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TRMC studies at NREL

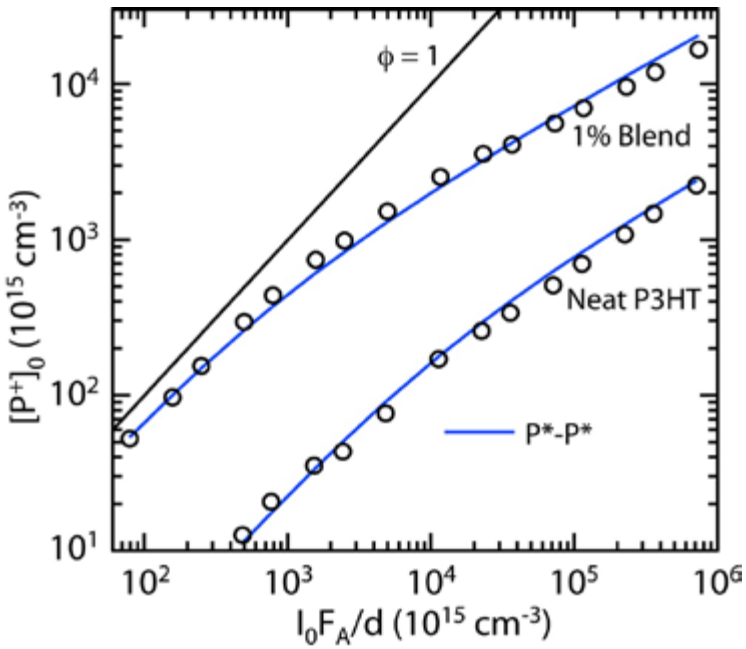
Quenching of excitons by holes in poly(3-hexylthiophene) films

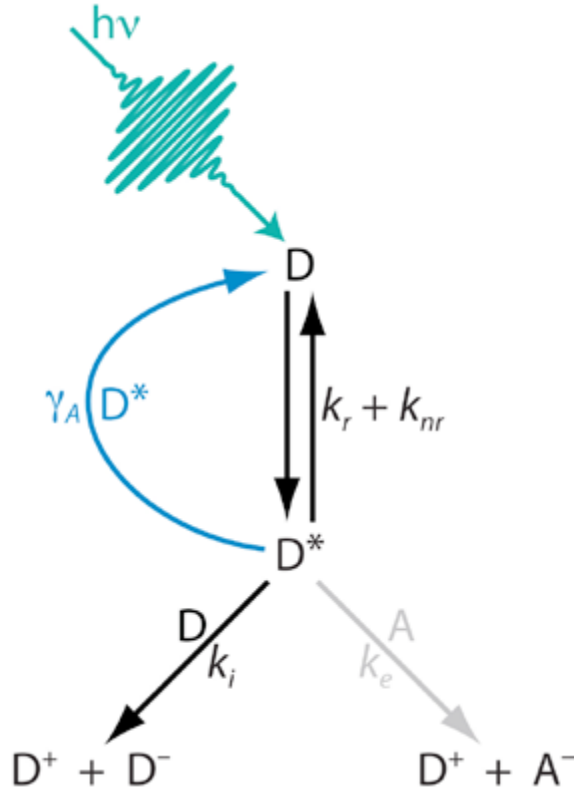
J. Phys. Chem. C; **2008**, *112*, 9865-9871
DOI: 10.1021/jp7113412

Andrew Ferguson, Nikos Kopidakis, Sean Shaheen[†], Garry Rumbles
Departmen o Physic & Astronomy, University o Denver

Thi wor wa funde b th Photochemistry an Radiation Research progra o th U.S. Departmen o Energy, Office o Science, Basic Energ Sciences, Division o Chemical Sciences, Geoscience an Biosciences, under Contrac No. DEAC36-99GO1033 t NREL.

Exciton-exciton annihilation

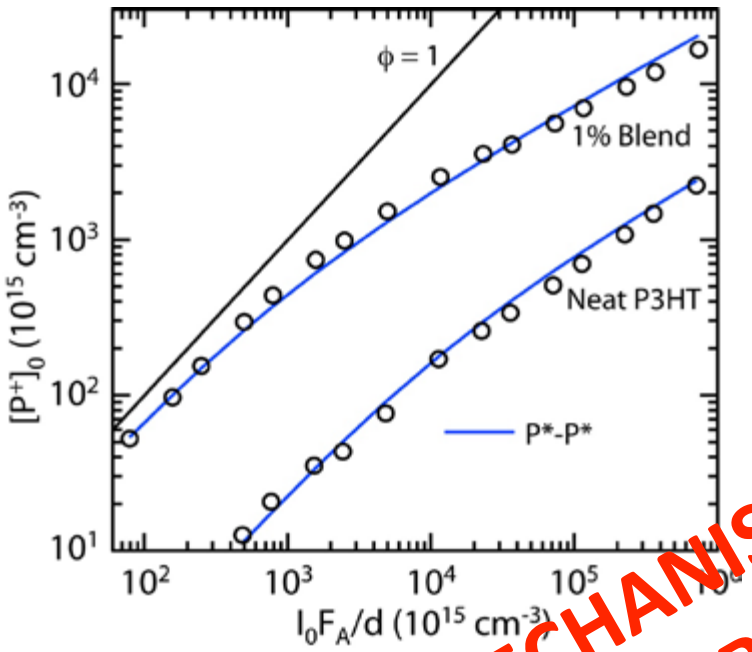


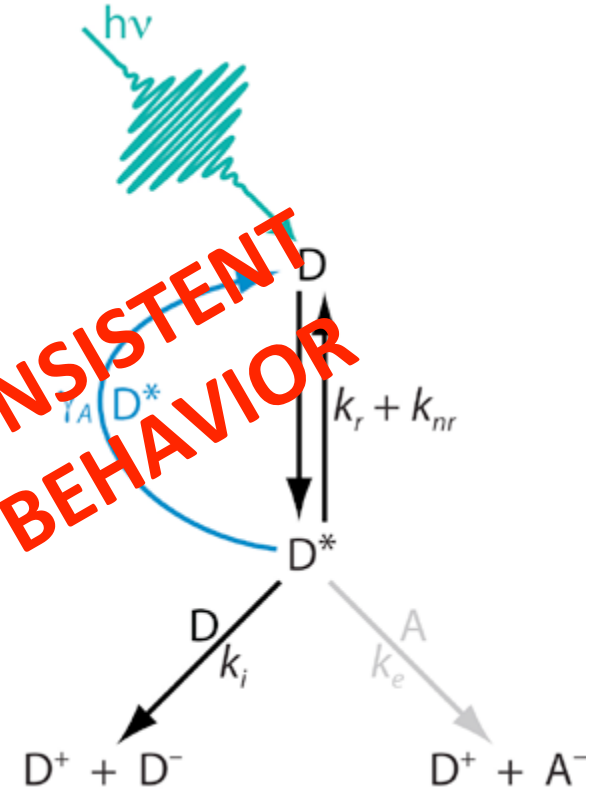


	P3HT	1% Blend
$k_e[A]$ (s^{-1})	--	9.2×10^9
γ_A (cm^3/s)	4.5×10^{-9}	1.0×10^{-6}

- Excitons **annihilate each other** at high excitation densities
  - mechanism **intrinsic** to the **polymer phase**
- However, upon the addition of **1% by weight** PCBM
  - rate **constant** must increase by **3 orders** of magnitude

