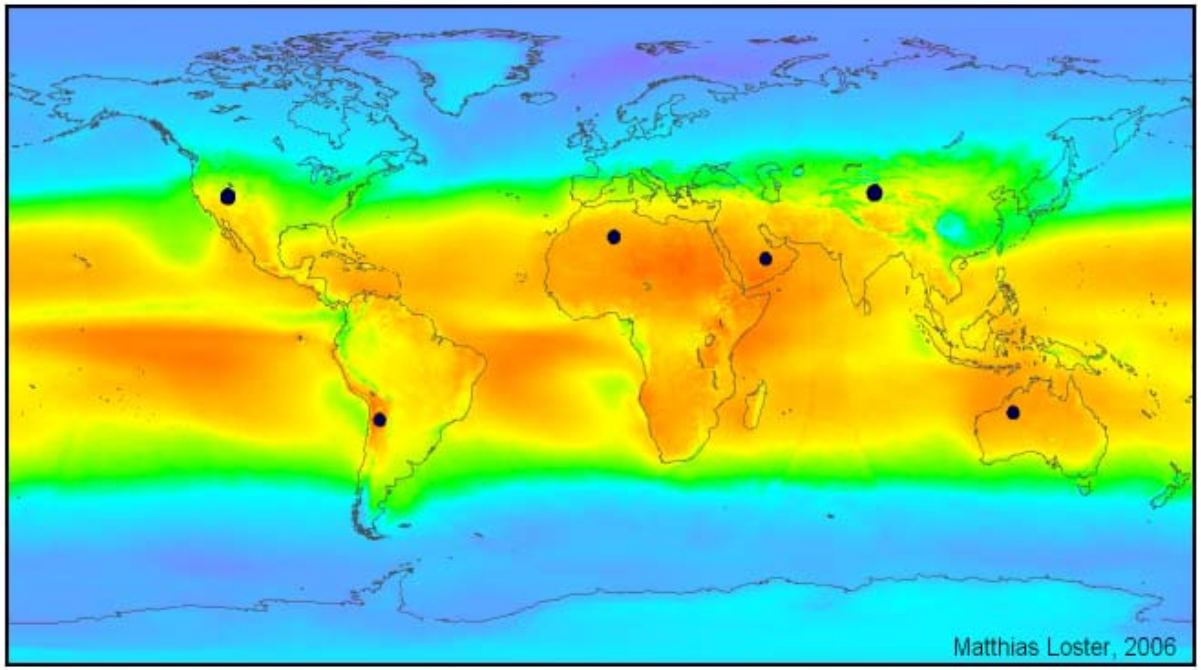


Σ● = 18 TWe

http://www.ez2c.de/ml/solar_land_area/

Exciton Fission for an Ultra-High Efficiency, Low Cost Solar Cell

Program Team PV

Josef Michl

University of Colorado, Boulder

michl@eefus.colorado.edu

May 24-27, 2010

Overview

Timeline

- Project start date: 2/1/2008
- Project end date: 7/31/2011
- Percent complete: 65%

Barriers

- Barriers addressed
  - **Material Utilization & Cost**
  - **Efficiency**

Budget

- Total project funding: $1,119,715
  - DOE share: $895,772
  - Contractor share: $223,943
- Funding received in FY09: $296,372
- Funding for FY10: $299,400

Partners

- Mark Ratner, Northwestern University
- Josef Michl, University of Colorado at Boulder

Challenges, Barriers or Problems

- Material Utilization & Cost

  Material and fabrication costs of dye-sensitized solar cells (DSSC's) are less than those of silicon-based solar cells, but their efficiency is low

- Efficiency

  The theoretical maximum efficiency of current DSSC's is ~30%, our aim is to improve this limit to ~45%

- Will help the Solar Program's goal of developing cost-competitive unsubsidized photovoltaics

Relevance

This project is focused on exploring and developing the next generation of PV technologies that will reach consumers beyond the SAI timeframe (post-2015)

OBJECTIVE

Fabrication of a photovoltaic cell that is inexpensive and highly efficient

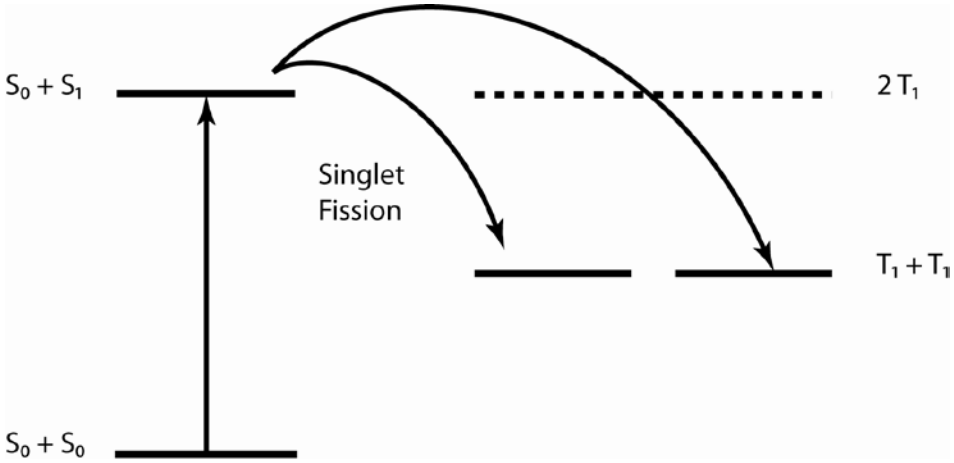
GOAL

Demonstrate that the conversion efficiency in a molecule-based photovoltaic cells can be increased by the use of sensitizers capable of singlet fission

IMPACT

Will significantly aid the Solar Program in accelerating the market competitiveness of solar electricity as industry-led teams compete to deliver solar systems that are less expensive, more efficient, and highly reliable

Singlet Fission (SF) for More Efficient Solar Cells



Singlet Fission (SF): one singlet exciton (S_1) is converted into two triplet excitons ($2T_1$); this requires two of more mutually coupled chromophores.

Maximum triplet quantum yield of 200%, getting two electronic excitations from a single photon. If it is possible to use the triplets for two independent separate injections, the photovoltaic current will be doubled for photons with enough energy. This is an organic analog of multiple photon generation.

EXAMPLES

Crystals

Anthracene - first observation**:** Singh, S.; Jones, W. J.; Siebrand, W.; Stoicheff, B. P.; Schneider, W. G. *J. Chem. Phys.* **42**, 330 (1965).

Tetracene - theoretical prediction: C.E. Swenberg, W.T. Stacy, *CPL* **2**, 327 (1968).

Tetracene – mag. field effect: R.E. Merrifield et al., *CPL* **3**, 155 (1969).

Pentacene/Tetracene - heterofission: N.E. Geacintov et al., *CPL* **11**, 504 (1971).

Tetracene/Anthracene - heterofission: K. von Burg, I. Zschokke-Granacher, *J. Chem. Phys*. **70**, 3807 (1979).

Polymers, oligomers, dimers (directly measured T yield)

Polydiacetylenes **(0.4%):** B. Kraabel et al., *Chem. Phys*. **227**, 83 (1998), Jundt et al., CPL 203, 37 (1993).

