Вычислительные методы в дизайне оптических материалов

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http://bit.ly/NanoSim
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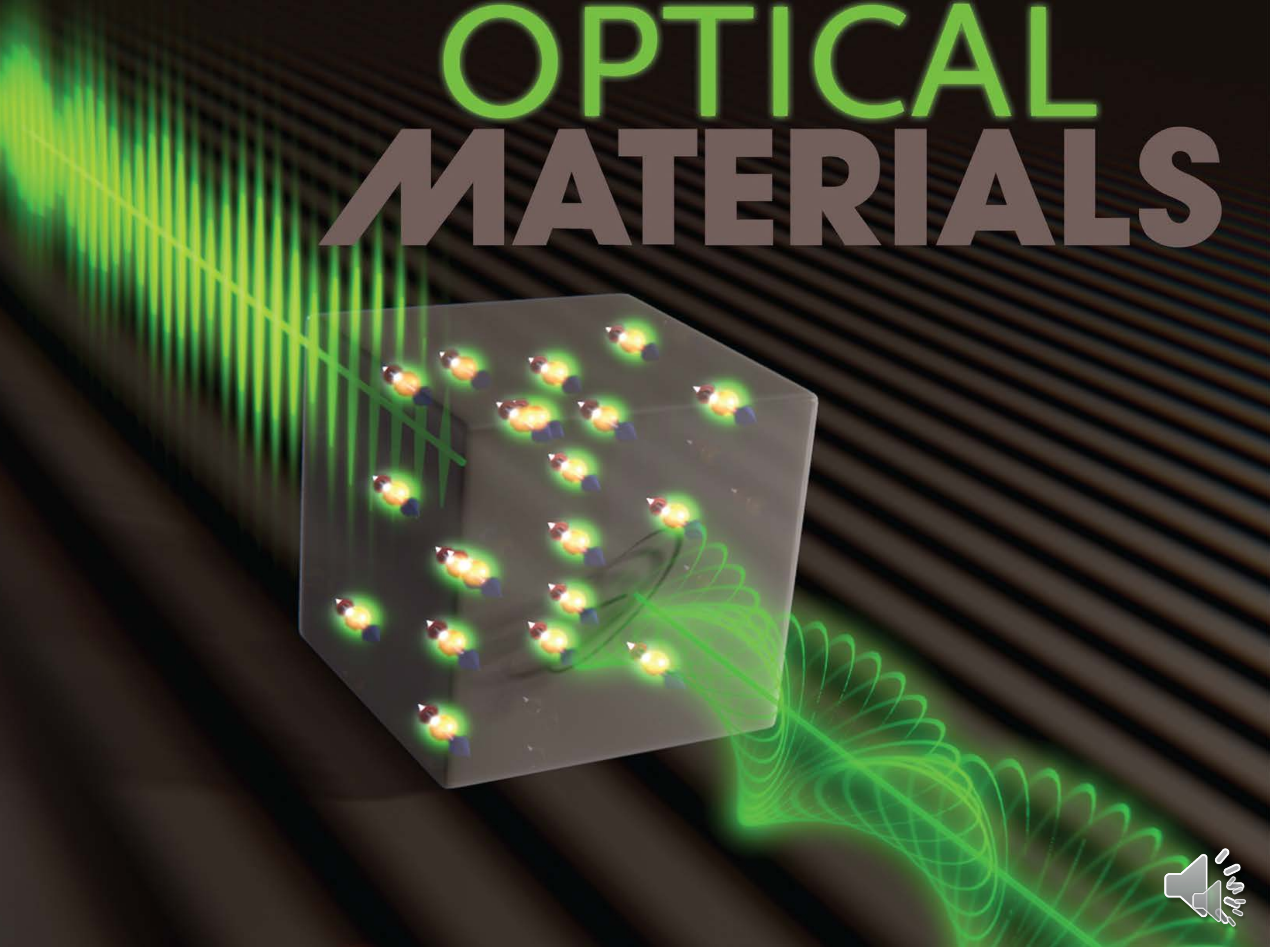
Central Florida: Orlando, FL

University of Central Florida is Second Largest in US (~60,000 students)

Ten largest public university campuses by enrollment as of Fall 2012			
Ranking	University	Location	Enrollment
1	Arizona State University [a]	Tempe, Arizona	60,169[1]
2	University of Central Florida [b]	Orlando, Florida	60,048[2]
3	The Ohio State University	Columbus, Ohio	56,387[3]
4	Texas A&M University [b]	College Station, Texas	53,337[4]
5	University of Texas at Austin [b]	Austin, Texas	52,186[5]
6	University of Minnesota	Minneapolis/Saint Paul, Minnesota	51,853[6]
7	Florida International University [b]	Miami, Florida	50,396[7]
8	University of Florida [b]	Gainesville, Florida	49,913[8]
9	Michigan State University	East Lansing, Michigan	48,906[9]
10	Pennsylvania State University	University Park, Pennsylvania	45,351[10]

IN THIS TALK

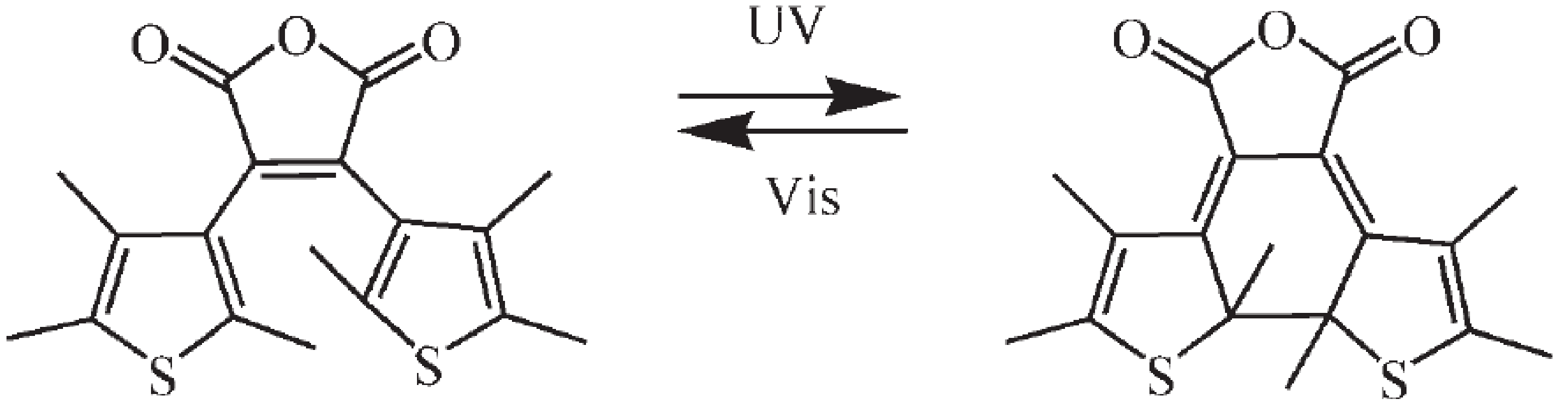
- Photochromic chromophores
- Optical data storage
- Two-photon absorption
- Prediction of photoswitching properties
  - Excited state surfaces
  - Kohn-Sham orbitals
- Two-photon absorbing photochrom


OPTICAL
MATERIALS

EXAMPLES OF OPTICAL MATERIALS

- Photovoltaics (light into electricity)
- Photosensitizers (light into triplets)
- Frequency doubling (red light into green light)
- Optical limiting (prevent photodamage)
- Optical switching (change properties under light)

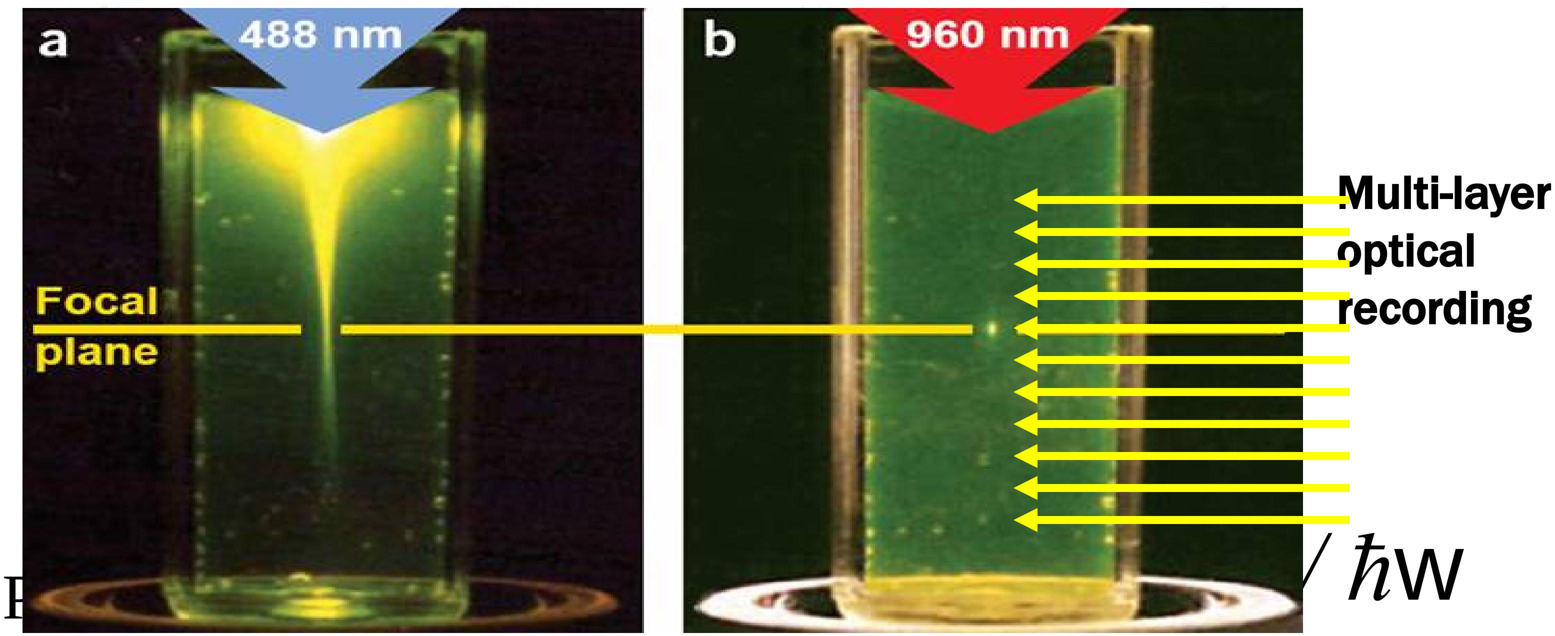
PHOTOCHROMIC MATERIALS FOR OPTICAL DATA STORAGE



Colorless **Colored**

Dithioarylethenes: the photochromic chromophores that are thermally stable and fatigue resistant