Exciton-exciton annihilation





MECHANISM INCONSISTENT WITH OBSERVED BEHAVIOR

	P3HT	1% Blend
$k_e[A]$ (s^{-1})	--	9.2×10^9
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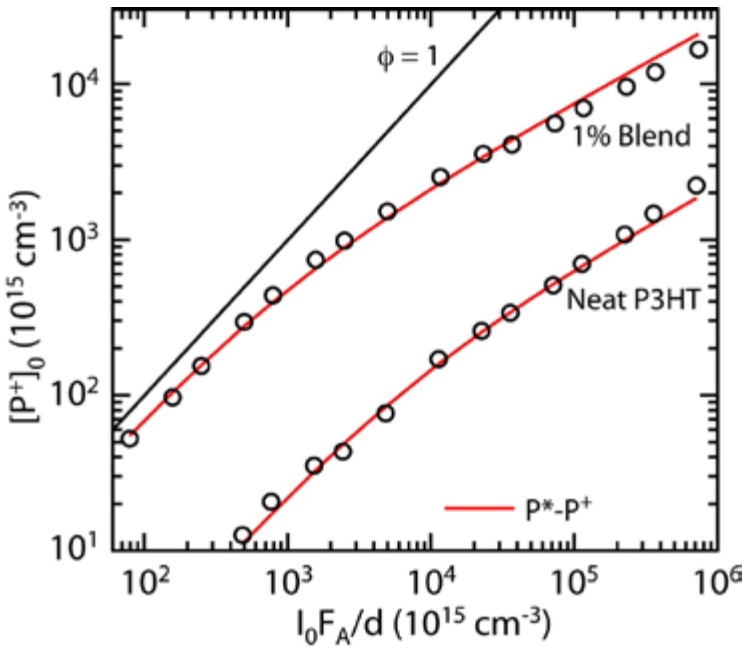
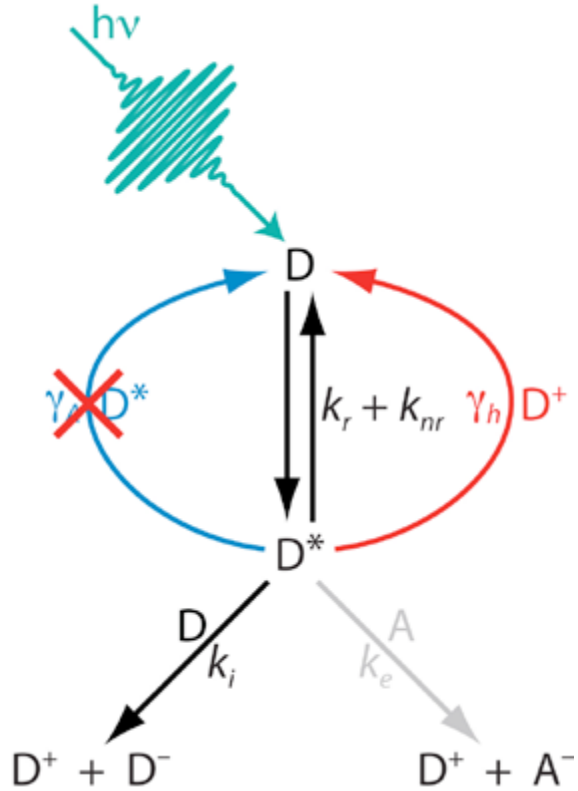
  - rate **constant** must increase by **3 orders** of magnitude

Exciton annihilation by mobile holes





	P3HT	1% Blend
$k_e[A]$ (s^{-1})	--	9.2×10^9
γ_A (cm^3/s)	--	--
γ_h (cm^3/s)	3.0×10^{-8}	3.0×10^{-8}

- Excitons **annihilated by mobile holes** at high excitation densities
- Addition of **1% by weight** PCBM
  - **single rate constant** describes process in neat polymer and blend

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TRMC studies at NREL

Dark Carriers, Trapping, and Activation Control of Carrier Recombination in Neat P3HT and P3HT:PCBM Blends

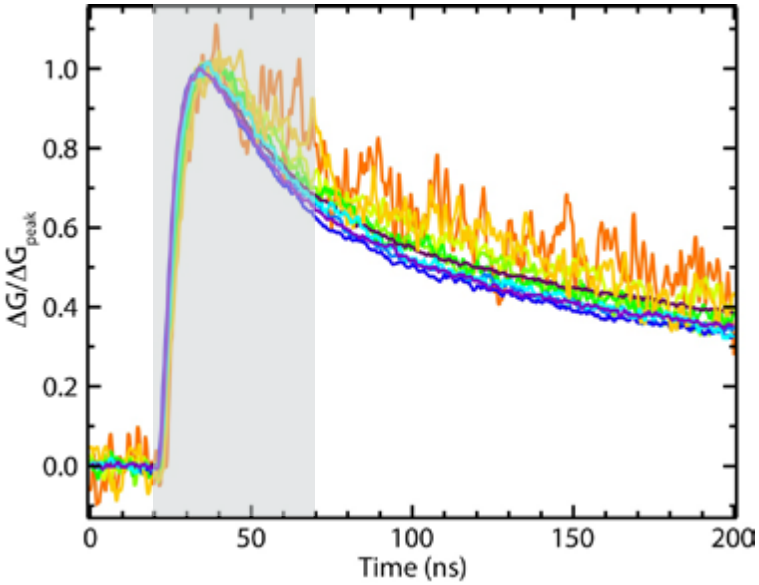
J. Phys. Chem. C; **2011**, *115*, 23134-23148
DOI: 10.1021/jp208014v

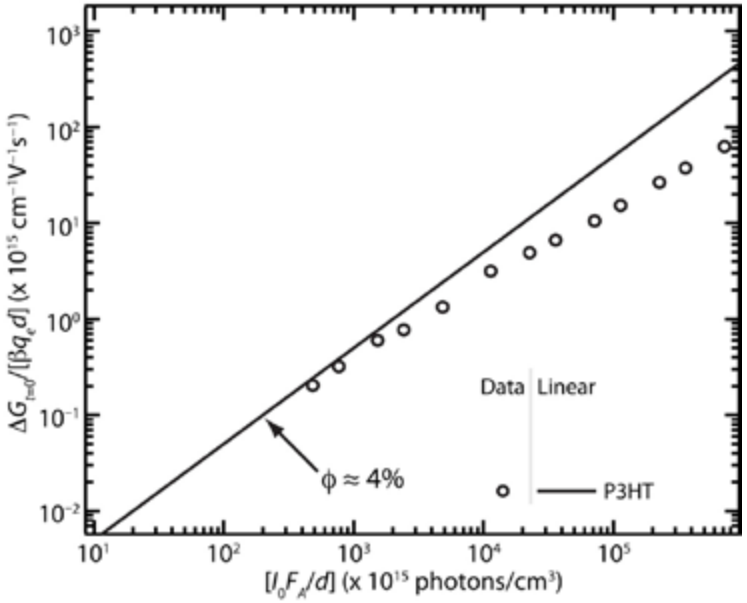
Andrew Ferguson, Nikos Kopidakis, Sean Shaheen[†], Garry Rumbles
Departmen o Physic & Astronomy, University o Denver

Thi wor wa funde b th Sola Photochemistry progra o th U.S Departmen o Energy, Office o Science, Basic Energ Sciences, Division o Chemica Sciences, Geosciences and Biosciences, under Contract No. DE-AC36-08GO2830 to NREL.

Photophysics in pristine P3HT

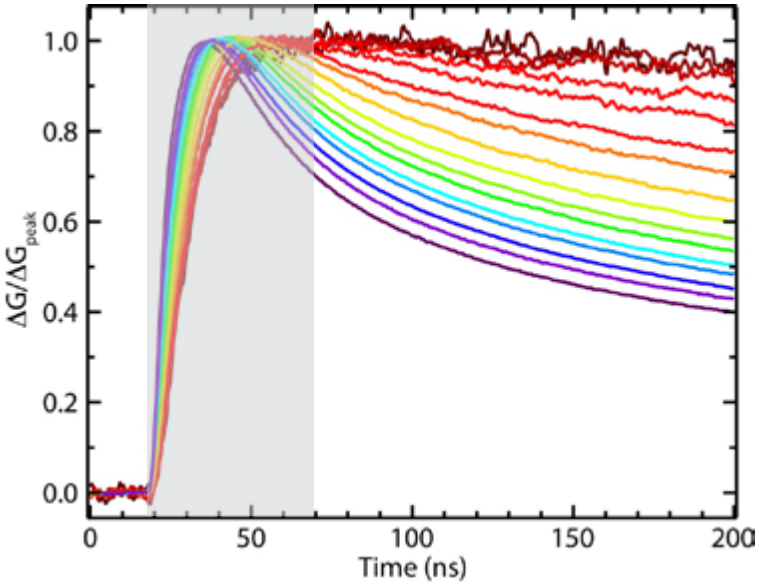
- Majority of photoinduced excitons **decay** *to* **ground state** or **quenched by carriers** at high excitation densities
  - **small**, but finite, yield of **intrinsic**, **long-lived** mobile holes
- **High density** of **dark carriers** in pristine P3HT
  - **electrons trapped**
  - **holes** form **equilibrium** between **trapped** and **mobile**
- Photoconductance **dynamics** determined by **dark carriers** and **traps**
  - **pseudo-first-order dynamics** due to large reservoir of dark carriers
- Photoinduced **holes perturb** equilibrium
  - equilibrium **re-established** within ≈50 ns
- Subsequent **leakage** and **re-equilibration**
  - due to **slow second-order recombination** with trapped electrons