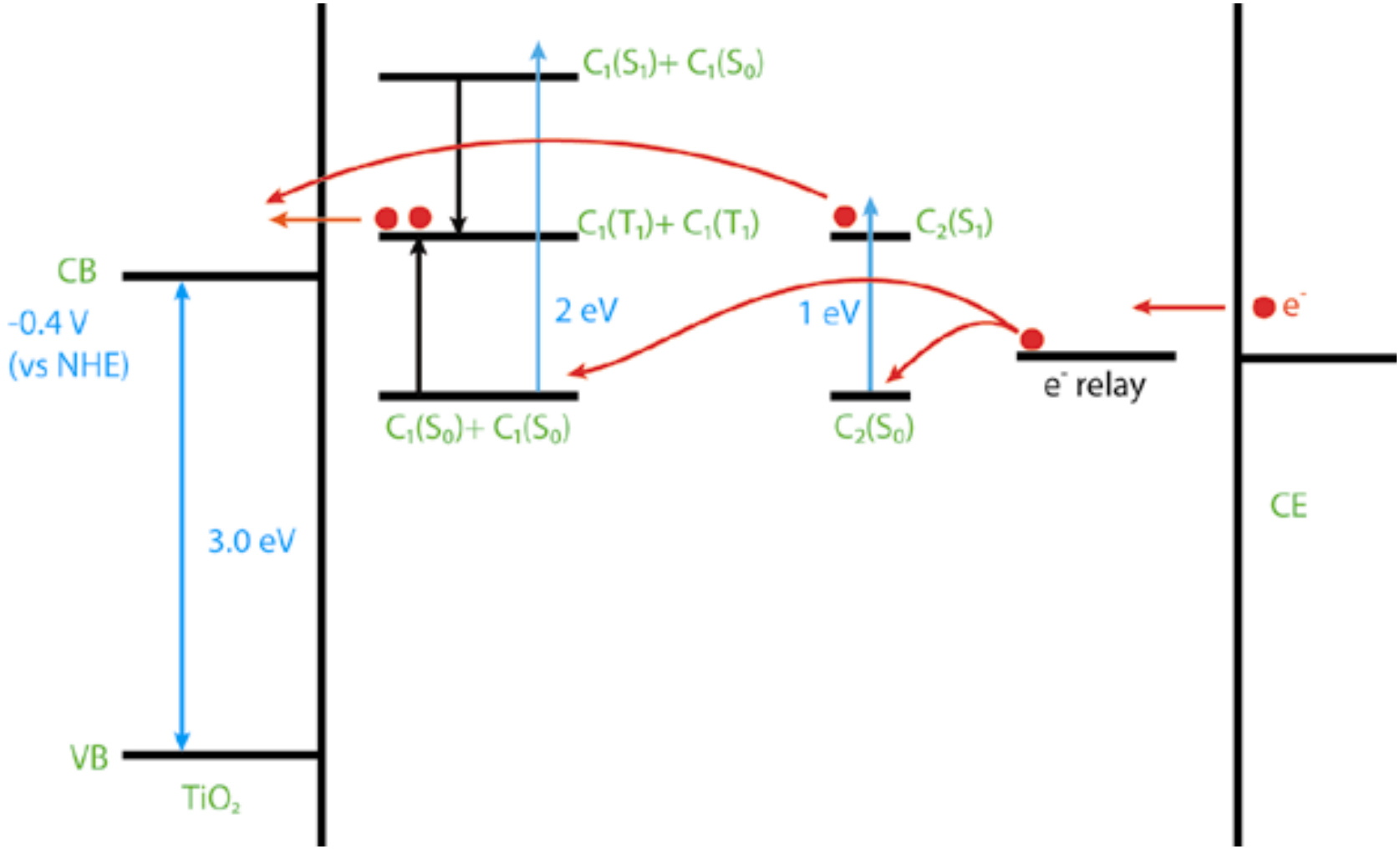
Poly(*p*-phenylene): M. Wohlgenannt et al., *Phys. Rev. Lett*. **82**, 3344 (1999).

Carotenoids **(5-30%):** Gradinaru et al., *PNAS*, **98**, 2364 (2001); E. Papagiannakis et al., *PNAS*, **99**, 6017 (2002).

Bistetracenylbenzene **(0-3%):** A.M. Müller et al., *CPL.* 421, 518 (2006), *JACS,* **129**, 14240 (2006).

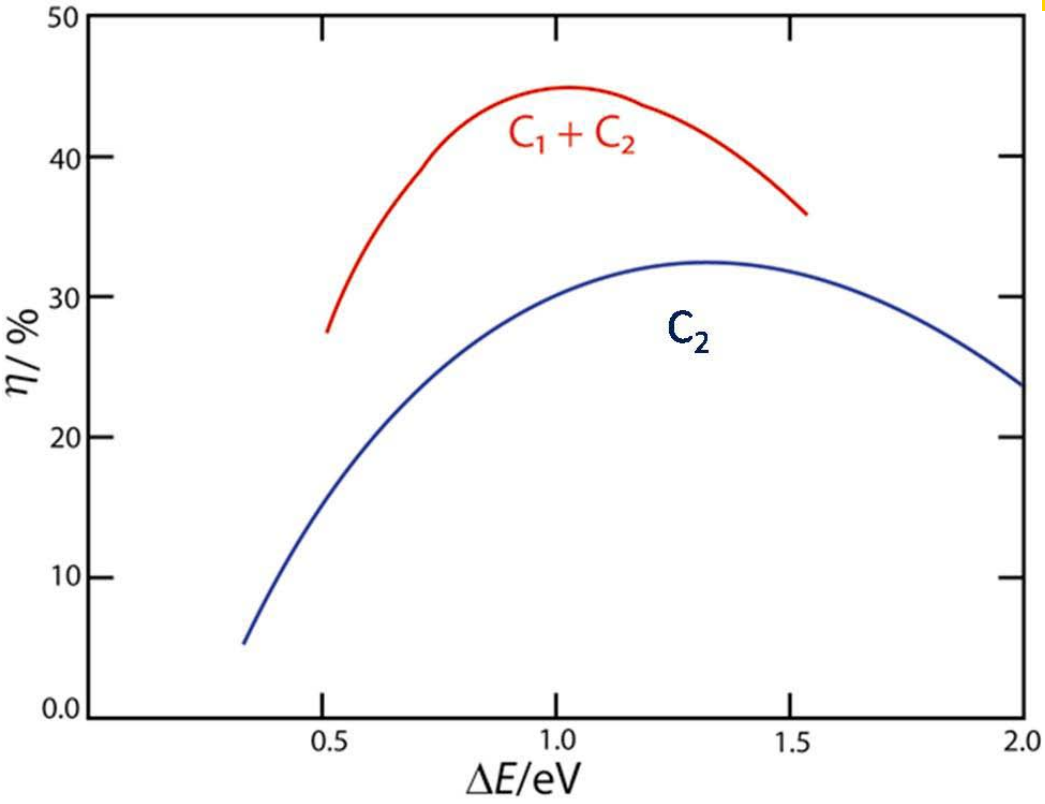
Bis(diphenylisobenzofurans **(0-9%):** J. Michl et al., *Proc. SPIE* **6656,** 66560E1 (2007).

Proposed SF Solar Cell



Bi-Layer Grätzel Cell: employing two sensitizers in optical series - C_1 (SF sensitizer) and C_2 (conventional sensitizer); no current matching is needed

Theoretical Cell Efficiencies



Cell with only C_2 (blue) and both C_1 and C_2 (red)

Assuming:

- 1 Sun illumination
- Full absorption of incident solar light above 1.1 eV
- Optimal charge collection efficiency

With 200% triplet quantum yield, theoretical efficiency increases by a factor of ~1.5
A triplet yield close to 200% is essential, otherwise there is no gain.
The right sensitizer needs to be found; yields close to 200% have never been demonstrated by a direct measurement (but have been inferred indirectly for crystalline tetracene, so there is hope)

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

What is Needed?

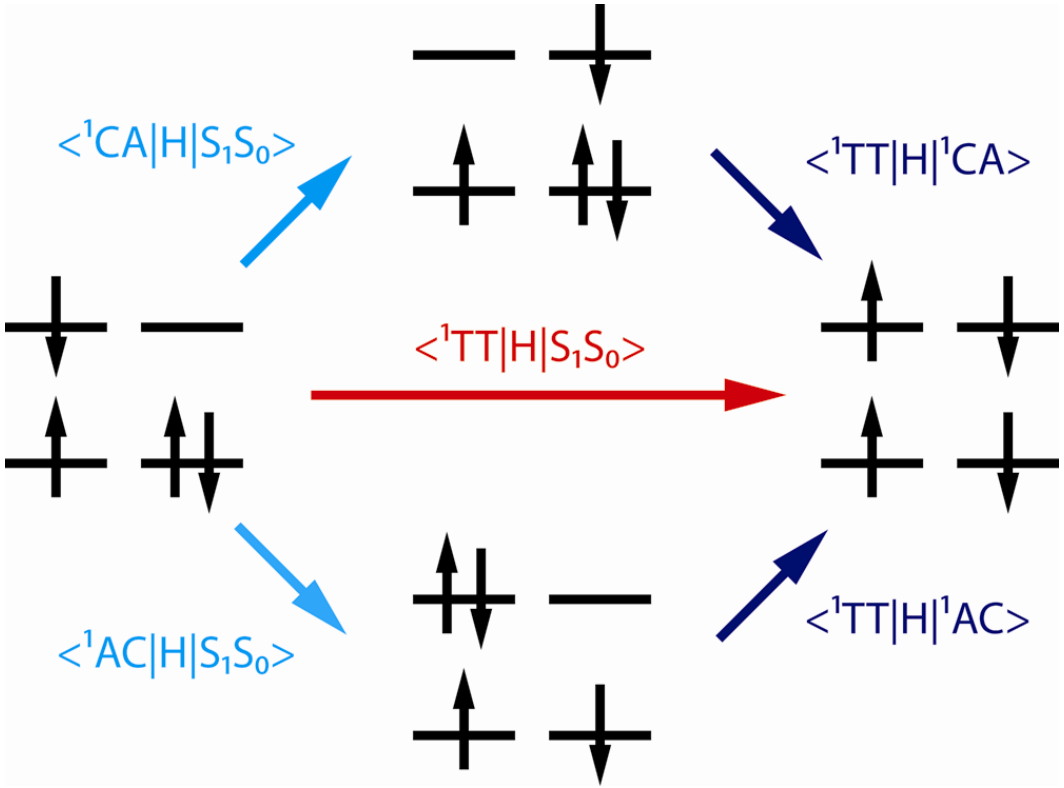
1) SELECT OPTIMAL CHROMOPHORE (GUIDELINES AVAILABLE)
   - ***E*(T$_2$) ≥ *E*(S$_1$) ≥ 2 *E*(T$_1$) = 2.0 - 2.2 eV** Paci et al. *J. Am. Chem. Soc.*, **2006**, *128*, 16546
     i. alternant hydrocarbons (all previously studied cases)
     ii. biradicaloids (present research)
   - **high ε up to UV region, high stability, low cost**

