UNIVERSITY OF CAMBRIDGE

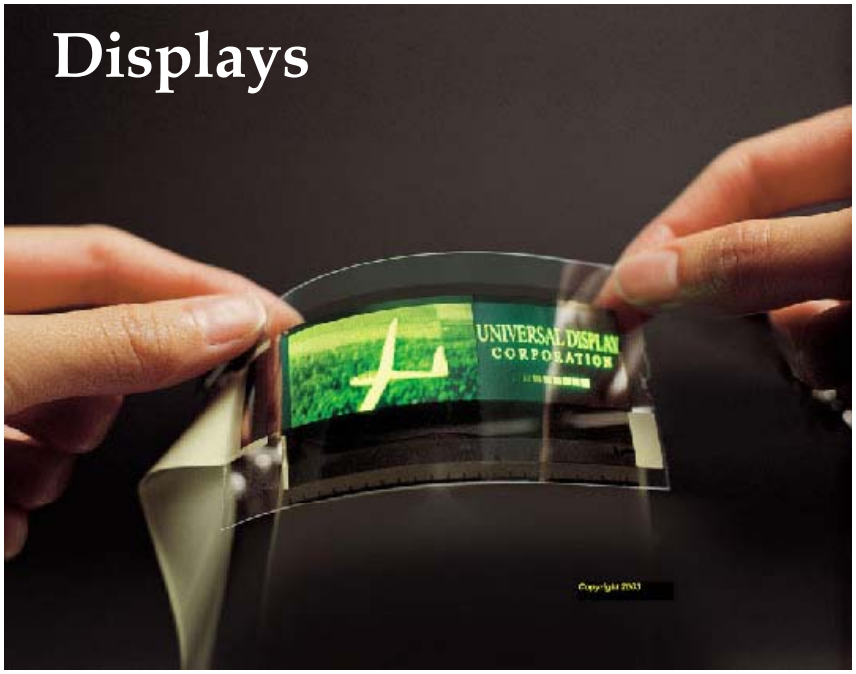
Фонд Дмитрия Зимина
Династия

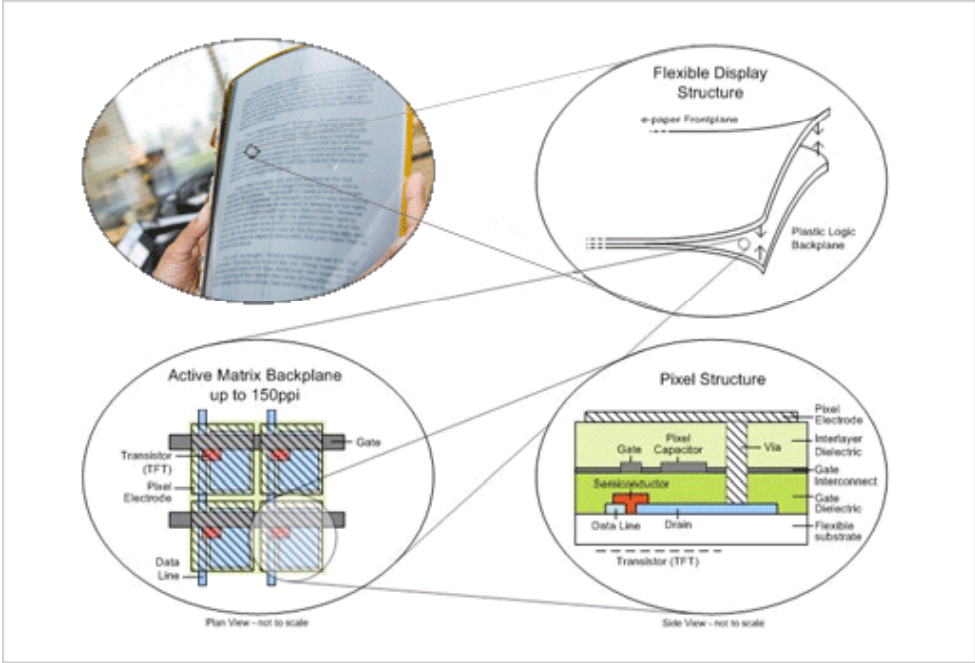
Cavendish laboratory

К вопросу о «горячей диссоциации» экситонов в органических полупроводниках

Артем Бакулин

Plastic electronics





Transistors

Solar cells

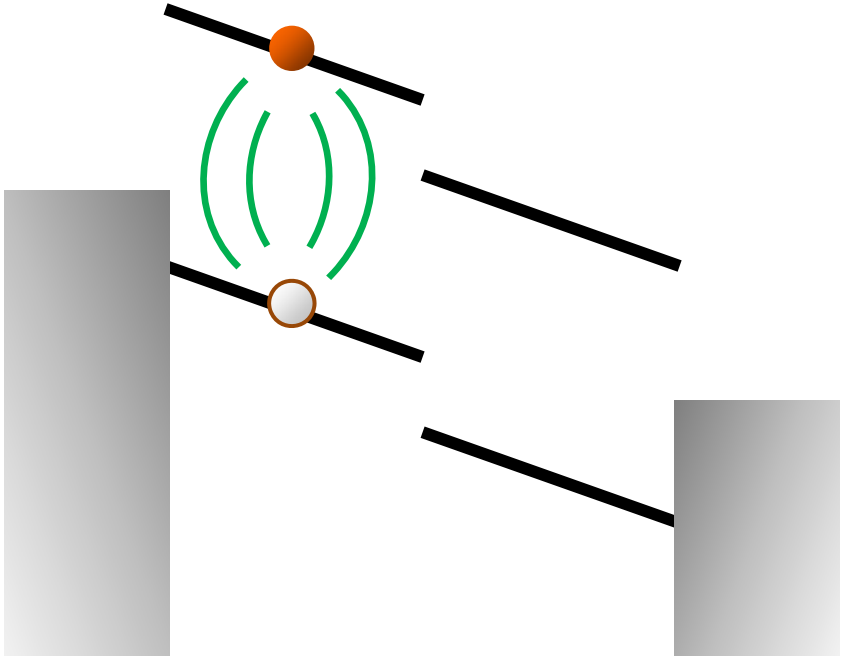
- Recent “hot” debates about the “hot” dissociation

- Our “direct” measurements of the “hot” state relaxation

- Possible outlook

Exciton Dissociation Bulk heterojunctions

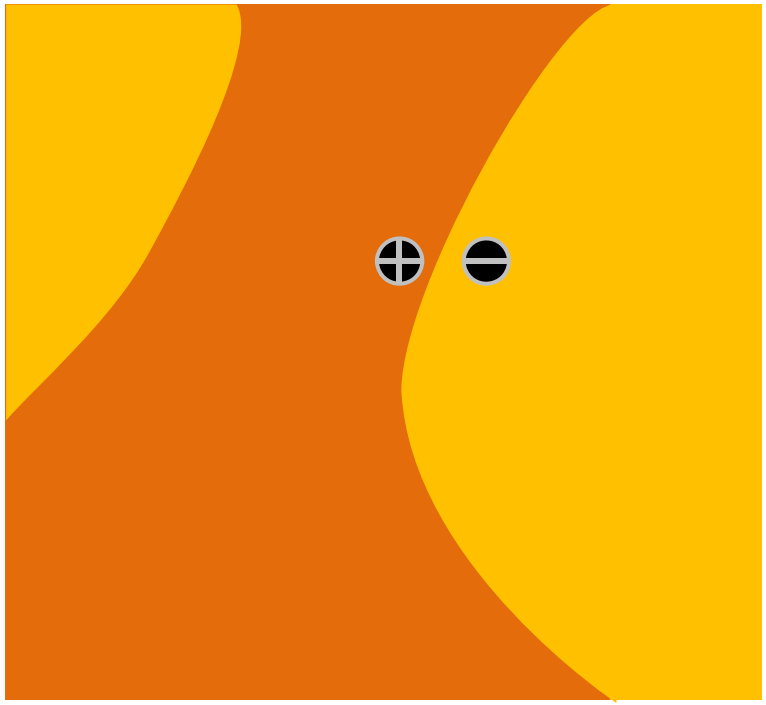
- Exciton is generated and diffuses to interface