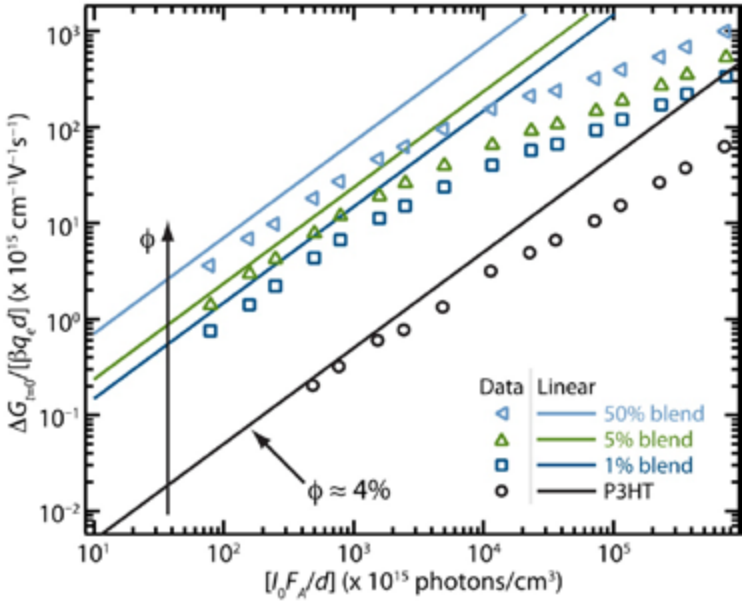




Photophysics in P3HT:PCBM blends (1)

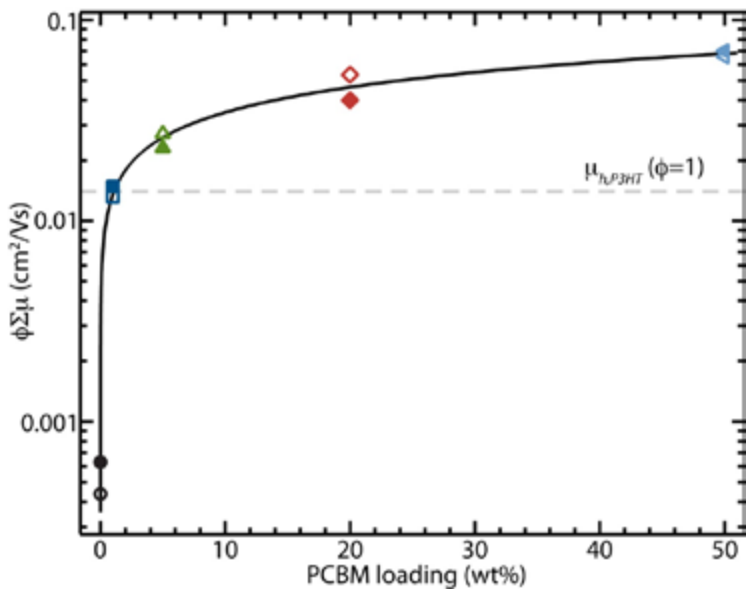
- Photoinduced excitons **rapidly quenched** by **electron transfer** to an acceptor (PCBM)
  - excitons still **quenched by carriers** at high excitation densities
- Intensity-dependent photoconductance **dynamics** determined mainly by **photoinduced carriers**
  - **second-order dynamics**
- Photoinduced **holes still perturb** equilibrium
  - equilibrium **re-established** within ≈50 ns

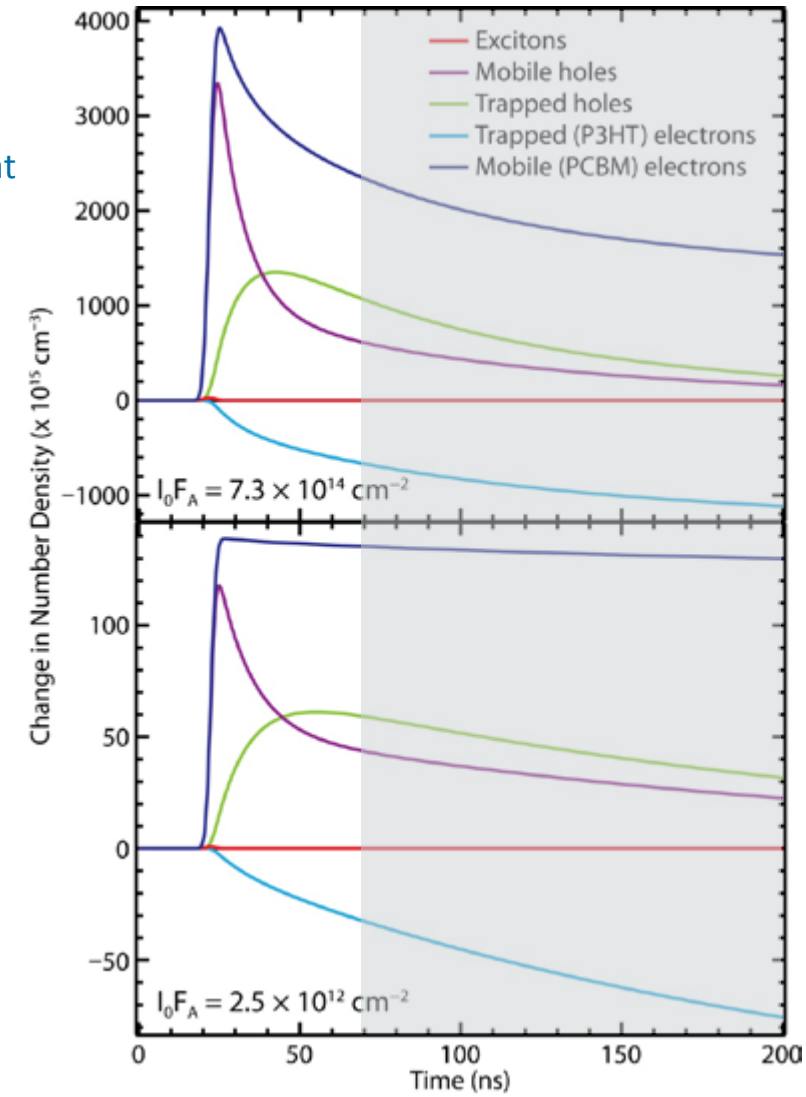




Photophysics in P3HT:PCBM blends (2)

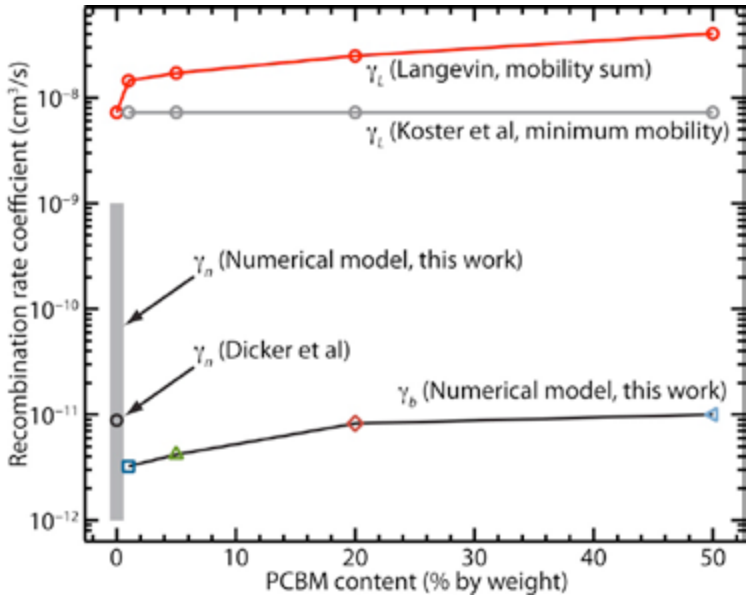
- Photoinduced **electrons** now **contribute** to **photoconductance**
  - PCBM **aggregates** formed even at **low loadings**
  - electron contribution **dominates** at **high loadings** and at **long times**

