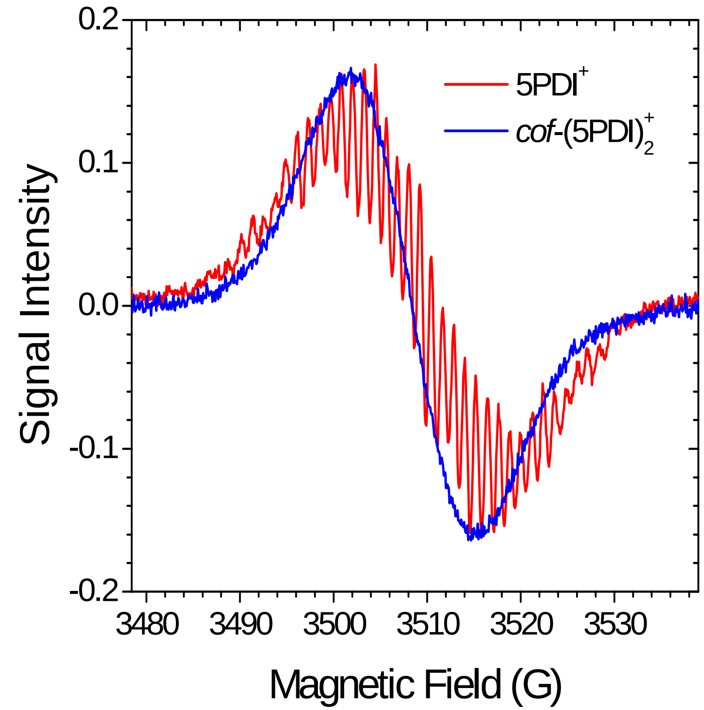
However, in MCH $\Delta A > 0$ suggests that 5PDI anion is present and photoinduced electron transfer occurs

Ultrafast optical spectroscopy shows that quantitative photoinduced electron transfer occurs between stacked non-covalent monomers….



Preliminary EPR results on the cation radical of the *cof*-$(5PDI)_2$ reference molecule show that the charge hops between the two 5PDI molecules.

