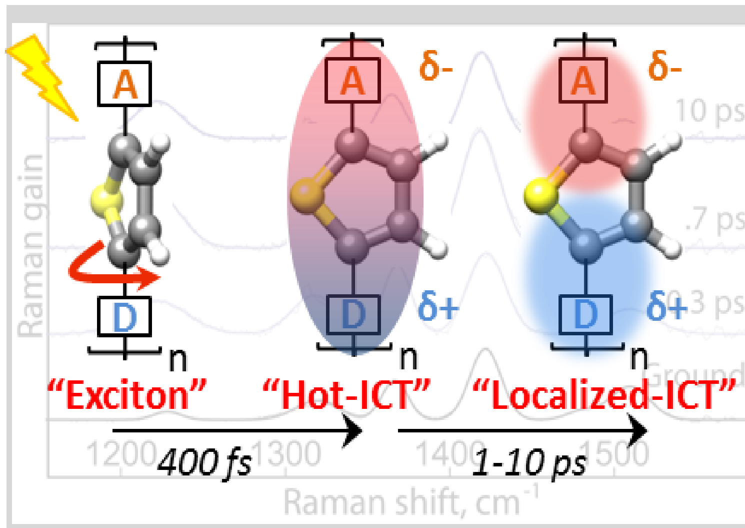
Raman Tracking of Charge Transfer States in Molecular Systems



ASET Colloquium @ TIFR, Mumbai on 14th July 2017

Jyotishman Dasgupta

Department of Chemical Sciences

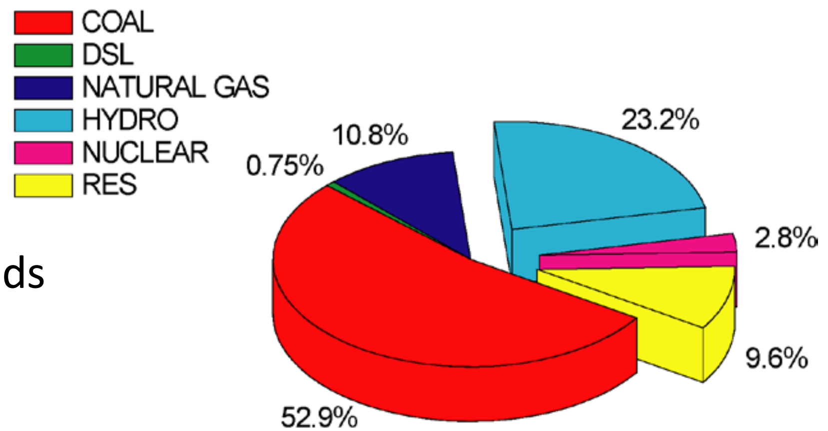
Tata Institute of Fundamental Research, Mumbai

Energy Status in INDIA: Need Renewable Sources

2010 : 160000 MW production

30 % power loss at distribution

2016: 18,500 villages and 50 million households without power



2010 Data Govt. of India

Electrical Energy needs for India in 2030:

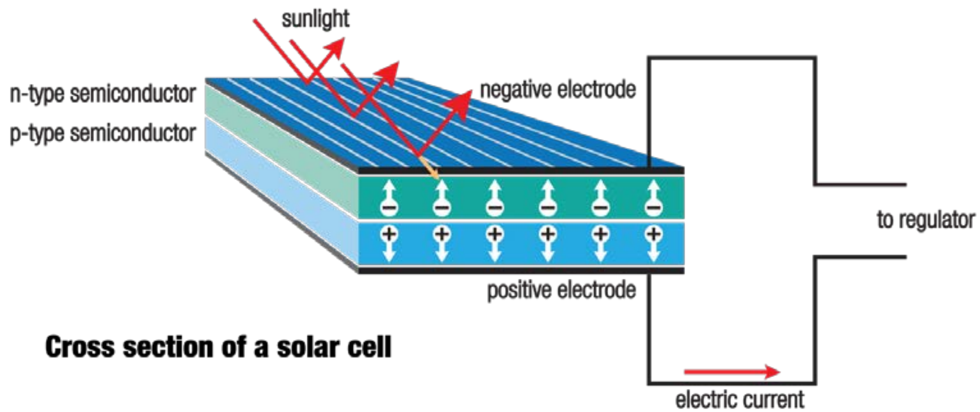
800,000 MW power (5 x the current production)

Primary commercial energy in 2030:

1400 mtoe (3x the current consumption)

The Government plans to achieve 100 GW solar power by 2022

Solar Energy Conversion: Photovoltaics



$$\text{Solar cell efficiency (\%)} = \frac{\text{Power out (W)} \times 100\%}{\text{Area (m}^2\text{)} \times 1000\ \text{W/m}^2}$$

1839 Becquerel discovered the Photovoltaic effect

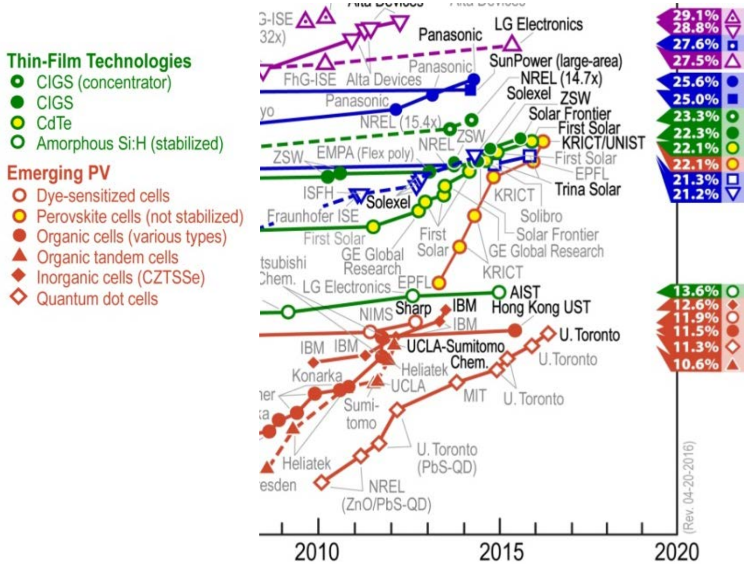
Interfacing materials with distinct electron affinities or Fermi energies

Light absorption >1.1 eV at the p-n junction leads to photocurrent

Current efficiencies > 25% for crystalline Si and ~10% for amorphous Si

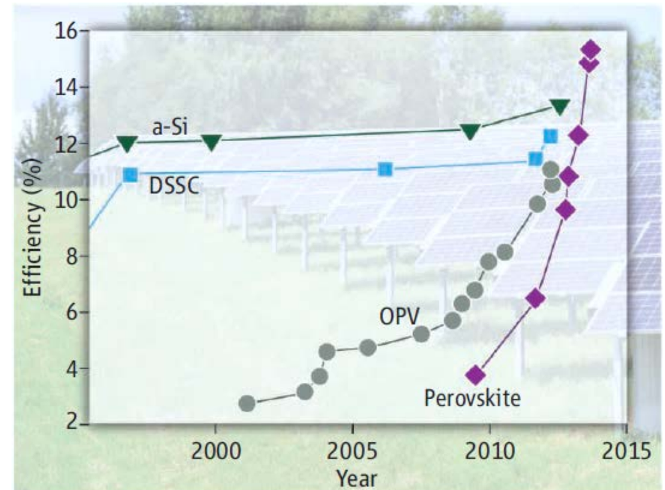
Current Si technology is Rs 30/KWh but we want Rs 5/KWh

Photovoltaics: Looking beyond Si



NREL chart

https://www.nrel.gov/pv/assets/images/efficiency-chart.png



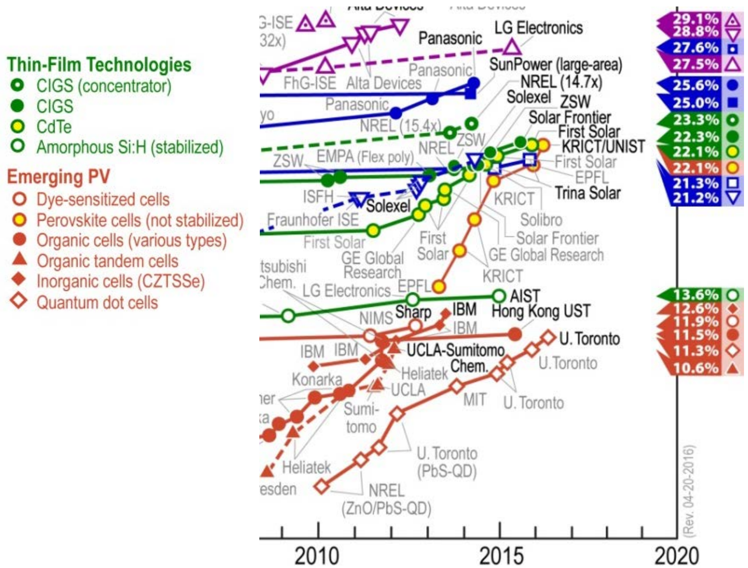
Gary Hodes, *Science,* **2014**

Cheap materials: Molecular? LARGE Absorption cross-section?

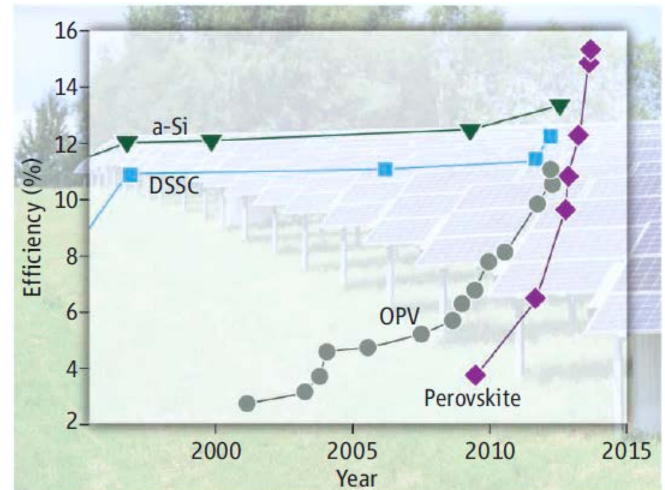
Interface Engineering: Solution process? Device Architecture?

New mechanisms: Singlet Fission or Multiple Exciton Generation

Photovoltaics: Looking beyond Si



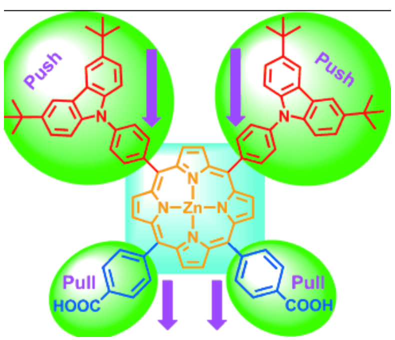
NREL chart



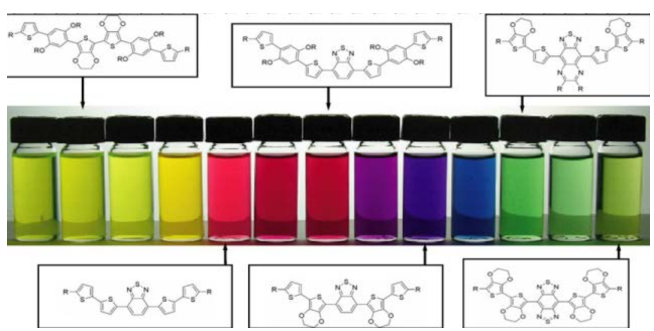
Gary Hodes, *Science,* **2014**

https://www.nrel.gov/pv/assets/images/efficiency-chart.png

Small Molecules

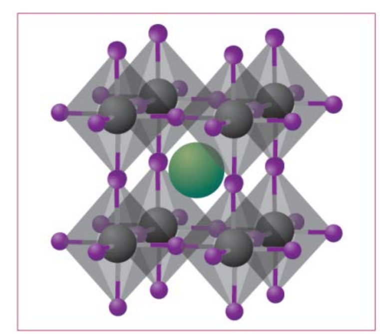


Conjugated Polymers



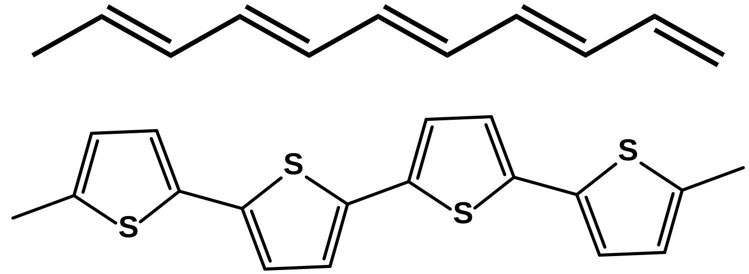
Quantum Dots

Pervoskite



Figures courtesy: Google Images

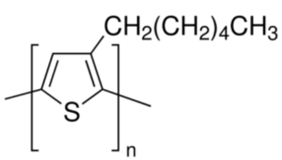
Organic Semiconductors: Tunable Bandgaps



Conjugated polymers!!!

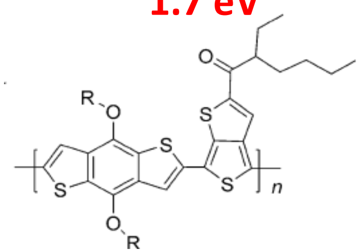
Bandgap can easily be tuned by introducing different chemical groups in polymer skeleton

High Bandgap Polymers
~2 eV



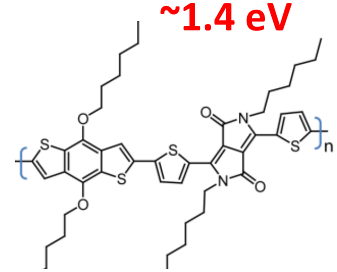
P3HT

Medium Bandgap Polymers
~1.7 eV



PBDTTT-C

Low Bandgap Polymers
~1.4 eV

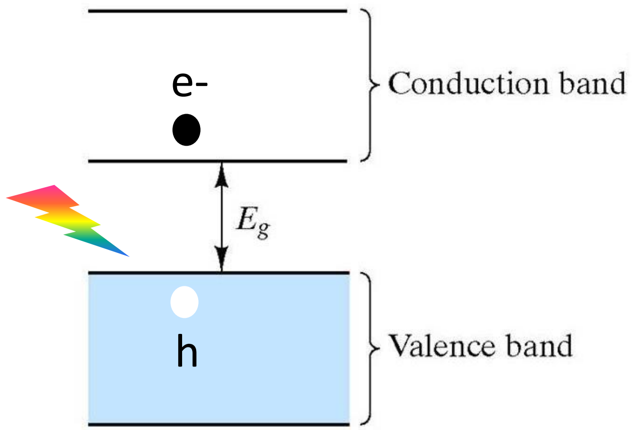


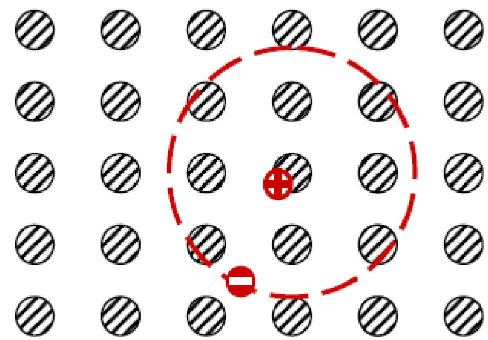
TDPP-BBT

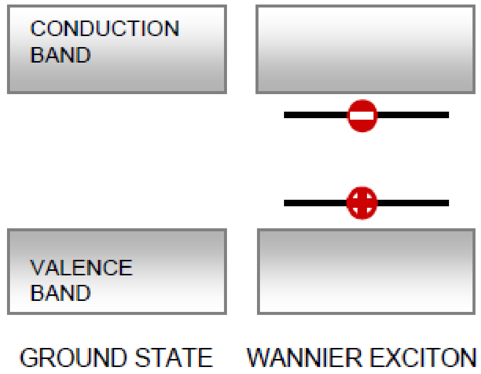
bandgap decreases

Polymer chemists: Klaus Mullen, Alan Heeger, Richard Friend, N. Sariciftci, Fred Wudl and more

Excitons : The Si advantage!







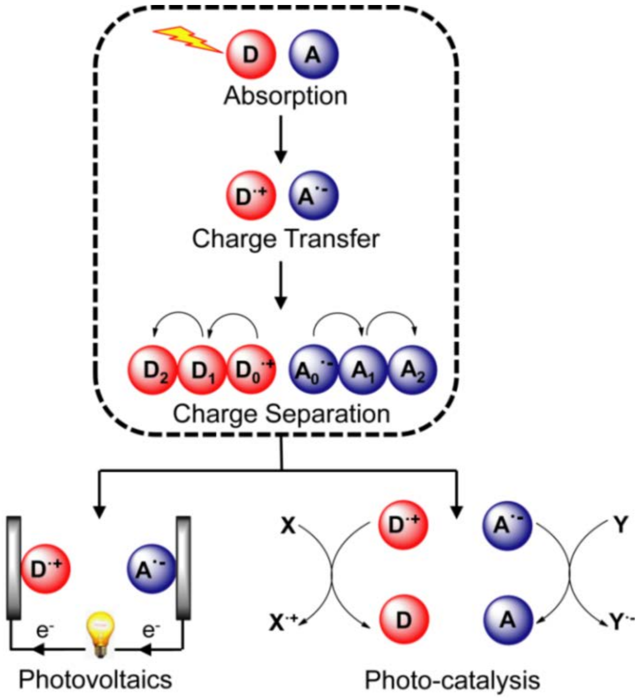
Pope and Swenberg

Charge-less particles (*electron-hole* bound pairs) that can diffuse

Excitons in Silicon
Radius ~ 10-20 nm
Binding energy ~ 10 meV

If the binding energy is comparable to room temperature
Easy to generate *FREE* charges!