TWO-PHOTON (2PA) ABSORPTION MAY HELP IN MULTILAYER RECORDING

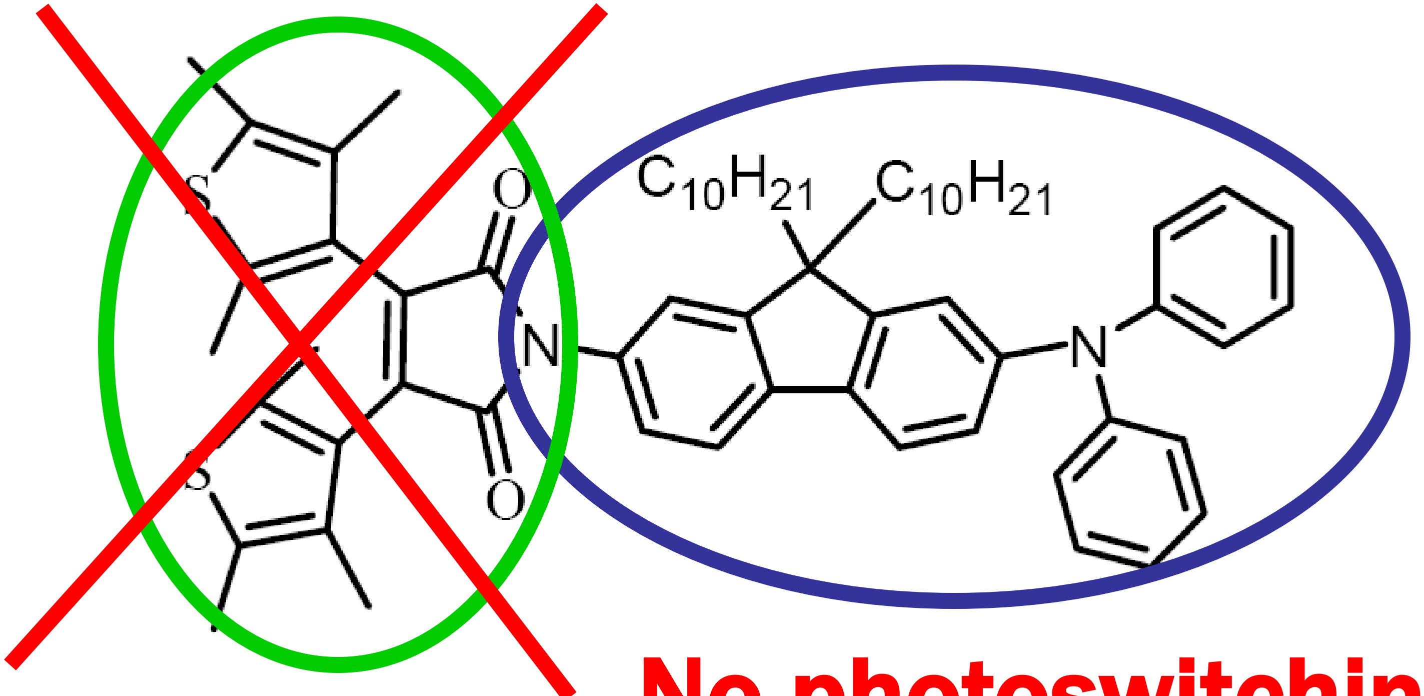


P_{1P} … $/ \hbar w$

Proof of concept: Kawata, *Proc. IEEE*, 87, 2009 (1999)

PRACTICALLY USEFUL MATERIALS NEED LARGE 2PA CROSS-SECTIONS

2PA absorber

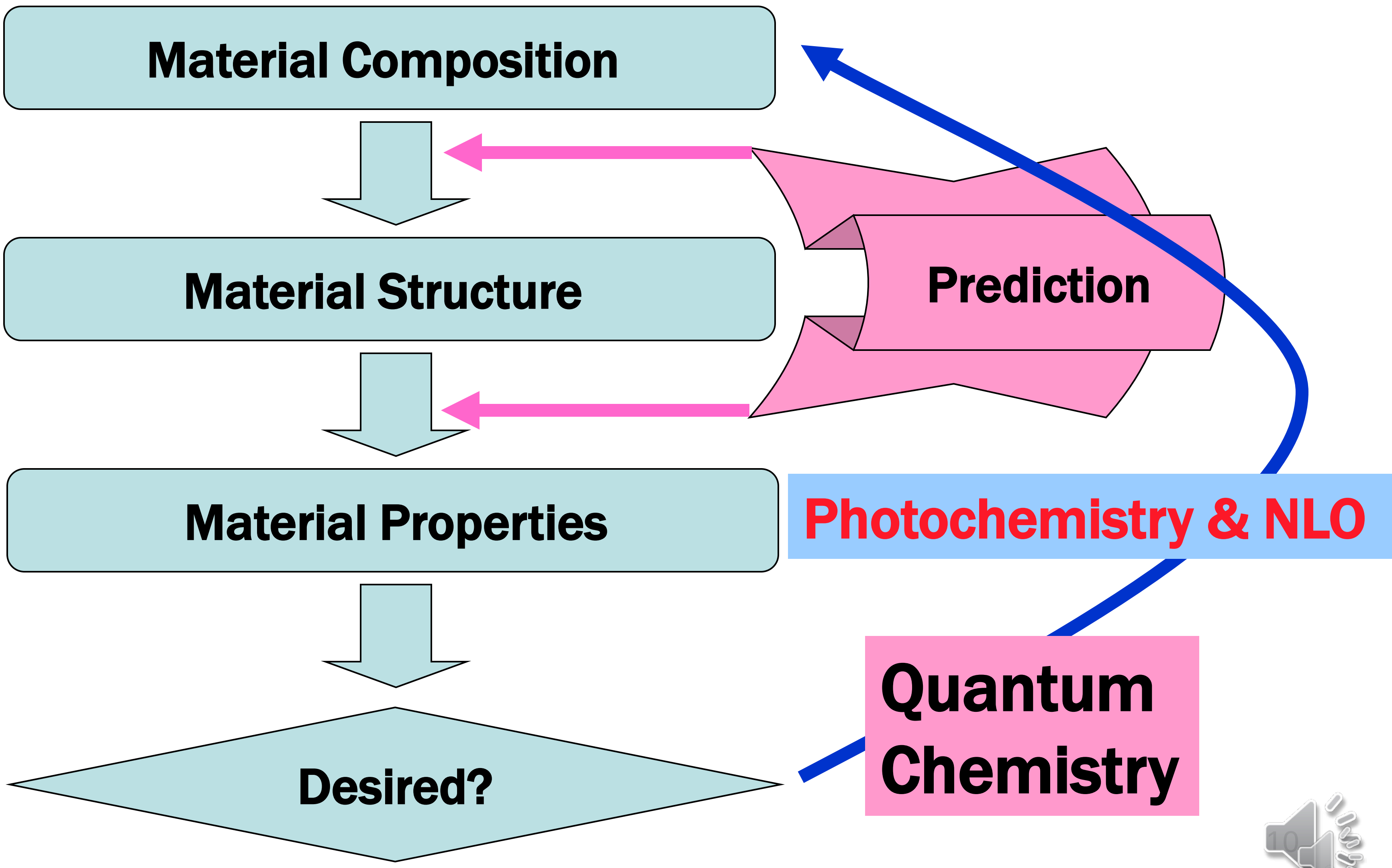


No photoswitching in this molecule

Ultrafast photoswitch

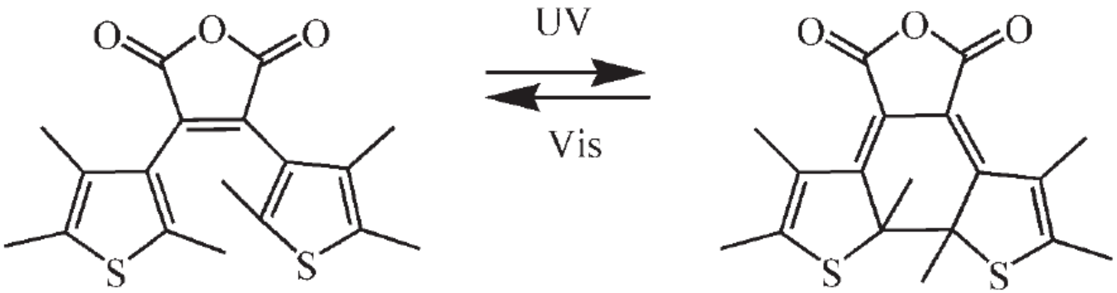
Experiment: Belfield, *unpublished* (2005)

INVERSE PROBLEM IN MATERIALS DESIGN

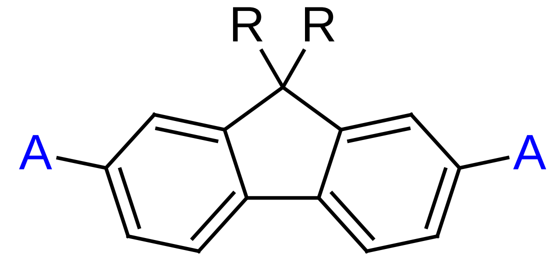


HOW TO COMBINE THE PHOTOCHROMISM WITH 2PA SUCCESSFULLY?

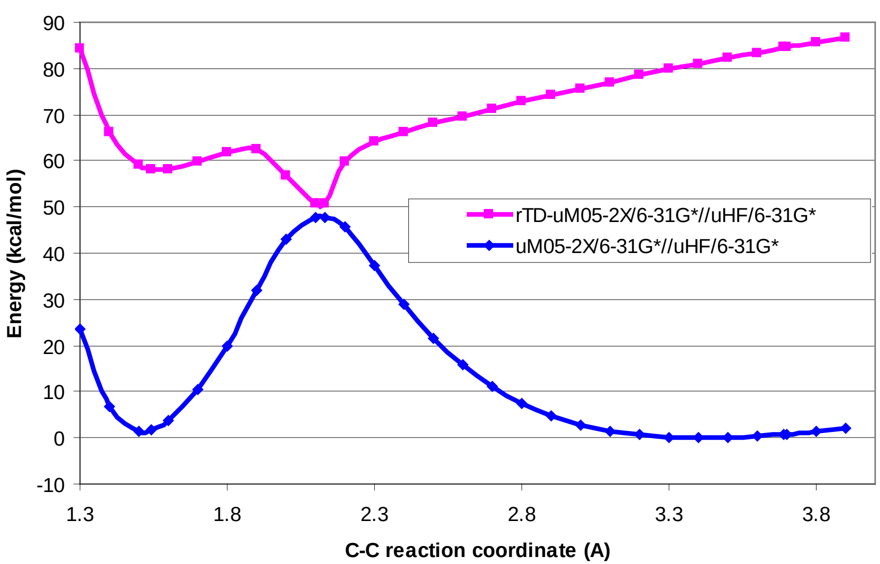
Efficient photoswitching



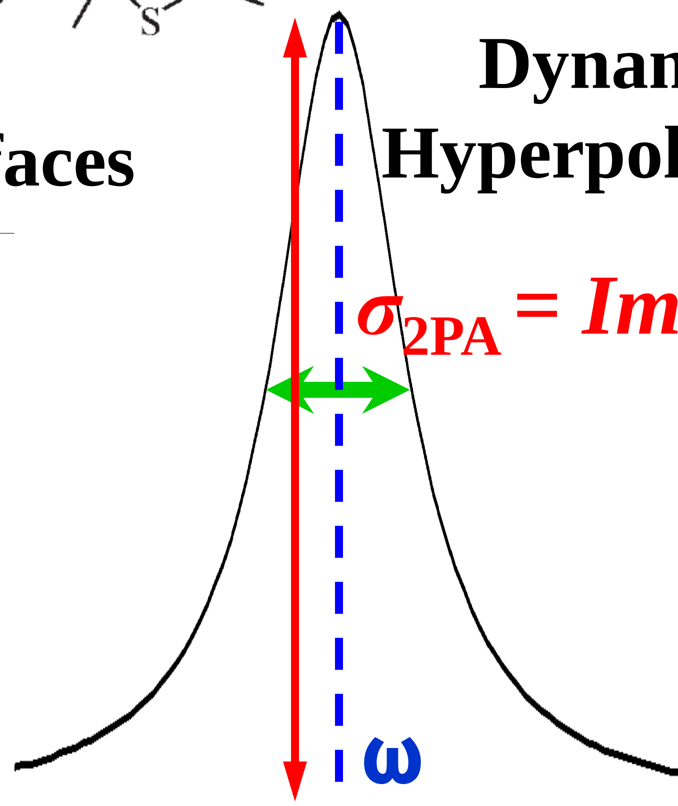
Large 2PA cross-sections



Ground and Excited State Potential Energy Surfaces



Dynamic Second Hyperpolarizability



$$\sigma_{2PA} = Im\langle\gamma\rangle$$

VERTICAL ABSORPTION

TD-DFT (LINEAR RESPONCE) IS USED TO PREDISCT ABSORPTION SPECTRA

Ground state: density functional DFT

↓

Excited states: linear response TD-DFT

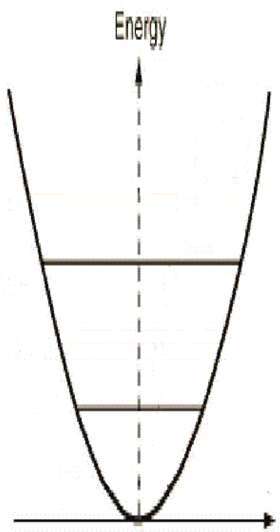
$$\chi_i - orbitals$$

$$total\_density : \rho = \sum_i n_i \chi_i^2$$

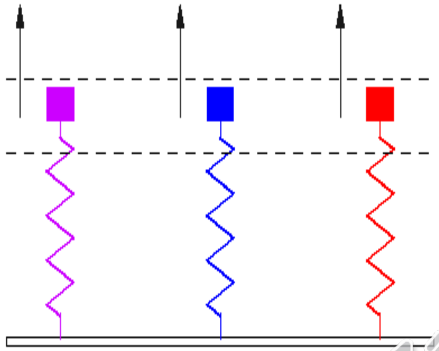
$$excitation\_energies : \Omega_\alpha$$