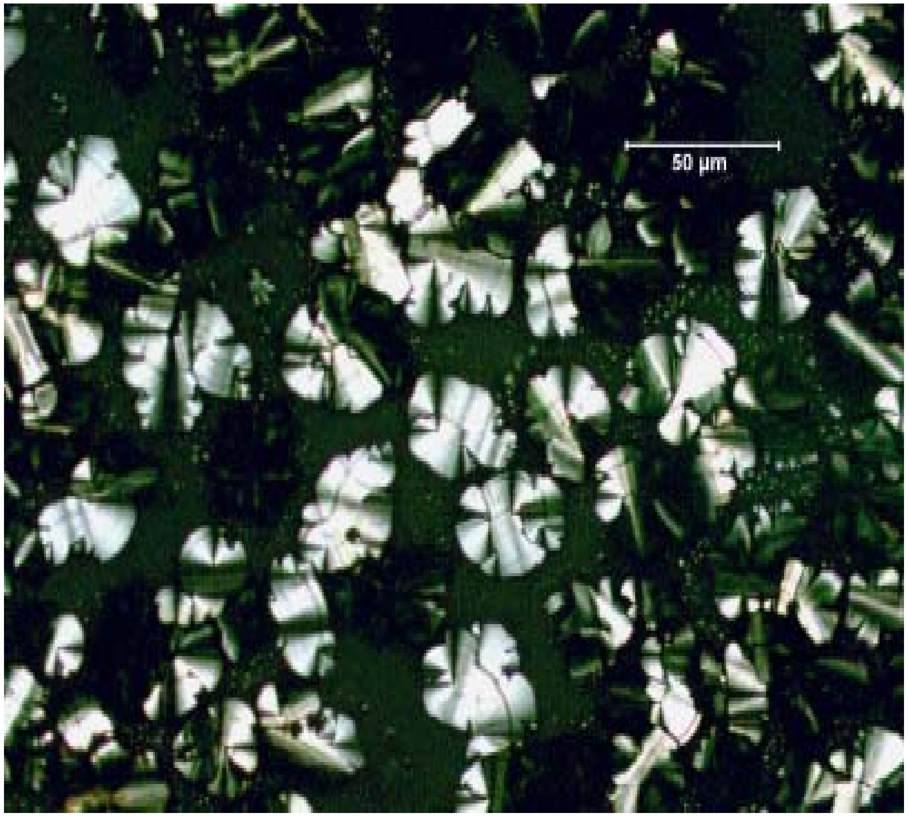




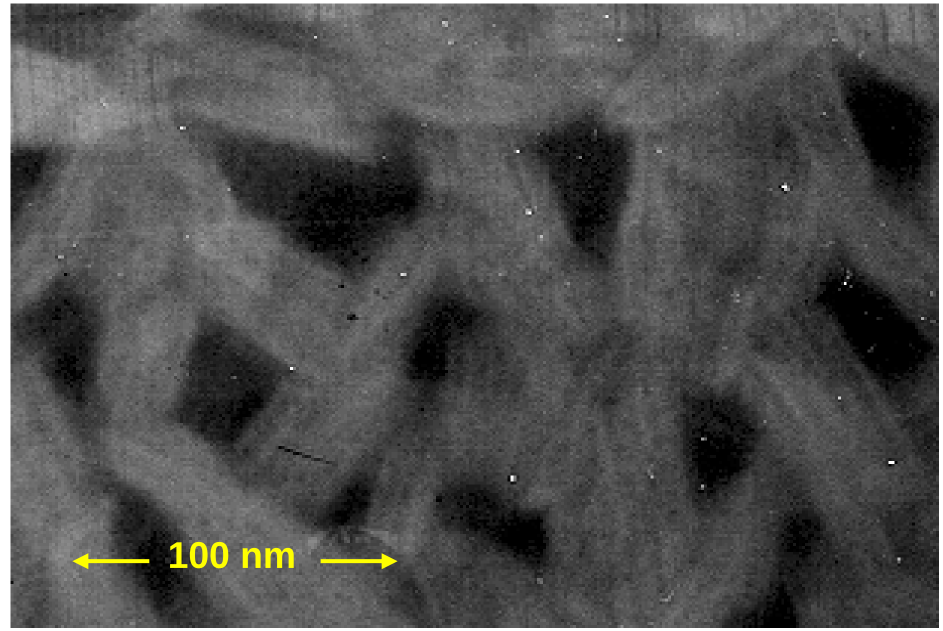
Michael Tauber

Self-Assembly of 5PDI-LC in the Liquid Crystal State

Polarized Optical Microscopy

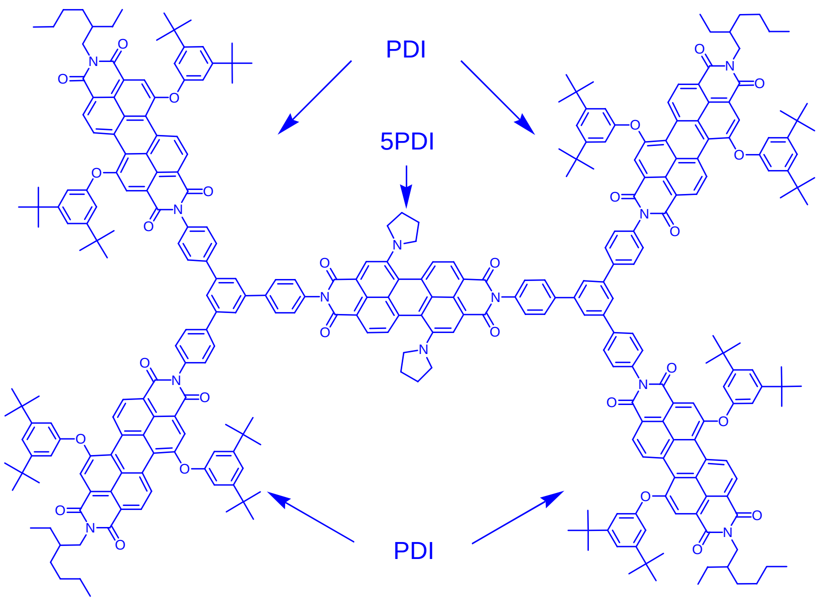


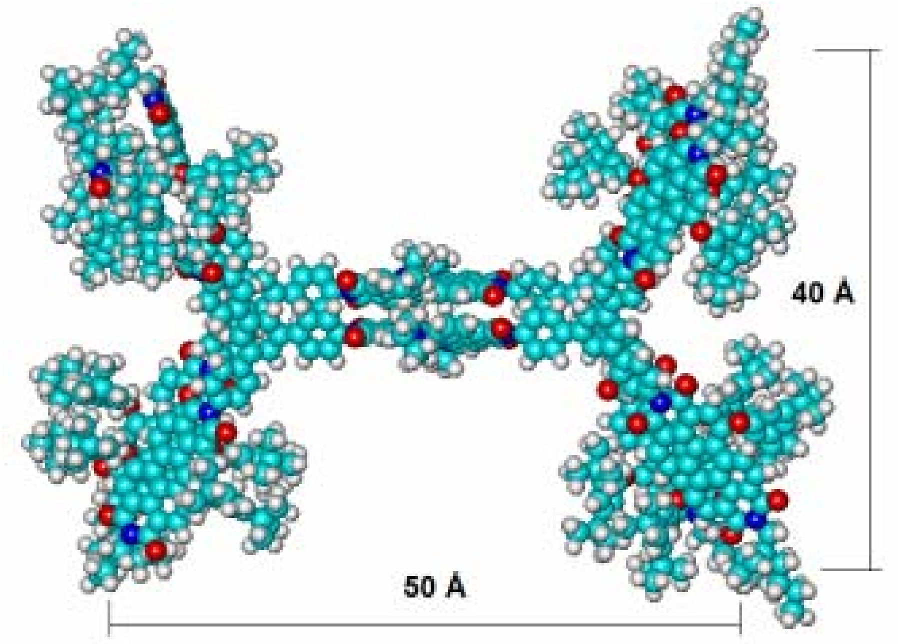
TEM Image

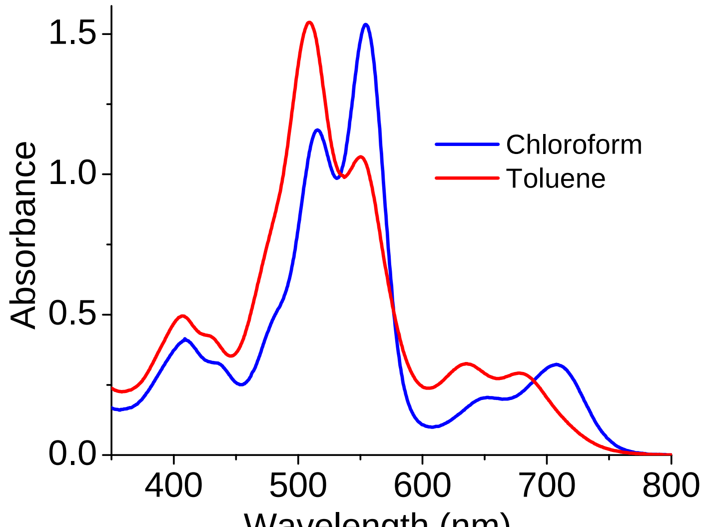


K - (-50) – LC - 265ºC (DSC)
WAXD shows columnar order with intercolumnar distance of 31.8 Å

Combining Light-harvesting and Charge Separation in a Self-assembled Artificial Photosynthetic system Based on Perylenediimide Chromophores



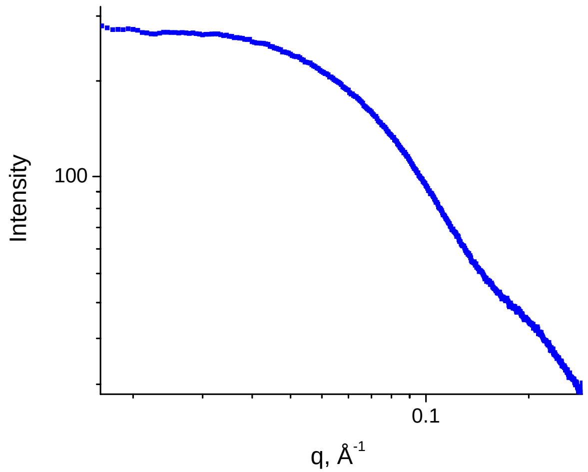




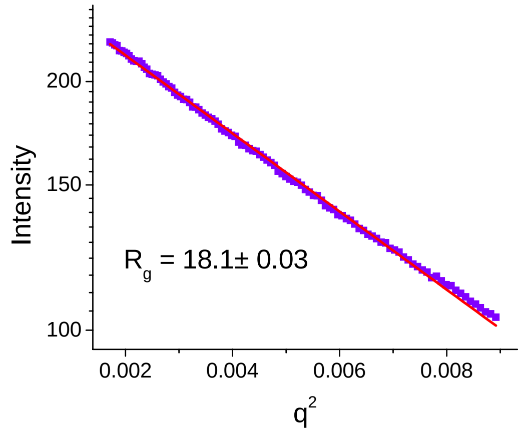
B. Rybtchinski et al., *J. Am. Chem. Soc*. (in press).