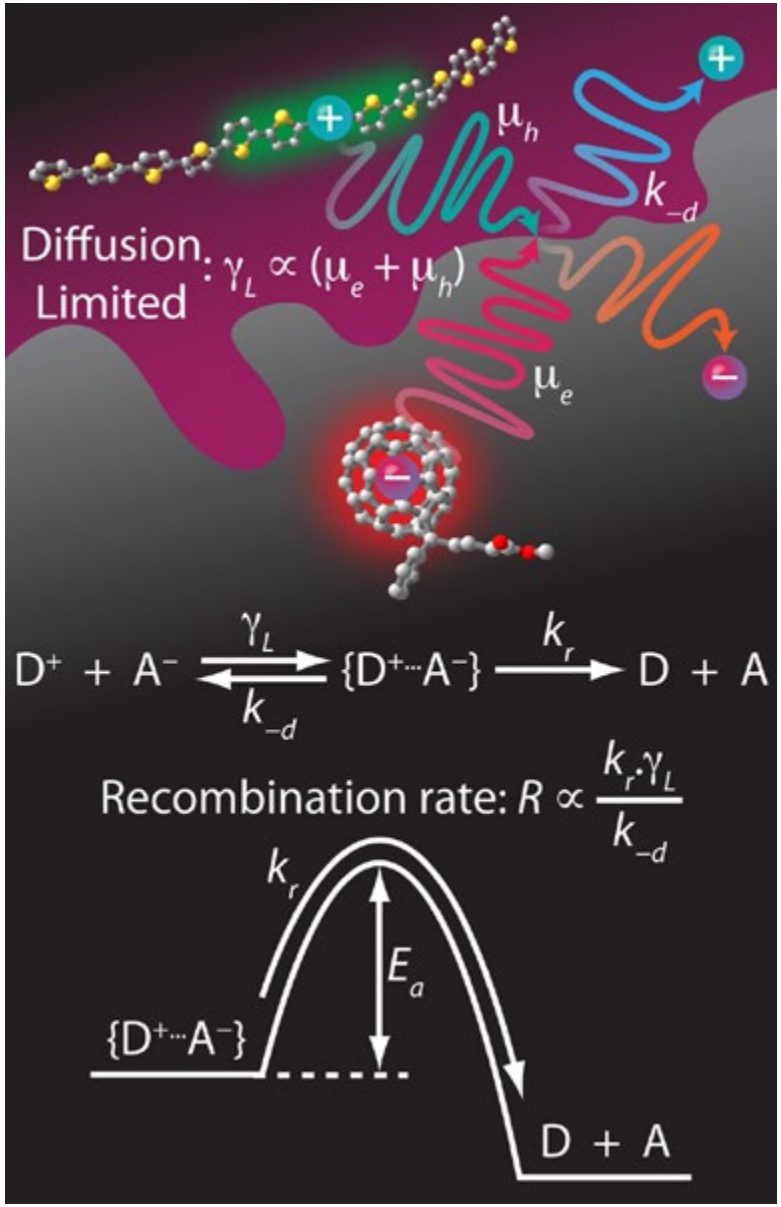




Hindered carrier recombination in P3HT and P3HT:PCBM

- **Recombination rate coefficient** several **orders of magnitude smaller** than predicted by Langevin-based models
  - carrier **recombination** is **activation controlled** (even in pristine P3HT)
  - **energetic barrier** exists at the **interface** that **severely hinders carrier recombination**





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TRMC studies at NREL

The Influence of Solid-State Microstructure on the Origin and Yield of Long-Lived Photogenerated Charge in Neat Semiconducting Polymers

J. Polym. Sci. B Polym. Phys.; **2012**, *50*, 27-37
DOI: 10.1002/polb.22379

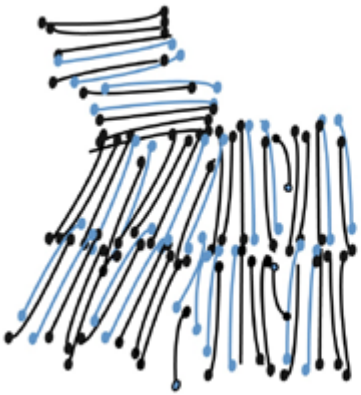
Obadiah G. Reid, Jennifer A. Nekuda-Malik[†], Gianluca Latini[‡], Smita Dayal, Nikos Kopidakis, Carlos Silva[#], Natalie Stingelin[†], Garry Rumbles

Departmen o Materials, Imperial Colleg London
Cente fo Biomolecula Nanotechnologies @UNILE Istitut Italian d Tecnologia
Departmen o Physics, Université de Montréal

Thi wor wa funde b th Sola Photochemistry progra o th U.S Departmen o Energy, Office o Science, Basi Energ Sciences, Division o Chemica Sciences, Geosciences an Biosciences, under Contrac No. DE-AC36-08GO2830 t NREL. Contrac Number DE-SC0001342:001.

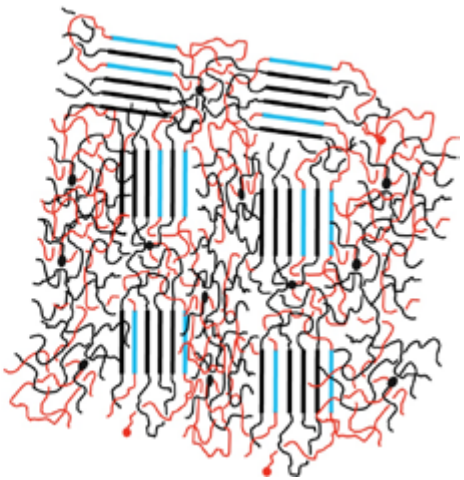
P3HT may assume two distinct classes of microstructure

paraffinic

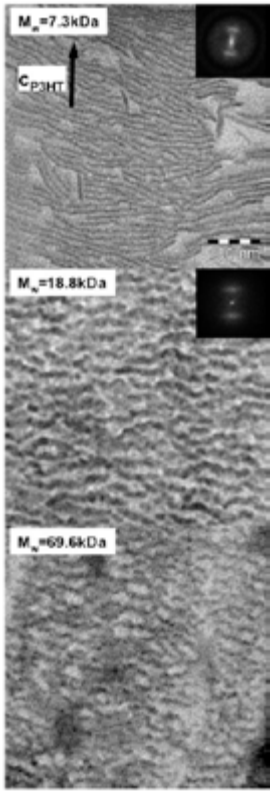


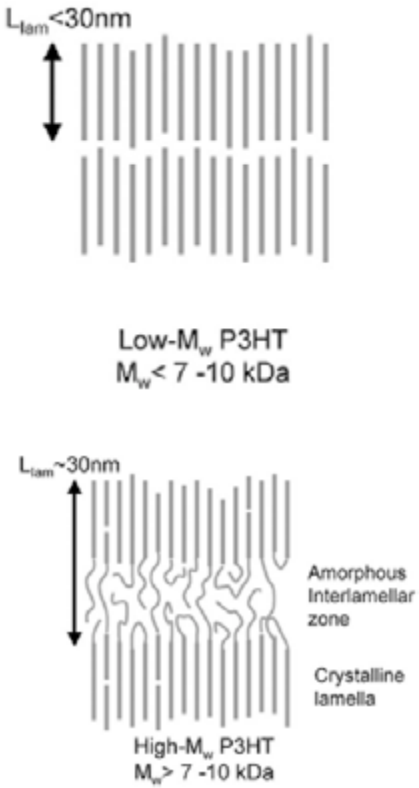
Low molecular weight.
Oligomers. No entanglement

semi-crystalline



High molecular weight.
Polymers. Entanglement.

