

Photophysics of Multi- chromophoric Systems: Small Oligomers and Polymers in Solution and Film

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Outline

- Introduction
- Experimental
- Structures of the Arrays
- Polymer Photo-physics
- Conclusion



Introduction

- We desire to make devices and materials.
- We need to move charge or energy long distances.
- How do we correlate solution phase data with solid state results? How do you move from molecular studies to material sciences?
- Can we determine principles of molecular design?
- Can we correlate the photo-physics with the solid state materials properties?

(Photophysical) Experimental Techniques



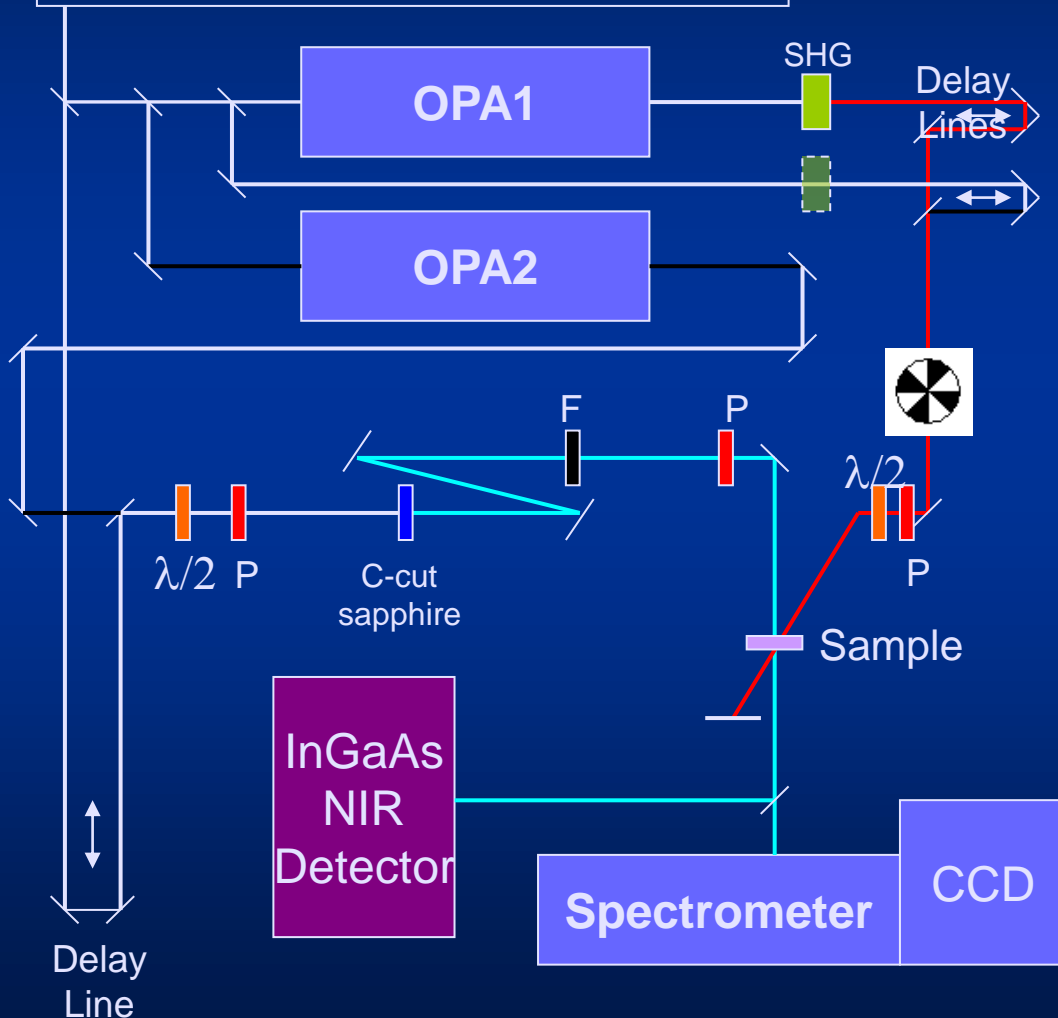
- Steady state measurements
 - UV-VIS
 - Fluorescence
- Time resolved measurements
 - Fluorescence (35 ps- seconds)
 - **Femtosecond transient absorption (300 fs- 6 ns)**
 - Nanosecond transient absorption (10 ns- μ s)

FS-TA



Ti:S Oscillator and Regen (CPA-2001)

$\lambda = 775 \text{ nm}$, 1kHz, ~800 mW



White light probe centered at $\lambda = 775 \text{ nm}$.

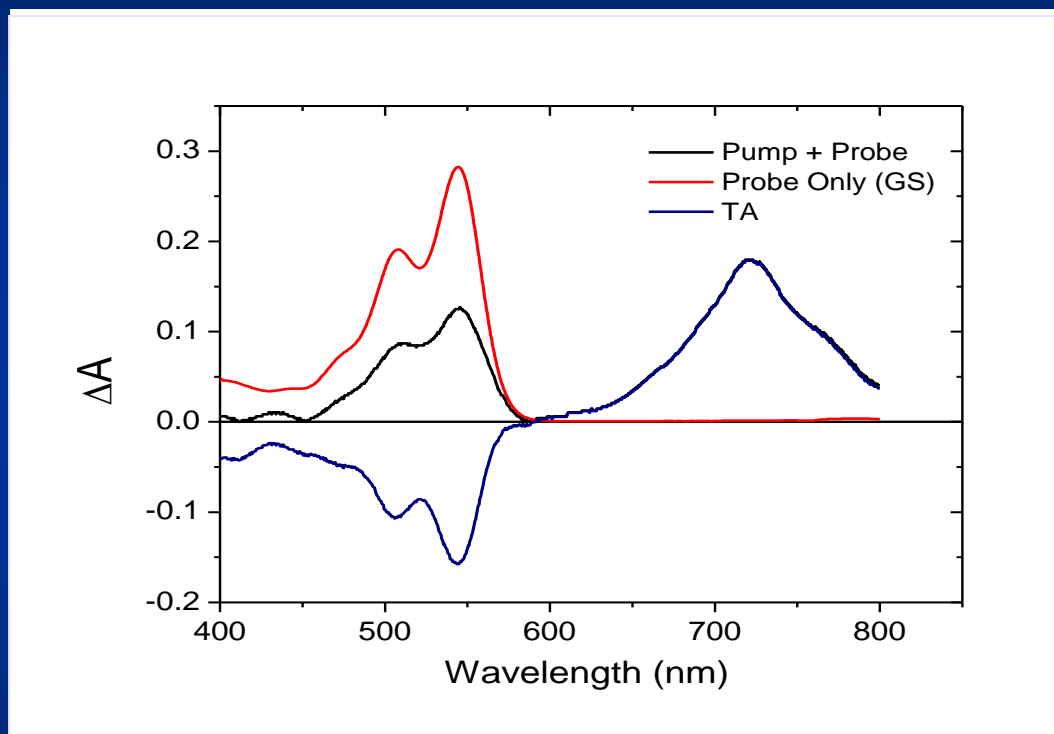
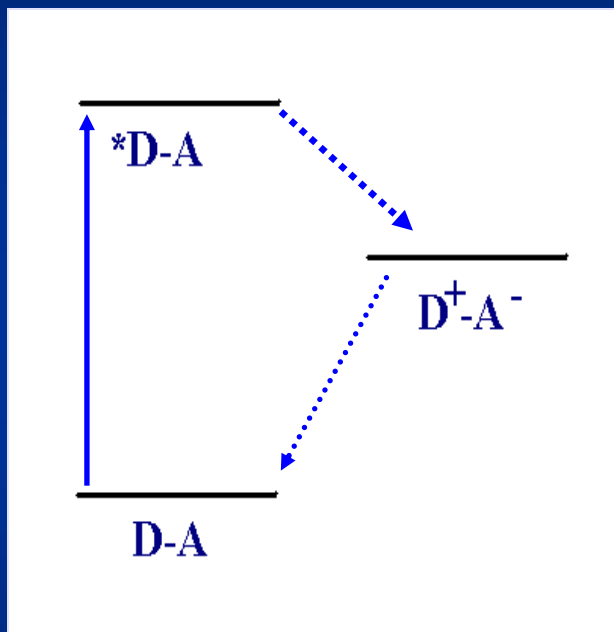
Visible excitation: OPA1 provides tunable light from ~550 to 710 nm; 775 nm or 338 nm pulses are available by bypassing the OPA

CCD camera provides 400-1100 nm detection capability

Redirection of probe to an InGaAs detector extends detection wavelengths through ~ 1800 nm.



