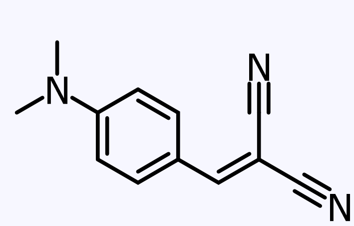
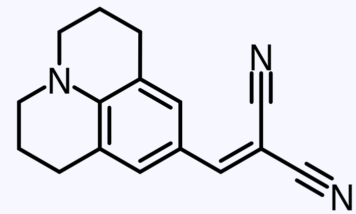
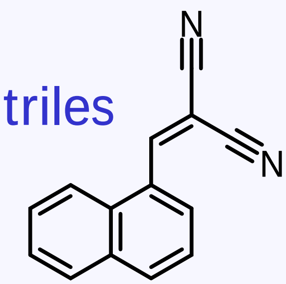
Push-Pull "Molecular Rotors" as Local Friction Probes

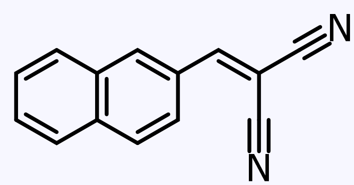
Probes We've Studied:

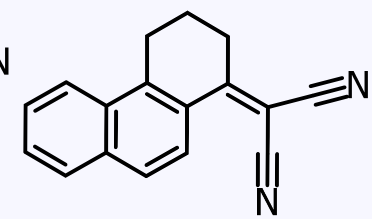
1. Benzylidene Malononitriles
2. Naphthylmethylene Malononitriles
3. CCVJ
4. Thioflavin T





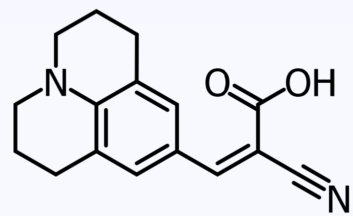


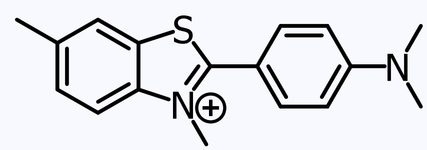




Our Interests:

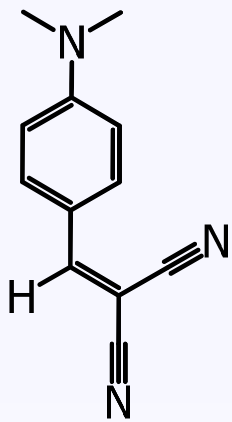
- ❑ Mechanism?
- ❑ What's Being Reported?
- ❑ Friction on Reaction?

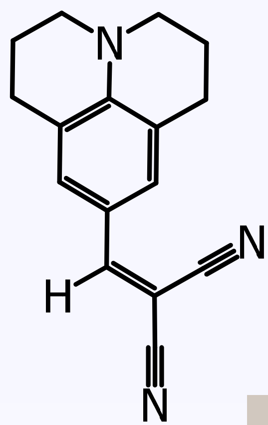




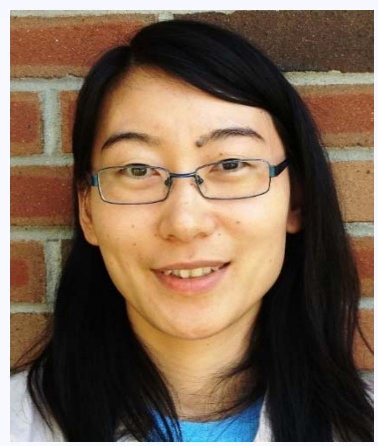
Hui Jin, Chet Swalina, Min Liang,
Chris Rumble, Jens Breffke, & Mark Maroncelli
Penn State

1: Benzylidene Malononitriles





Hui Jin

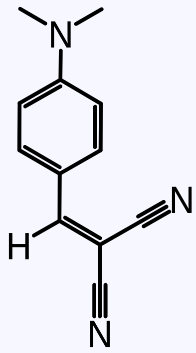


Min Liang

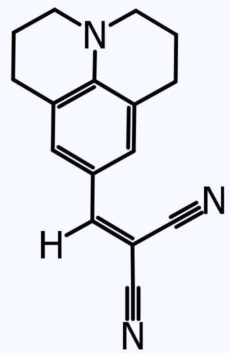
Chet Swalina

Some Background

DMN



JDMN

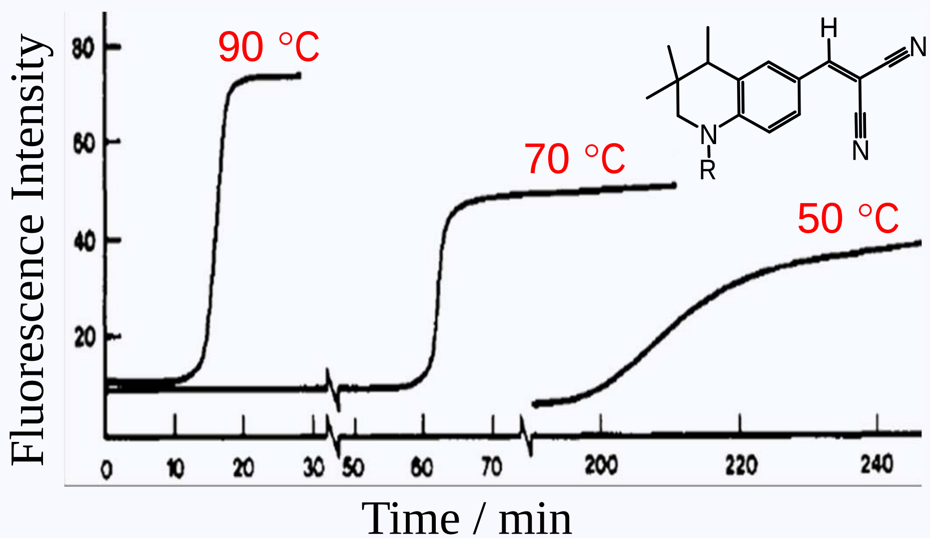


- CT character to $S_0 \rightarrow S_1$; large β

  μ_0~9 D, μ_1~18 D
- weakly fluorescent in most solvents

  φ_f ~10^{-3}-10^{-4}; τ_f ~1 ps
- $S_1 \rightarrow S_0$ sensitive to local fluidity or free volume of environment
- introduced in early 1980s by Loutfy and Law as environmental fluidity probe
- used to probe local fluidity in:
  - liquids
  - polymers
  - ionic liquids
  - host-guest assemblies
  - biological systems

Polymerization of MMA

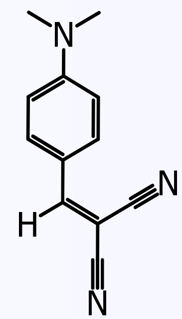


Loutfy, *Macromolecules* **14**, 270 (1981).

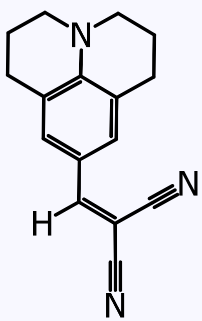
Spectra & Solvatochromism

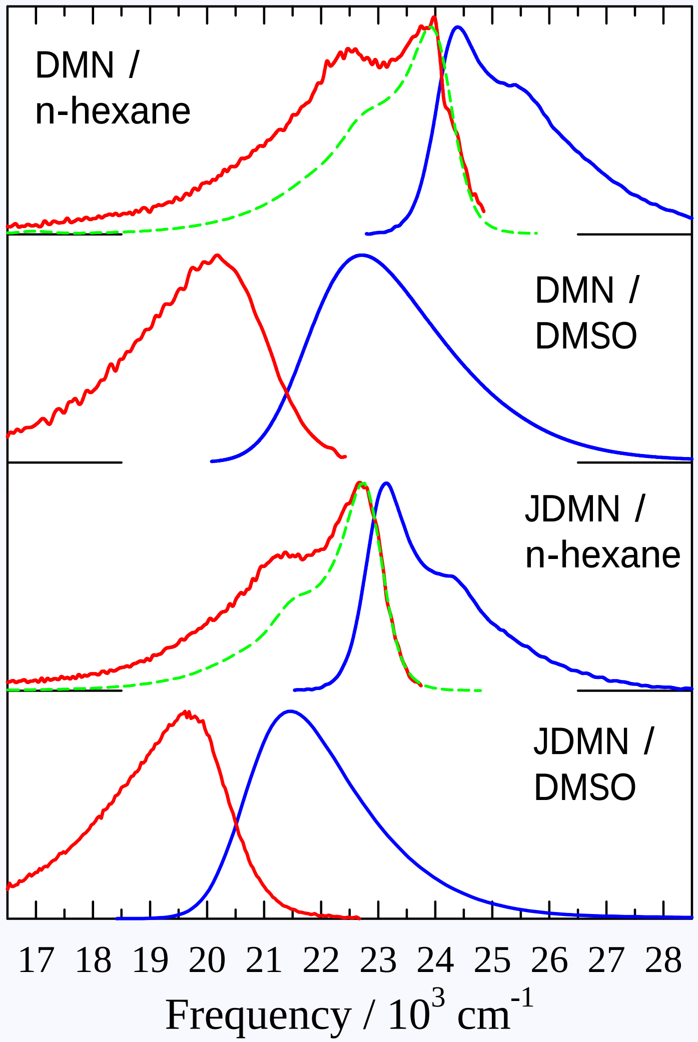
Representative Spectra

DMN



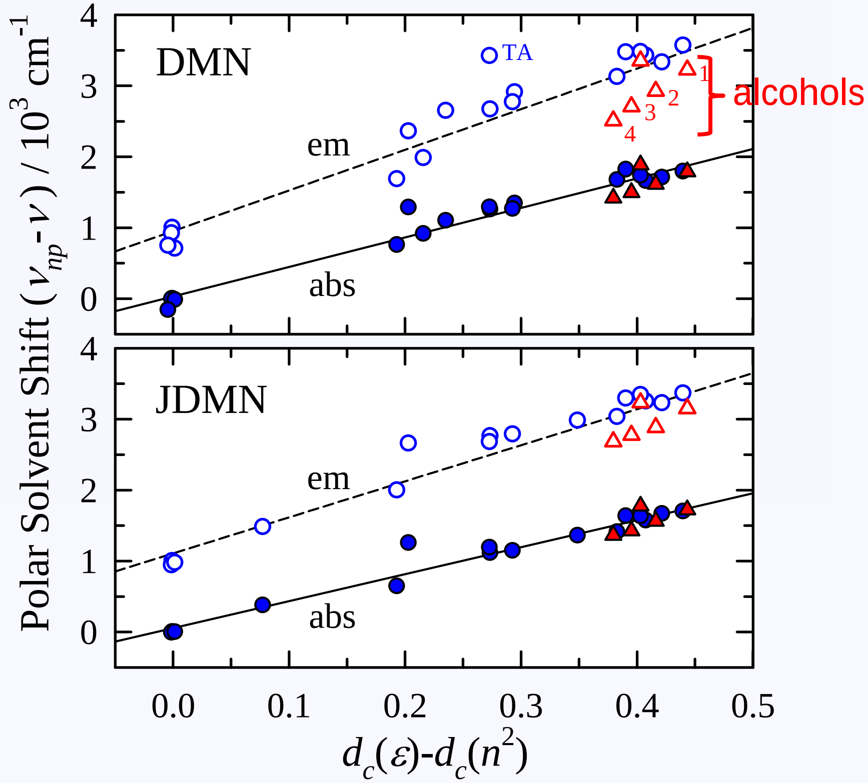
JDMN





Jin et al., *JPCB* **114**, 7565 (2010).

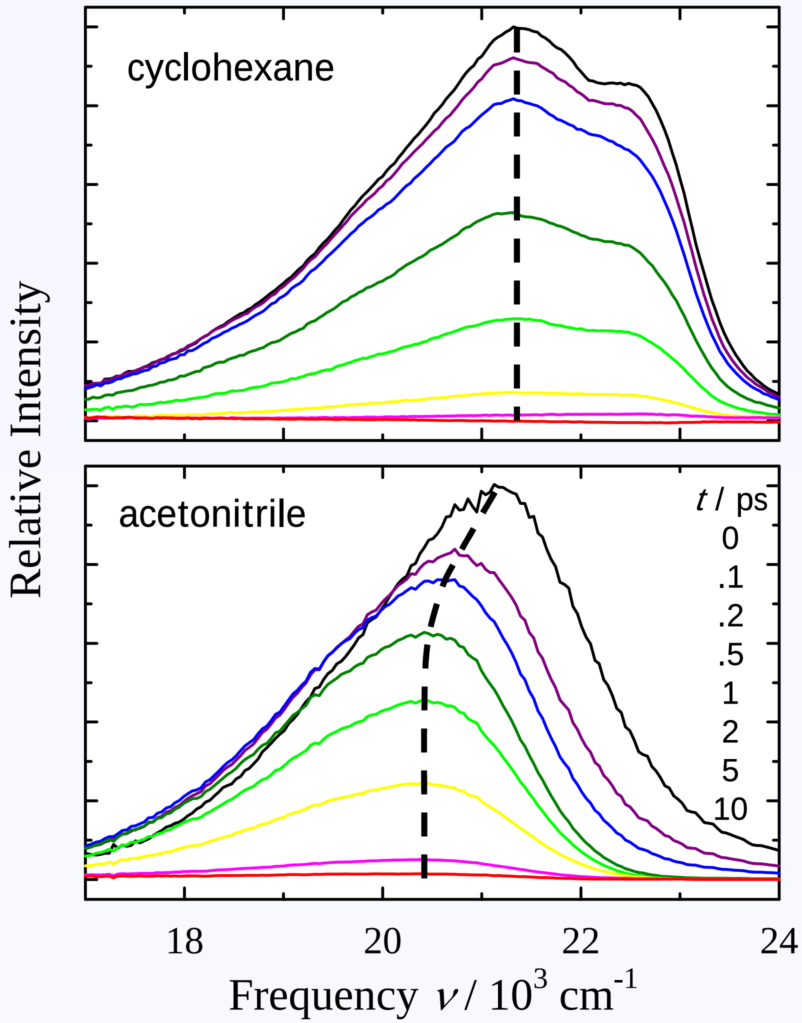
Dielectric Correlations



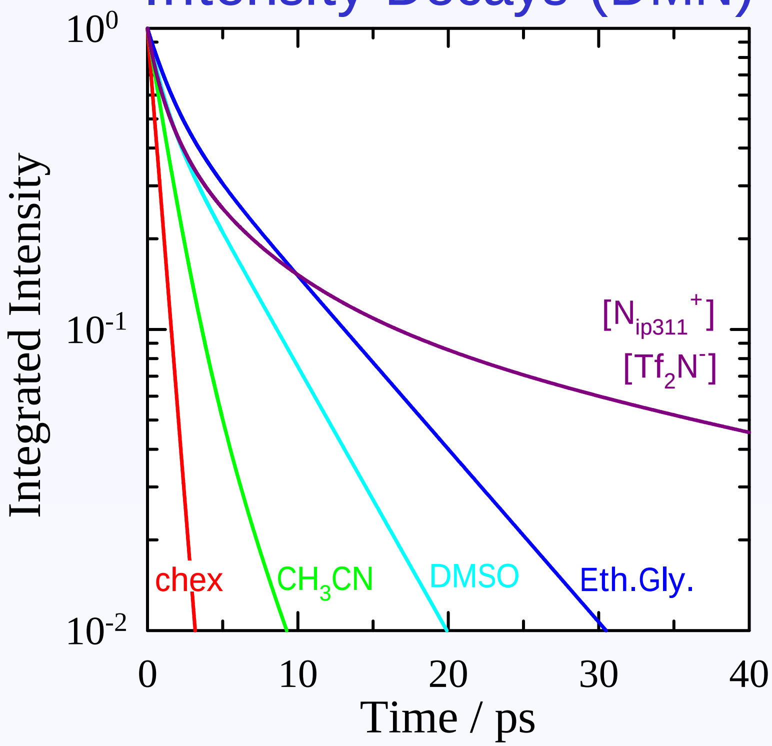
- ➢ DMN, JDMN spectra similar except for $\Delta\nu$
- ➢ absorption shifts indicate $\Delta\mu$=7-8 D, consistent with electrochromism
- ➢ emission shifts smaller than expected

fs-Time-Resolved Emission (25 °C)

