NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Probing solar photoconversion using flash-photolysis time-resolved microwave conductivity (FP-TRMC)

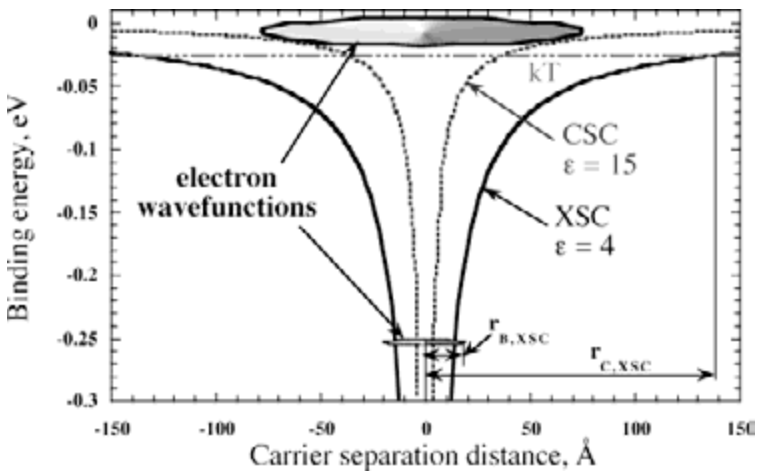
Chemical & Nanosciences Group
Chemical & Materials Science Center

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

TRMC users

- **PI: Garry Rumbles**
- Current users
  - Rebecca Callahan (liquid crystal donor materials)
  - Ryan Crisp (semiconductor NC films)
  - Andrew Ferguson (polymer:fullerene & polymer:SWCNT blends)
  - Nikos Kopidakis (polymer:fullerene & polymer:SWCNT blends; sensitized oxides)
  - Bryon Larson (polymer:perfluoroalkyl fullerene systems)
  - Hilary Marsh (conjugated polymers)
  - Alex Nardes (polymer:small molecule blends)
  - Obadiah Reid (TRMC technique development; conjugated polymers)
- Alumni
  - Jorge Piris (built NREL's original TRMC system; sensitized oxides)
  - Dominick Bindl (SWCNT/fullerene bilayers)
  - David Coffey (fundamental charge-transfer processes)
  - Smita Dayal (semiconductor NCs; polymer:semiconductor NC blends)
  - Josh Holt (polymer:SWCNT blends)

Excitonic semiconductors



B. A. Gregg, S.-G. Chen, R. A. Cormier, *Chem. Mater.* **16** (2004) 4586.

- Photoexcitation generates **excitons**
  - Exciton binding energy ca. 200 meV
- **Small** diffusion constant*
  - $D \approx 0.25–5 \times 10^{-3}$ cm^2s^{-1}
- **Short** exciton lifetime**
  - $\tau \approx 0.2–1$ ns

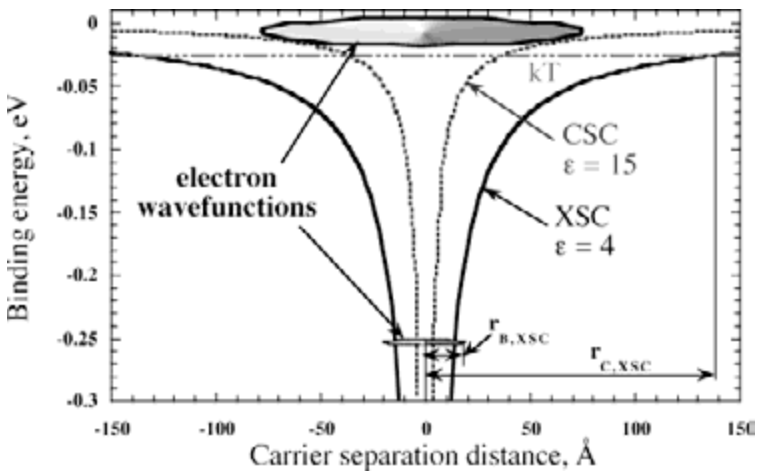
* P.E. Shaw, A. Ruseckas, I. D. W. Samuel, *Adv. Mater.* **20** (2008) 3516.

** L. Magnani, G. Rumbles, I. D. W. Samuel, K. Murray, S. C. Moratti, A. B. Holmes, R. H. Friend, *Synth. Met.* **84** (1997) 899.

Length scales:

- **Short** exciton diffusion length
  - $L = \sqrt{D\tau} \approx 5 – 10$ nm
- Absorption depth
  - $1/\alpha \approx 100$ nm
- **Exciton bottleneck**

Excitonic semiconductors



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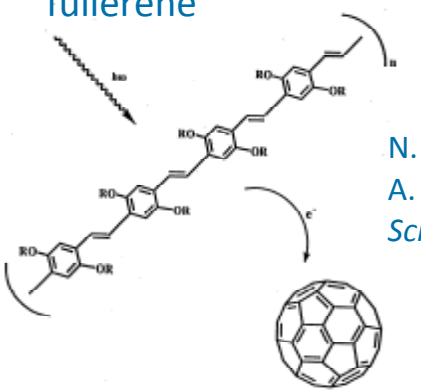
Potential solution:

- Efficient exciton dissociation, due to electron transfer from conjugated polymer to fullerene



N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, *Science* **258** (1992) 1474.

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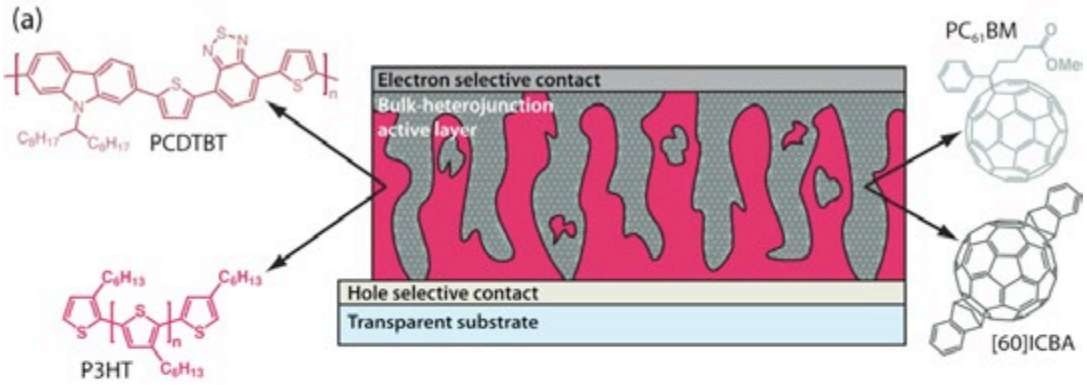
The *bulk heterojunction* (donor-acceptor blend)



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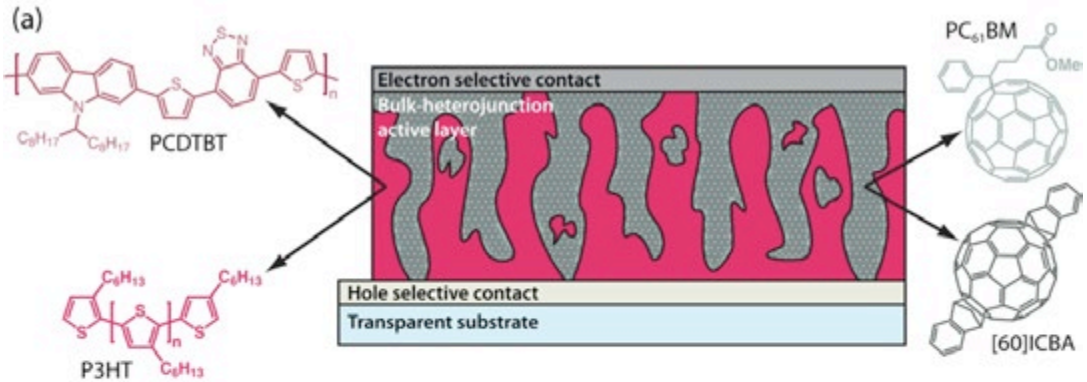

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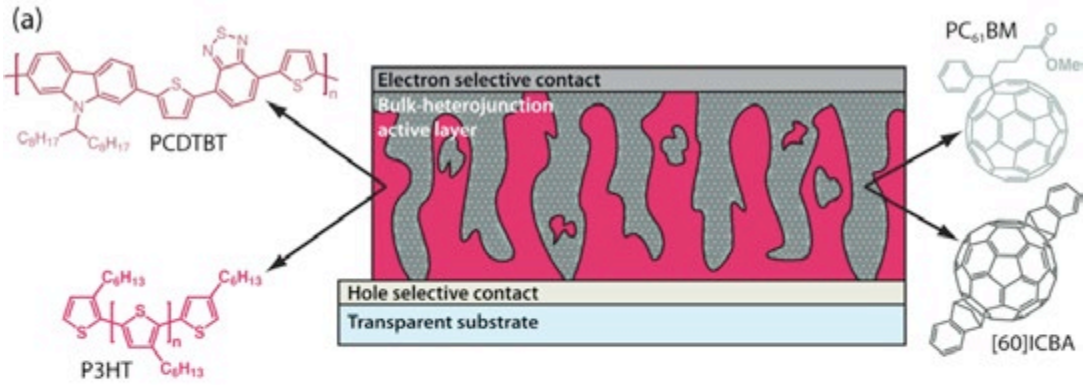
Solution:

- Exploit **efficient** electron transfer
  - Nanostructured blend of conjugated polymer and fullerene derivative

Practical difficulties:

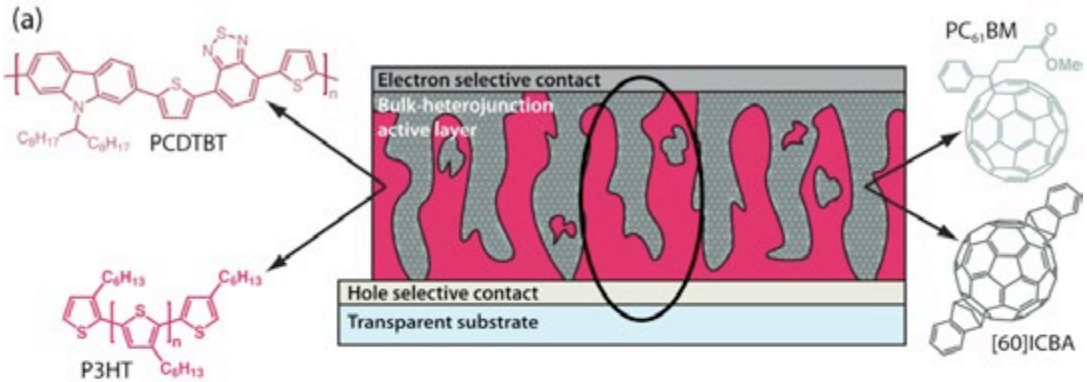
- **Controlling** the nanomorphology
  - Need domain size comparable to *L*
  - Maintain percolation pathways to collect carriers
- **Predicting** electronic structure of blend

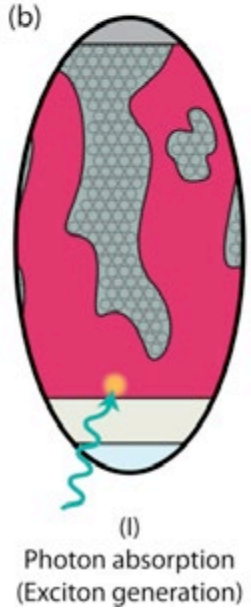
Photoinduced processes in a bulk heterojunction



D + A

Photoinduced processes in a bulk heterojunction

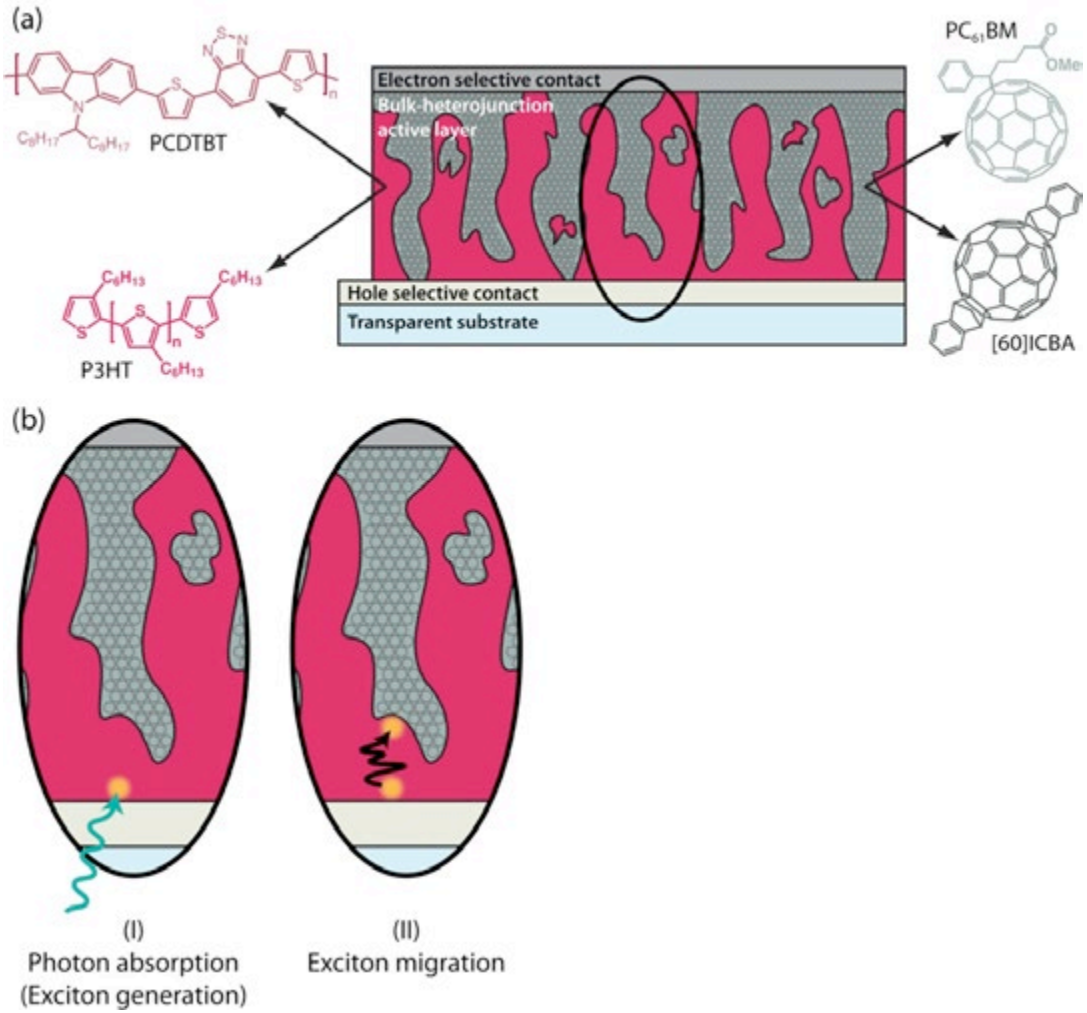




$$D + A \xrightarrow{\eta_A} D^* + A$$

photon absorption
(exciton generation)