$$transition\_densities : \xi_\alpha$$

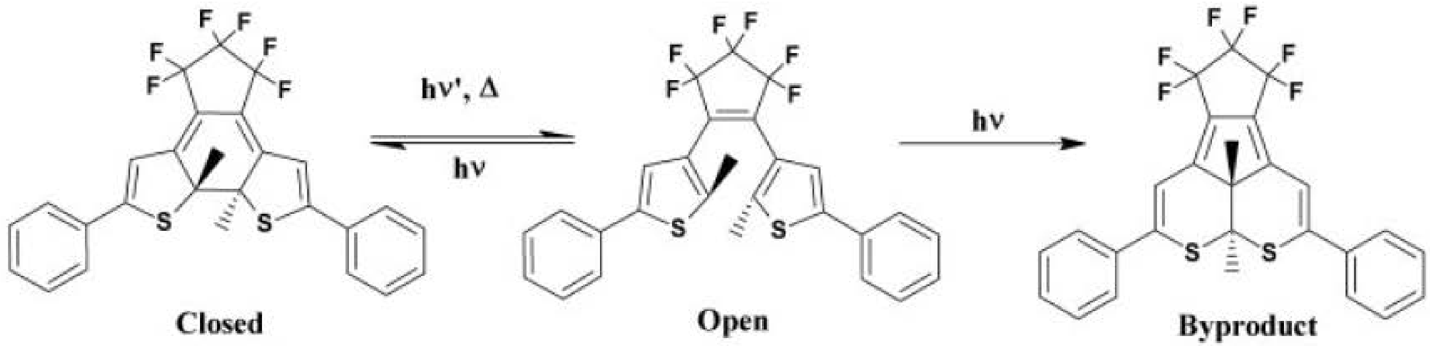
$$\mu_{0,\alpha} = Tr(\mu \xi_\alpha)$$



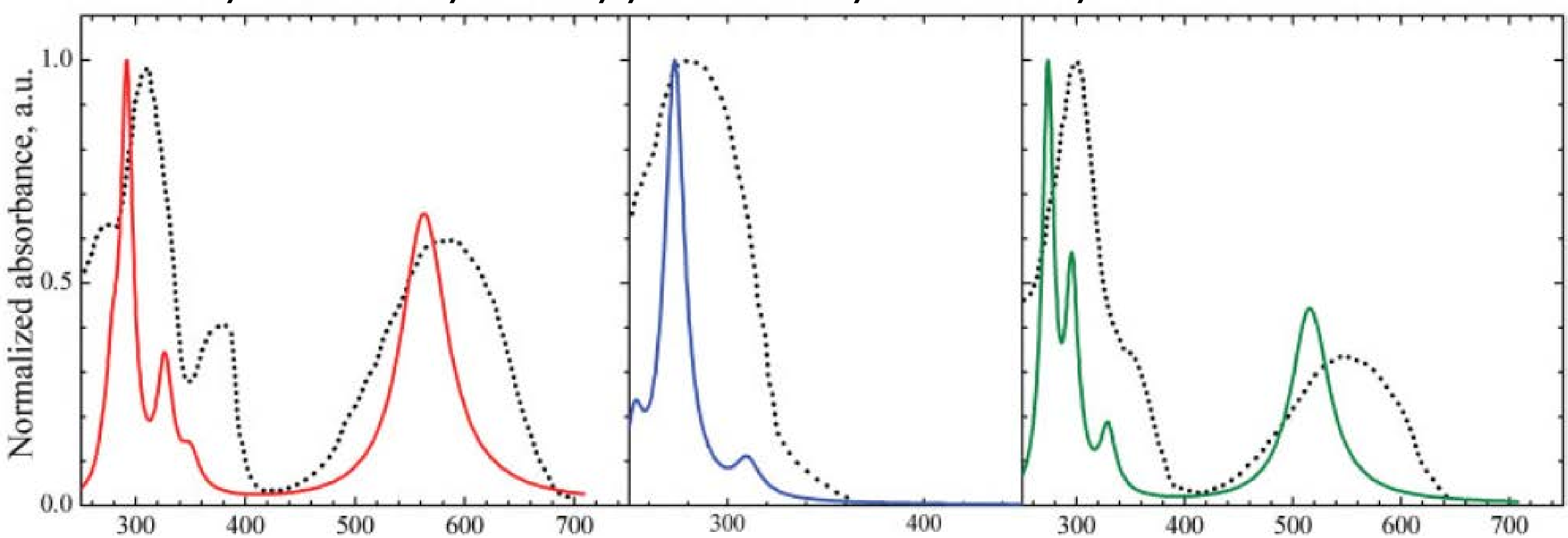
disturb electron density with external field, assume harmonic potential, find resonances



TIME-DEPENDENT rDFT PREDICTS ABSORPTION SPECTRA WELL



TD-M05/6-31G*/PCM//M05-2x/6-31G*/PCM level of theory



Patel, Mikhailov, Belfield, Masunov, *Int. J. Quant. Chem. 109*, 3711 (2009)

Experiement: Irie, et al., *Chem. Commun.*, 747 (1999)

TWO-PHOTON ABSORPTION (2PA) NEEDS LARGE STATE-TO-STATE TRANSITION DIPOLES

2PA cross-section in Sum-Over-State formalism:

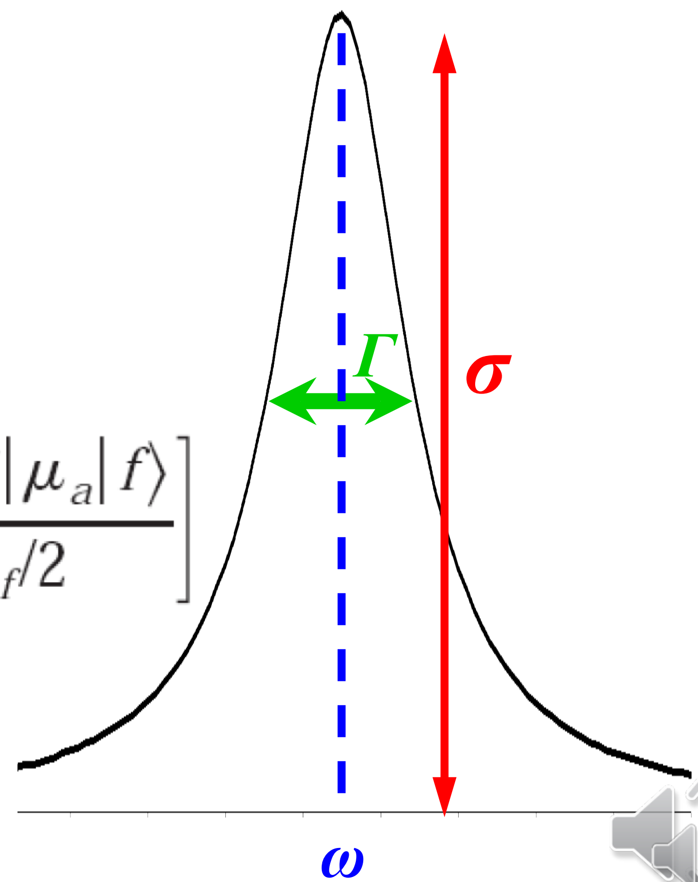
$$\sigma^{\text{TPA}} = \frac{4\pi^2 a_0^5 \alpha}{c_0} \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{\text{TP}}$$

$$\delta_{\text{TP}}^{L} = 6(S_{zz})^2$$

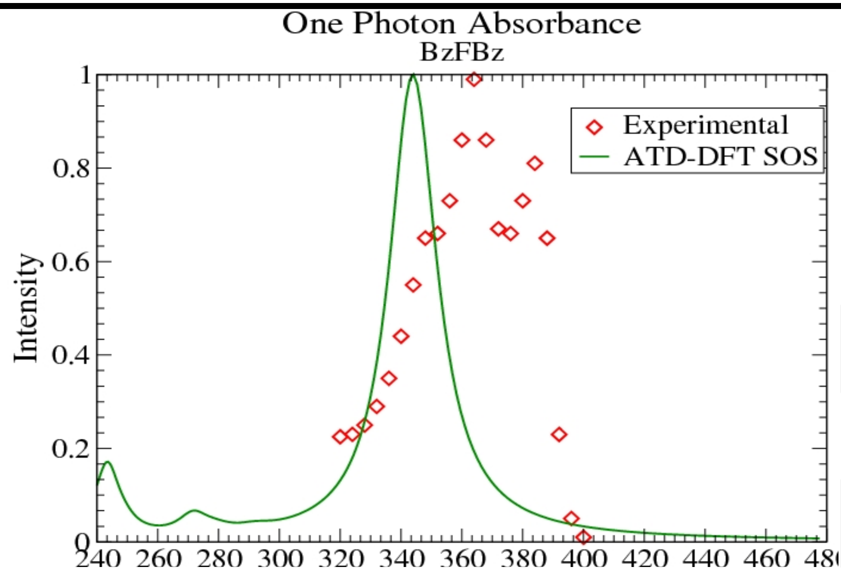
$$S_{ab} = \sum_i \left[\frac{\langle 0|\mu_a|i\rangle\langle i|\mu_b|f\rangle}{\omega_i - \omega_f/2} + \frac{\langle 0|\mu_b|i\rangle\langle i|\mu_a|f\rangle}{\omega_i - \omega_f/2} \right]$$

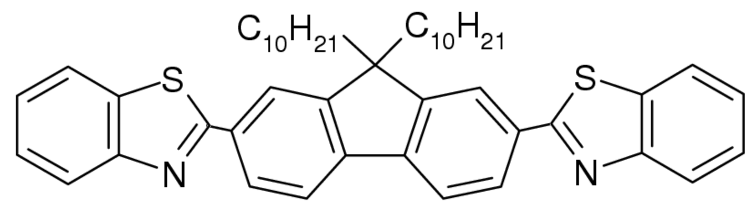
State to State Transition Dipole moments:

$$\mu_{ee'}^{z} = < e \,|\, z \,|\, e' >$$

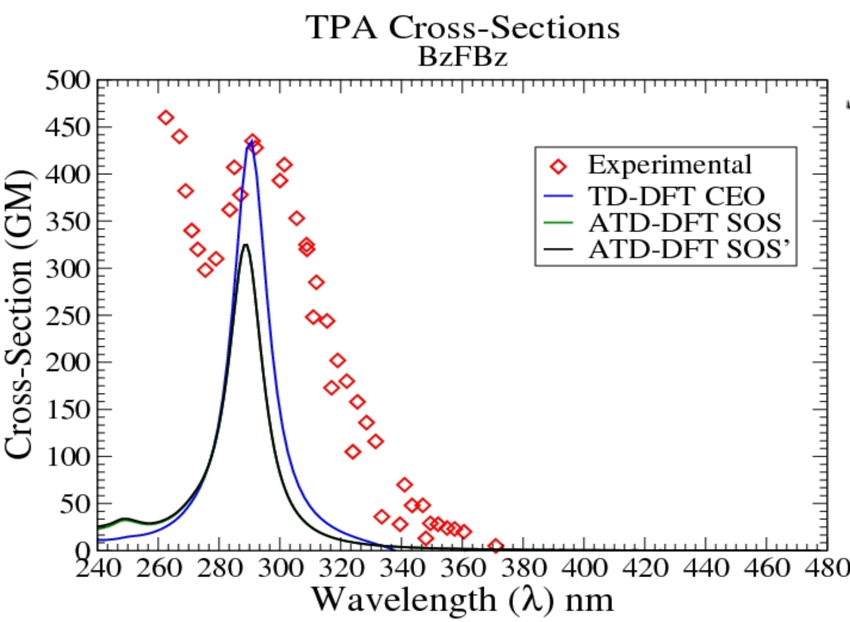


OUR ATDA-DFT APPROACH ACCURATELY PREDICTS 2PA CROSS-SECTIONS





BzFBz		X-dip.	Y-dip.	Z-dip.	Dip. M.
S0-S1	345.27	0.0000	-4.3856	0.0000	4.3856
S1-S2	293.14	0.0000	1.4393	0.0000	1.4393
S1-S4	289.87	0.0000	-4.8998	0.0000	4.8998