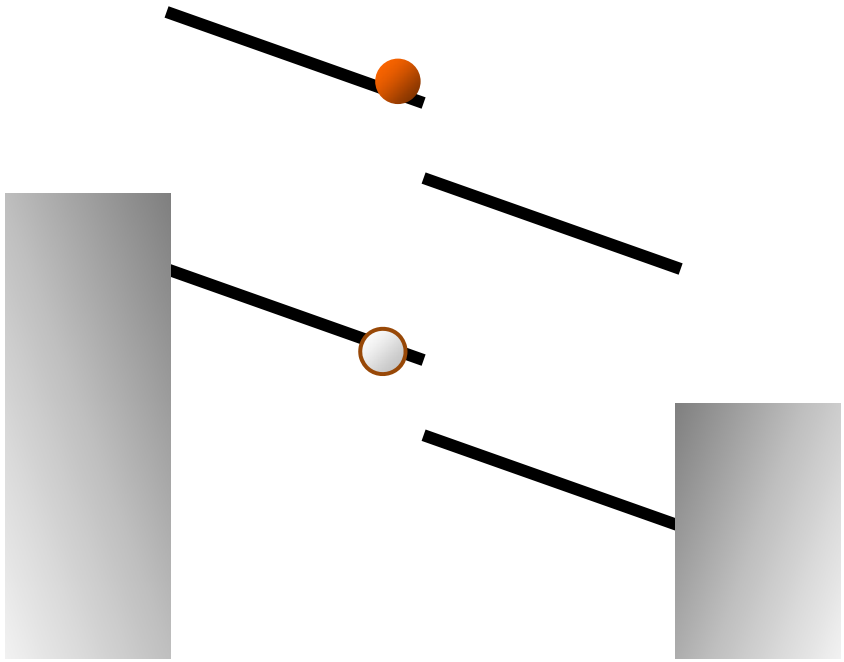


Hole transporter / Electron transporter

Exciton Dissociation Bulk heterojunctions

- Charge is transferred across the junction

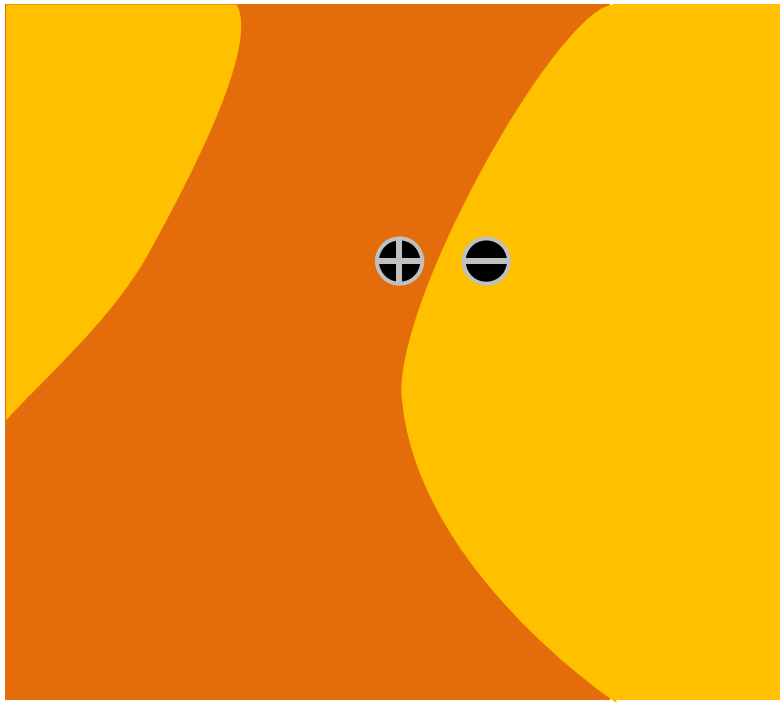


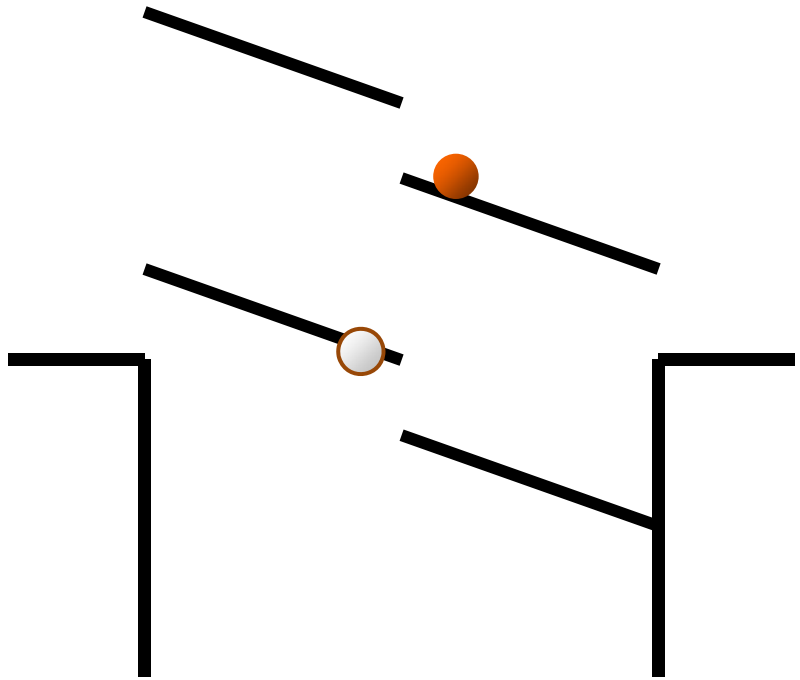


Hole transporter / Electron transporter

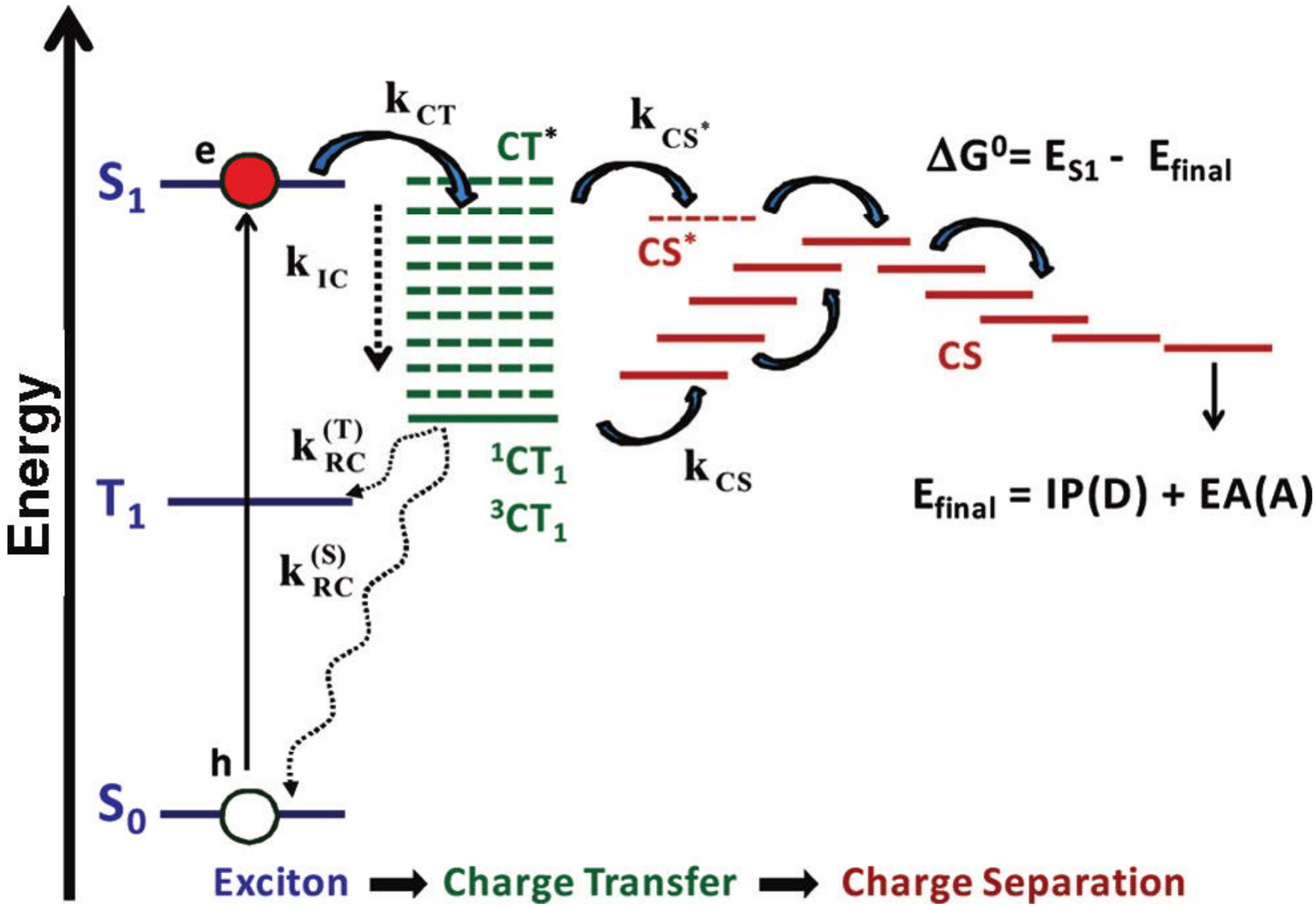
Exciton Dissociation at Bulk heterojunctions

- Charges drift to the electrodes

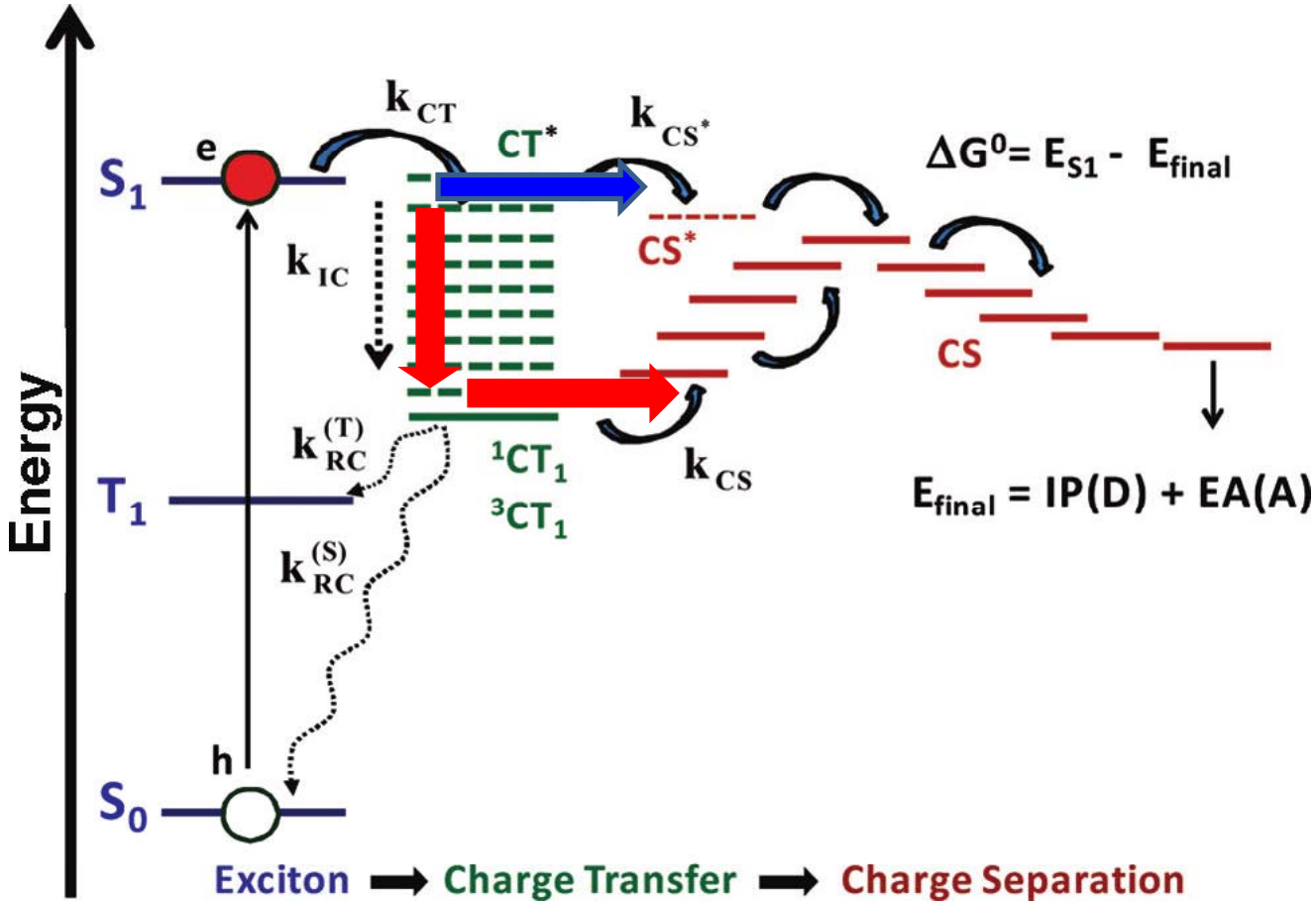




Hole transporter / Electron transporter



'Molecular Understanding of Organic Solar Cells', BREDAS et al, **Accounts Of Chemical Research, Vol. 42, No. 11 November 2009 1691-1699**