Small-Angle X-ray Scattering Structural Studies of 2 x 10^{-4}M 5PDI-PDI_4 in Toluene Solution

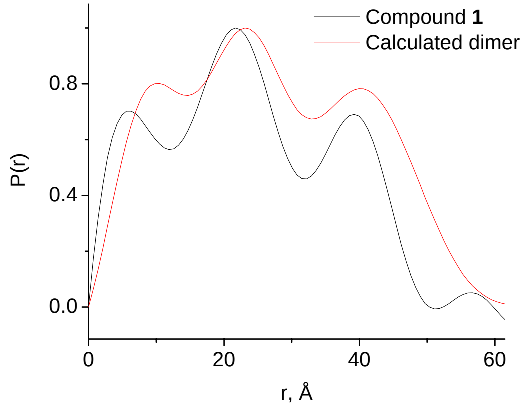
Scattering Intensity

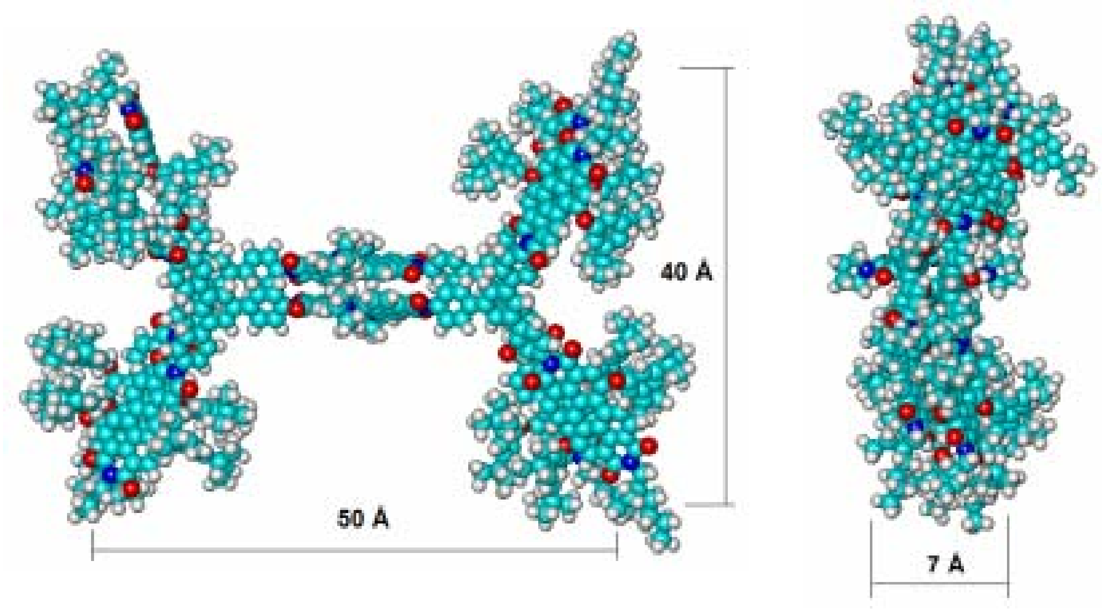


Guinier Plot



PDF Plot





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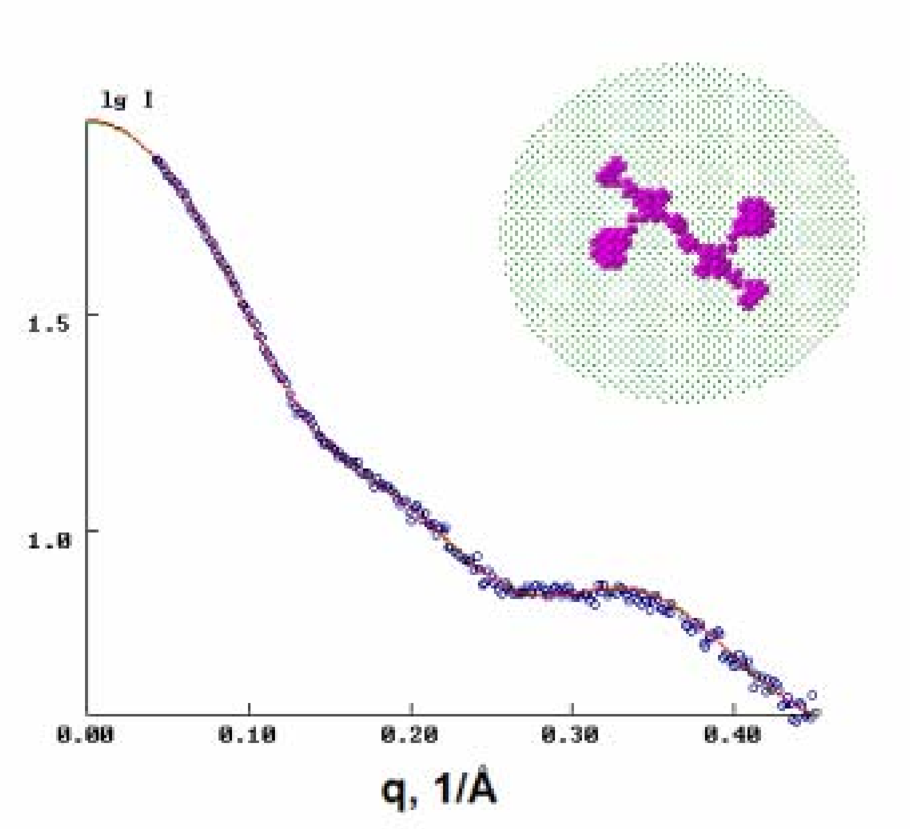