Kerr Gated Emission of DMN



Intensity Decays (DMN)



Solvent	η/cP	τ_0/ps	β	$\langle\tau\rangle$ /ps
cyclohexane	0.9	0.7	1	0.7
CH_3CN	0.3	1.5	0.94	1.5
DMSO	2	3.0	0.79	3.4
ethylene elycol	17	3.9	0.75	4.6
$[N_{ip311}^+]$ $[Tf_2N^-]$	113	2.5	0.63	3.5

Jin et al., *JPCB* **114**, 7565 (2010).

τ_{rxn} & Fluorescence Quantum Yields

- good estimates reaction times ≅ lifetimes from QYs if k_{rad} is known

$$\tau_f^{-1} = k_{rad}(\varphi_f^{-1} - 1) \cong \tau_{rxn}^{-1}$$

k_{rad} from time-resolved emission:

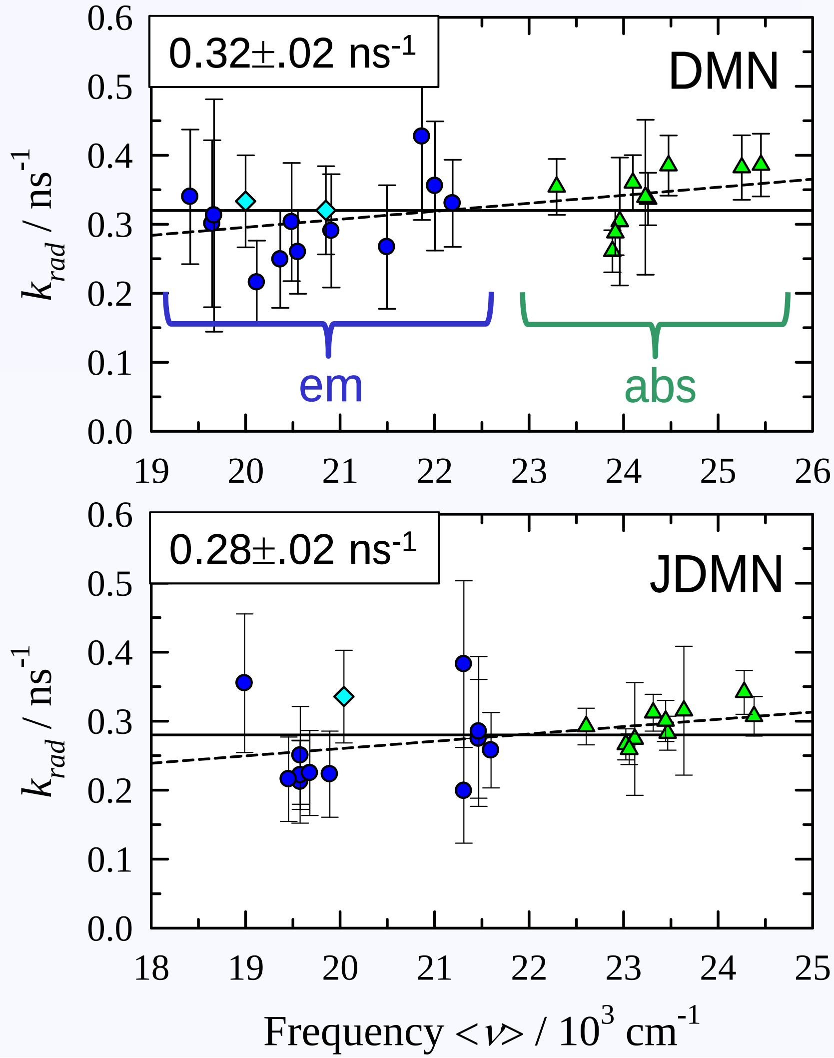
$$k_{rad} = \frac{\varphi_f}{< \tau_f >}$$

k_{rad} from absorption:

$$k_{rad} / \mathrm{s}^{-1} \cong 2.88 \times 10^{-9} n^2 (\tilde{\nu}_{em}^3 / \mathrm{cm}^{-3}) \otimes \int_{S_1} \frac{\varepsilon(\nu)/(\mathrm{M}^{-1}\mathrm{cm}^{-1})}{\nu} d\nu$$

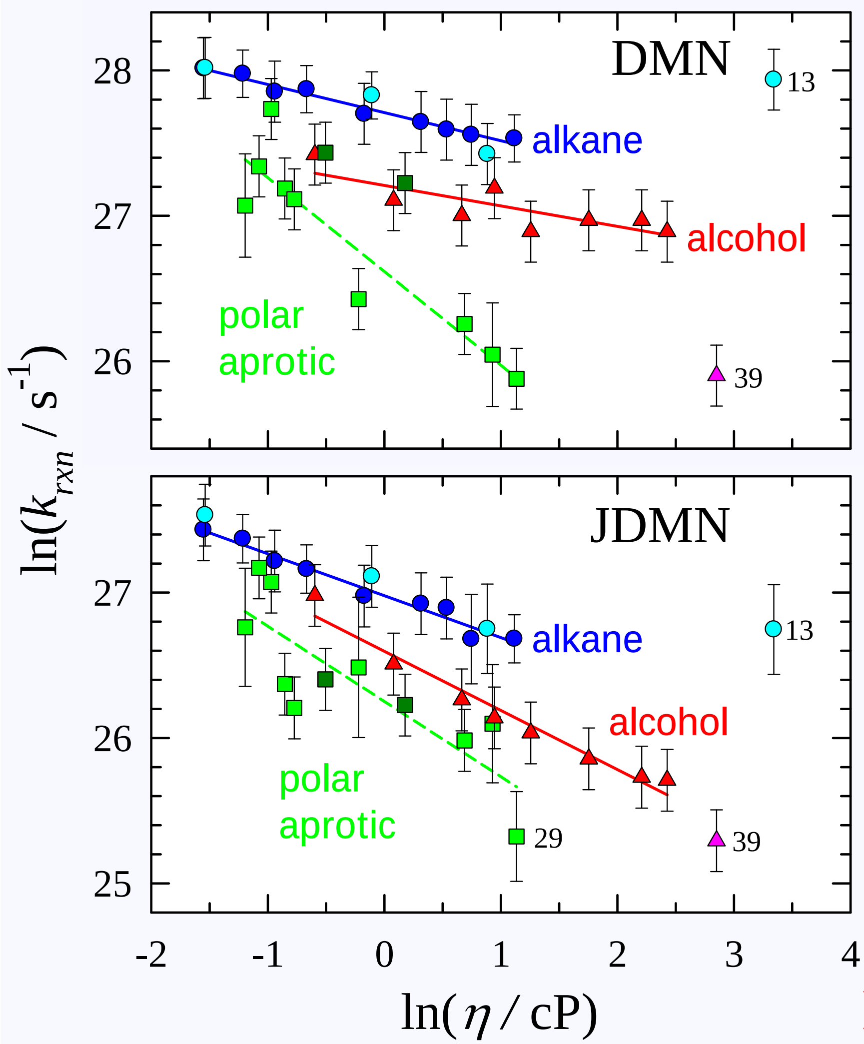
- $\varphi_f < 10^{-3}$ (challenging)
- k_{rad} solvent independent
- $M_{01} = M_{10} = 6.6 \pm 0.2$ D, the same for both solutes

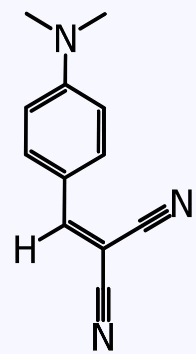
k_{rad} in Assorted Solvents

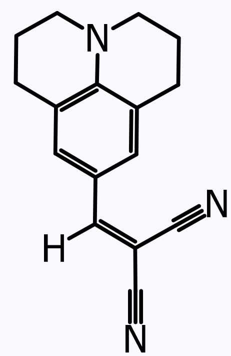


Survey of Reaction Rates

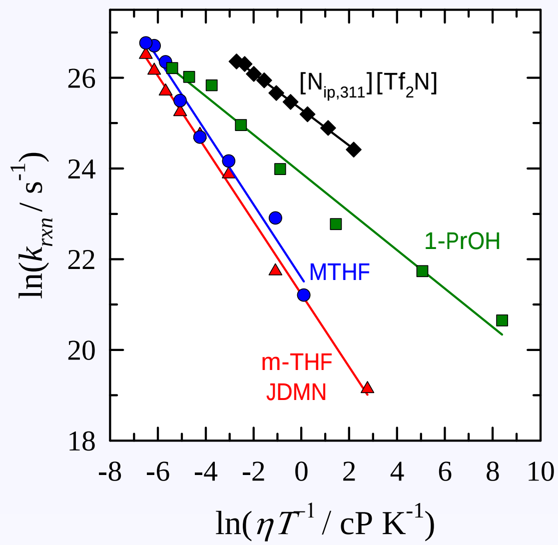
33 Solvents @ 25 °C



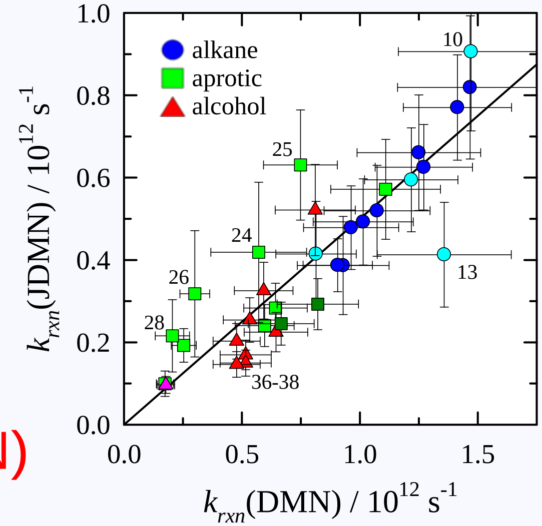




T Dependence



JDMN vs DMN



- $k(DMN) \sim 2k(JDMN)$
- $k/T \propto \eta^{-p}$ with $p<1$

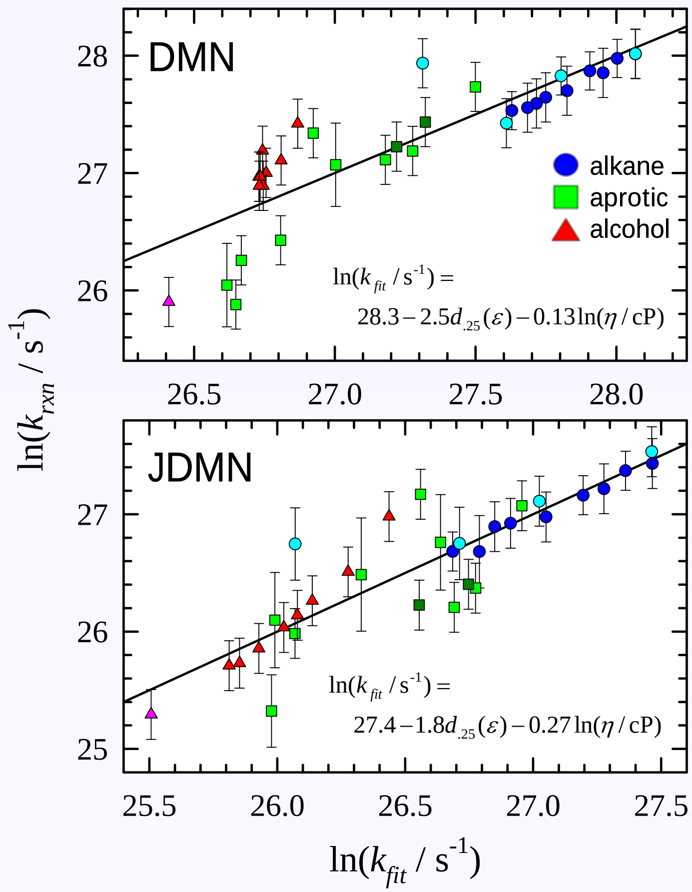
Viscosity Exponents, Polarity

Viscosity Exponents $k_{rxn}/T \propto \eta^{-p}$

solvent	T/K	η/cP	#	p
		DMN		
n-alkanes	298	0.2−3	9	0.19
n-alcohols	298	0.6−11	8	0.14
2-methyltetrahydrofuran	125−298	0.5−34	8	0.69
ethyl acetate	295−349	0.3−0.4	7	1.1
dimethyl phthalate	298−378	2−14	9	0.43
1-propanol	135−298	2−3 × 10^5	8	0.39
glycerol	297−366	6−1040	8	0.61
$[N_{ip311}][Tf_2N]$	258−338	22−2300	9	0.40
		JDMN		
n-alkanes	298	0.2−3	9	0.29
n-alcohols	298	0.6−11	8	0.41
n-alcohols	293	0.5−11	10	0.29
alcohols + glycerol	RT	2−1000	14	0.59
alcohols + glycerol	298	4−290	9	0.58
ethylene glycol + glycerol	RT	50−1000	6	0.59
2-methyltetrahydrofuran	125−298	0.5−34	8	0.78
ethyl acetate	295−341	0.3−0.4	10	1.00
dimethyl phthalate	297−396	1−14	14	0.49
glycerol	277−381	12−7100	19	0.73
glycerol	293−373	69−6800	18	0.71
7 imidazolium ionic liquids	263−343	10−700	11	0.35−.69

