Electron- and Photo-Induced Processes for Molecular Energy Conversion Group

Picosecond pulse radiolysis applied to energy research

MIT-BNL Mini-workshop
Brookhaven National Lab, NY
July 26, 2017

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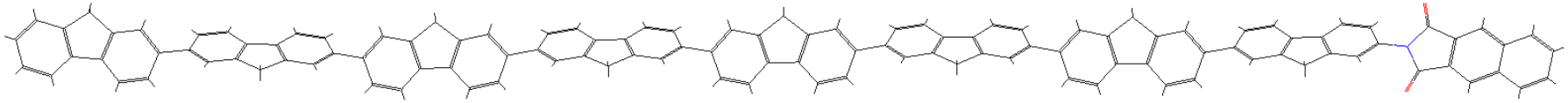
Brookhaven National Laboratory



Pulse radiolysis / radiation chemistry are powerful tools for studies of chemical reactivity

Make solute radical ions rapidly: ps, faster? Observe reactions on the ps timescale

- Electron transfer in small molecules, assemblies
- Transport of charges in conjugated polymers
- Primary radiolysis products and reactions

Radical ions can be studied free of counter charges

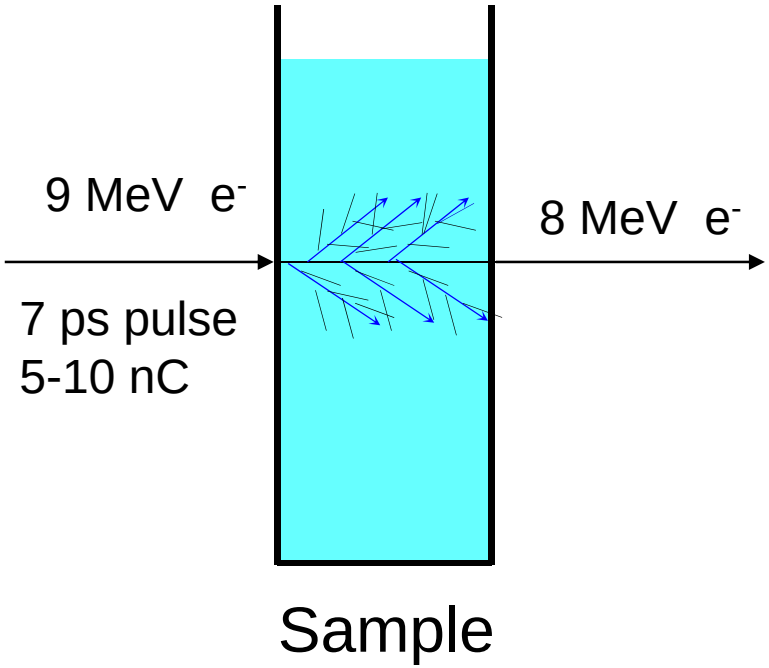
- Energetics & reactions
- Electrochemistry without salts, low polarity solvents

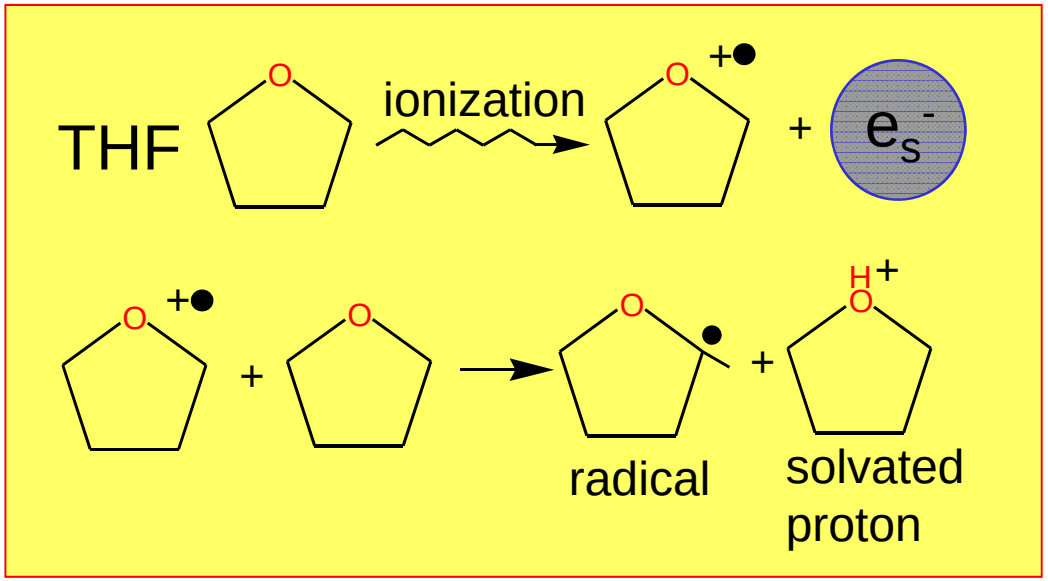
Radiolysis provides routes to unique transient species difficult to produce/study in other ways