Transient Absorption



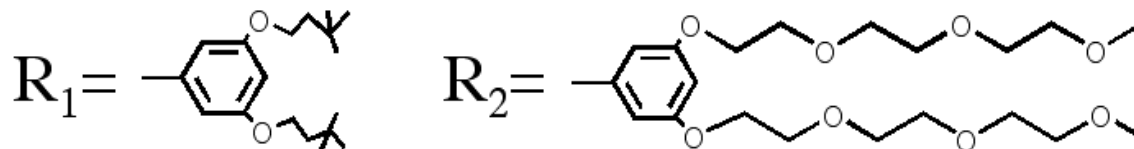


Porphyrin Oligomers

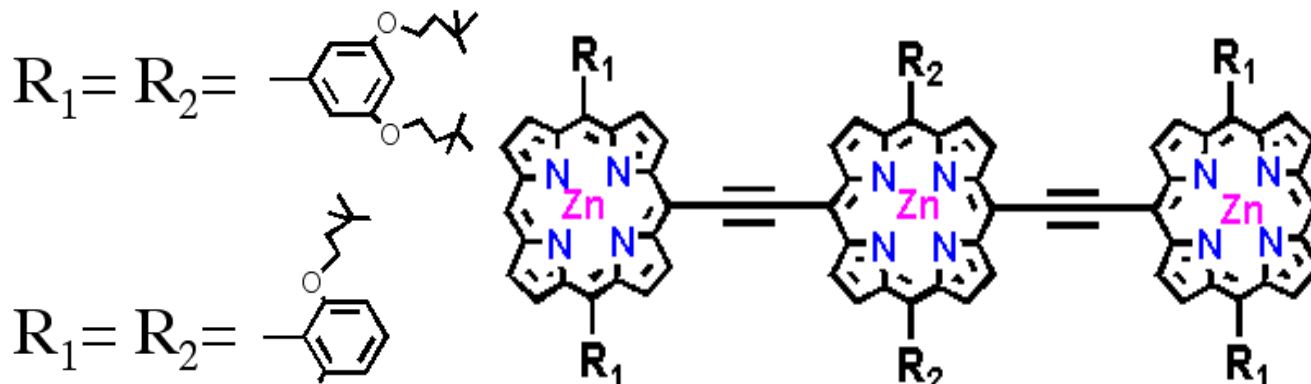


Different Substituents

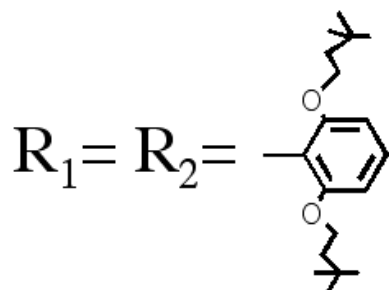
DDD



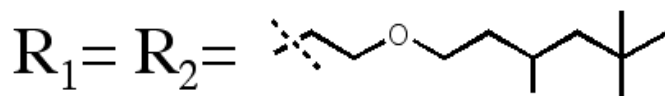
3,5



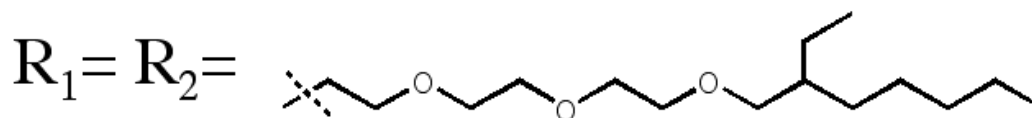
2,6



O1



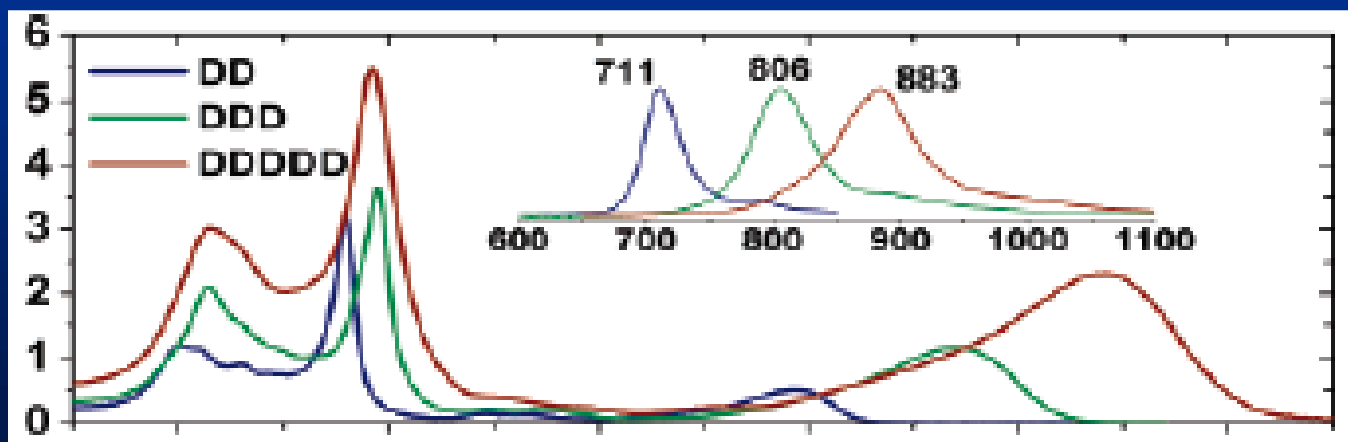
O3



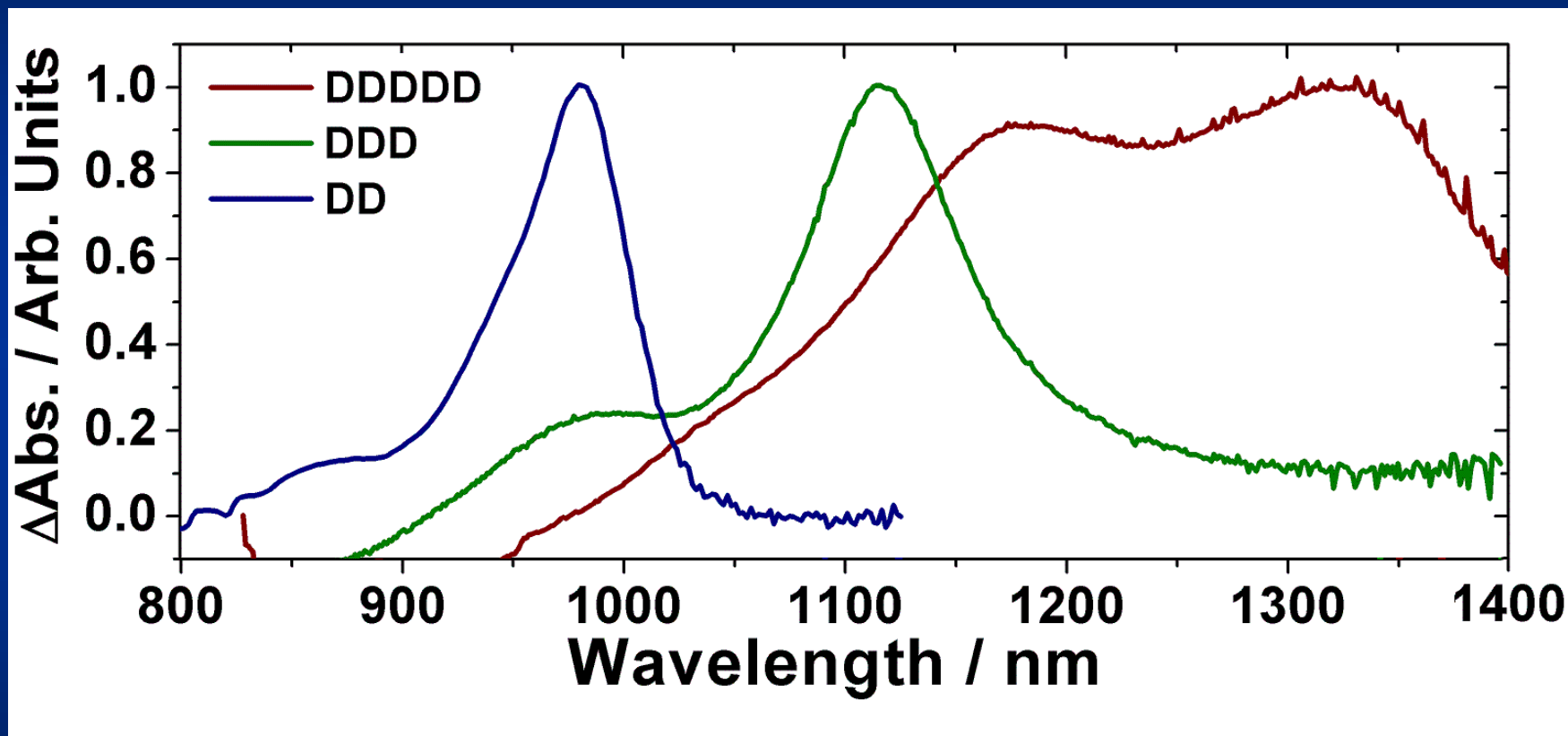


The “DD” Series

	λ_{\max} ($S_0 \rightarrow S_1$) [nm] ^a	ϵ_g @ λ_{\max} ($S_0 \rightarrow$ S_1) [M ⁻¹ cm ⁻¹]	λ_{\max} ($S_1 \rightarrow S_0$) [nm] ^a	Φ_f ^b	λ_{\max} ($S_1 \rightarrow S_n$) [nm] ^{a,c}	τ_F ^d (τ_o) ^e [ns]
DD	695 (1085)	51400	711 (810)	0.16 (0.03)	980 (656)	1.09 (17.6)
DDD	770 (1380)	116000	806 (875)	0.22 (0.03)	1120 (750)	1.13 (7.32)
DDDDD	842 (1563)	230000	883 (955)	0.14 (0.01)	1325 (1980)	0.45 (3.56)

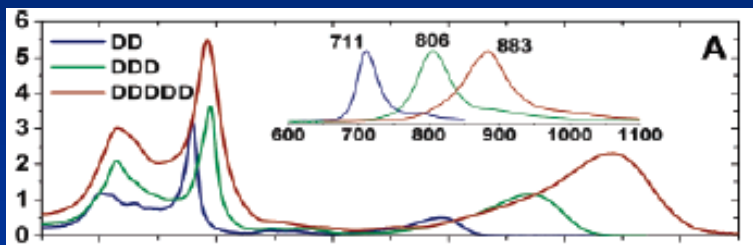