Photoinduced processes in a bulk heterojunction



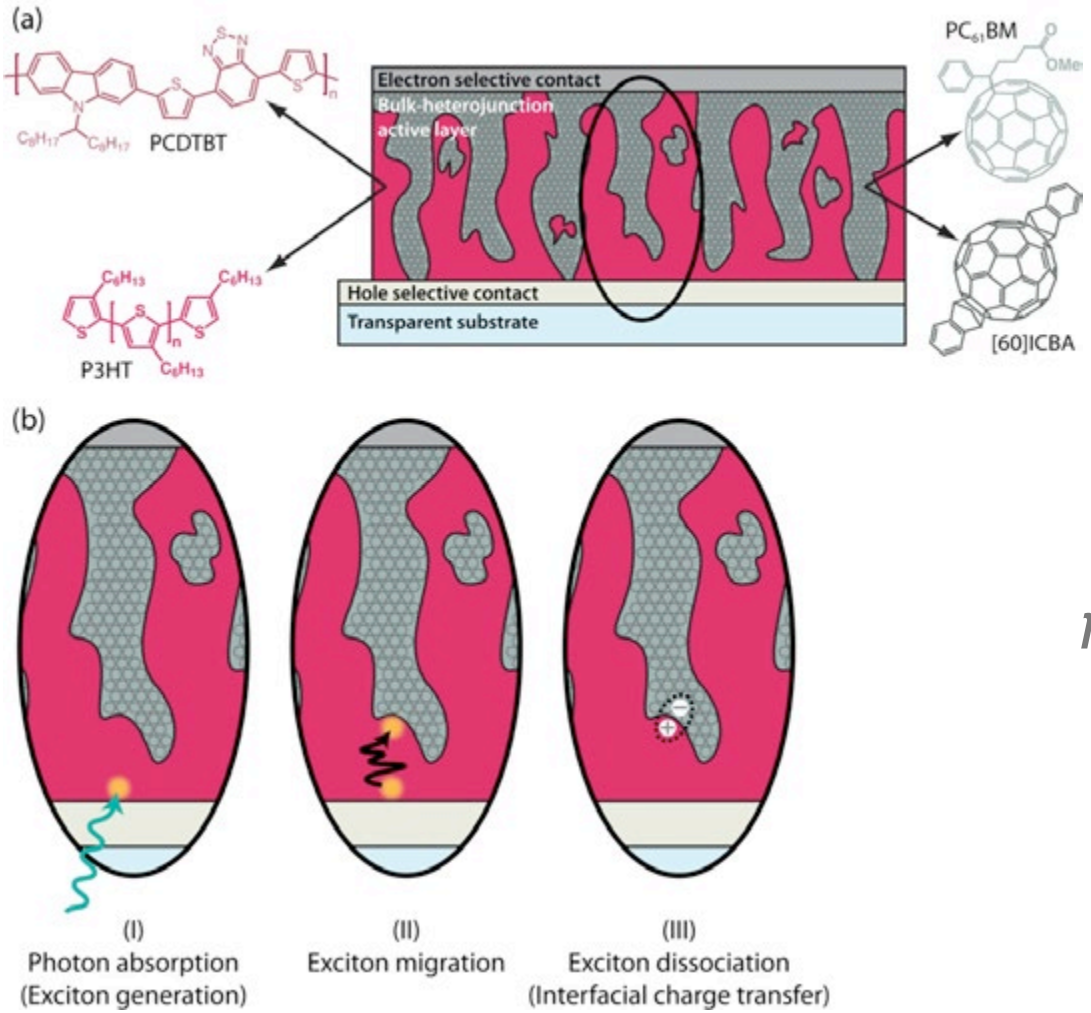
$$D + A \xrightarrow{\eta_A} D^* + A$$

photon absorption (exciton generation)

$$\xrightarrow{\eta_{diff}}$$

exciton migration

Photoinduced processes in a bulk heterojunction



$$D + A \xrightarrow{\eta_A} D^* + A$$

photon absorption (exciton generation)

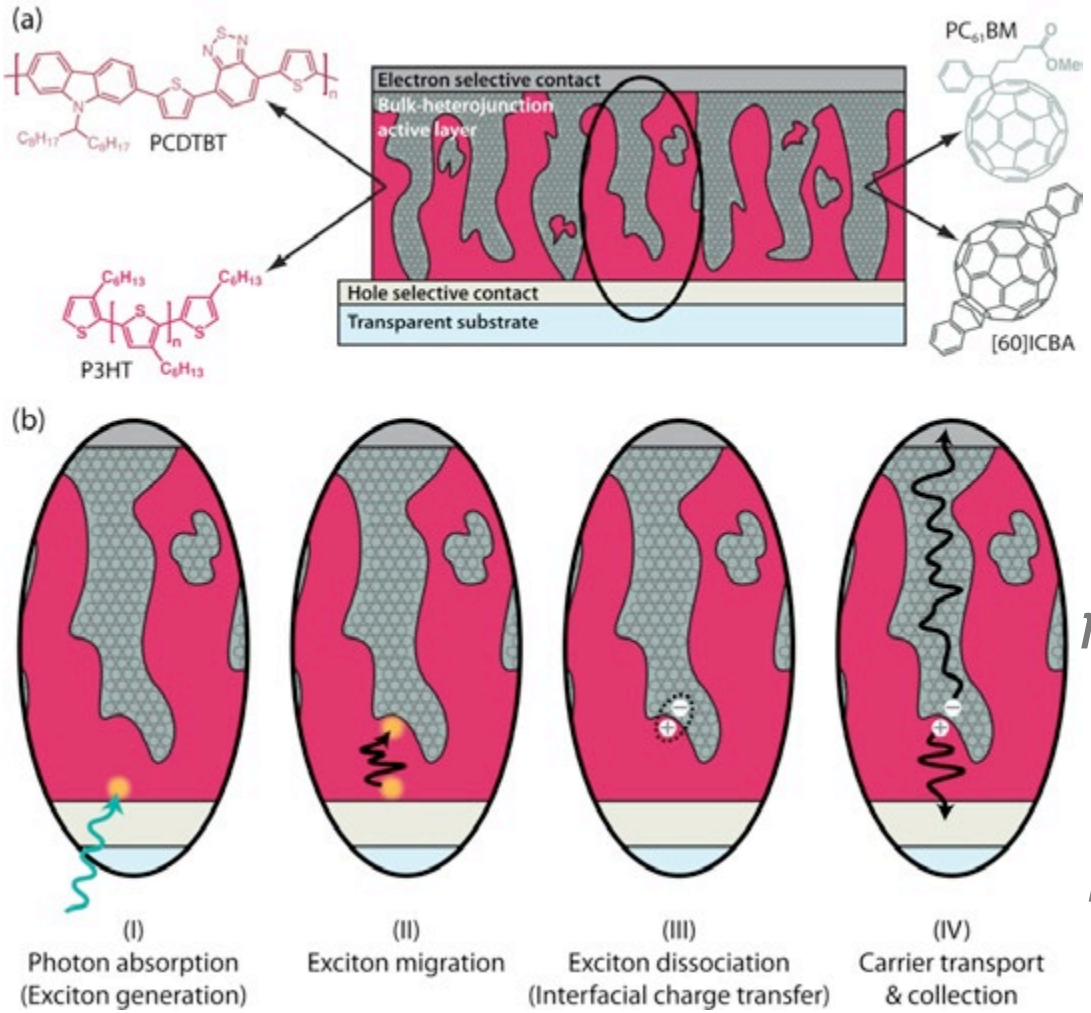
$$D^* + A \xrightarrow{\eta_{diff}} \{D^{*}\cdots A\}$$

exciton migration

$$\{D^{*}\cdots A\} \xrightarrow{\eta_{diss}} \{D^{+}\cdots A^{-}\}$$

exciton dissociation

Photoinduced processes in a bulk heterojunction



$D + A$

η_A ↓ photon absorption (exciton generation)

$D^* + A$

η_{diff} ↓ exciton diffusion

$\{D^* \cdots A\}$

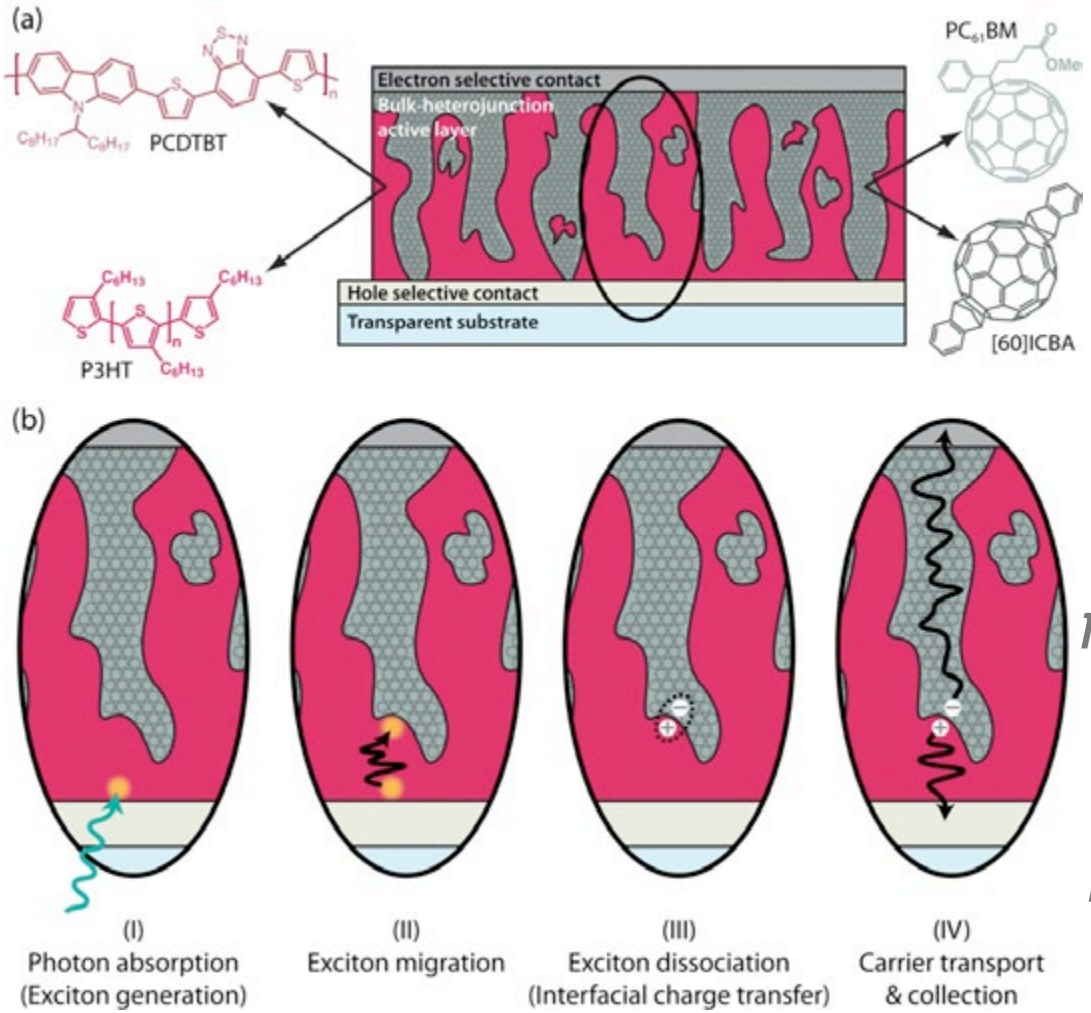
η_{diss} ↓ exciton dissociation

$\{D^+ \cdots A^-\}$

η_{sep} ↓ free carrier generation

$D^+ + A^- \xrightarrow{\eta_{coll}}$ Carrier collection

Photoinduced processes in a bulk heterojunction



$$D + A \xrightarrow{\eta_A} D^* + A$$

$$D^* + A \longrightarrow D + A$$

$$D^* + A \xrightarrow{\eta_{diff}} \{D^* \cdots A\}$$

$$\{D^* \cdots A\} \longrightarrow D + A$$

$$\{D^* \cdots A\} \xrightarrow{\eta_{diss}} \{D^+ \cdots A^-\}$$

$$\{D^+ \cdots A^-\} \longrightarrow D + A$$

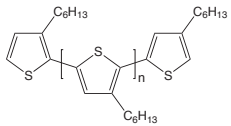
$$\{D^+ \cdots A^-\} \xrightarrow{\eta_{sep}} D^+ + A^-$$

$$D^+ + A^- \xrightarrow{\eta_{coll}} \text{Carrier collection}$$

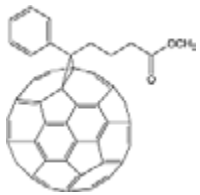
loss pathways

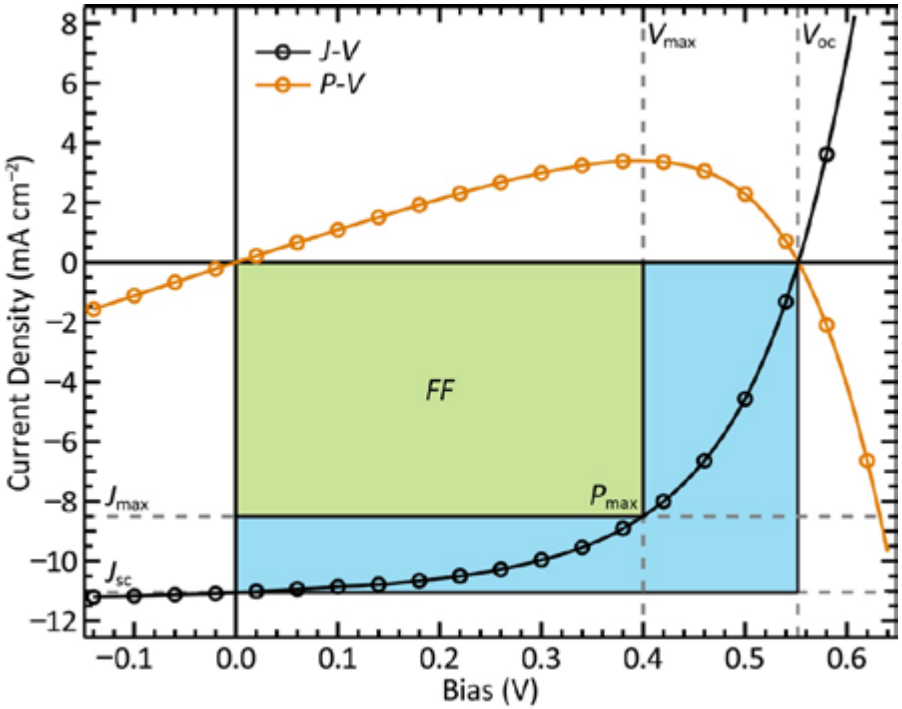
Photovoltaic device operation

D=



A=





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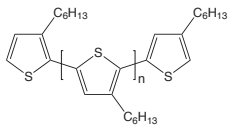