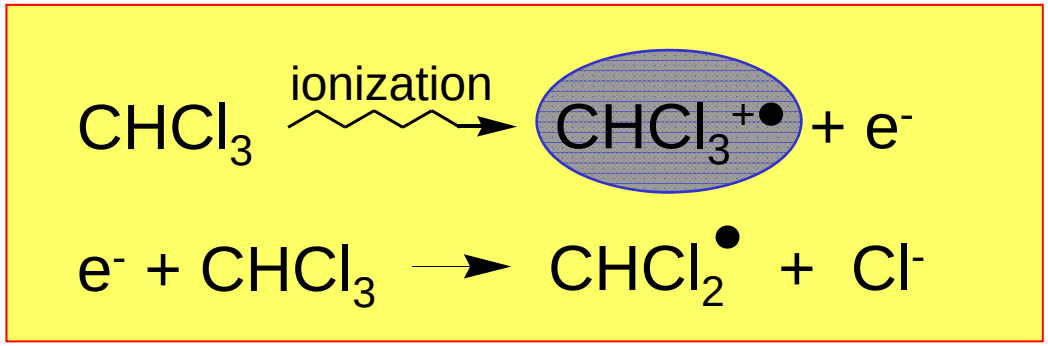
Excited states from direct excitation and recombination

- Triplets can be made rapidly, without singlet precursors

Charge attachment by Pulse Radiolysis





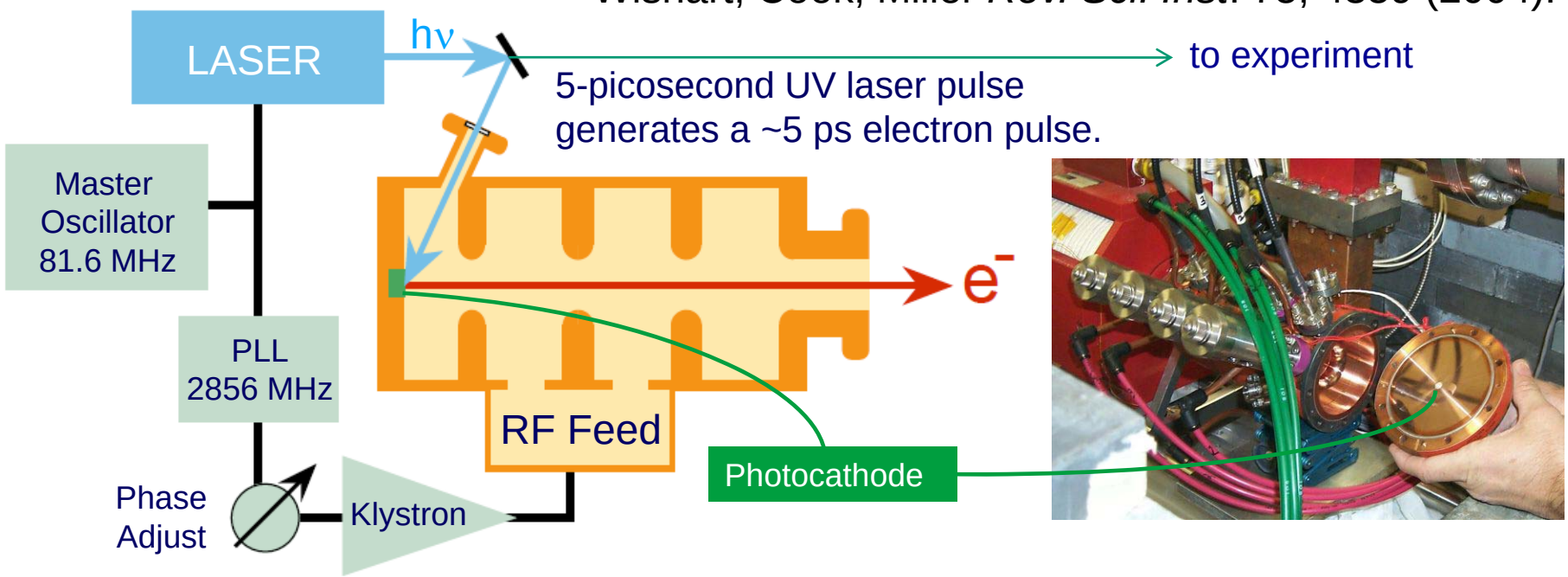


Attach e^- or h^+ to a solute, but it takes time (diffusion, or ?)