Viscosity+Polarity Correlation

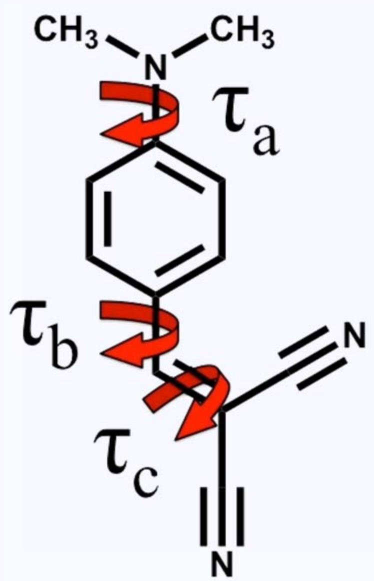
$$\ln k_{rxn} \cong a - bf(\varepsilon) - c\ln\eta$$

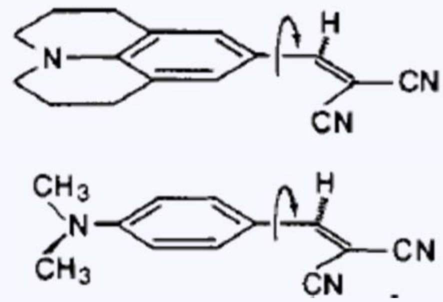


➢ both fluidity "1/η" and polarity play important roles

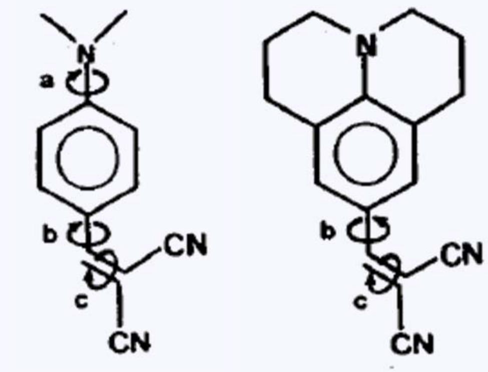
Jin et al., *JPCB* **114**, 7565 (2010).

What's the Mechanism?

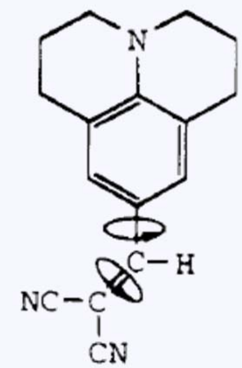




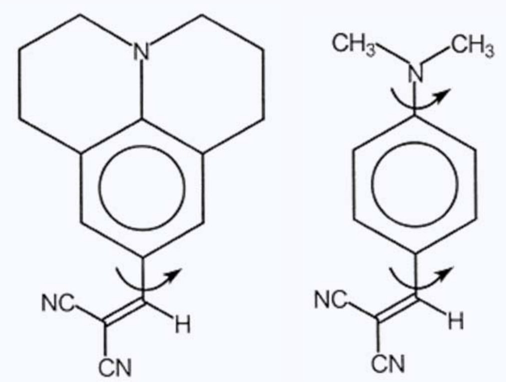
Loutfy (1982)



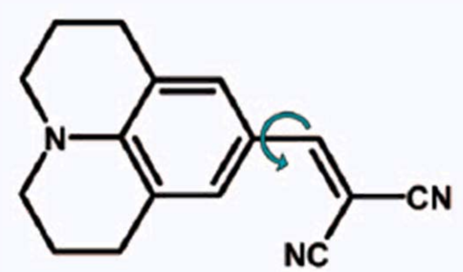
Mqadmi (1990)



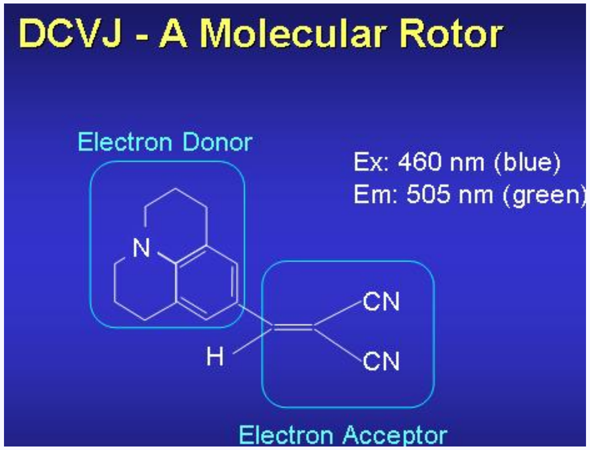
Torkelson (1995)



Drickamer (1998)

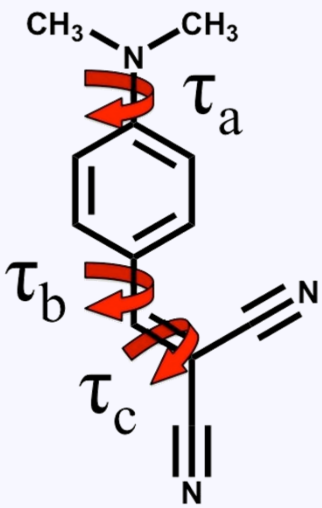


Samanta (2008)



Haidekker (2009)

Gas-Phase Torsional PES of S_1 DMN

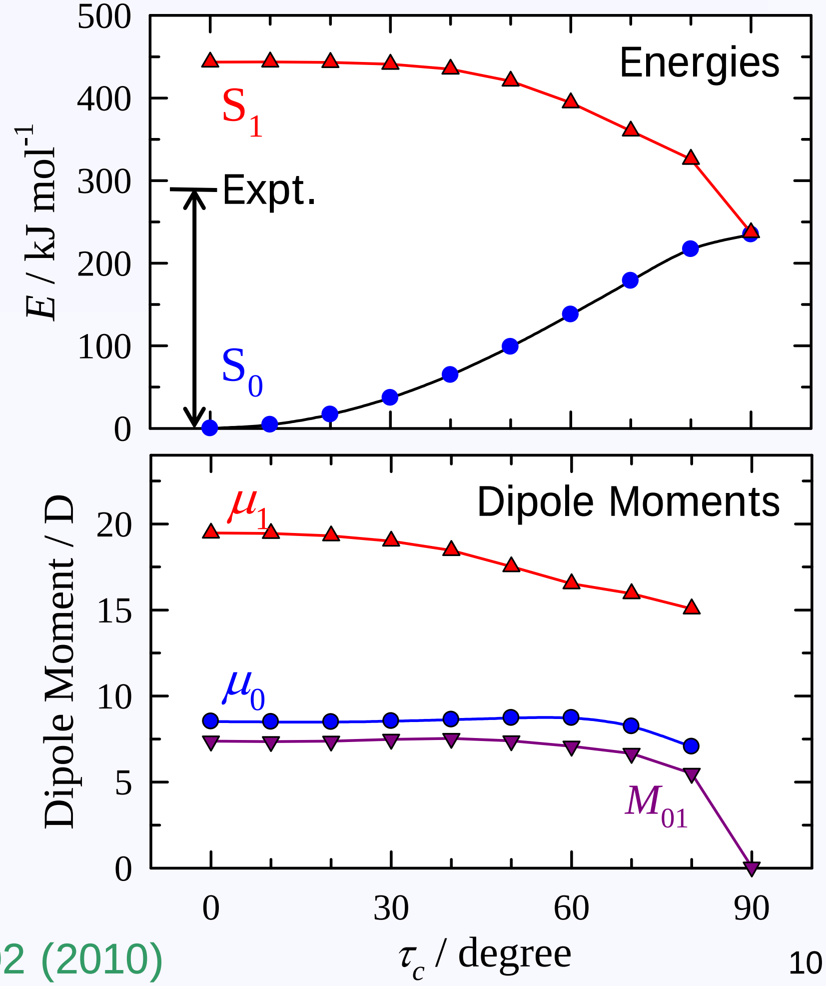


- τ_c is primary reaction coordinate
- scanned at SA2-CAS(12,11)/6-31G(d) level (S_0 optimized geometries)

Details of PES Search

- search of S_1 @ RI-CC2/def2-TZVP level located minima at τ_a=90° and τ_b~ τ_c~20°, but no τ_b=90° TICT state
- (a TD-B3LYP located a τ_b-TICT state, but LC corrections eliminated it)
- a CIS search did not reveal a τ_b TICT state; instead a conical intersection with S_0 was found at τ_c=90°

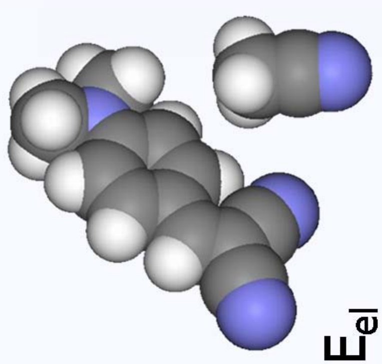
CAS-SCF Predictions

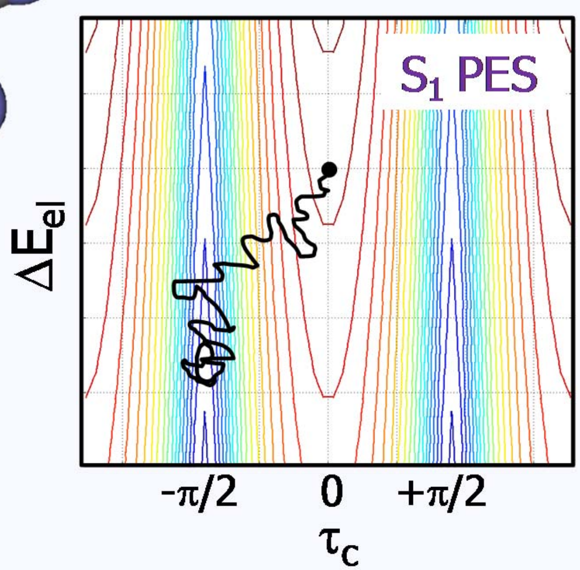


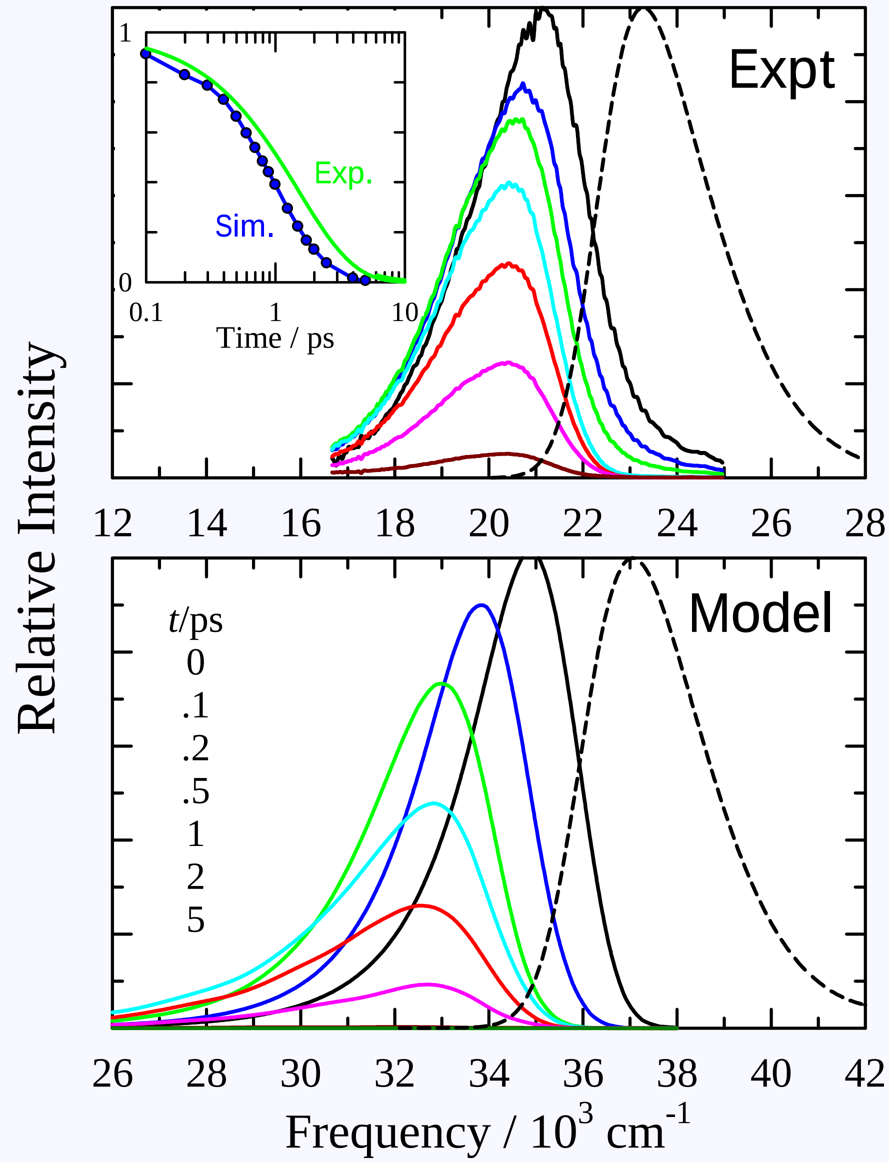
Swalina & Maroncelli, *JPCC* **114**, 5602 (2010)

Preliminary MD Simulations

- explore solvent effect by combining QM E(τ_c) with classical solvent bath via molecular dynamics simulations
- semi-rigid solute (τ_c only)
- 108 CH_3CN solvent molecules
- 2000 n.e. trajectories on U_1
- terminate when $|\tau_c|$=85°