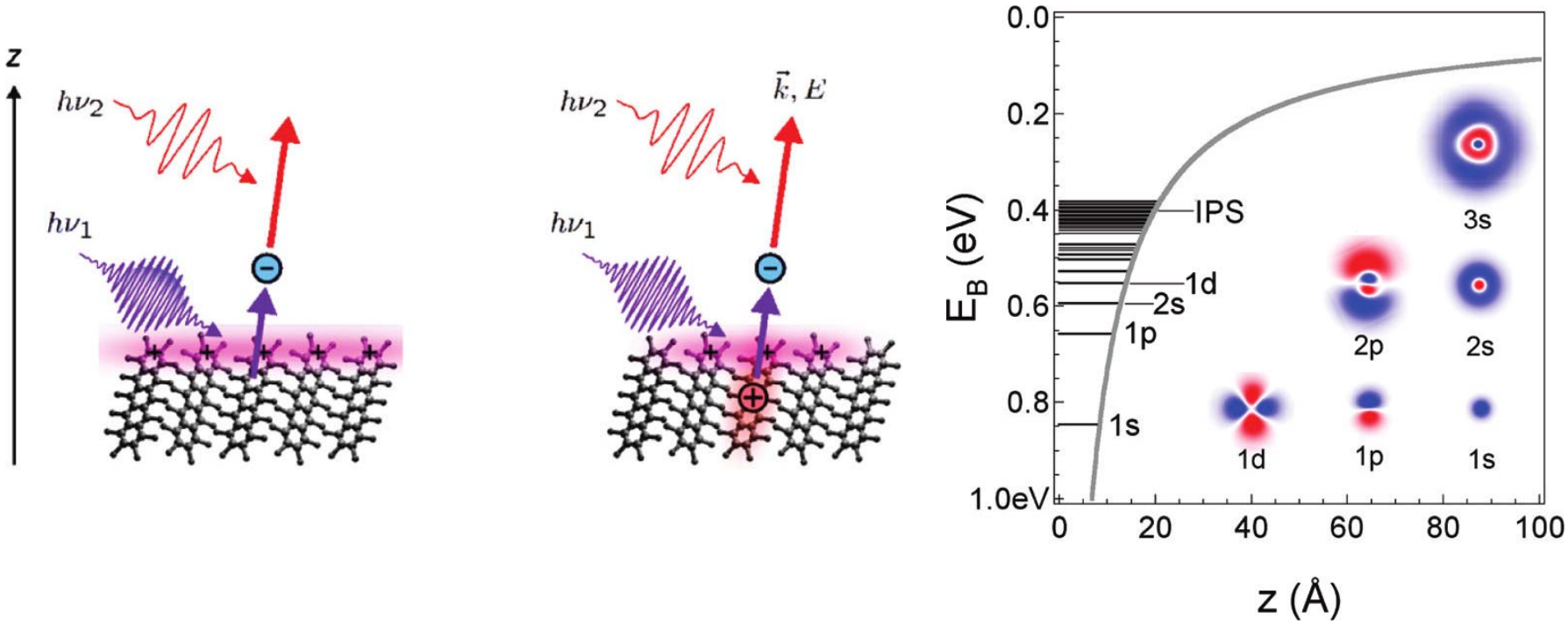
Question: What is the role of the CT state in charge separation in OPVs?

The possible answers:-

1)It's a ditch: Once you relax through the CT manifold charges can't be extracted. Need to go through 'Hot CT states' to create charge.

2) Charge can be efficiently generated even from the lowest CT state.

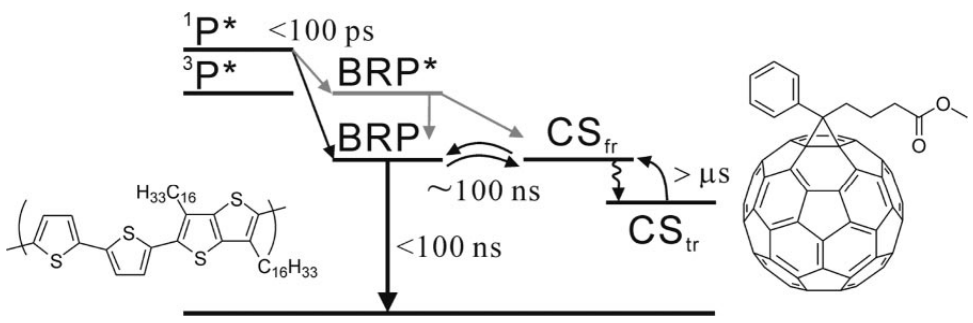
Evidence for Hot CT states 1



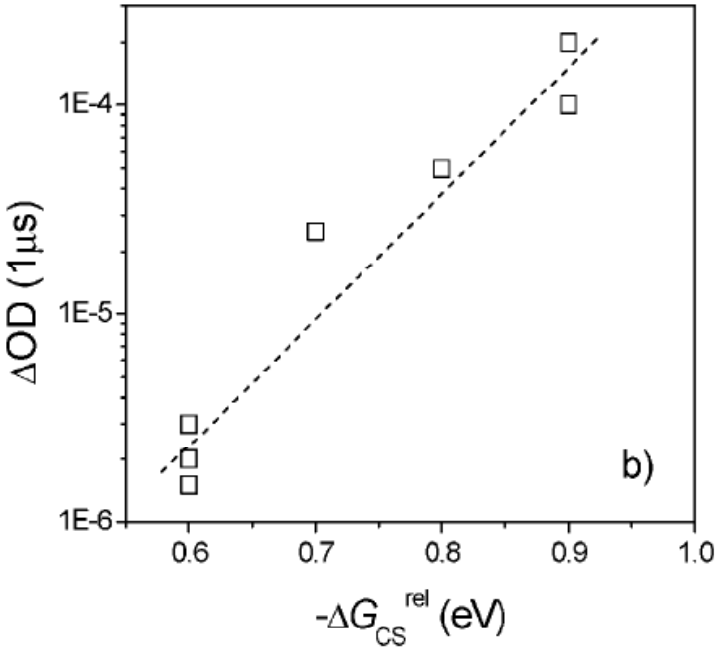
1. Time-resolved two-photon photoemission (TR-2PPE) spectroscopy used to extract CT energies for Pentacene monolayer on Bi(111) surface.
2. CT binding energies between 0.1-0.5eV.

Zhu et.al. **Accounts Of Chemical Research Vol. 42, No. 11 November 2009 1779-1787**

Evidence for Hot CT states 2



Series of polythiophenes mixed with varying amounts of PCBM.

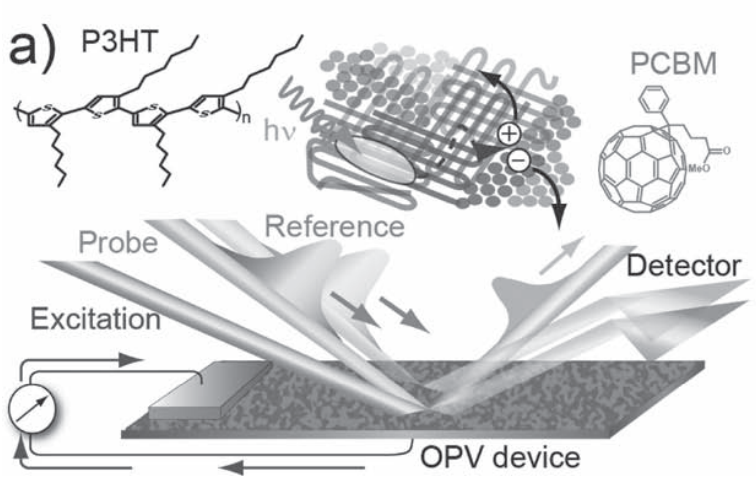


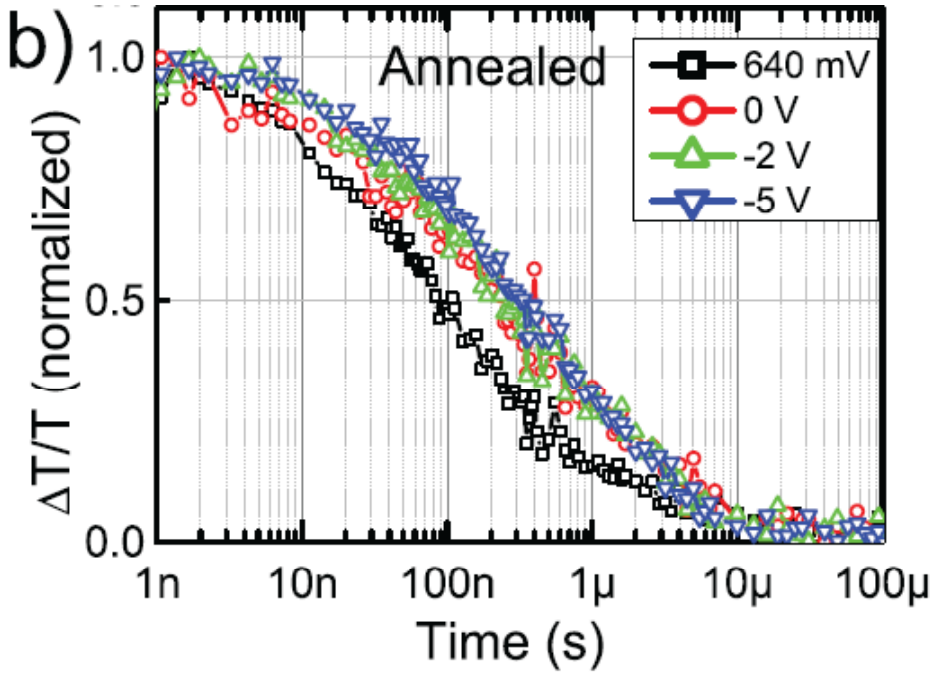
ΔGCS: the difference in energy between the singlet exciton and the dissociated charge-separated state.

Transient Absorption measurements suggest that dissociation is through 'Hot CT' state.