NIR Band- Marker for structural inhomogeneity in the excited state?



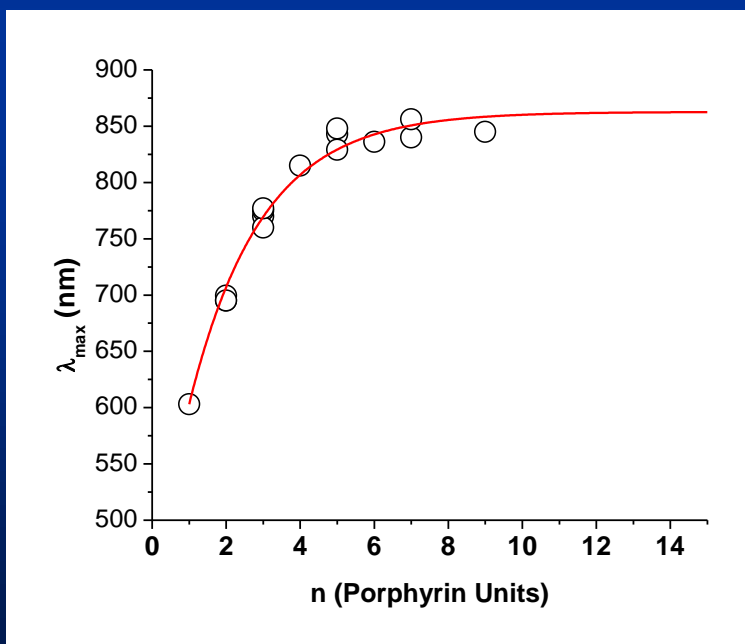
Exceptional Near-Infrared Fluorescence Quantum Yields and Excited-State Absorptivity of Highly Conjugated Porphyrin Arrays, Duncan, Susumu, Sinks, and Therien, *JACS*, ASAP

Tuning the Bandwidth- Adding Porphyrin Units



Using the method of Meier et al., the λ_{\max} vs. n was fit with:

$$\lambda_i(n) = \lambda_{i,\infty} - (\lambda_{i,\infty} - \lambda_{i,1})e^{-b_i(n-1)}$$



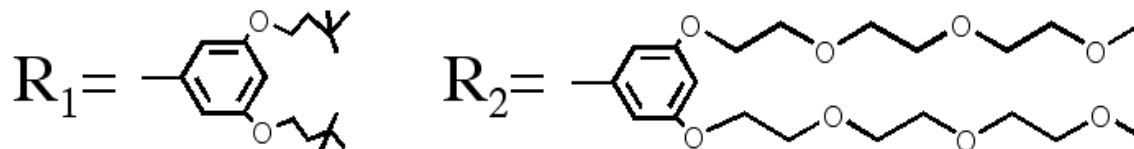
$$\lambda_{i,\infty} = 863 \text{ nm}$$

$$b = 0.5$$

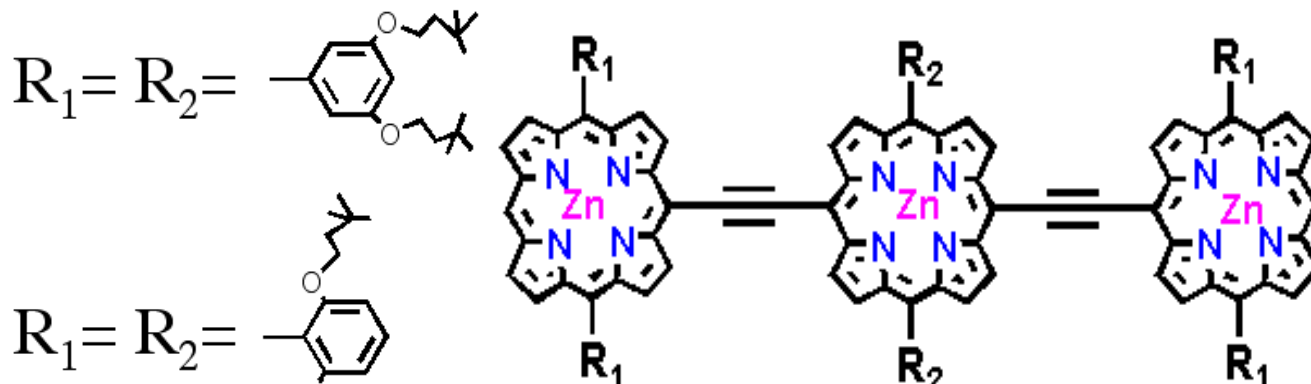


Different Substituents

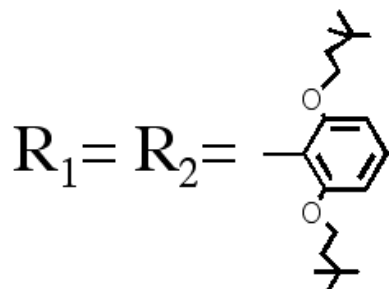
DDD



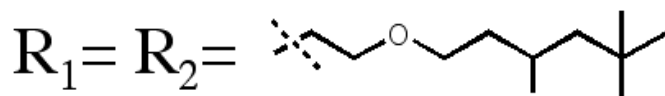
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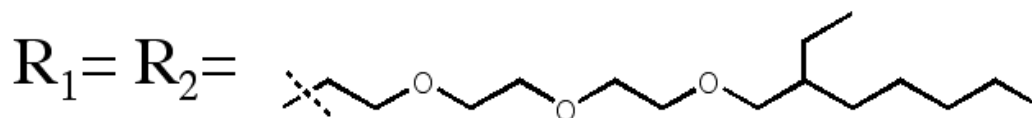
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O1