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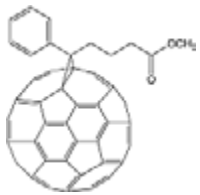
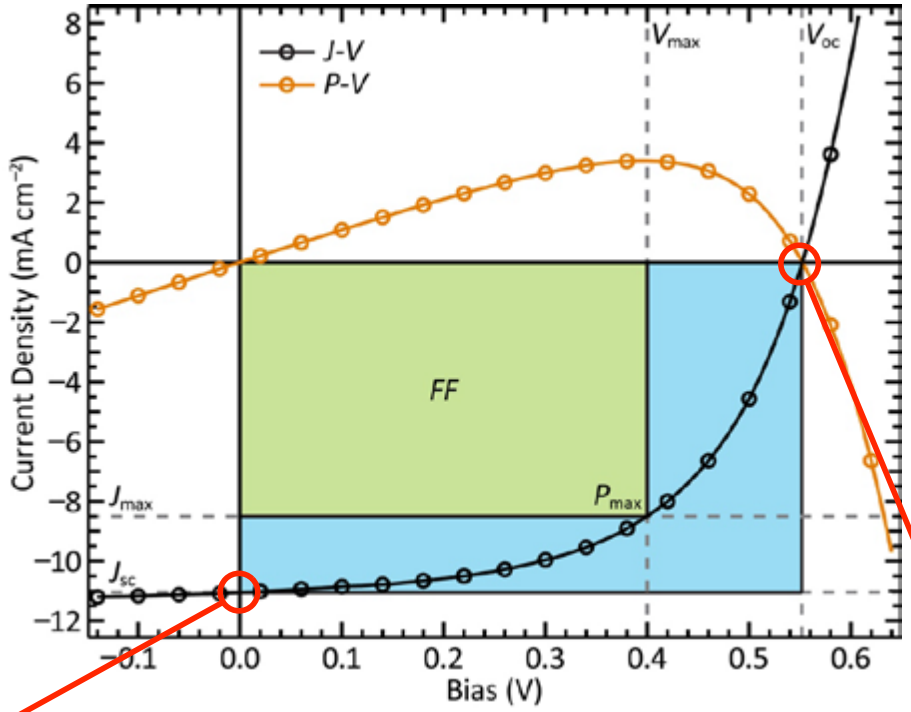


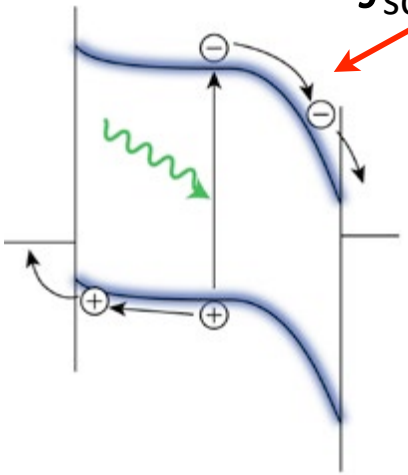


$$P_{max} = J_{max} \times V_{max}$$

$$PCE(\eta_P) = \frac{P_{max}}{P_{inc}} = \frac{J_{max} \times V_{max}}{P_{inc}}$$

$$\eta_P == \frac{J_{sc} \times V_{oc} \times FF}{P_{inc}}$$

J_{sc}



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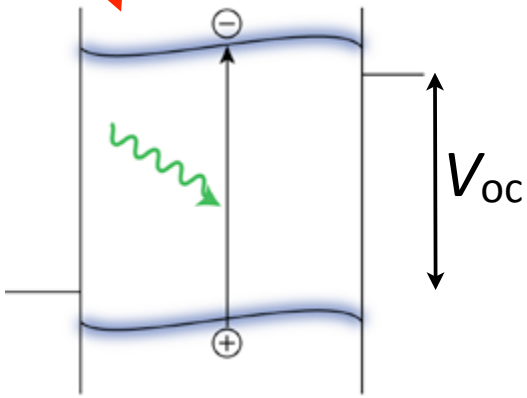
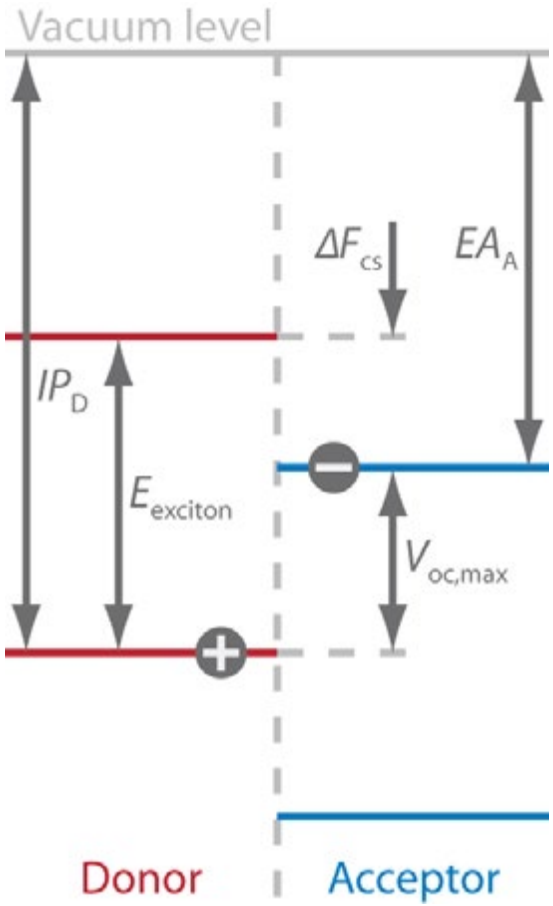
  - Nanostructured blend of conjugated polymer and fullerene derivative

V_{oc}



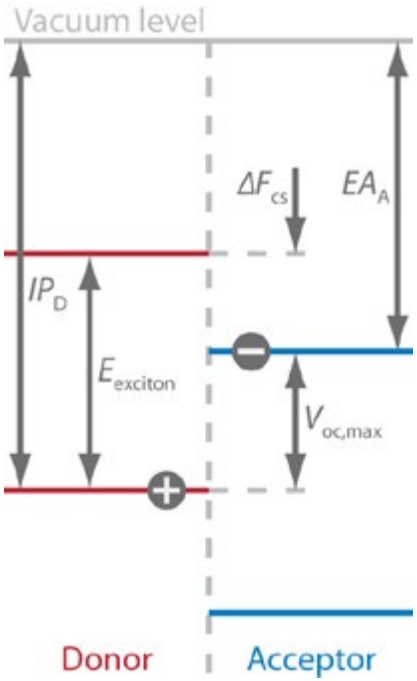
Mobile charge carrier generation in a bulk heterojunction



Energetics:

- **Maximize** voltage output
  - $V_{oc,\max} = \left| IP_D - EA_A \right|$
- Maintain **driving force** for carrier separation
  - $\Delta F_{cs} = E_{exciton} - \left| IP_D - EA_A \right|$
  - Importance of ΔF_{cs}?

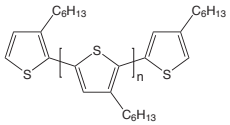
The naivety of device measurements (1): novel acceptors



	Reduction potential vs. C_{60} (V)
PCBM	-0.09
mono-indene-C_{60}	-0.21
bis-indene-C_{60}	-0.25
tris-indene-C_{60}	-0.45

EA_A decreases,
ΔF_{cs} decreases,
V_{oc} should increase

D=



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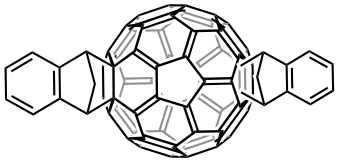

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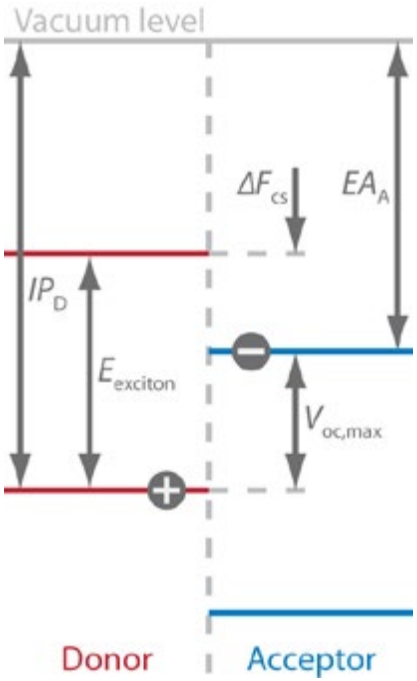

	Reduction potential vs. C_{60} (V)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PCBM	-0.09	0.56	11.05	56	3.40
mono-indene-C_{60}	-0.21	0.69	10.56	54	3.92
bis-indene-C_{60}	-0.25	0.78	10.82	56	4.65
tris-indene-C_{60}	-0.45				

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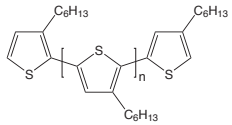

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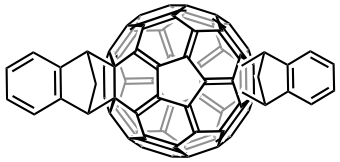

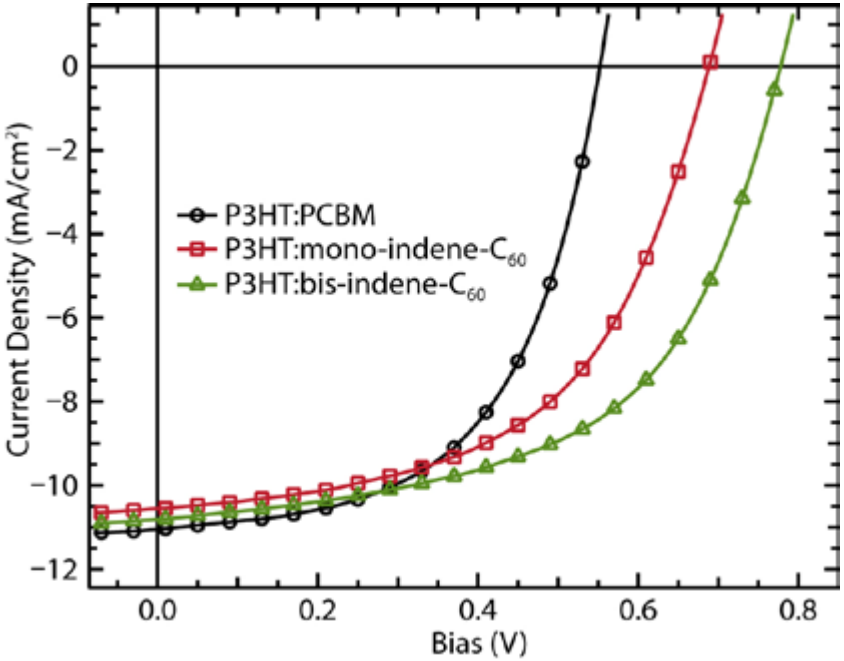

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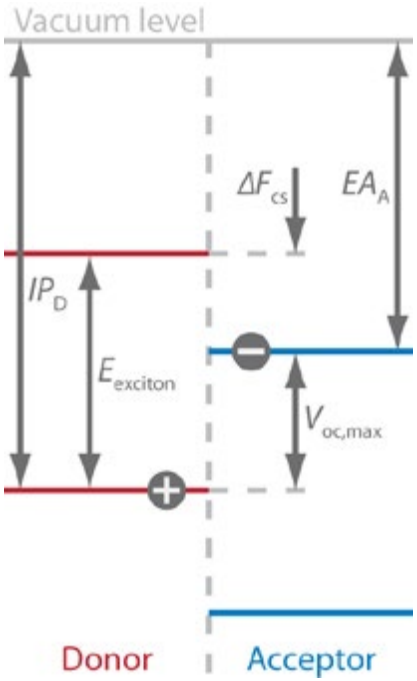

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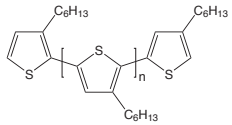
tris-indene-C_{60}	-0.45	0.69	1.86	40	0.51

D=



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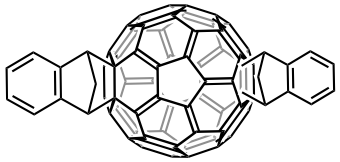
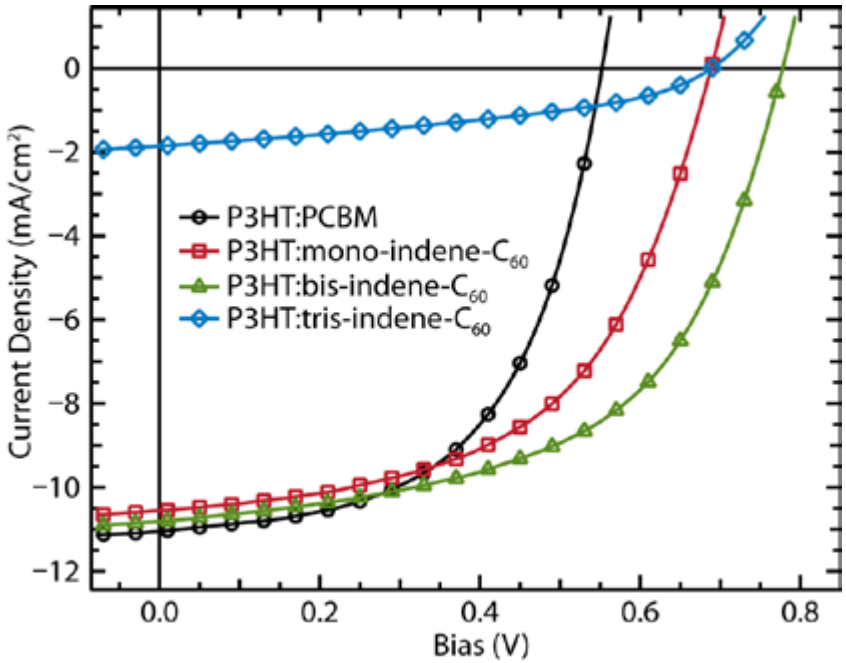


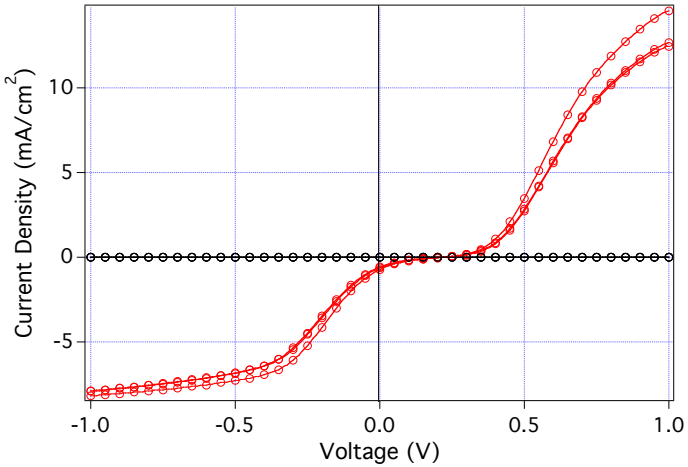


What limits the tris-indene-C_{60} device performance?