Durrant et al, **JACS. 2008, 130, 3030**

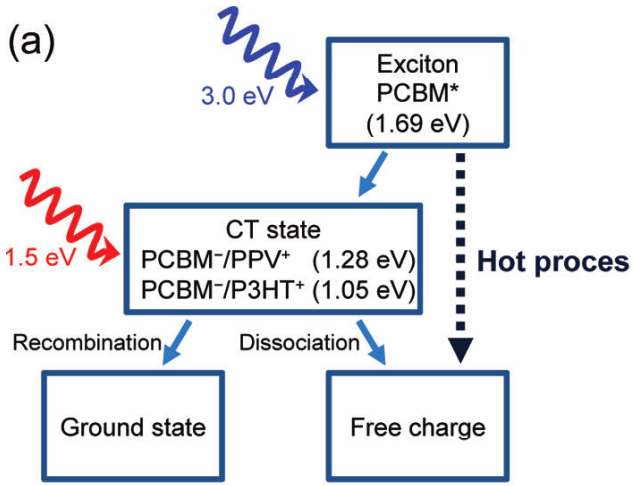
Evidence against Hot CT states 1

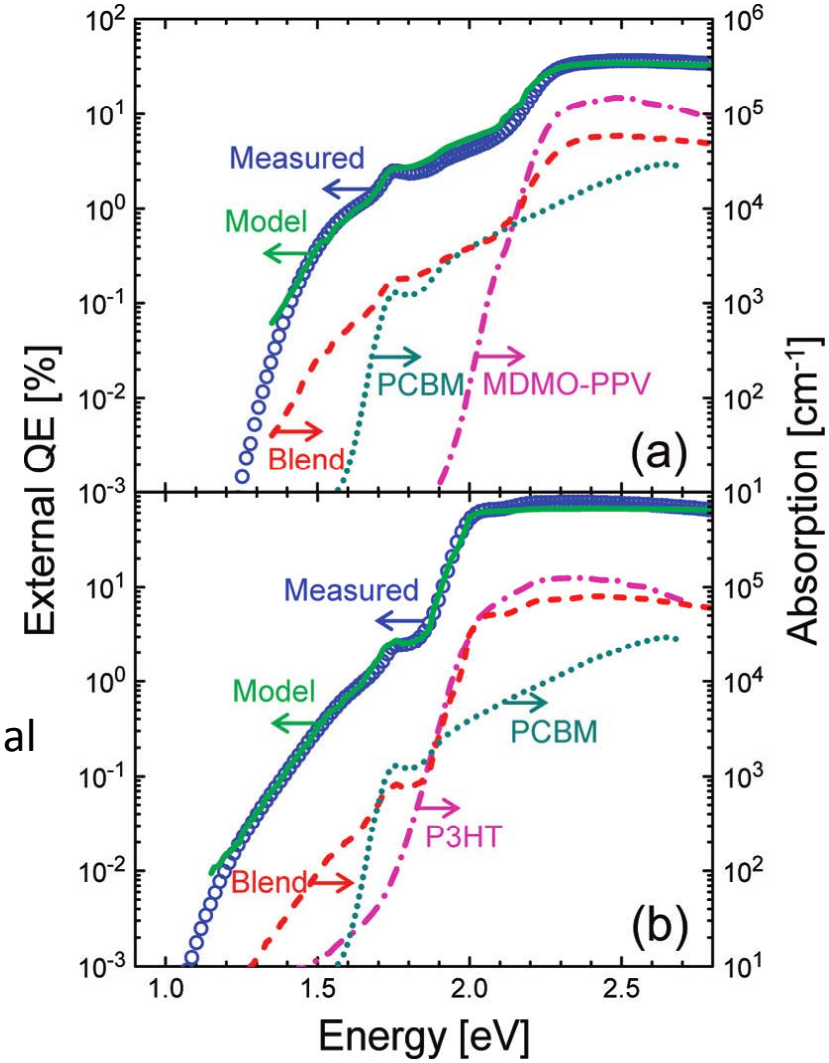




Direct Measurement of Electric Field-Assisted Charge Separation in Polymer:Fullerene Photovoltaic Diodes, R. Alex Marsh , Justin M. Hodgkiss , and Richard H. Friend, ***Adv. Mater. 2010***

Evidence against Hot CT states 2

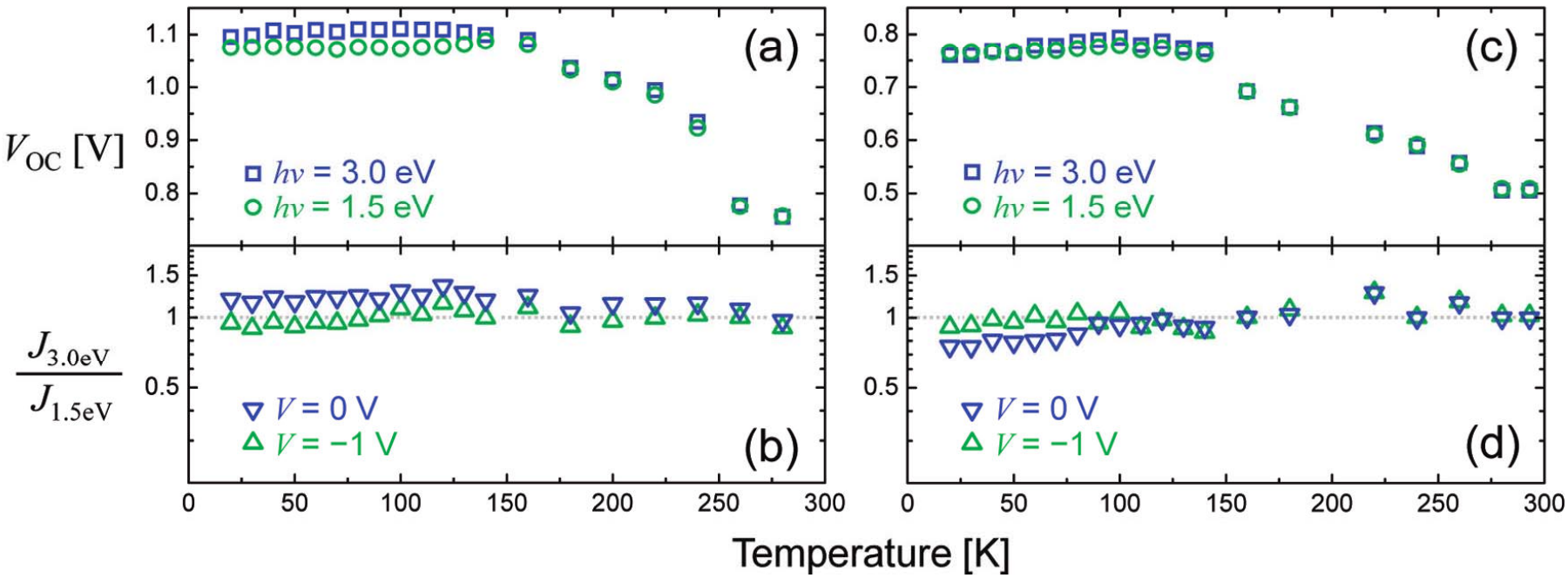




1. EQE measured via Fourier-transform photocurrent spectroscopy (FTPS).
2. Absorption measured using photothermal deflection spectroscopy (PDS)

Charge Transfer State Versus Hot Exciton Dissociation in Polymer-Fullerene Blended Solar Cells, Baldo et.al, **JACS (2010)**.