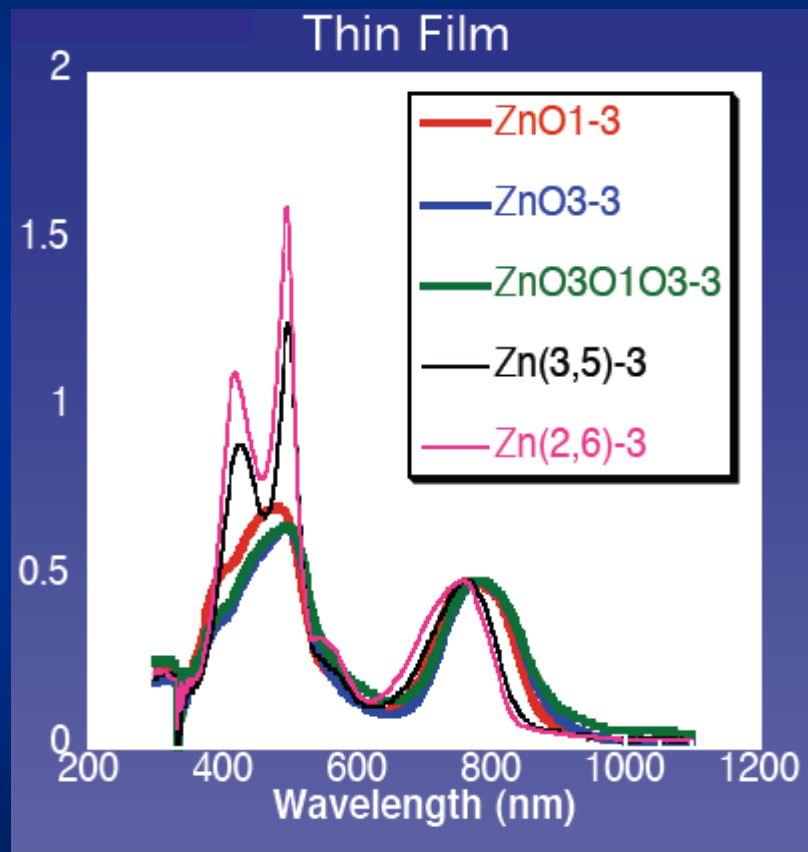
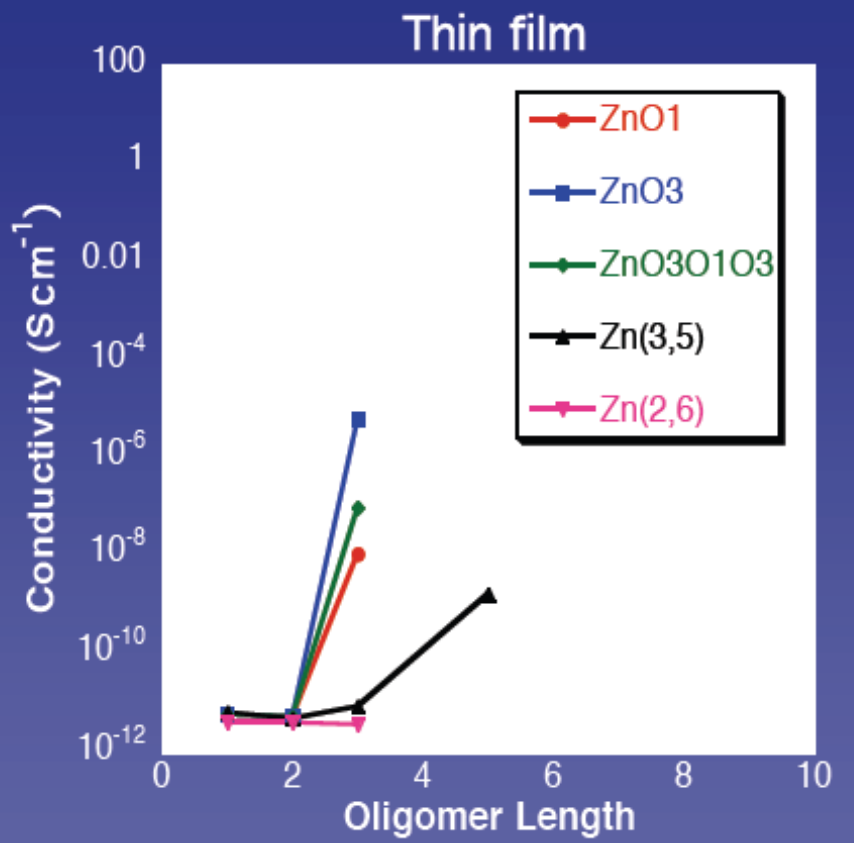


O3





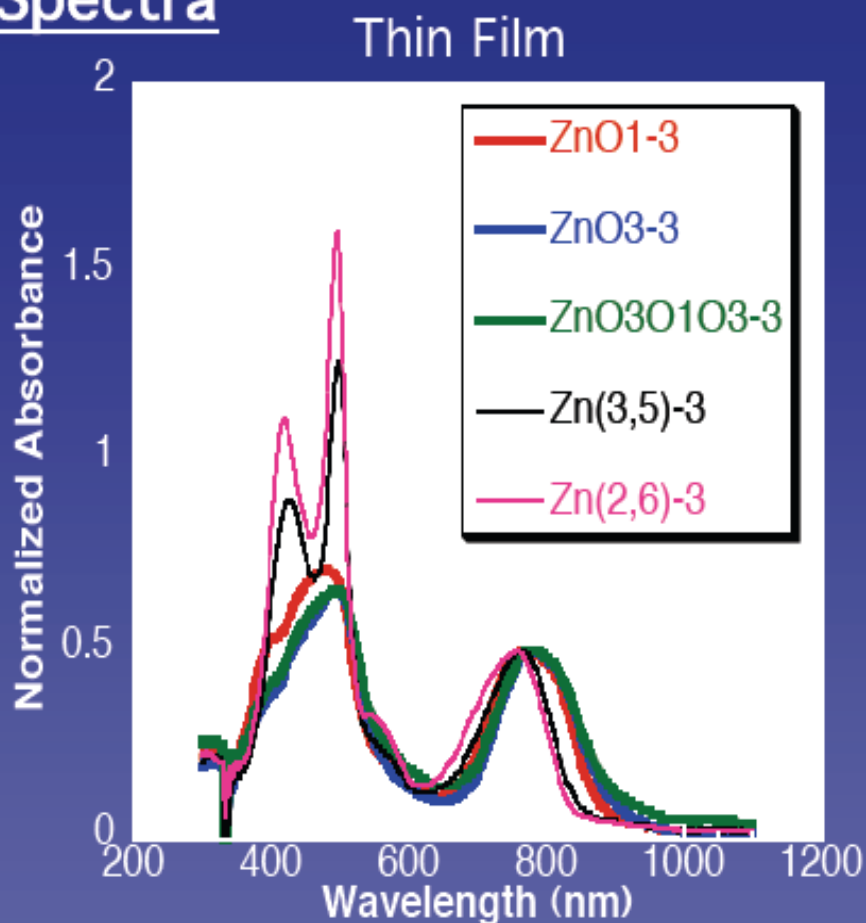
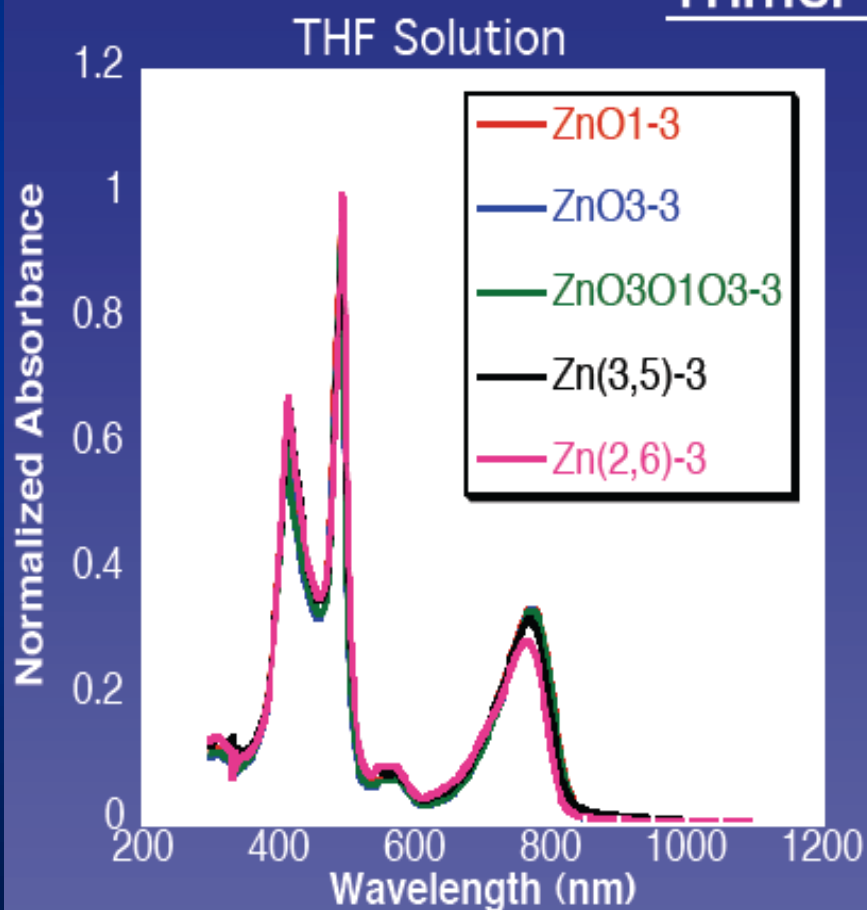
Large Impact in the Solid State!