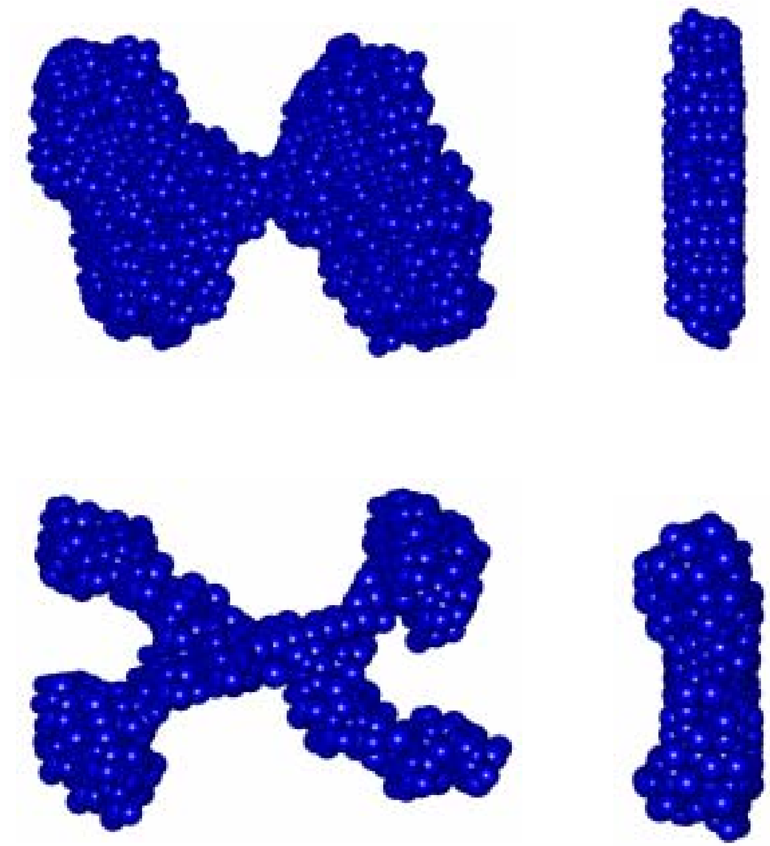
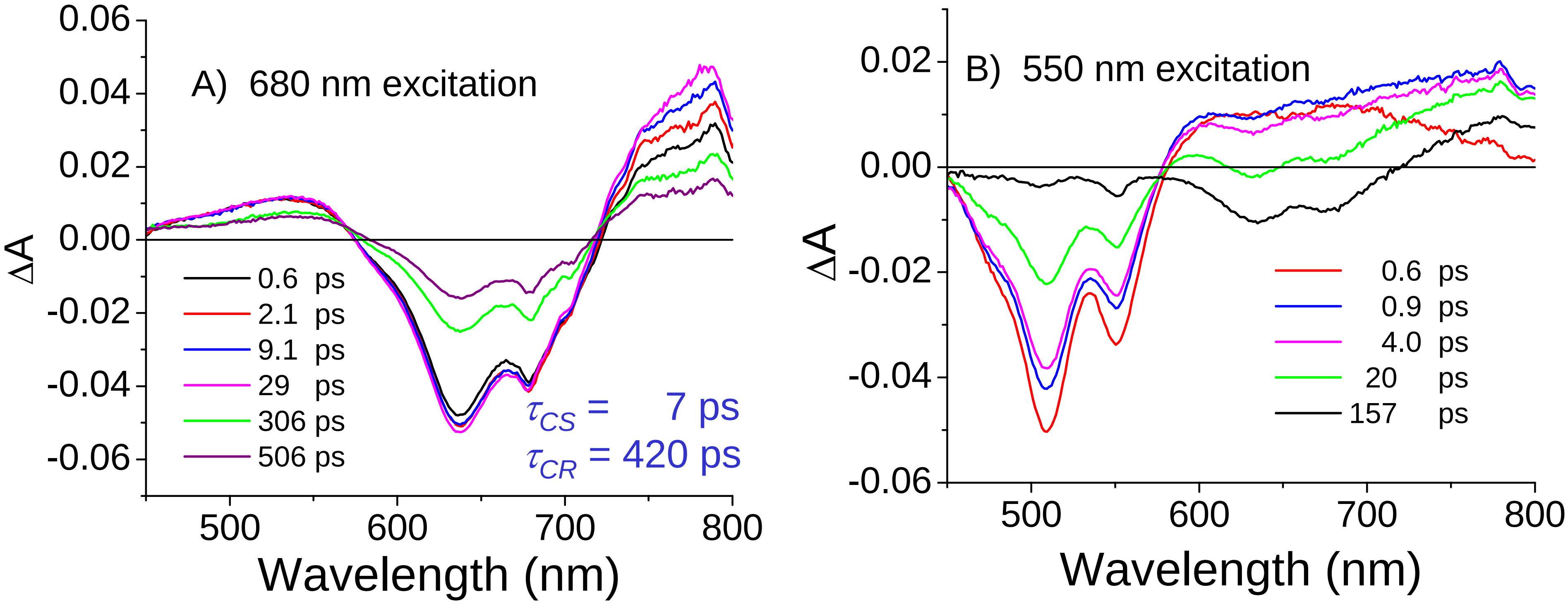
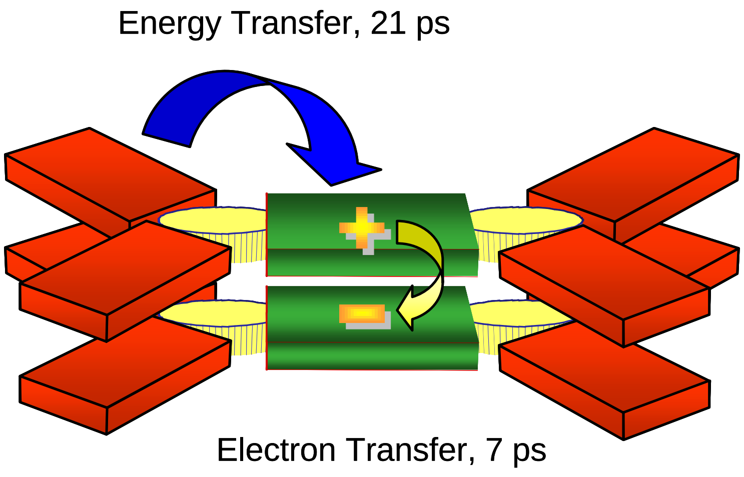
Simulated Annealing Reconstruction of the Aggregate Shape



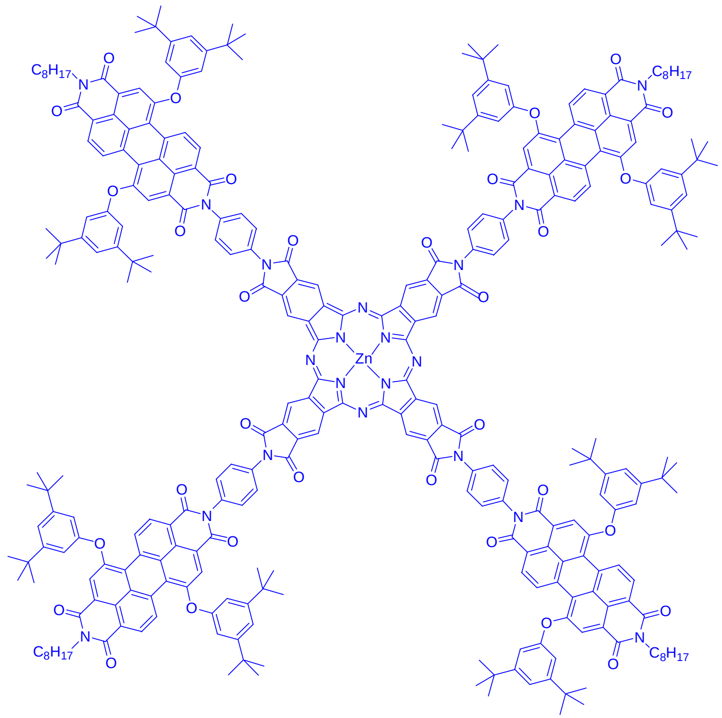


Transient Absorption Spectra of $(5PDI\text{-}PDI_4)_2$ in Toluene following Laser Excitation at 680 nm and at 550 nm