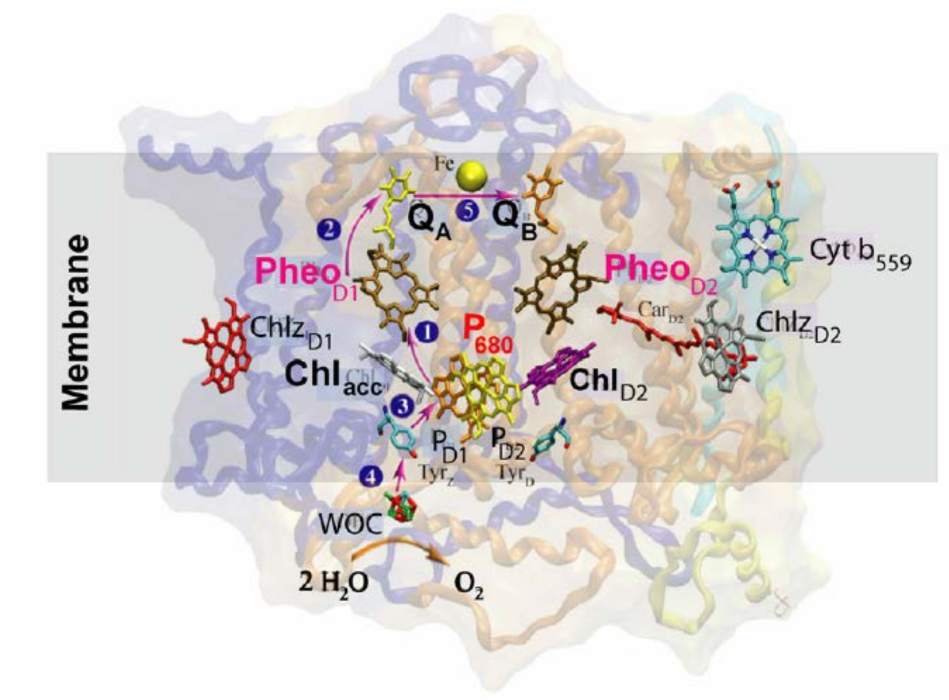
Charge Generation in Organics: The Central Dogma



Exciton binding energy: 400 - 1000 meV

Exciton radius: <1 nm i.e. on the backbone of the molecule

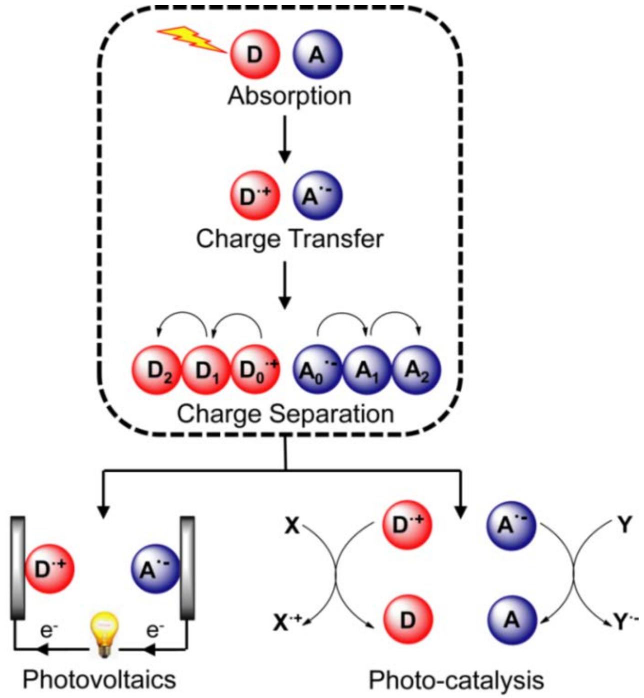
Charge Generation in Organics: The Central Dogma



Photosynthesis operates with multiple organic chromophores

Charge Transfer step key to FREE charges!

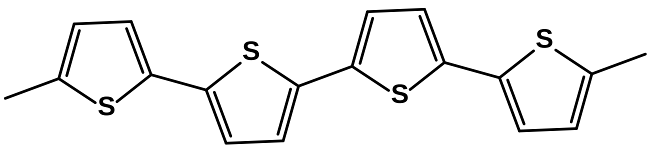
Charge Generation in Organics: The Central Dogma



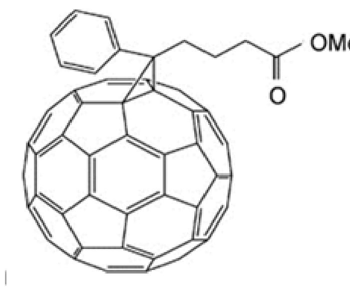
Stitching Donor-Acceptor Interfaces critical!

Charge Transfer step key to FREE charges!

Conceptual Idea of OPVs: Solution processing

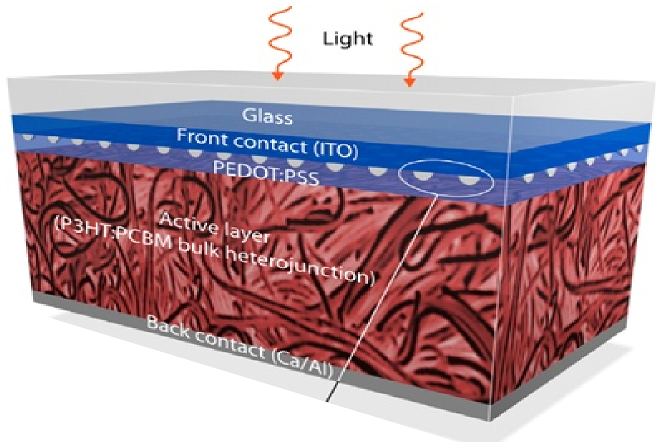


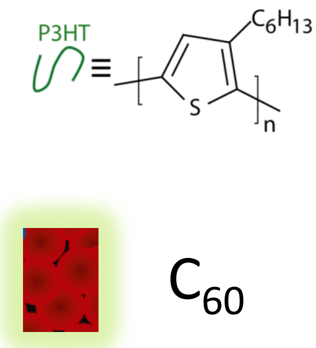
Richard Friend
Alan Heeger

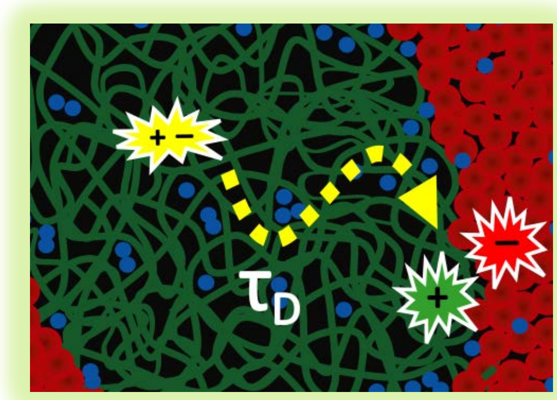


Polymer Donor

Fullerene Acceptor



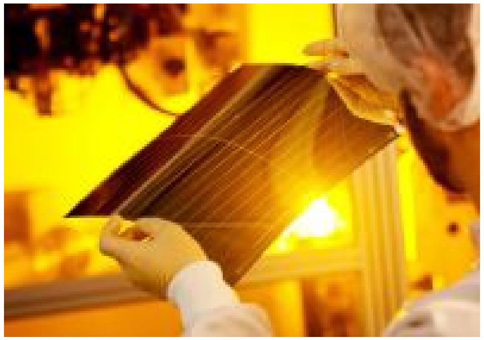




Simple spin casting on electrodes helps make these devices!

Key: *Heterojunction architecture*

Organic Photovoltaics: Current Trends

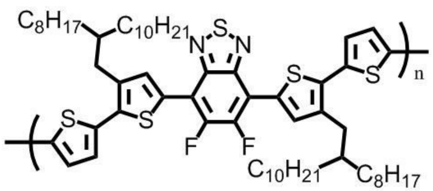


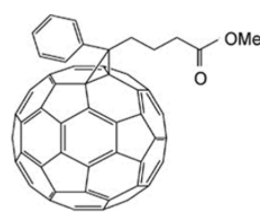
Donor-π-Acceptor Polymer/ Fullerene

OPV efficiency of 13.2%

2016 Press release from Heliatek Inc

Fullerene-based





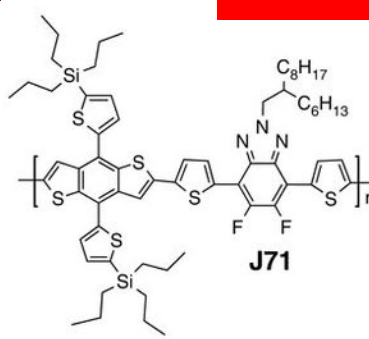
Dinesh Kabra, IIT Bombay

OPV Efficiency ~ 9%

0.77 V from Bandgap of 1.6 eV

unpublished results

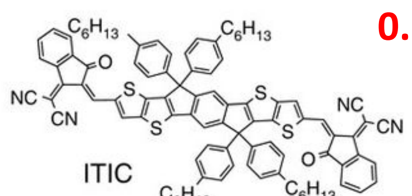
Non-Fullerene based



J71

OPV efficiency of 11.4 %

0.96 V from Bandgap of 2.16 eV

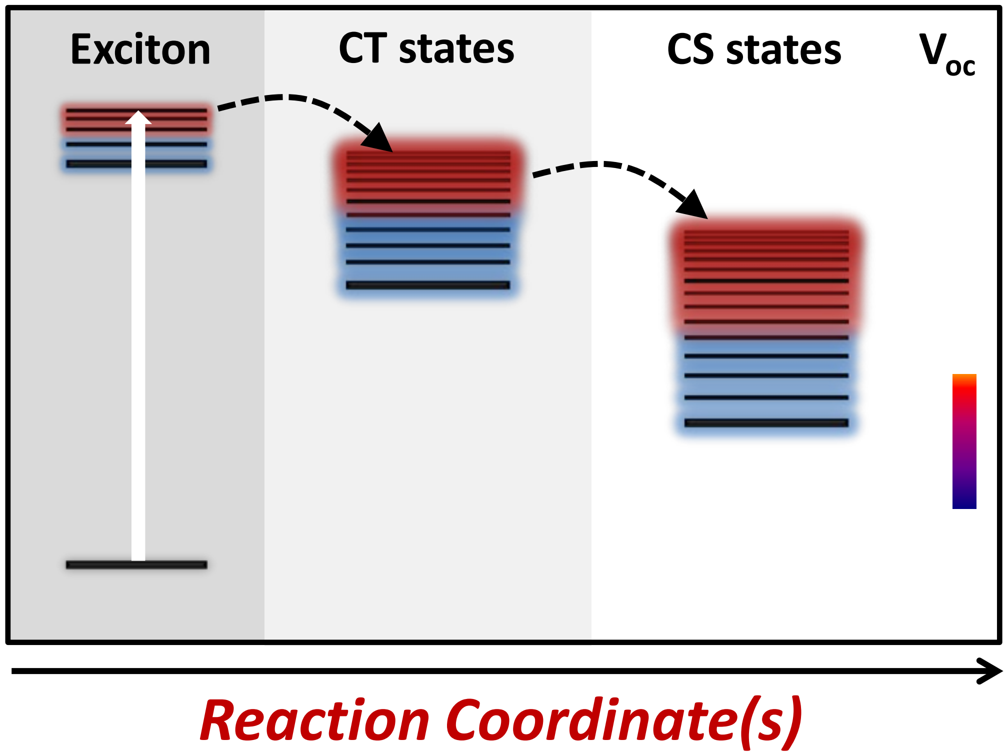


ITIC

Chinese Academy of Sciences

Nature Communications, **7**, 13651 (2016)

Charge Generation and Energy Loss in OPVs!



Loss of e … **action**

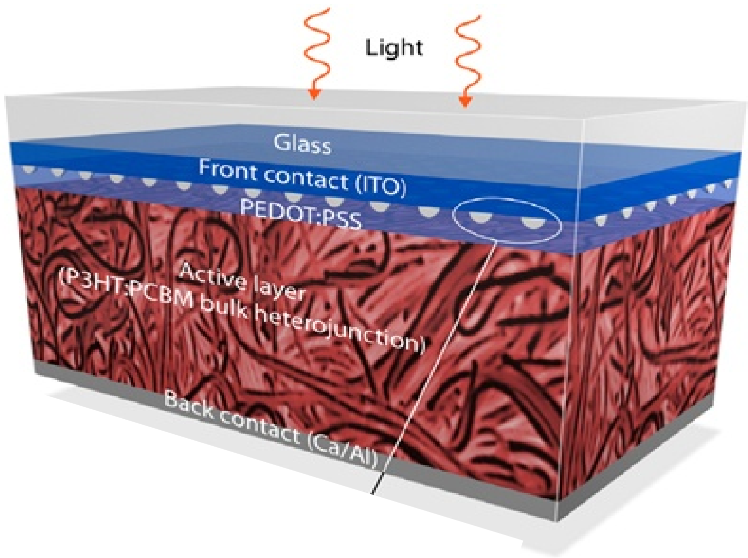
Relaxation … wed down

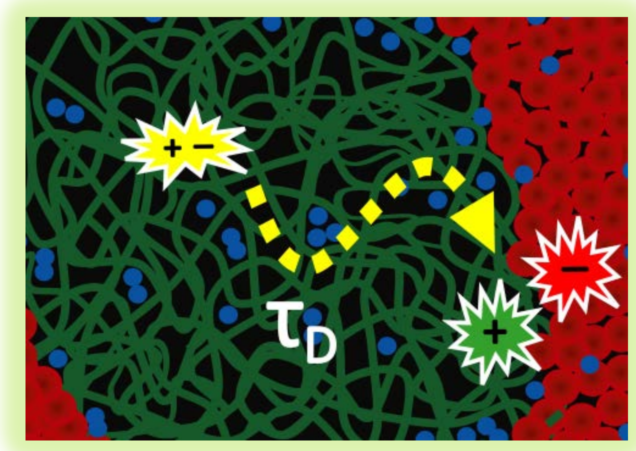
$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \times 100\%$$

Multi-exciton generation for increasing the efficiency

Singlet Fission can generate multiple Triplet EXCITONS!

Inside a BHJ Solar Cell: *Polymer:Fullerene* Interfaces!



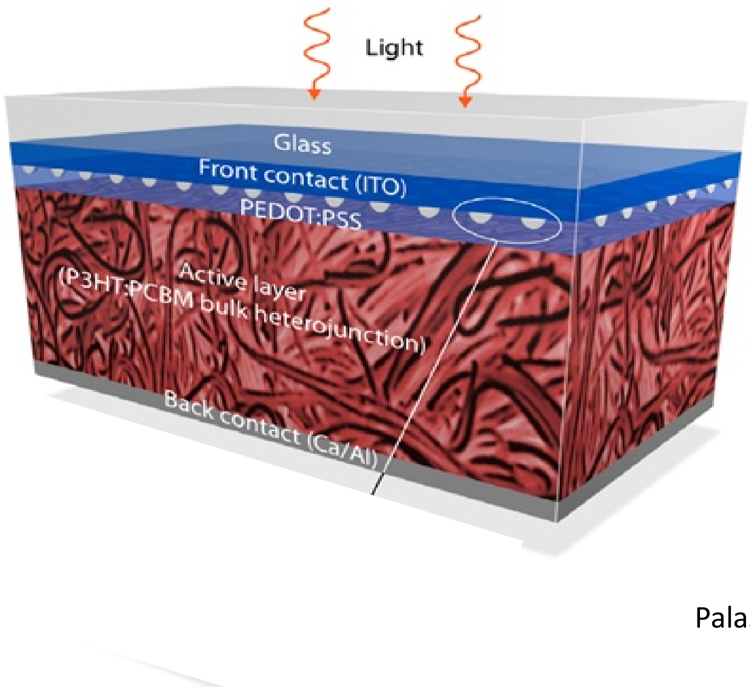


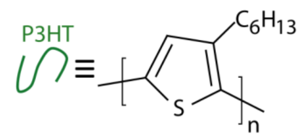
Solvent engineering of the morphology very critical for efficient charge extraction

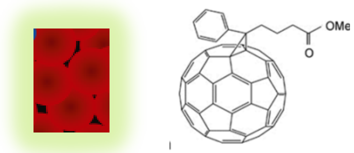
Early studies: Sariciftci and co-workers; Heeger and co-workers (2001)

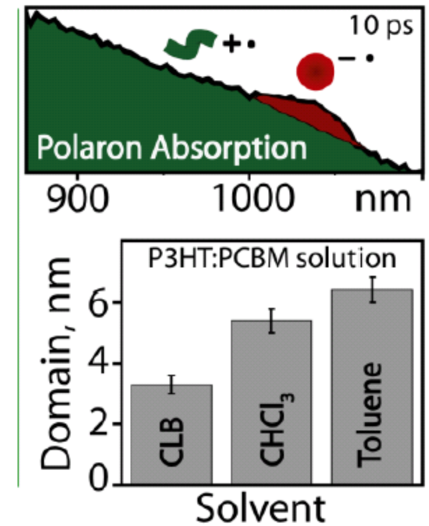
Ternary phase as a seed: Janssen and co-workers (2013, 2015); Dasgupta and co-workers (2016)

Inside a BHJ Solar Cell: *Polymer:Fullerene* Interfaces!









Palas Roy, Ajay Jha and Jyotishman Dasgupta; *Nanoscale* 2016, **8**, 2768-2777

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Ternary phase as a seed: Janssen and co-workers (2013, 2015); Dasgupta and co-workers (2016)

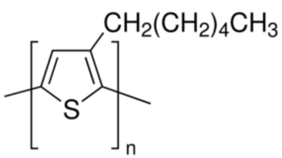
Limits to energy conversion: Track the *Singlet Excitons* and *Charge Generation*

Bulk TA measurements: Natalie Banerjee, Eric Vauthey; Heeger and co-workers; Ito and co-workers

Exciton Imaging: Libai Huang and co-workers; Naomi Ginsberg and group; Dario Polli and co-workers Papanikolas and co-workers

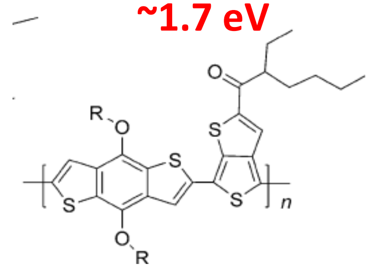
Low-bandgap Polymers: Donor-Acceptors Stitched!

High Bandgap Polymers
~2 eV



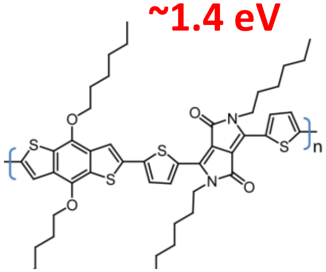
P3HT

Medium Bandgap Polymers
~1.7 eV



PBDTTT-C

Low Bandgap Polymers
~1.4 eV



TDPP-BBT

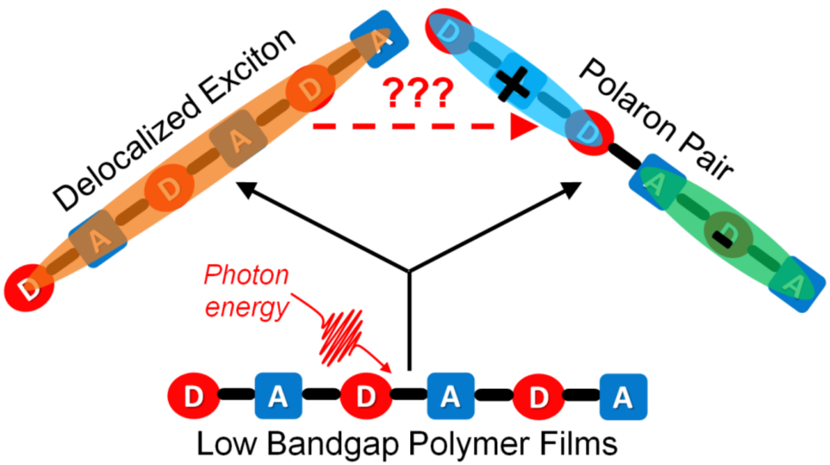
bandgap and exciton lifetime decreases

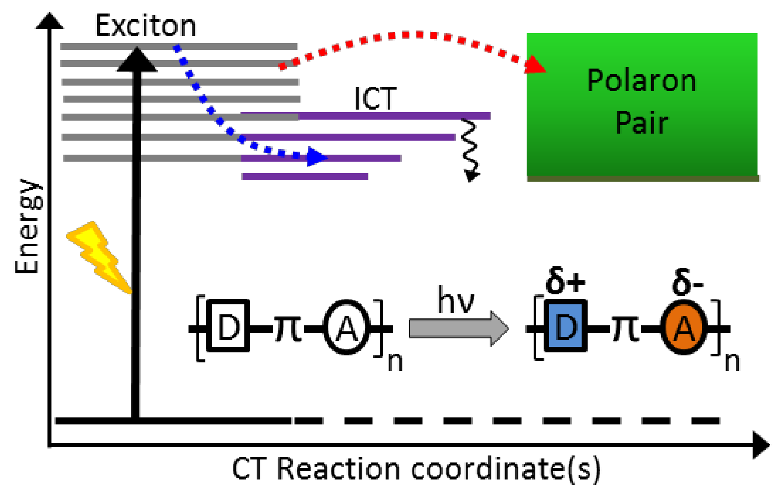
DONOR-(π BRIDGE)-ACCEPTOR

Chemical design incorporates these ideas!