The Laser-Electron Accelerator Facility (LEAF):
A collaborative user facility

9 MeV, 5-10 ps electron pulses with synchronized ~100 fs laser beams

Wishart, Cook, Miller *Rev. Sci. Inst*. 75, 4359 (2004).



2856 MHz microwave power: 15 MW

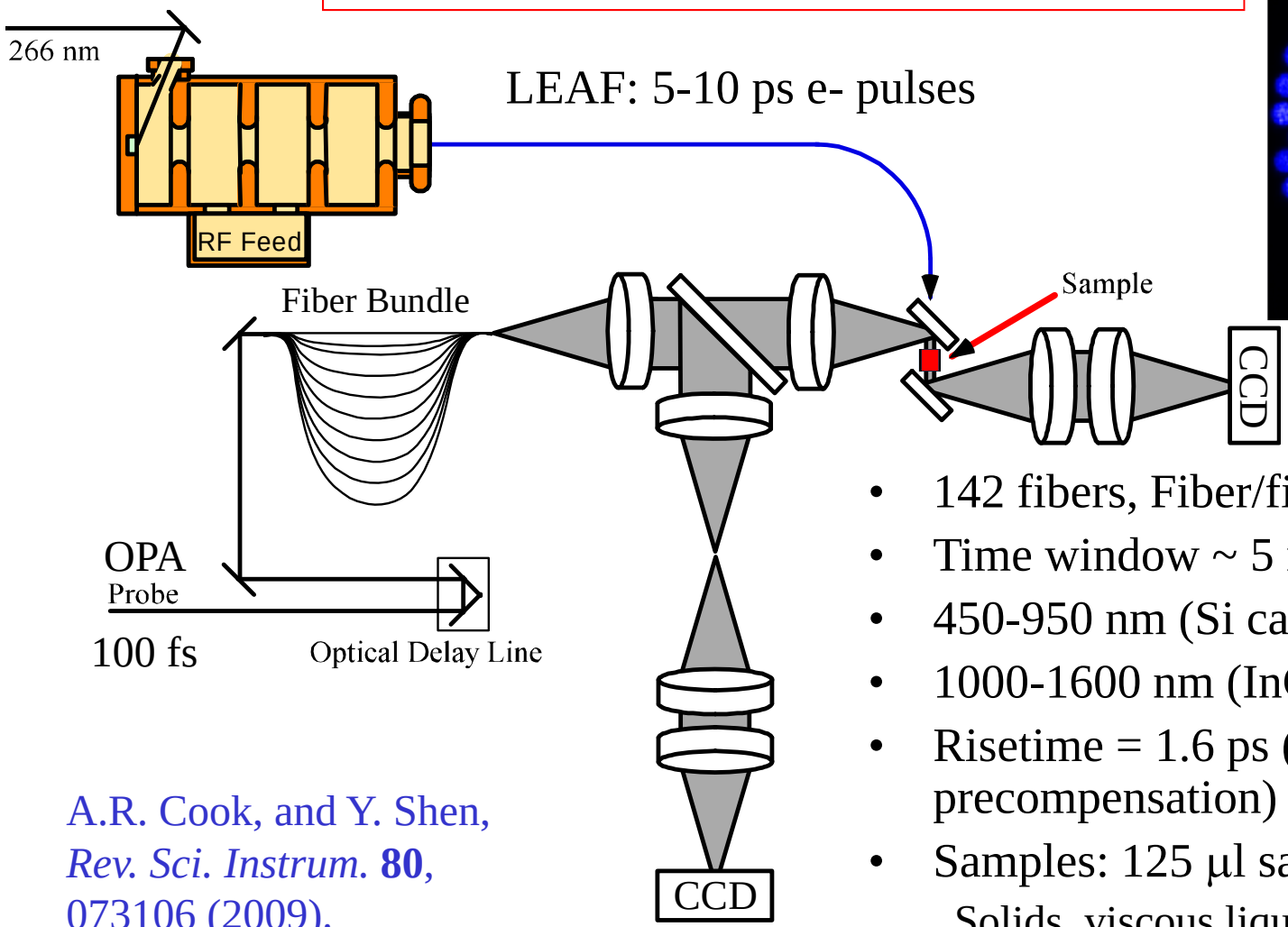
Additional tools: 2 MeV
Van de Graaff, Cobalt-60