2) SELECT OPTIMAL INTER-CHROMOPHORE COUPLING (GUIDELINES UNDER DEVELOPMENT)
   - **Fast singlet fission, no competing processes**

3) OPTIMIZE TRIPLET EXCITON SEPARATION AND ELECTRON INJECTION (GUIDELINES NEEDED)
   - **independent triplets, no recombination**
   - **no charge injection from S$_1$**
   - **fast charge injection from T$_1$**
   - **no triplet quenching by holes**

GO/NO-GO: Has a sensitizer been found that produces a high triplet yield by singlet fission (at least 10%)? **Yes, ~200±30% triplet yield**

Interchromophore Coupling Guidelines under Development



$\langle {}^1TT|H|S_1S_0\rangle = (3/2)^{1/2}\,[(l_A l_B)||(l_A h_B) - (h_A h_B)||(h_A l_B)]$

$\langle {}^1CA|H|S_1S_0\rangle = \langle l_A|F|l_B\rangle + 2(h_A l_A)||(h_A l_B) - (h_A h_A)||(l_A l_B)$

$\langle {}^1AC|H|S_1S_0\rangle = -\langle h_A|F|h_B\rangle + 2(h_B l_B)||(h_A l_B) - (l_B l_B)||(h_A h_B)$

$\langle {}^1TT|H|CA\rangle = (3/2)^{1/2}[\langle l_A|F|h_B\rangle + (l_A h_B)|l_B l_B) - (l_A h_B)||(h_A h_A)]$

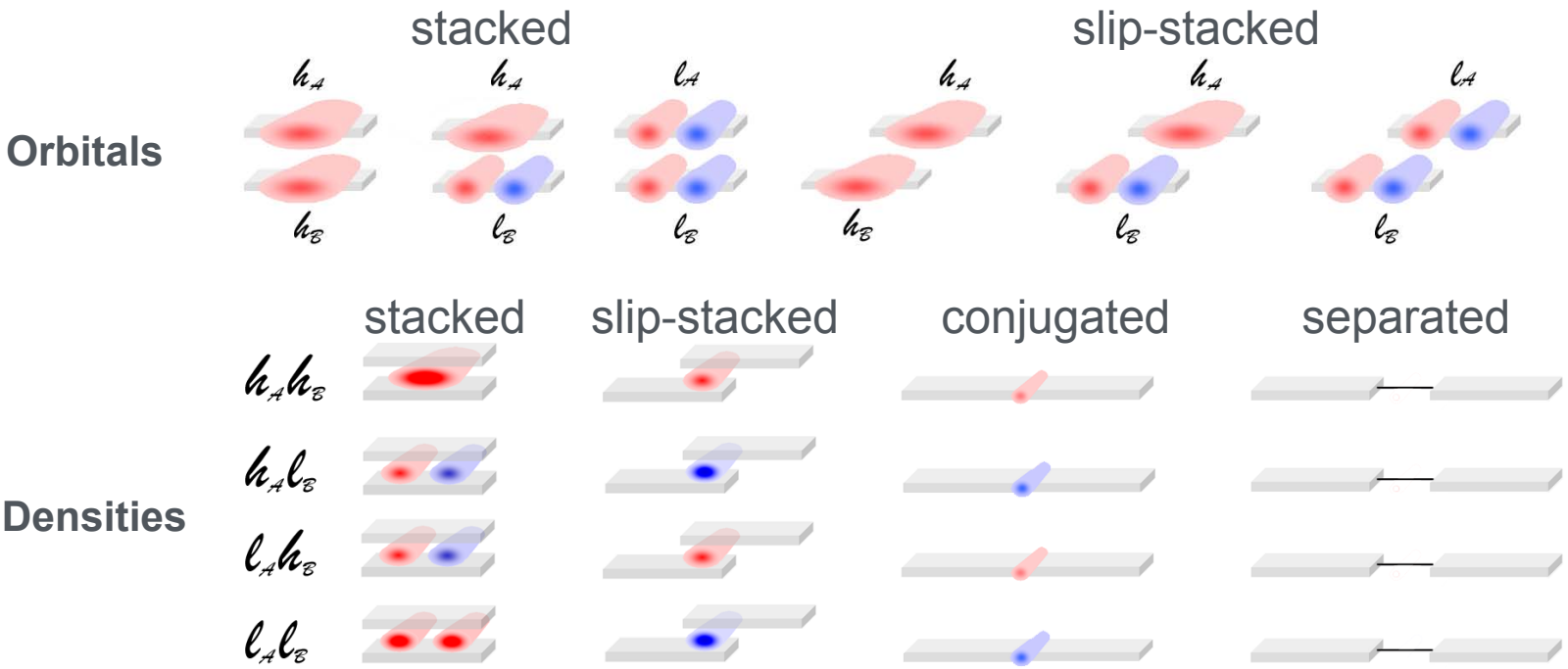
$S_1S_0 \rightarrow {}^1(TT)$: (i) directly (H2) or (ii) indirectly via charge transfer states (H1+H2)

(i) Direct Coupling

Qualitative Guidelines - Maximizing

$$\iint [l_A(1)l_B(1)|e^2/r_{12}|h_B(2)l_A(2) - h_A(1)h_B(1)|e^2/r_{12}|h_A(2)l_B(2)]d\tau_1\tau_2$$