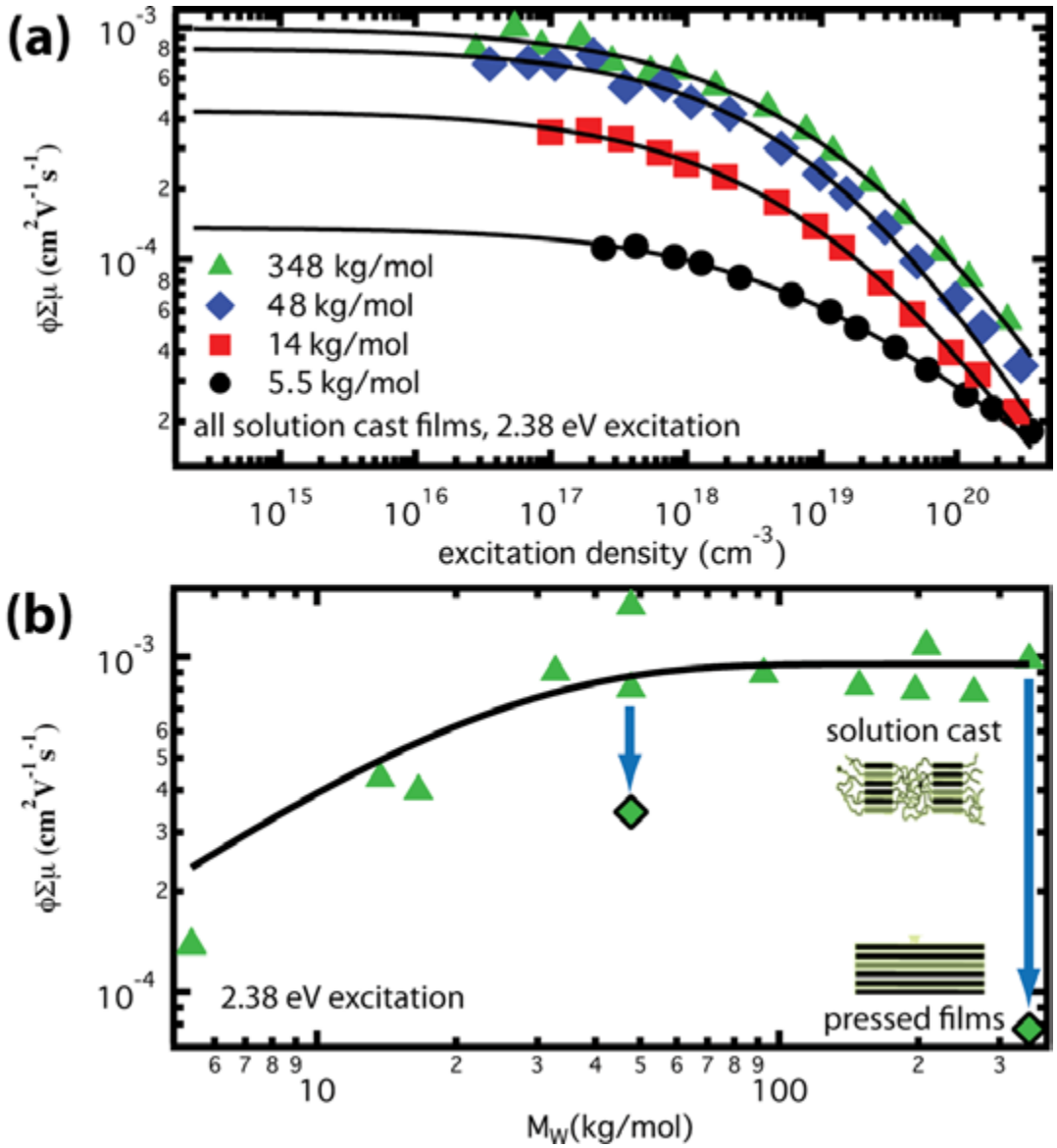




M. Brinkmann, P. Rannou,
Adv. Funct. Mater. **17** (2007) 101.

- **Molecular weight** (M_w) provides a powerful **"knob"** which can be used to tune the **solid-state microstructure**
  - **Low M_w** P3HT forms a **paraffinic phase** of **disconnected extended-chain crystals**
  - **High M_w** P3HT forms a **semicrystalline** two-phase system of **crystals** and **interconnected amorphous domains**

Microstructure determines the yield of free photogenerated charge



- The **photoconductivity** measured via TRMC **depends** sensitively on the **molecular weight** of the polymer.
- The **TRMC mobility** is **independent** of **polymer microstructure** [1], thus, **variations** in the **yield-mobility product** with molecular weight are due to changes in the **yield**.
- **Carrier yield** is **maximized** in samples with **co-existing crystalline and amorphous phases** (semicrystalline), and minimized for a single-phase polycrystalline samples (paraffinic).
- We propose that **carrier separation** occurs at the **interface** between **amorphous** and **crystalline** phases.
- **Decreasing the interface** between amorphous and crystalline domains through pressing the films **reduces** the **carrier yield**.

[1] G. Dicker, "Photogeneration and Dynamics of Charge Carriers in the Conjugated polymer poly(3-hexylthiophene)." Technische Universiteit Delft. PhD Dissertation.

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TRMC studies at NREL

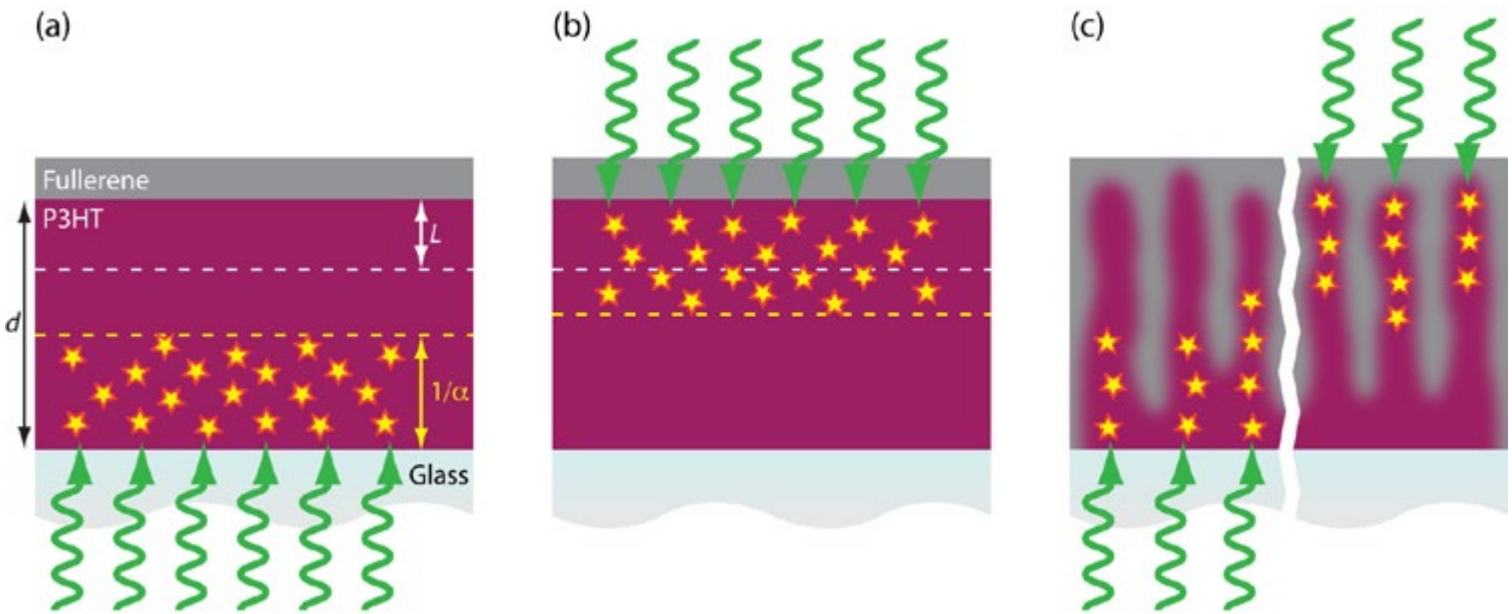
Photoinduced Charge Carrier Generation and Decay in Sequentially Deposited Polymer/Fullerene Layers: Bulk Heterojunction vs Planar Interface

J. Phys. Chem C; **2012**, *116*, 7293-7305
DOI: 10.1021/jp212390p

Alexandre M. Nardes, Alexander L. Ayzner[†], Scott R. Hammond, Andrew J. Ferguson, Benjamin J. Schwartz[†], Nikos Kopidakis
Departmen o Chemistr an Biochemistry, University o California, Los Angeles

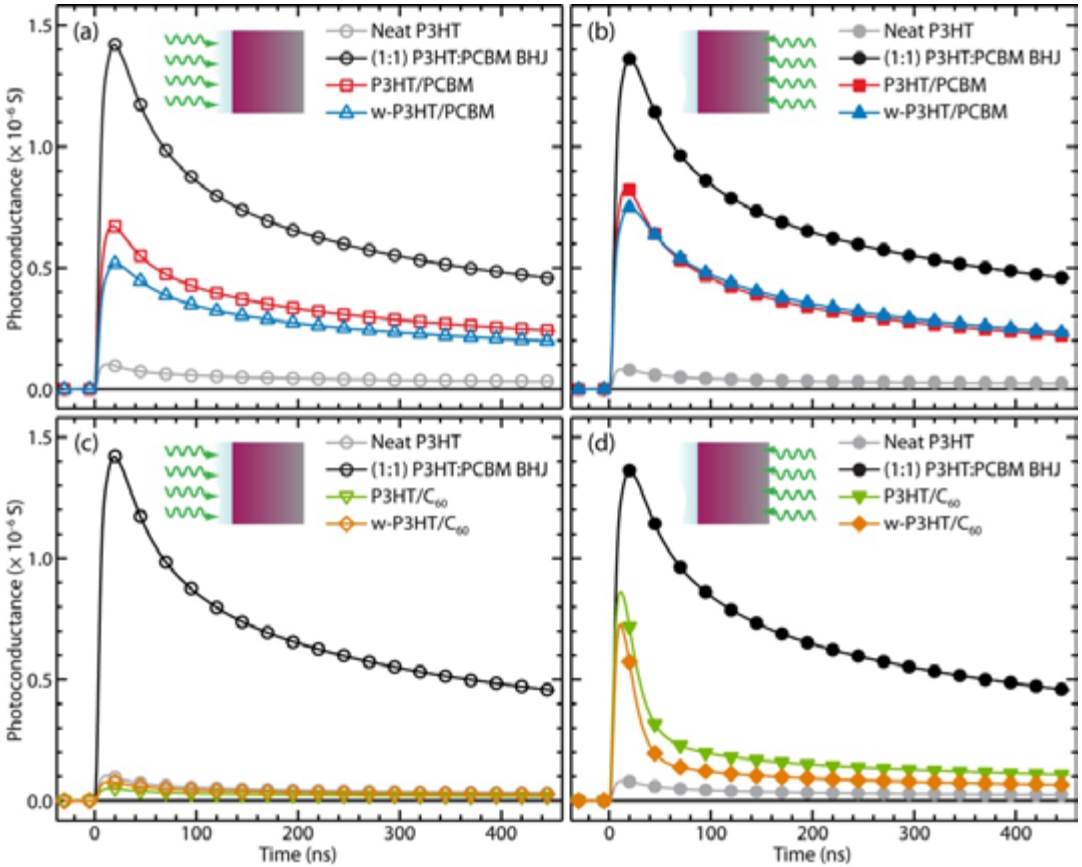
Thi wor wa supported as par of th Energy Frontier Research Cente "Molecularly Engineered Energy Material (MEEMs) funde b th U.S Departmen o Energy, Office o Science, Office o Basic Energy Science unde Contrac Number DE-SC0001342:001.