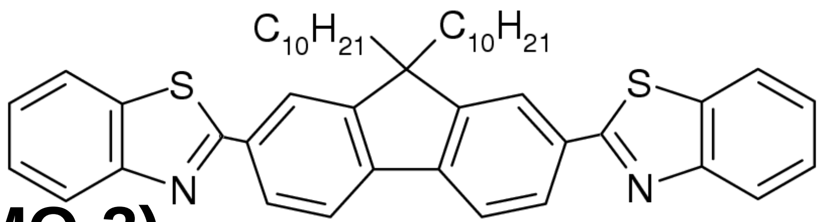


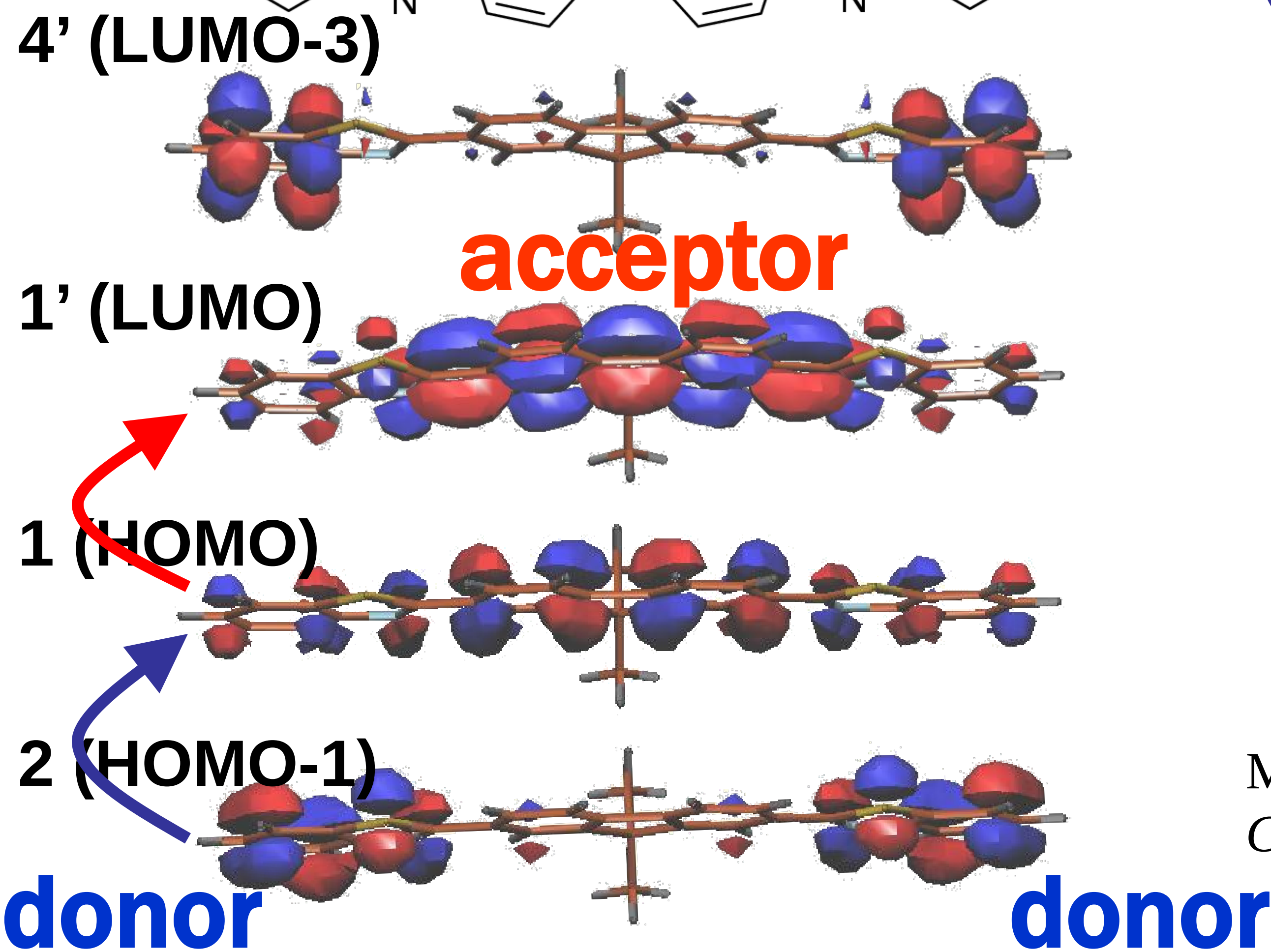
$$S_{ab} = \sum_i \left[\frac{\langle 0|\mu_a|i\rangle\langle i|\mu_b|f\rangle}{\omega_i - \omega_f/2} + \frac{\langle 0|\mu_b|i\rangle\langle i|\mu_a|f\rangle}{\omega_i - \omega_f/2} \right]$$

Tafur, Mikhailov, Belfield, Masunov, *Lecture Notes Comp. Sci.* 5545, 179 (2009)

UCF NSTC

$\mu_{\alpha\beta}$ ALLOW 2PA ANALYSIS IN TERMS OF ORBITALS





S4= (1-4')+(2-1')

S2= (2-1')

S1= (1-1')

S0

Masunov, Mikhailov, *Eur. J. Chem.*, 1(2), 142 (2010)

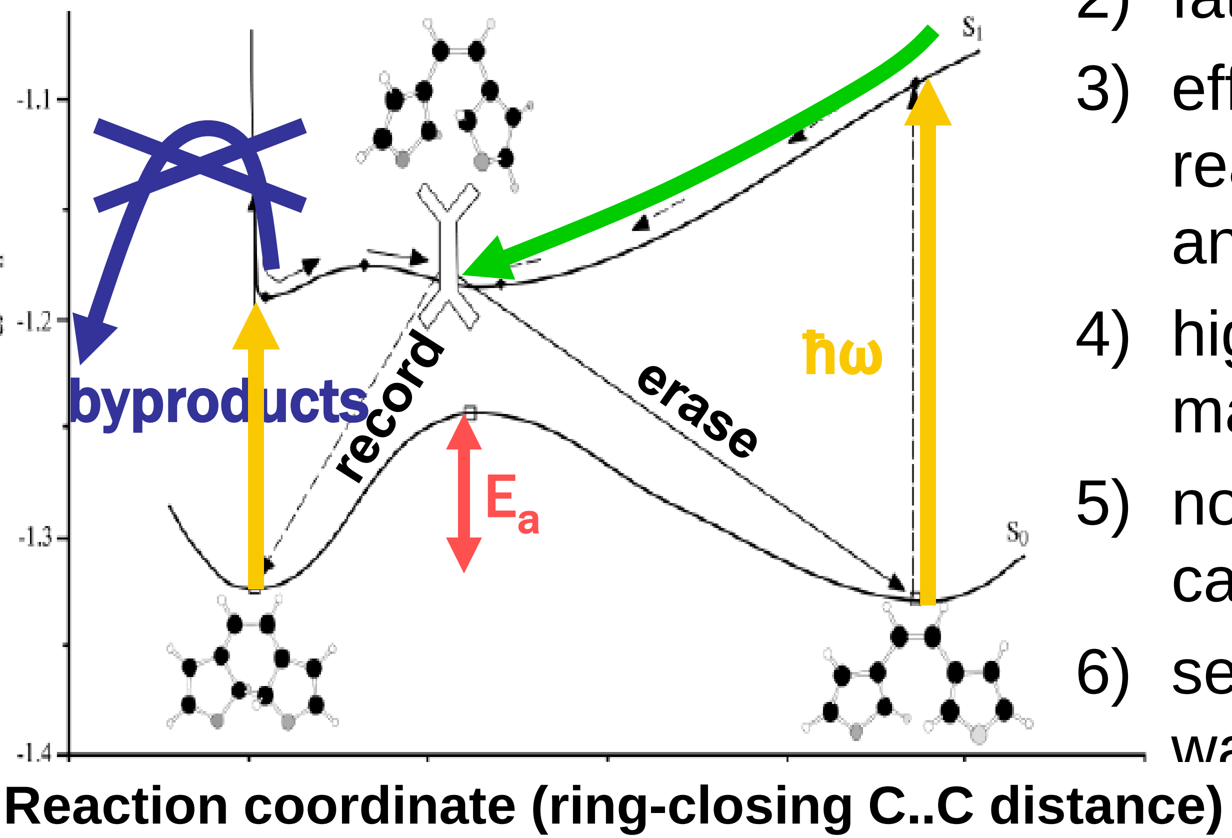
EXCITED STATE POTENTIAL SURFACES

POTENTIAL ENERGY SURFACES IN RATIONAL DESIGN OF PHOTOCHROMIC MATERIALS

Practical requirements to photochromic materials (from M. Irie, *Chem. Rev.* **100**, 1685 (2000)):

1) thermal stability;
2) fatigue resistance;
3) efficient photochromic reactivity: high sensitivity and rapid response;
4) high solubility in polymer matrices;
5) non-destructive readout capability;
6) sensitivity at diode laser wavelengths

CASSCF(10,10)/6-31G* data from M. Boggio-Pasqua, M. Ravaglia, M. J. Bearpark, M. Garavelli, and M. A. Robb, *J. Phys. Chem. A*, *107,* 11139 (2003)