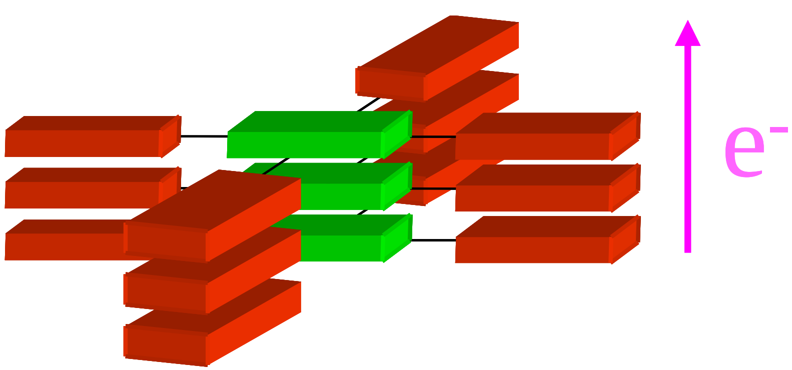


Self-Assembled n-Type Semiconductor Fibers



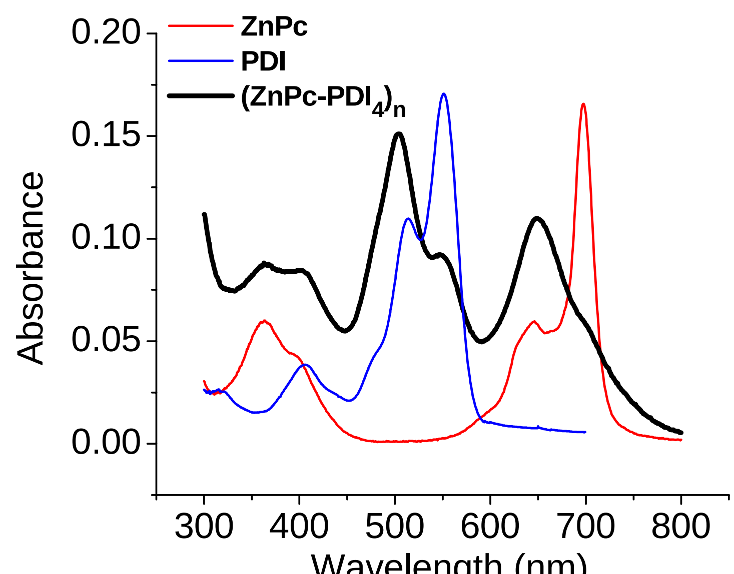
ZnPc-PDI$_4$

- ZnPc-PDI$_4$ self-assembles into cofacial stacks that form long fibers.
- The ZnPc core and the PDI peripheral groups both absorb light strongly.
- The ZnPc core is an unusual electron-deficient phthalocyanine because its intrinsic imide groups make it an excellent electron acceptor (E_{RED} = -0.45 V vs. SCE).
- Thus the entire assembly is an n-type material.



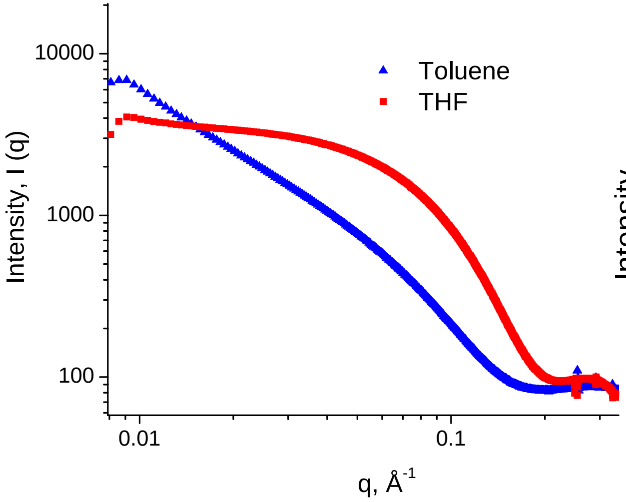
X. Li et al., *J. Am. Chem. Soc*. (in press).