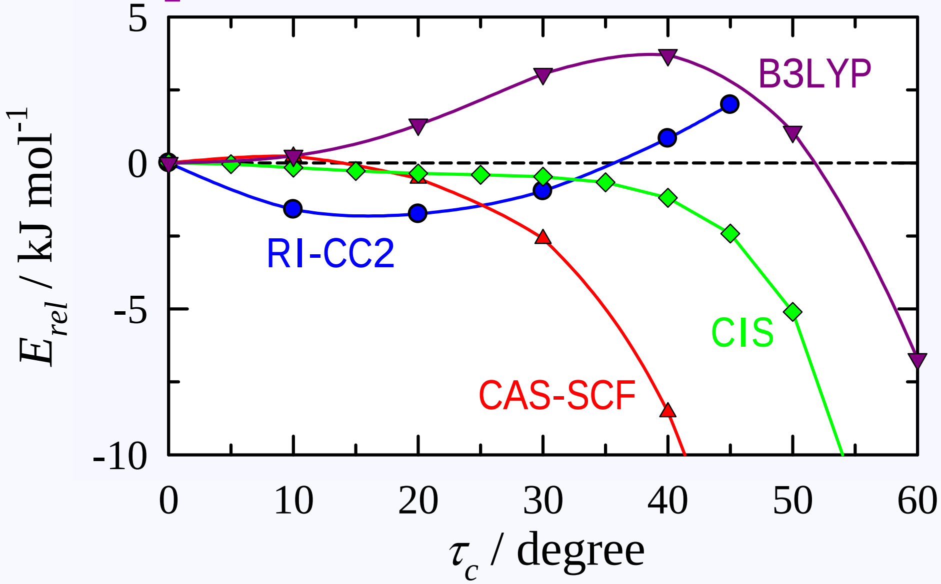


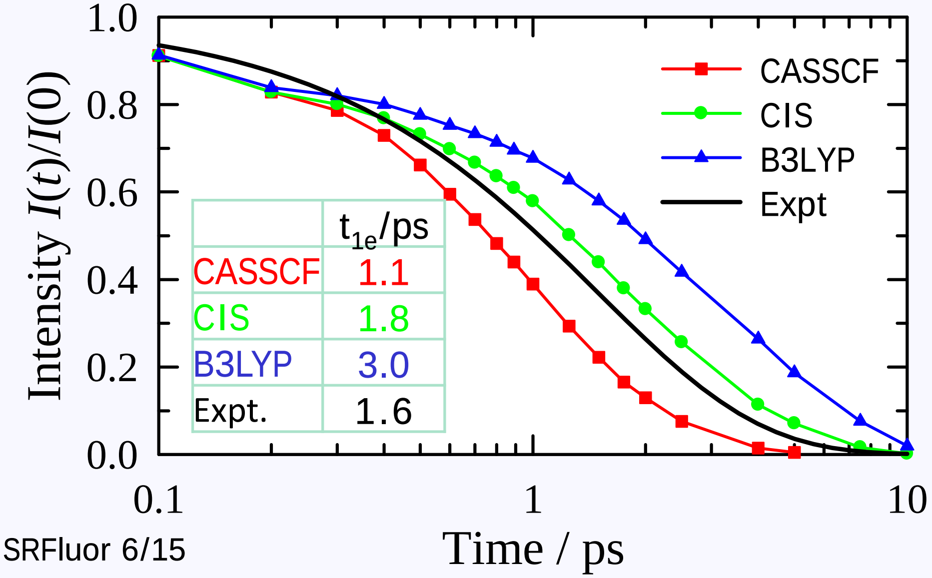


Swalina & Maroncelli, *JPCC* **114**, 5602 (2010)

Variations with τ_c PES & Solvent

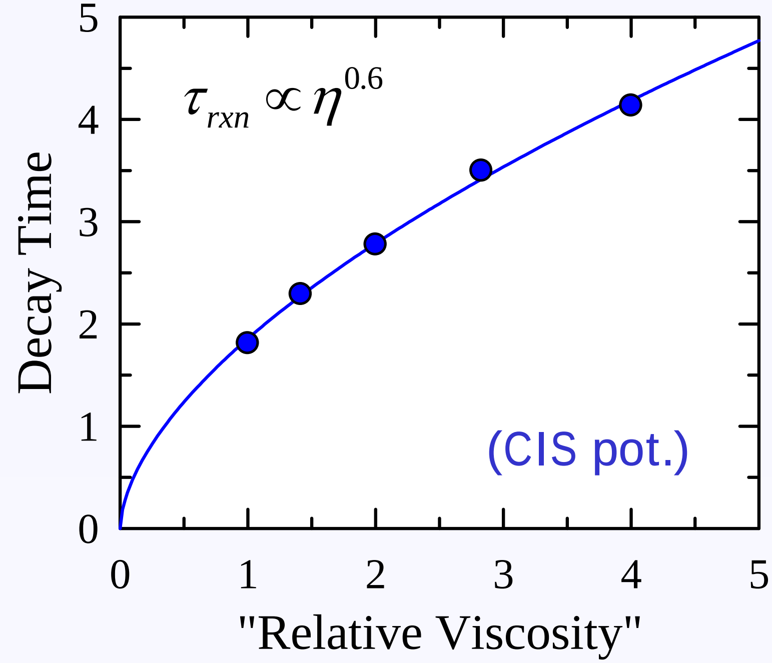
S_1 Potentials & Their Dynamics





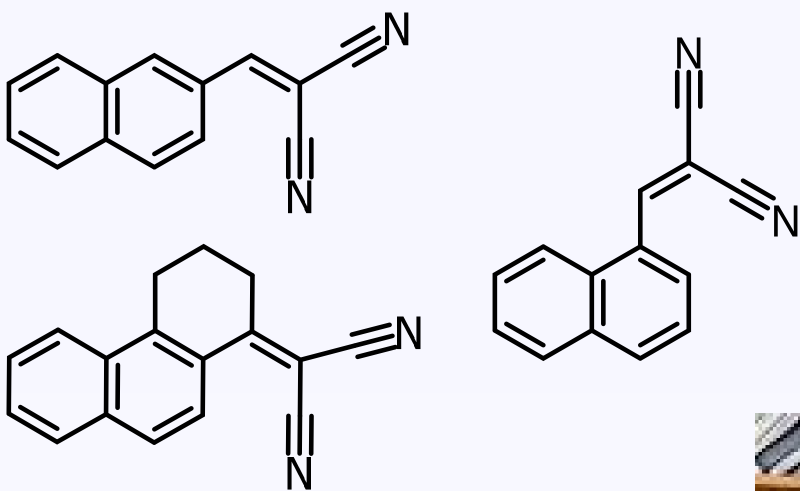
	t_{1e}/ps
CASSCF	1.1
CIS	1.8
B3LYP	3.0
Expt.	1.6

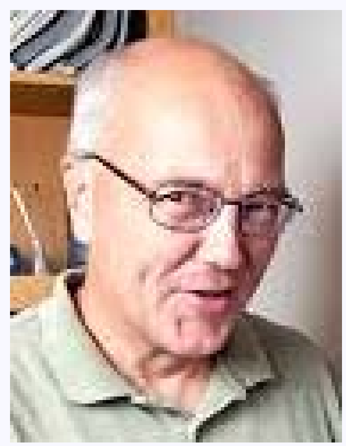
Viscosity Dependence



- dynamics are sensitive to k_BT-level variations in $E(\tau_c)$
- viscosity variation & DMN/JDMN difference like experiment
- overall approach is promising

2: Naphthylmethylene Malononitriles

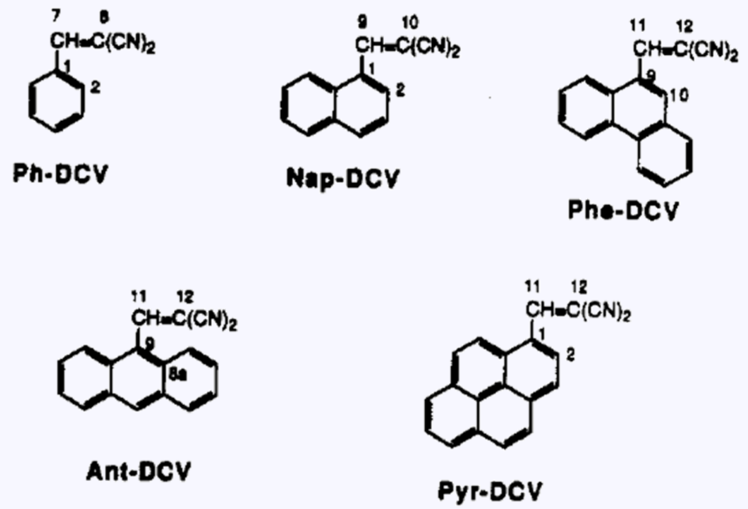




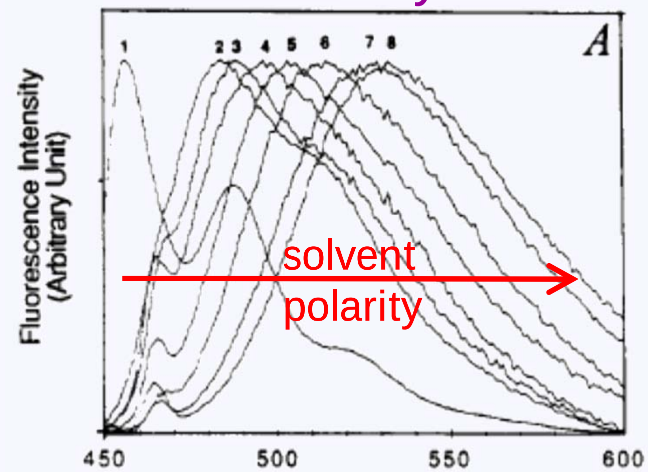
Brian Williams

Jens Breffke

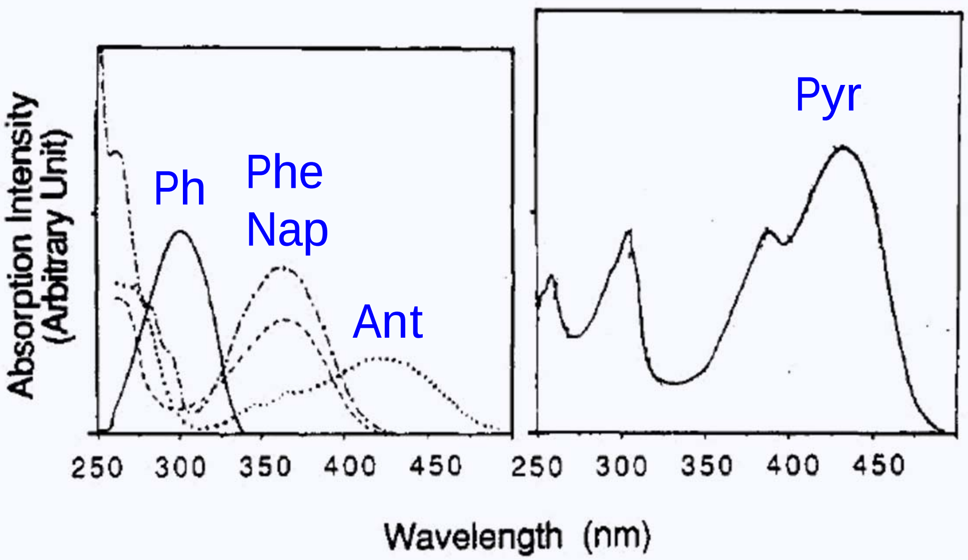
Prior Work, Schanze & Co.