These polymers work as OPV materials possibly because of strong ICT

Excitons Dynamics in Donor-π-Acceptor Polymers



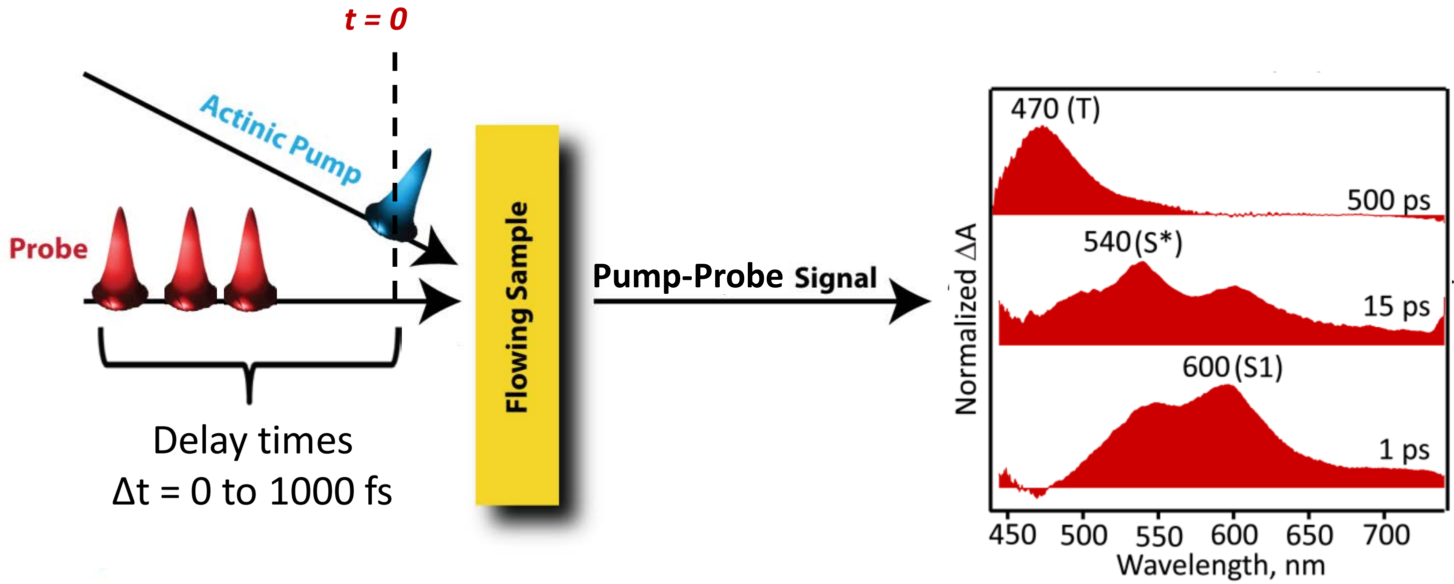


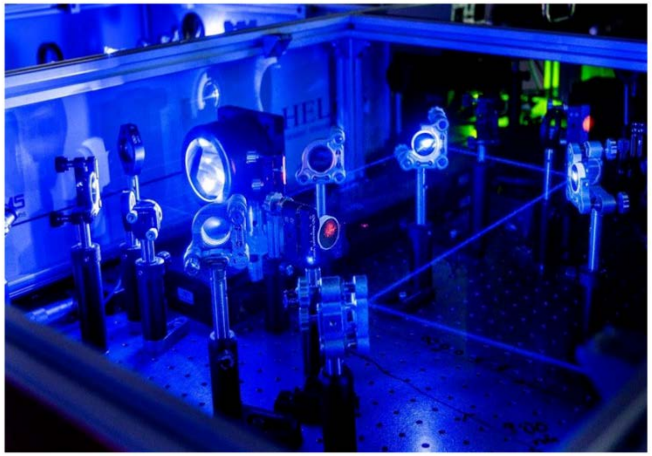
Exciton dissociation and dynamics key towards optimizing charges!

The Fundamental Question is:

What is the reaction coordinate for Exciton-to-Charges reaction?

Tracking of Excited States: Transient Absorption



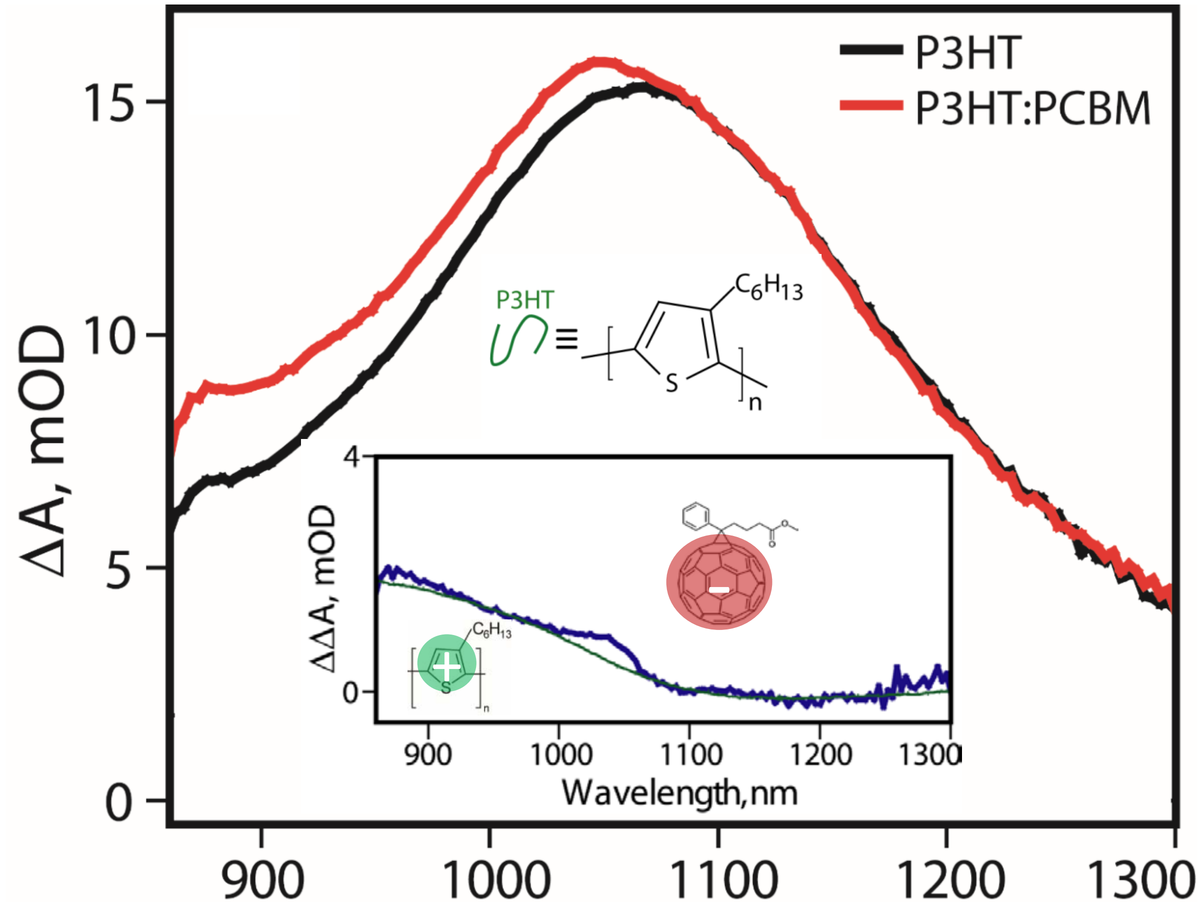


Femtosecond Pump-Probe experiment:

Creates a temporal map of RAPID events

With ~50 fs resolution we can watch events till nanoseconds

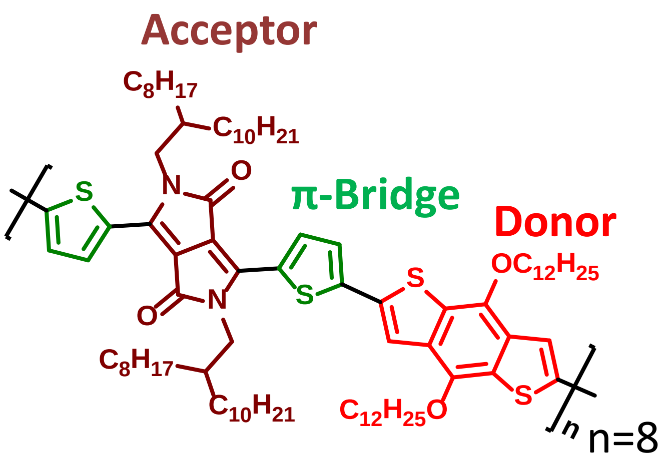
Tracking *Excitons* and *Charges:* Pump-Probe Data



Palas Roy et al. *Nanoscale* **2016**, 8, 2768-2777

Broad features in electronic absorption features limits the understanding

Complexity of Structure and Transitions: D-π-A polymer

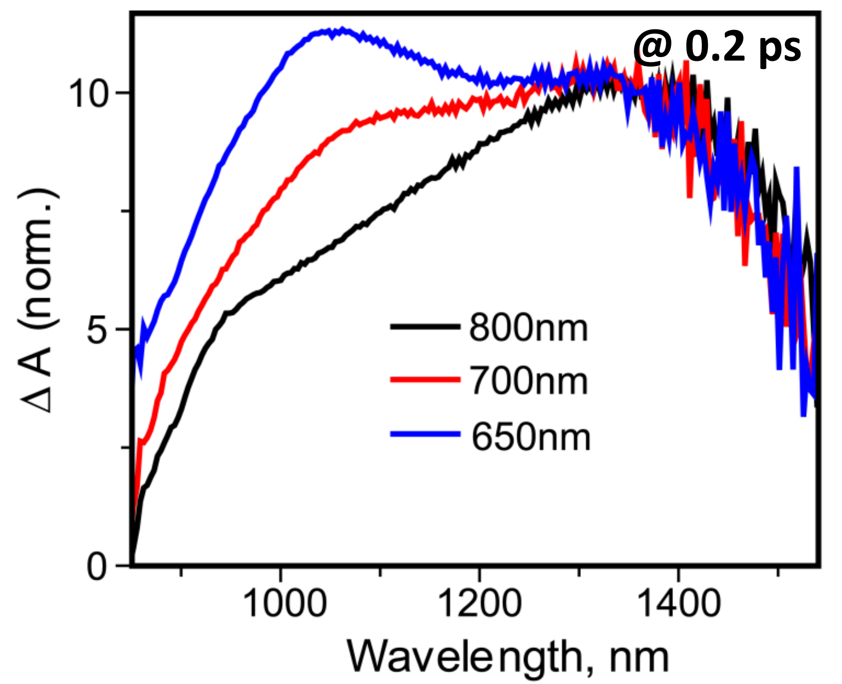


TDPP-BBT

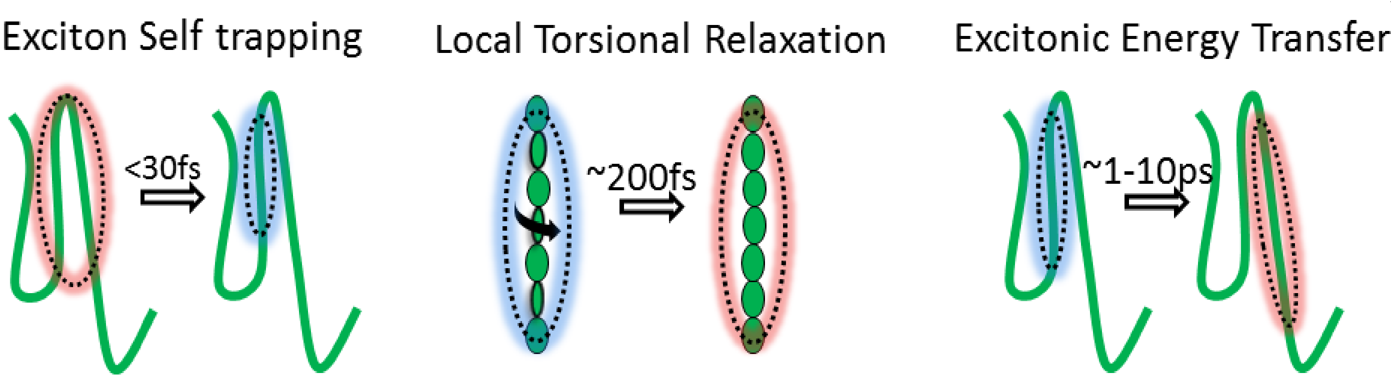
Higher conformational degrees of freedom

Multiple excited states!

with Prof. Satish Patil, IISc Bangalore



Exciton Dynamics: How to resolve then?



Adapted from Greg Scholes and co-workers, *Chem. Mater.* 2010

Time-resolved Vibrational Spectroscopy

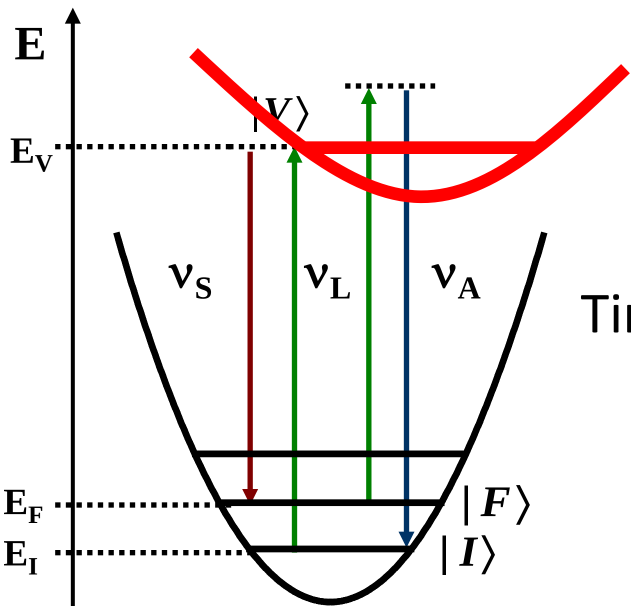
Will track the structural changes happen once the Exciton is generated

Can we track the reaction coordinate for Relaxation?

RAMAN SPECTROSCOPY and Resonance Effect

Sir C.V. Raman

Electronic Resonance Effect on Raman intensities!



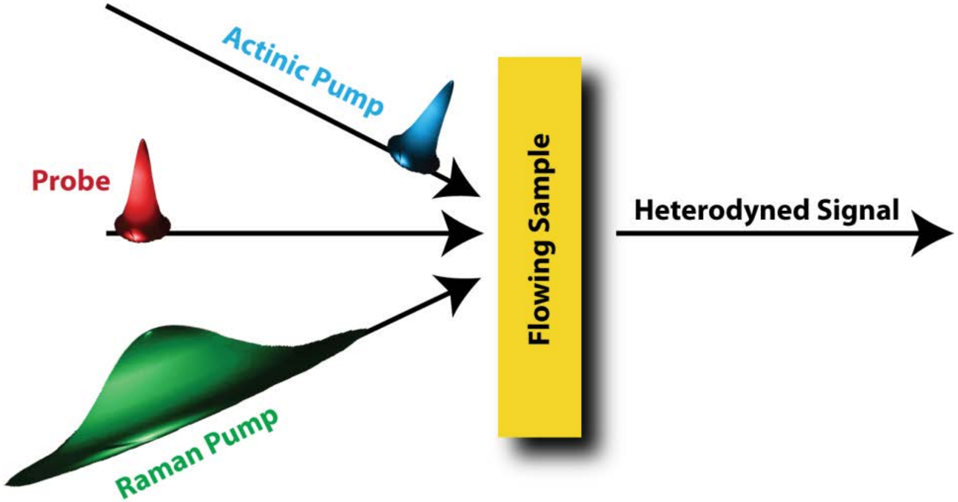
$$\sigma_{Ram} = k^* E_L E_s^3 M^4 \left| \sum_v \frac{\langle f|v\rangle \langle v|i\rangle}{(E_V - E_I - E_L - i\Gamma)} \right|^2$$

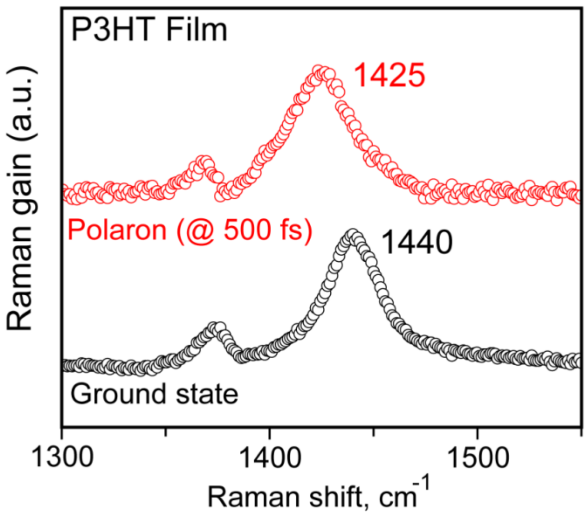
Time-resolved studies limited to picosecond regime

$$\Delta\nu \approx \frac{15\ cm^{-1}}{ps}$$

1 ps ~ 15 cm^{-1} vs 100 fs ~ 150 cm^{-1}

Femtosecond Stimulated Raman Spectroscopy





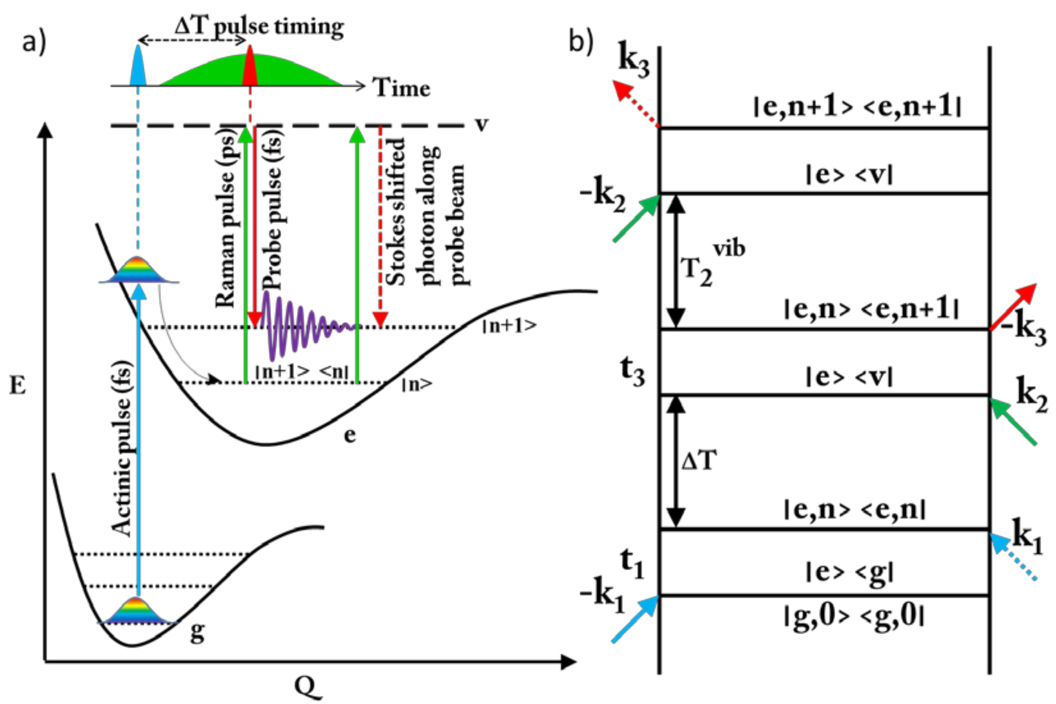
Concept: *Rich Mathies (UC Berkeley)*
M. Yoshizawa (University of Tokyo)