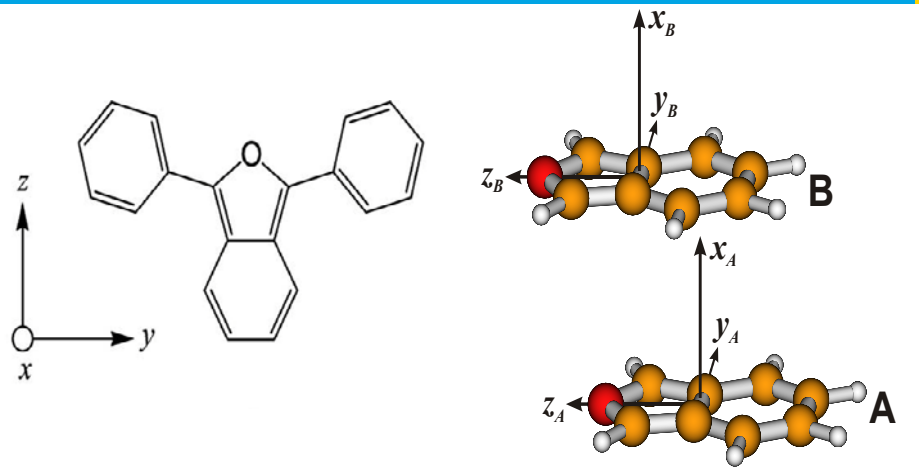
CHROMOPHORES A and B

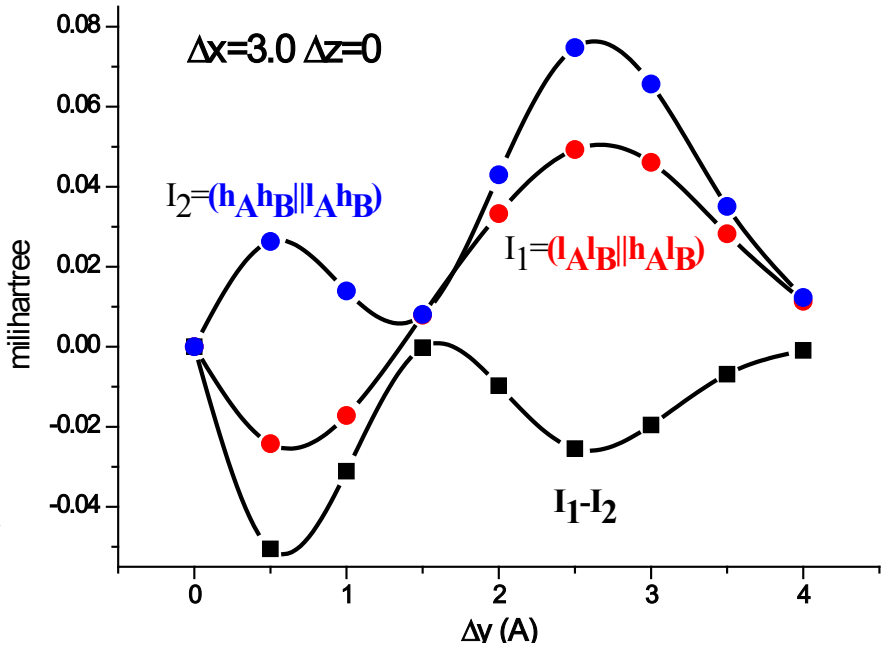


$$(l_A l_B|e^2/r_{12}|l_A h_B) - (h_A h_B|e^2/r_{12}|h_A l_B)$$

"Slip-Stacked" chromophores have the largest direct coupling matrix element

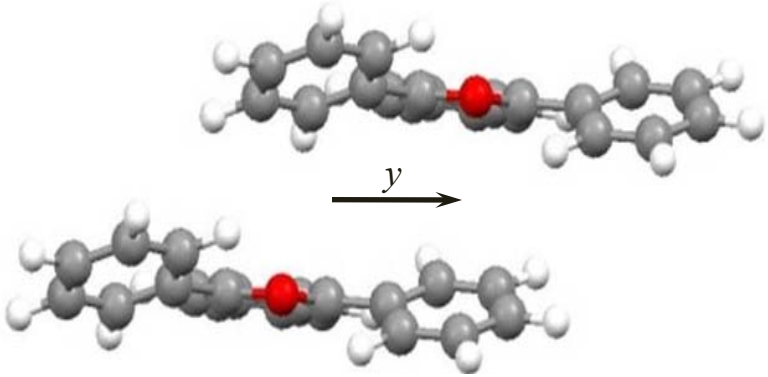
Slip-Stacked Chromophores

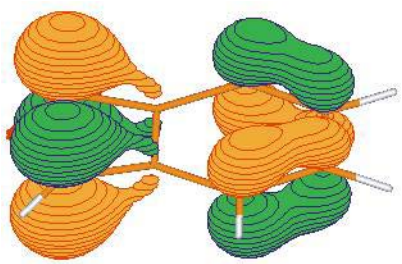




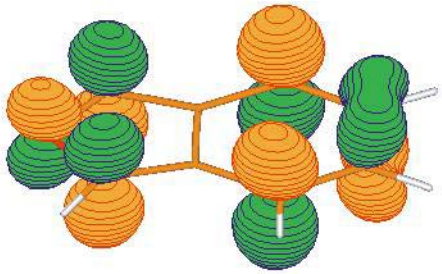
CALCULATED SINGLET FISSION DIRECT COUPLING MATRIX ELEMENT AS A FUNCTION OF SLIP ALONG *y*

CRYSTAL PACKING





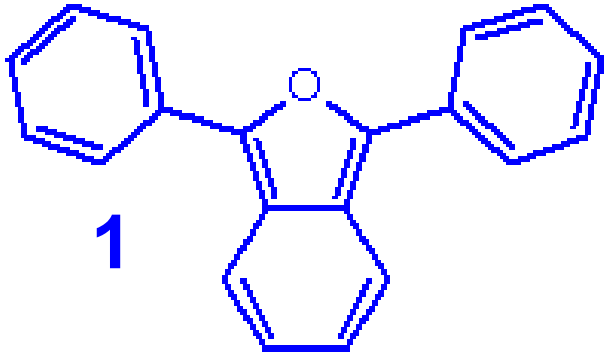
HOMO



LUMO

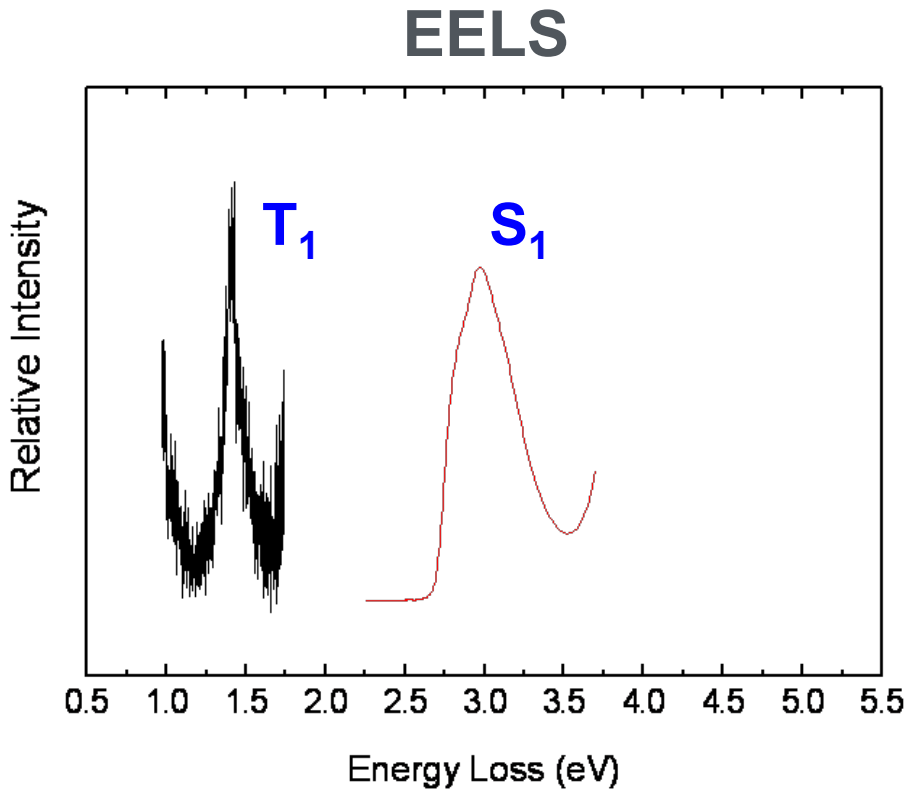
As in the crystal, an offset of 0.5 Å in the direction of the electronic dipole moment is ideal