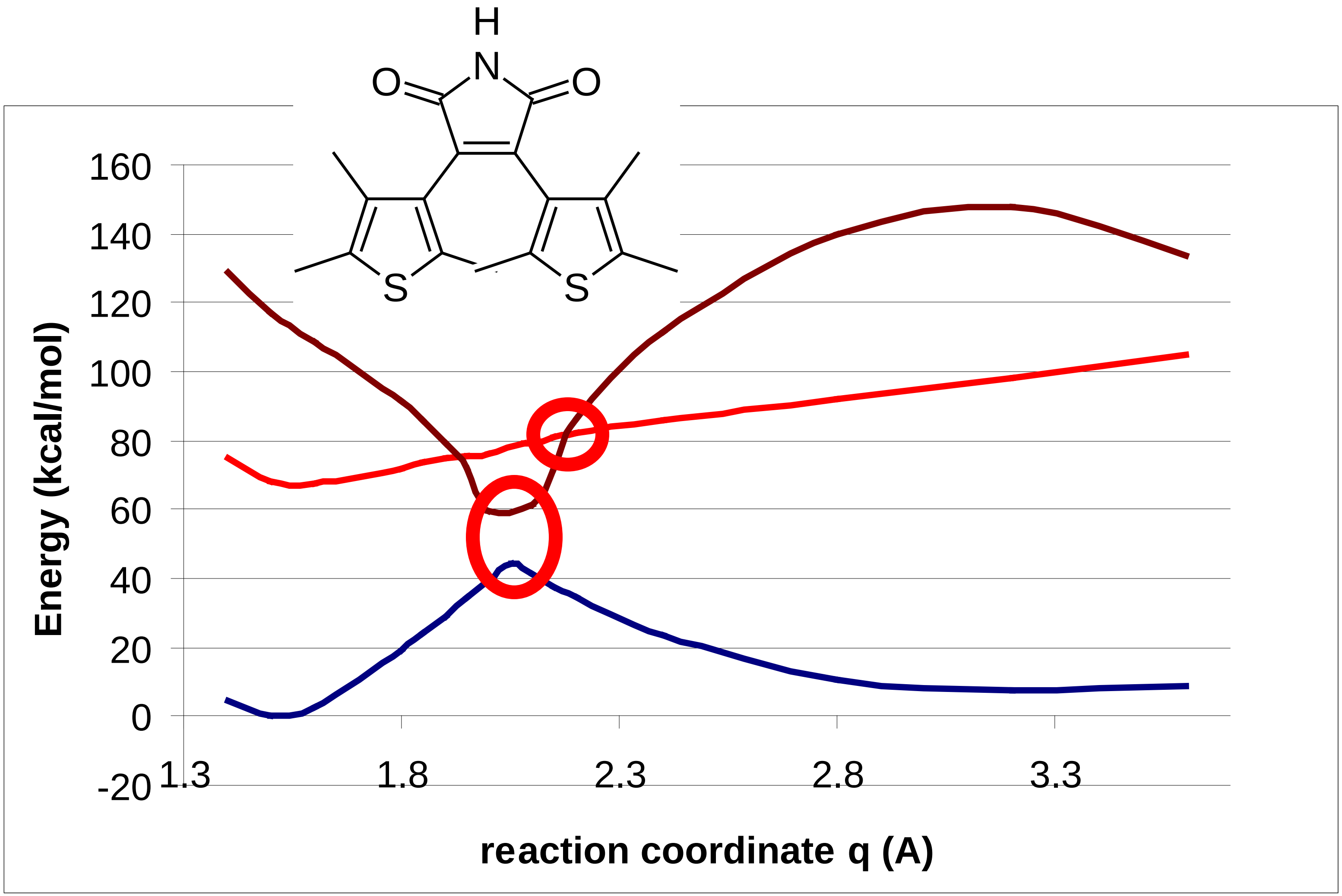


UCF NSTC

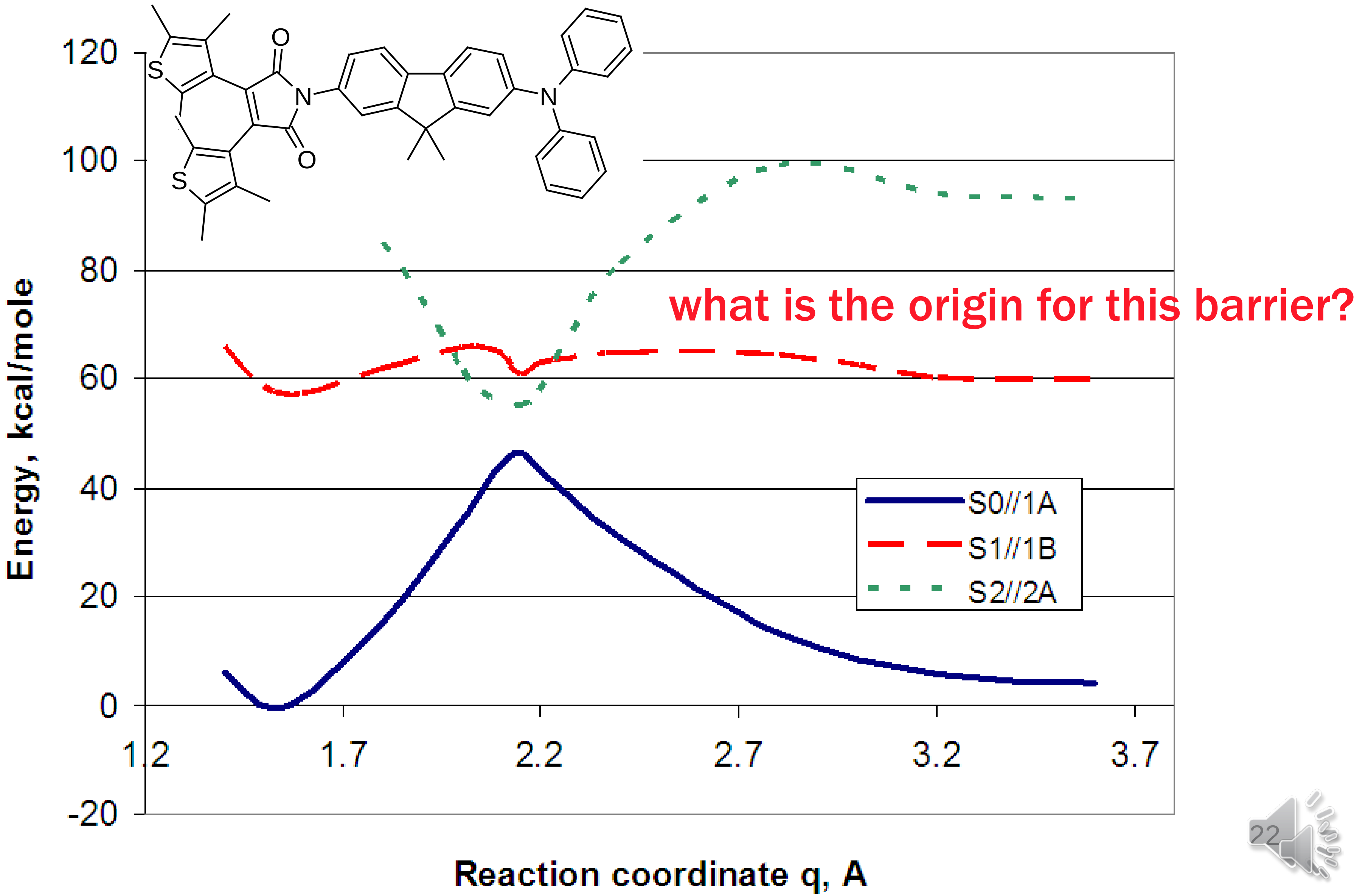
POTENTIAL ENERGY SURFACE (PES)

1. Relaxed scan along the bond forming distance
2. Ground state geometry and energy at uDFT level
3. Single excited state geometry at α-STS level
4. Double excited state geometry at αβ-STS level
5. Single excitation energy at rTD-DFT level
6. Double excitation energy as rTD-DFT*2
7. We use Truhlar's M05-2X functional