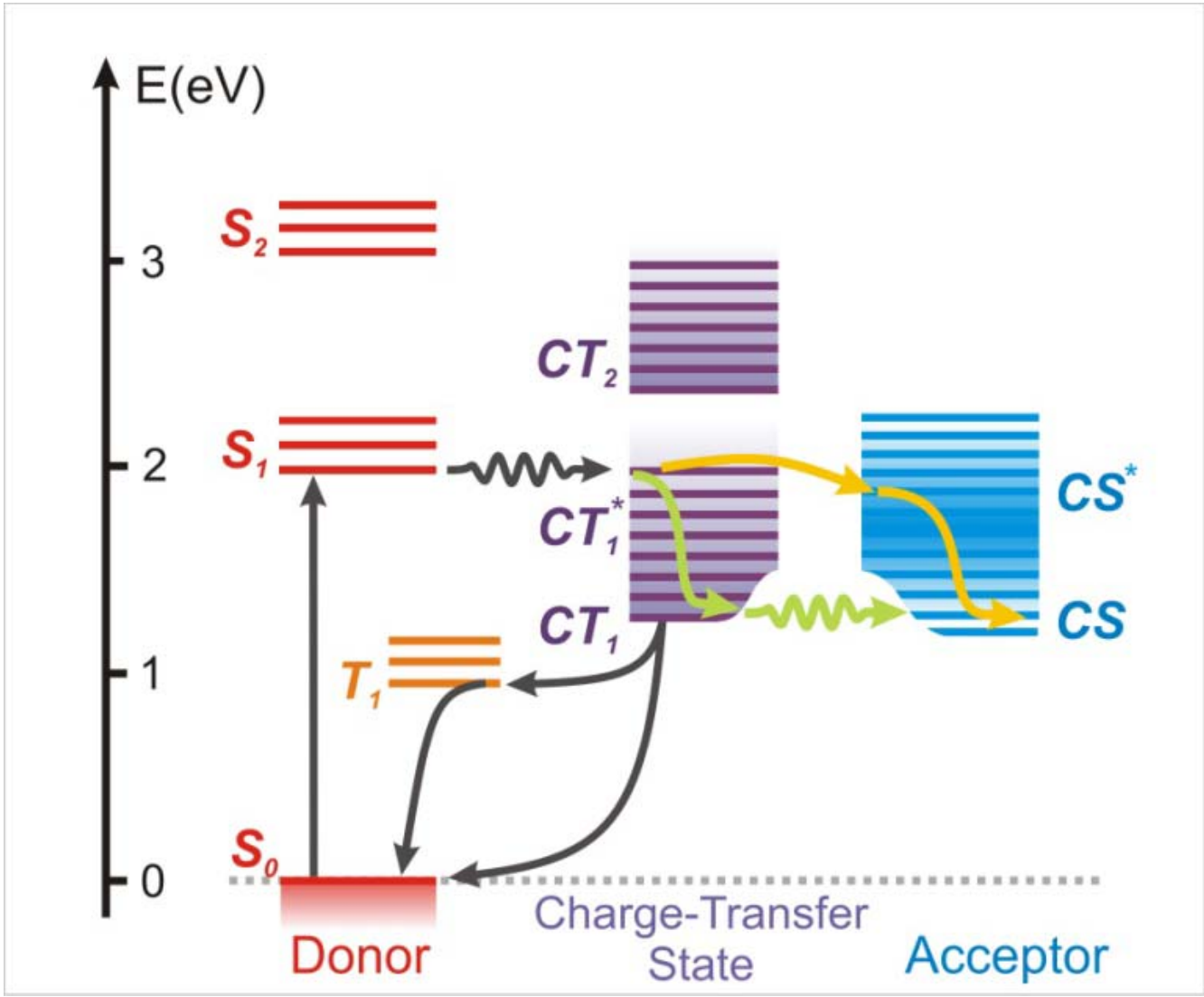
Evidence against Hot CT states 2



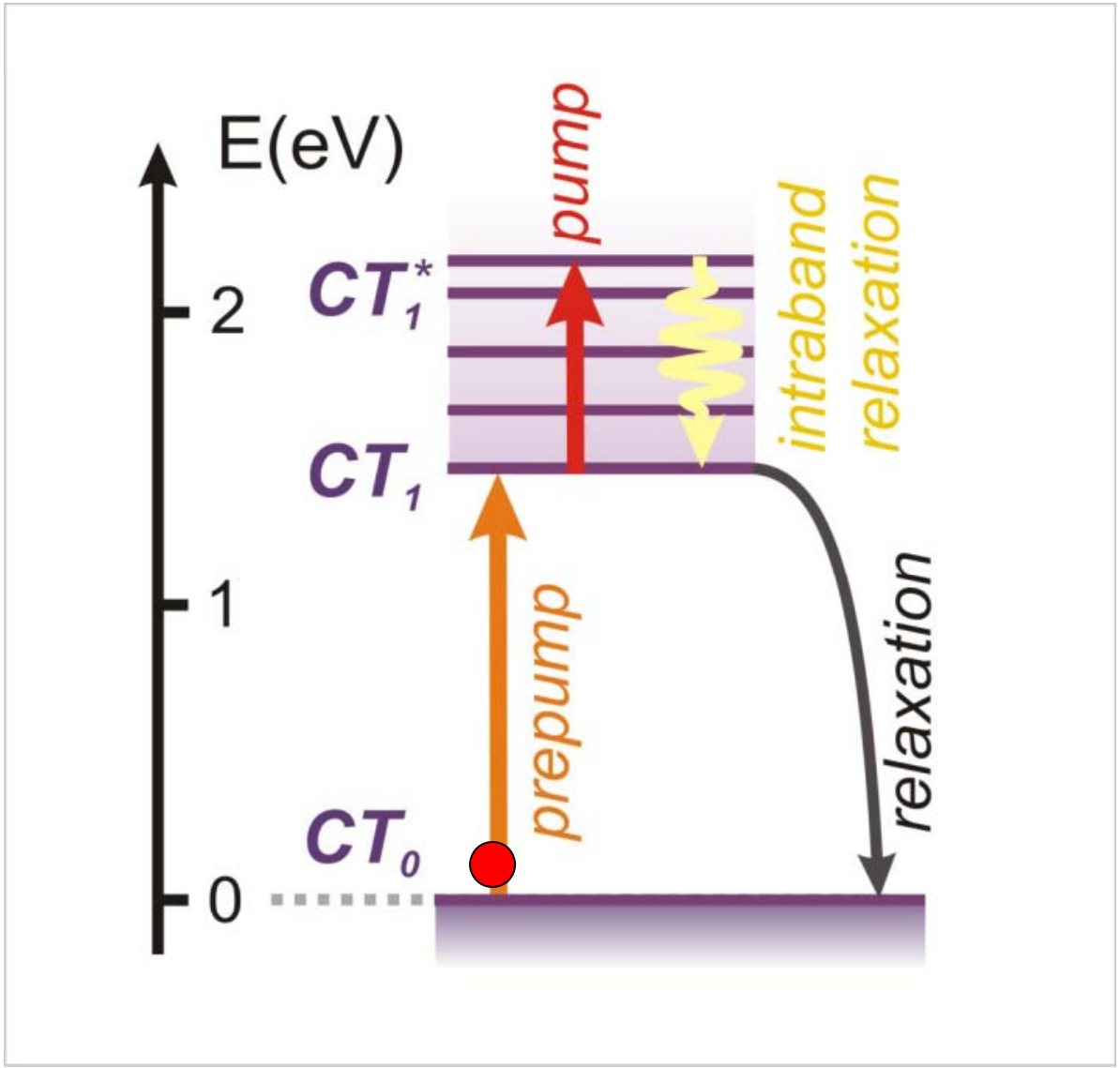
1. Some difference in CT vs Exciton photocurrent at low temperature but no difference at room temperature.
2. Conclusion: Every optically accessible exciton and CT state exhibits a similar probability of charge generation or recombination.

Charge Transfer State Versus Hot Exciton Dissociation in Polymer-Fullerene Blended Solar Cells, Baldo et.al, **JACS (2010)**.

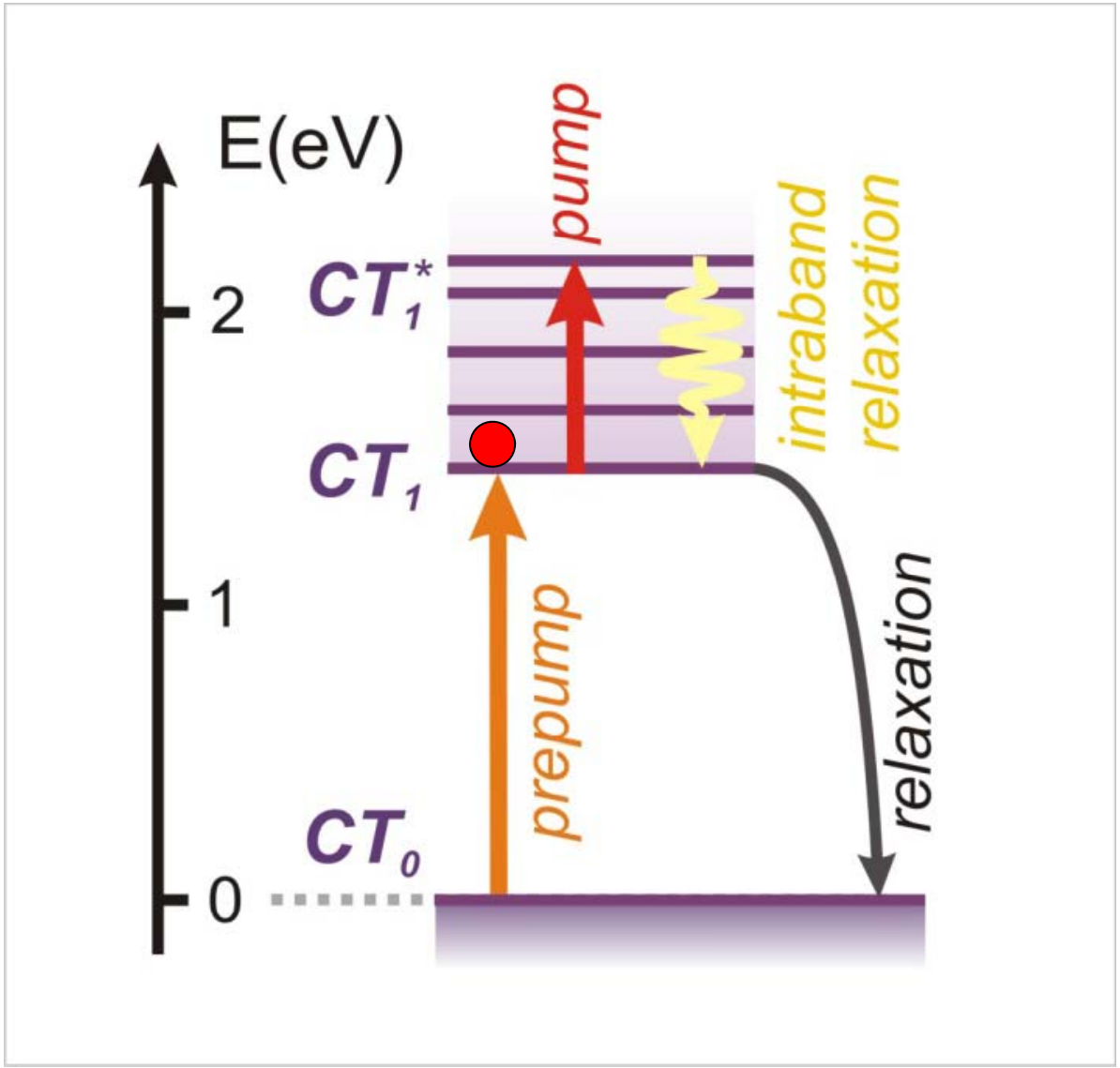
General picture of photon-to-charge conversion in organic semiconductors



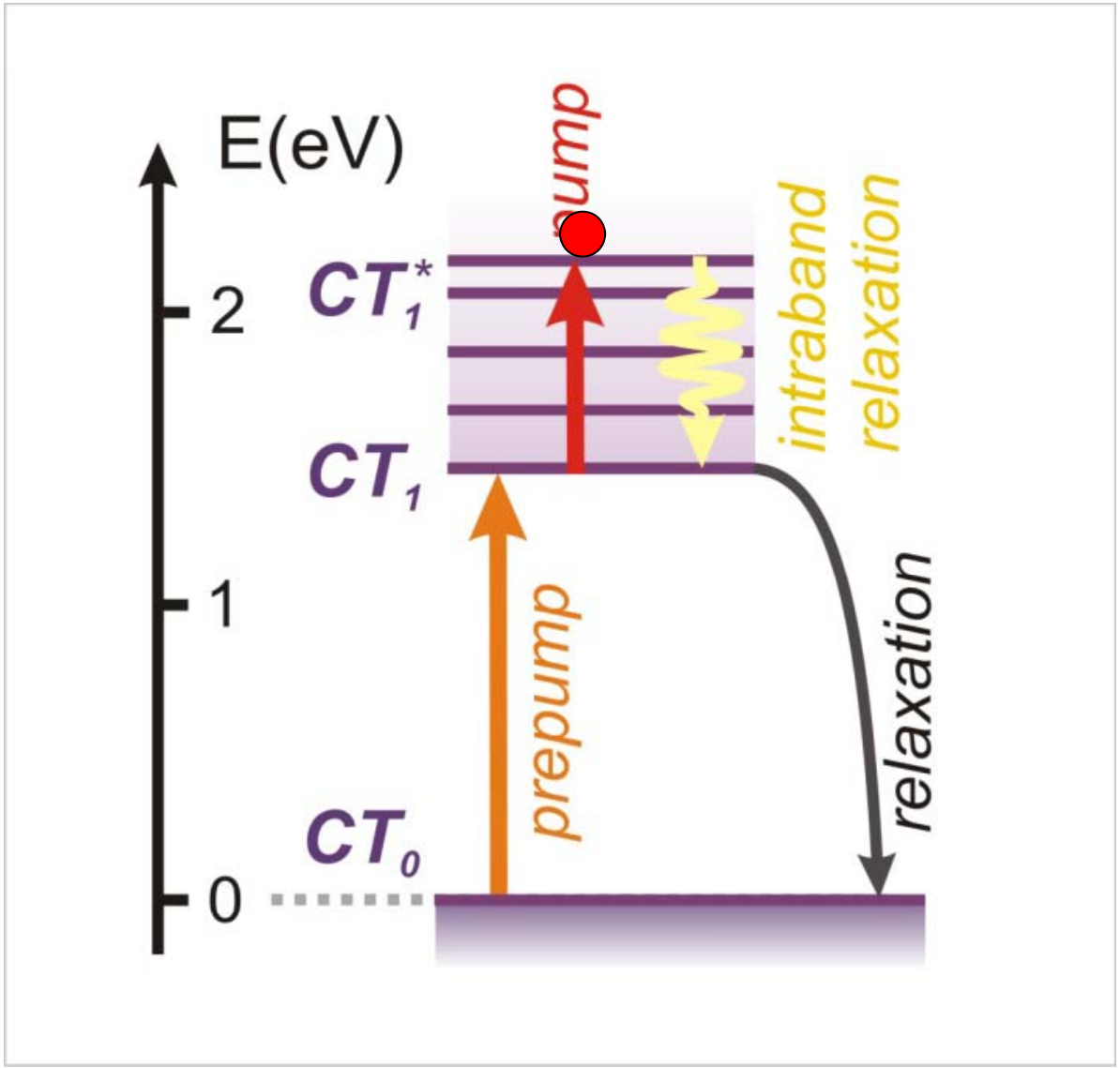
The way to measure intraband (hot state) relaxation time