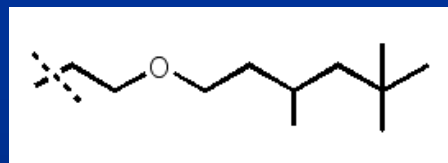


UV-Vis Spectra

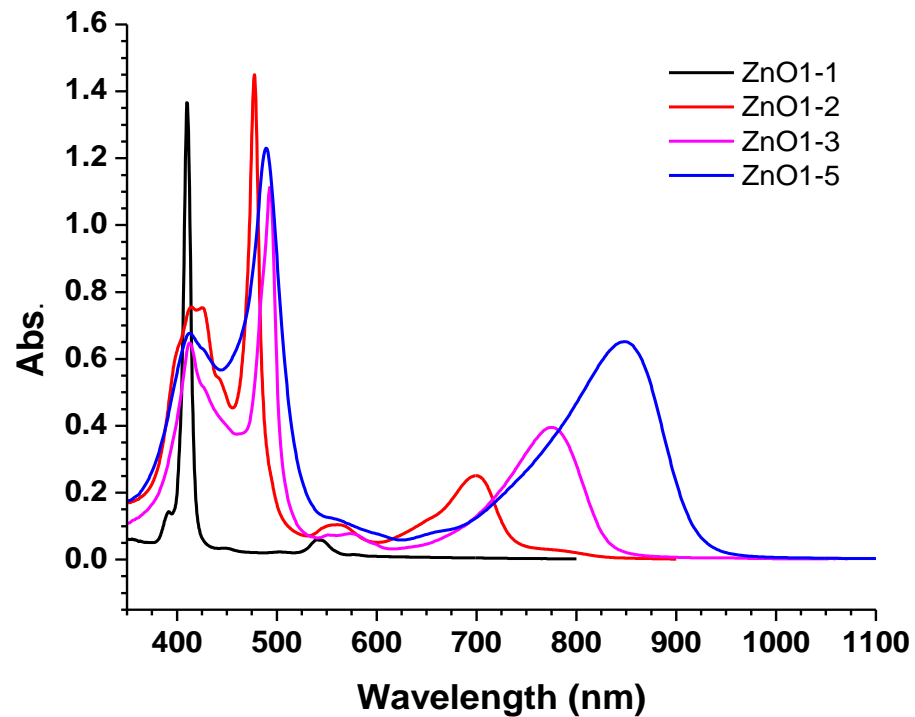
Trimer Spectra



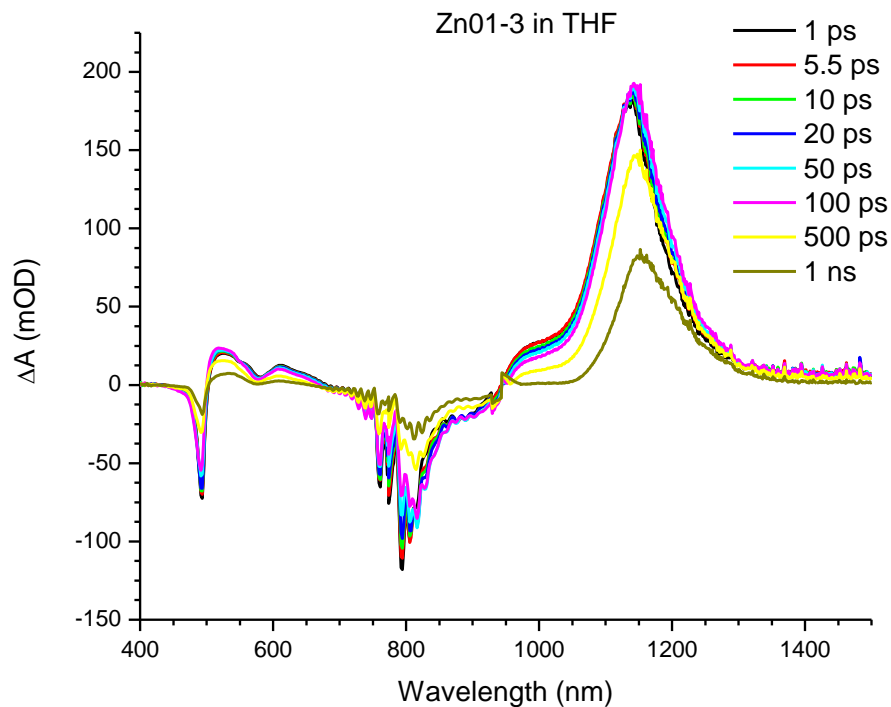
“O1” Series in Solution



Absorption Spectra



Transient Absorption of ZnO1-3 in THF

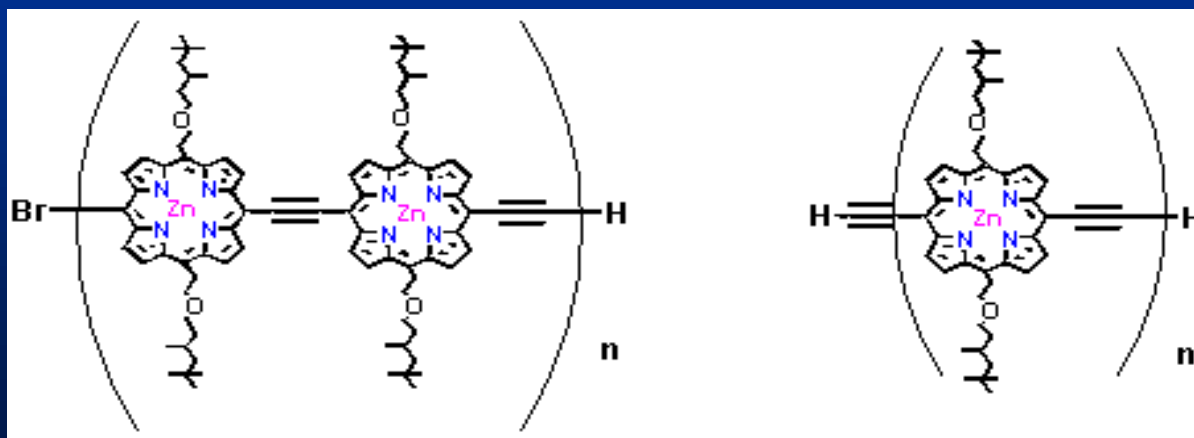


Global fitting indicates two main time constants: 63 ps and 800 ps. This is somewhat shorter than those reported for the DDD series, which found three time constants of 70 ps, 130 ps, and 1.24 ns