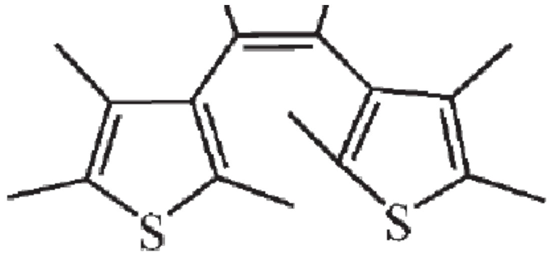
PHOTOREACTIVE PES HAS SMOOTH SLOPES TO INTERSECTION POINTS



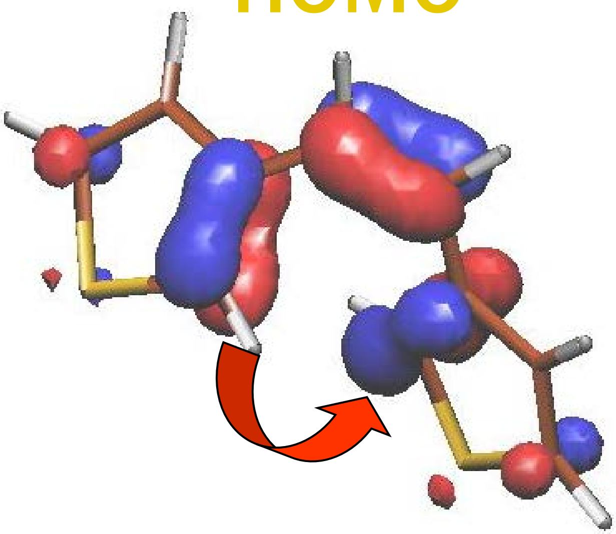
BARRIERS ON PES MAKE THE MOLECULE PHOTOINACTIVE



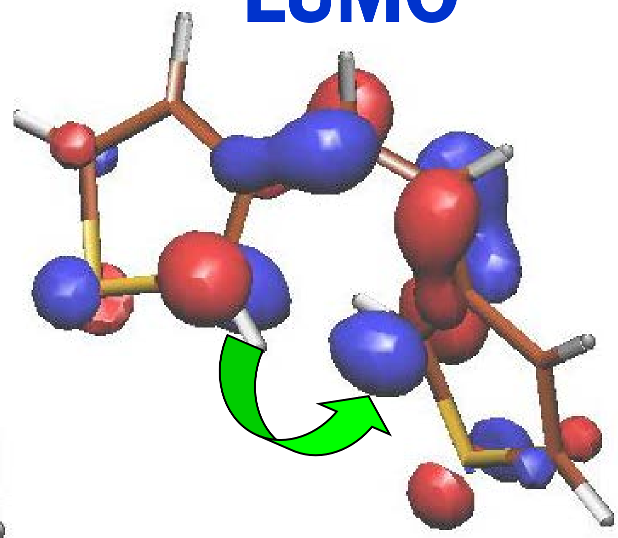
HOMO/LUMO ORBITAL TOPOLOGY ENSURES THE LOWEST STATE IS REACTIVE

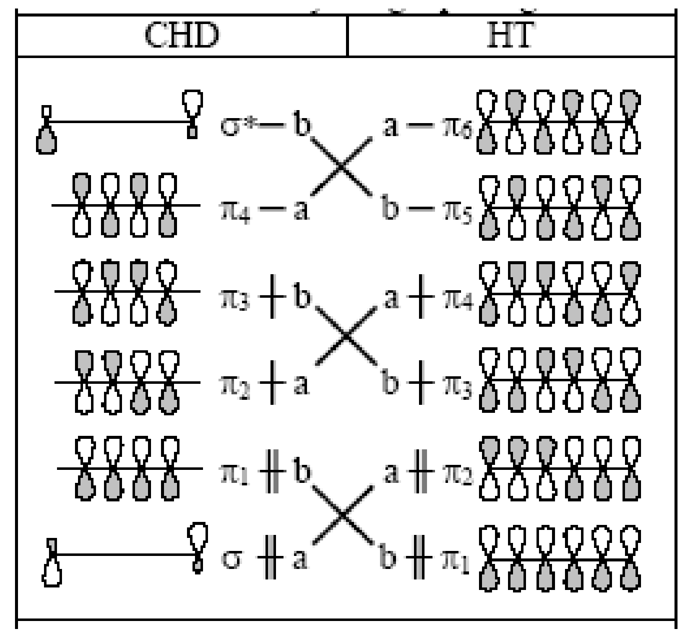


HOMO



LUMO

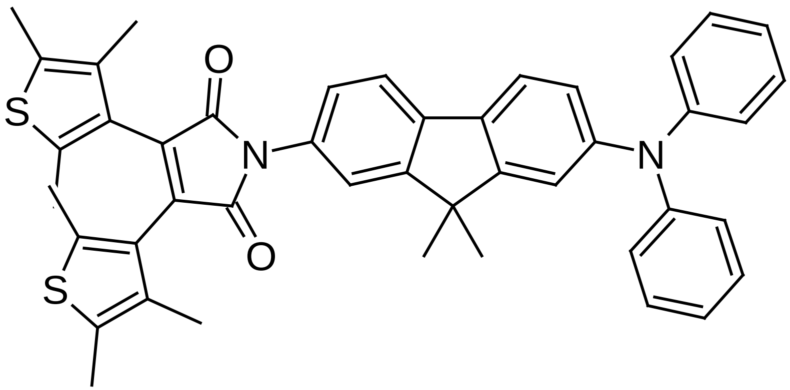




antibonding

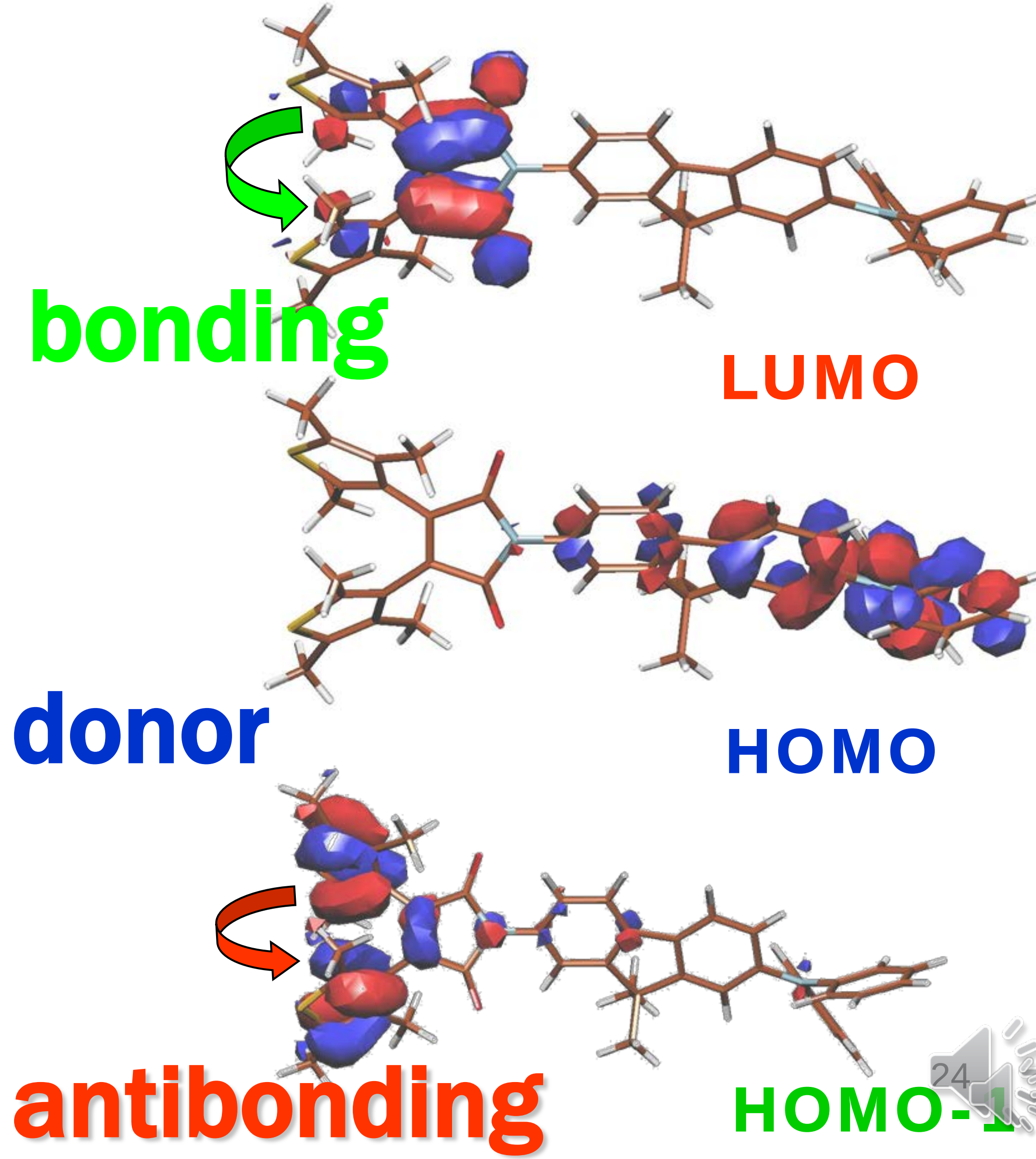
bonding

ELECTRONIC STRUCTURE OF THE PROTOTYPE



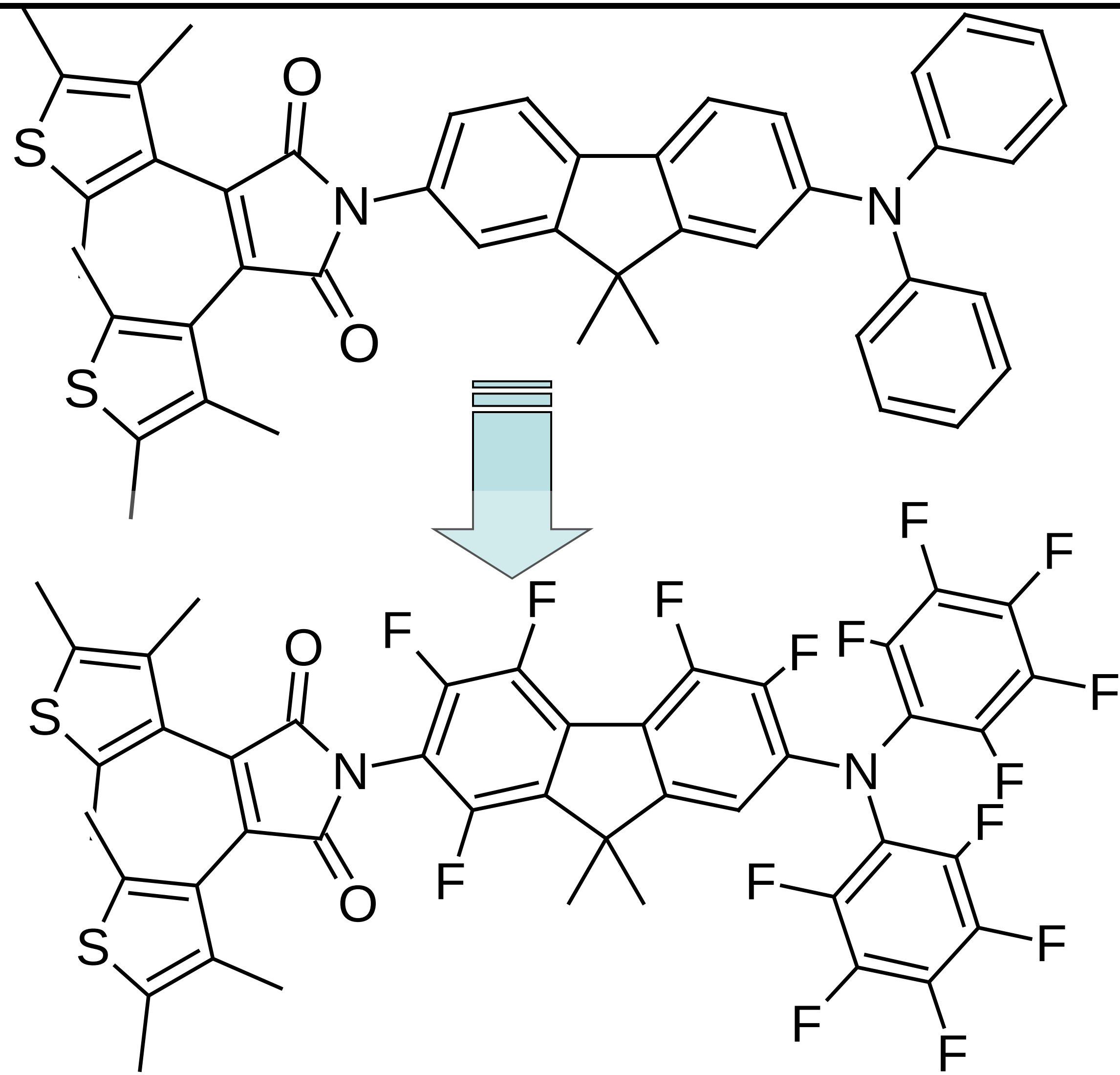
Donor HOMO of 2PA pendant percolates HOMO-LUMO gap of the photoswitch.

This produced barrier on S_1 PES



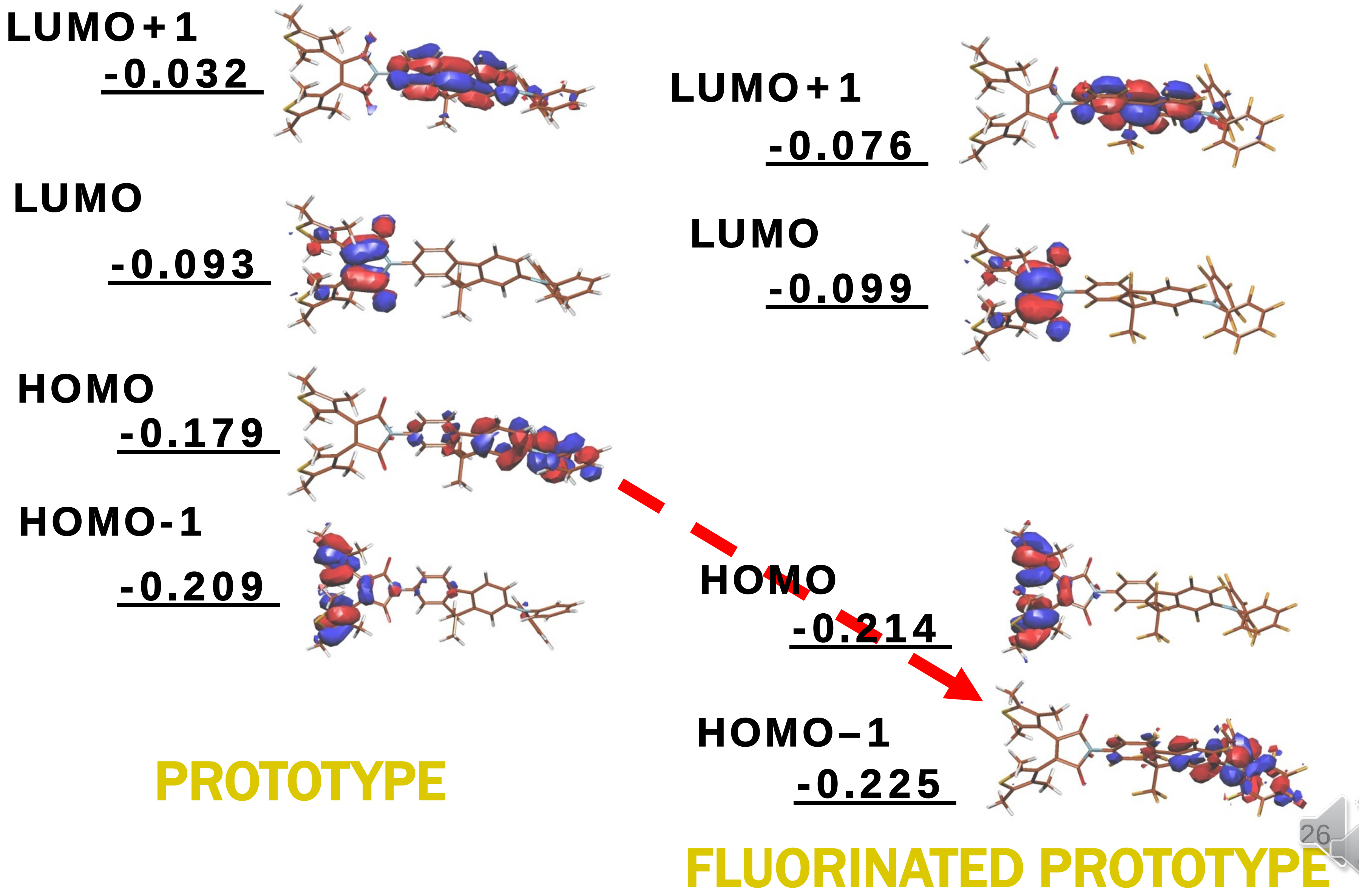
SOLUTION PROPOSED

To stabilize the donor MO below the photoswitch HOMO (e.g. by perfluorination of the 2PA pendant group)

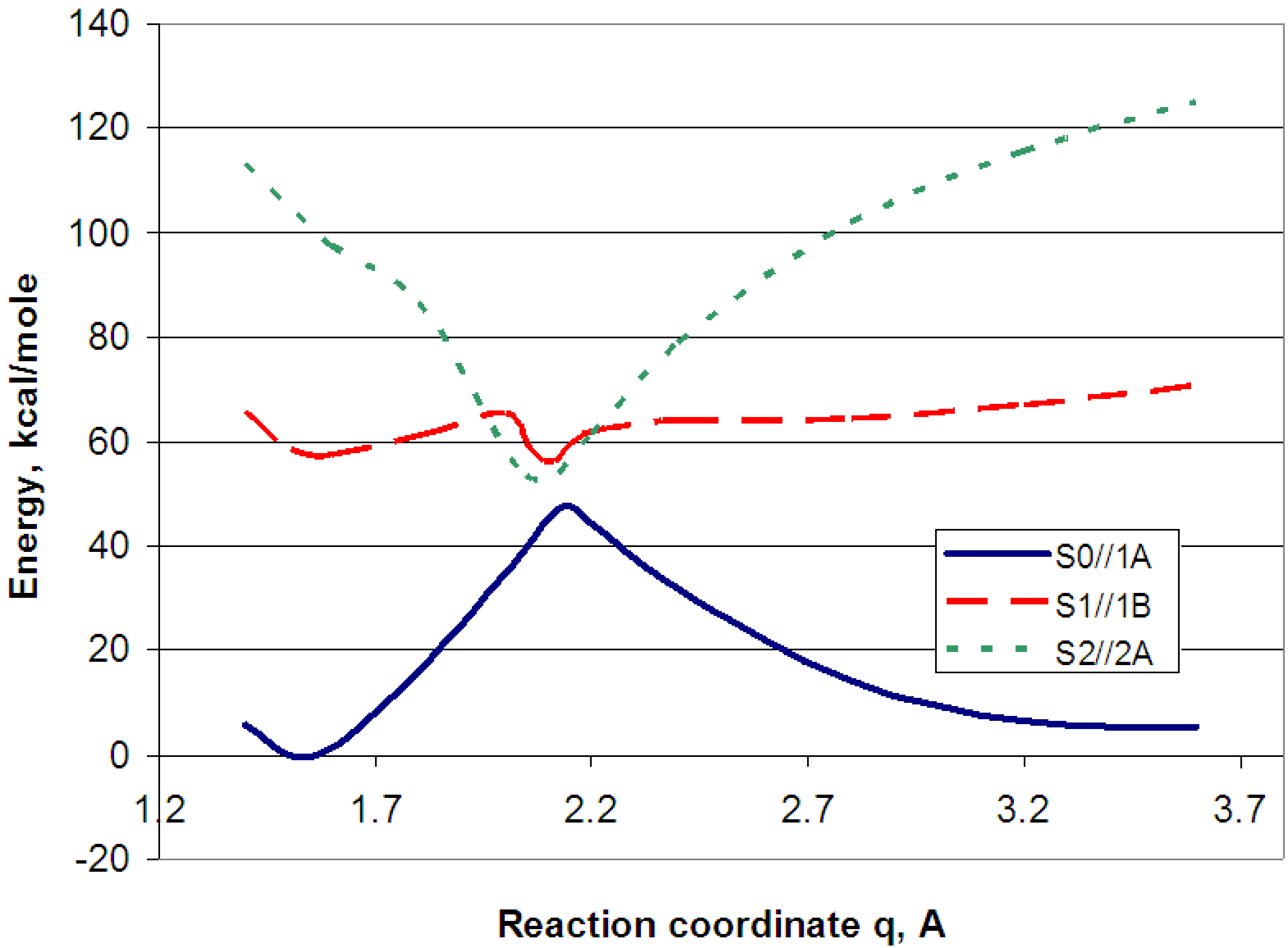


Mikhailov, Belfield, Masunov, *J Phys Chem* A, 113(25), 7080(2009)