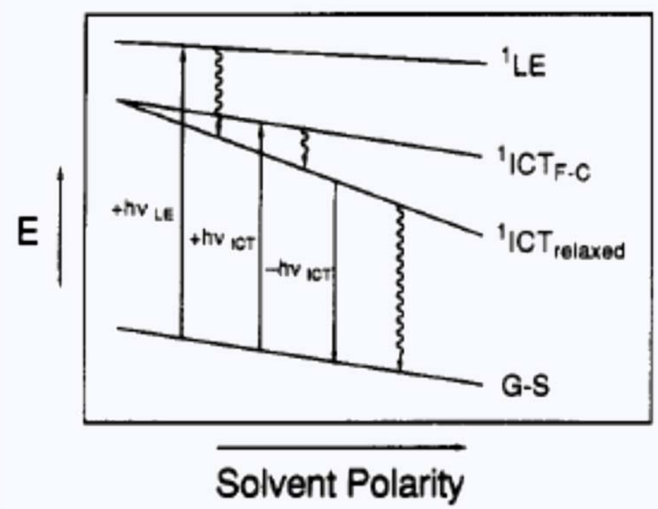
Emission of PyrDCV



Absorption Spectra



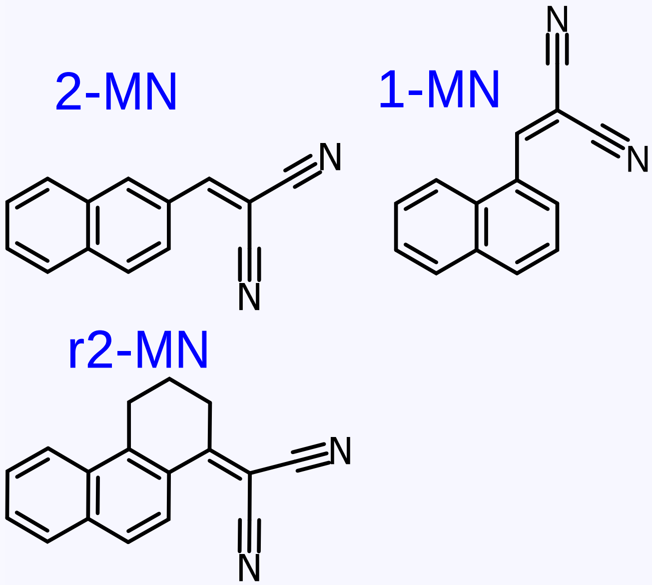
Interpretation

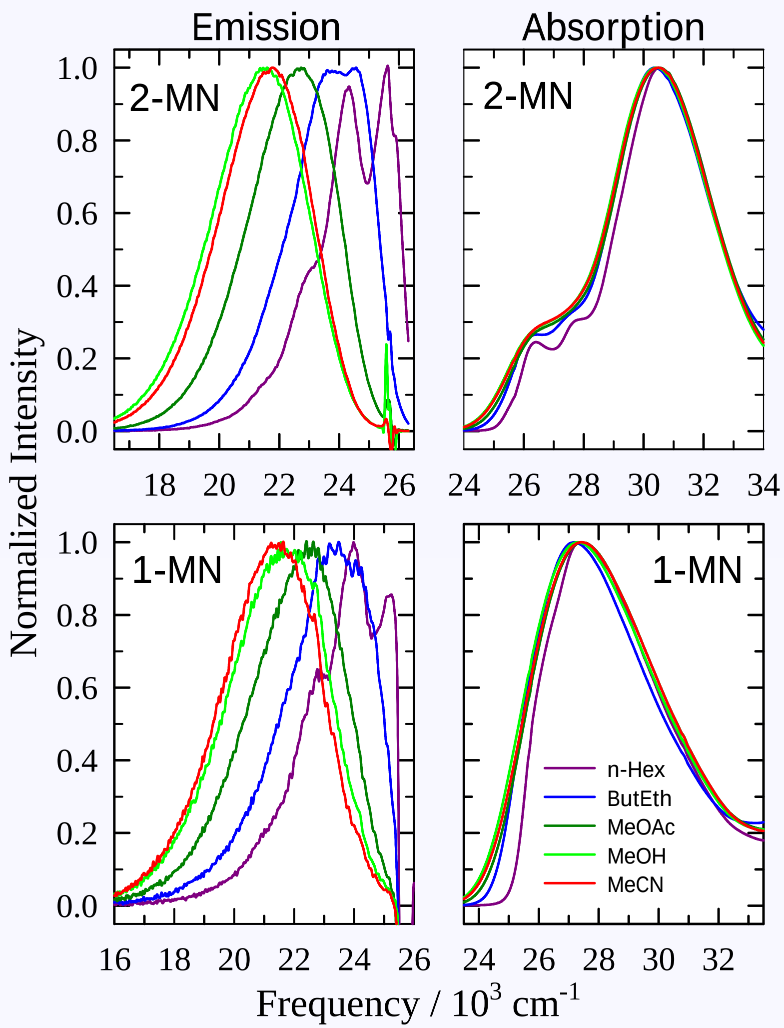


"prob. TICT"

Katritzky, ..., Schanze, *J. Phys. Chem.* **95**, 5737 (1991).

Our Work





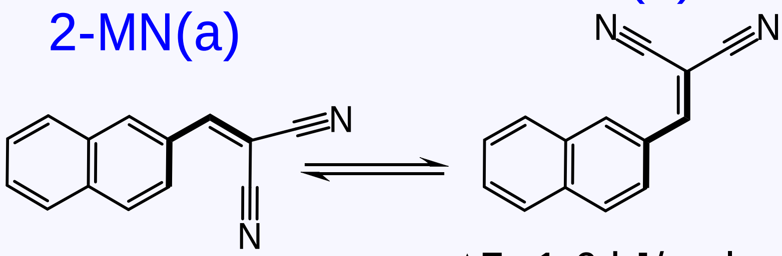
- DFT calculations
- survey of solvatochromic shifts, quantum yields, transition moments in 11 solvents of varying polarity
- emission lifetimes on ps & fs timescales

Breffke, Williams, & Maroncelli, *J. Phys. Chem. B* **119**, (2015) [10.1021/jp509882q].

Conformer Possibilities

2-MN(a)

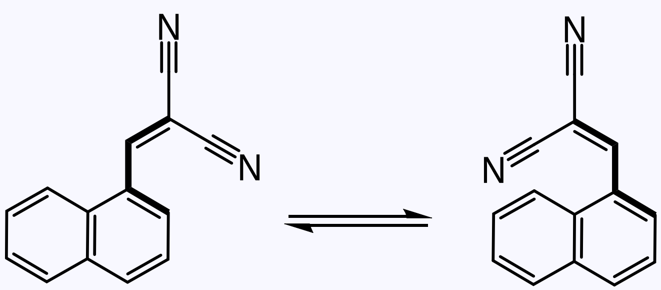
2-MN(b)



ΔE~1-6 kJ/mol

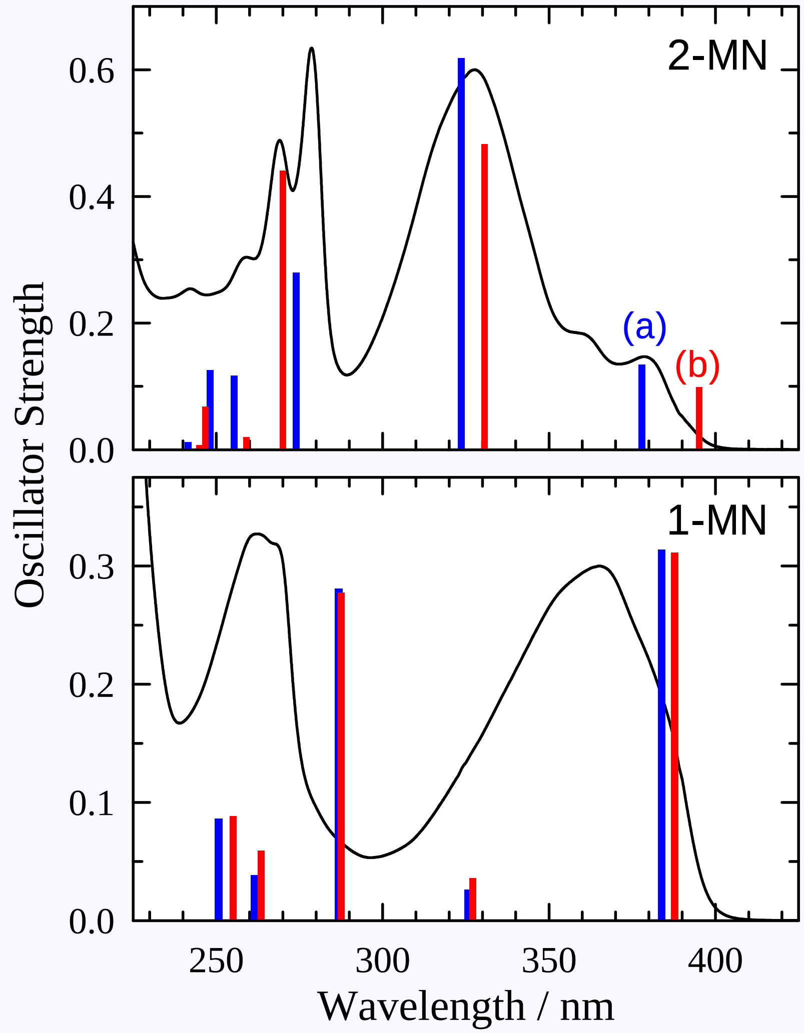
1-MN(a)

1-MN(b)



ΔE~6-13 kJ/mol

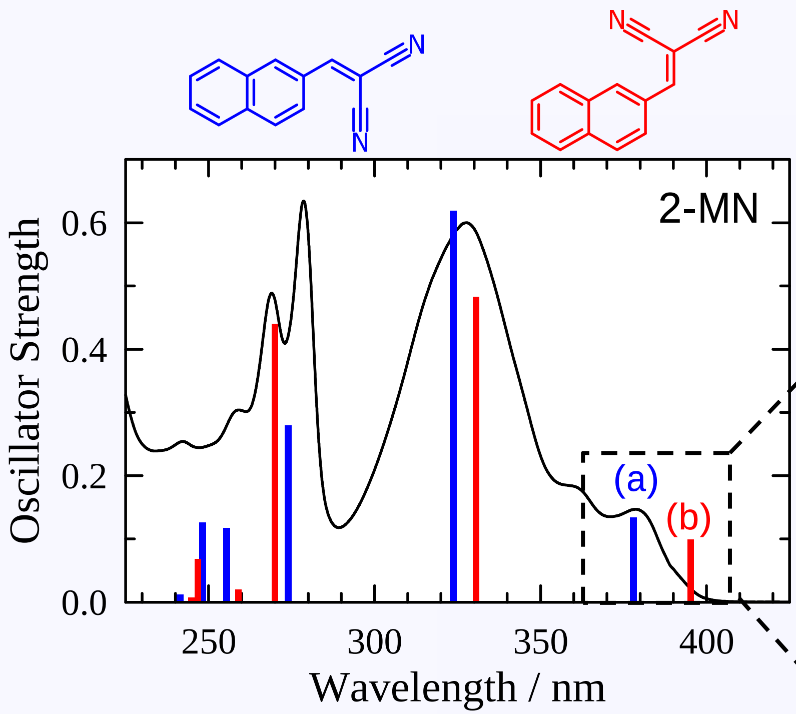
Observed & Calculated Absorption

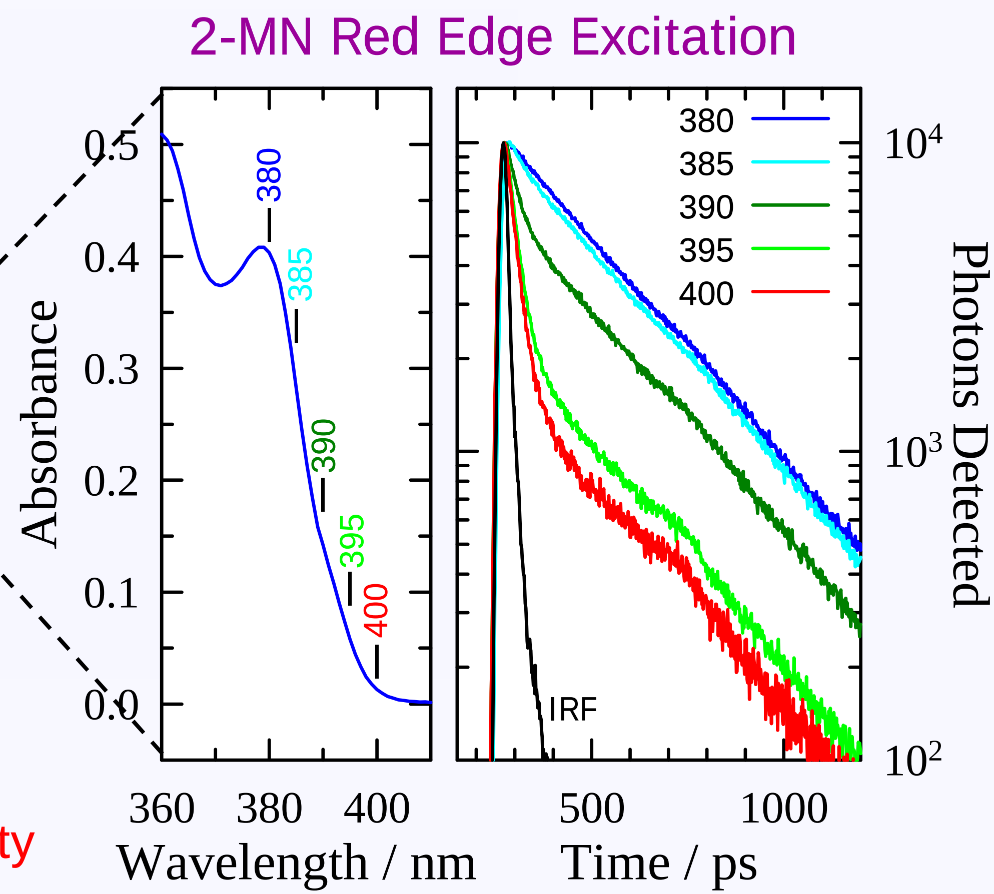


Breffke et al., *J. Phys. Chem. B* **119**, (2015) [10.1021/jp509882q].

1-MN: no sign of multiple conformers in any solvent

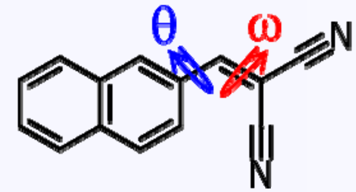
2-MN: hints of multiple emitting species only in nonpolar and weakly polar solvents



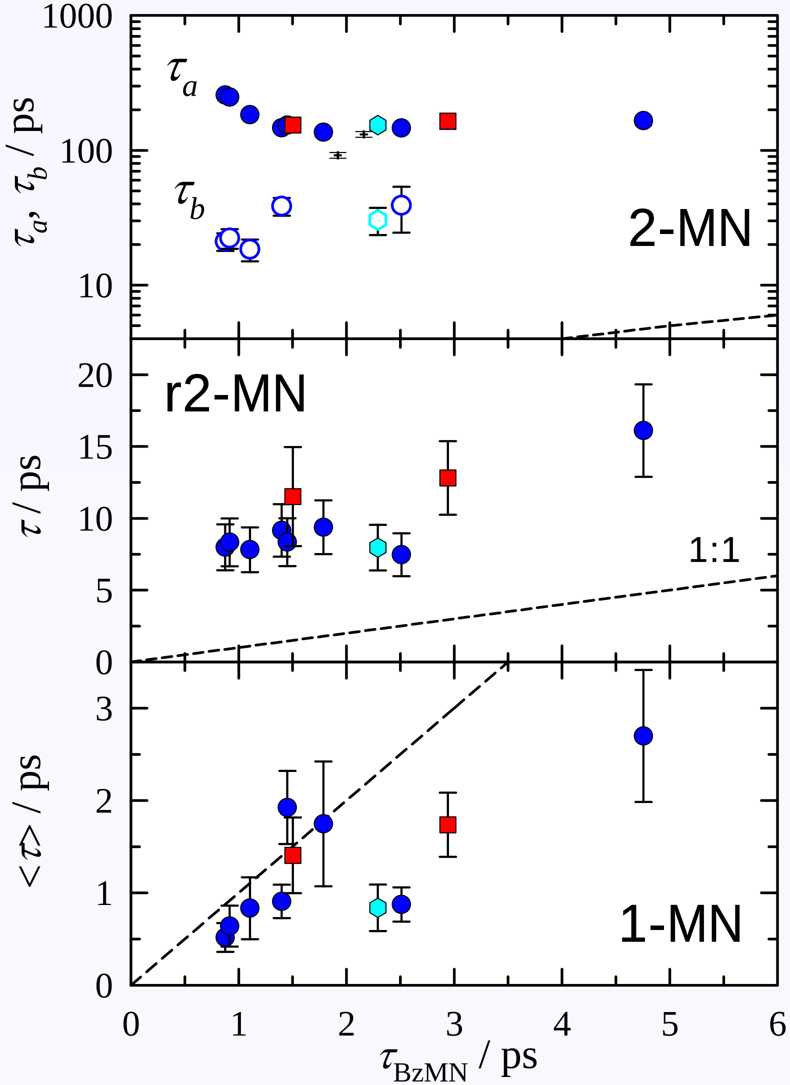


- ➢ assign fast decay component to 2-MN(b)
- ➢ $\Delta G_{b\text{-}a}$ increases with solvent polarity such that 2-MN(a) dominates in highly polar solvents