ZnPc-PDI$_4$ Absorbs 300-800 nm Light

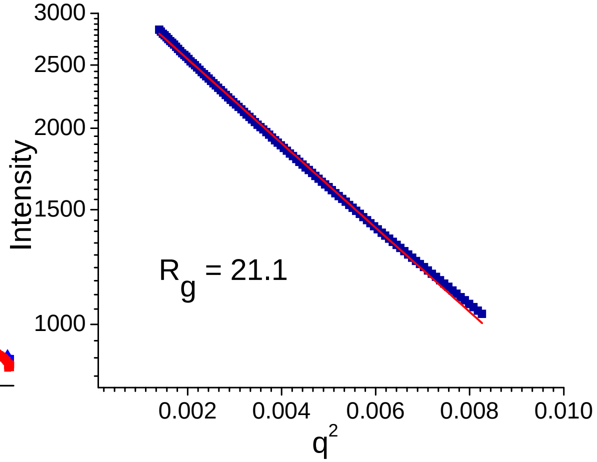


Small-Angle X-ray Scattering Structural Studies in Solution

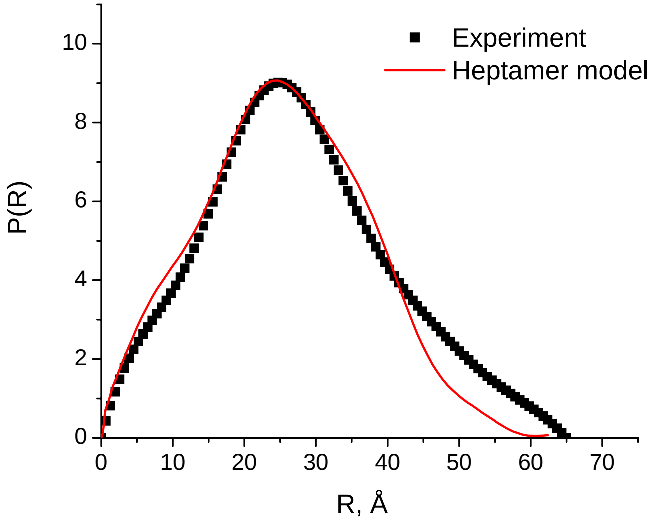
Scattering Intensity

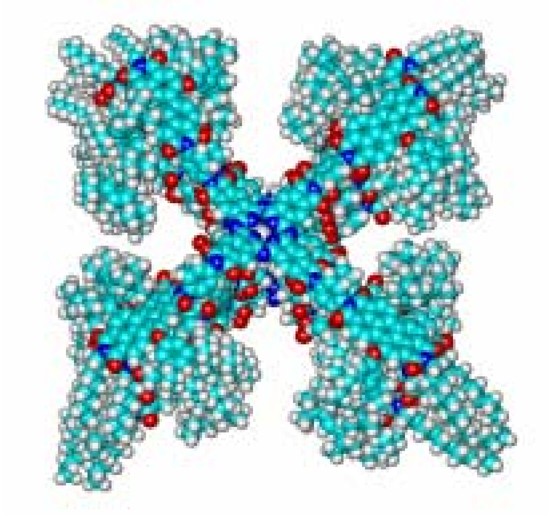


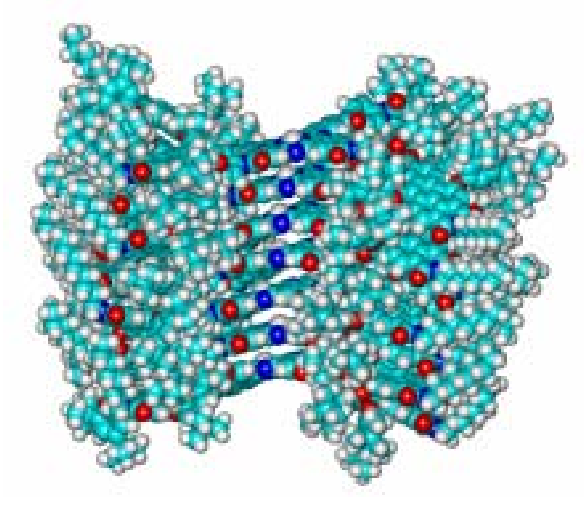
Guinier Plot



PDF Plot

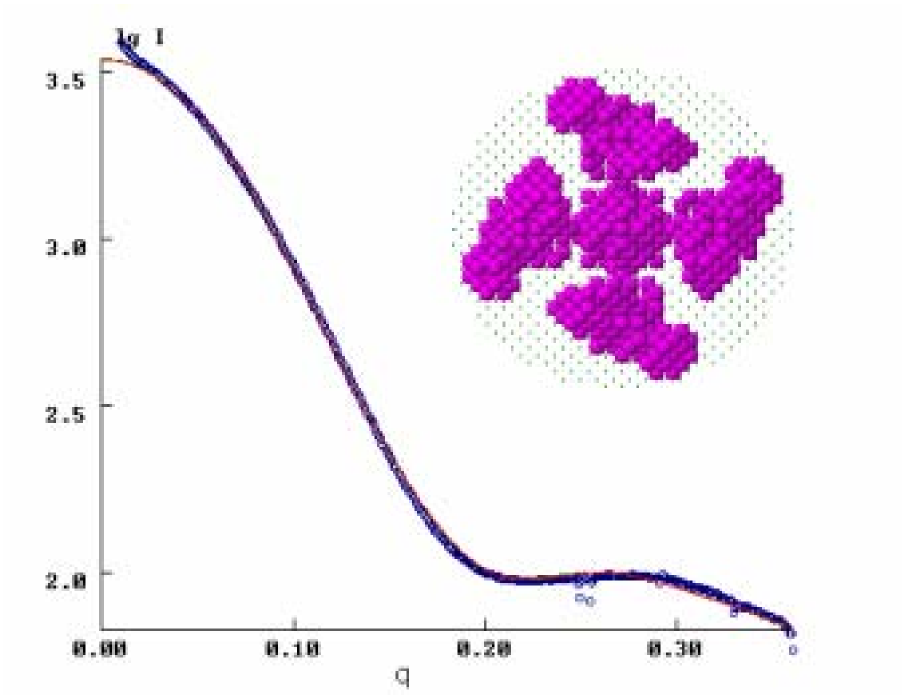


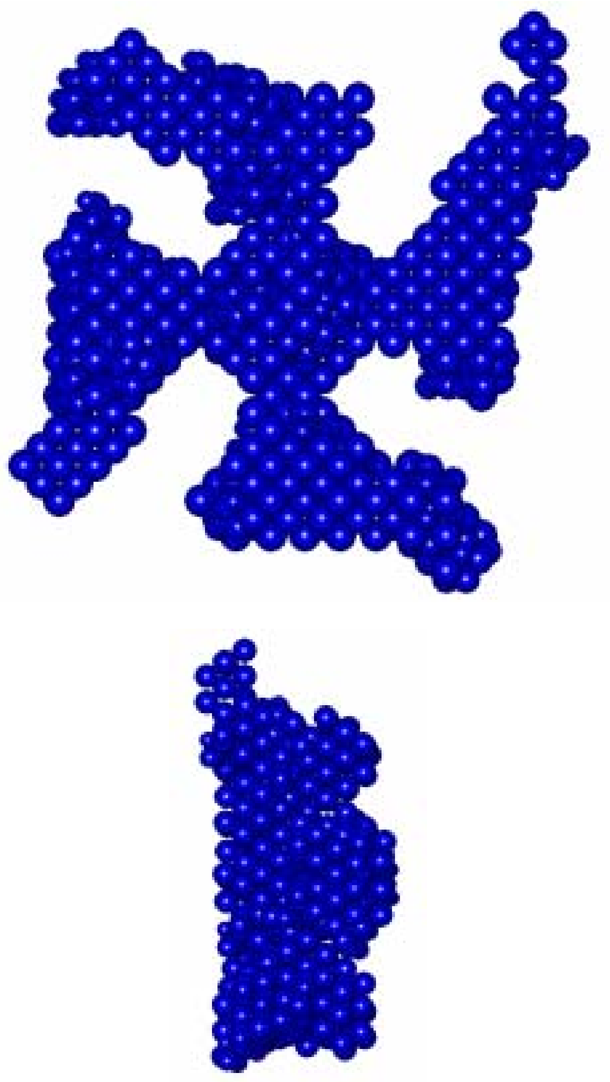




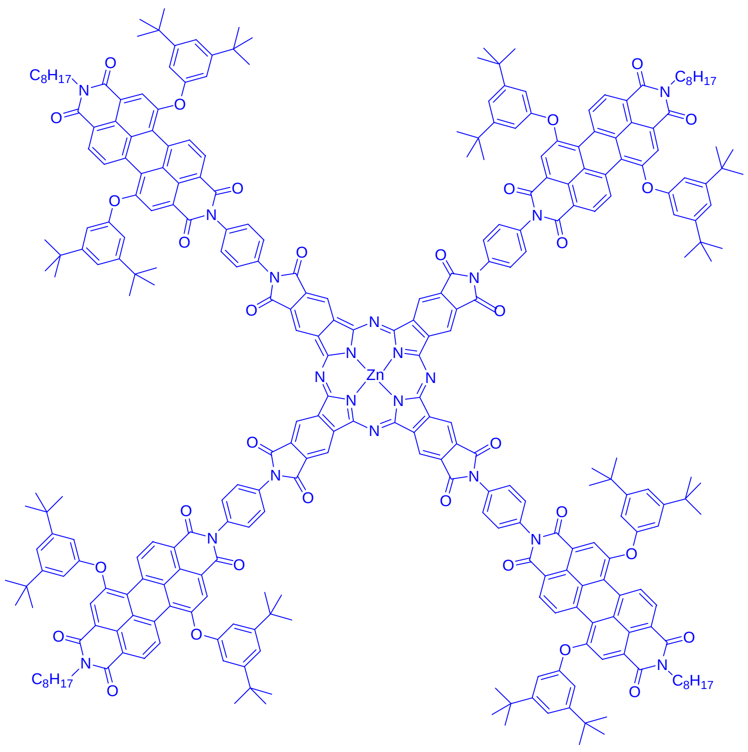
Small-Angle X-ray Scattering Studies in Solution