Palas Roy

Kukura, McCamant and Mathies, *Annu. Rev. Phys. Chem*. (2007)
Dasgupta, Fronteira, Fang and Mathies in *Encyclopaedia of Biophysics* (2012)
Ajay Jha and JD, *ISRAPS Bulletin* (2013)
Hoffman and Mathies, *Acc. Chem. Res.* (2016)
Palas Roy, Shreetama Karmakar and JD in *Handbook of Molecular Spectroscopy* (2017)

3 pulses needed: Raman pump on top of the two other pulses

Femtosecond Stimulated Raman Spectroscopy



Kukura, McCamant and Mathies, *Annu. Rev. Phys. Chem*. (2007)
Dasgupta, Fronteira, Fang and Mathies in *Encyclopaedia of Biophysics* (2012)
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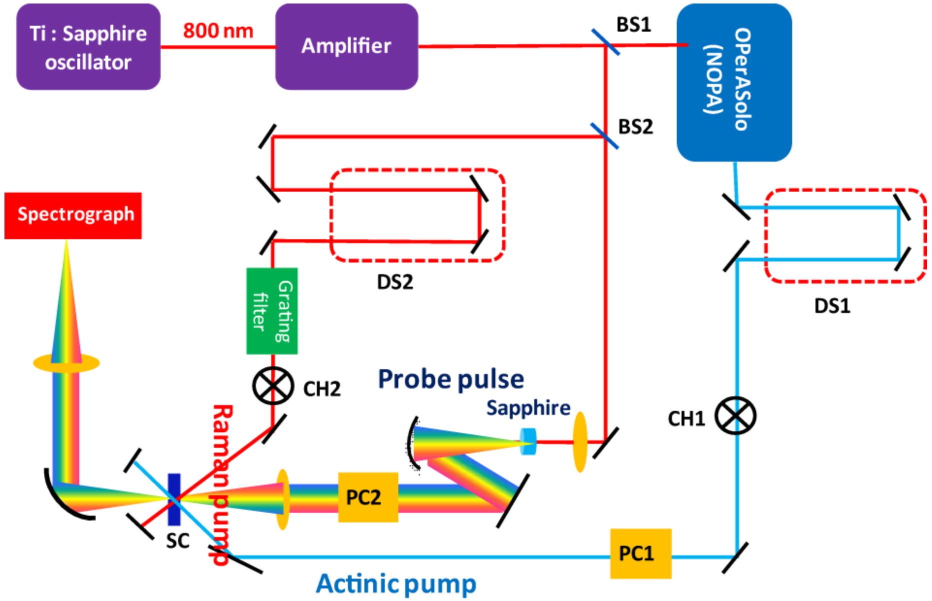
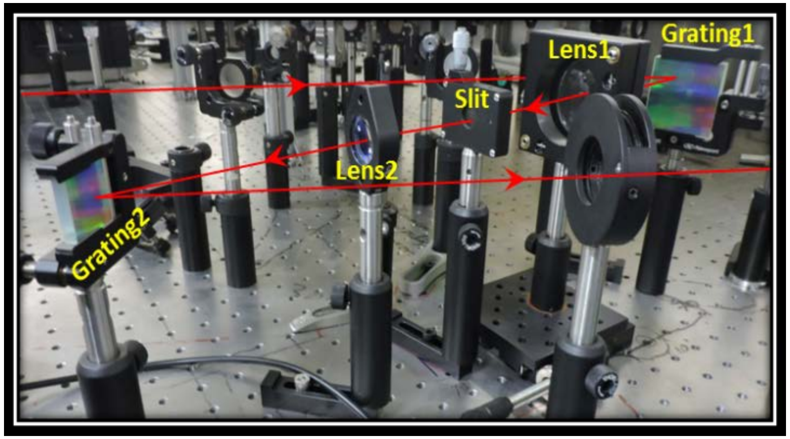
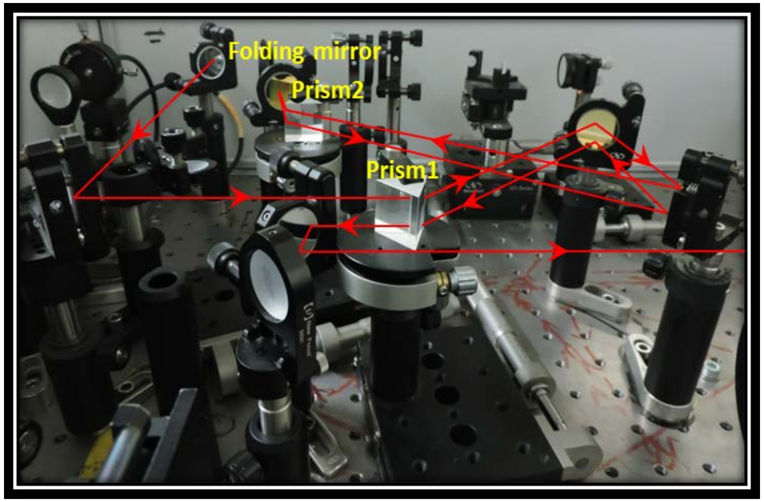
At TIFR: Our FSRS set-up



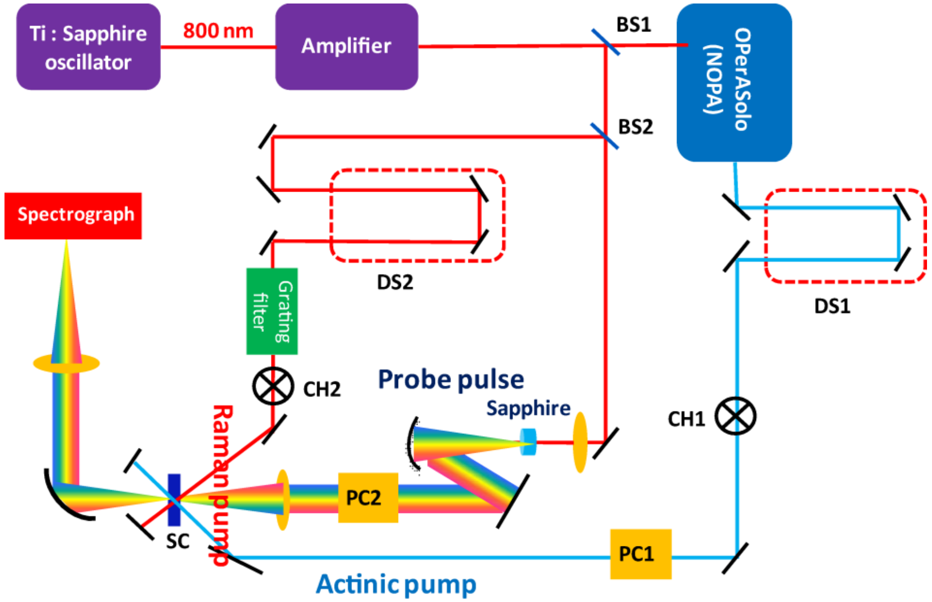


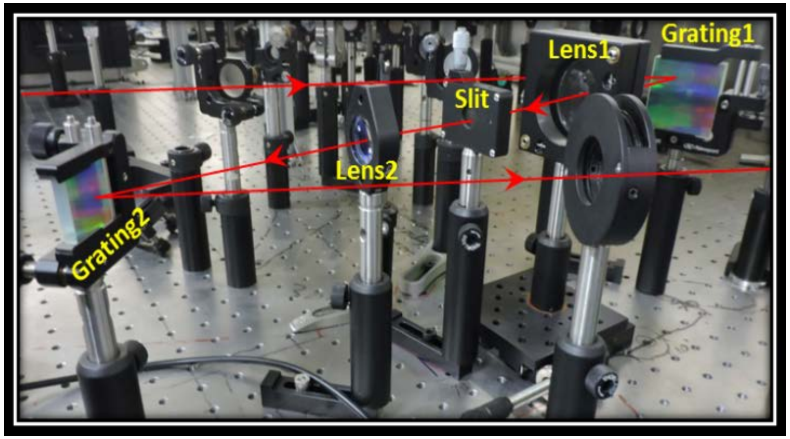
Grating Filter for Raman pump



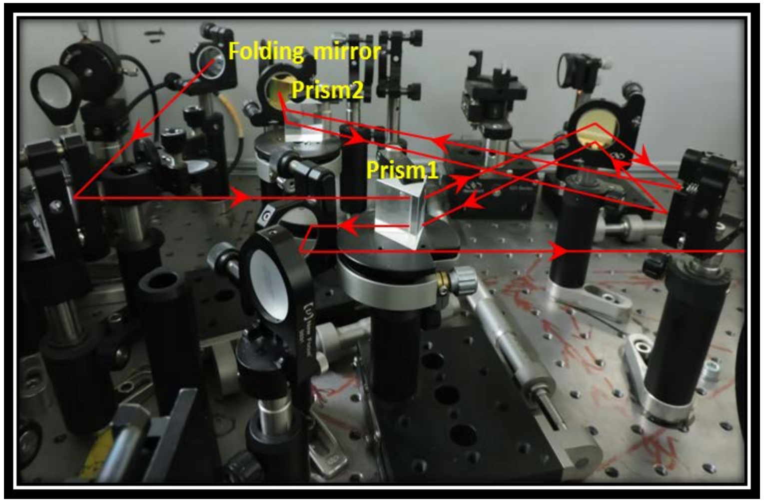
Palas Roy, Ajay Jha, Vineeth Benyamin and Thulasi Ram

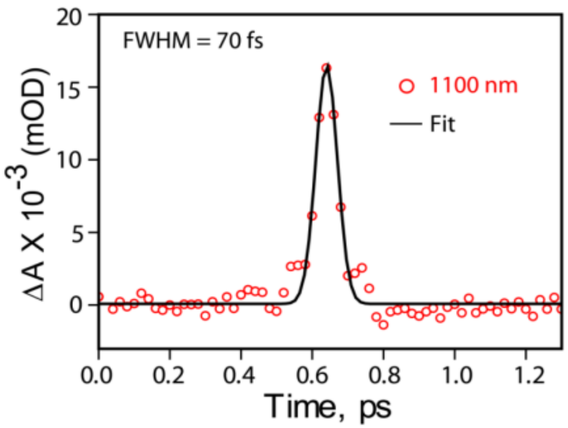
At TIFR: Our FSRS set-up

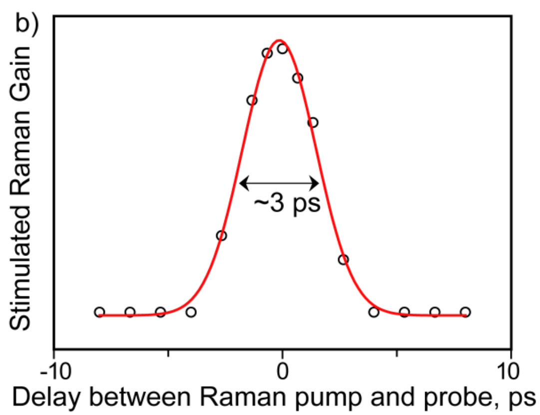




Grating Filter for Raman pump

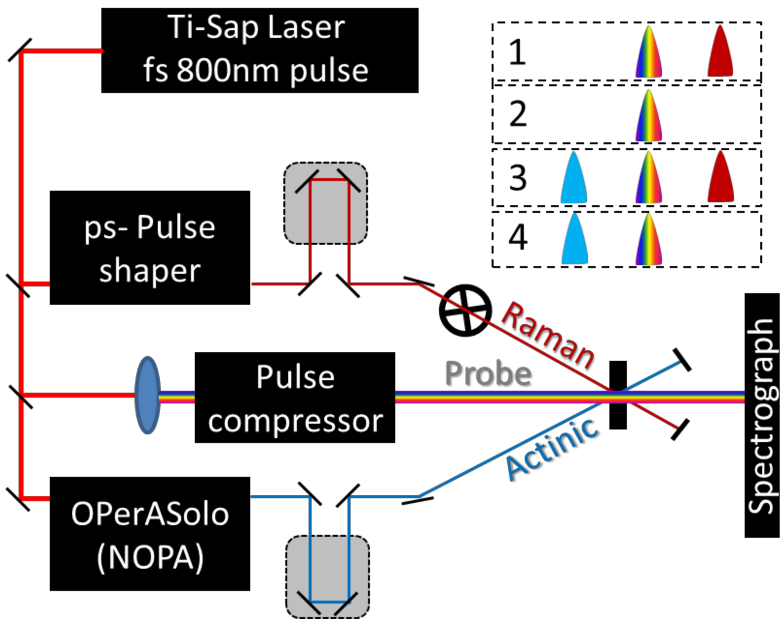


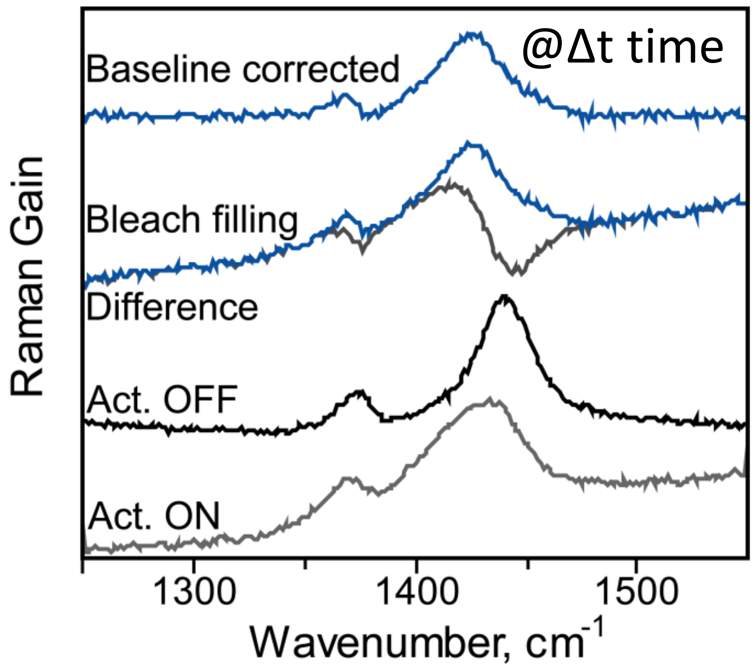




Palas Roy, Ajay Jha, Vineeth Benyamin and Thulasi Ram

At TIFR: Our FSRS set-up with NIR probe





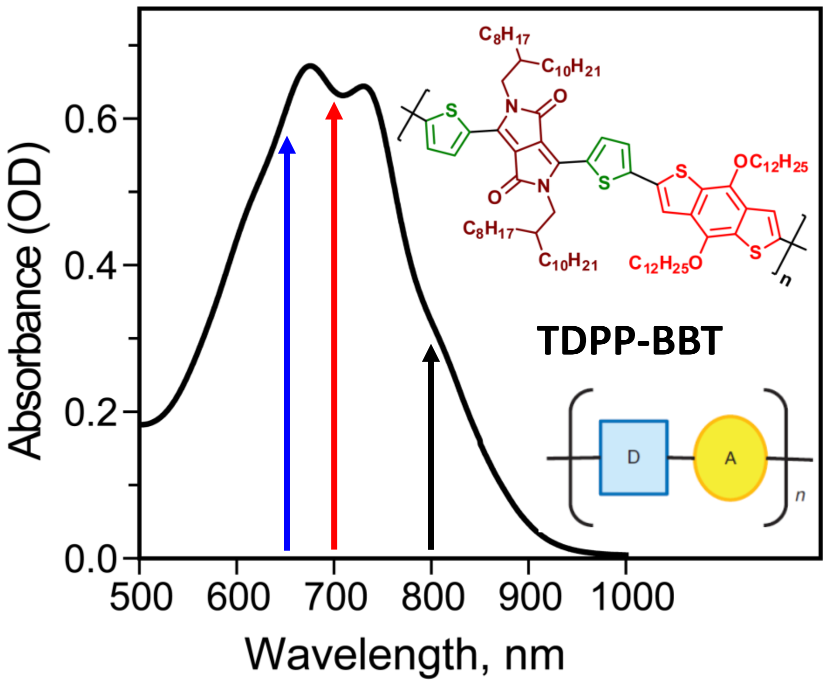
fs-Actinic pulse
Starts the Photochemistry
10-500 nJ/pulse

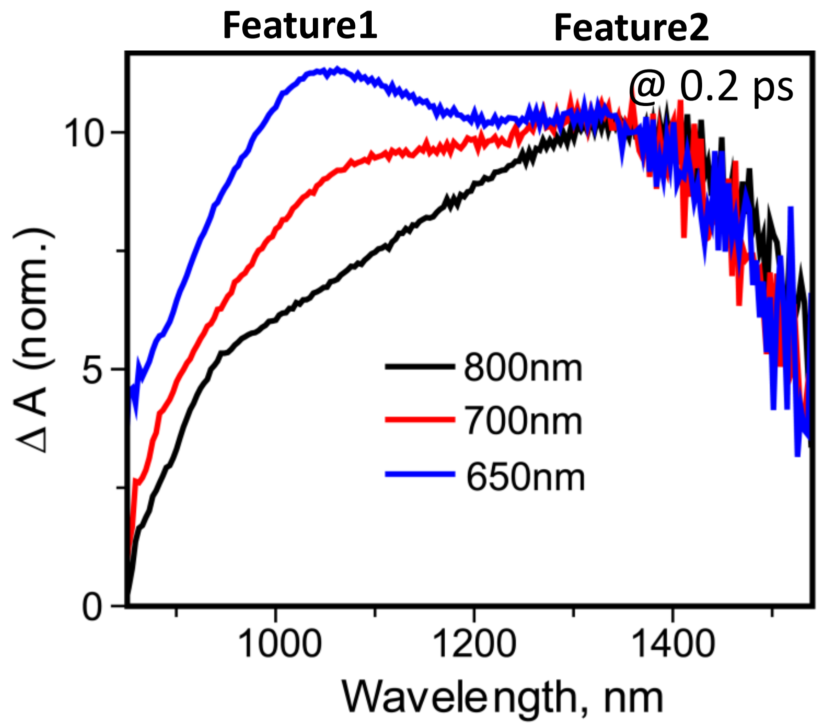
ps-Raman Narrow band pulse
Spectral width (~10 cm^{-1})
0.5 to 1 µJ/pulse; 780-840 nm

fs-Probe Broadband pulse
Pulse width(~15 fs)
800-1200 nm; 20 nJ/pulse

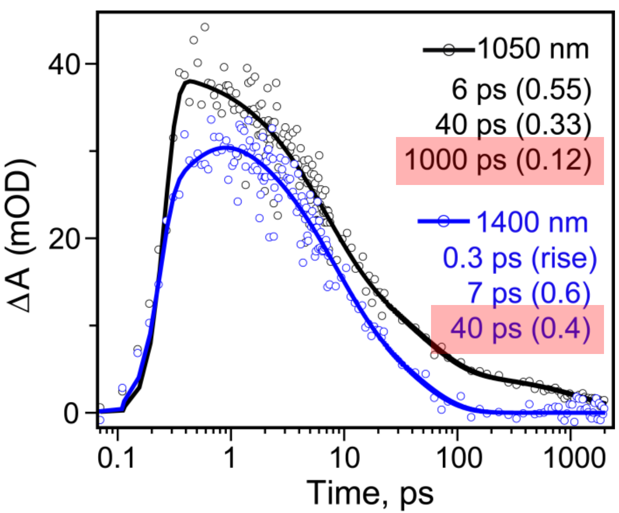
Excited state FSRS can be plotted by filling in the GS contribution