Excited States of a Designed Model Chromophore, 1



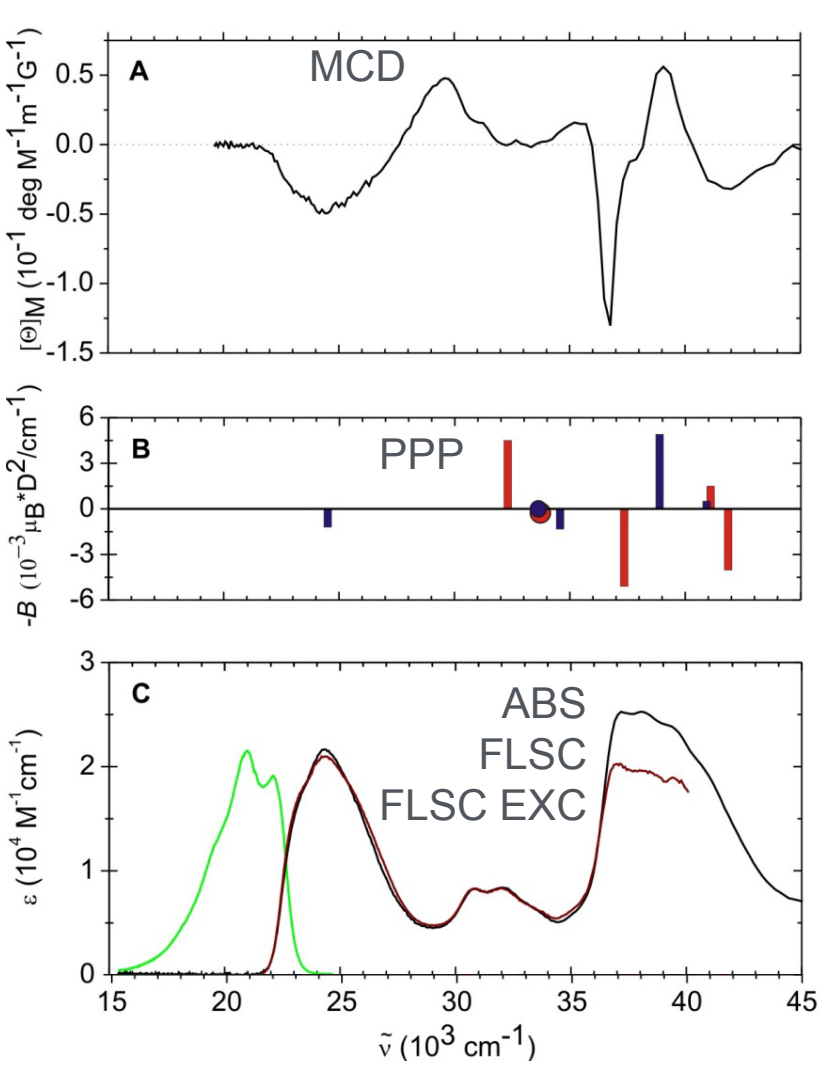
$S_0 - S_1$

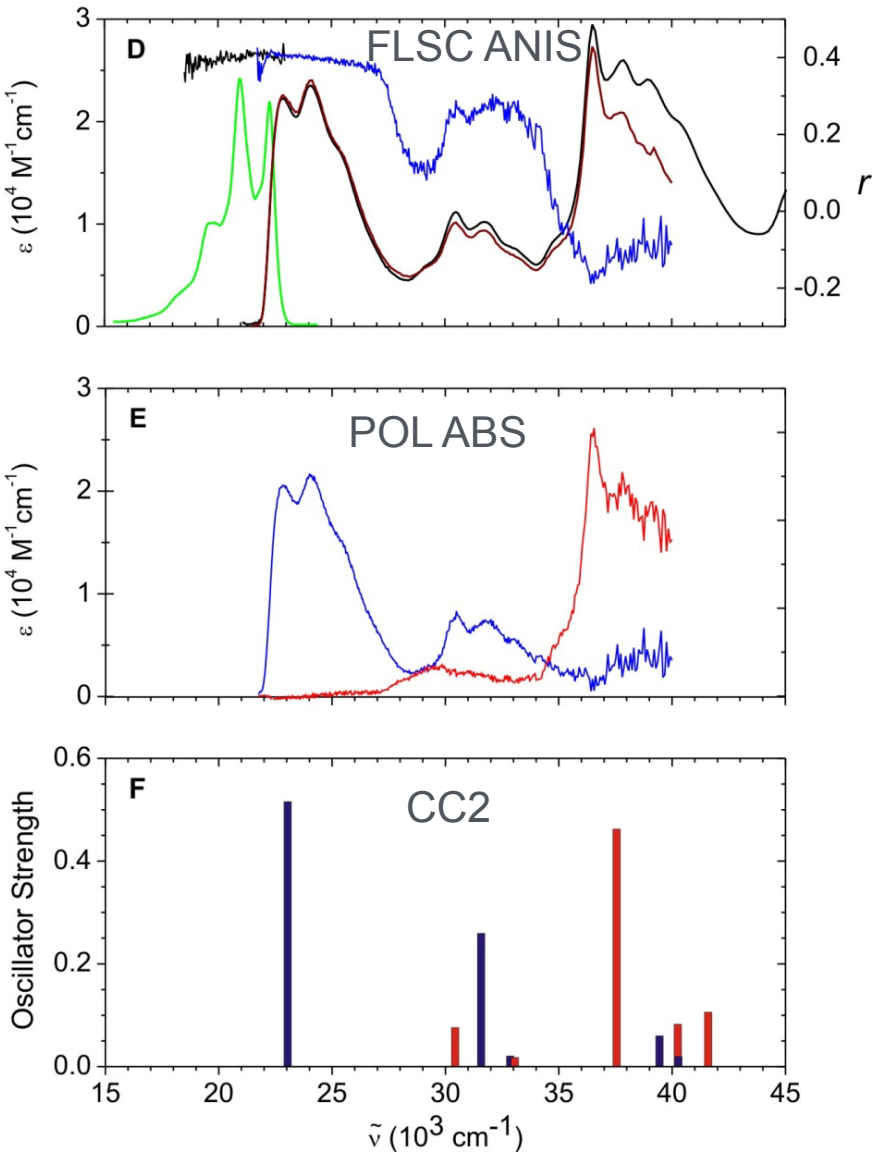
Calculated by:
PPP
TD-DFT
SORCI
CC2
CASPT2



Schwerin et al, *J. Phys. Chem. A* **2010**, *114*, 1457.

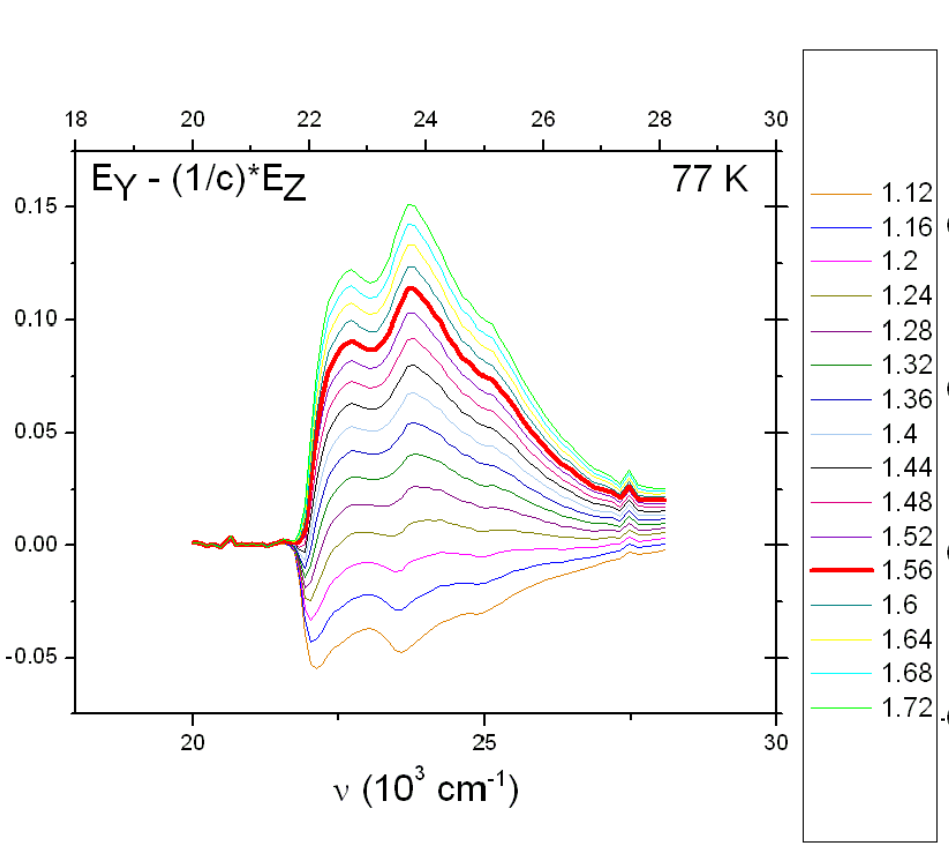
Spectral Calculations and Solution Photophysics of 1