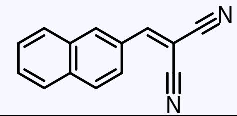
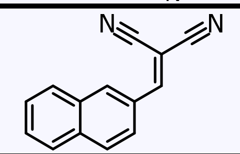
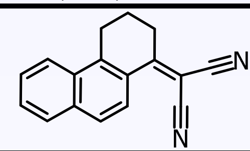
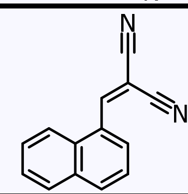
Fluorescence Lifetimes



x-MN vs DMN/JDMN Lifetimes

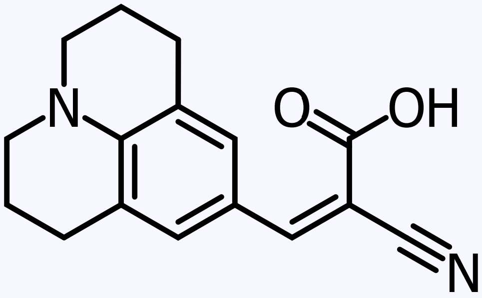


Lifetimes & S_0 Structure

		τ_{fl}/ps	θ	ω
2-MN(a)		~100	6°	0
2-MN(b)		~30	25°	0
r2-MN		~10	34°	1°
1-MN(a)		~1	43°	6°

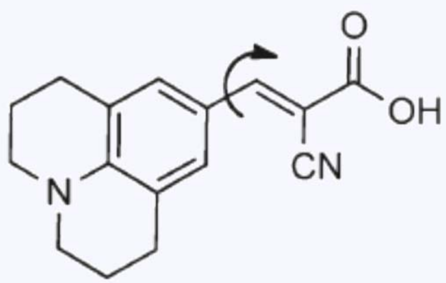
- decay mechanism is isomerization (ω) & IC as in the benzylidene case
- θ and ω coordinates are coupled
- pretwisting/strain in S_0 is reflected in decay rates (S_1 isomerization PES)

3: CCVJ (A Cautionary Tale)



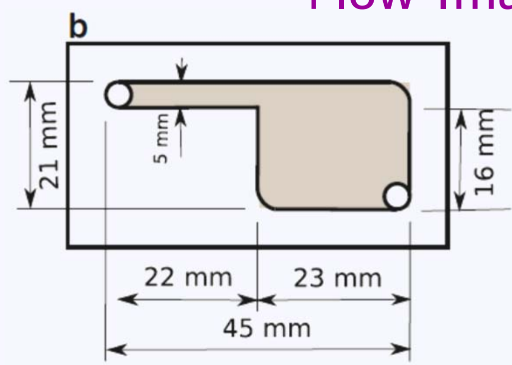
Chris Rumble

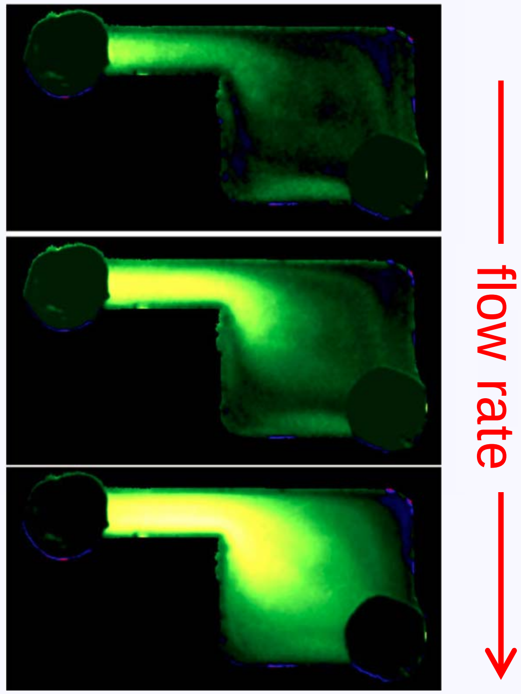
CCVJ as a Local Flow Sensor



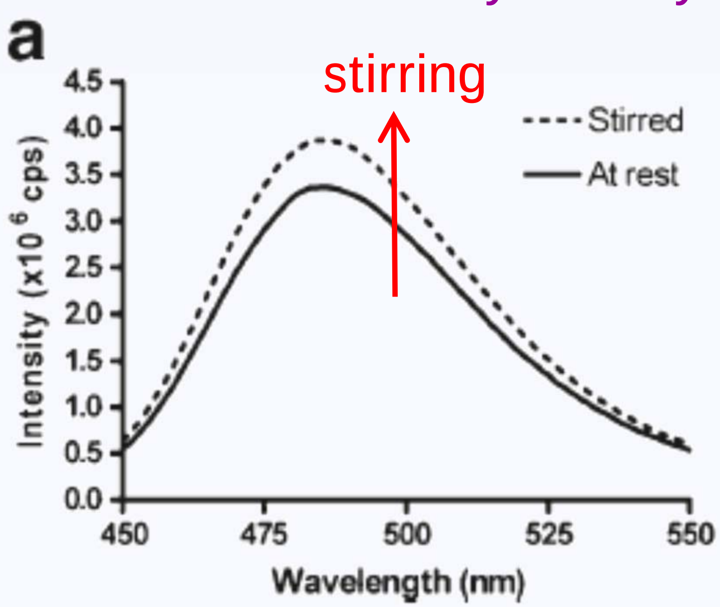
CCVJ

Flow Imaging





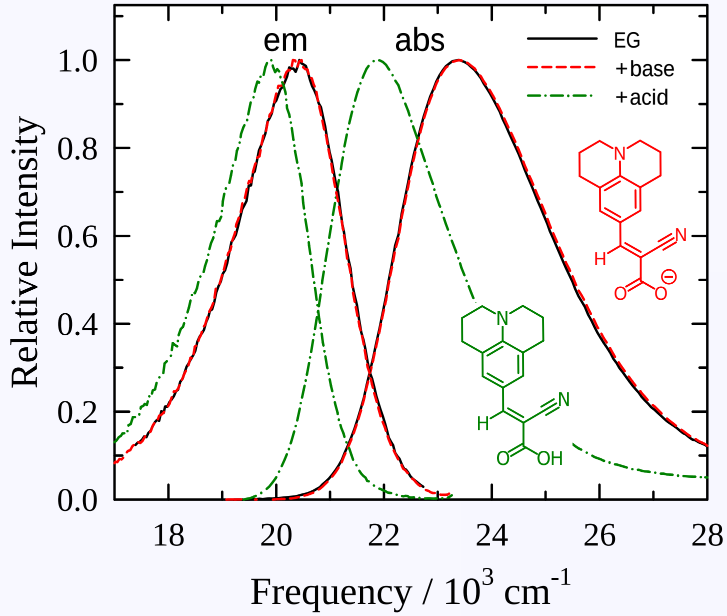
Emission of CCVJ in Ethylene Glycol



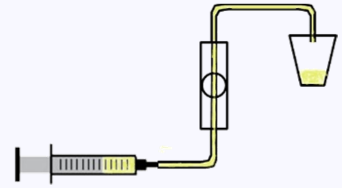
- not an effect of photobleaching
- deactivation via TICT mechanism
- proposed molecular mechanism in which shear stress/flow influences TICT process

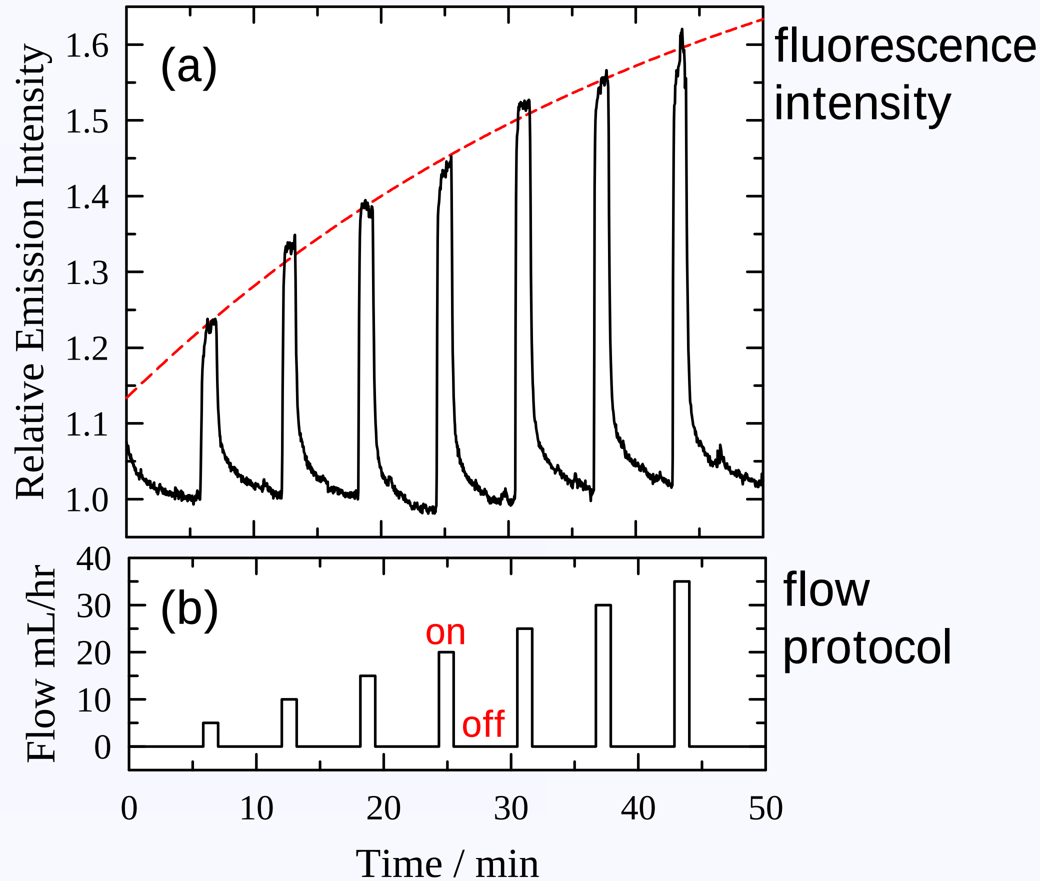
Haidekker et al., *Sensor Lett.* **3**, 42 (2005); *J Fluoresc.* **20**, 1087 (2010).

Protonation State?

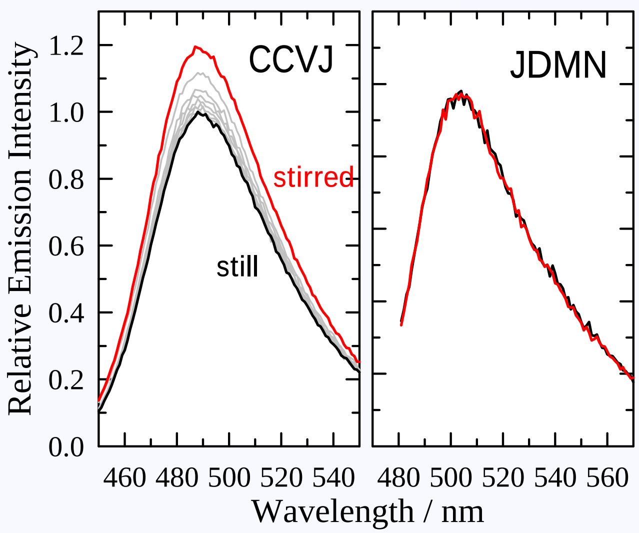


Effect of Flow





Effect of Stirring

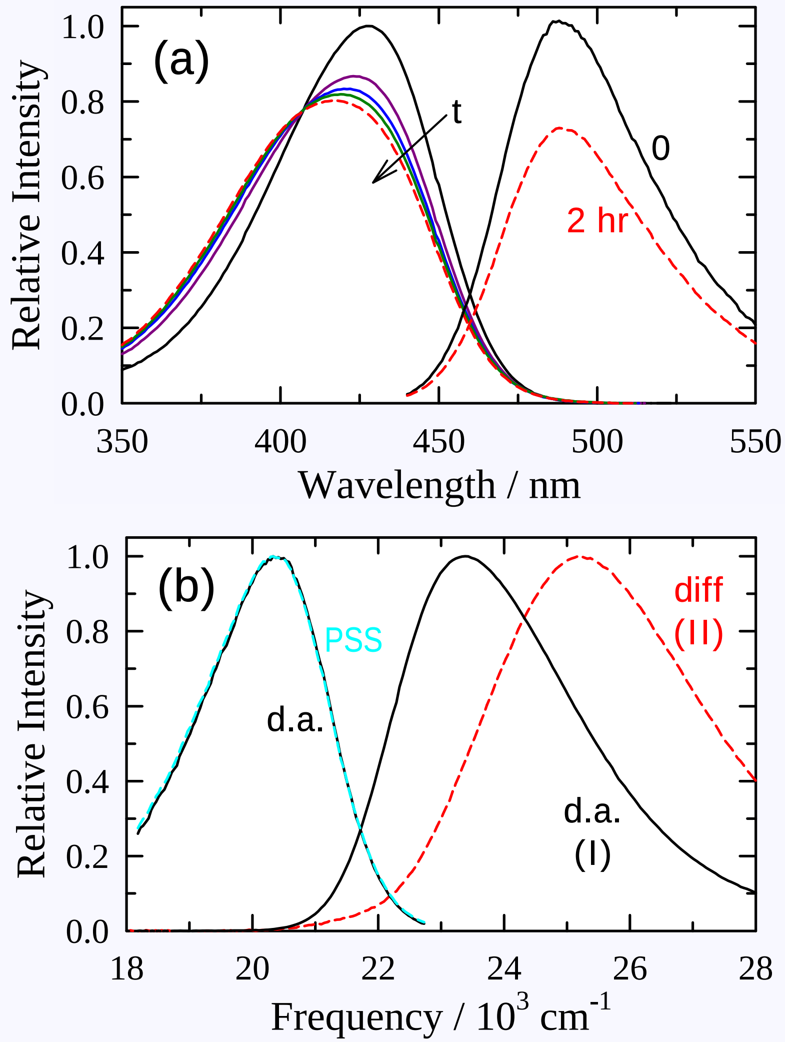


- ➢ anion is the relevant species in pure alcohols & water; speciation varies in other solvents
- ➢ stirring and flow effect confirmed