- Energetics
  - Is ΔF_{cs} too small?
    - Inefficient charge carrier generation
  - Are there states that facilitate efficient carrier recombination?
- Nanomorphology
  - Poor charge carrier transport?

The naivety of device measurements (2): contact issues

ITO/PEDOT bottom contact
LiF/Al top contact



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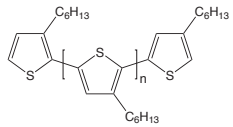

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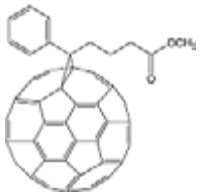
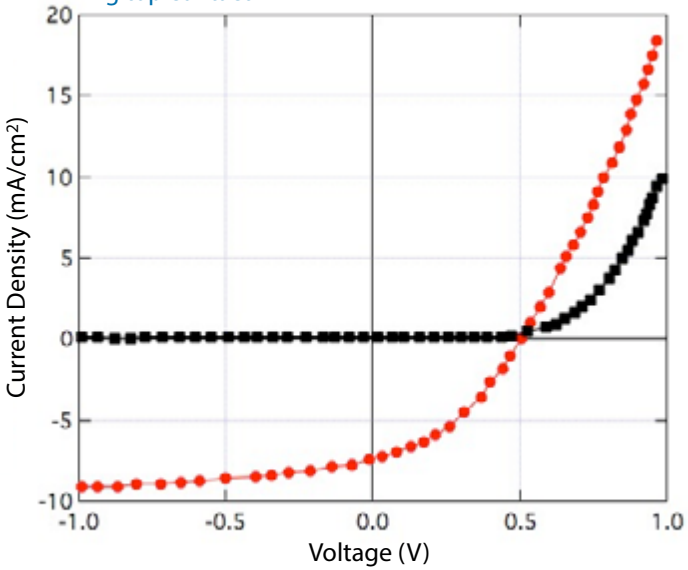
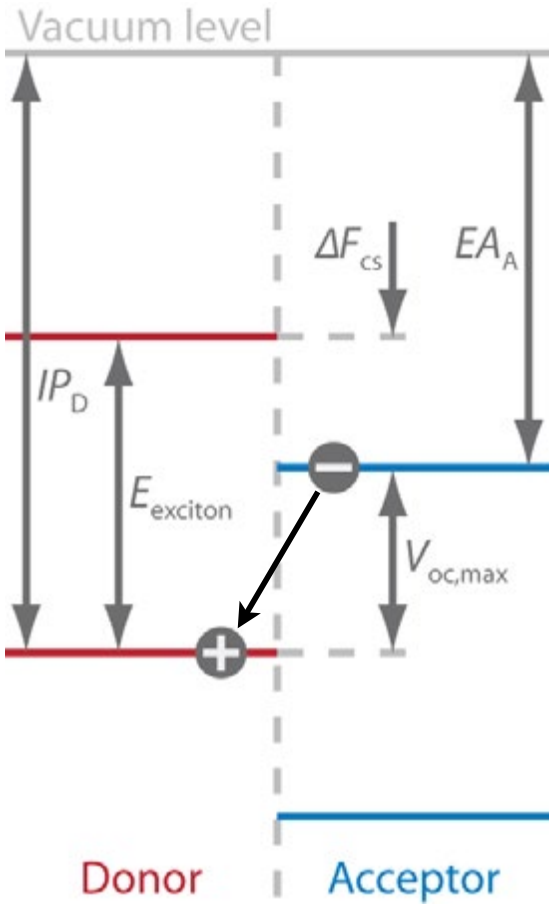


ITO/ZnO bottom contact
Ag top contact



- Contacts dramatically influence device performance
  - Large parameter space for:
    - Device architecture
    - Carrier transport layers
    - Carrier selective contacts

Carrier loss mechanisms in BHJs (1): recombination



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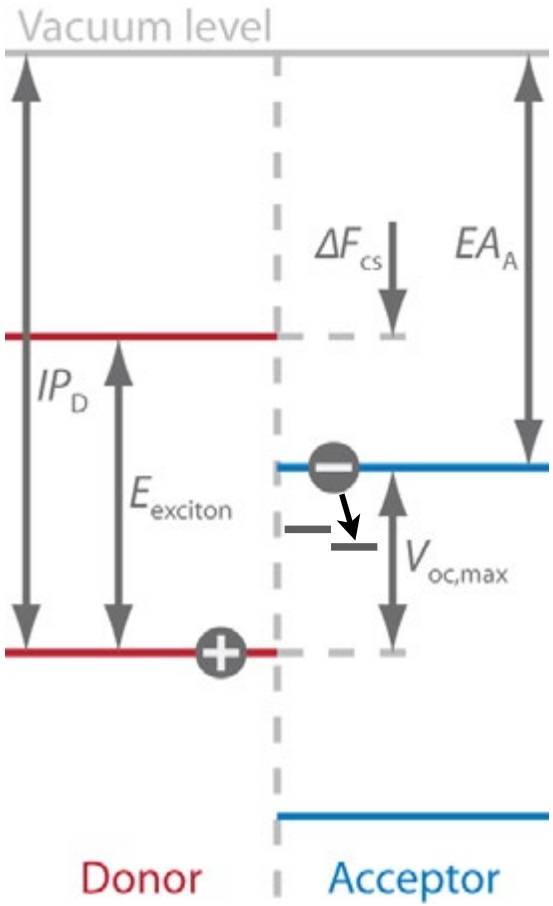
Loss mechanisms:

- **Recombination**
  - **Geminate** (interfacial charge-transfer state)
  - **Second-order** (free carriers)

Carrier loss mechanisms in BHJs (2): trapping



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Loss mechanisms:

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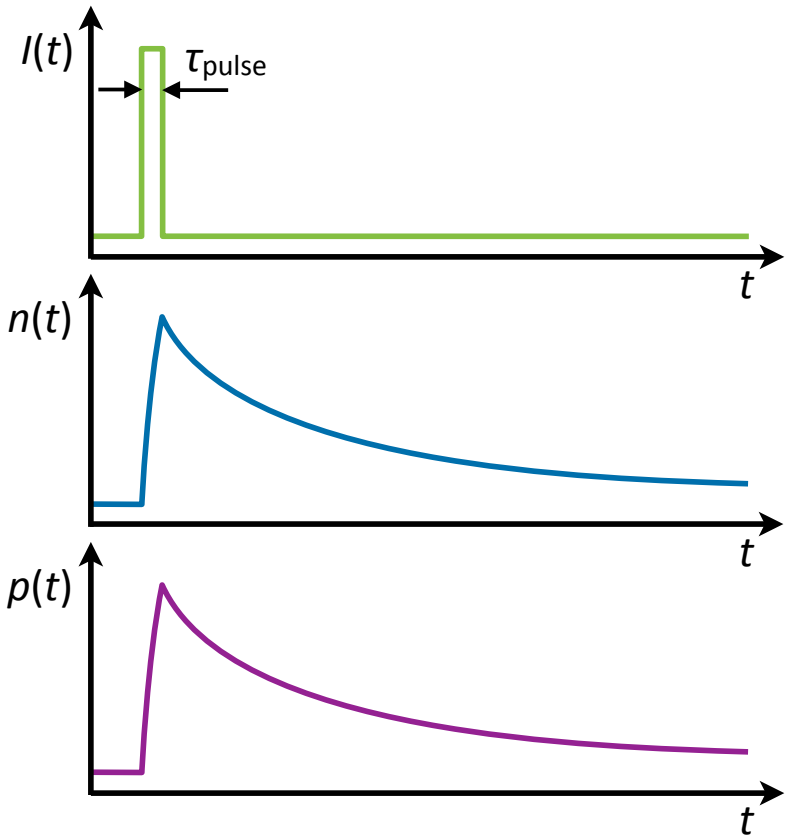
  - **Geminate** (interfacial charge-transfer state)
  - **Second-order** (free carriers)
- **Trapping**

Probing photoinduced charge carrier dynamics

Desired features:

- No contacts
- Time-resolved measurement
  - $n(t)$, $p(t)$: time-dependent **free** (**mobile**) carrier densities
  - n_{peak}, p_{peak}: free carrier **generation rate** (**efficiency**)
  - $n(t)$, $p(t)$ for $t>\tau_{pulse}$: carrier **loss mechanisms**
  - Relevant time scale: > 100 ps to µs



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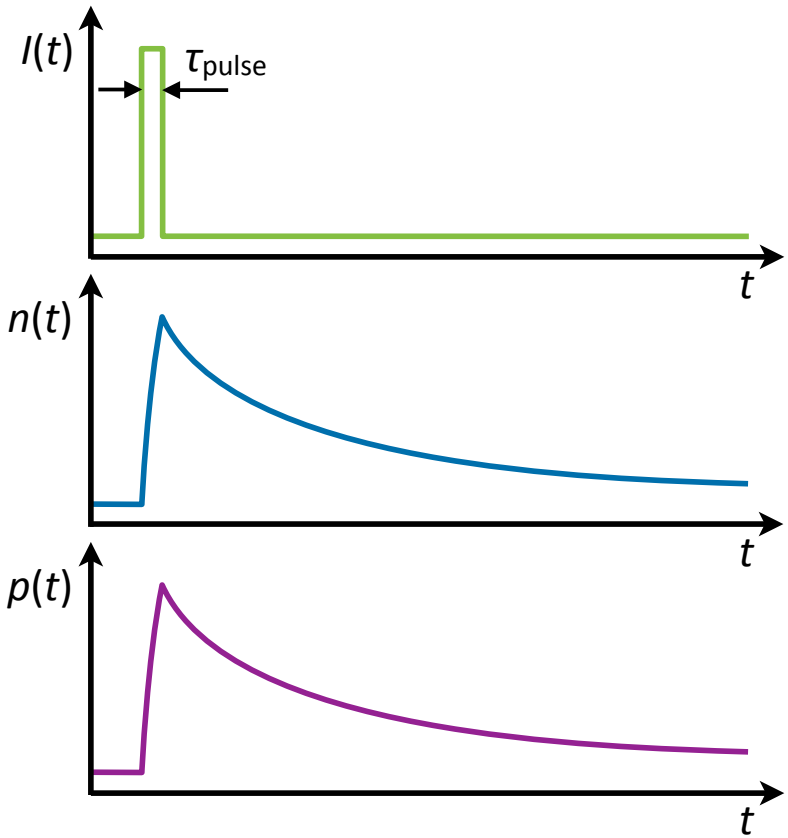
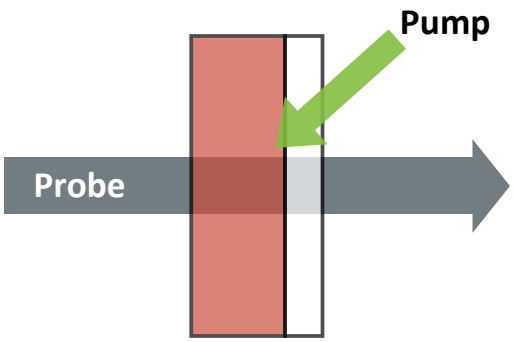
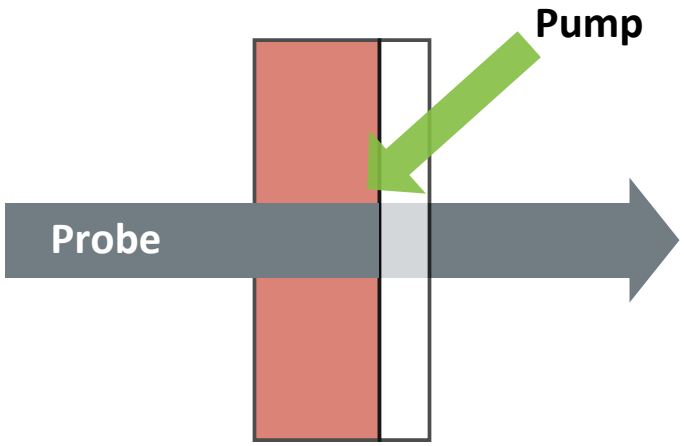
- Time-resolved measurement
  - $n(t)$, $p(t)$: time-dependent **free** (**mobile**) carrier densities
  - n_{peak}, p_{peak}: free carrier **generation rate** (**efficiency**)
  - $n(t)$, $p(t)$ for $t>\tau_{pulse}$: carrier **loss mechanisms**
  - Relevant time scale: > 100 ps to µs





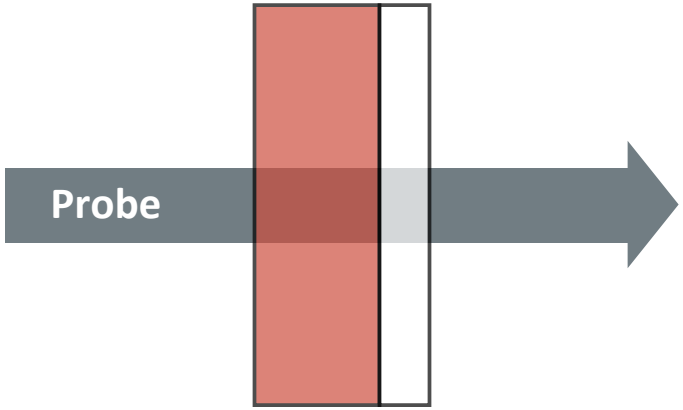
- General methodology: **"pump-probe"** technique
  - Time-resolved terahertz spectroscopy (TRTS)
    - Typically sub-ns
  - Transient absorption spectroscopy (TAS)
    - Typically sub-10 ns
  - Flash photolysis
    - Typically ns – ms
  - **Flash-photolysis time-resolved microwave conductivity (FP-TRMC)**
    - Typically ns – ms

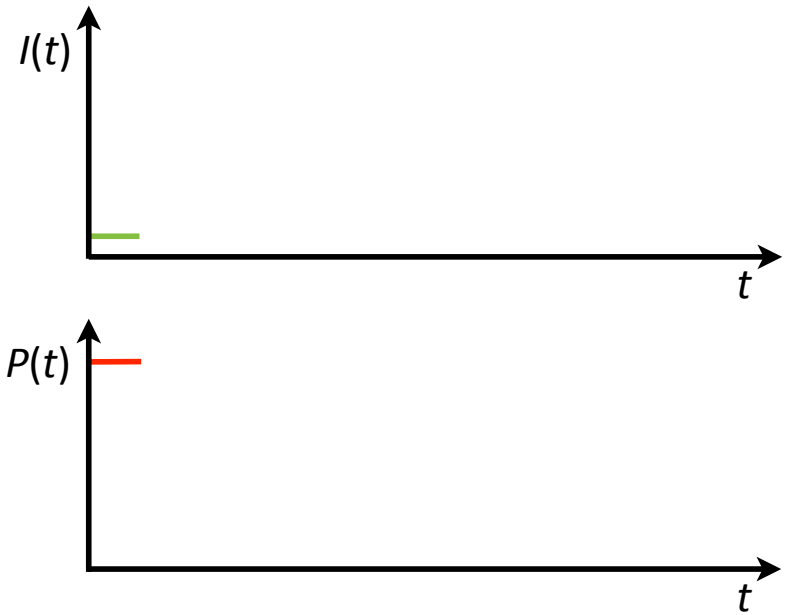
Pump-probe measurements



- General methodology: **"pump-probe"** technique
  - Pulsed optical pump
  - Time-resolved terahertz spectroscopy (TRTS)
    - Terahertz probe
    - Time-dependent photoconductivity
  - Transient absorption spectroscopy (TAS)
    - Optical probe
    - Excited state dynamics
  - Flash photolysis
    - Optical probe
    - Excited state dynamics
  - **Flash-photolysis time-resolved microwave conductivity (FP-TRMC)**
    - Continuous microwave probe
    - Time-dependent photoconductivity