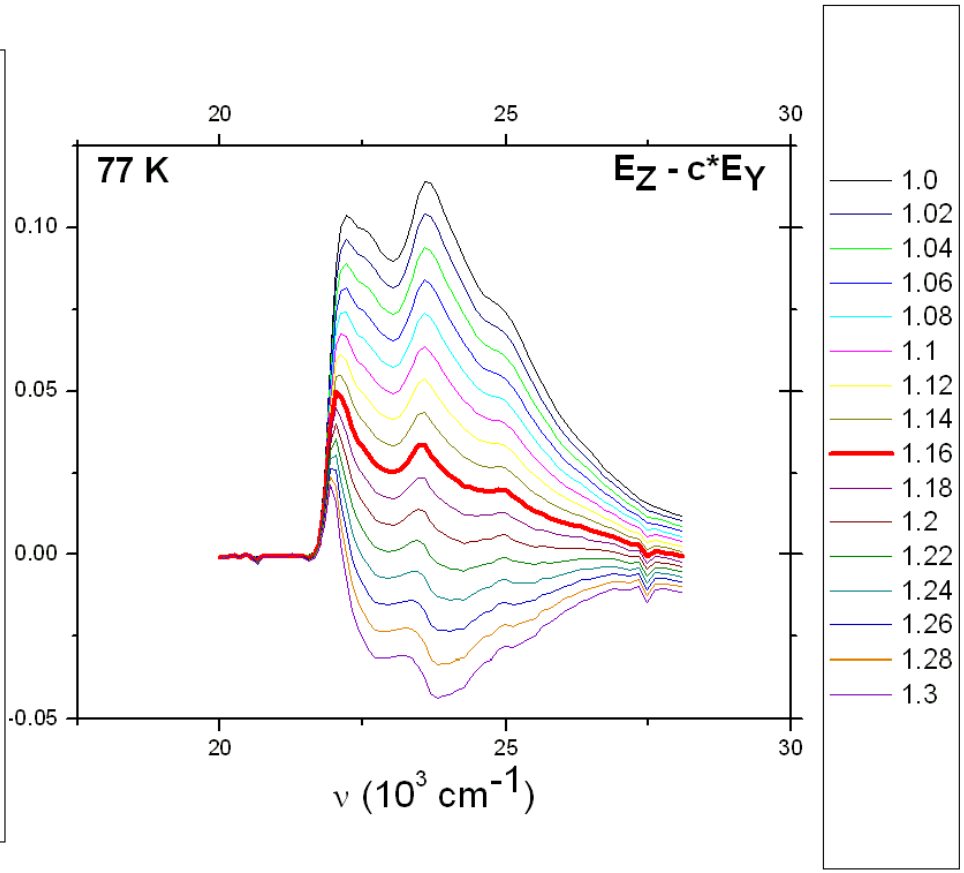




Schwerin et al, *J. Phys. Chem. A* **2010**, *114*, 1457.

Photophysics of 1 Continued



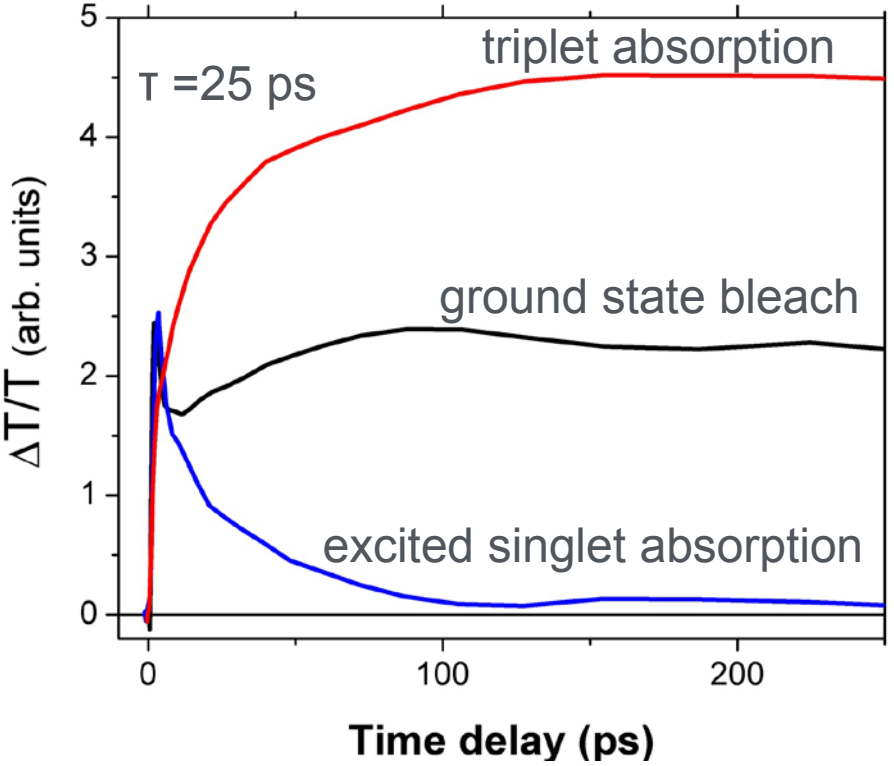


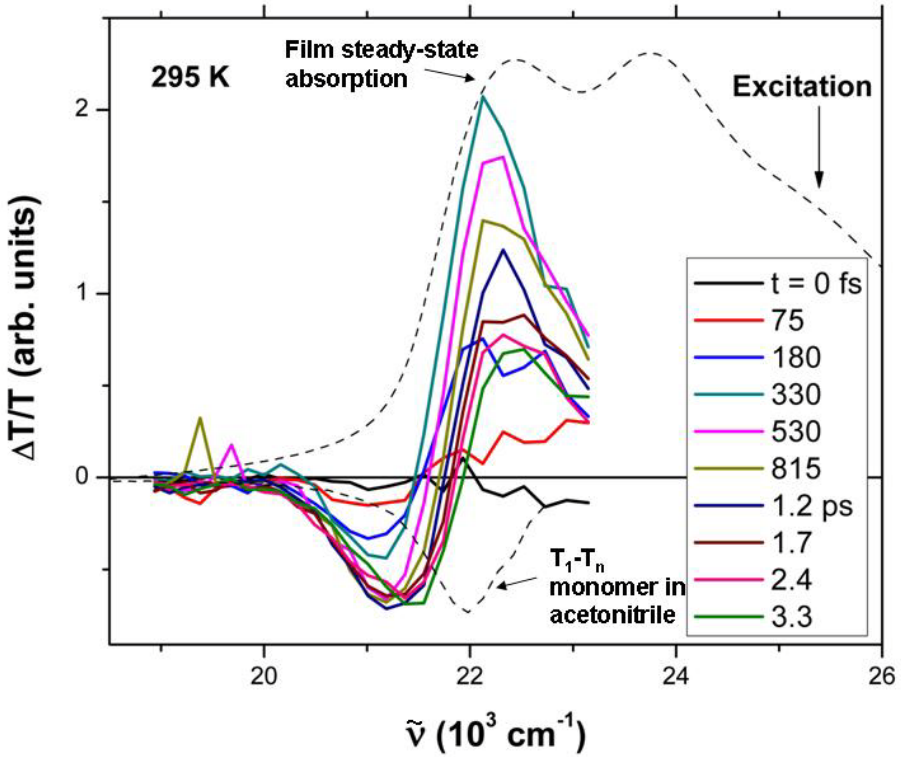
red curves:
S_0 - S_1 transition in C_2 and C_s conformers from linear dichroism in stretched polyethylene film at 77 K

Schwerin et al, *J. Phys. Chem. A* **2010**, *114*, 1457.