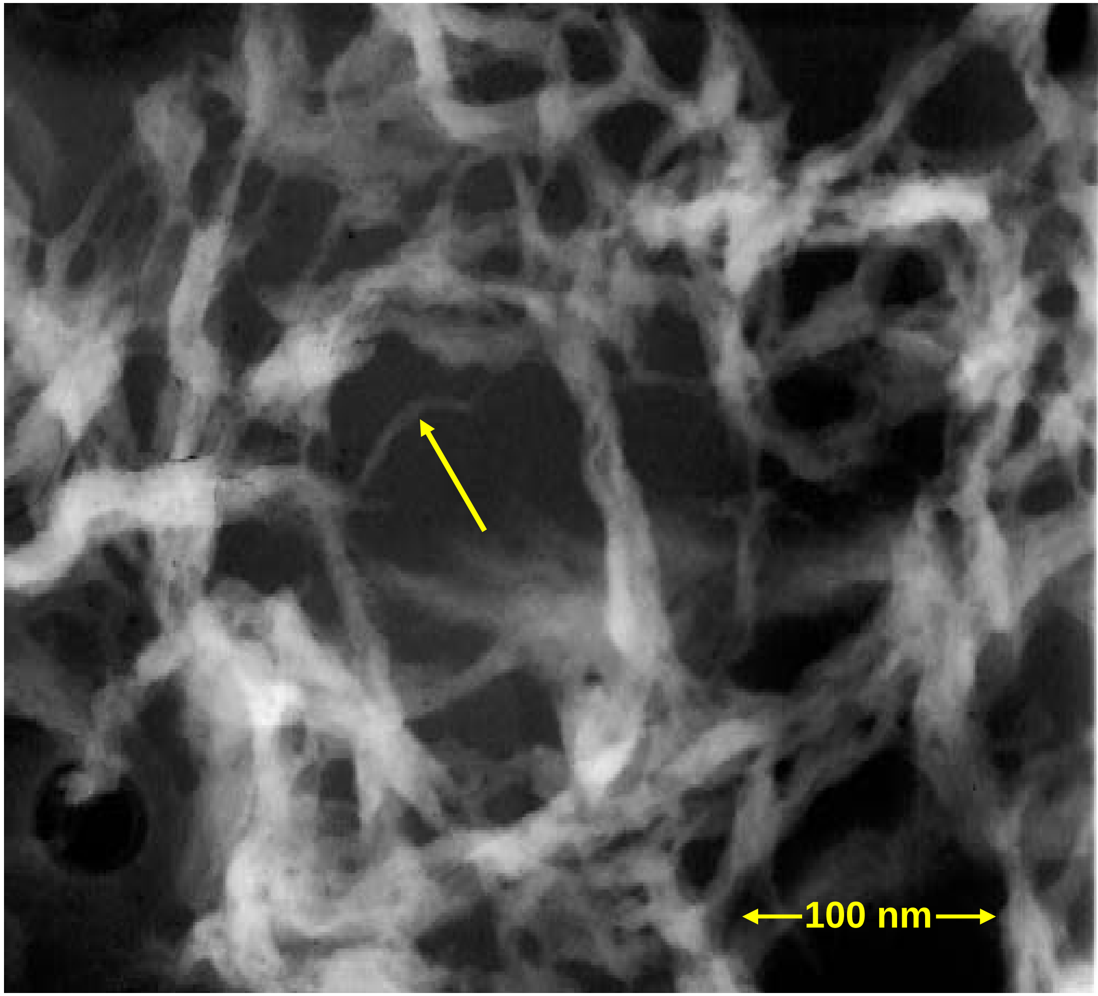
Simulated Annealing Reconstruction of the Aggregate Shape



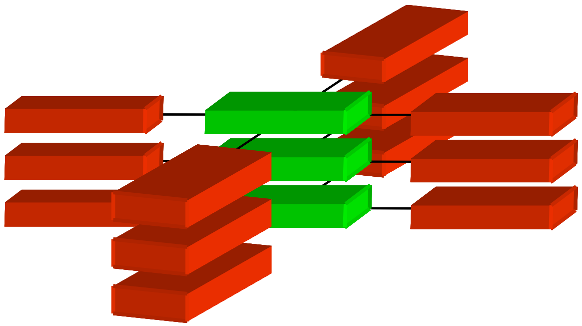


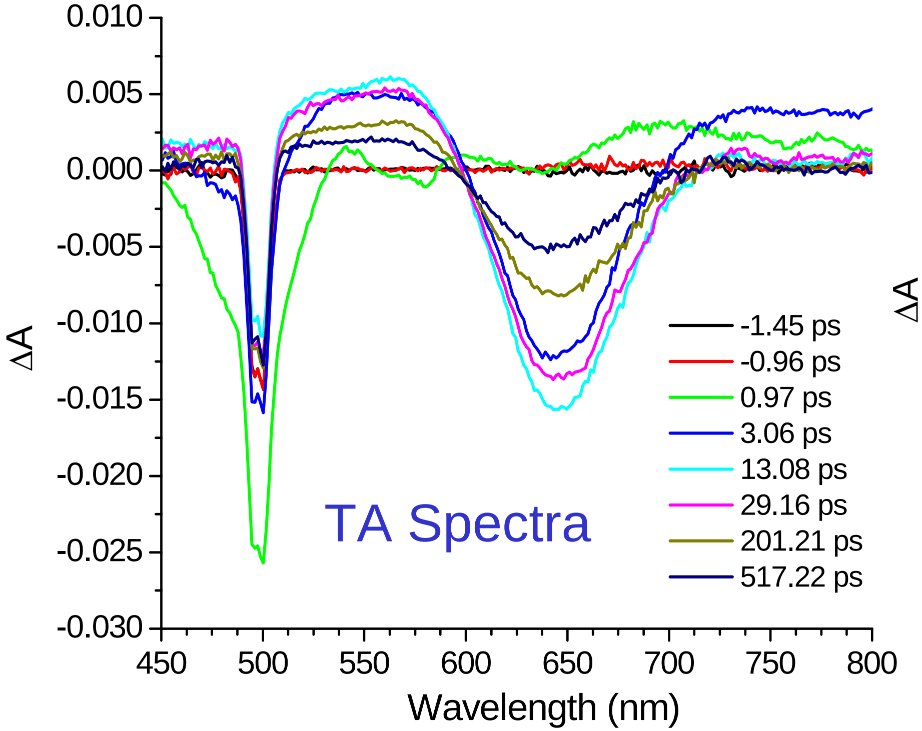
TEM Image of ZnPc-PDI$_4$ Fibers. Arrow Points to a Fiber only 5 nm Wide, One Molecular Width!