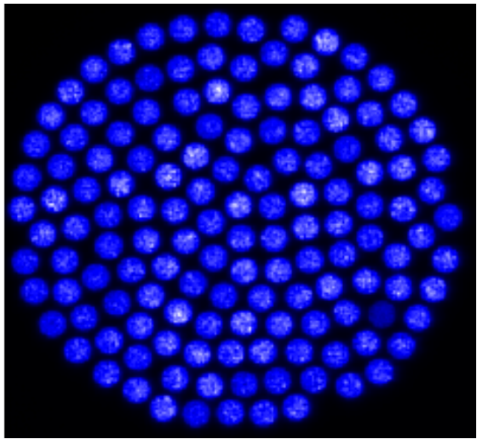
Key experimental methods:

Transient absorption: (1-2ns) 200-2600nm
Pulse probe, OFSS (10 ps), MIR (40ns)
Microwave conductivity

Optical Fiber Single-Shot Detection (OFSS) System

Spatial Encoding of Temporal Information



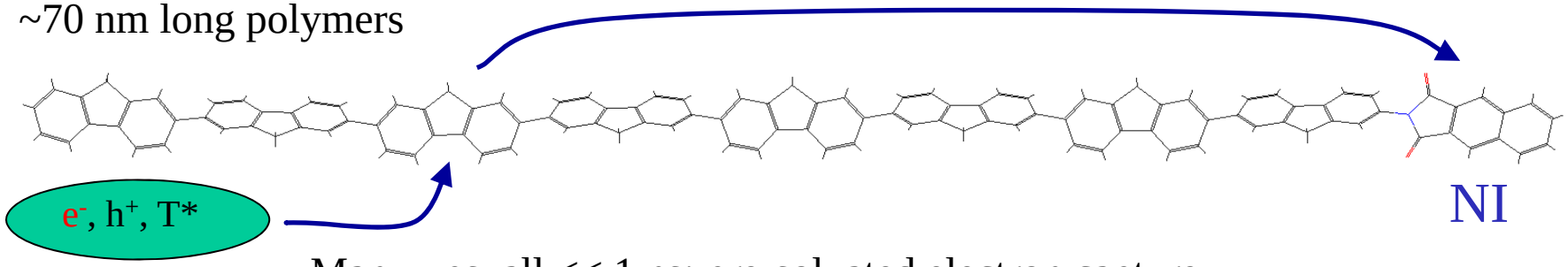


- 142 fibers, Fiber/fiber $\Delta \sim 5+$ ps
- Time window ~ 5 ns
- 450-950 nm (Si cameras)
- 1000-1600 nm (InGaAs cameras)
- Risetime = 1.6 ps (0.5 ps with precompensation)
- Samples: 125 μl samples (no flow)
  Solids, viscous liquids, precious samples

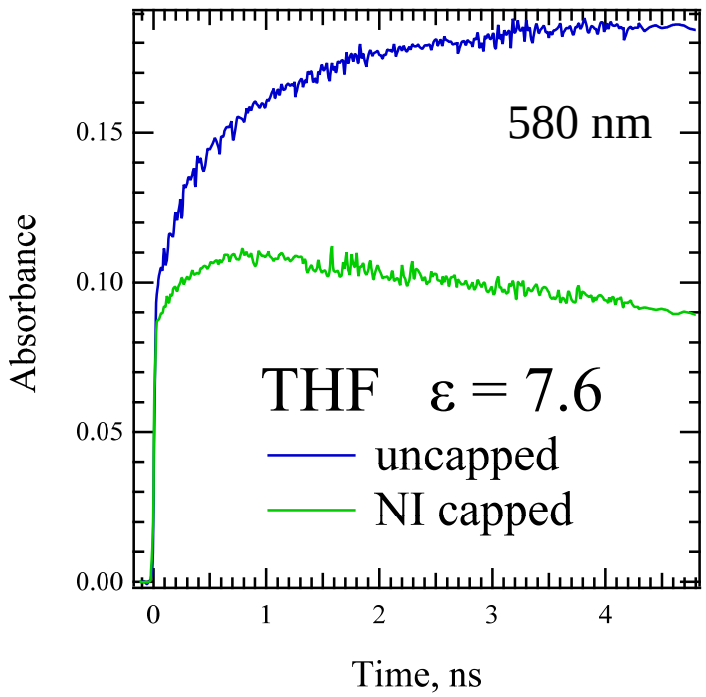
A.R. Cook, and Y. Shen, *Rev. Sci. Instrum.* **80**, 073106 (2009).