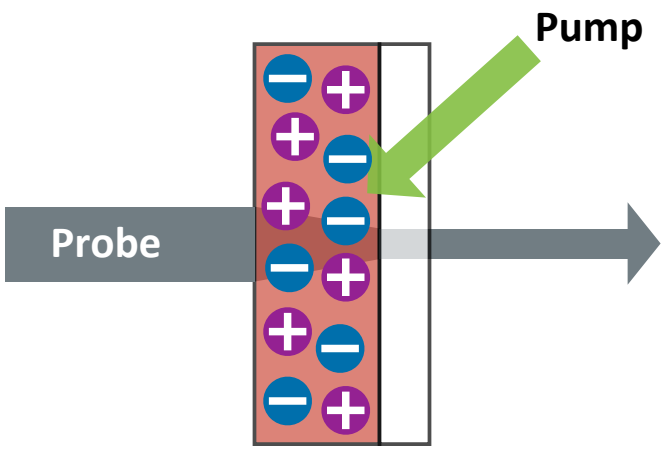
Microwave absorption probe of photoresponse

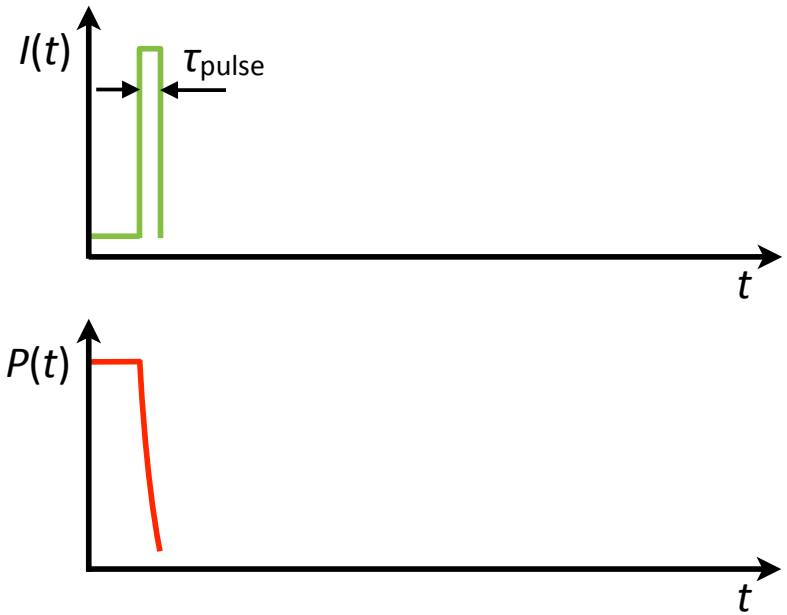




- **Flash-photolysis time-resolved microwave conductivity (FP-TRMC)**
  - Continuous microwave probe
    - Power, *P*

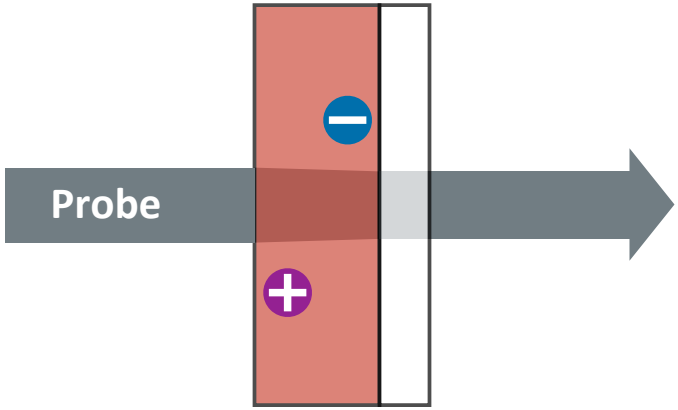
Microwave absorption probe of photoresponse

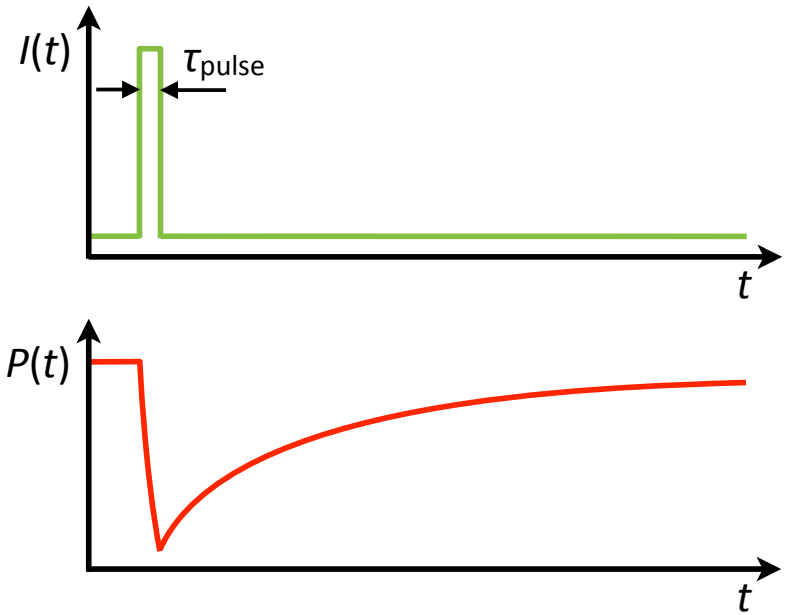




- **Flash-photolysis time-resolved microwave conductivity (FP-TRMC)**
  - Continuous microwave probe
    - Power, P
  - Optical pump "on"
    - Laser pulse (τ_{pulse} ~ 5 ns; Intensity = I_0)
  - Photoinduced carriers **absorb** microwave probe
    - ΔP_{peak}

Microwave absorption probe of photoresponse



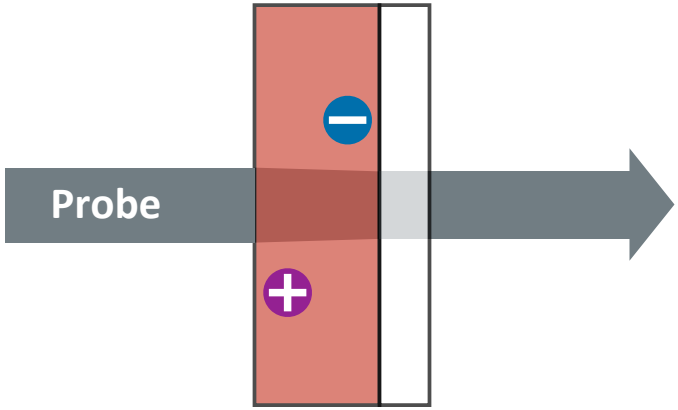


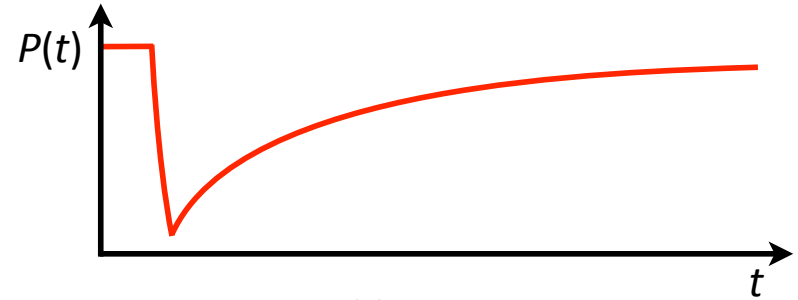
$$\frac{\Delta P(t)}{P} = -K.\Delta G(t)$$

$$\Delta G(t) = \beta q_e.d.\left[n(t)\mu_e + p(t)\mu_h\right]$$

- **Flash-photolysis time-resolved microwave conductivity (FP-TRMC)**
  - Continuous microwave probe
    - Power, P
  - Optical pump "on"
    - Laser pulse (τ_{pulse} ~ 5 ns; Intensity = I_0)
  - Photoinduced carriers absorb microwave probe
    - ΔP_{peak}
  - Optical pump "off"
  - Carrier loss mechanisms restore microwave probe power
    - $\Delta P(t)$

Microwave absorption probe of photoresponse





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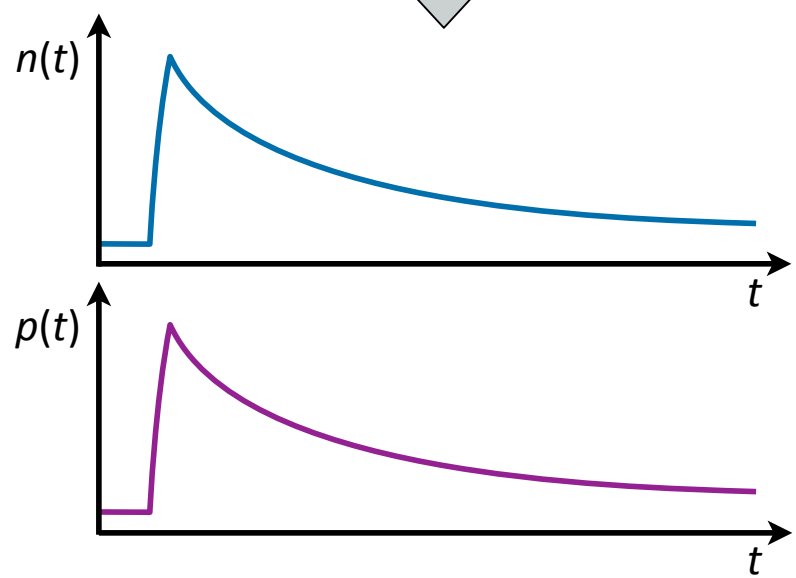
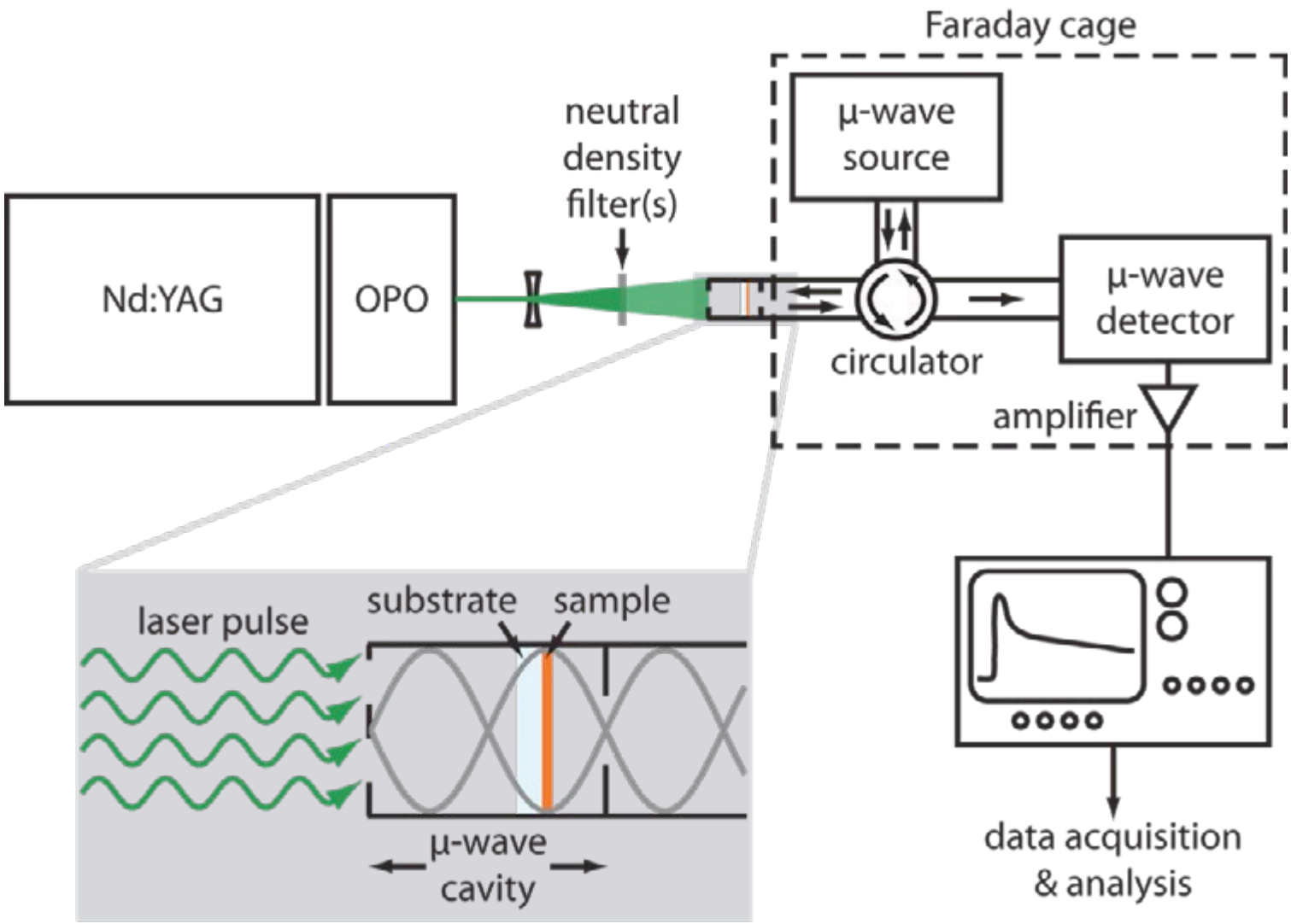
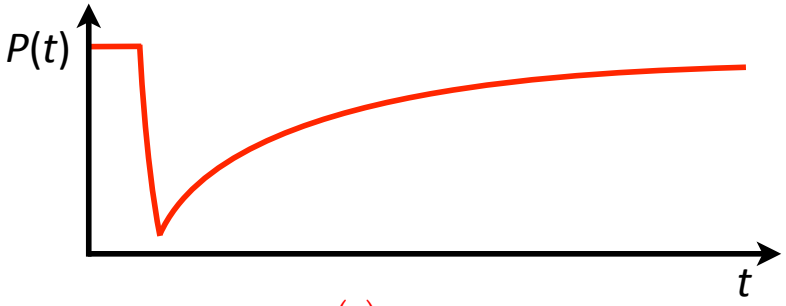