Singlet Fission in Thin Film of Neat Solid 1

TRANSIENT ABSORPTION KINETICS AT 77K



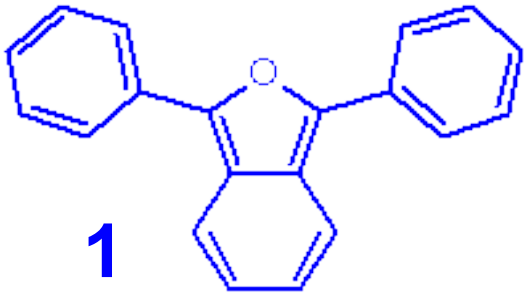


positive peaks: bleach of the ground state
negative peaks: triplet absorption

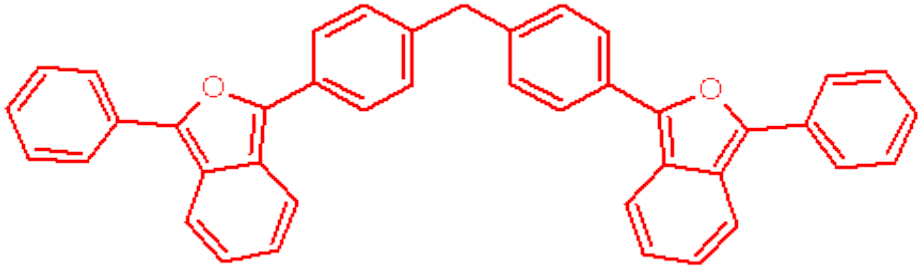
TRIPLET YIELD AT 77 K: 200±30%

(ii) Indirect Coupling

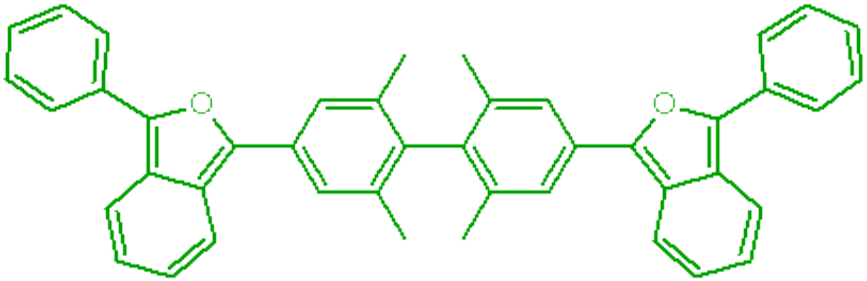
CONJUGATED CHROMOPHORES
WEAKLY AND STRONGLY COUPLED DIMERS OF 1



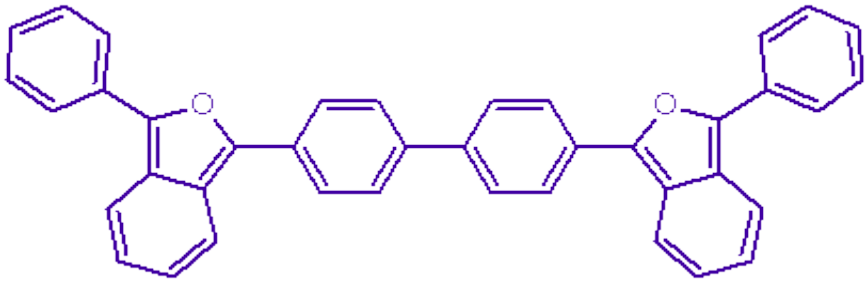
1



2 W

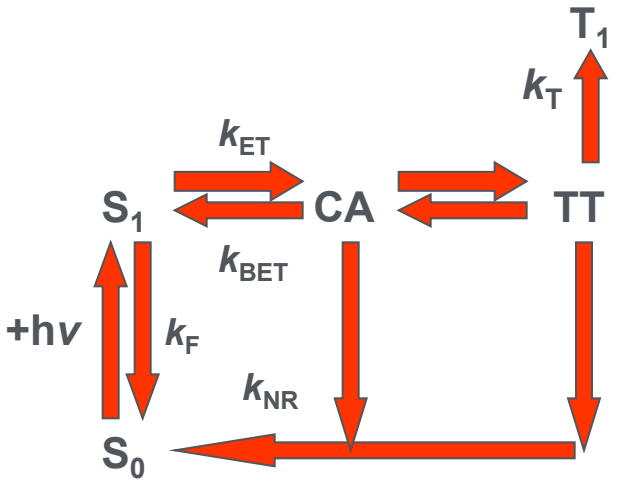


3 W

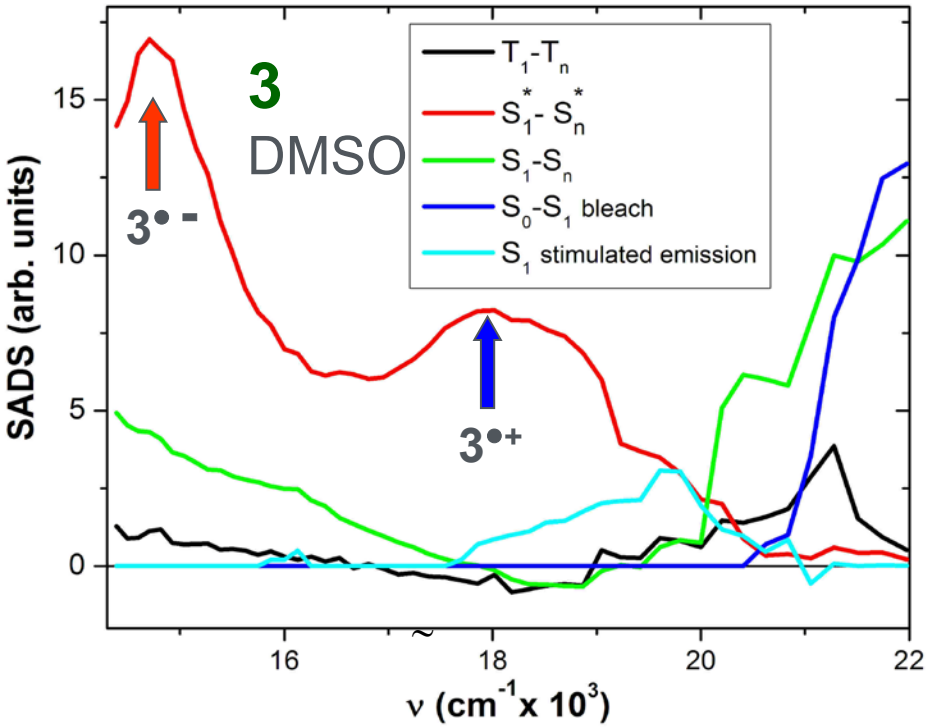


4 S

Two-Step Fission via a CT State



1. RT: S_1 and CA are equilibrated
CA is ~1.8 kcal/mol below S_1
2. LT: S_1 to CA is rate limiting,
E_a = 3 kcal/mol
3. Φ_T increases at LT



RT rate constants (1/ns)	k_F	k_{ET}	k_{BET}	k_{NR}	k_T
2 DMSO	0.23	1.8	2.8	~1.0	~0.10
3 DMSO	0.25	3.8	4.9	~0.8	~0.09

decay time of CA = rise time of T-T absorption, they are temperature independent

FIRST OBSERVATION OF TWO-STEP SINGLET FISSION, BUT TRIPLET YIELDS ARE SO FAR ONLY UP TO 9%

Triplet Exciton Separation

- Before the triplets diffuse apart: if T-T coupling is weak, they behave as two T_1; if it is significant, ^1TT is block diagonal in H_{elst} and yields S,T,Q
- Promotion of triplet separation needs to be studied and design guidelines developed
- The nine S,T,Q sublevels need to be close in energy; they are mixed by H_{ss}
  - If the two chromophores symmetry equivalent, only S and Q mix
  - Magnetic field effects (H_{Zeeman})
- The nine sublevels need to lose coherence to separate the two triplets
  - Those with S character can decay into S_1 or S_0
  - Those with T or Q character ca decay into T_1
  - Q levels could be long-lived and perhaps observable?

The Unusual Photophysics of 4

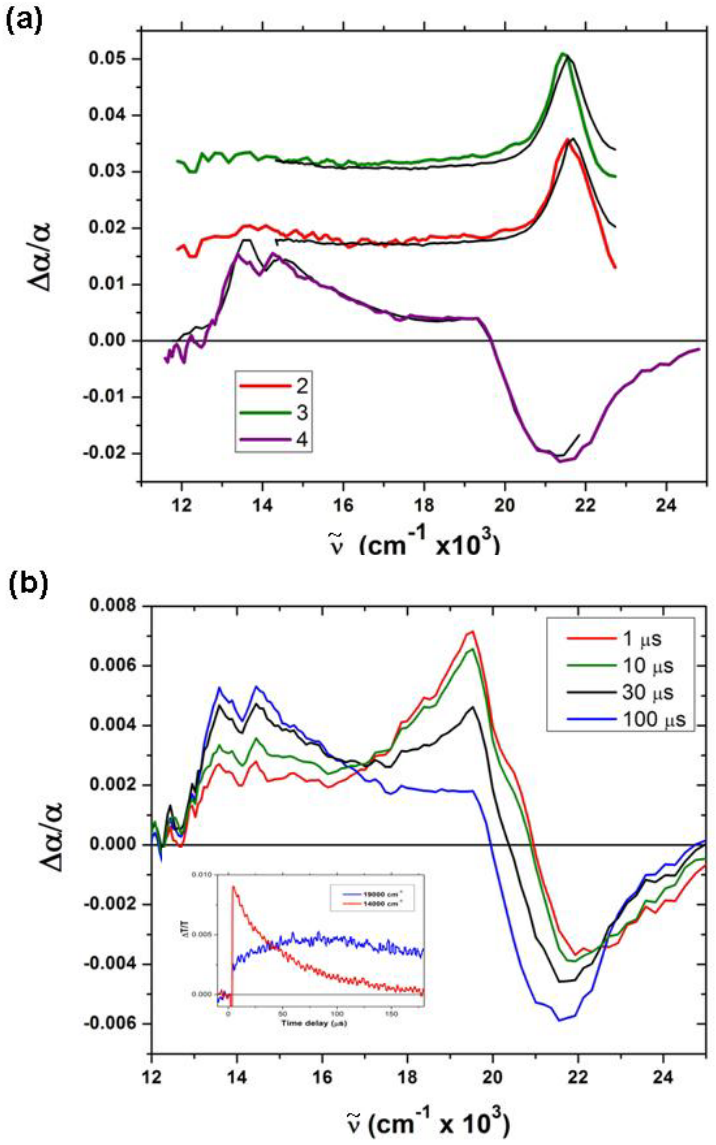
Triplet-triplet absorption
in DMSO (**2**, **3**)
in toluene (**4**)