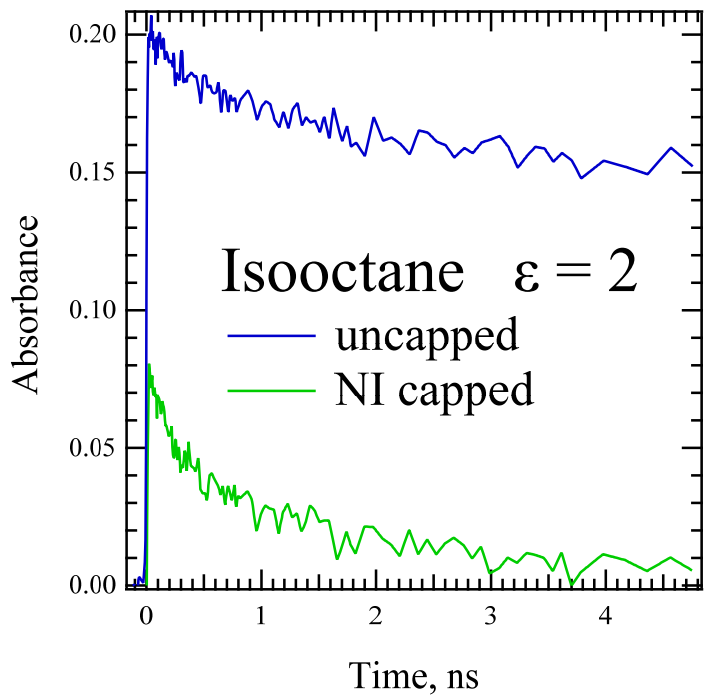
Does the environment have a large impact on charge transport in conjugated polymers?

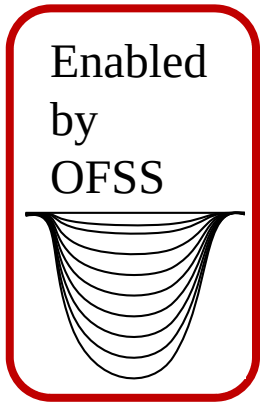
~70 nm long polymers



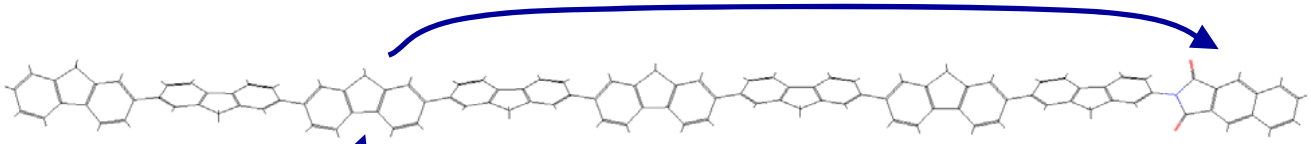
Many ~ps, all << 1 ns: pre-solvated electron capture





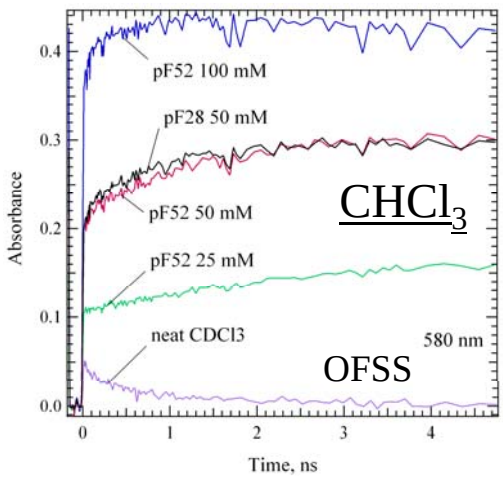


Can holes be captured faster than diffusion ?



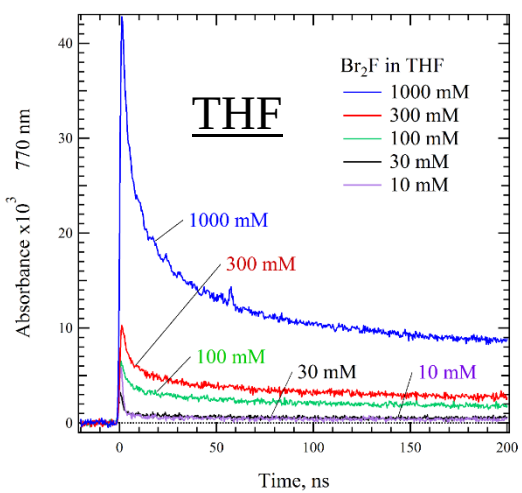
e^-, h^+, T*

Diffusion of solvated holes is slow, limits time resolution!



Yield rivals pre-solvated electron capture !

Cook, Bird, Asaoka, Miller, *J. Phys. Chem. A* **2013**, *117*, 7712-7720.