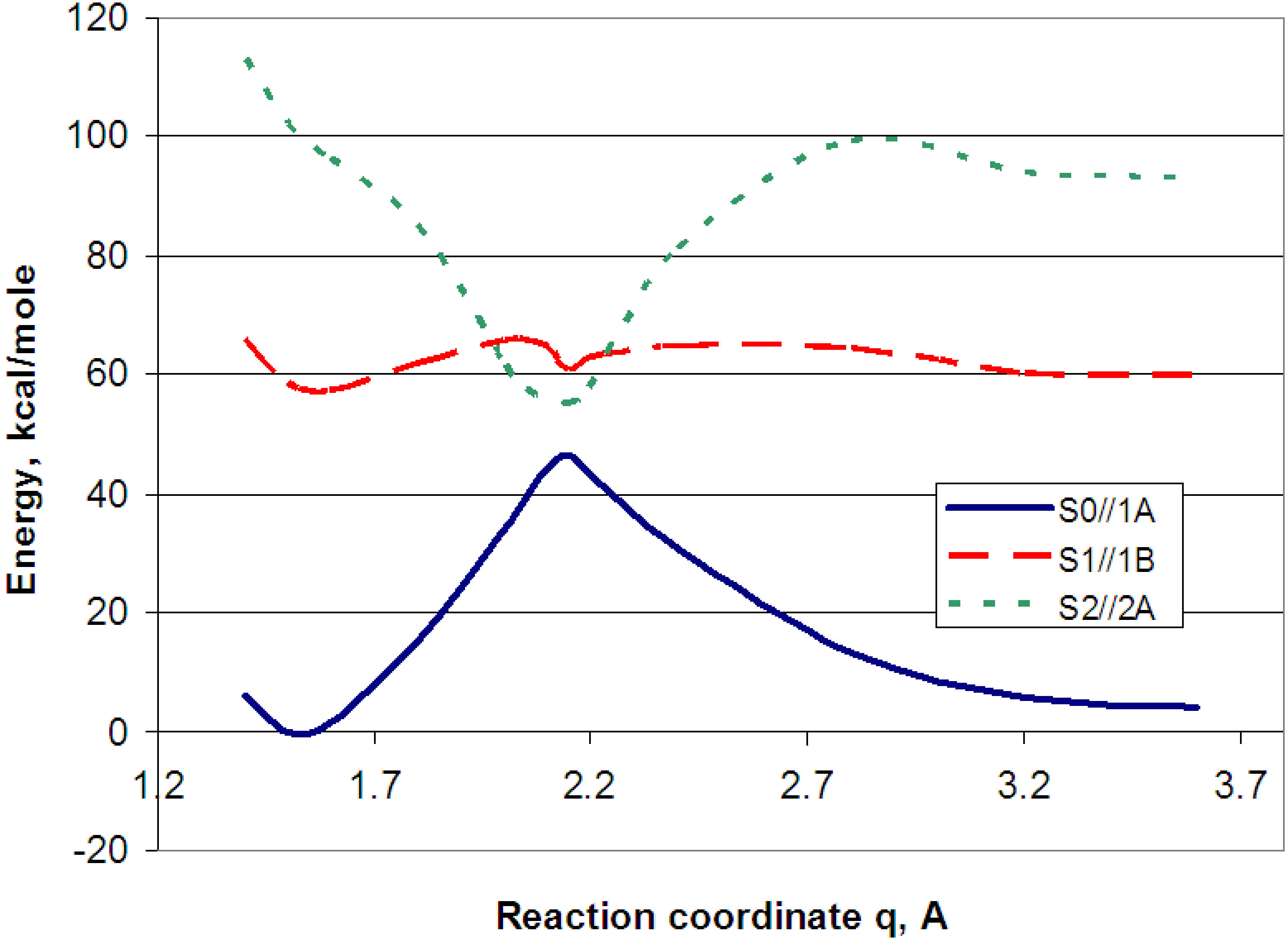
ORBITAL ENERGIES INDICATE THE FIRST EXCITED STATE TO BE PHOTOREACTIVE



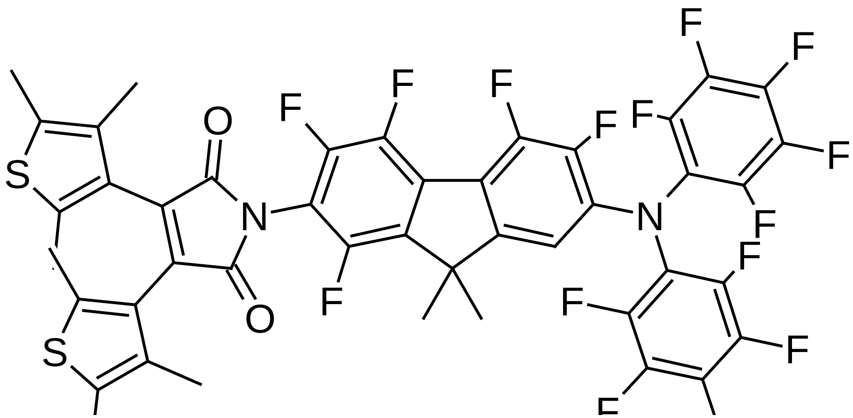
PES AT rTD-uM05-2X/6-31G* LEVEL AFTER FLUORINATION

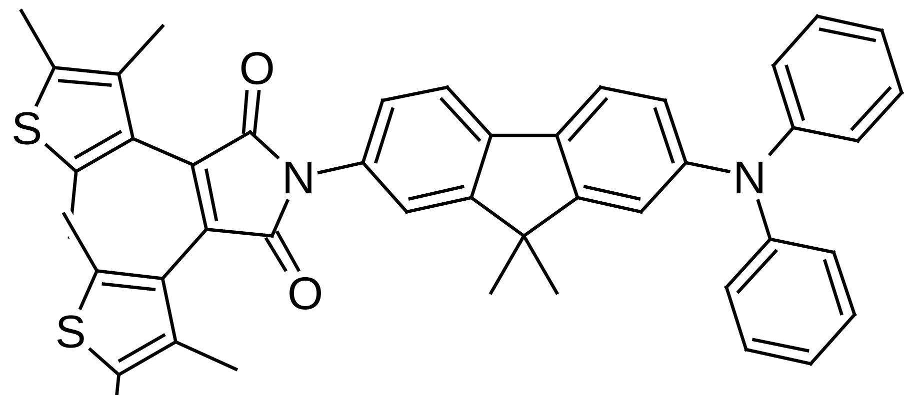


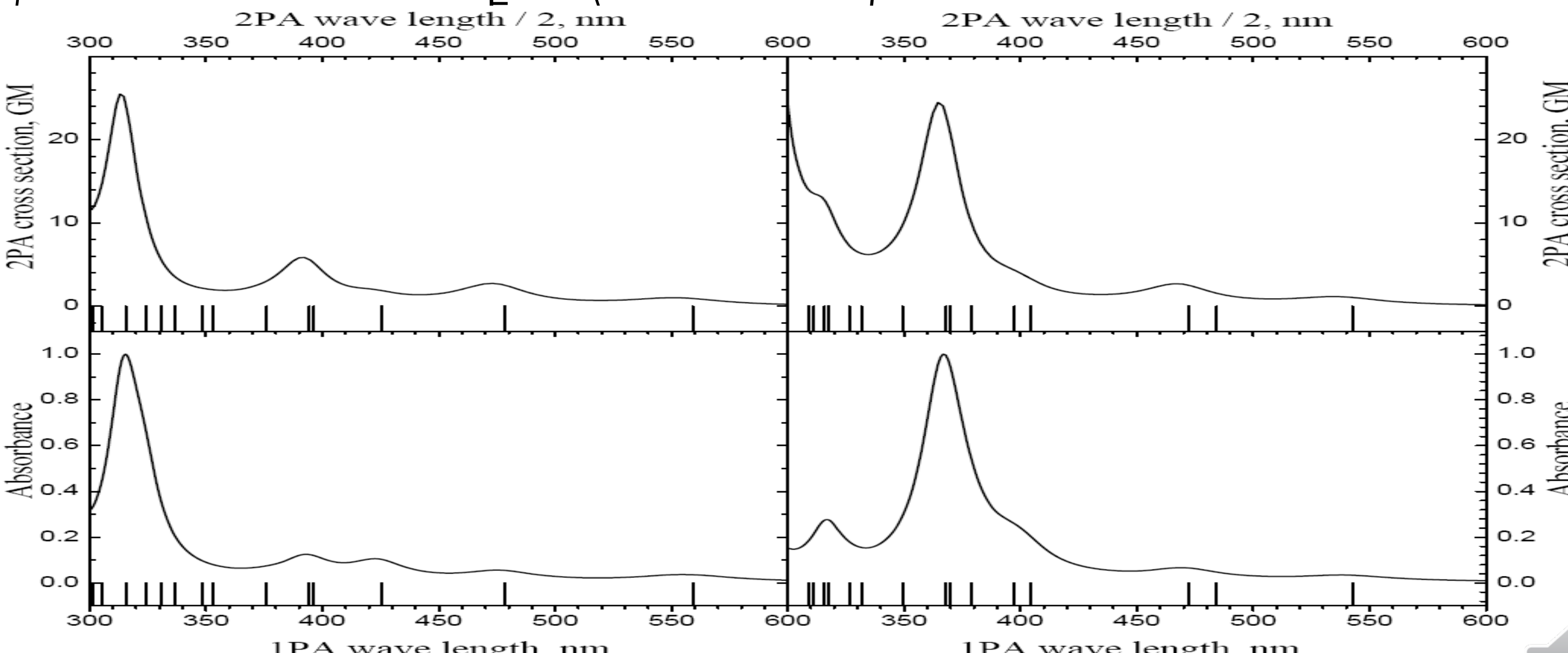
PES at rTD-uM05-2X/6-31G* LEVEL BEFORE FLUORINATION