- **Flash-photolysis time-resolved microwave conductivity (FP-TRMC)**
  - Continuous microwave probe
    - Power, P
  - Optical pump "on"
    - Laser pulse (τ_{pulse} ~ 5 ns; Intensity = I_0)
  - Photoinduced carriers absorb microwave probe
    - ΔP_{peak}
  - Optical pump "off"
  - Carrier loss mechanisms restore microwave probe power
    - $\Delta P(t)$

FP-TRMC apparatus



Photoconductance transients & The TRMC figure of merit: $\phi\Sigma\mu$



$$\frac{\Delta P(t)}{P} = -K.\Delta G(t)$$

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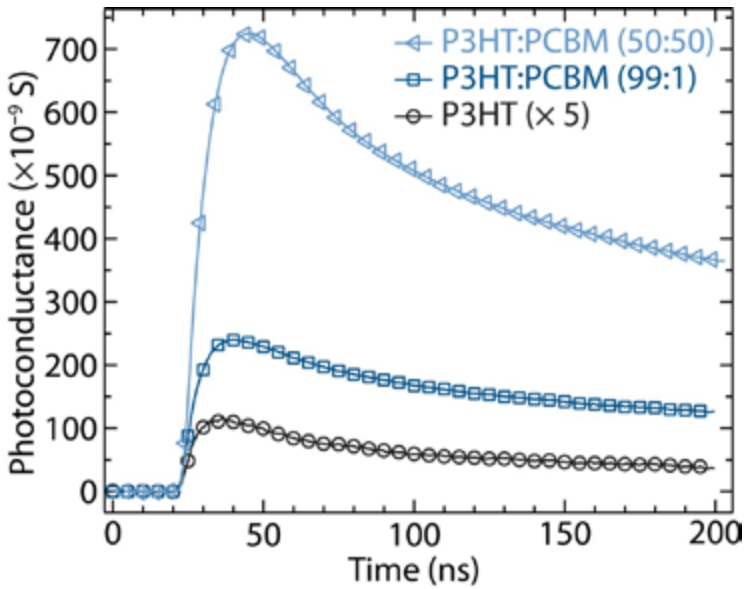
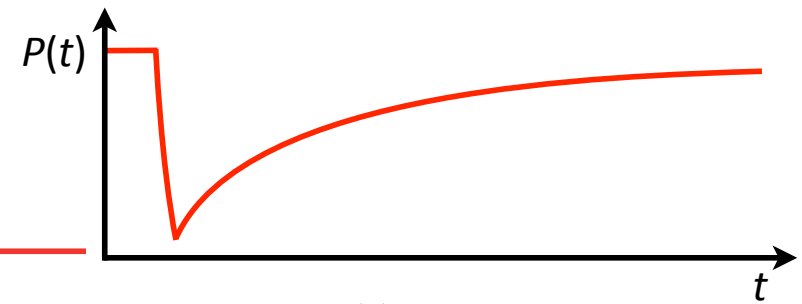
Photoconductance transients & The TRMC figure of merit: $\phi\Sigma\mu$





$$\frac{\Delta P(t)}{P} = -K.\Delta G(t)$$

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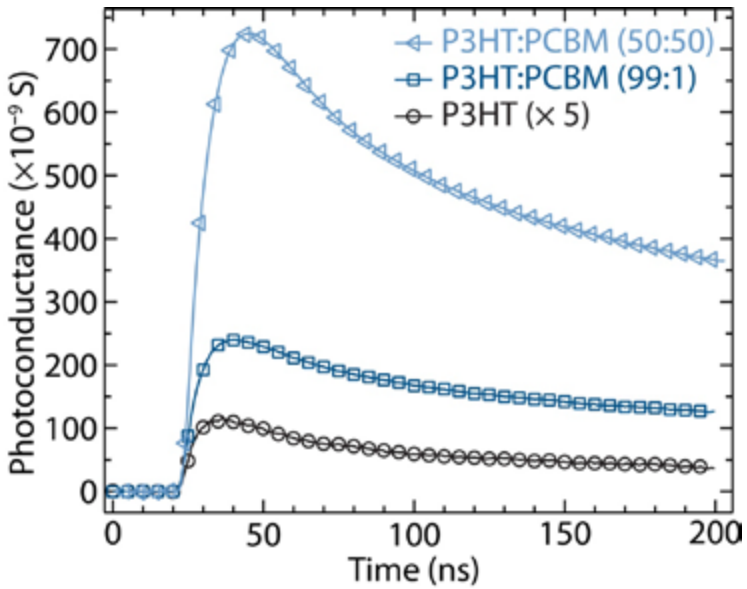
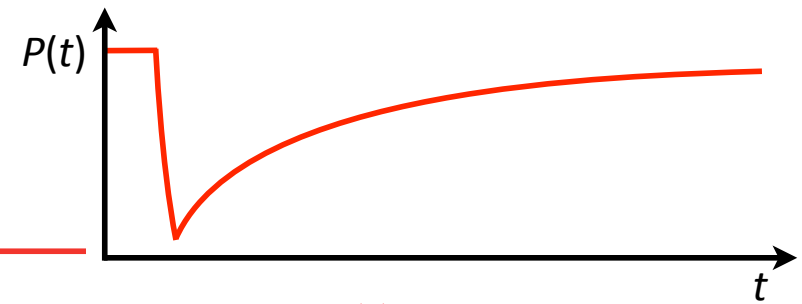
Photoconductance transients & The TRMC figure of merit: $\phi\Sigma\mu$





$$\frac{\Delta P(t)}{P} = -K.\Delta G(t)$$

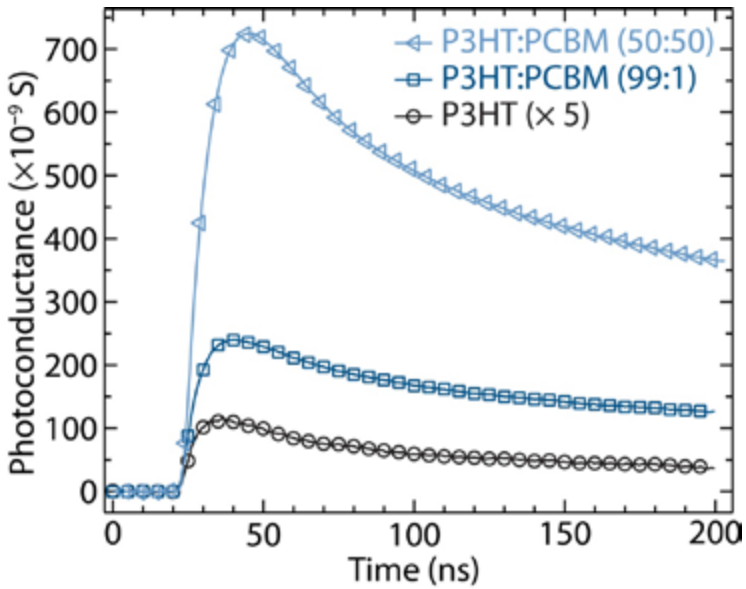
$$\Delta G(t) = \beta q_e.d.\left[n(t)\mu_e + p(t)\mu_h\right]$$

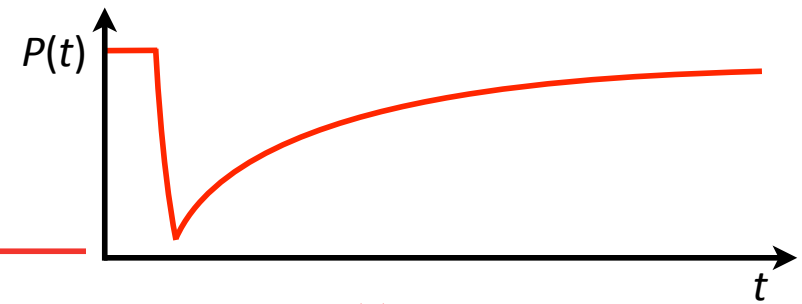
$$n_{t=0} = p_{t=0} = \frac{I_0 F_A}{d}\phi$$

$$\Delta G_{t=0} = \beta q_e I_0 F_A \phi(\mu_e + \mu_h)$$

$$\phi\Sigma\mu_i = \frac{\Delta G_{t=0}}{\beta q_e I_0 F_A}$$

Photoconductance transients & The TRMC figure of merit: $\phi\Sigma\mu$





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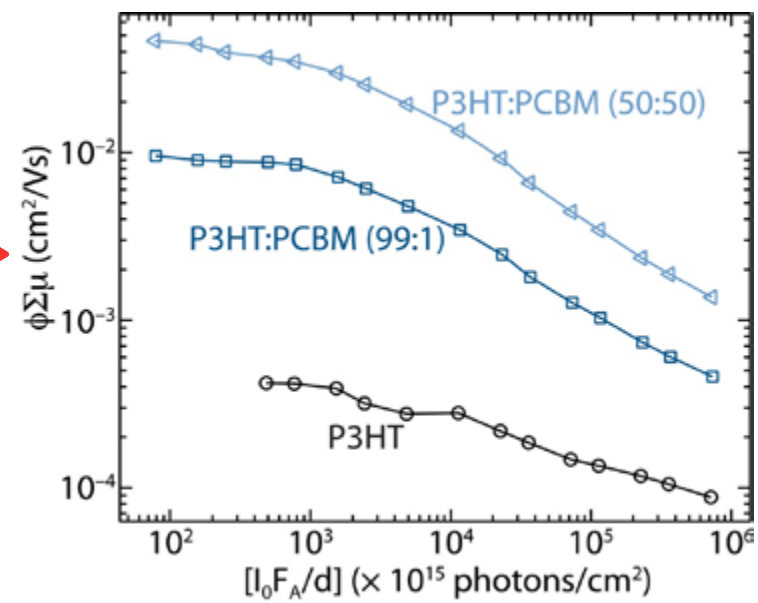
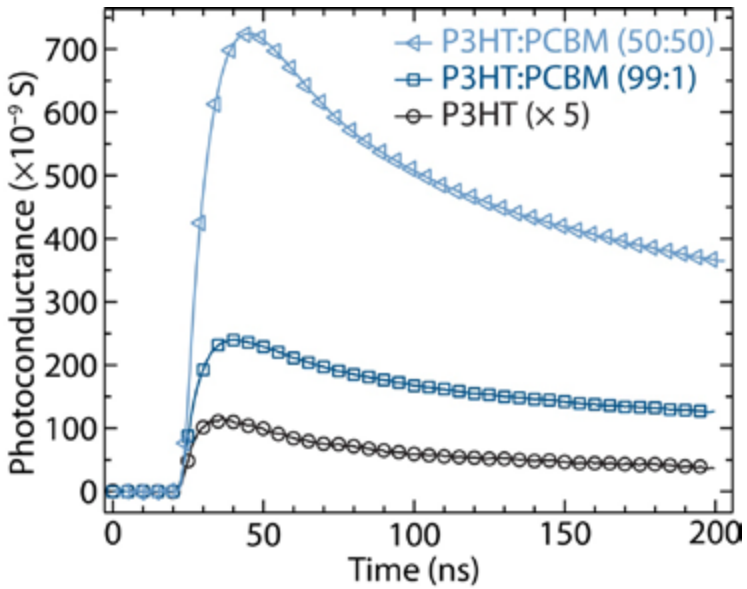
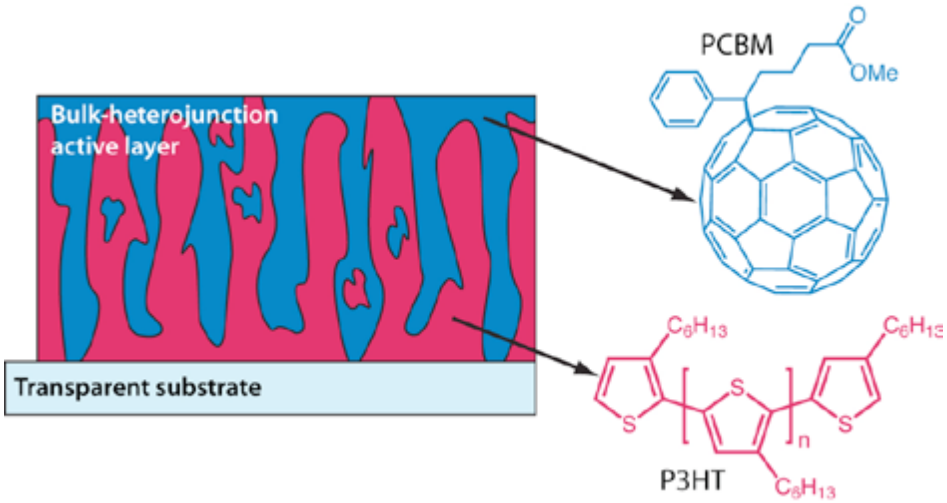
$$\phi\Sigma\mu_i = \frac{\Delta G_{t=0}}{\beta q_e I_0 F_A}$$

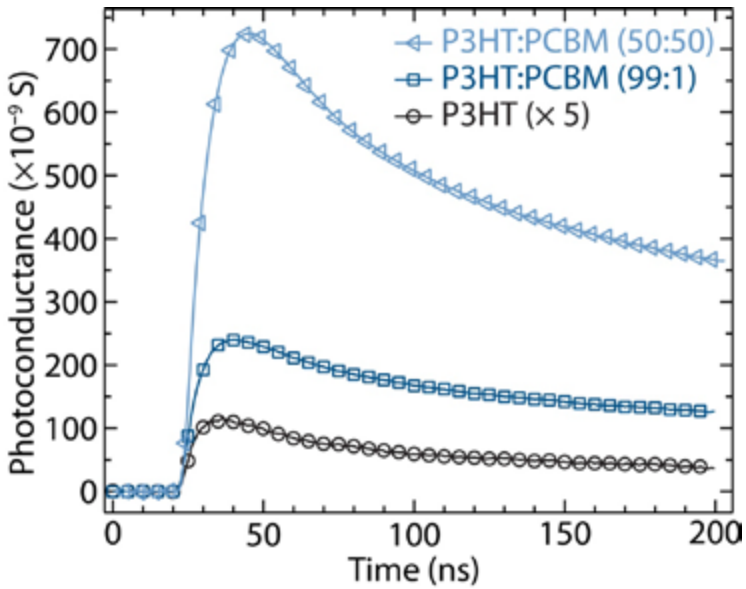


Extracting photocarrier dynamics from photoconductance transients





Extracting photocarrier dynamics from photoconductance transients



$$n_{t=0} = p_{t=0} = \frac{I_0 F_A}{d}\phi$$

Free carrier yield and exciton lifetime known/ measured for neat polymer (donor) $\phi_n ; \tau_n$