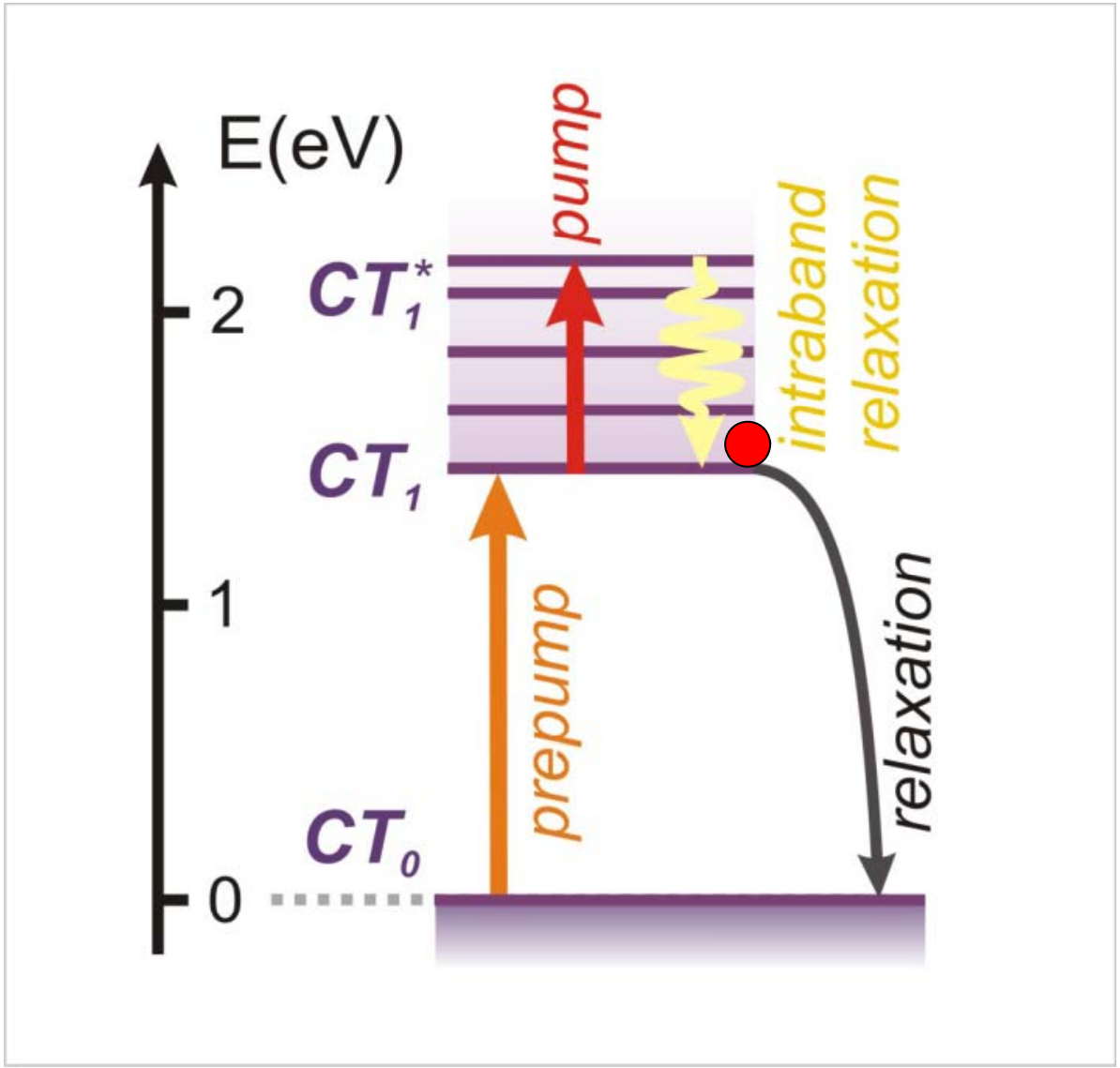
The way to measure intraband (hot state) relaxation time



The way to measure intraband (hot state) relaxation time

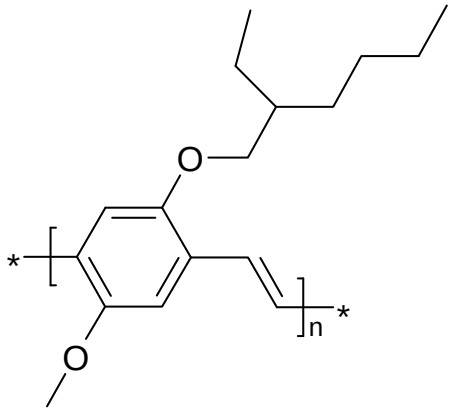


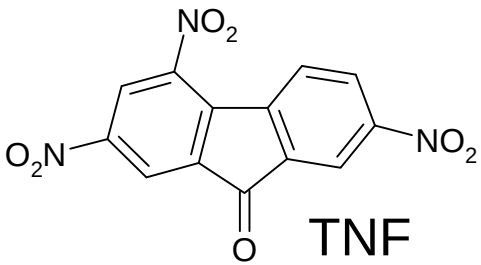
The way to measure intraband (hot state) relaxation time