Nature of the excited states present: TA

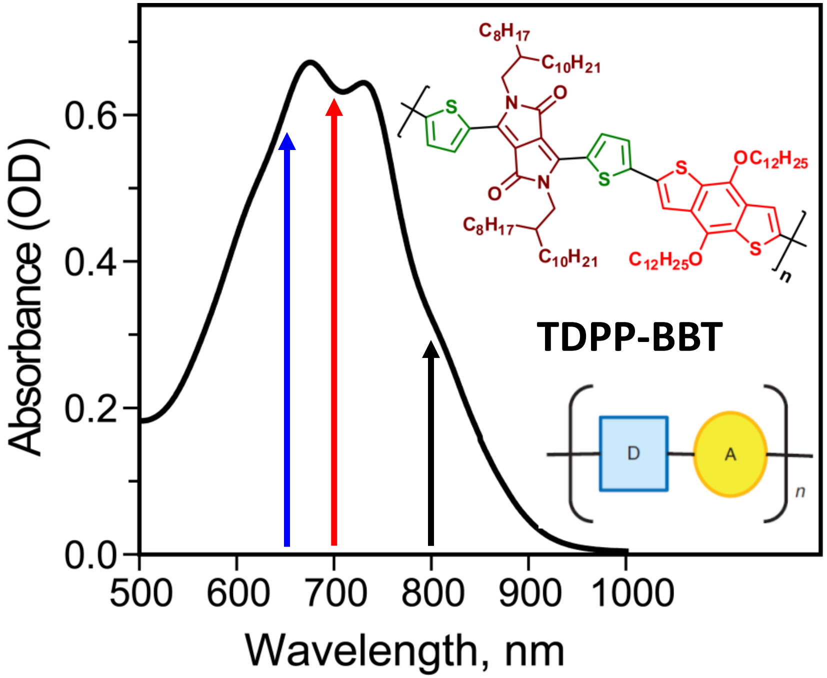


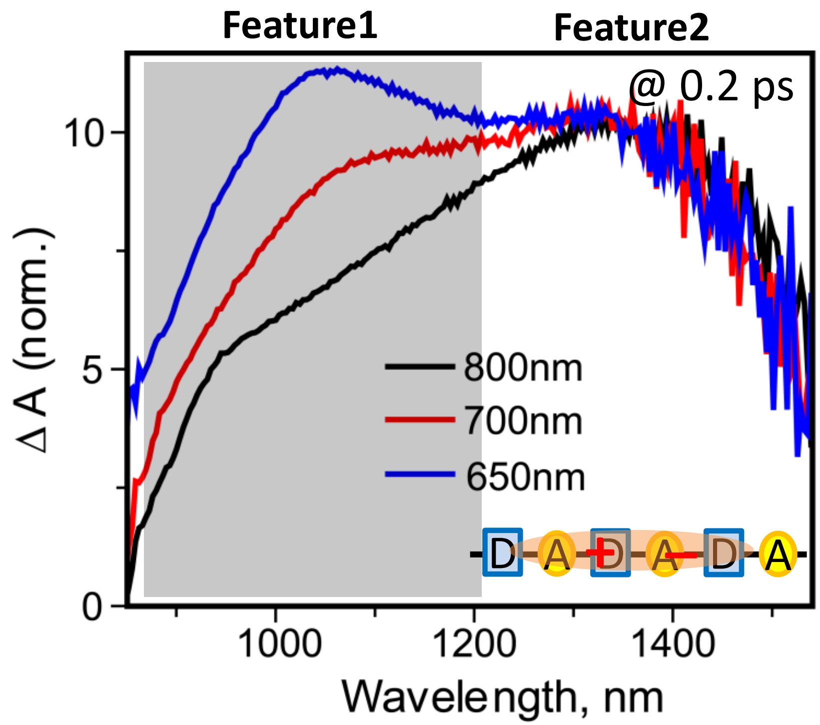


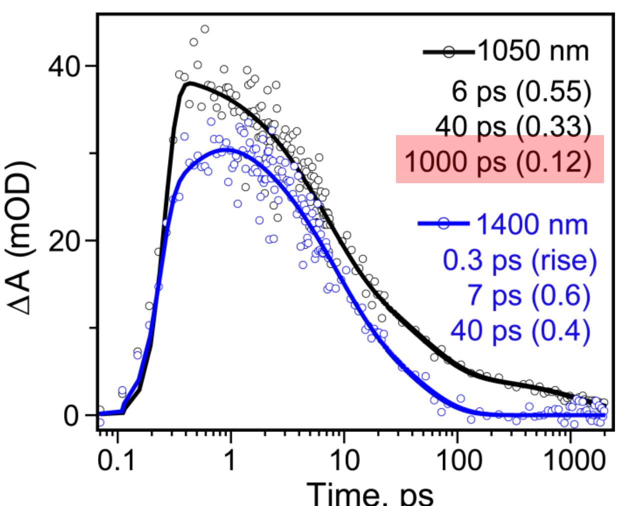
Conformational heterogeneity

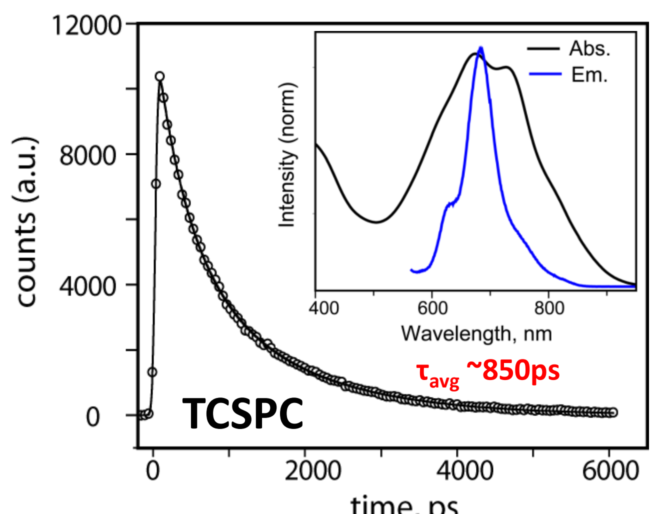


Nature of the excited states present: TA



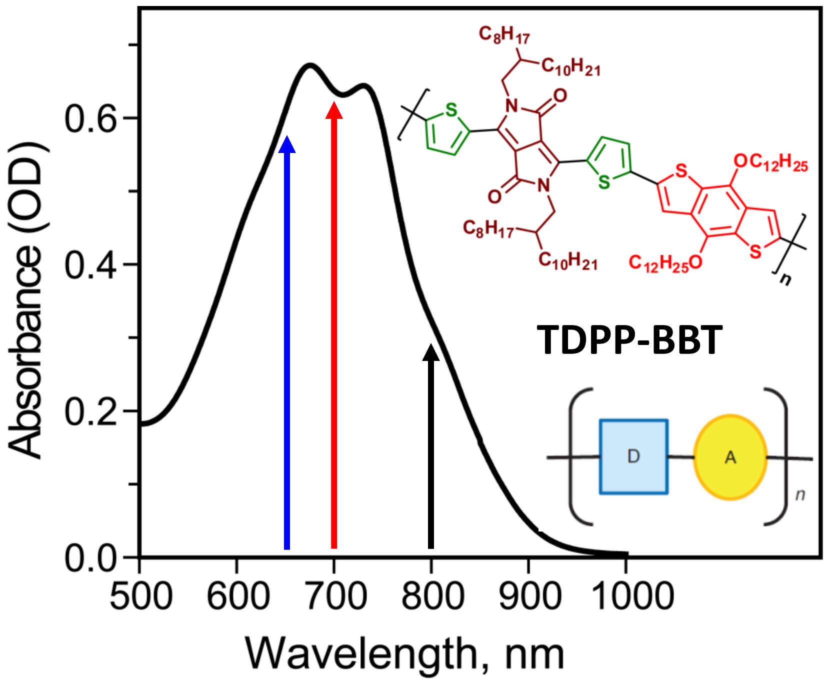


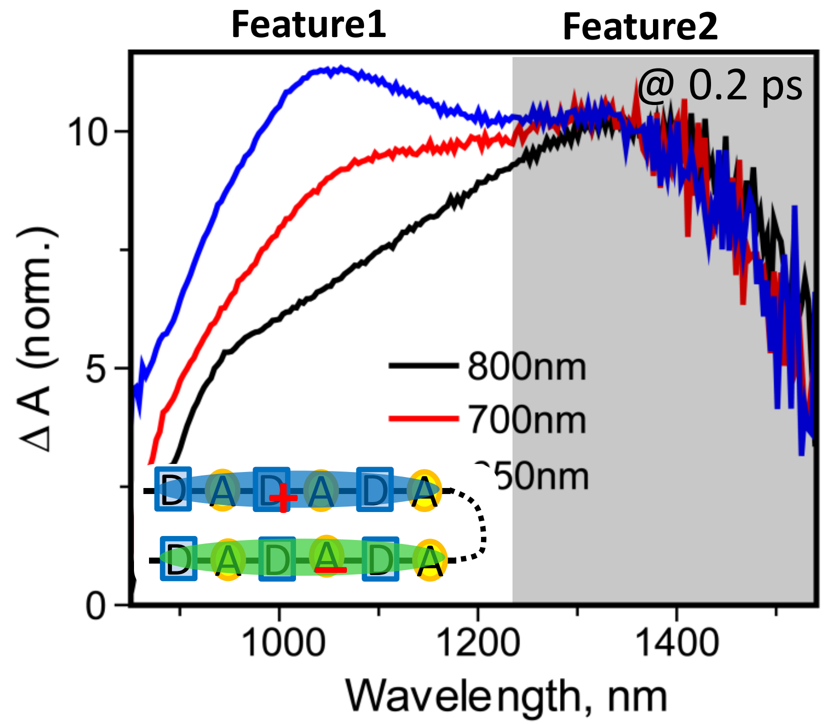


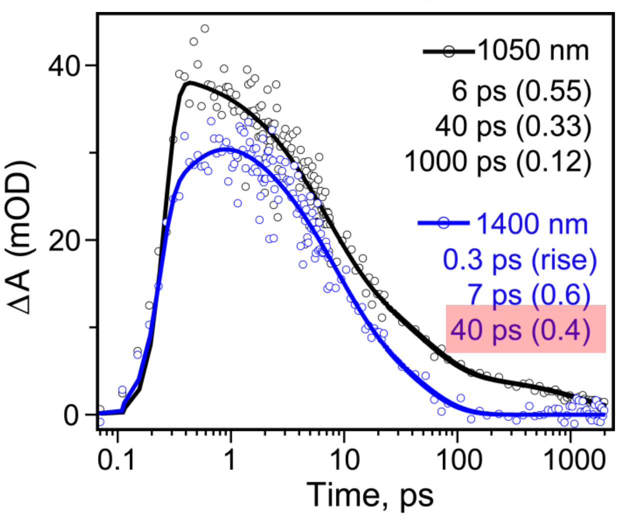


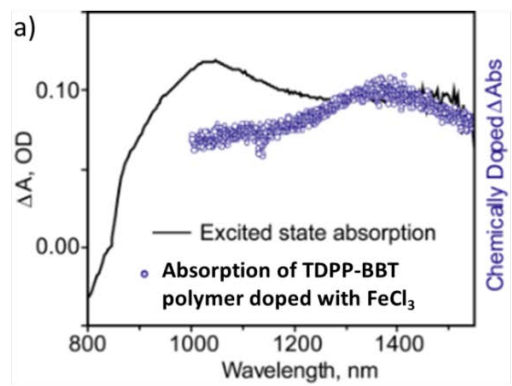
Feature 1:
Long lived singlet
Exciton

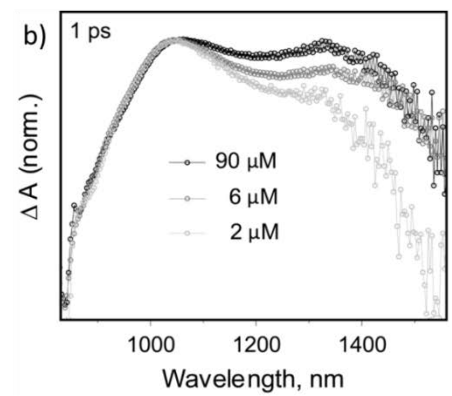
Nature of the excited states present: TA