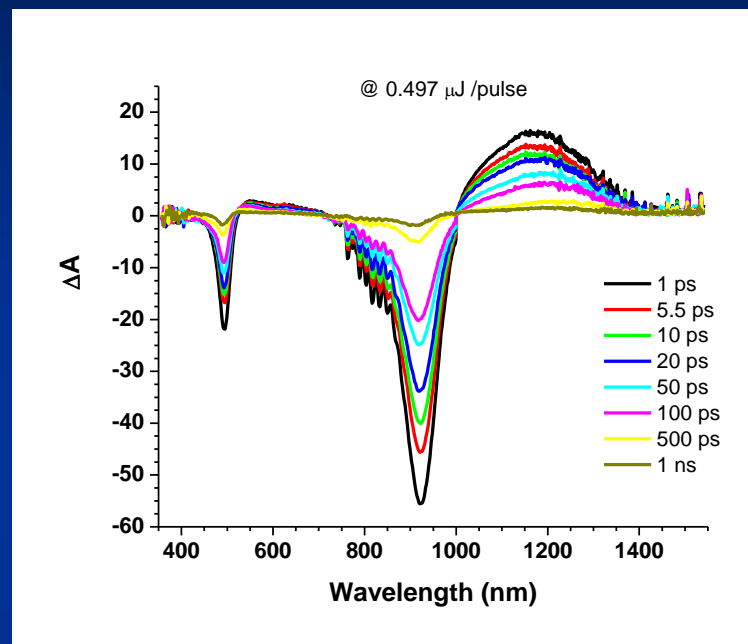
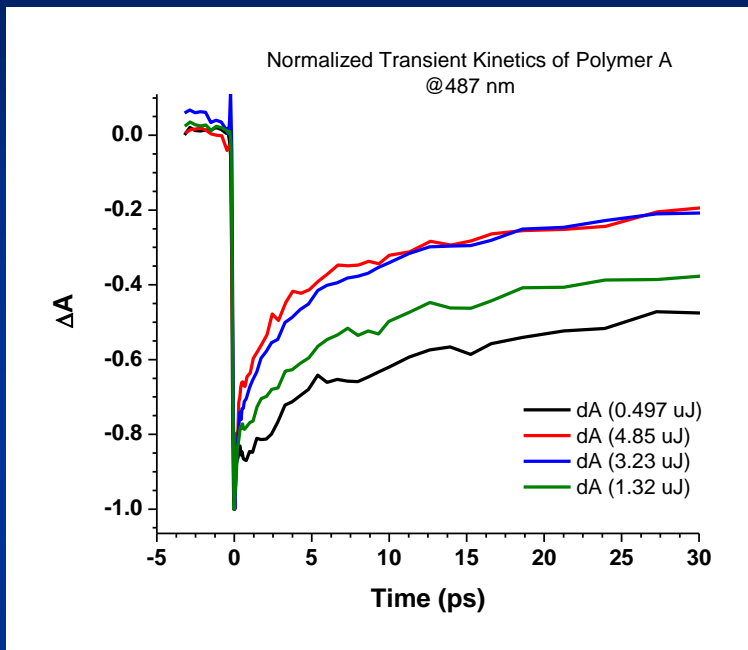
ZnO1-polymers

Batch	Cat.	λ_{\max} (nm)	Cond.
A	AsPh ₃	911	4
B	AsPh ₃	896	1
C	PPh ₃	876	2
D	P(Cyclo)	904	3
ZnO1-3		777	5





Polymer A

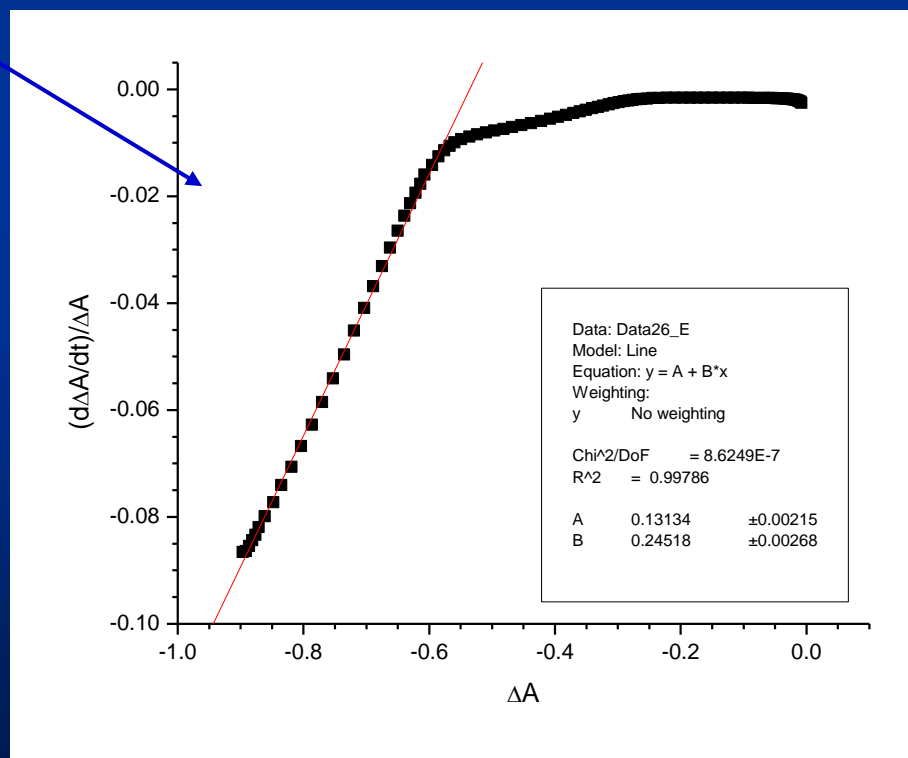
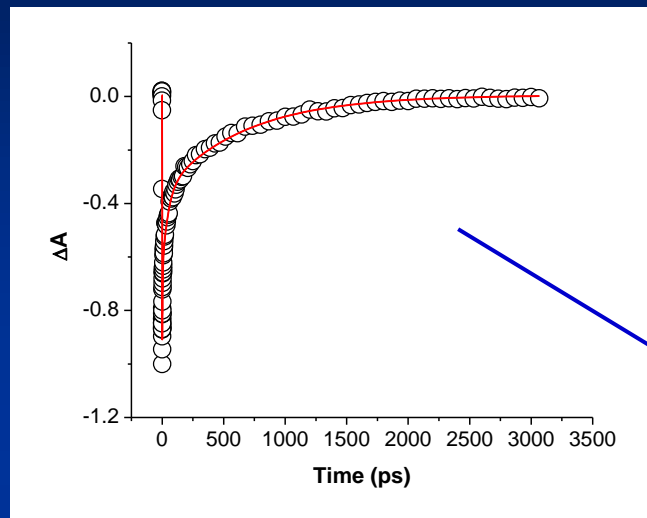


Global fit produces 2-3 time constants:

Low power: 6.9 ps, 203 ps, and very long lived component



Second Order Kinetics



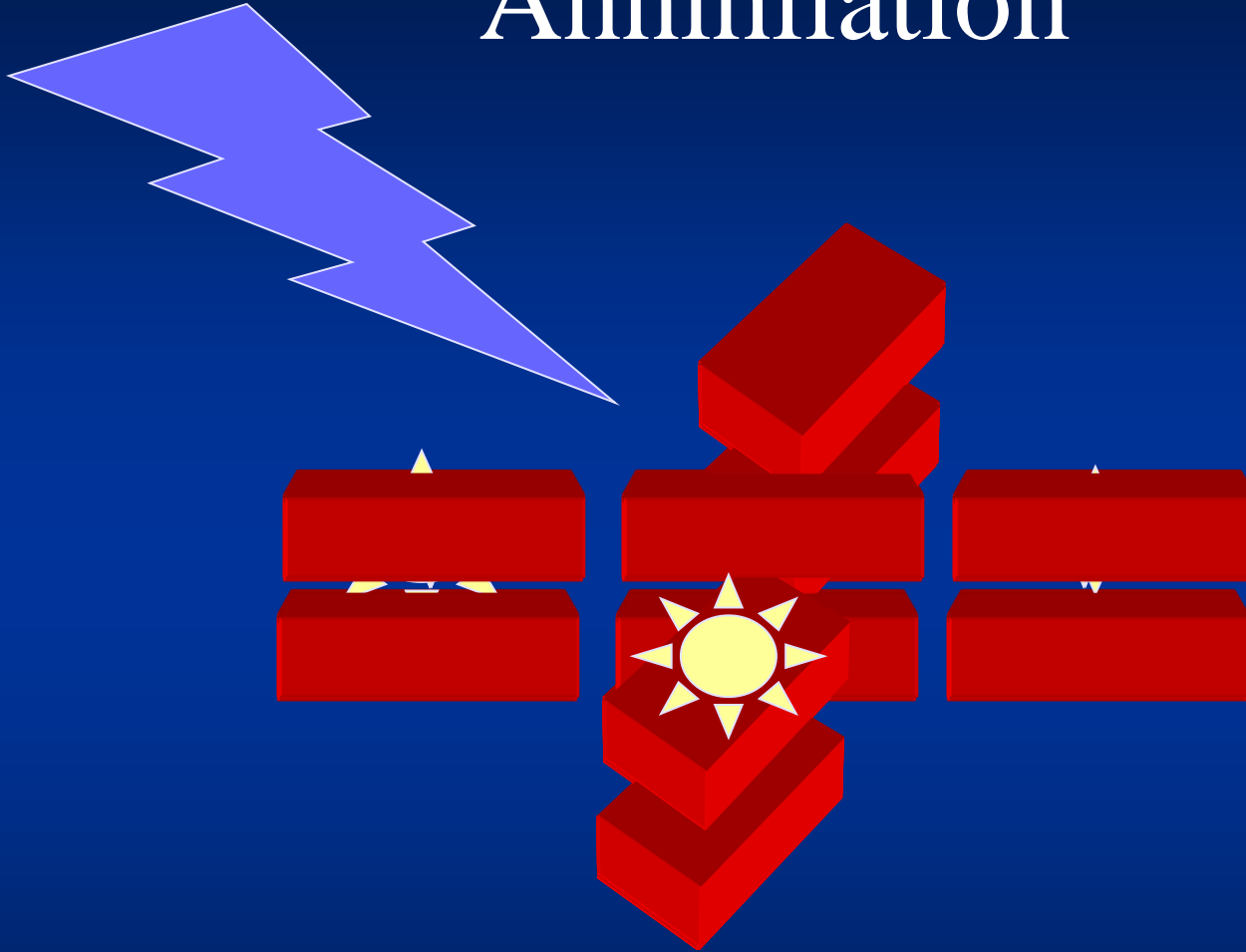
Singlet-Singlet Annihilation (or fusion)



- When an assembly of chromophores are photo-excited by a laser, numerous chromophores in the assembly may be excited.
- If the chromophores are in good communication, the excitons can migrate to each other and interact. $*S + *S \rightarrow S + **S$
- This higher excited singlet state (**S) generally quickly dumps energy to re-form the first excited singlet state.
- The net result is the destruction of one exciton and the preservation of one exciton



Annihilation





Annihilation

- Annihilation is well known in the literature.
- First seen in PS
- Bimolecular process- second order kinetics
- Should be power dependent
- Can, in theory, back out the number of chromophores involved
- Indication of good electronic coupling



Annihilation Analysis

Assume a simple kinetic model where the annihilation rate is *time independent* (γ_2) and defined as a pseudo-first order rate (rate per pair of excitons) per Paillotin et al.*

$$\frac{dn}{dt} = \gamma_1 n - \frac{1}{2} \gamma_2 n^2$$

* Paillotin et al., *Biophys. J.*, 25, 513-534



ZnO1-polymers

Batch	Cat.	λ_{\max} (nm)	cond	γ_1 ($\times 10^{12}$ 1/s)
A	AsPh3	911	4	211
B	AsPh3	896	1	11.3
C	PPh3	876	2	44.4
D	P(Cyclo)	904	3	93.1
ZnO1-3		777	5	N/A



Linear Chain Model

- $\tau_a = [N(N-1) * \tau_{hop}] / 6$
 - Where N = number of sites sampled, τ_a = annihilation time constant, and τ_{hop} is the exciton lifetime at each site
- Assuming no chain-chain interactions, which may not be correct.
- Let us assume that the hopping rate is the same in these systems (and it is 1 fs) and calculate a hypothetical “n”

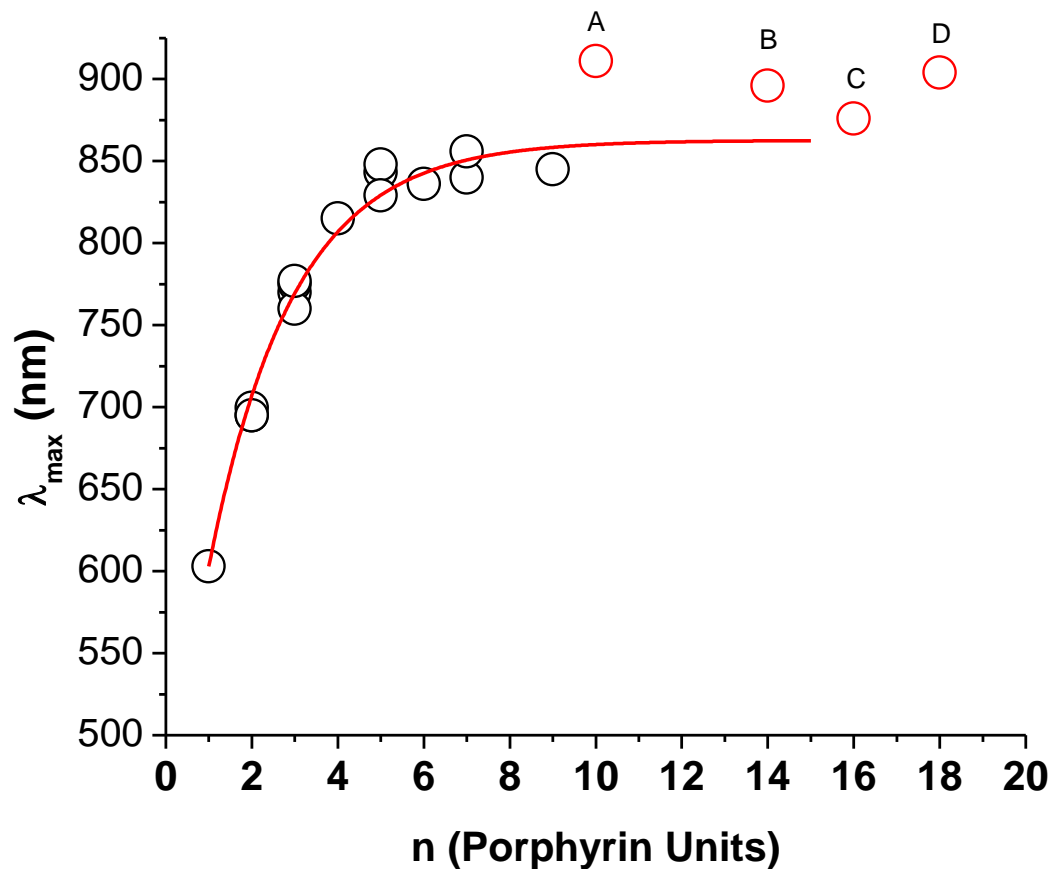


ZnO1-polymers

γ_1 ($\times 10^{12}$ 1/s)	n	Batch	Cat.	λ_{\max} (nm)	cond
11.3	23	B	AsPh3	896	1
44.4	12	C	PPh3	876	2
93.1	8	D	P(Cyclo)	904	3
211	6	A	AsPh3	911	4