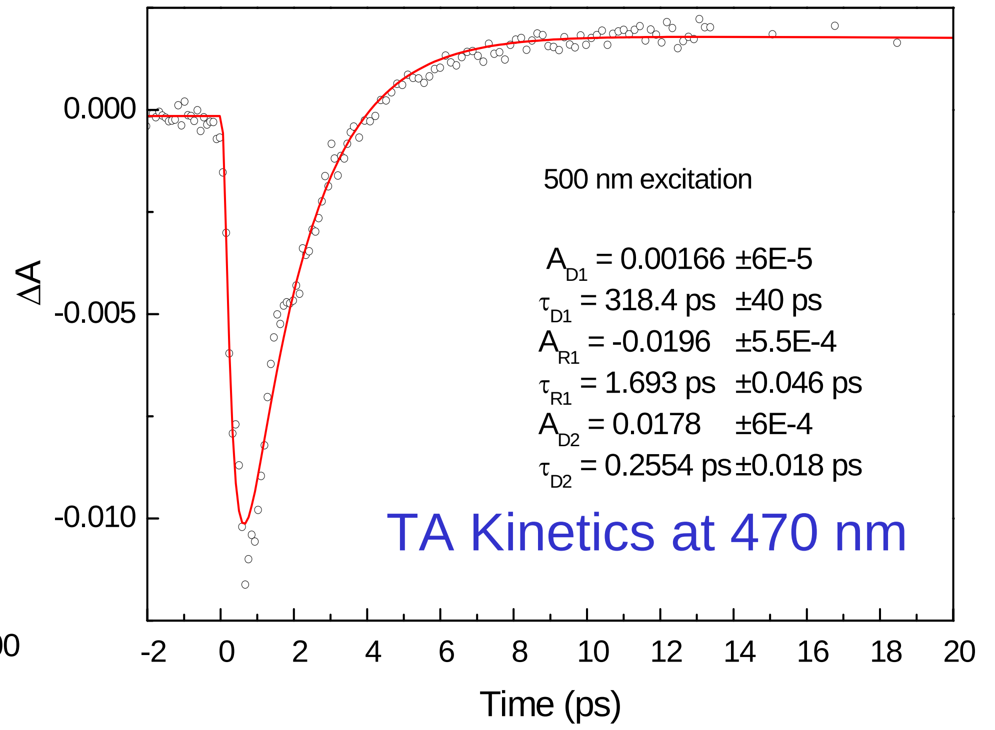




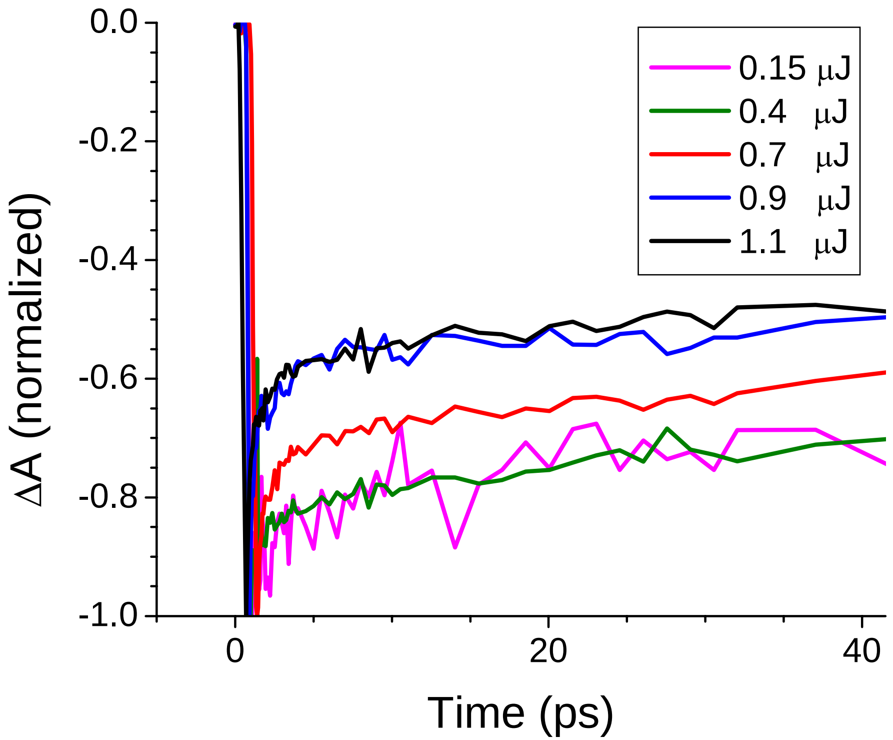
Photophysics of $(ZnPc(PDI)_4)_n$ Aggregates in Toluene







Singlet-Singlet Annihilation within $(ZnPc\text{-}PDI_4)_n$ Provides Evidence for Exciton Hopping Throughout the Assembly



$$-\frac{d\Delta A}{dt} = \gamma_1 \Delta A + \frac{1}{2}\gamma_2 (\Delta A)^2$$

For a one-dimensional linear array:

$$\tau_a = 2\gamma_2^{-1} = (N(N-1)/6)\tau_{hop}$$

τ_a = 1.1 ps, so that if N = 7, then τ_{hop} = 160 fs

Since lifetime of the exciton within ZnPc aggregates is 260 ps, A hopping time of τ_{hop} = 160 fs implies that the excitation can visit more than 1600 sites (or hop through aggregates that are more than 0.5 μm long) within its lifetime.

Summary:

- Photoexcitation of self-assembled, stacked 5PDI chromophores results in symmetry breaking in the excited state resulting in quantitative charge separation.

- Self-assembly of two types of robust perylenediimide chromophores 5PDI (red-absorber) and PDI (green absorber) are used to produce an artificial light-harvesting antenna structure that in turn induces self-assembly of a functional special pair that undergoes ultrafast, quantitative charge separation, $(5PDI\text{-}PDI_4)_2$.

- A new n-type material based on $ZnPc\text{-}PDI_4$ self-assembles into long ordered fibers driven primarily by a strong interactions between the PDI molecules. Studies of singlet-singlet annihilation indicate that exciton migration occurs throughout the structures.