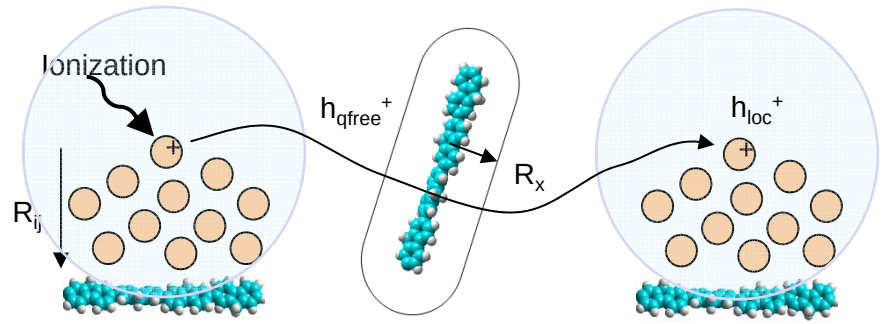


Yield up to 50%

Capture < 0.5 ps !!!

Fundamental process in radiation chemistry?

Pre-solvated hole capture !



Current work:

Mechanism? Short-lived delocalized holes or rapid hopping prior to solvation?

How to control, and capture large yields on high IP solutes?

How does this impact critical nuclear separations processes? Unexpected degradation route?

Fast triplets?? Enables rapid measures of rapid triplet transport!

Recombination of $pF^{+\bullet}$ made by pre-solvated hole capture?

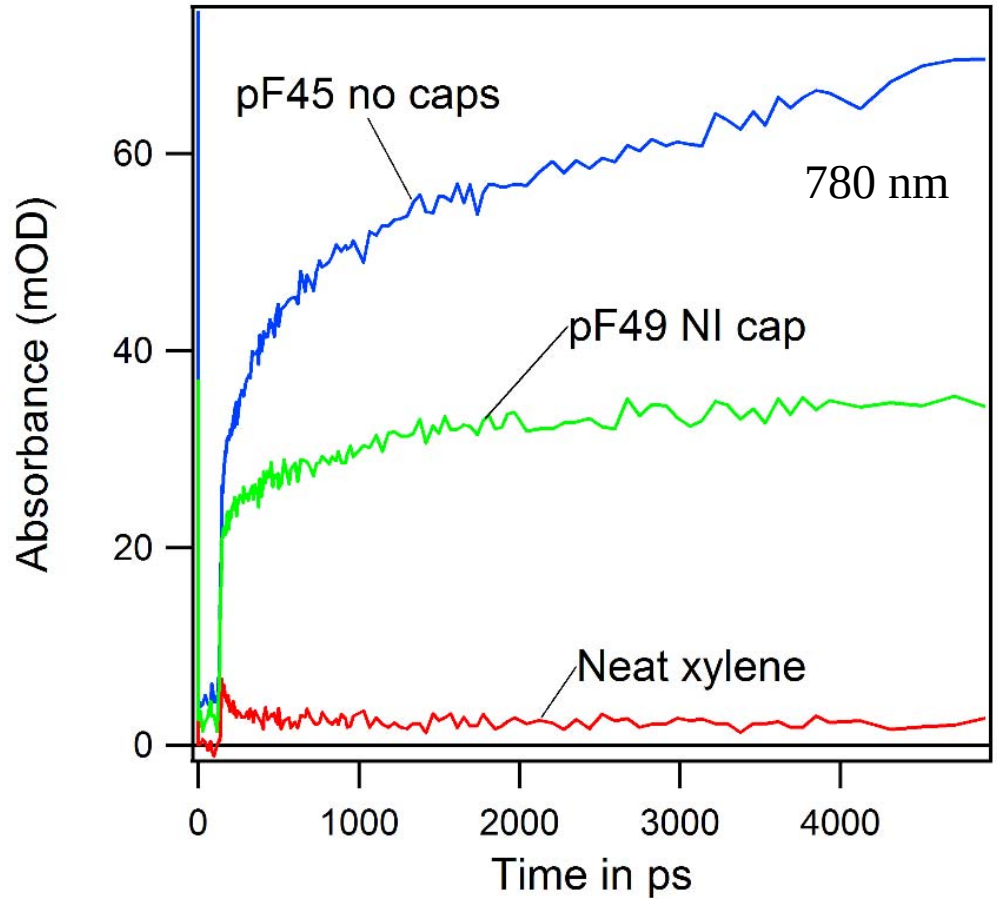
$pF^{+\bullet}$ + e-, $pF^{-\bullet}$ -> $^3pF^*$

Triplets < 10 ps ?

Special to polymers?
Energetics & Yield?

Triplet (Dexter) transport faster than singlets (Dexter+Förster) ??

Triplets reach endcaps in < 7 ns. 42 nm !