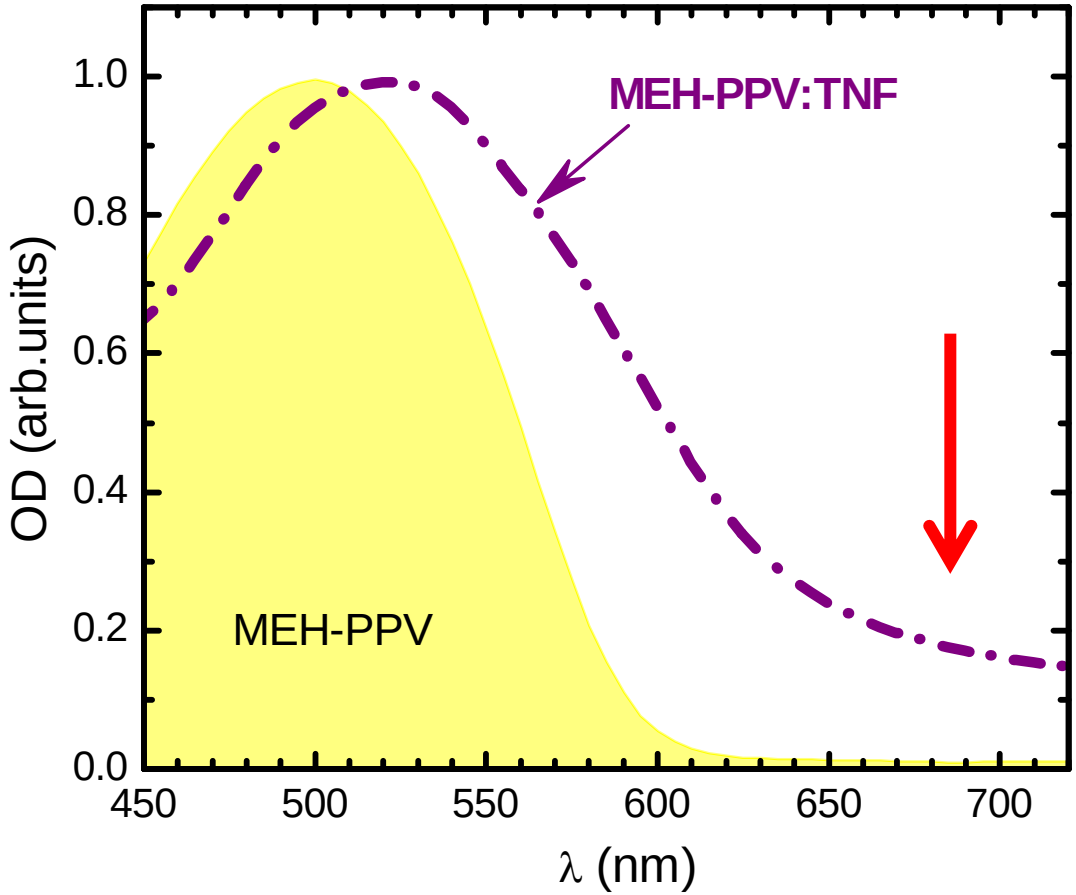
Selective excitation of CT state

MEH-PPV

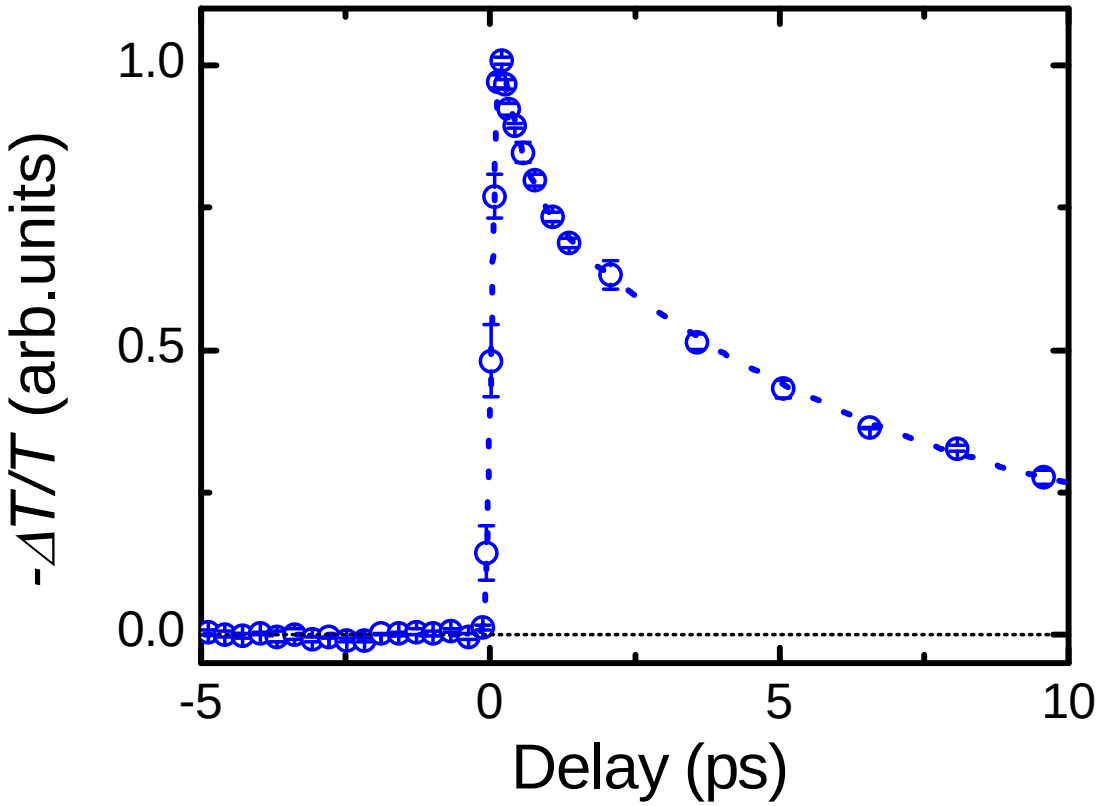


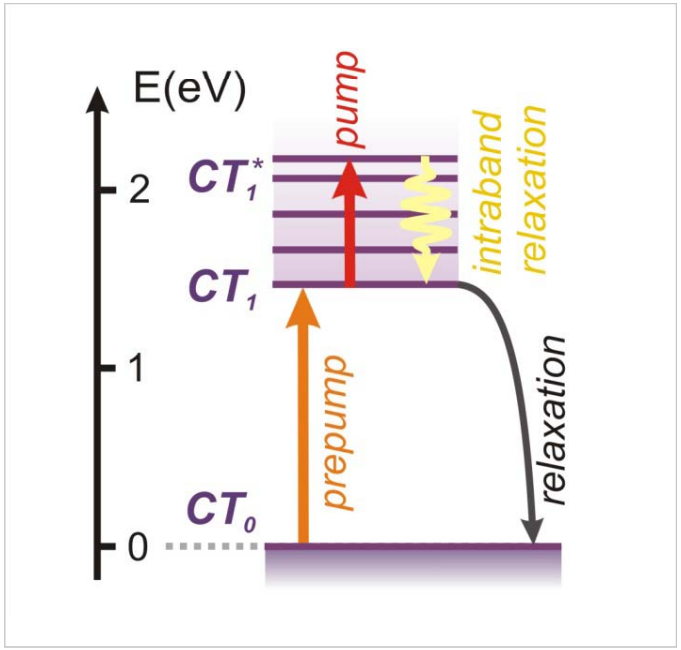


TNF



Ultrafast PIA in CTCs

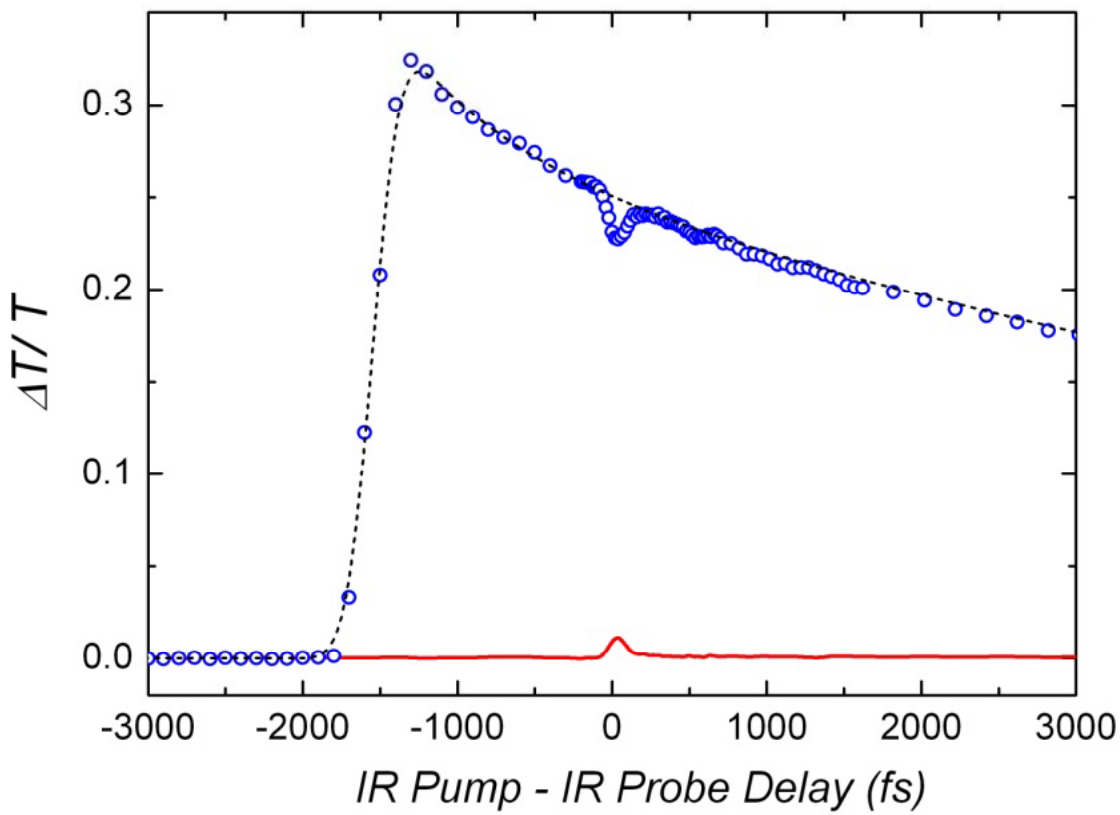


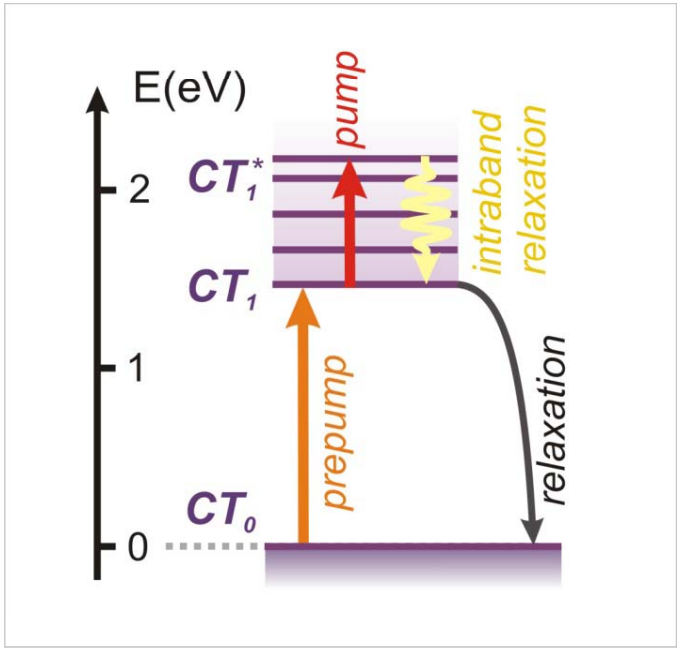


- Fast geminate recombination

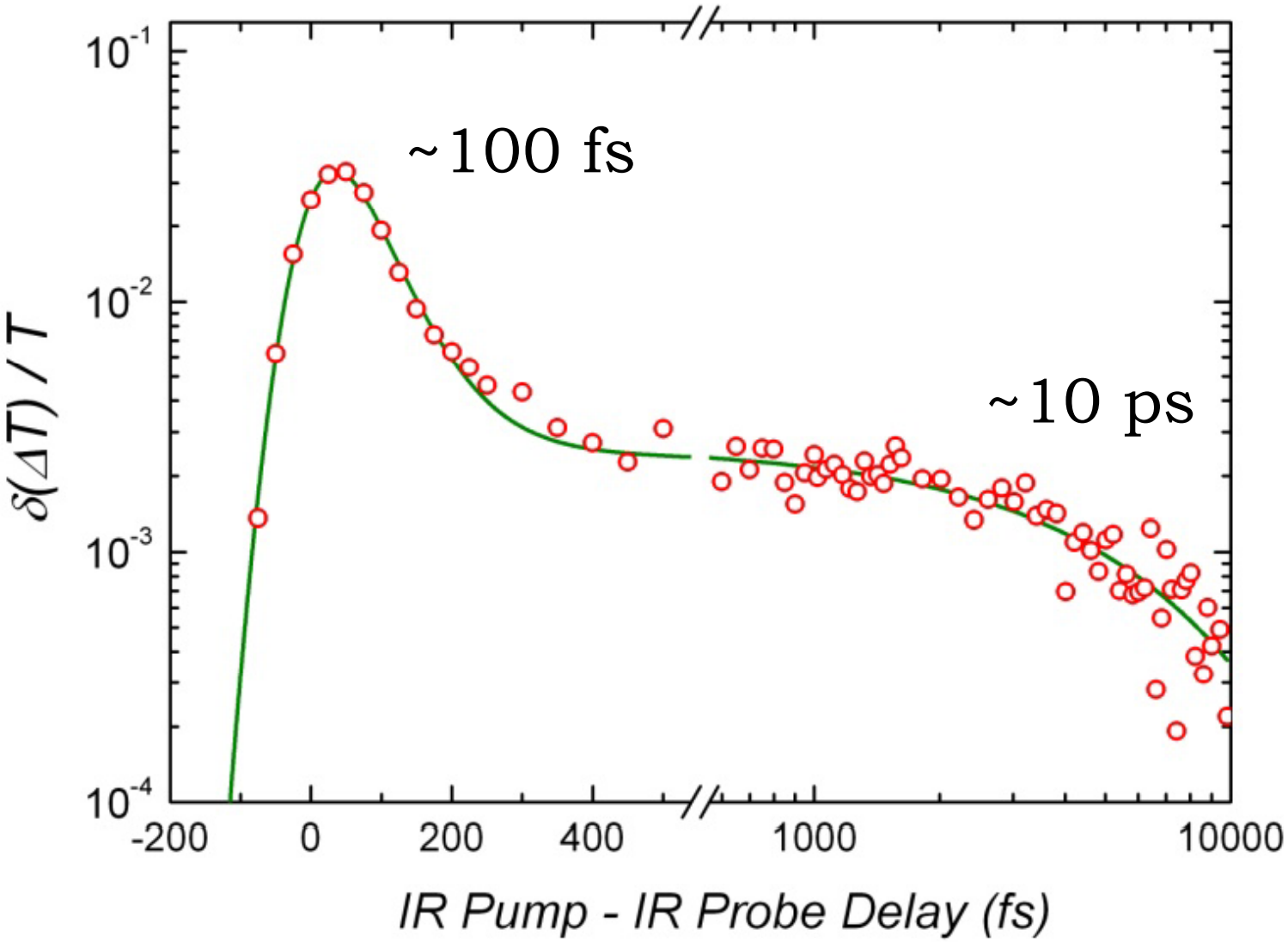
J. Phys. Chem. B **112**, 13730 (2008)