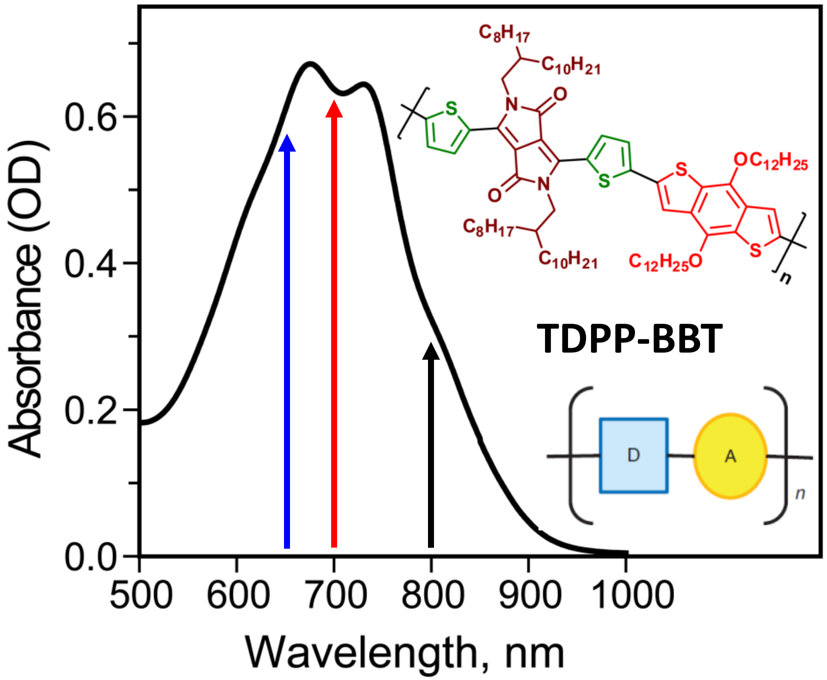


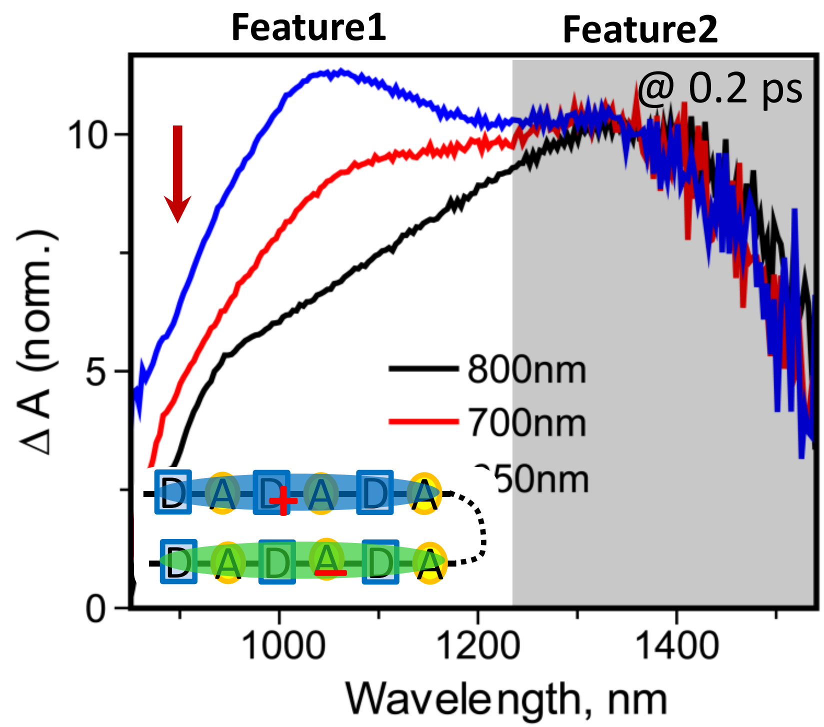


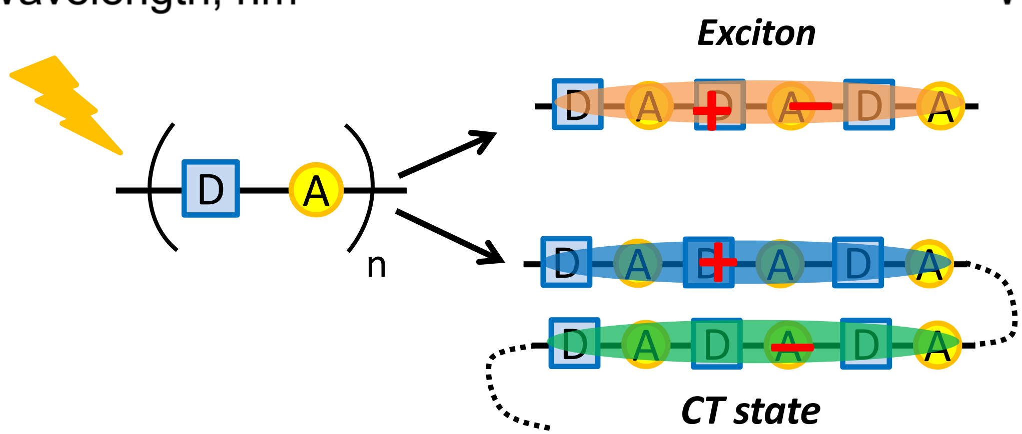


Feature 2: Polaron Pair or CT state

Nature of the excited states present: TA

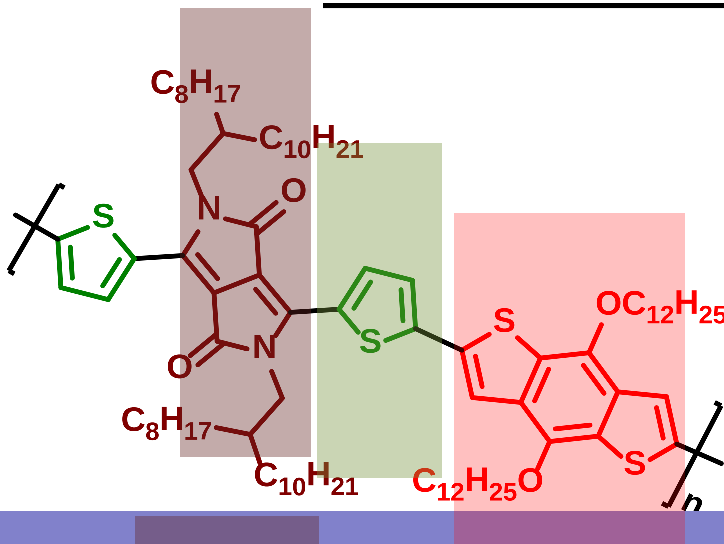


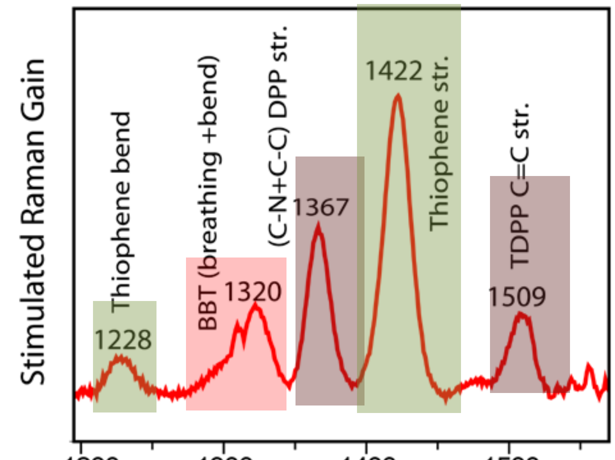


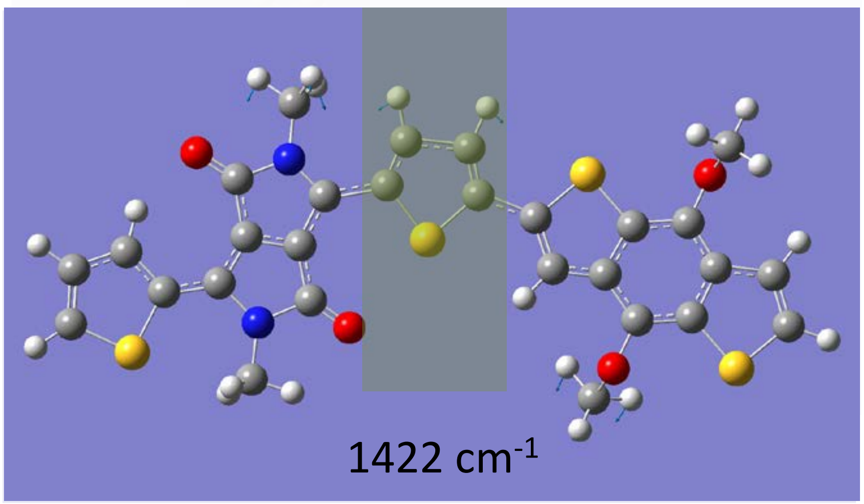


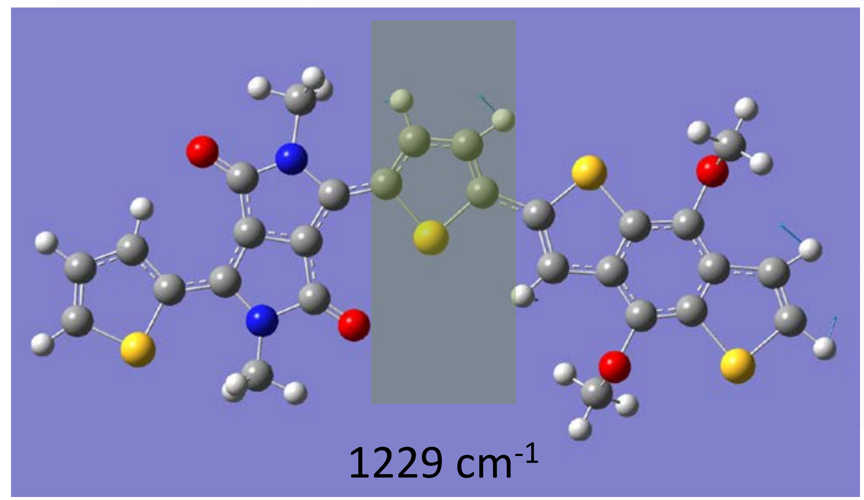
Can we selectively probe the Exciton?

Ground state Raman of TDPP-BBT



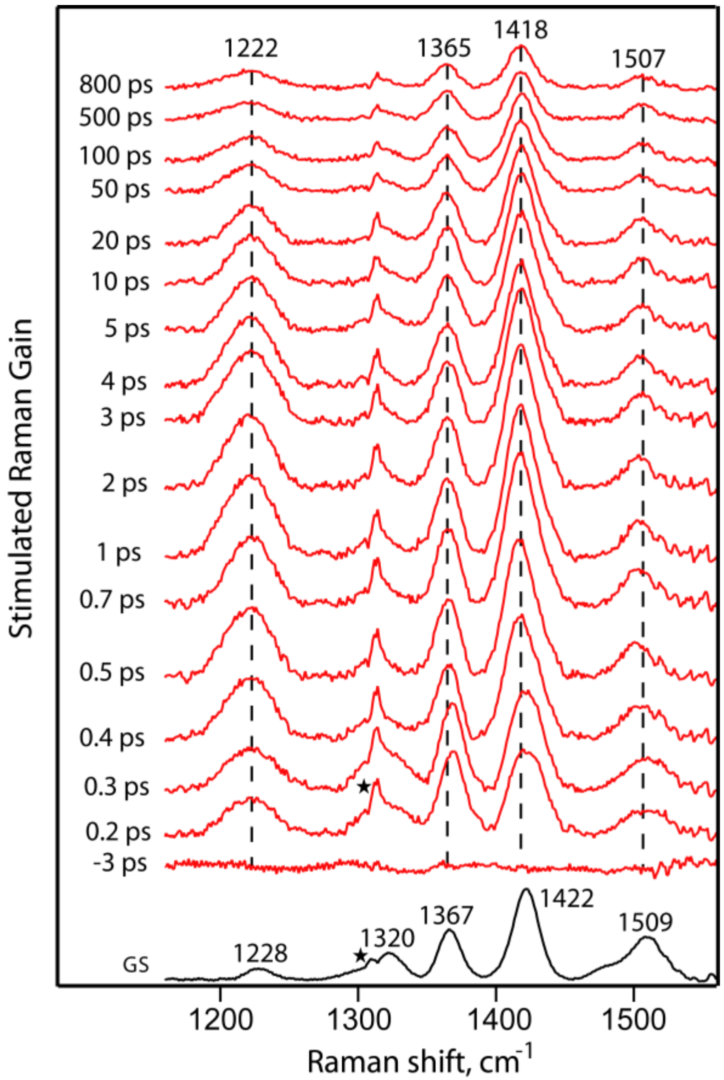




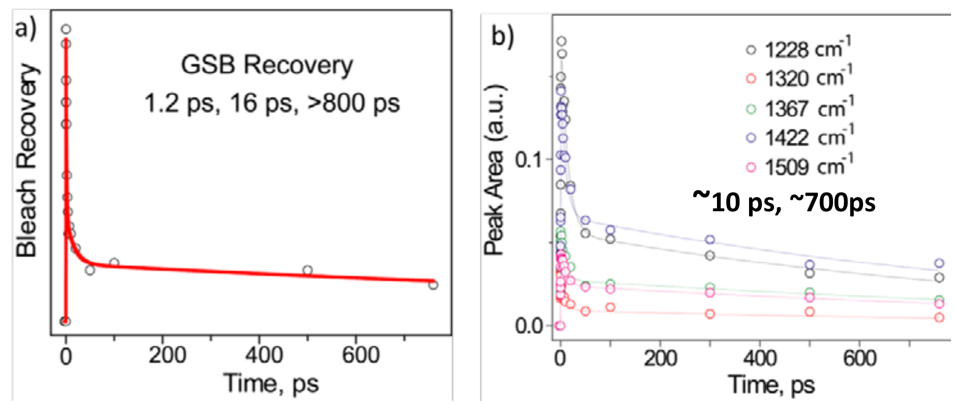


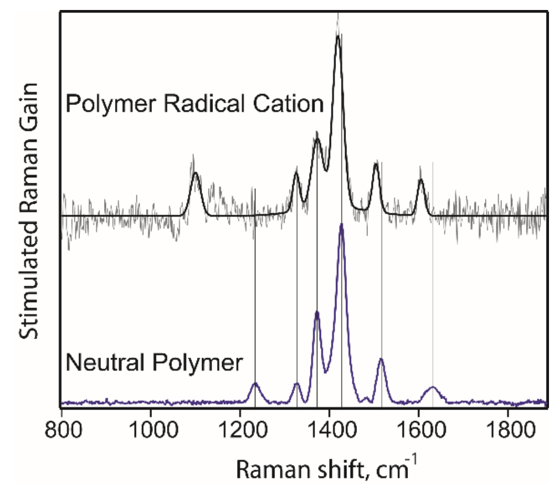
IMPORTANT for todays talk!!!

Raman Snapshots of the Polymer with 816 nm Pump



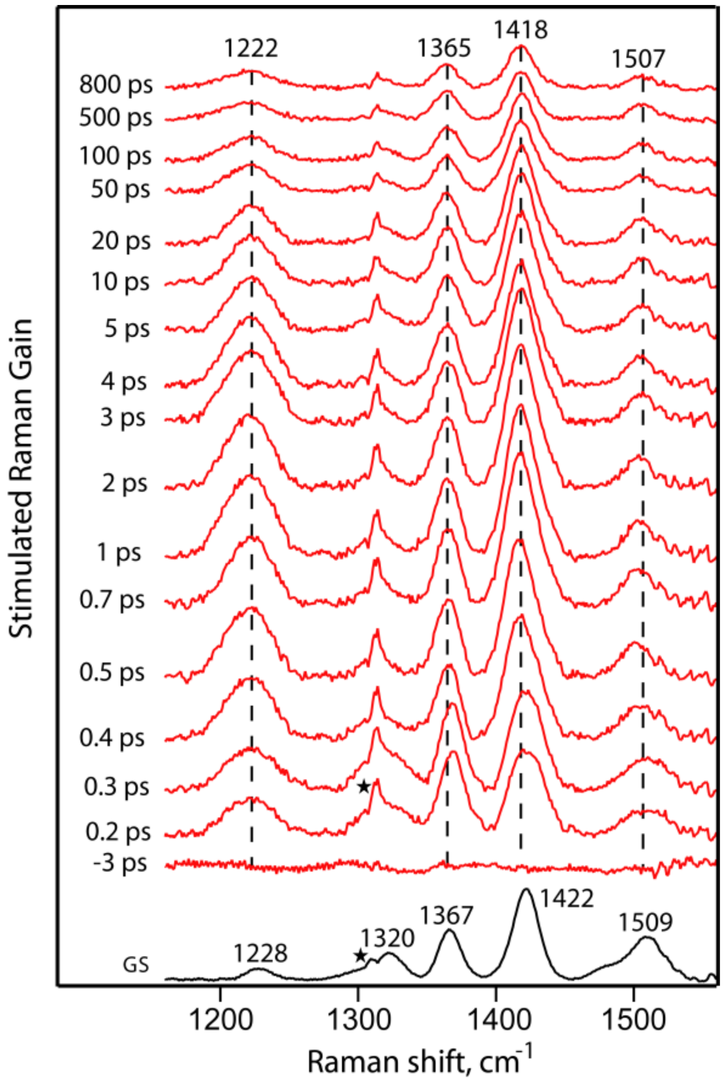
Lifetime of the State



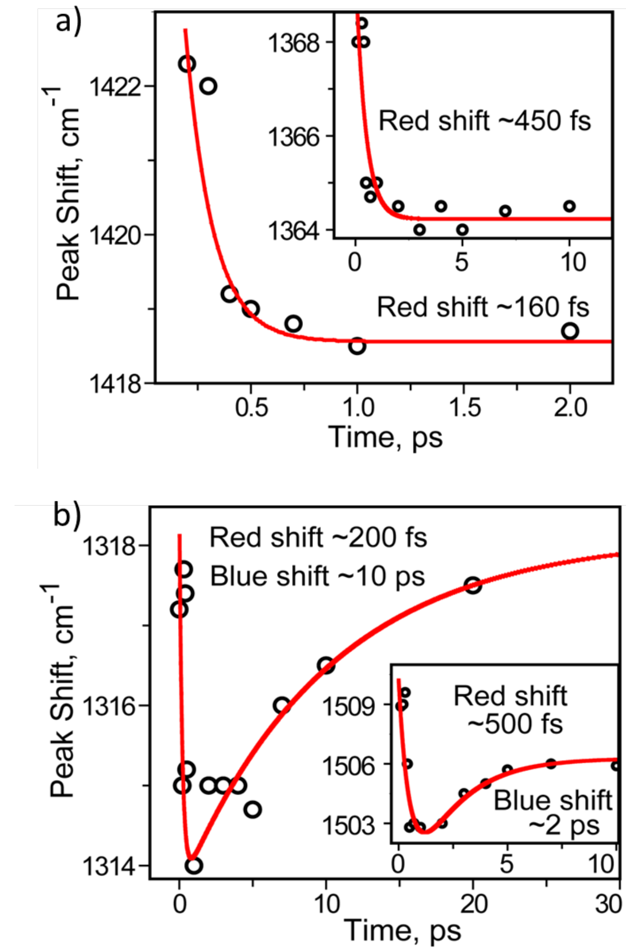


It is an **EXCITON** we are in resonance with!!!

Raman Snapshots of the Exciton!

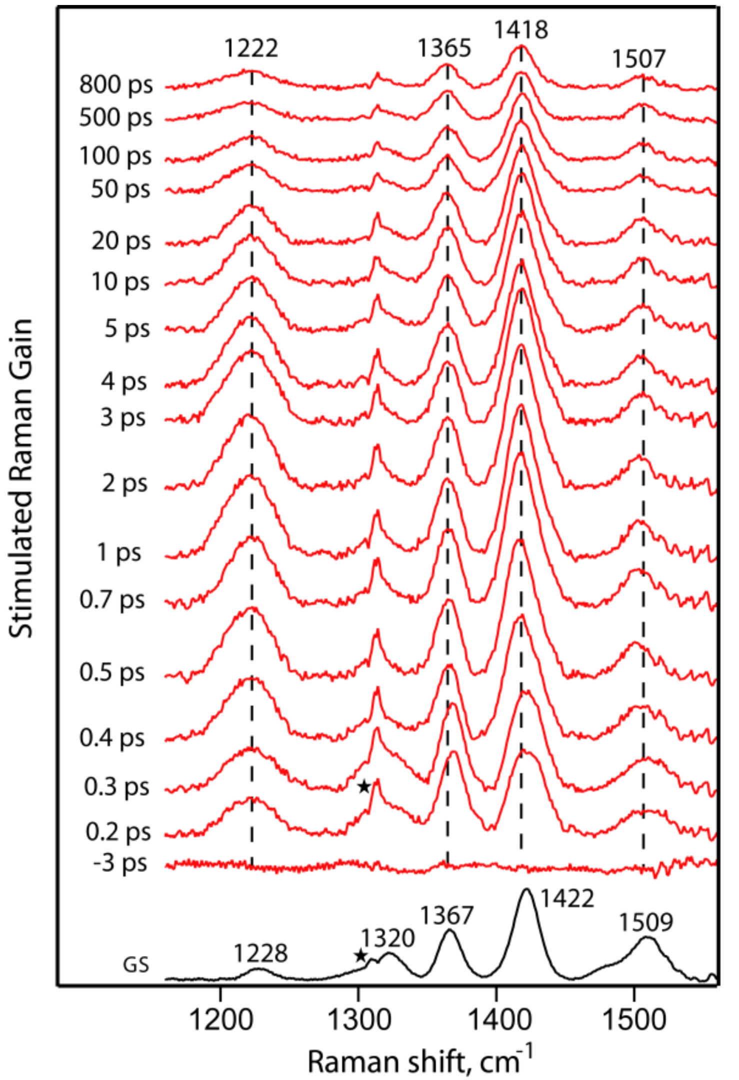


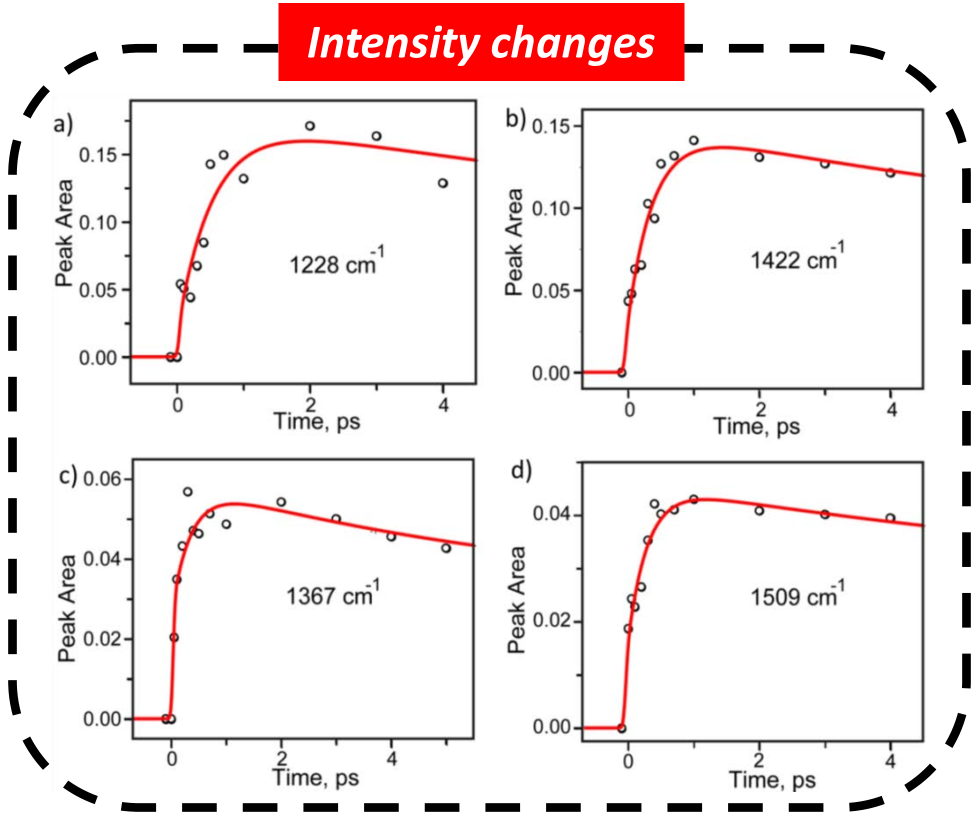
Frequency changes

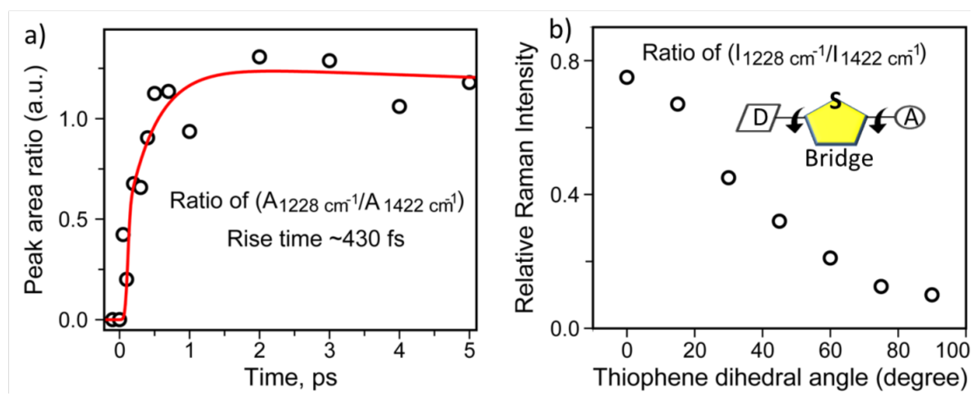


Enhanced **conjugation** in the backbone

Raman Snapshots of the Exciton!