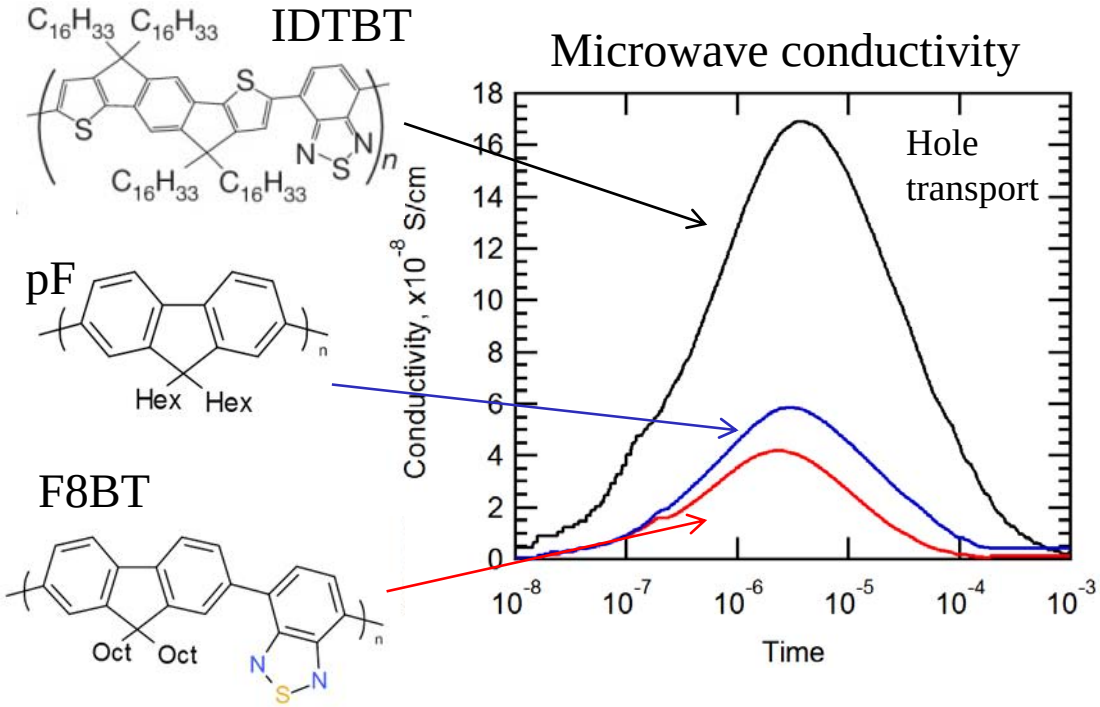
What controls charge transport along molecular wires?

Matt Bird

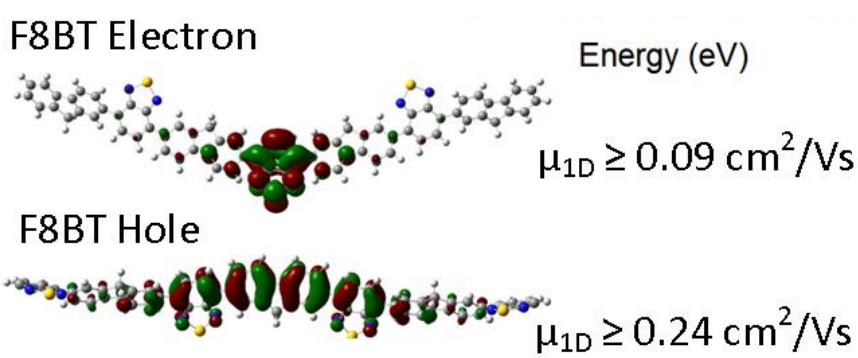
<u>Current Interests:</u>
Effect of molecular structure?

Do localized charges impede transport?

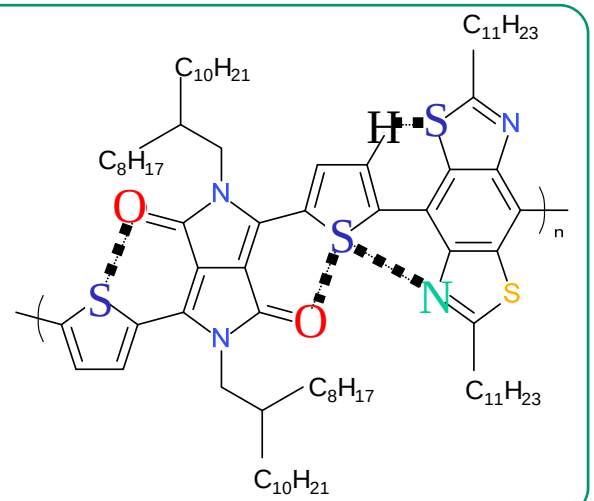
Can non-bonded interactions increase mobility?