Observation of CT state cooling

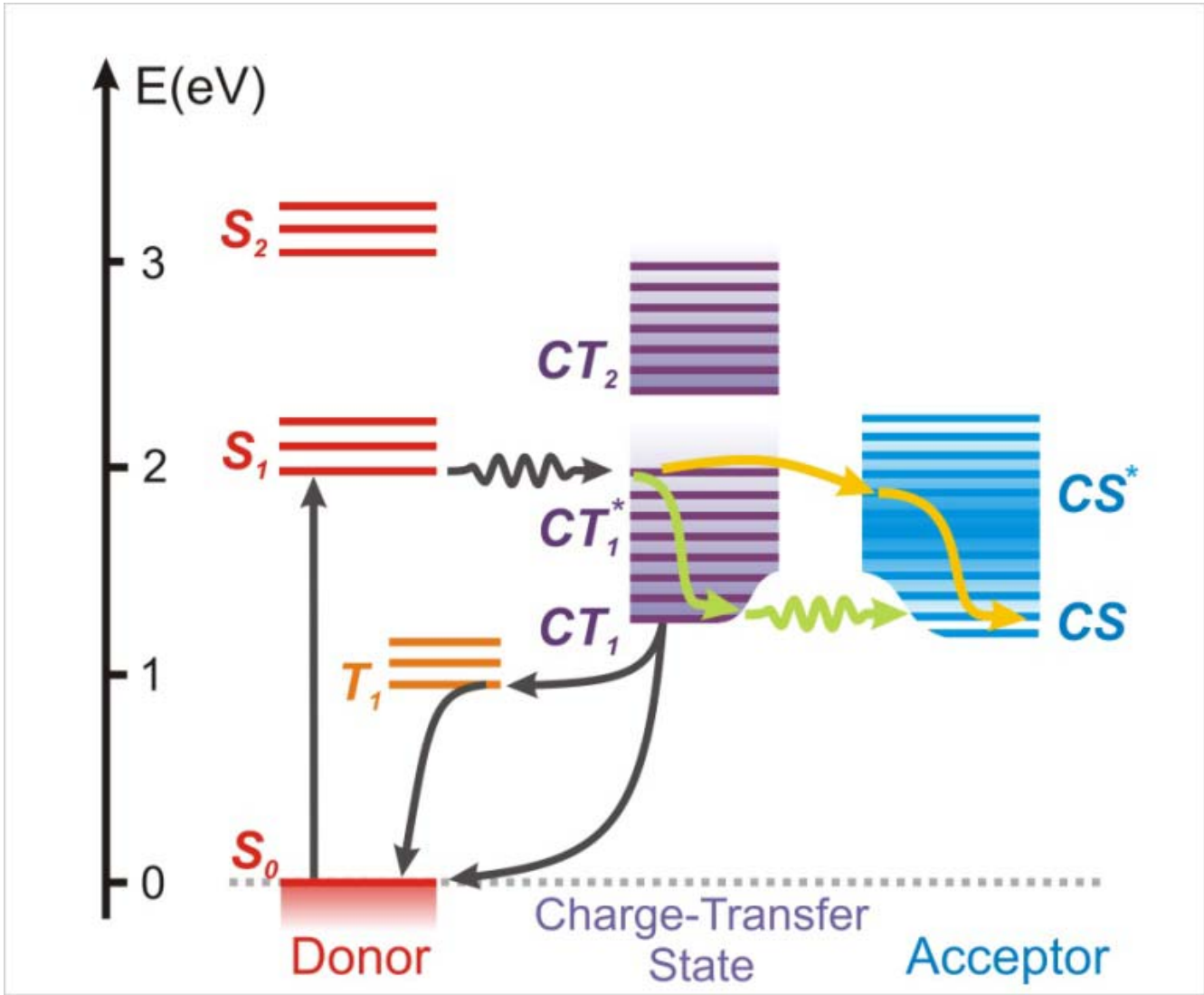




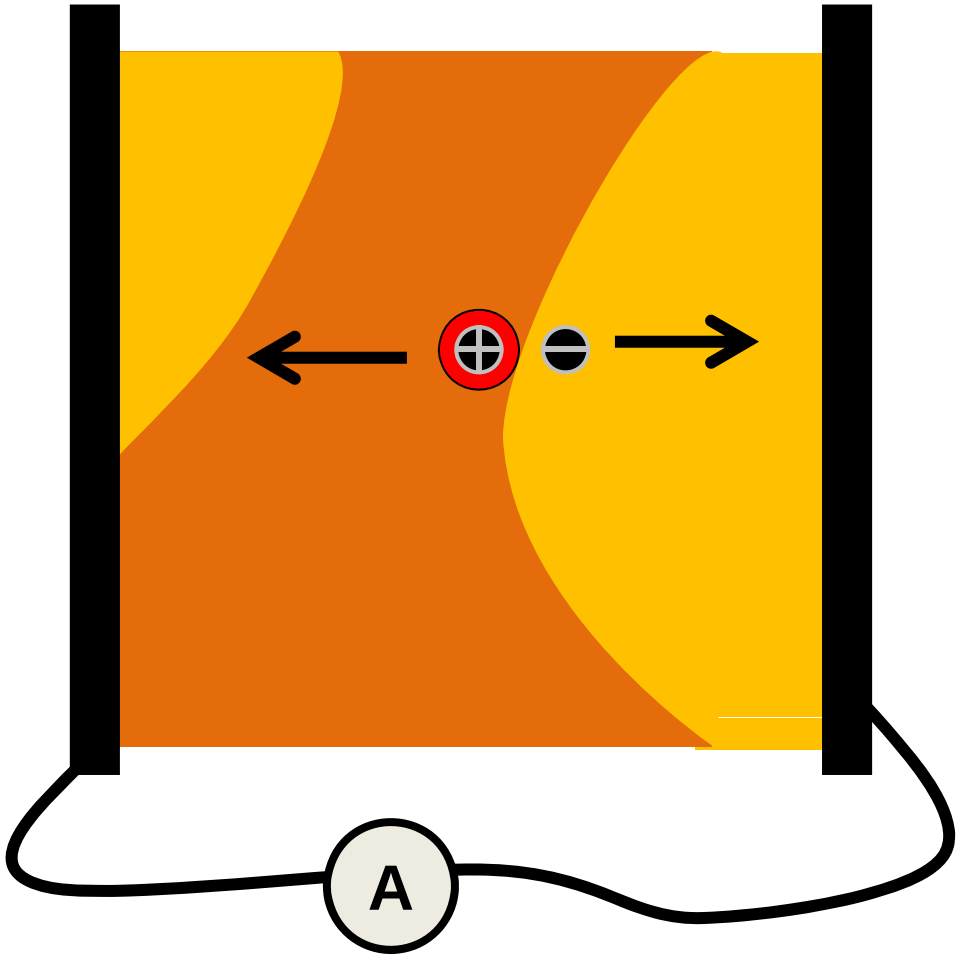
Kinetics of intraband relaxation

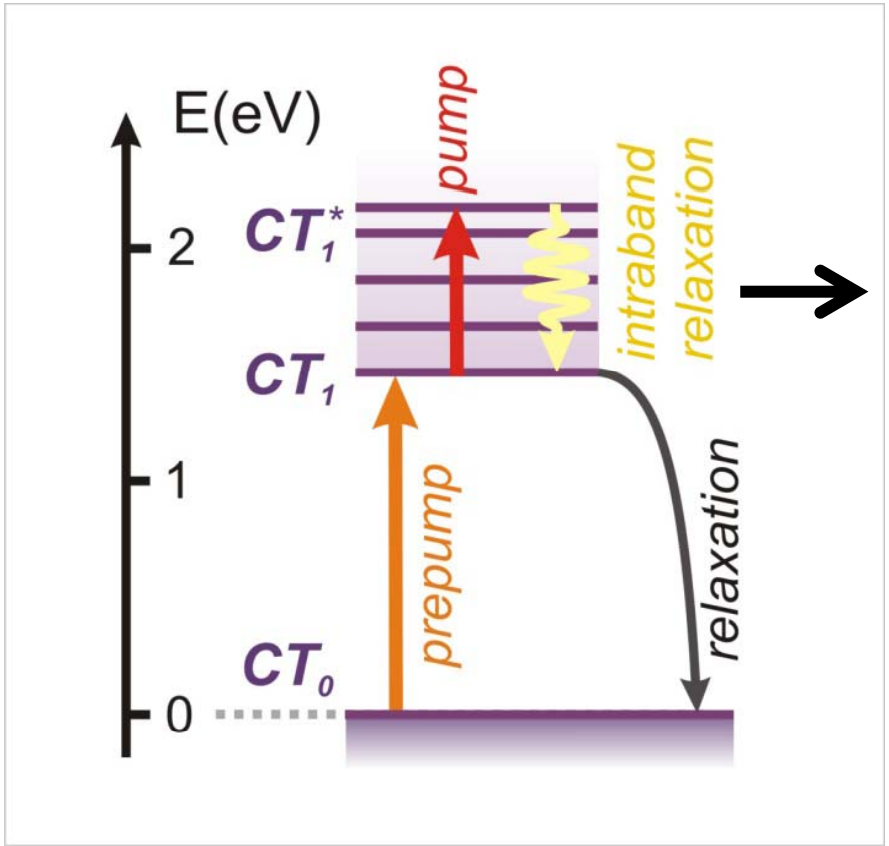


Intraband relaxation - dominative channel in charge generation



Possible perspective – “warm-up” induced Photocurrent





Conclusions

- Lots of theory and experiments point to the need for a hot dissociation

- even relaxed CT states can efficiently generate charge.

- Ultrafast relaxation of “hot” charge-transfer state is very efficient

- **The energy of CT state is important**

Acknowledgements

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- **Jenny Clark**
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University of Groningen
Zernike Institute
for Advanced Materials

Спасибо за внимание!

Papers

- Hot CT states not important:-

- *Charge Transfer State Versus Hot Exciton Dissociation in Polymer-Fullerene Blended Solar Cells,* Baldo et.al, **JACS (2010)**.
- *Compositional and Electric Field Dependence of the Dissociation of Charge Transfer Excitons in Alternating Polyfluorene Copolymer/Fullerene Blends*, Janssen et al. **JACS (2008), 130, 7721**.
- *The Relation Between Open-Circuit Voltage and the Onset of Photocurrent Generation by Charge-Transfer Absorption in Polymer*, Manca et al. **Adv. Funct. Mater. 2008,18, 2064–2070**.
- *Direct Measurement of Electric Field-Assisted Charge Separation in Polymer:Fullerene Photovoltaic Diodes***,** R. Alex Marsh , Justin M. Hodgkiss , and Richard H. Friend*, **Adv. Mater. 2010***

- Hot CT states are important:-

- Durrant et al, **JACS. 2008, 130, 3030 &** *Charge Photogeneration in Organic Solar Cells***, Chem Rev.**
- Zhu et.al. **PRL 101, 196403 (2008) & Accounts Of Chemical Research Vol. 42, No. 11 November 2009 1779-1787**
- Bredas et al, **Accounts Of Chemical Research, Vol. 42, No. 11 November 2009 1691-1699**.