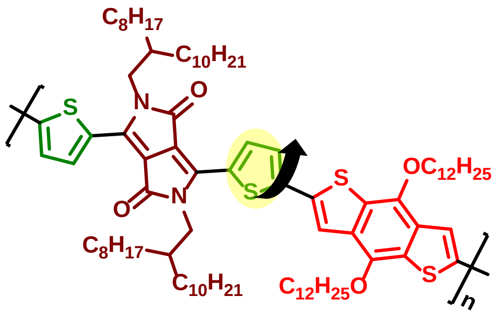




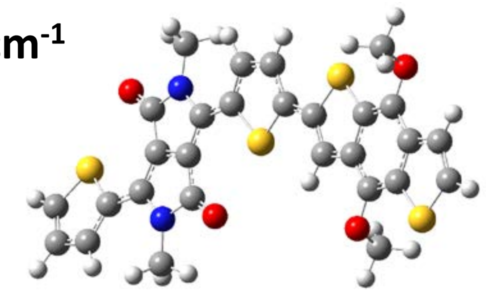
Enhanced Intensity in 1228 cm^{-1} mode due to planarization

Direct visualization of Bridge planarization

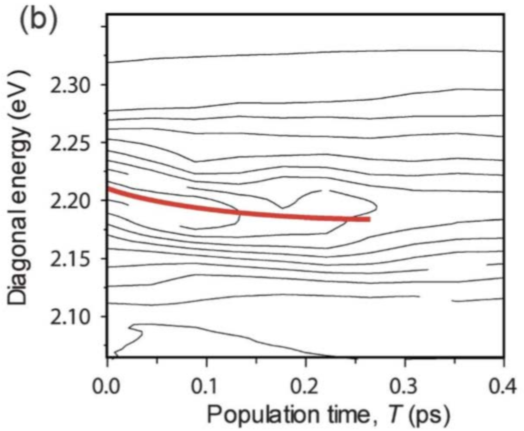
Planarization of the Bridge Thiophene in D-B-A!!

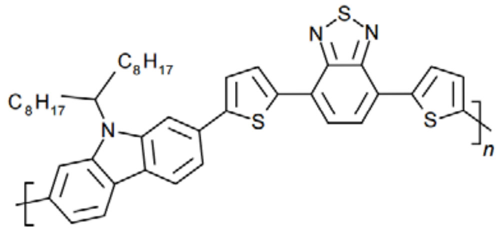


125 cm^{-1}



Local torsional relaxation leads to
enhanced conjugation & Raman cross-section

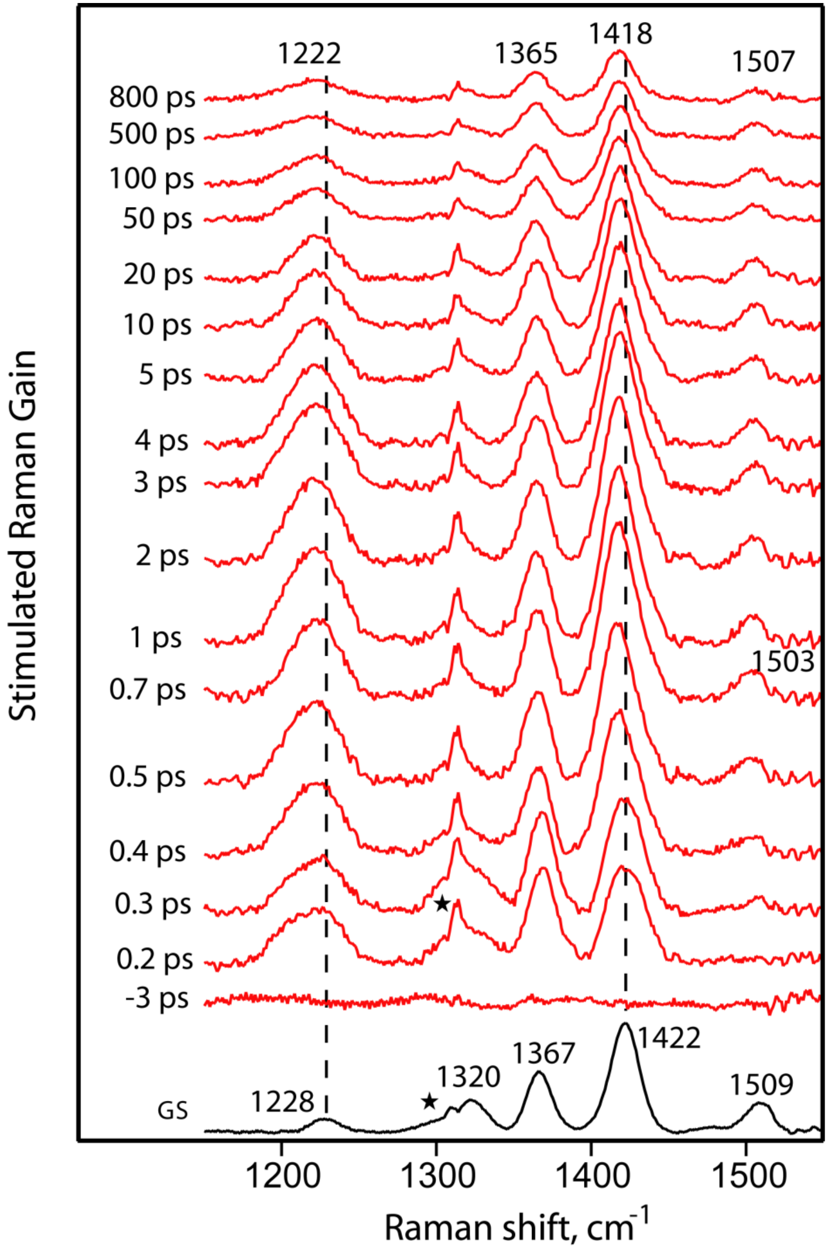


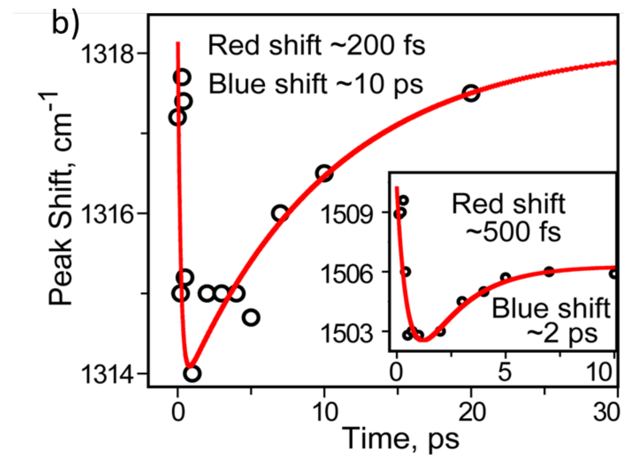


G. Scholes and coworkers, *Chem. Sci.,* 2012, **3**, 2270

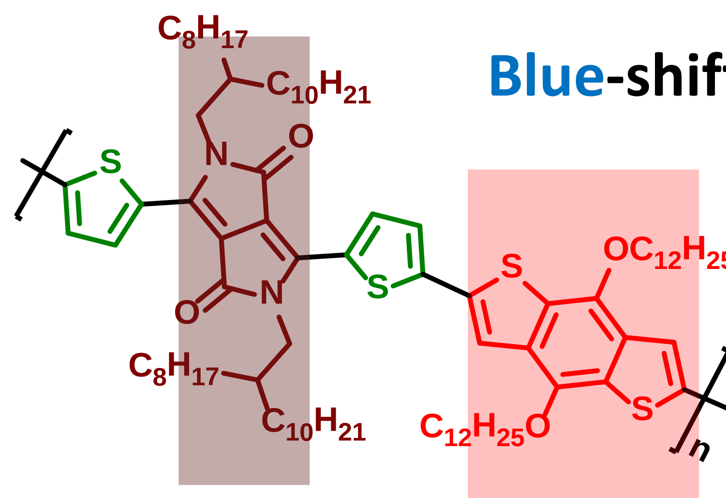
2D-eelctronic spectroscopy on CT states implied relaxation based on red-shift

Localization of the Exciton and its CT character





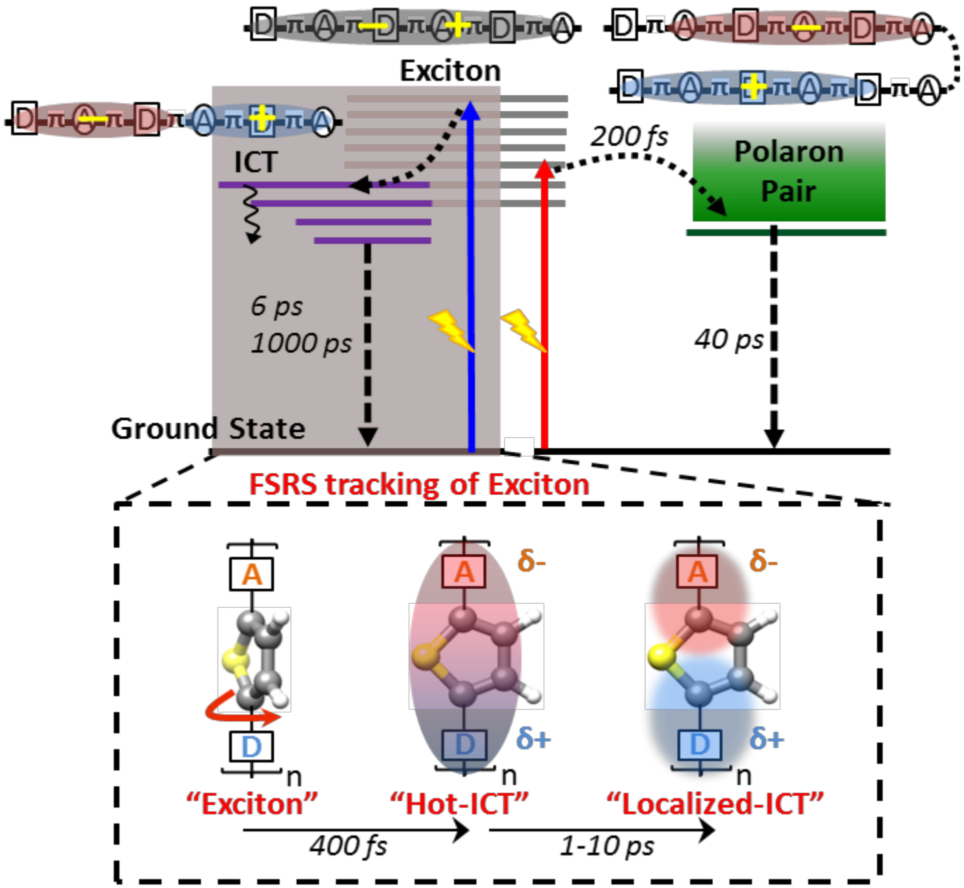
Blue-shift



Cooling Within ~1 (DPP) and ~10 ps (BBT)

Summary: Direct observation of Bridge Planarization

Selectively probing Exciton using FSRS and correlating to TA

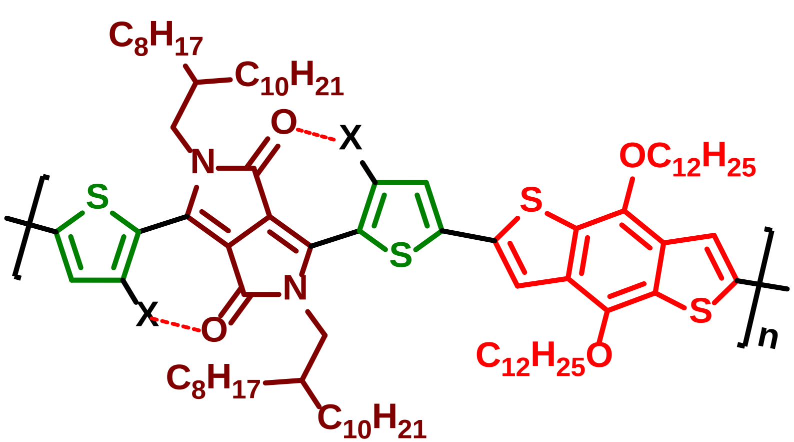


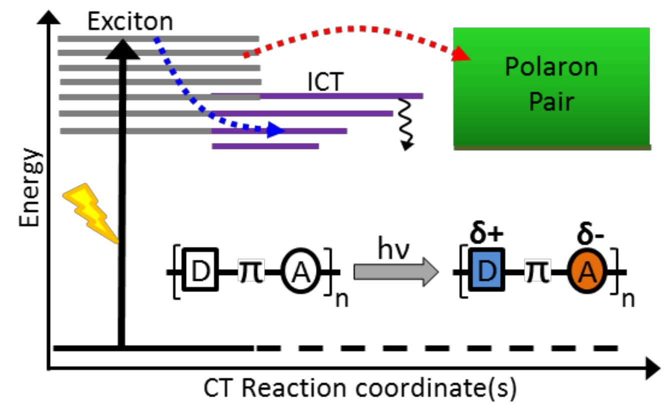
Palas Roy et al. *under revision*

Initial planarization leading to conjugation and thus the ICT character

OPV lessons: Target Backbone Torsions

Charge Transfer vs Relaxation





Palas Roy et al. *under revision*

Slowing the relaxation dynamics to allow charge transfer from hot states!

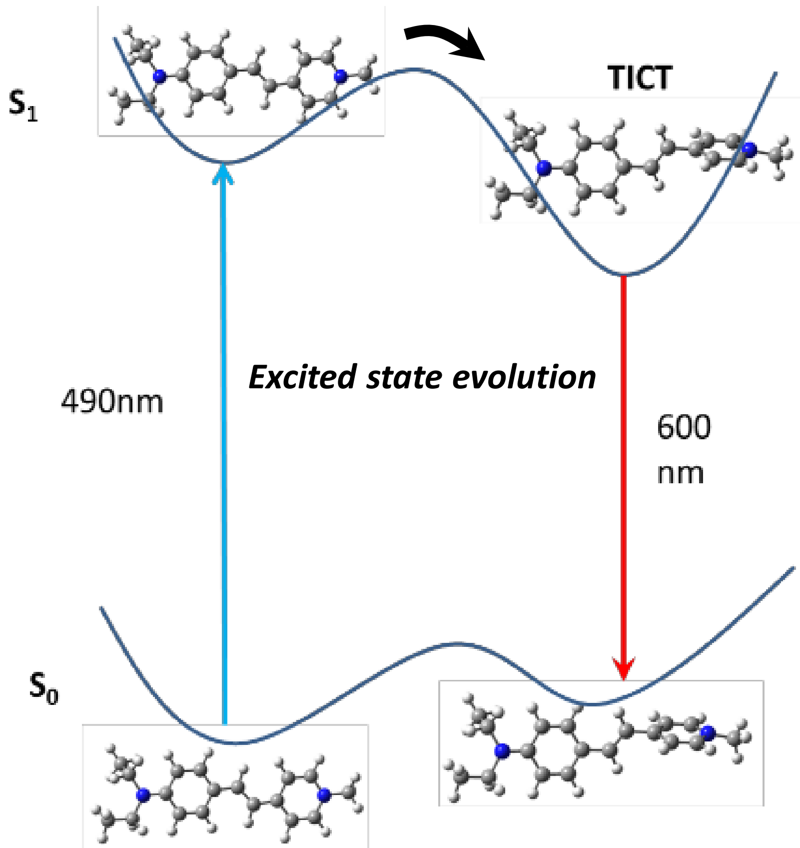
Side-chain engineering to align the Donor and Acceptor to ensure large CT yields.

RELAXATION channels in CT and CS states are being interrogated!

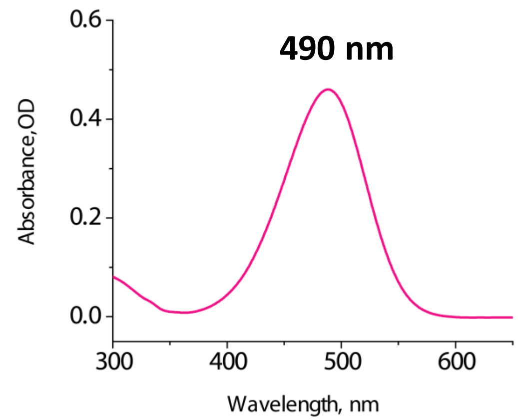
Twisted-Intramolecular CT state in Staining Dyes?

Dr. A. Dharmadhikari, TIFR

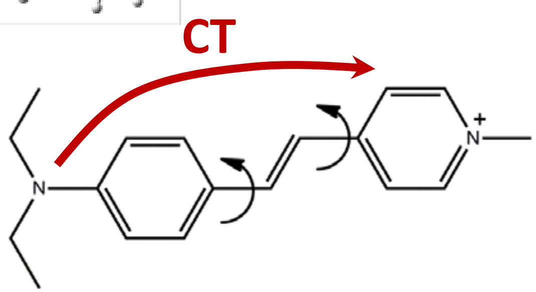
Dharmadhikari, A., et al.
Appl Phys B (2004) **79**, 235



Dr. Shreetama **Mr. Abhinandan**



DEST



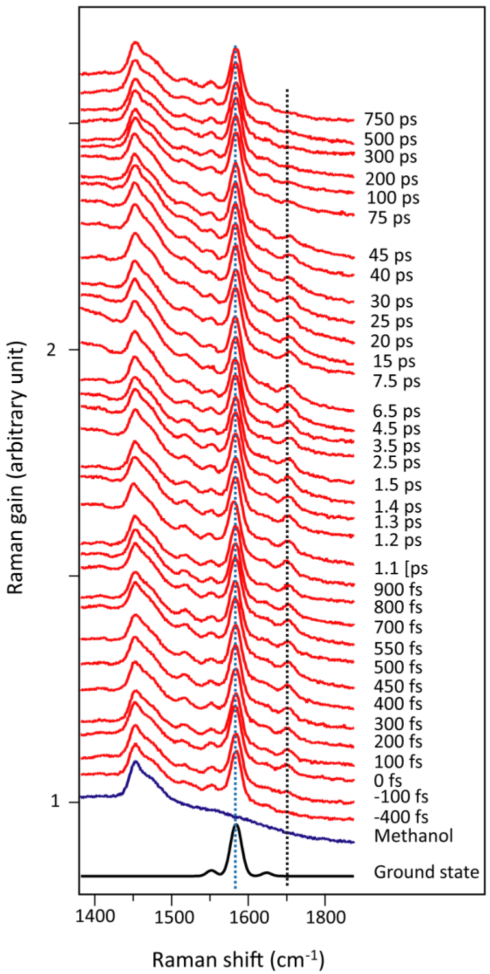
N,N-diethyl-N'-methyl-stilbazolium cation

TICT state is emissive

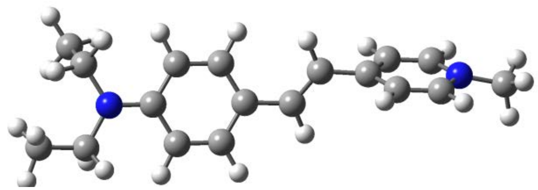
Stokes shifted!