Push-pull polymer



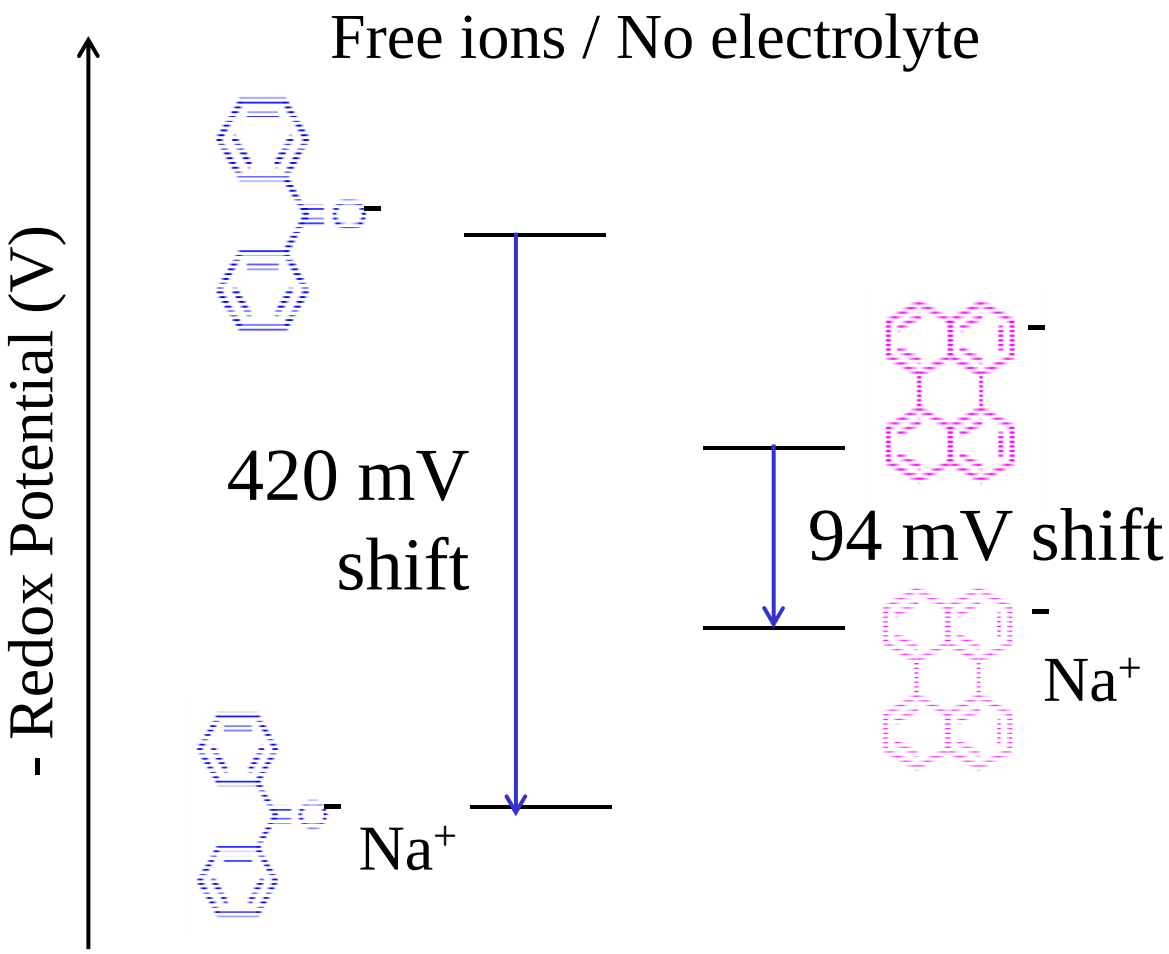
Planarized by non-bonded interactions



M. Bird, J. Bakalis, S. Asaoka, H. Sirringhaus, J. R. Miller *J. Phys. Chem. C*, Article ASAP

How do electrolytes, used in cyclic voltammetry, effect measured redox potentials?

Matt Bird



C.V. conditions, 0.1M electrolyte

Pulse radiolysis enables determining redox potentials without salts, and in low polarity media

Large effect of charge delocalization on redox shift. Magnitude depends on nature of ions

M. Bird, T. Iyoda, N. Bonura, J. Bakalis, A. Ledbetter, J. Miller, J. Electrochem. D, submitted.

Thanks!

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Diane Cabelli

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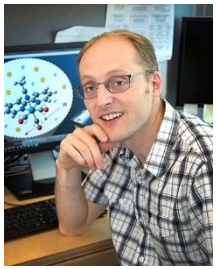
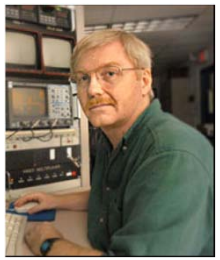

David Grills

Sergei Lymar

John Miller


James Wishart

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