The exciton bottleneck



- In a **bilayer geometry** there is a distinct **mismatch** between the **absorption depth** (1/α) and the **exciton diffusion length** (*L*)
- For a **thick P3HT film** ($d > 1/\alpha \gg L$) illumination at the:
  - **P3HT/substrate interface** (a) produces excitons that **cannot reach** the **dissociation interface** with fullerene
  - **P3HT/fullerene interface** (b) produces excitons which **can** predominantly **reach** the **dissociation interface**
- In a film where the **P3HT** (donor) and **fullerene** (acceptor) **materials mix** (c) the yield of **exciton dissociation** should be essentially **independent** of **illumination direction**

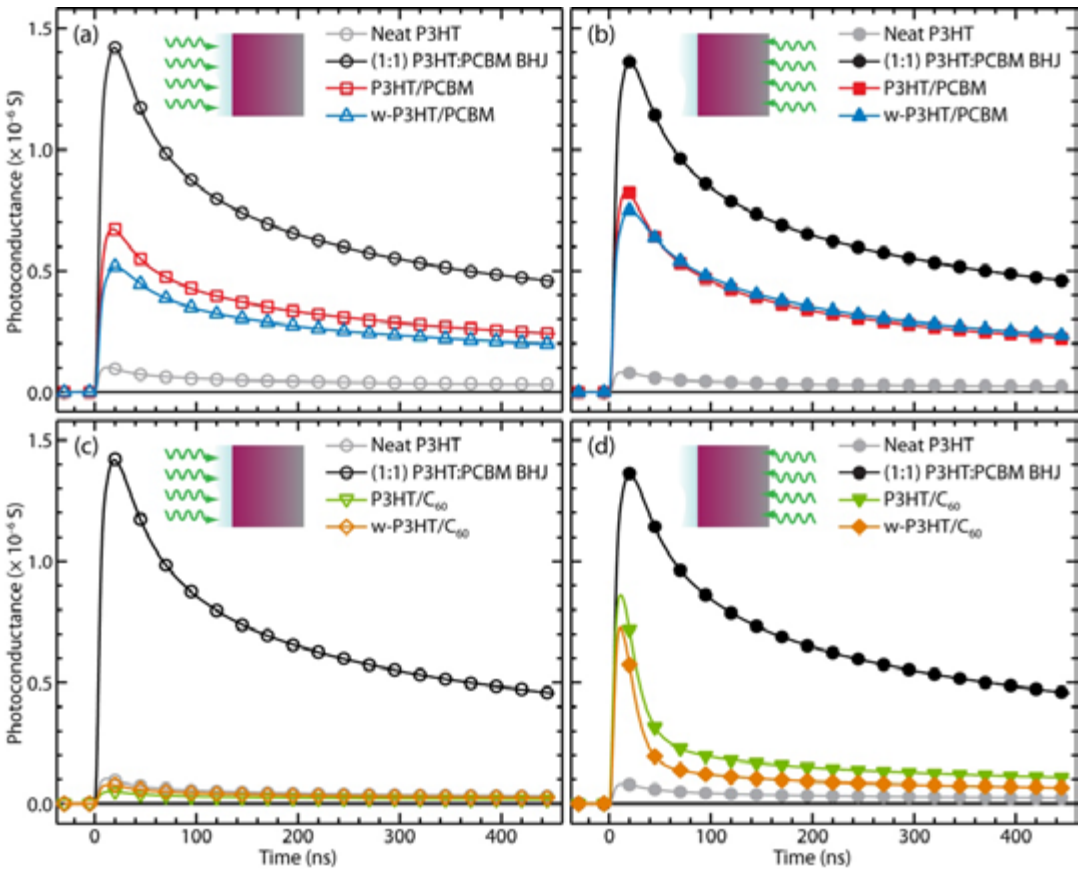
Probing the exciton bottleneck with TRMC

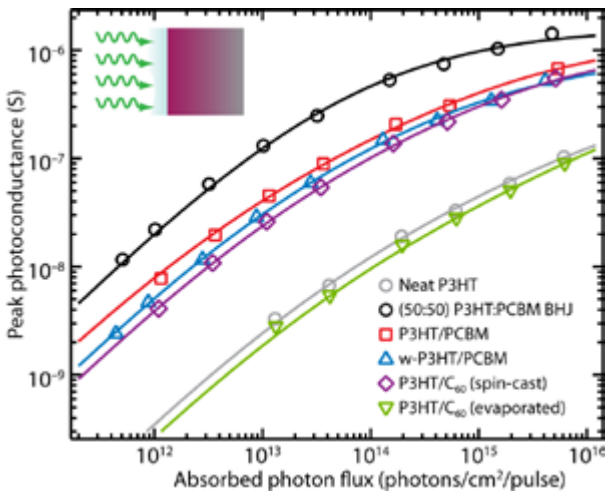


- For samples where the **fullerene** is **solution-deposited** (PCBM) onto P3HT the **photoconductance signal** is essentially **independent** of **illumination direction**
  - indicates that **PCBM mixes** effectively into the **underlying P3HT layer**

- For samples where the **fullerene** is **thermally-evaporated** (C_{60}) onto P3HT the **photoconductance signal** is **significantly larger** for **illumination** at the **P3HT/C_{60} interface**
  - **mixing** is far **less effective**

Probing the exciton bottleneck with TRMC





- **Photoconductance signal** approaches that of **optimized bulk heterojunction** (BHJ) (50:50 weight %) for **sequentially solution-deposited layers**

- For samples where the **fullerene** is **solution-deposited** (PCBM) onto P3HT the **photoconductance signal** is essentially **independent** of **illumination direction**
  - indicates that **PCBM mixes** effectively into the **underlying P3HT layer**

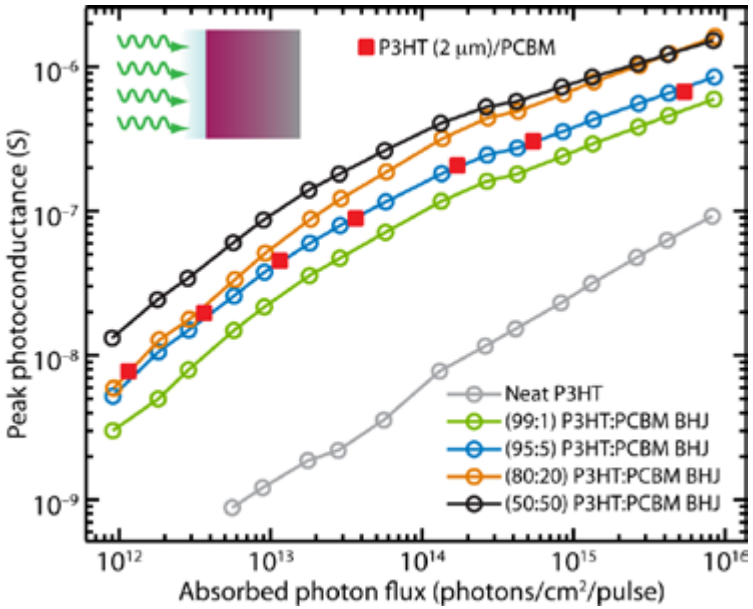
- For samples where the **fullerene** is **thermally-evaporated** (C_{60}) onto P3HT the **photoconductance signal** is **significantly larger** for **illumination** at the **P3HT/C_{60} interface**
  - **mixing** is far **less effective**

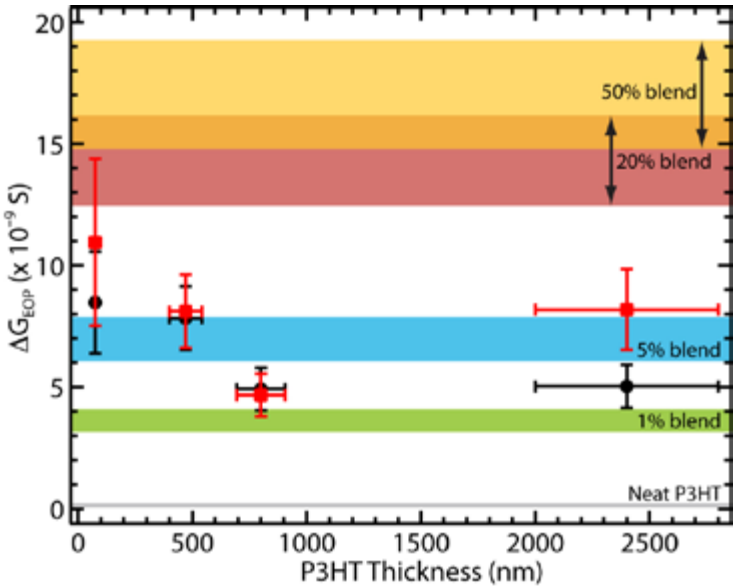
Effective fullerene loading ratio in graded P3HT/PCBM 'bilayers'