MODIFICATION DOES NOT AFFECT 2PA





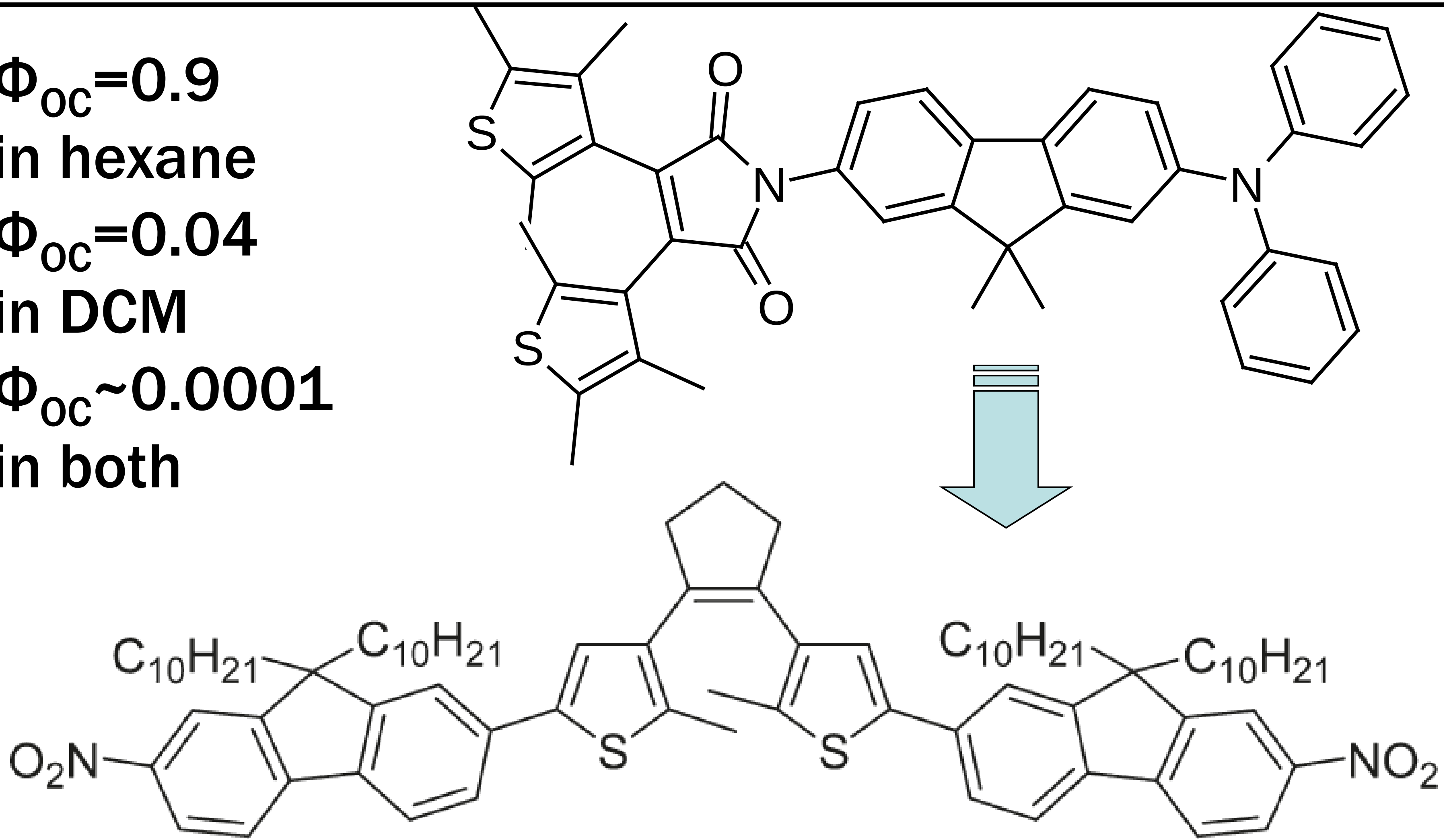


ANOTHER SOLUTION FOUND

Φ_{oc}=0.9 in hexane

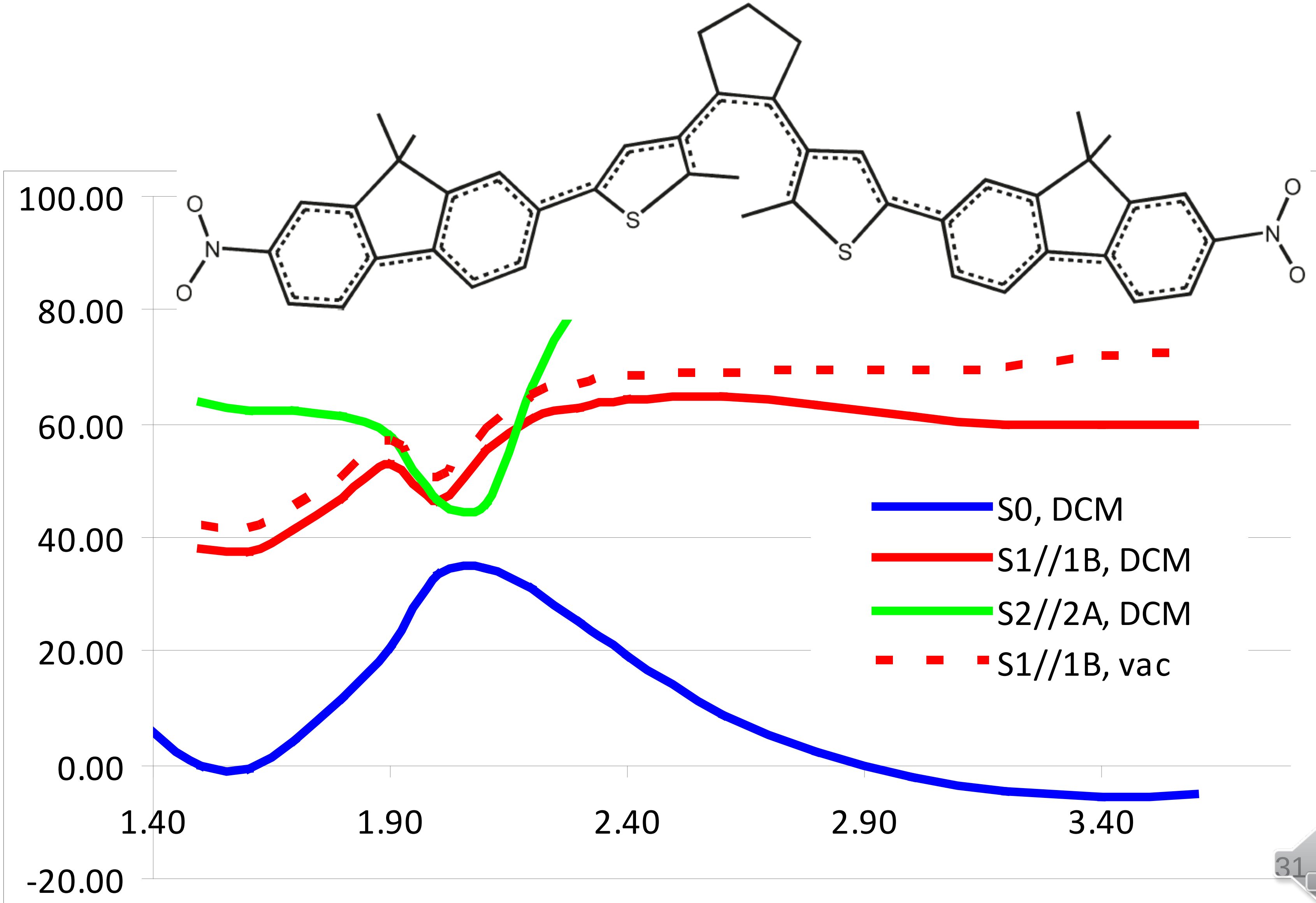
Φ_{oc}=0.04 in DCM

Φ_{oc}~0.0001 in both

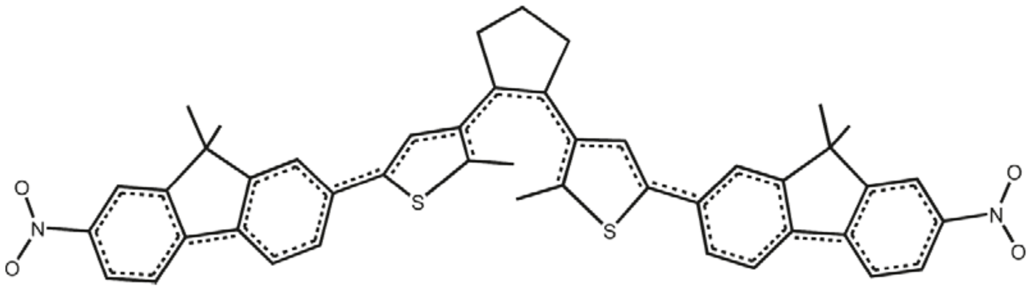


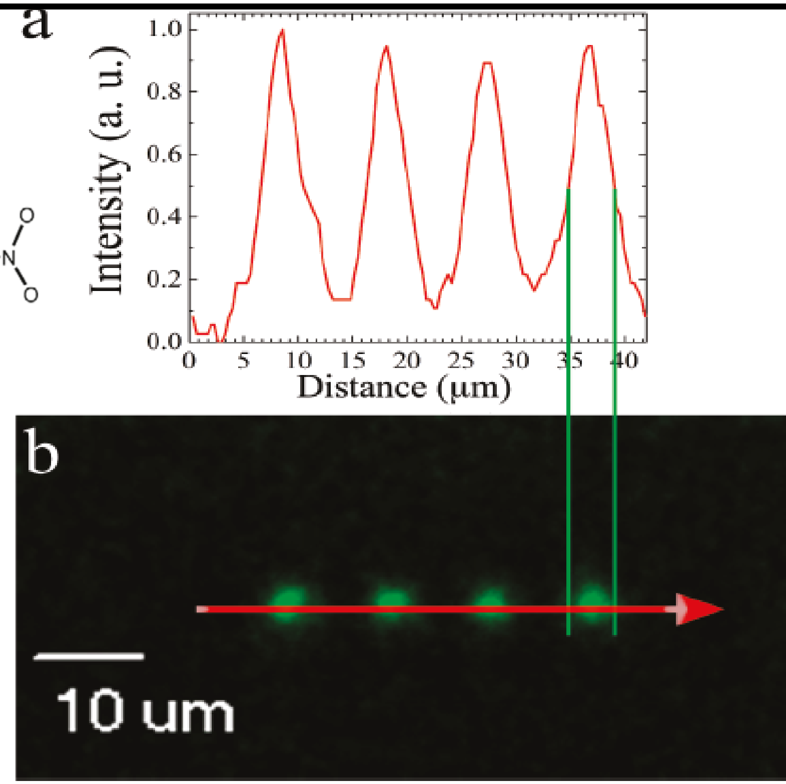
Luchita, Bondar, Yao, Mikhailov, Yanez, Przhonska, Masunov, Belfield, *ACS Appl. Mat. & Interfac.*, 3(9), 3559 (2011)

POTENTIAL SURFACE



2PA RECORDING DEMONSTRATED





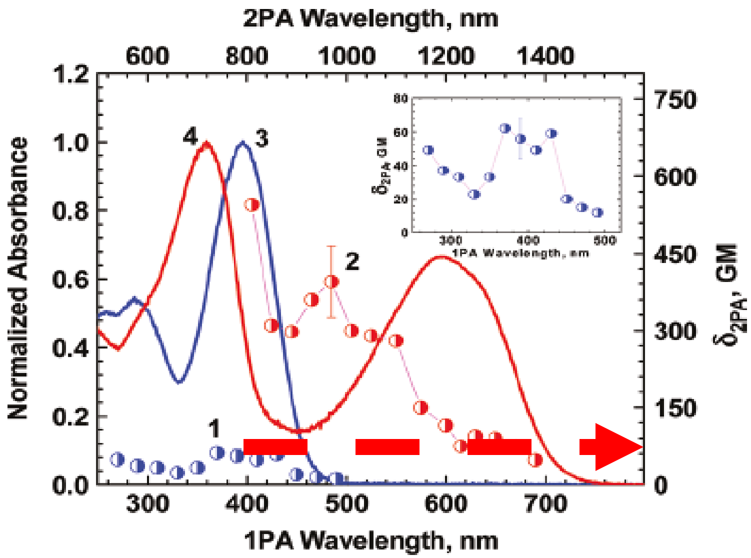


Figure 7. 2PA spectra of the OF (1) and CF (2) with corresponding linear one-photon absorption spectra of the OF (3) and CF (4) of 1 in DCM. The inset is a scaled 2PA contour of the OF (curve 1).

Figure 9. (a) Inverted signal intensity versus distance (μm) along (b) pixels traced by red arrow. Voxels recorded in photoreactive material consisting (b) of 1 and Rhodamine 6G in PMMA. Two-photon recording by inducing conversion OF to CF. Fluorescence of Rhodamine 6G was interrogated for two-photon fluorescence readout. After channel inversion, green pixels show the area within the material where fluorescence intensity was a minimum.

Luchita, Bondar, Yao, Mikhailov, Yanez, Przhonska, Masunov, Belfield, *ACS Appl. Mat. & Interfac.*, 3(9), 3559 (2011)

CONCLUSIONS

- Unrestricted DFT appears to be necessary to build smoothe surfaces of both ground and excited states
- Approximate second-order TD-DFT method allows for both quantitative prediction and qualitative understanding of 2PA spectra and photoreactivity
- Failure of the prototype 2PA photoswitch was explaind based om PES and orbital topology; simple chemical modification was suggested to correct it
- New 2PA photoswitch based A-π-A design was found to be sensitive to solvent polarity

Thank you