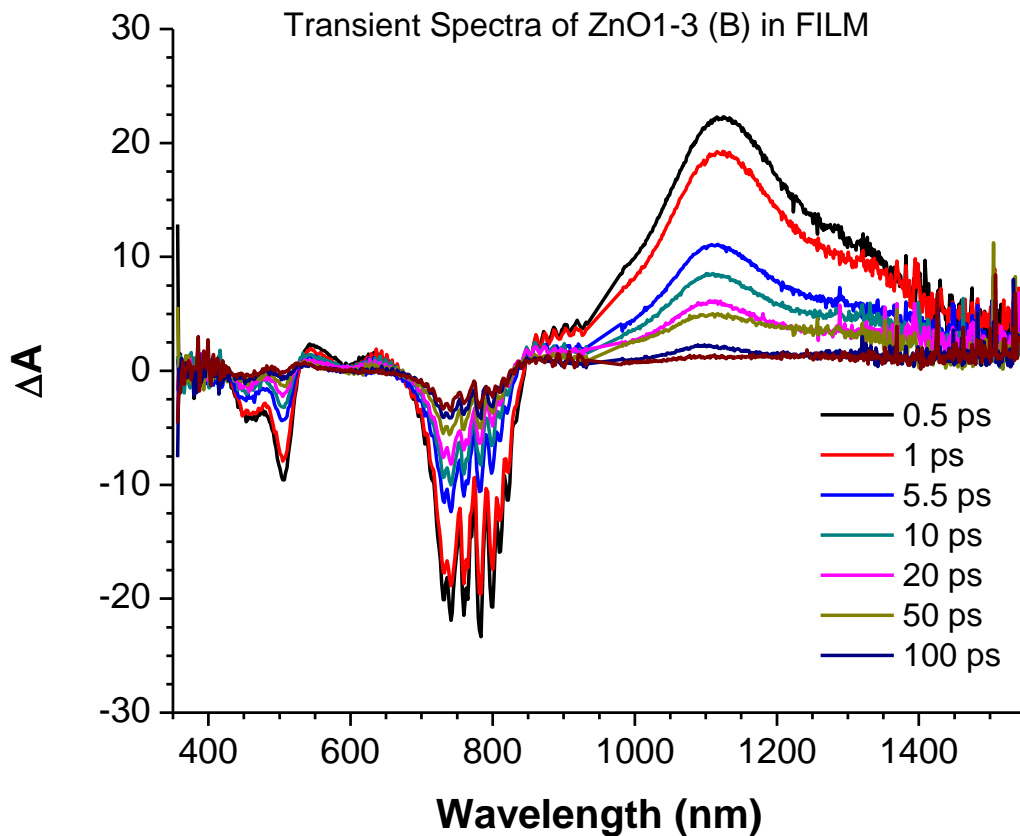
Note: if we assume the hopping rate is the same for all the polymers, then a larger annihilation rate means a shorter chain (with a linear chain model).

Why Chain-Chain Interactions?





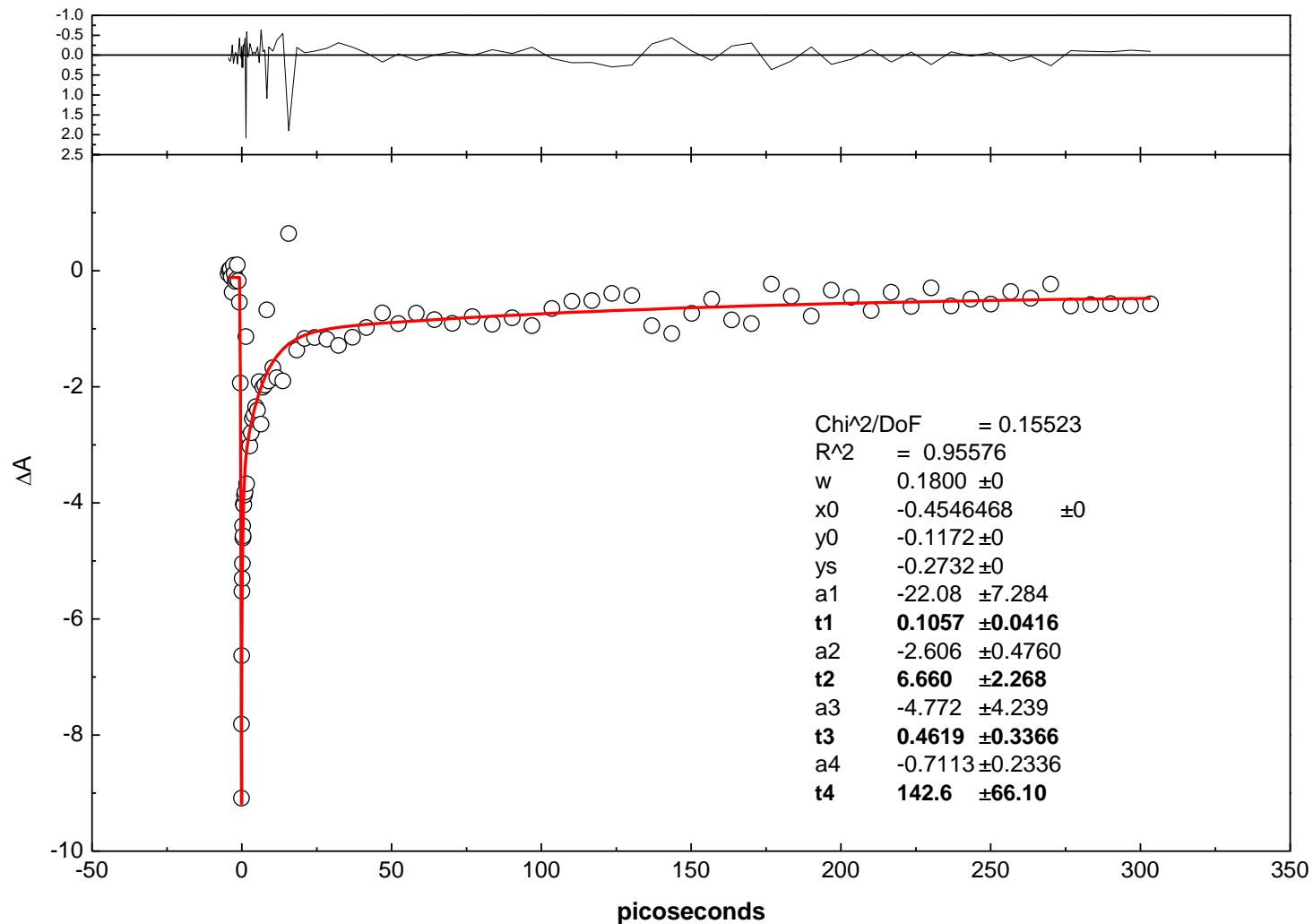
Thin Films



Rapid
deactivation of
the excited state
(non-linear with
power). Subtle
dynamic
differences
between films,
but the spectra
show differences
base on sol.
group



Transient Kinetics of ZnO1-3 (B) in FILM @ 458.9 nm





Conclusions

- Annihilation data correlates very well with preliminary conductivity data.
 - Does this mean that intrachain communication is key?
 - Or is this another indication that some polymers form aggregates (and interchain communication is important?)
- More structural information is needed to correlate with the photo-physical data
 - Is our n vs. λ plot saturated at ~ 860 nm, or do we just need more data?
 - Do we have chain-chain interactions?
- Films show fast deactivation pathway
 - Is this annihilation or something else?
 - How do we test this?

Acknowledgements



**Prof. Michael Therien &
Prof. Robin Hochstrasser**

Wasielewski Group/
Northwestern University
Wenhao Liu

**Paul Frail
Timothy V. Duncan**

Dr. Michael Tauber
Randall Goldsmith

Prof. Paul J. Angiolillo
St. Joseph's University

Funding

NIH

NIH Ruth L.

Kirschstein NRSA Fellowship