- The **peak photoconductance** signal for **solution-deposited PCBM** onto a 2 µm thick P3HT underlayer is **comparable** to a **bulk heterojunction** containing **5% by weight PCBM**

- Analysis of the **peak photoconductance** signal as a function of P3HT **underlayer thickness** suggest that:
  - for the **thinnest P3HT underlayer** (≈ 75 nm) the **photoconductance signal** corresponds to a **BHJ** with between **5 and 20% by weight PCBM**
    - consistent with **neutron scattering**[1] and **reflectivity**[2] studies of the **miscibility** of **PCBM** into **P3HT**

- These observations provide **guidelines** for the **control** of **microstructure** to accelerate the development of organic photovoltaic devices





[1] W. Yin, M. Dadmun, *ACS Nano.* **5** (2011) 4756.
[2] H. Chen, R. Hegde, J. Browning, M. D. Dadmun, *Phys. Chem. Chem. Phys.* **14** (2012) 5635.

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TRMC studies at NREL

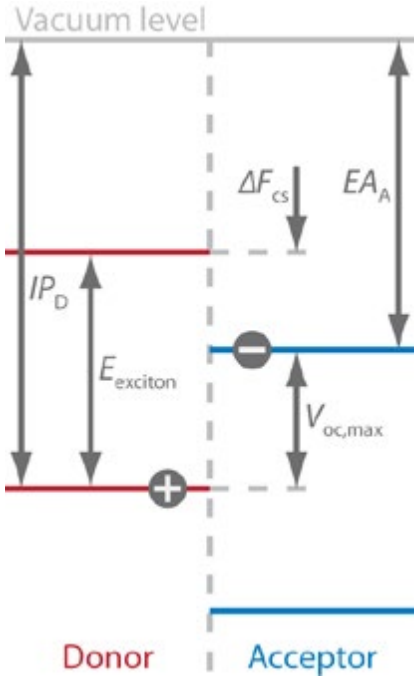
Beyond PCBM: Understanding the Photovoltaic Performance of Blends of Indene-C_{60} Multiadducts with Poly(3-hexylthiophene)

Adv. Funct. Mater. **2012**
DOI: 10.1002/adfm.201200336

Alexandre M. Nardes, Andrew J. Ferguson, James B. Whitaker†, Bryon W. Larson†, Ross E. Larsen, Klára Maturová, Peter A. Graf, Olga V. Boltalina†, Steven H. Strauss†, Nikos Kopidakis
Departmen o Chemistry, Colorado Stat University

Thi wor wa supported as par of th Energy Frontier Research Cente "Molecularly Engineere Energ Material (MEEMs) funde b th U.S Department o Energy, Office of Science, Office o Basi Energ Science unde Contrac Number DE-SC0001342:001.

Maximizing V_{oc}: Tuning the acceptor LUMO position



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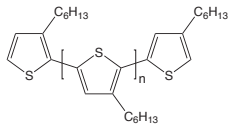

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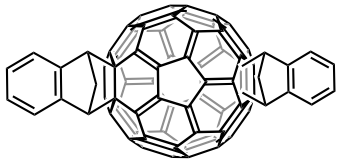


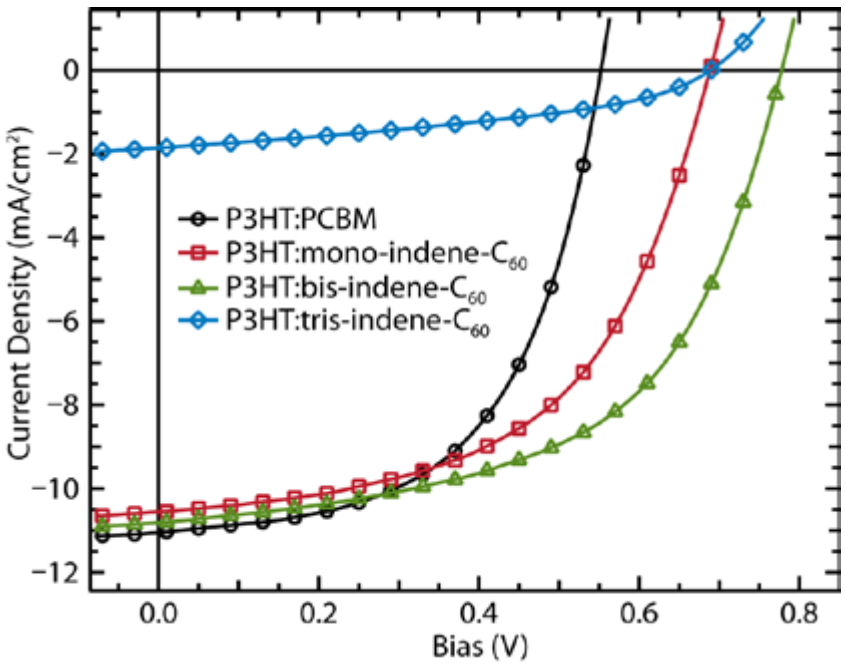
Substituted fullerenes:

- Replacement of the **methyl 5-phenylpentanoate** group in PCBM with an **indene** group **shifts the LUMO toward vacuum**
  - Corresponds to **reduced electron affinity**
- Subsequent addition of a **second** and **third indene** unit to the fullerene cage **further reduces the electron affinity**

- Reducing the electron affinity should:
  - **Increase the V_{oc}** of the PV device, BUT
  - Could also **decrease the driving force for exciton dissociation**, ΔF_{cs}

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

tris-indene-C_{60}: drastic deterioration in device performance

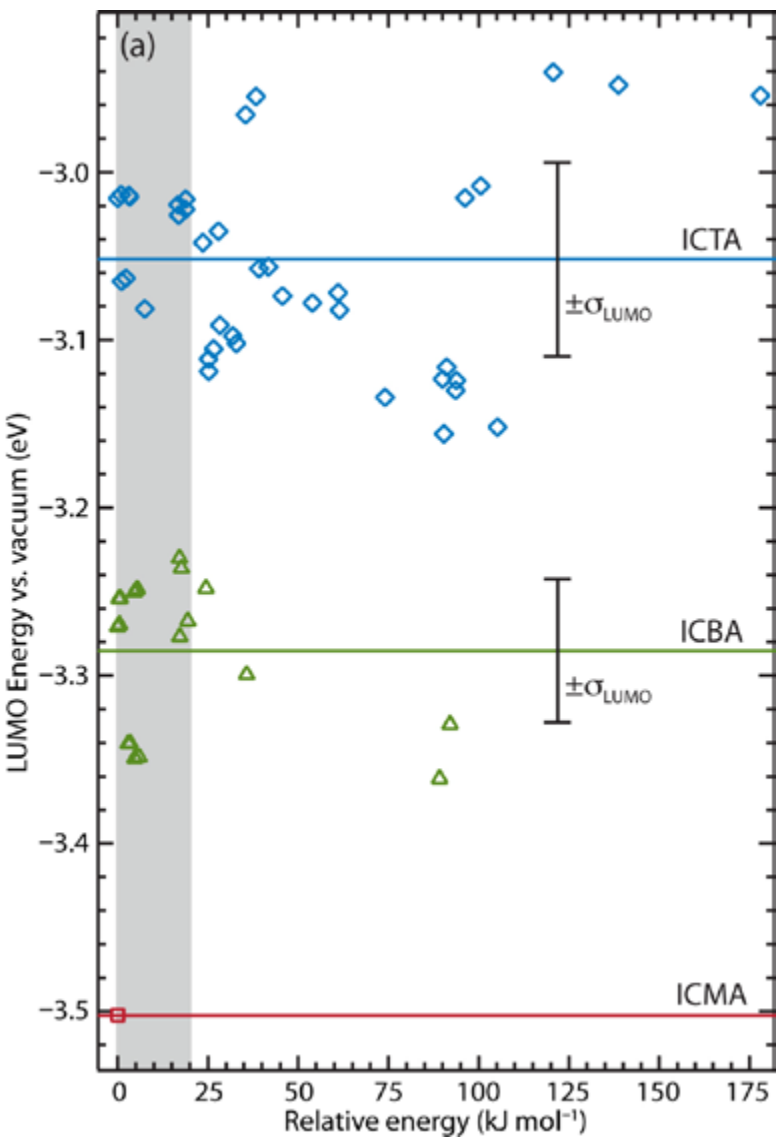


Current density-voltage data:

- **mono-** and **bis-indene-C_{60}** derivatives follow the predicted trend
  - **V_{oc}** of the PV device **increases**
  - Small **reduction in J_{sc}**
- **tris-indene-C_{60}** derivative exhibits poor performance
  - **V_{oc}, J_{sc}** and **FF** all **deteriorate**
- Device measurements **cannot elucidate** whether **energetics** (inefficient charge carrier generation or enhanced carrier recombination) or **nanomorphology** (poor carrier transport) limit device performance

	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} (ICMA)	-0.21	0.69	10.56	54	3.92
bis-indene-C_{60} (ICBA)	-0.25	0.78	10.82	56	4.65
tris-indene-C_{60} (ICTA)	-0.45	0.69	1.86	40	0.51

Isomers of fullerene multi-adducts



A number of **addition patterns** are possible when **multiple substituents** are bound the the fullerene cage:

- **23** possible isomers for **bis-indene-C_{60}**
- **53** possible isomers for **tris-indene-C_{60}**

Calculations based on **density functional theory** indicate that:

- the **spread in LUMO energies** for the tris-adduct is only **marginally larger** than the bis-adduct
  - for **isomers within 20 kJ mol^{-1}** of the most stable isomer the **spread is actually smaller**

- This observation suggests that the **poor performance** of devices employing **tris-indene-C_{60}** are **not limited** by **isomers with deeper LUMO energies**

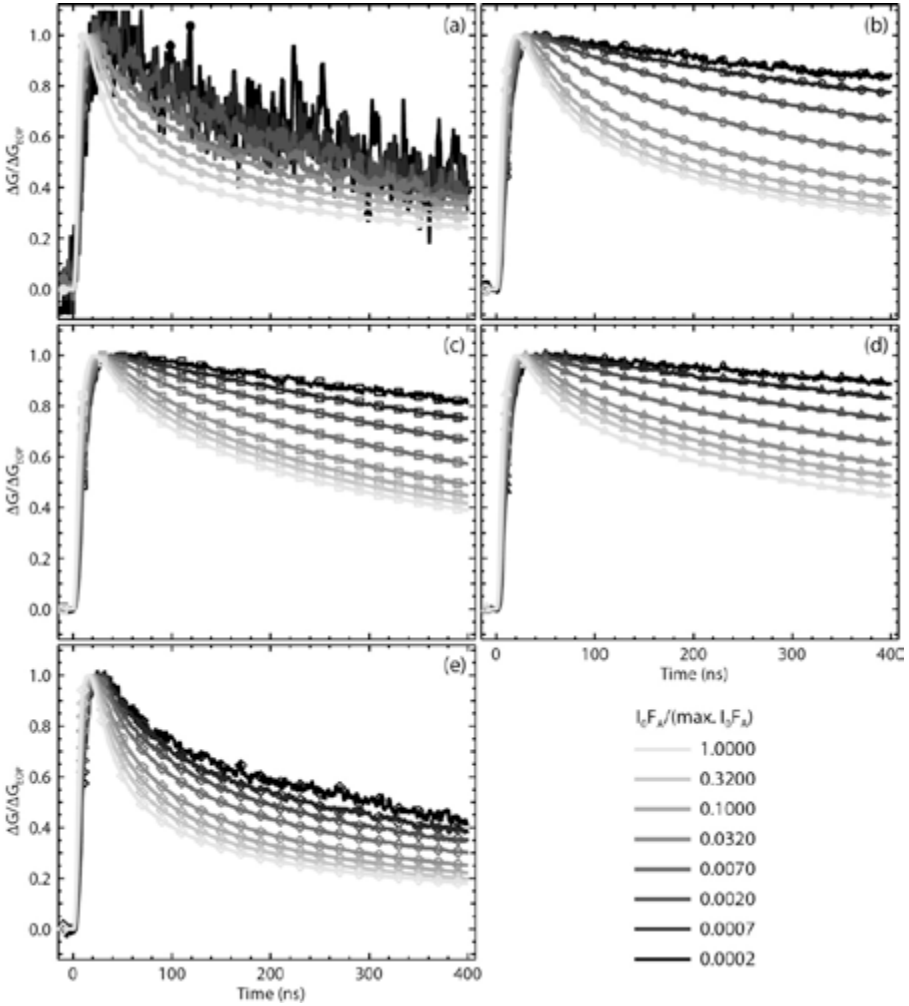
Photoconductance transients

Intensity dependence of **photoconductance transients** of P3HT blended with **PCBM, mono-indene-C_{60} and bis-indene-C_{60}** all indicate contribution from **electrons in acceptor domains**:

- **long-lived** photoconductance signal
- **large spread** in photoconductance transients

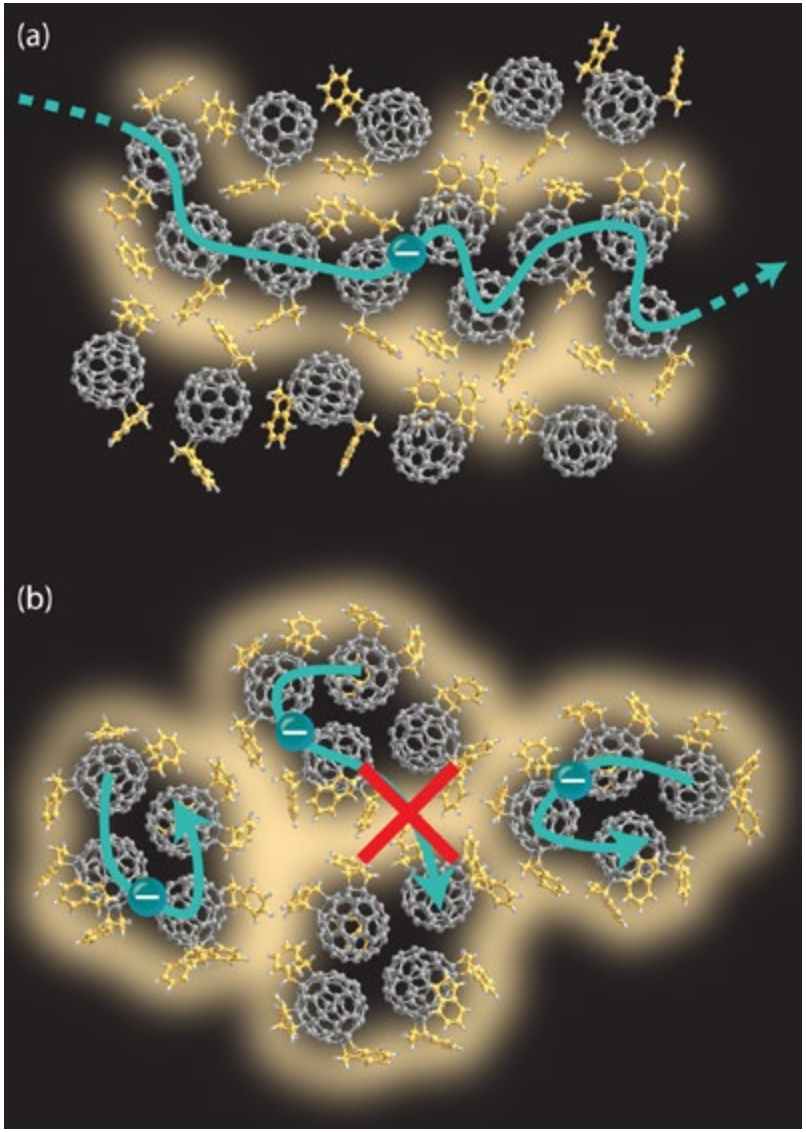
Blend of **P3HT with tris-indene-C_{60}** exhibits intensity-dependent **photoconductance transients** similar to **pristine polymer**:

- **smaller spread** in photoconductance transients
  - electron mobility **reduced** in **tris-indene-C_{60} domains**



Hindered electron transport

Simple cartoons arranging different isomers of bis-indene-C_{60} and tris-indene-C_{60} into disordered domains indicate that:

- it is possible to form **'chains'** of **bis-indene-C_{60}** where the fullerene cages can **couple strongly**
- **clusters** of **tris-indene-C_{60}** are quickly **covered** by the **insulating indene** solubilizing units
  - **coupling** between **neighboring clusters** is **hindered, reducing** both the **local** and **macroscopic** electron mobility

Strategies to **modify fullerene derivatives** with **multiple substituents** should consider the possible **impact on electronic coupling** between neighboring fullerene cages and/or clusters