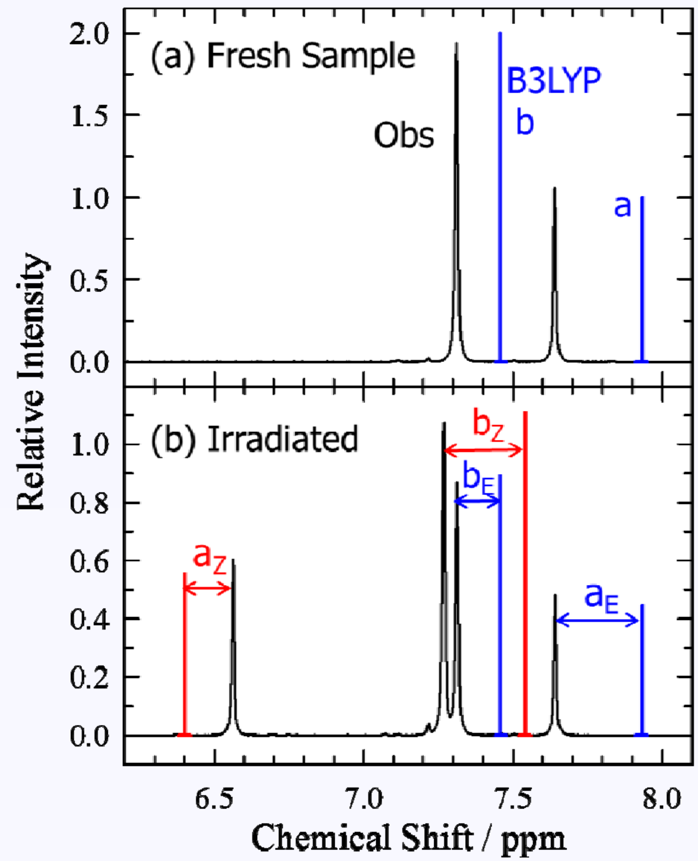
Rumble et al., *J. Phys. Chem. A* **116**, 10786 (2012).

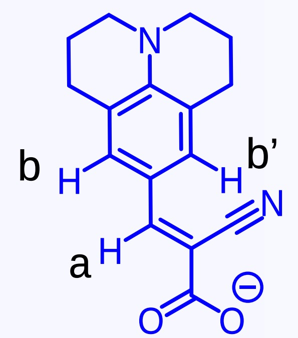
Photoisomerization Mechanism

Effect of Irradiation

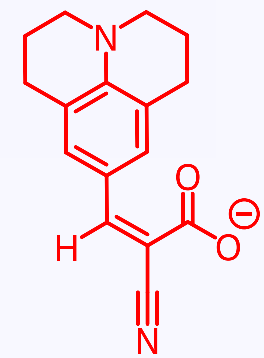


^{1}H NMR Spectra Obs & Calc.





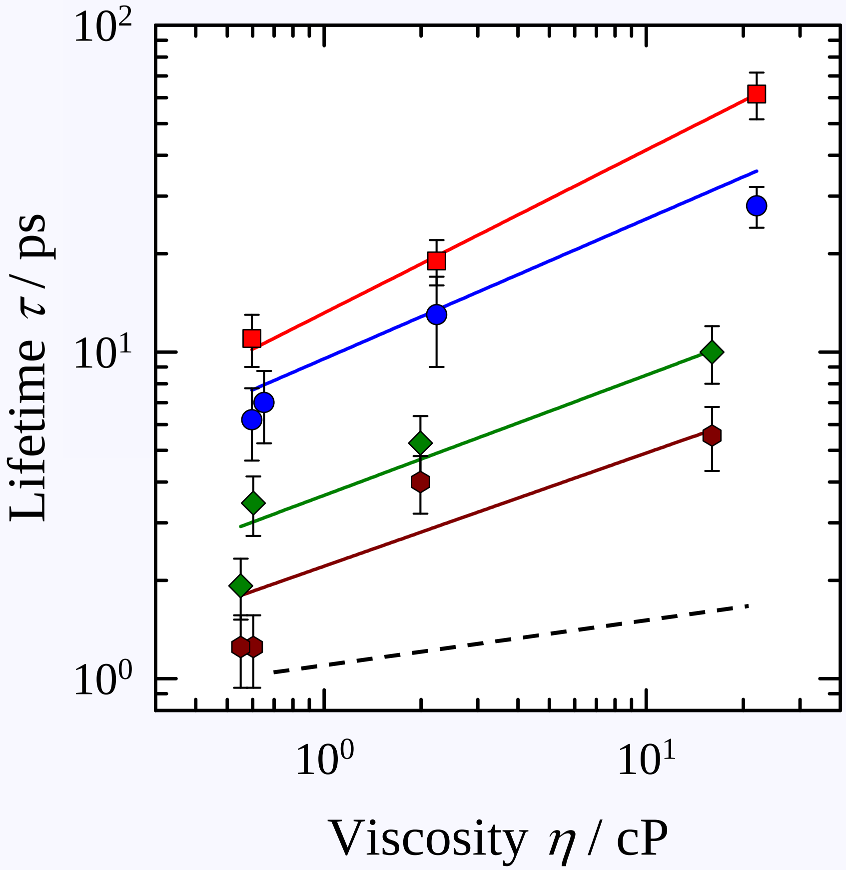
E Isomer (I)

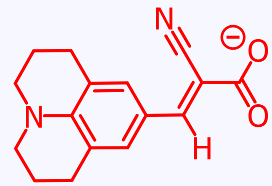


Z Isomer (II)

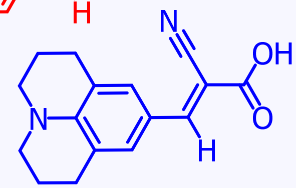
- irradiation leads to long-lived and virtually non-fluorescent photoproducts
- NMR confirms photoreaction is E→Z isomerization

Fluorescence Lifetimes

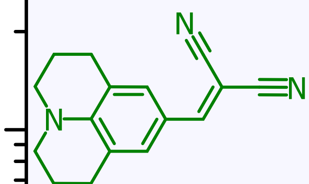




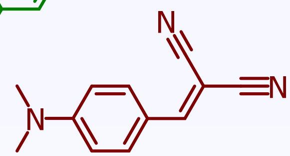
CCVJ$^-$



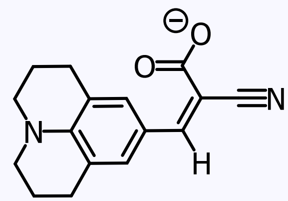
CCVJ^0



JDMN



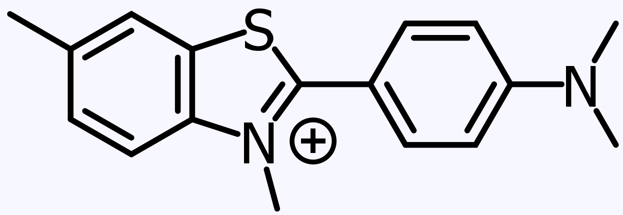
DMN



(Z-CCVJ$^-$)

- CCVJ similar to DMN, JDMN but slower
- $\tau \propto \eta^p$ with p~0.4 for all 4 species
- shorter lifetime of Z isomer likely due to significant nonplanarity in S_0
- *caution is needed with asymmetric substitutions*

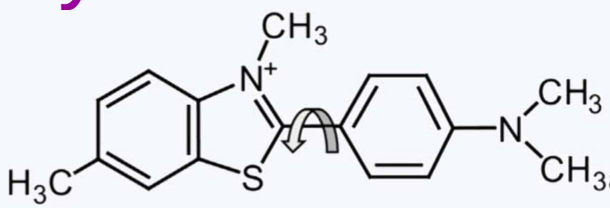
4: Thioflavin T

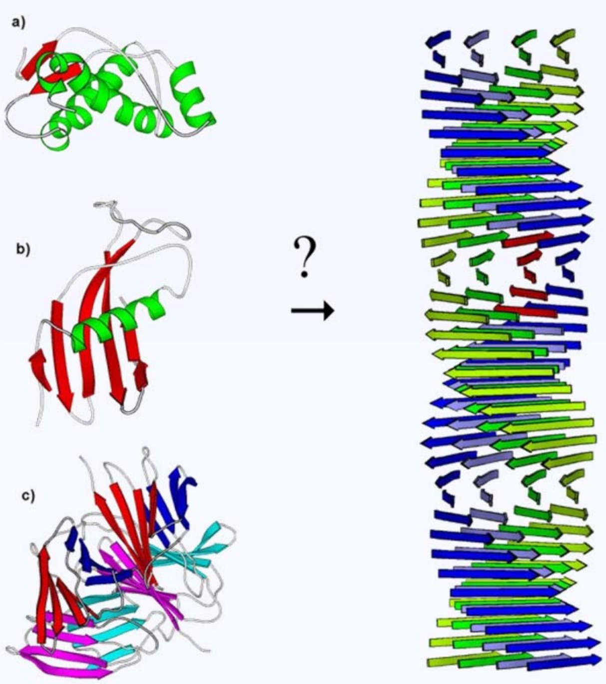


Jens Breffke

ThT$^+$ as Sensor for Amyloid Fibrils

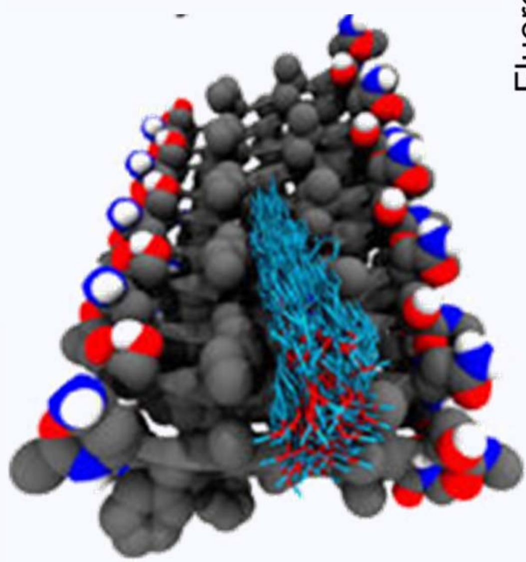
- ❑ introduced in 1945 for detecting amyloid fibrils
- ❑ still standard dye for monitoring fibrillization kinetics





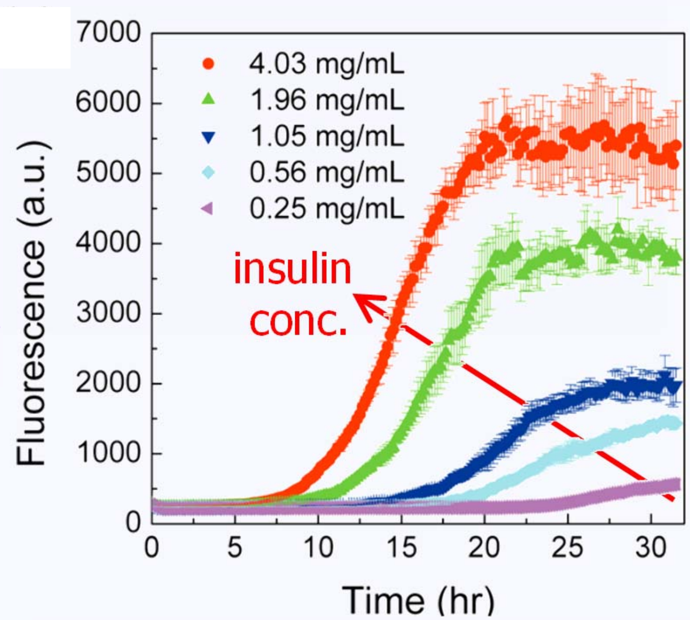
http://www.humpath.com/spip.php?article13252

MD of Dye Binding



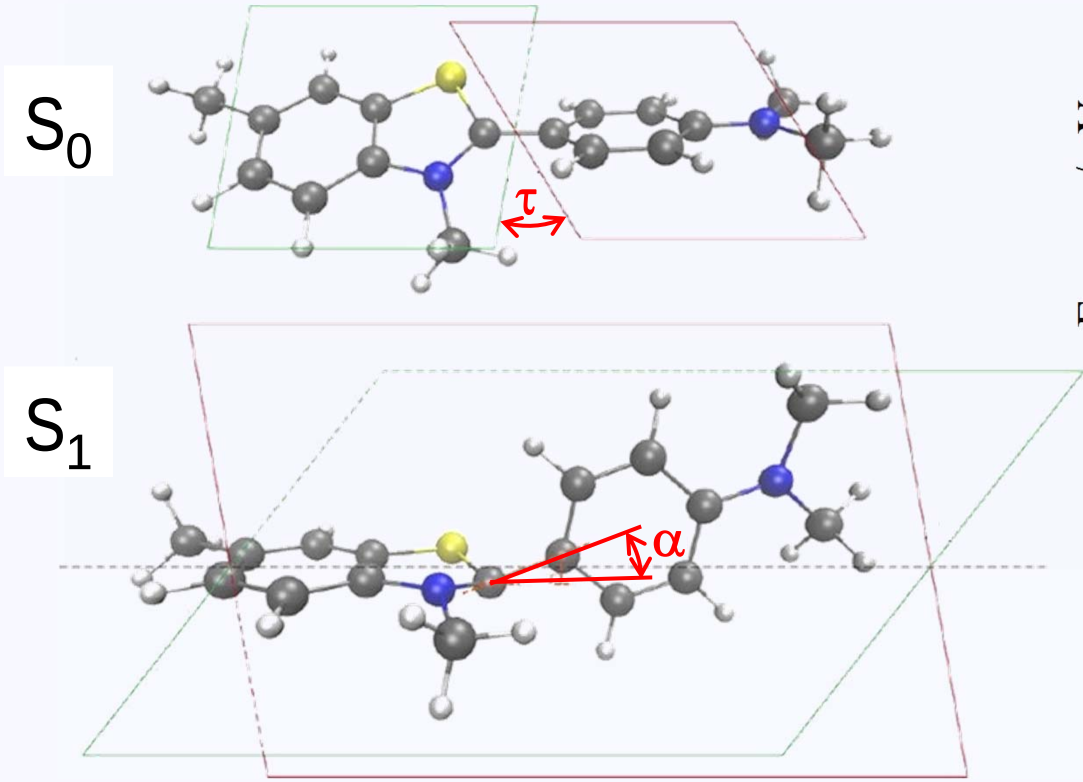
Skeby et al. *JACS* **135**, 15144 (2013)