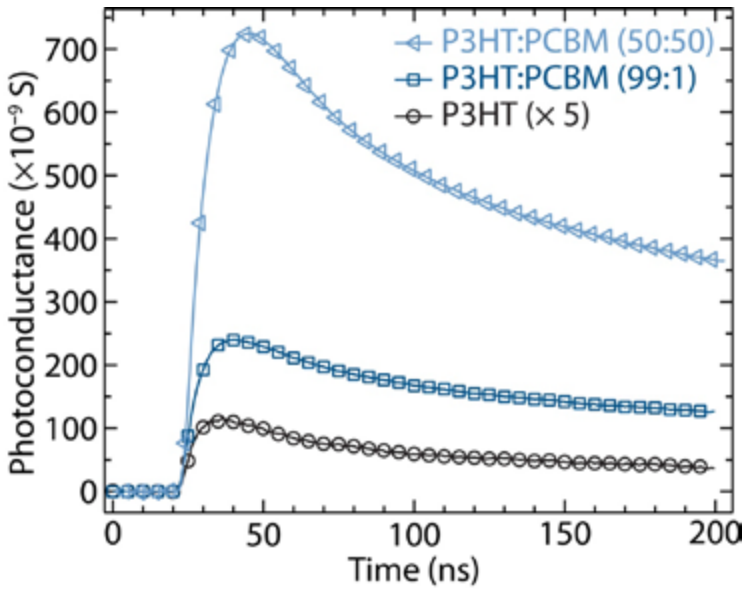
Exciton lifetime measured for the specific blend (donor:acceptor bulk heterojunction) τ_b

Free carrier yield in blend

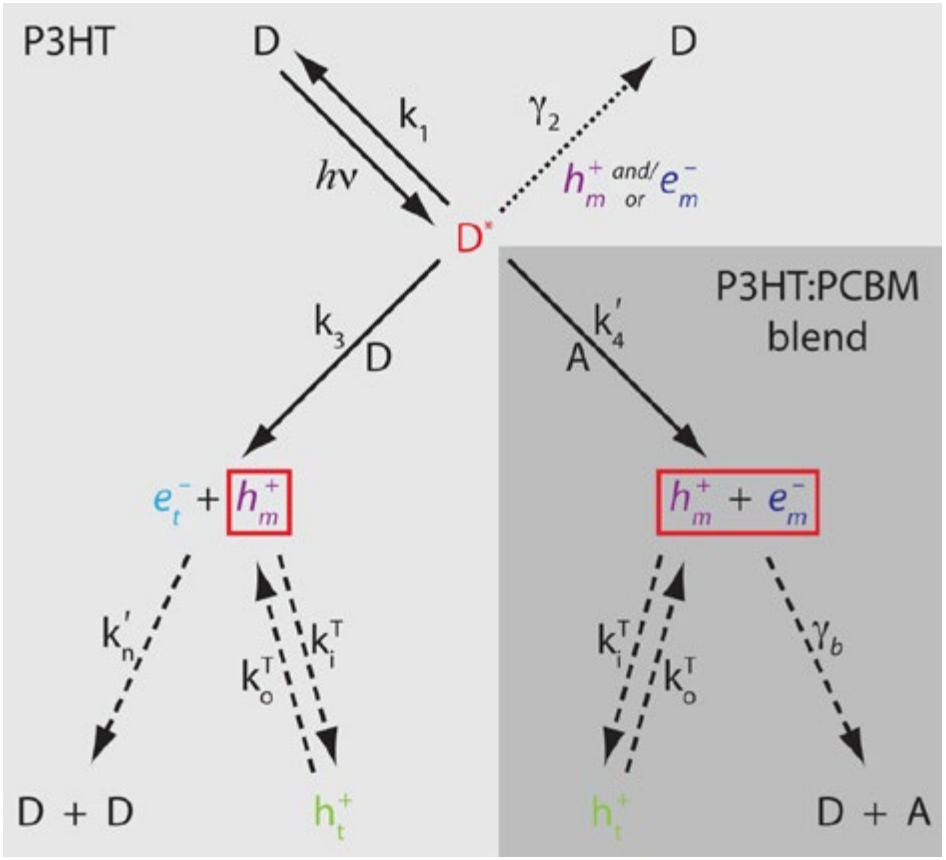
$$\phi_b = 1 - \frac{\tau_b}{\tau_n}\left(1 - \phi_n\right)$$

- Determine free carrier yield, ϕ

Extracting photocarrier dynamics from photoconductance transients



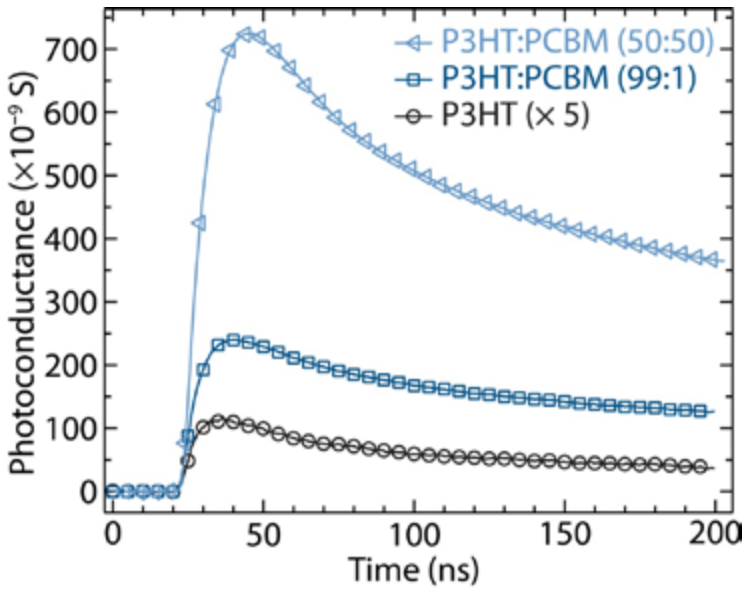
- Determine free carrier yield, ϕ
- Formulate kinetic scheme with relevant generation/loss processes



$$\frac{dn}{dt} = \text{...(relevant generation/loss rates for electrons)}$$

$$\frac{dp}{dt} = \text{...(relevant generation/loss rates for holes)}$$

Extracting photocarrier dynamics from photoconductance transients



$$\frac{dn}{dt} = \ldots\text{(relevant generation/loss rates for electrons)}$$

$$\frac{dp}{dt} = \ldots\text{(relevant generation/loss rates for holes)}$$

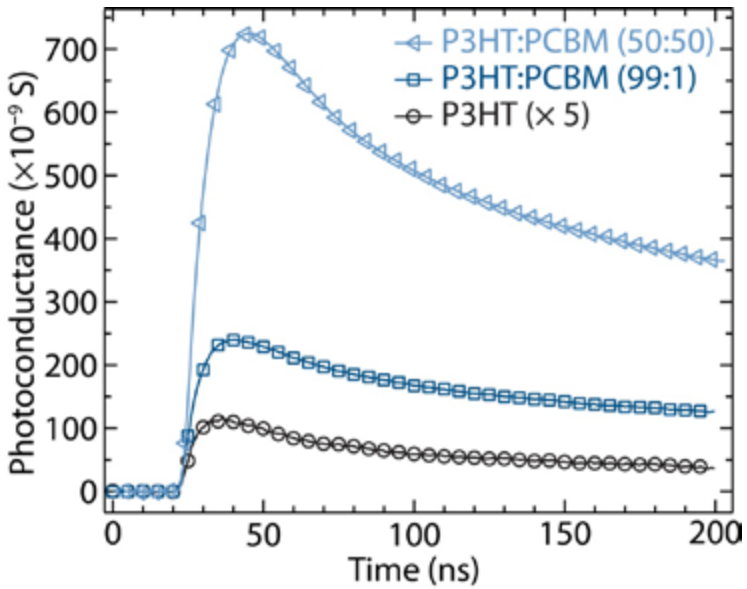
integrate rate equations (often numerically)

$$n(t) = \ldots$$

$$p(t) = \ldots$$

- Determine free carrier yield, ϕ
- Formulate kinetic scheme with relevant generation/loss processes
- Solve for $n(t)$, $p(t)$

Extracting photocarrier dynamics from photoconductance transients



- Determine free carrier yield, ϕ
- Formulate kinetic scheme with relevant generation/loss processes
- Solve for $n(t)$, $p(t)$
- Fit to photoconductance transients as a function of incident light intensity

$$\frac{dn}{dt} = \ldots\text{(relevant generation/loss rates for electrons)}$$

$$\frac{dp}{dt} = \ldots\text{(relevant generation/loss rates for holes)}$$

integrate rate equations (often numerically)

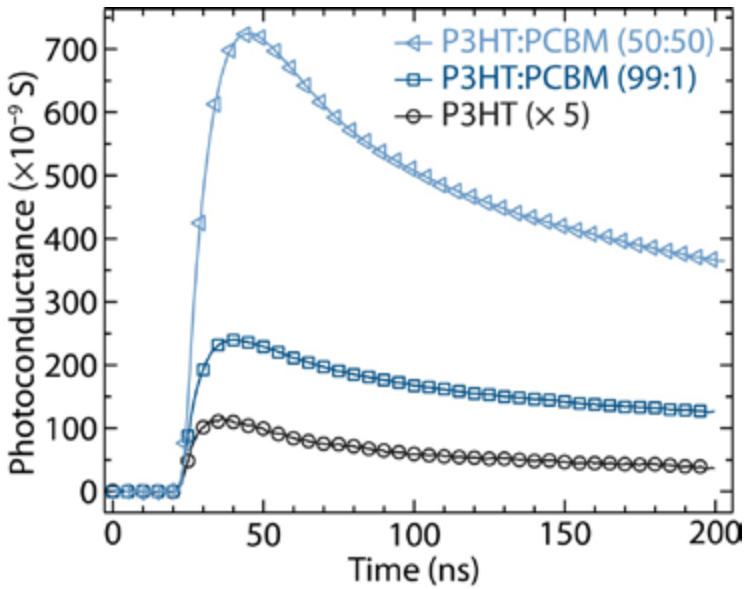
$$n(t) = \ldots$$

$$p(t) = \ldots$$

need μ_e & μ_h

$$\Delta G(t) = \beta q_e d.[n(t)\mu_e + p(t)\mu_h]$$

Extracting photocarrier dynamics from photoconductance transients



- Determine free carrier yield, ϕ
- Formulate kinetic scheme with relevant generation/loss processes
- Solve for $n(t)$, $p(t)$
- Fit to photoconductance transients as a function of incident light intensity
- Determine rate coefficients for photoinduced processes

$$\frac{dn}{dt} = \ldots\text{(relevant generation/loss rates for electrons)}$$

$$\frac{dp}{dt} = \ldots\text{(relevant generation/loss rates for holes)}$$

integrate rate equations (often numerically)