Twisted-Intramolecular CT state: A Raman Story

Pump-On



DEST



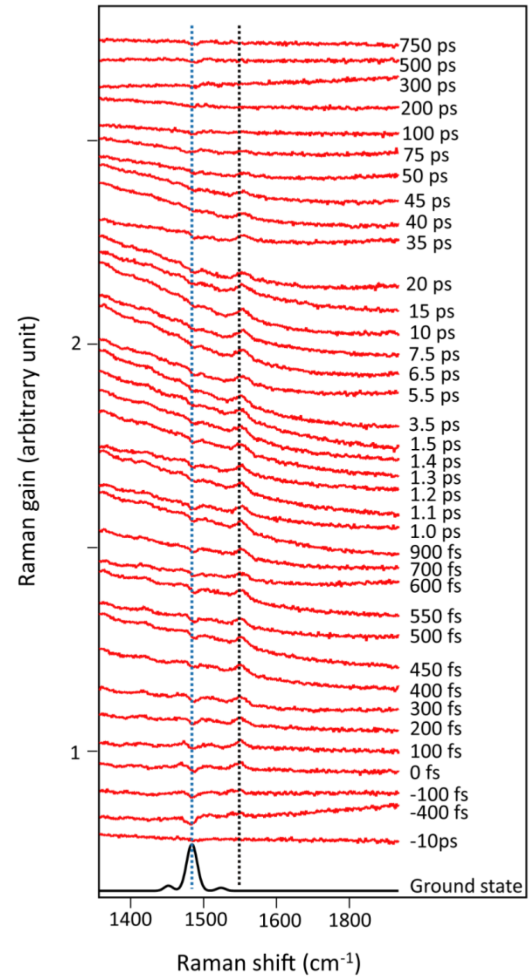
TD-DFT B3LYP basis: 6-31G+

Computational study on the excited state

1659 cm^{-1} and bond compression by 0.04 Å

First Raman signature of TICT state in Stilbazolium salt

"On" MINUS "Off"

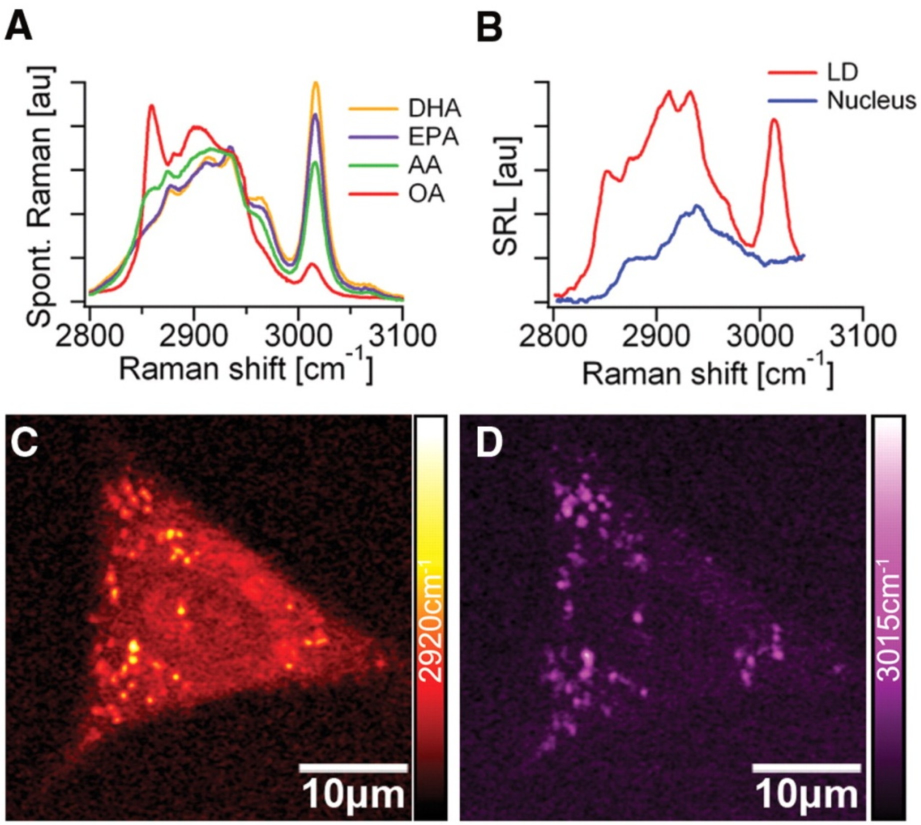


Viscosity dependent Raman signature:

Rise of the state and its Lifetime is affected

unpublished

Stimulated Raman Imaging: Label-free Idea



Ground state Raman spectrum useful for imaging lipids

Sunney Xie and colleagues *Science* (2008)

Explore the *Charge Transfer paradigm* for Chemical Work

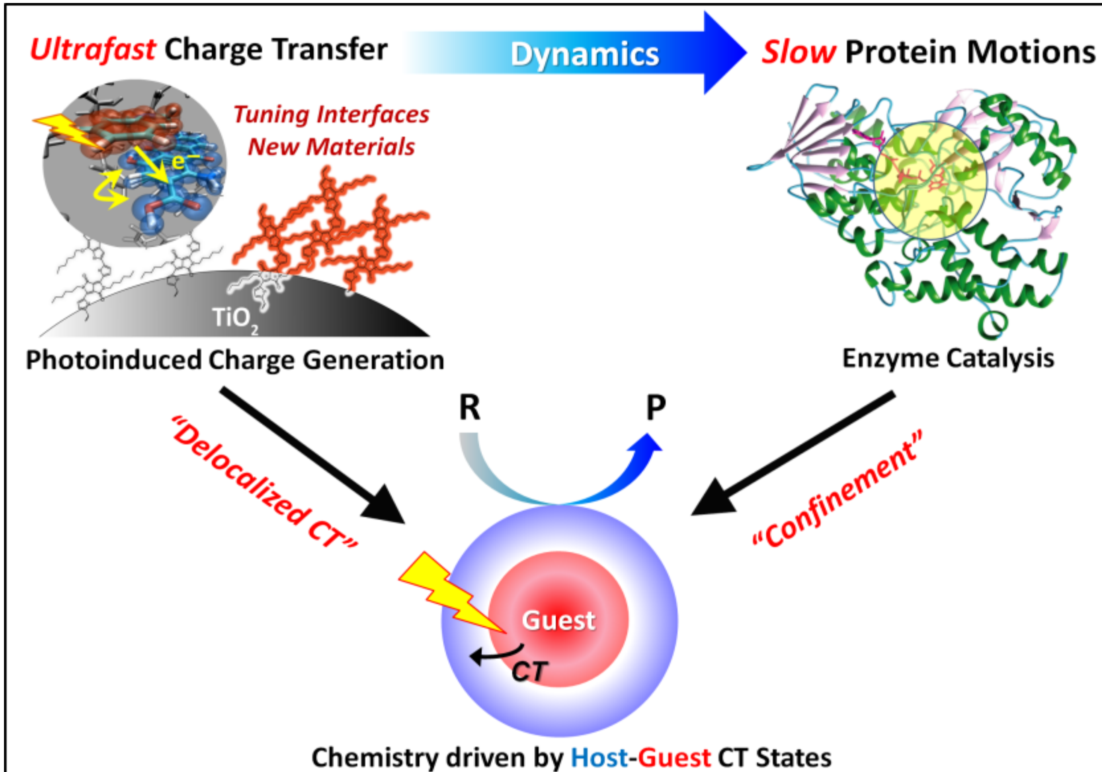
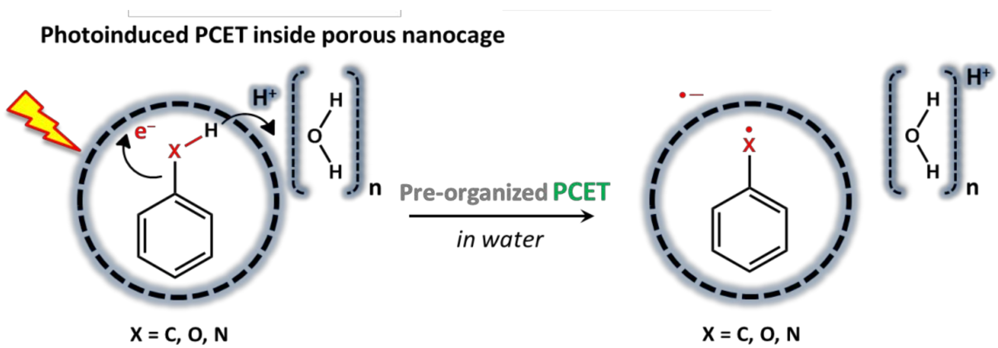


Figure 1. Schematic representation of our research program.



Acknowledgements: Our Group and Friends!!!

Collaborators

Prof. Satish Patil and Dr. B. Puttaraju (IISc Bangalore)
Prof. Anil Kumar (IIT Bombay)
Dr. Aditya Dharmadhikari (TIFR Mumbai)
Dr. Ravi Venkatramani (TIFR, Mumbai)
Dr. Vardharajan Srinivasan (IISER Bhopal)
Prof. ASR Koti (TIFR Mumbai)

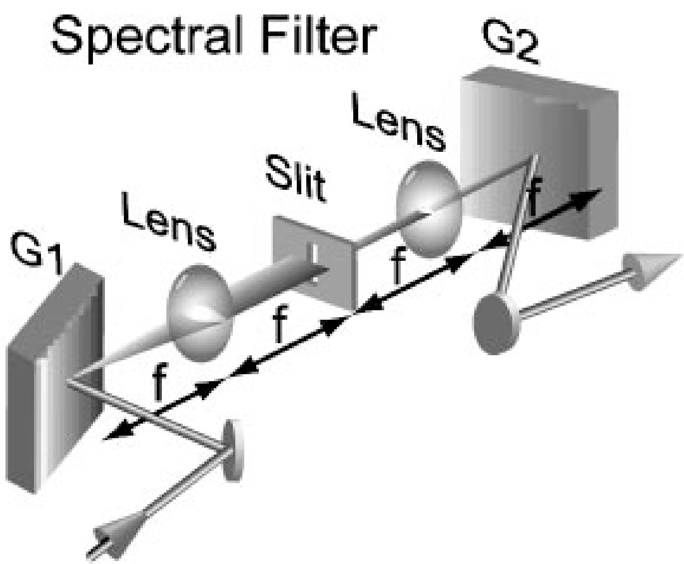
tata institute of fundamental research

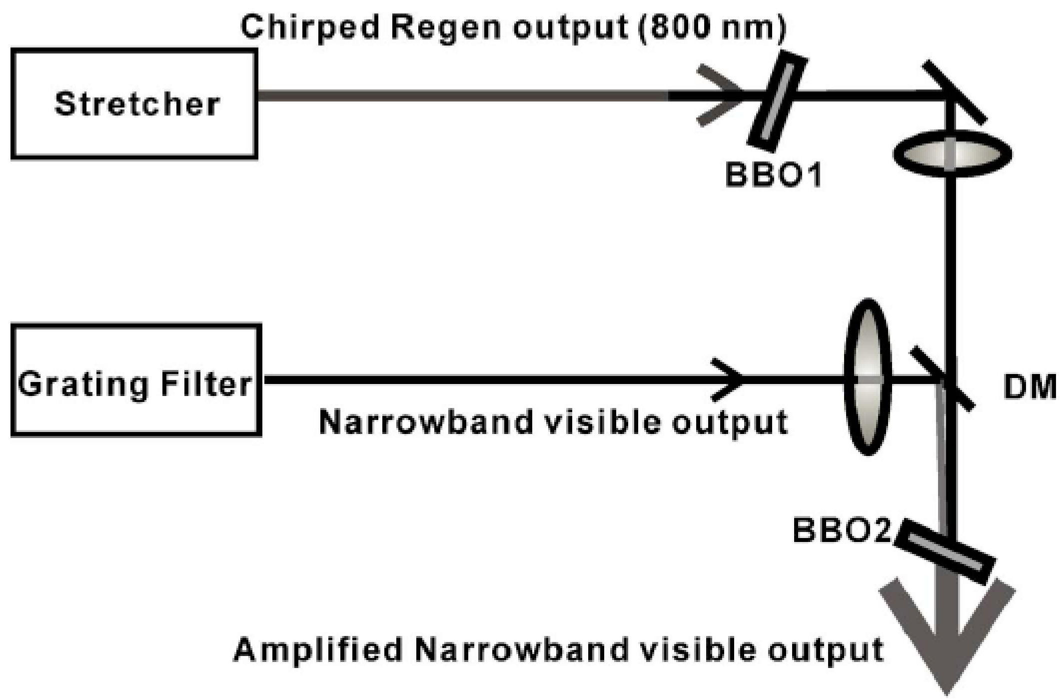
पऊवि DAE

Department of Chemical Sciences, TIFR

THANK YOU SATYA!

Raman Pump generation!





Efficiencies are poor (5% at best)

Other methods are being developed.

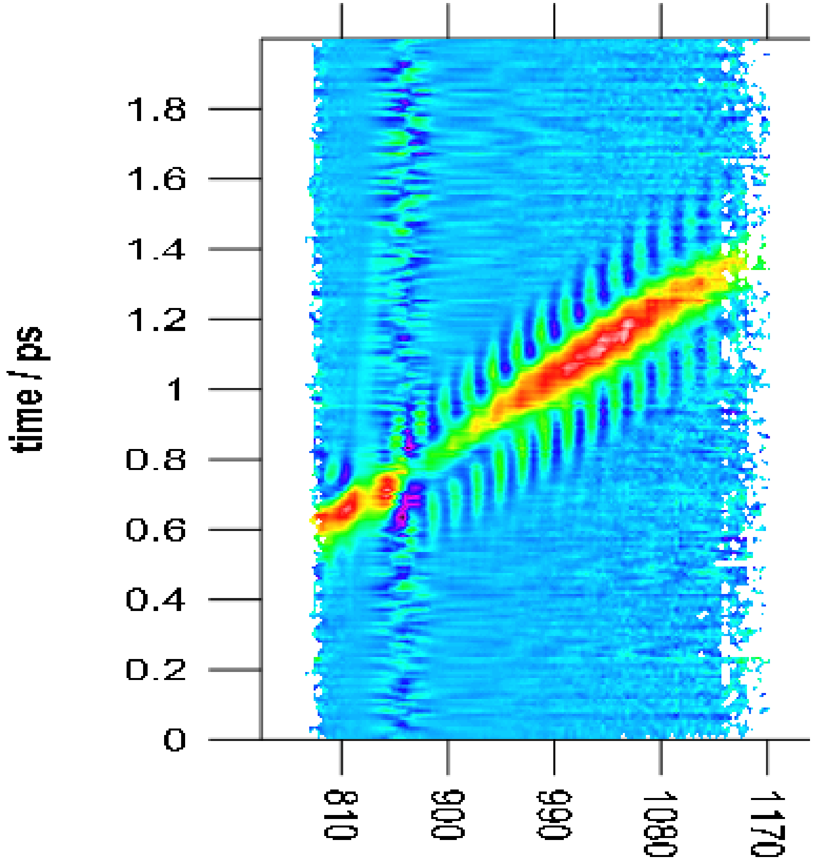
Optical Kerr Experiment(OKE)

Kerr effect is the change in refractive index of a material due to an external electric field. (Electro-optic effect)

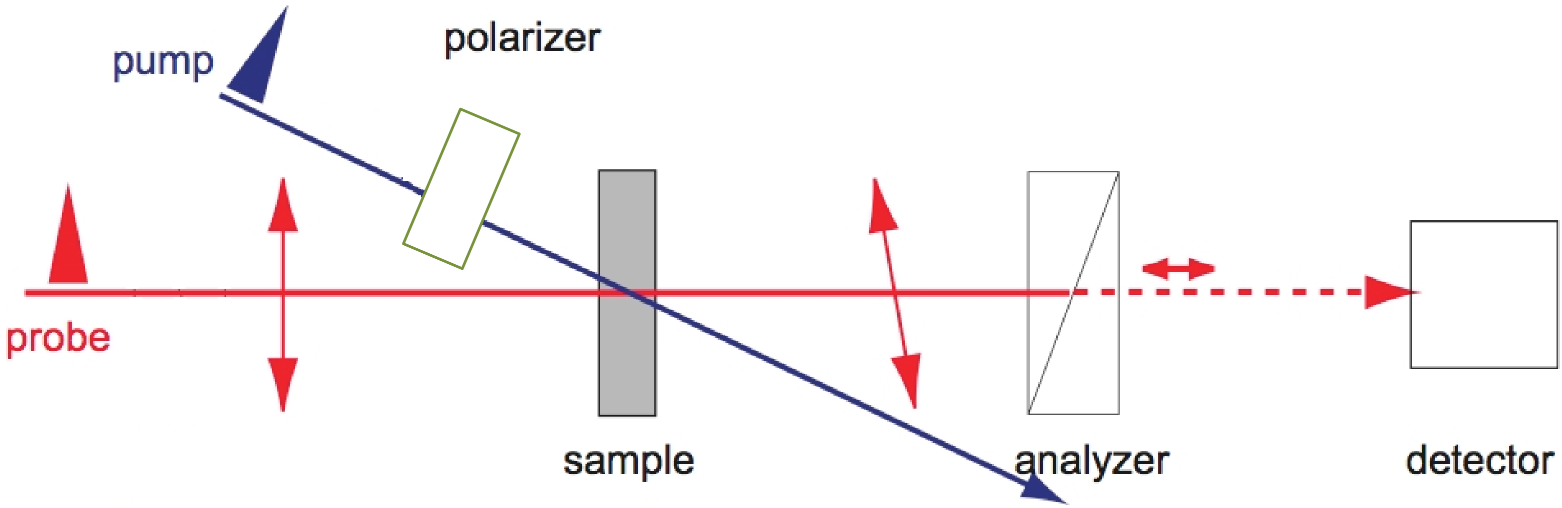
$$\Delta n = \lambda K E^2$$

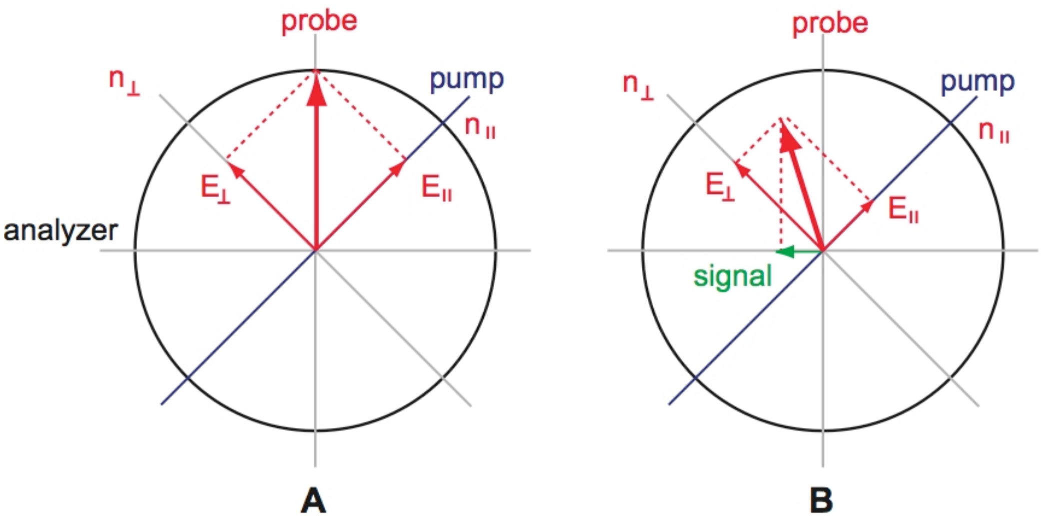
The material becomes birefringent and OKE is when the birefringence is induced by an optical pulse.

$$n = n_0 + \overline{n_2}\, I$$



OKE Setup





Polarization transfer takes place.