4: lifetime 220 µs

direct excitation: color
sensitized excitation: black

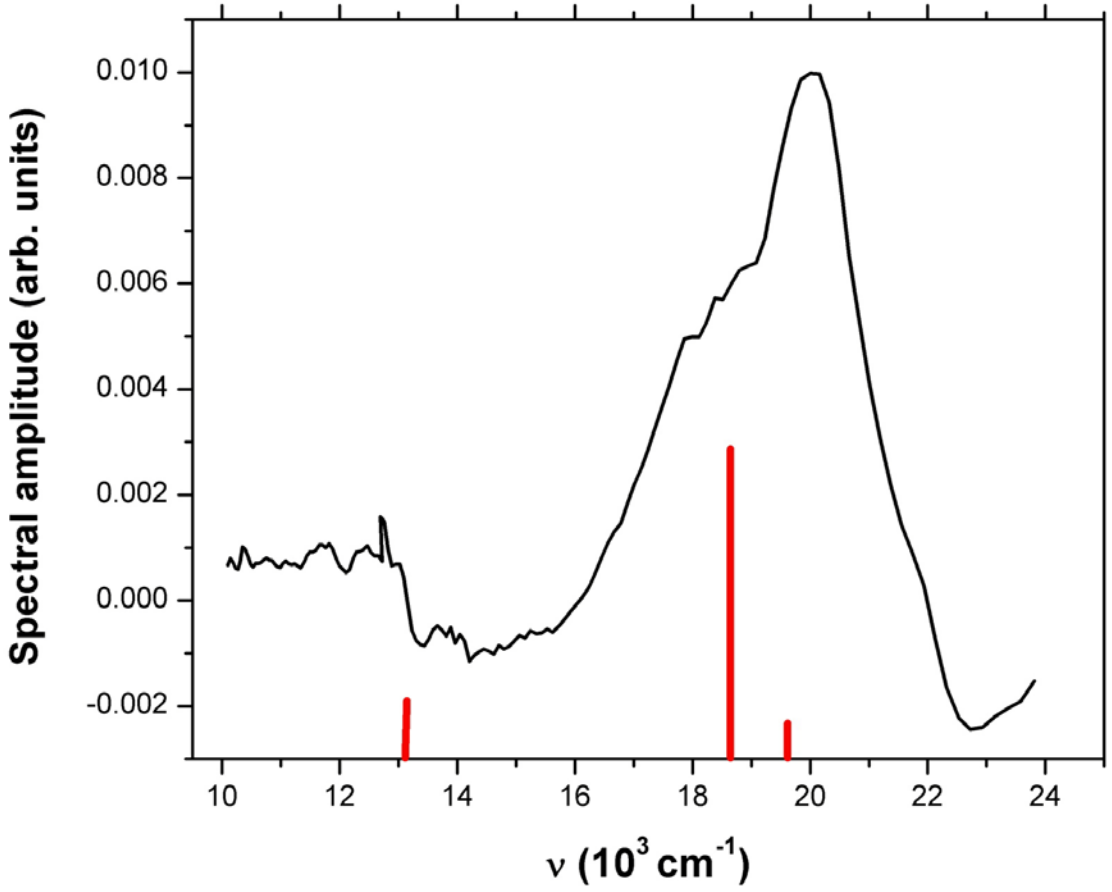
PHOTOINDUCED ABSORPTION OF 4 AS A FUNCTION OF DELAY TIME: SOLUTION

Time dependence of growing triplet-triplet and decaying **quintet-quintet** (?) absorption in toluene (**4**); time constant 40 µs
EPR confirmation experiments under way



Calculations: Quintet Assignment for a Second Long-Lived State of 4

40 µs ABSORPTION TRANSIENT FROM 4 AND TD-DFT CALCULATED Q_1-Q_n TRANSITIONS



Future Plans (FY 2011 and beyond)

- Continue theoretical exploration of singlet fission mechanisms, direct and mediated, and pursue new discoveries (e.g., EPR proof of quintet state)
- Use theoretical design guidelines to prepare new classes of singlet fission sensitizers: dimers, oligomers, polymers, aggregates, and nanocrystals; pay attention to stability and practical utility
- Complete the photophysical characterization of new SF sensitizers, get more accurate data for triplet yields
- Develop guidelines for designs that make the two triplets independent to perform two charge separations
- Synthesize larger amounts of favored sensitizers and modify them for adsorption on titanium dioxide
- Fabricate and test a SF Graetzel-type cell

Collaborations

- Mark Ratner
  - Subcontractor on the EERE project;
  - Northwestern University
  - Within the EERE Solar Program
  - An extremely close collaboration
- Arthur Nozik
  - Collaborator; funded from other sources
  - National Renewable Energy Laboratory
  - Outside of the EERE Solar Program
  - A very close collaboration
- Justin Johnson
  - Member of the Nozik team;
  - National Renewable Energy Laboratory
  - Outside of the EERE Solar Program
  - An extremely close collaboration
- Zdenek Havlas
  - International collaborator, funded from other sources; in part NSF OISE program
  - Institute of Organic Chemistry and Biochemistry AS CR, Prague, Czech Republic
  - Outside of the DOE Solar Program
  - A very close collaboration

Summary

1,3-Diphenylisobenzofuran - a new model chromophore for singlet fission

1. MONOMER IN SOLUTION

- no triplet formed upon direct excitation (no SF, negligible ISC), but it can be observed after energy transfer from triplet anthracene

2. MONOMER (AND ALL DIMERS) POLYCRYSTALLINE SOLIDS

- triplet formation by singlet fission, yield up to 200±30%

3. WEAKLY CONJUGATED DIMERS IN NONPOLAR SOLUTION

- no triplet formed (negligible SF and ISC)

4. WEAKLY CONJUGATED DIMERS IN POLAR SOLUTION

- up to 9% triplet formed via two-step SF with a dipolar intermediate

5. STRONGLY CONJUGATED DIMER IN SOLUTION

- the strong coupling causes $E(S_1) < 2E(T_1)$
- ~1.5% triplet and ~1.5% probable quintet formed by SF within <100 ps in competition with internal conversion when exciting above $2E(T_1)$; the quintet would be a novelty

Summary Table

Task #	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	PREDICT BATCH 1 NEW SF CHROMOPHORES	July 08	July 08	July 08	100%	
2	SYNTHESIS OF NEW SF CHROMOPHORES	July 08	July 08	July 08	100%	
3	EQUIPMENT SET UP AND TESTING	July 08	July 08	Apr 10	95%	STILL BEING FINE-TUNED
4	PREDICT A NEW SENSITIZER STRUCTURE	Jan 09	Jan 09	Dec 08	100%	
5	DEVELOP A DENSITY MATRIX FORMALISM CODE	Jan 09	Jan 09	Jan 09	100%	
6	SYNTHESIS OF A NEW SENSITIZER	Jan 09		Jan 09	100%	
7	SYNTHESIS OF A NEW CHROMOPHORE	Jan 09		Jan 09	100%	
8	AGGREGATE PREPARATION AND CHARACTERIZATION	Jan 09		Apr 10	90%	TRIPLET YIELD MEASUREMENTS REMAIN TO BE MADE
9	PREDICT NEW SENSITIZER STRUCTURES	Jul 09		Apr 09	100%	
10	SYNTHESIZE NEW SENSITIZERS	Jul 09		Apr 09	100%	
11	PREPARE NEW CHROMOPHORES	Jul 09		Mar 09	100%	
12	IMPROVED AGGREGATE FORMATION PROCEDURES	Jul 09	Jan 10		40%	THIS IS STILL UNDERWAY
13	MARCUS CODE FOR SF	Jan 10		10-Apr	100%	
14	SYNTHESIZE AND CHARACTERIZE NEW SENSITIZERS	Jan 10		10-Apr	100%	
15	FINALIZE AGGREGATE FORMATION PROCEDURES	Jan 10				

Budget

- Total project funding, $ 1 119 715, DOE $ 895 772, Univ. of Colorado, $ 223 943.
  - The project is on budget
  - Tasks that would be added if additional funding was provided: (i) a larger number of new classes of singlet fission sensitizers would be predicted, synthesized, and tested for efficiency. (ii) efforts would be started to optimize triplet separation and independent charge separation from each
  - Changes to tasks and activities in anticipation of the FY 2011 budget: added emphasis on the use of design guidelines that have been developed for the discovery of new classes of singlet fission sensitizers (we now have two new classes that look very promising computationally), and work on design for two independent triplet injections

Publications and Patent Applications

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