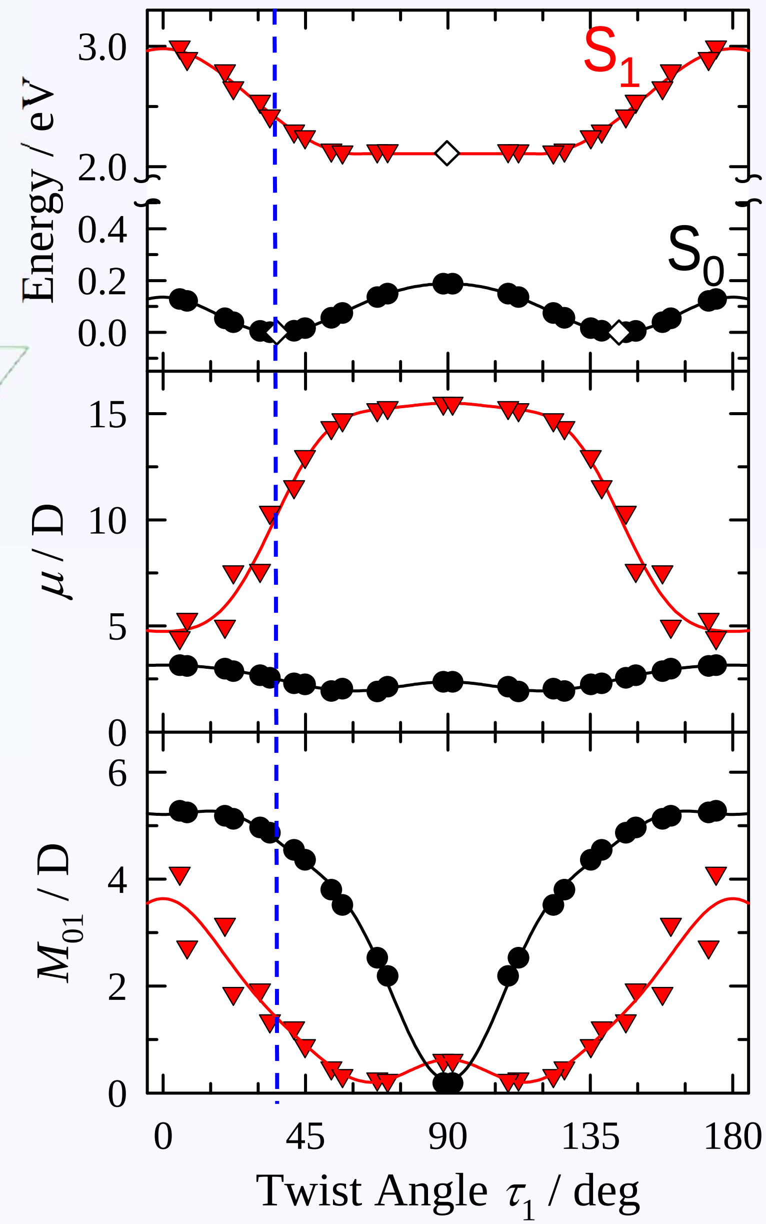
Insulin Fibrillization Kinetics



Hsu et al. *JPCB* **117**, 3459 (2013)

Electronic Structure Calculations



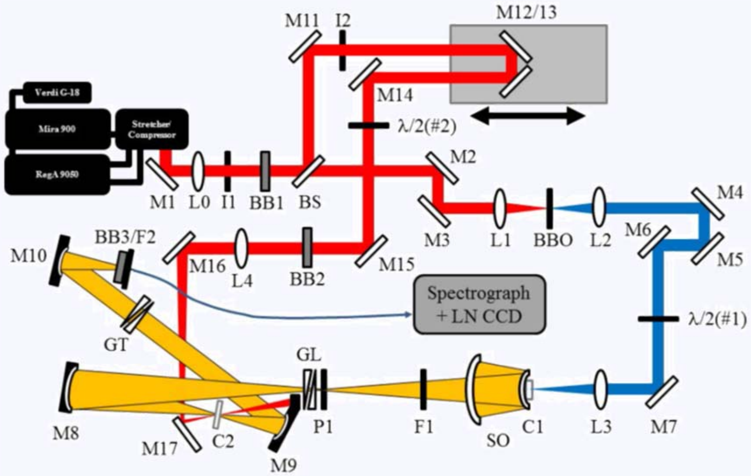


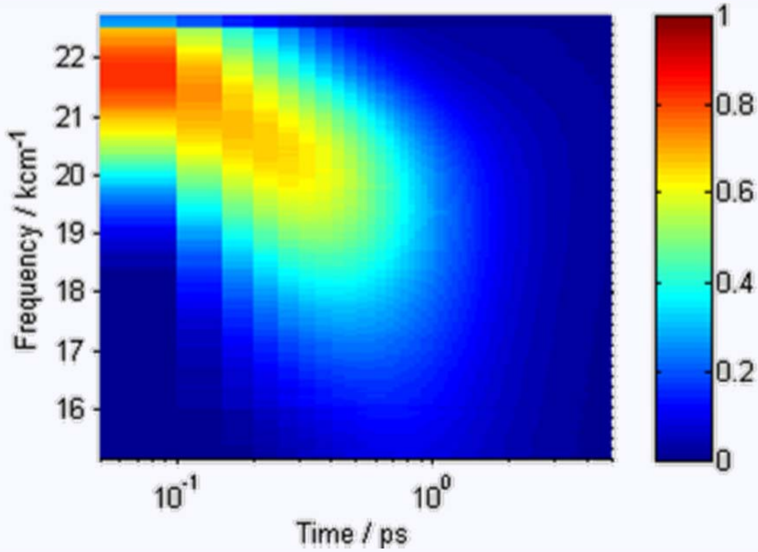
- in S_0 components planar with twist of $\tau=38°$
- in S_1 $\tau=90°$ and components bent by $\alpha=25°$
- large charge transfer character ($2 \rightarrow 15$ D)
- TICT state non-emissive (+ CI)

Ren et al., *JPCA* **117**, 6096 (2013).

TR Emission Spectra via Kerr Gating

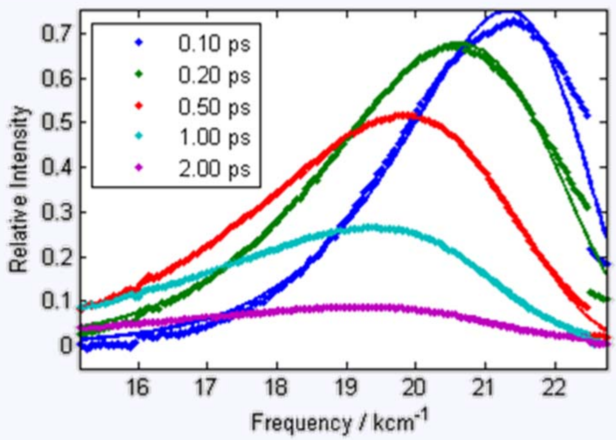
The Kerr-Gated Emission



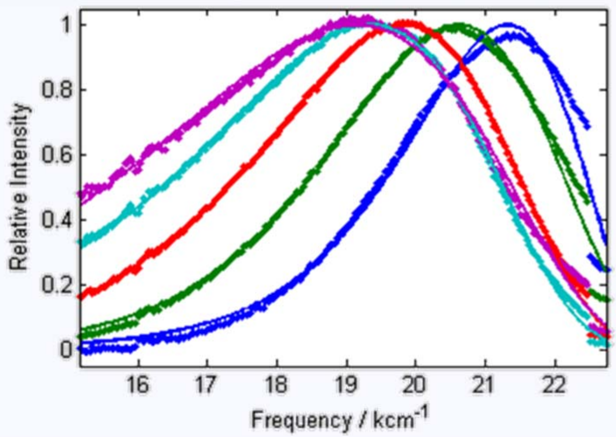


IRF ~350 fs; deconvolute to ~100 fs

ThT$^+$ in CH_3CN



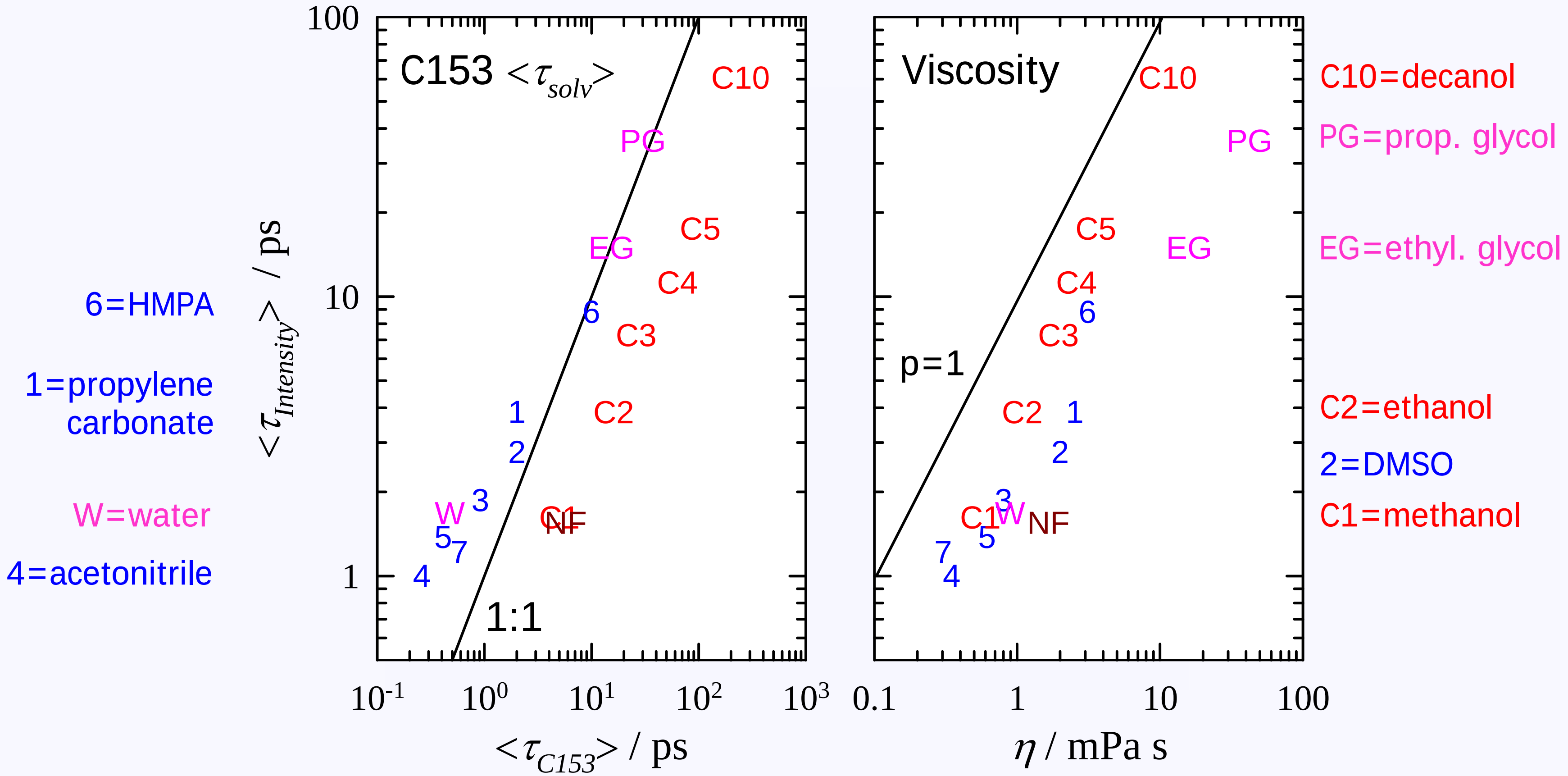
Normalized Spectra and Fits at These Times



- large Stokes shift + intensity loss
- intensity decays non-exponential
- marked red tail to emission

Solvent Dependent Lifetimes (25 °C)

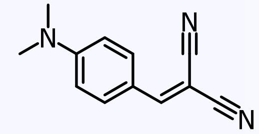
Correlations with Solvation Times and Viscosity

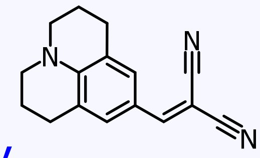


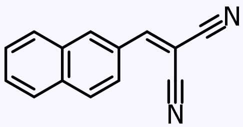
- decay times ≈ solvation times in many solvents but not in n-alcohols
- viscosity scaling nearly η^1 in n-alcohols; ps measurements of Huppert & co. show T, P dependence in n-alcohols also scales as $\sim\eta^1$

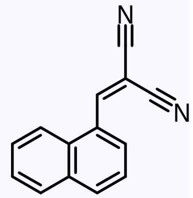
Summary

- the push-pull vinyl malononitriles & relatives we've studied share many common features:
  - highly solvatochromic
  - weakly fluorescent to rapid internal conversion
  - quantum yields & lifetimes sensitive to environmental fluidity (and polarity)
  - primary decay mechanism is twisting about vinyl linker

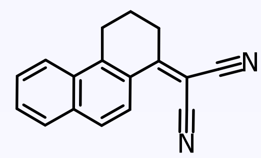




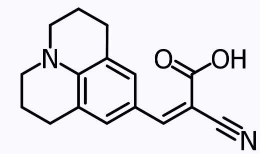




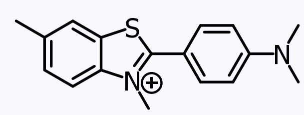
- quantum yields & lifetimes sensitive to environment: both fluidity and polarity
- in DMN and JDMN S_1 PES is relatively flat; lifetimes highly sensitive to small changes to PES; pretwisting important



- asymmetrically substituted may involve long-lived photoproducts so some care is necessary



- ThT^+ similar environmental sensitivity but mechanism is TICT process coupled to overall bend
- potentially better target for detailed modeling studies of environmental dependence



Acknowledgements

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Chris Rumble

ACS PRF

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