$$n(t) = \ldots$$

$$p(t) = \ldots$$

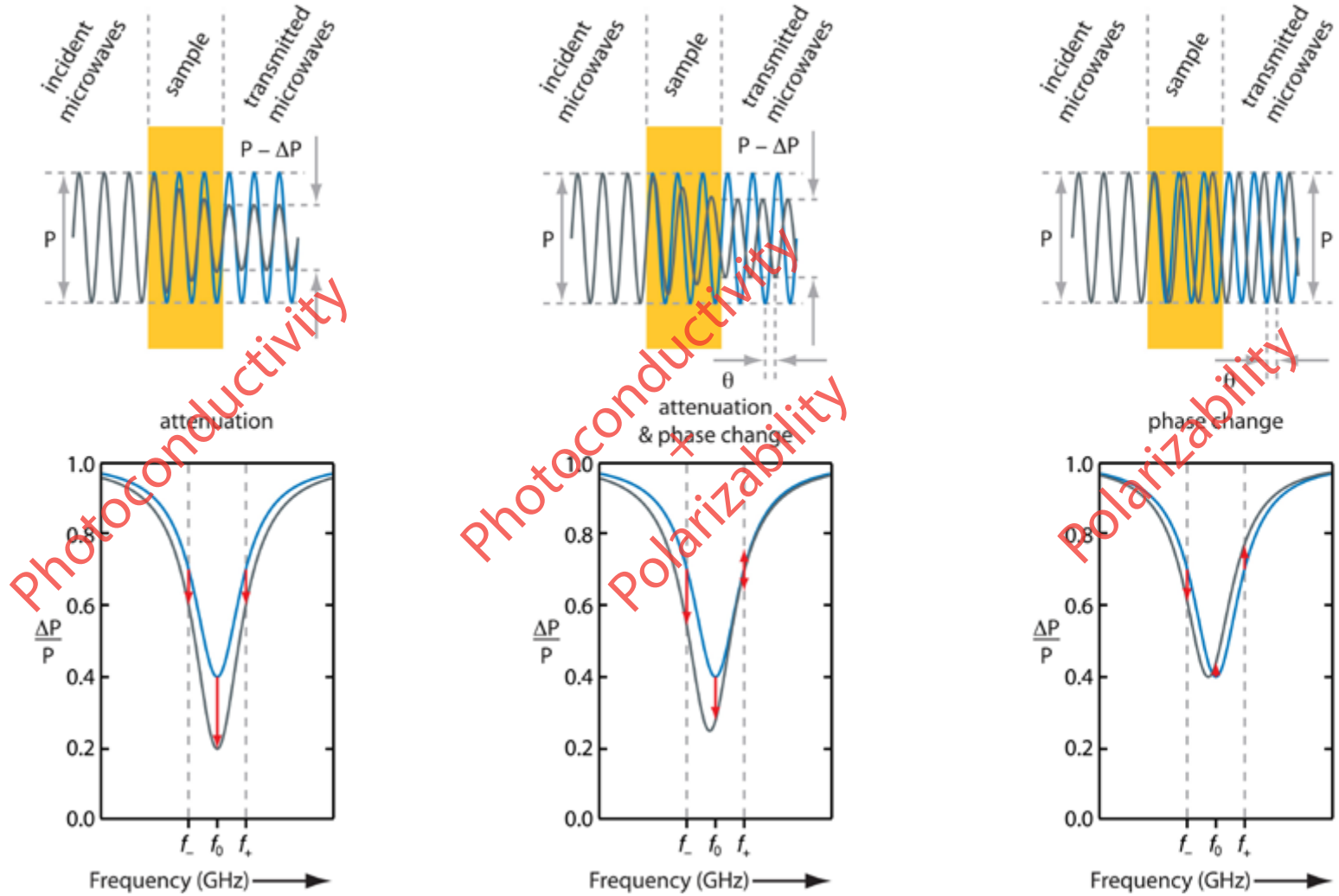
need μ_e & μ_h

$$\Delta G(t) = \beta q_e . d . [n(t)\mu_e + p(t)\mu_h]$$

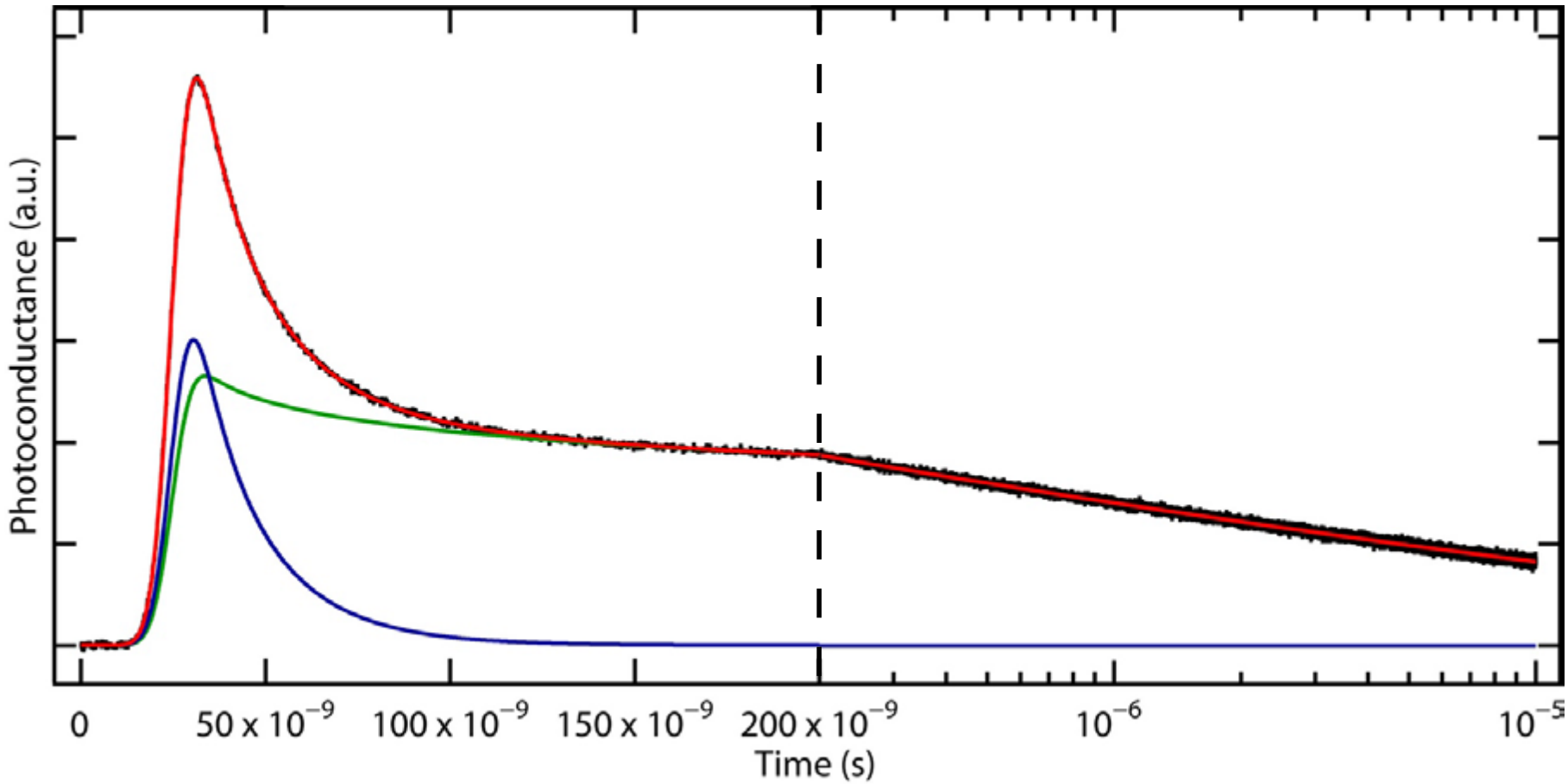
determine all k_i & γ_i

Photoinduced perturbation of microwave cavity resonance

Dark
After photoexcitation

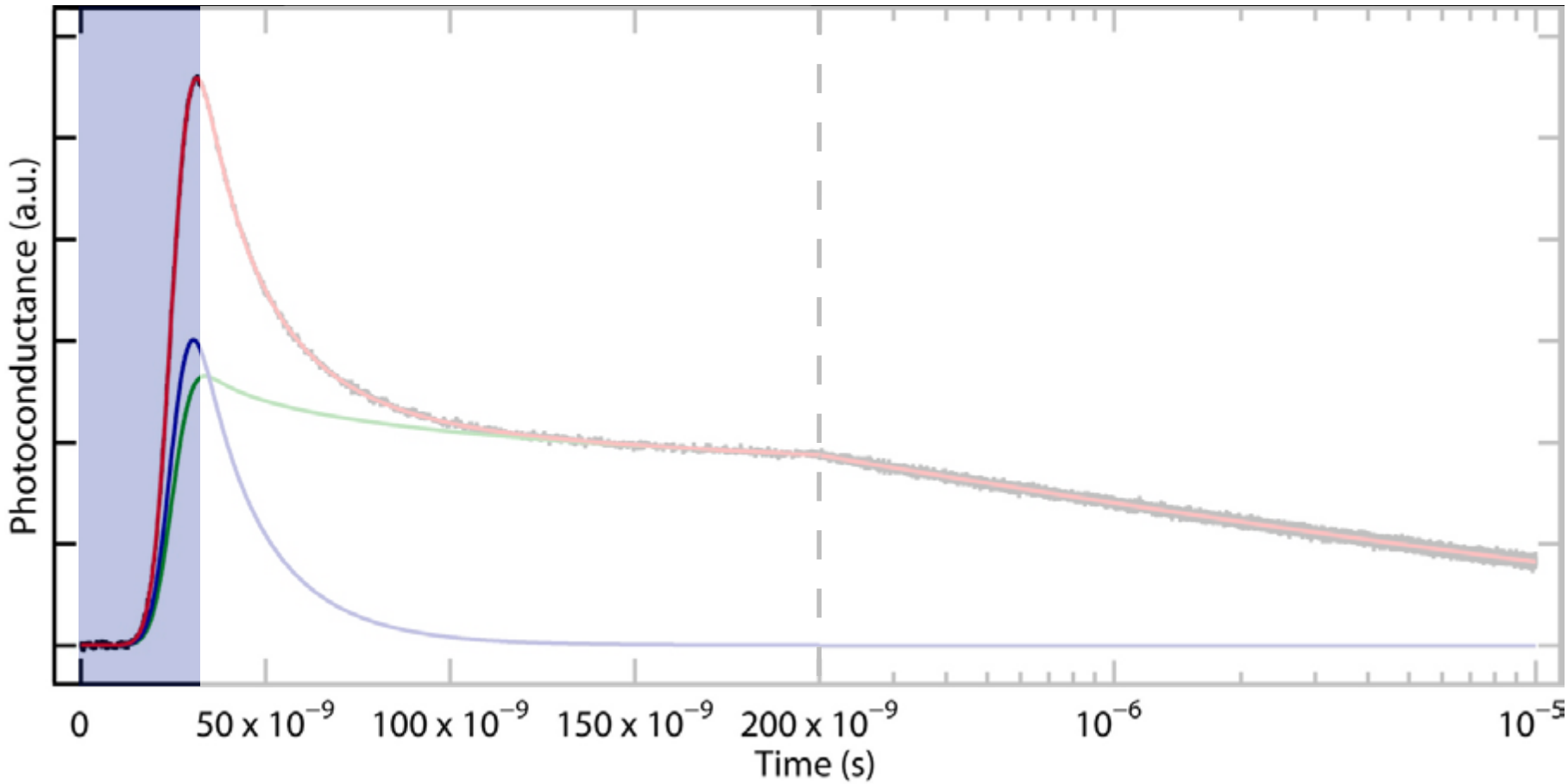


TRMC timescales



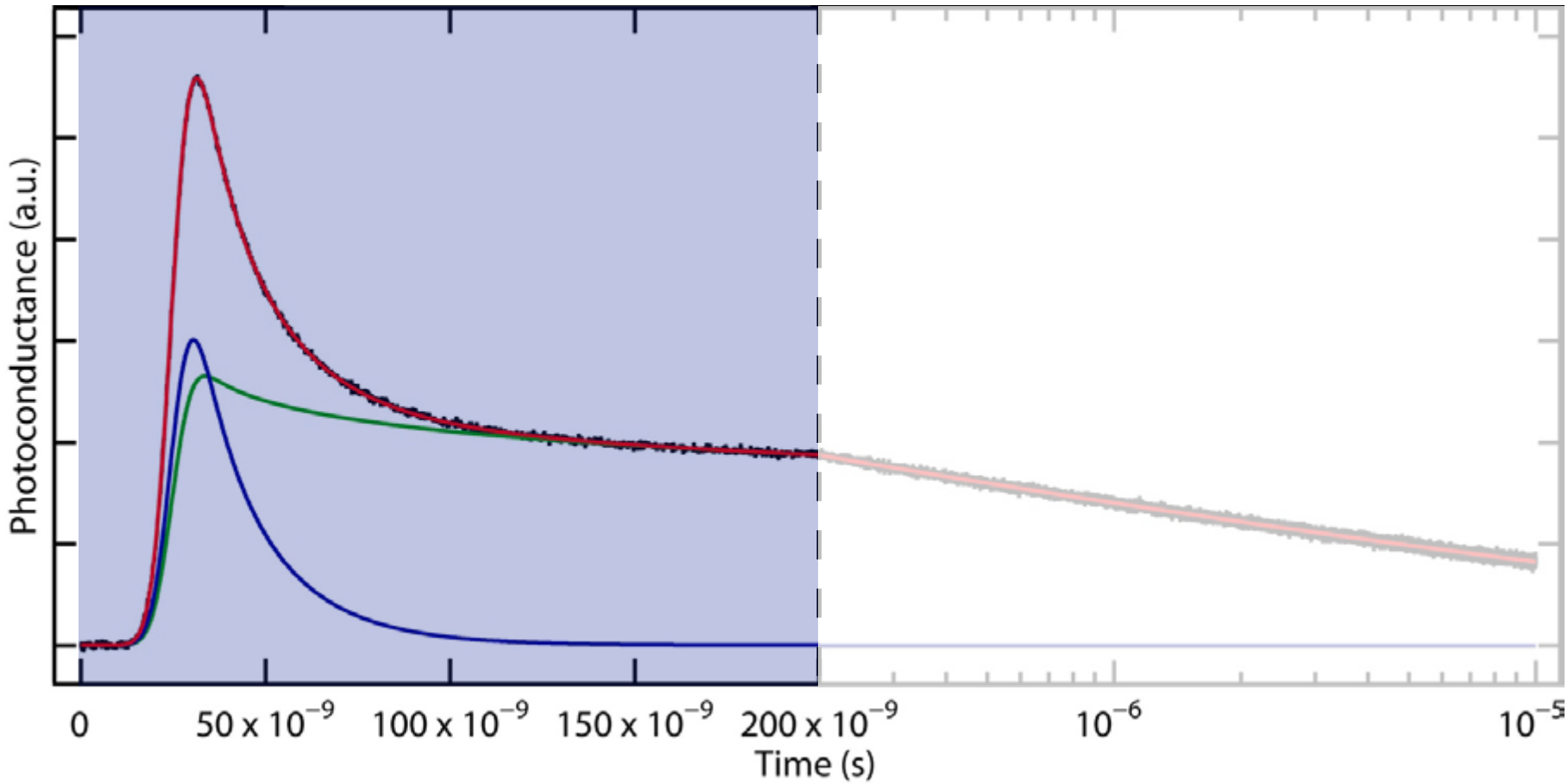
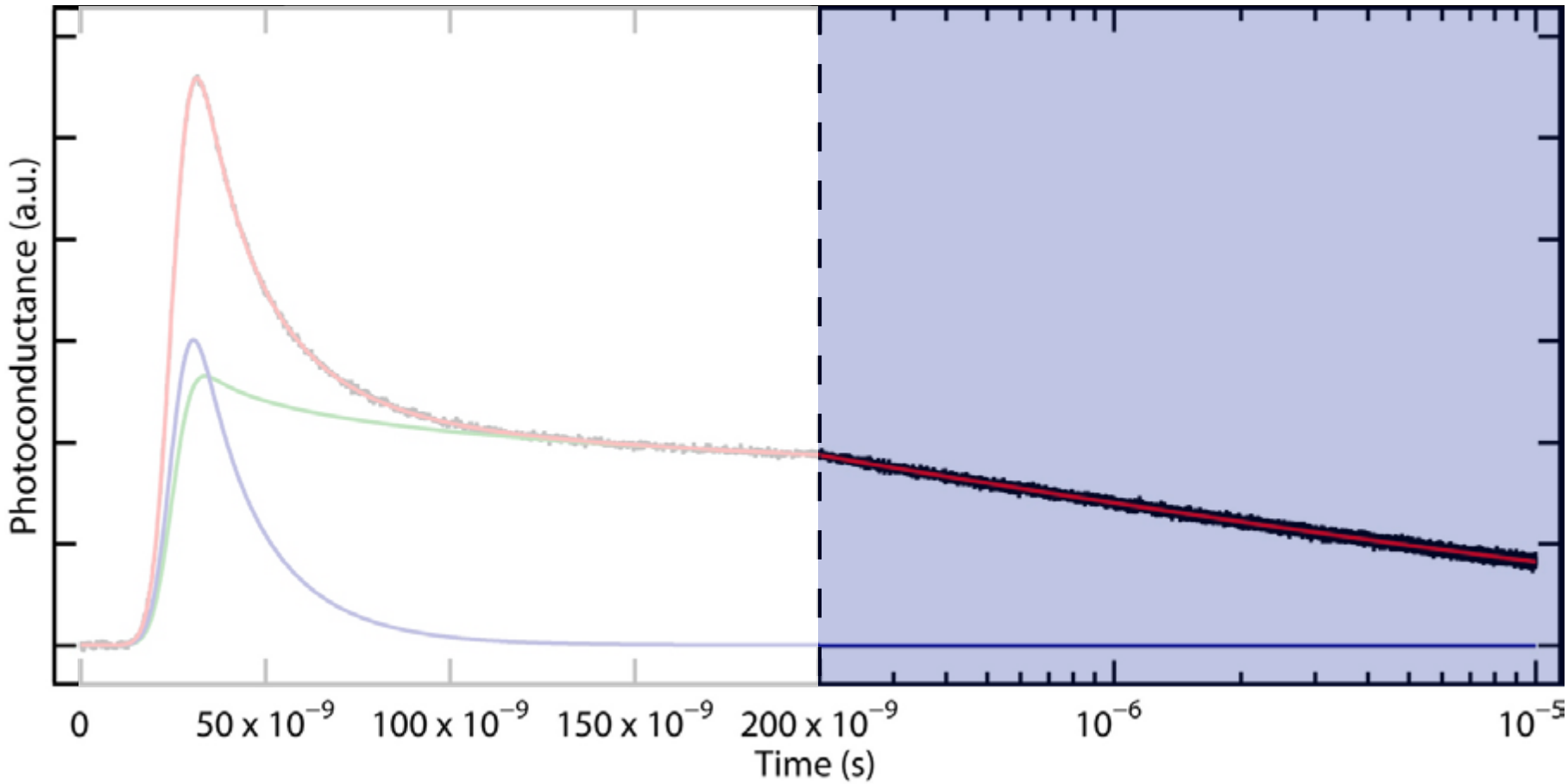
TRMC timescales

Timescale 1: Peak photoconductance (Carrier yield)



TRMC timescales

Timescale 2: Sub-microsecond carrier dynamics (Equilibration of trapped & mobile carriers)



Timescale 3: Microsecond carrier dynamics (Carrier trapping/de-trapping & recombination)