Organic Photovoltaics:
Current State of the Art and the Role of Delocalization

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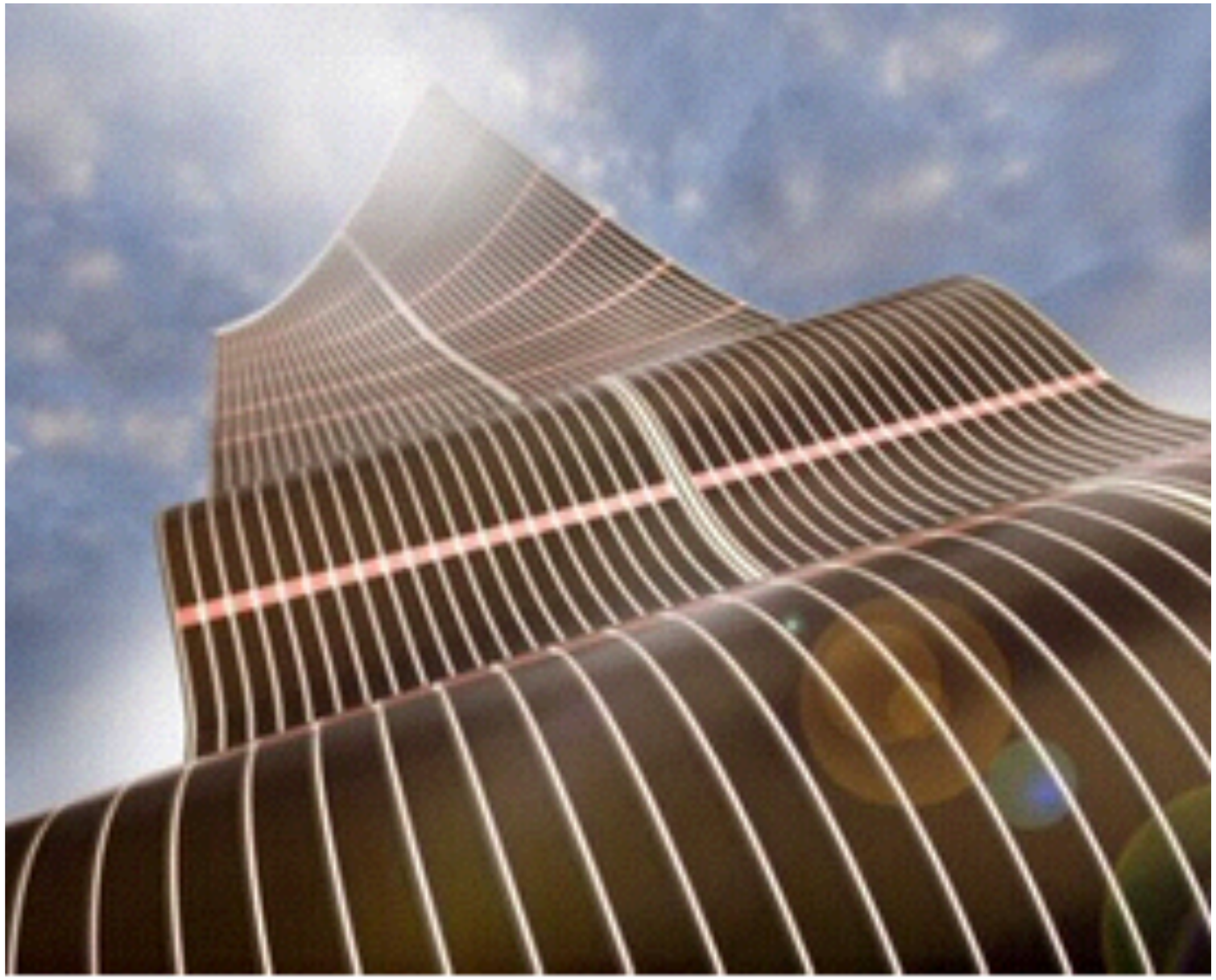
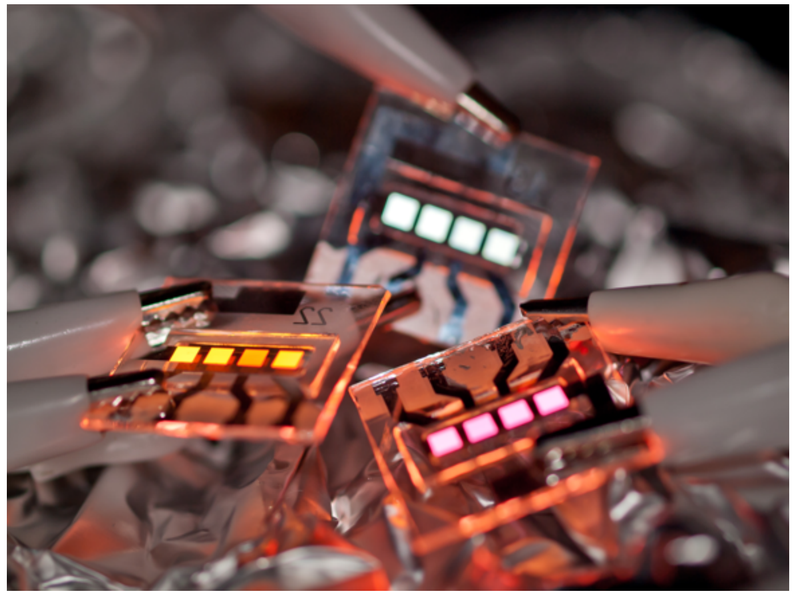
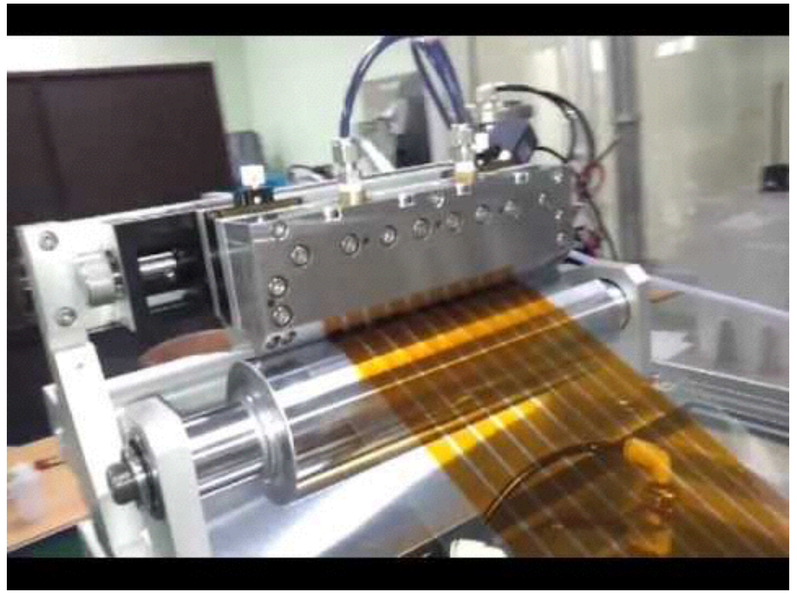
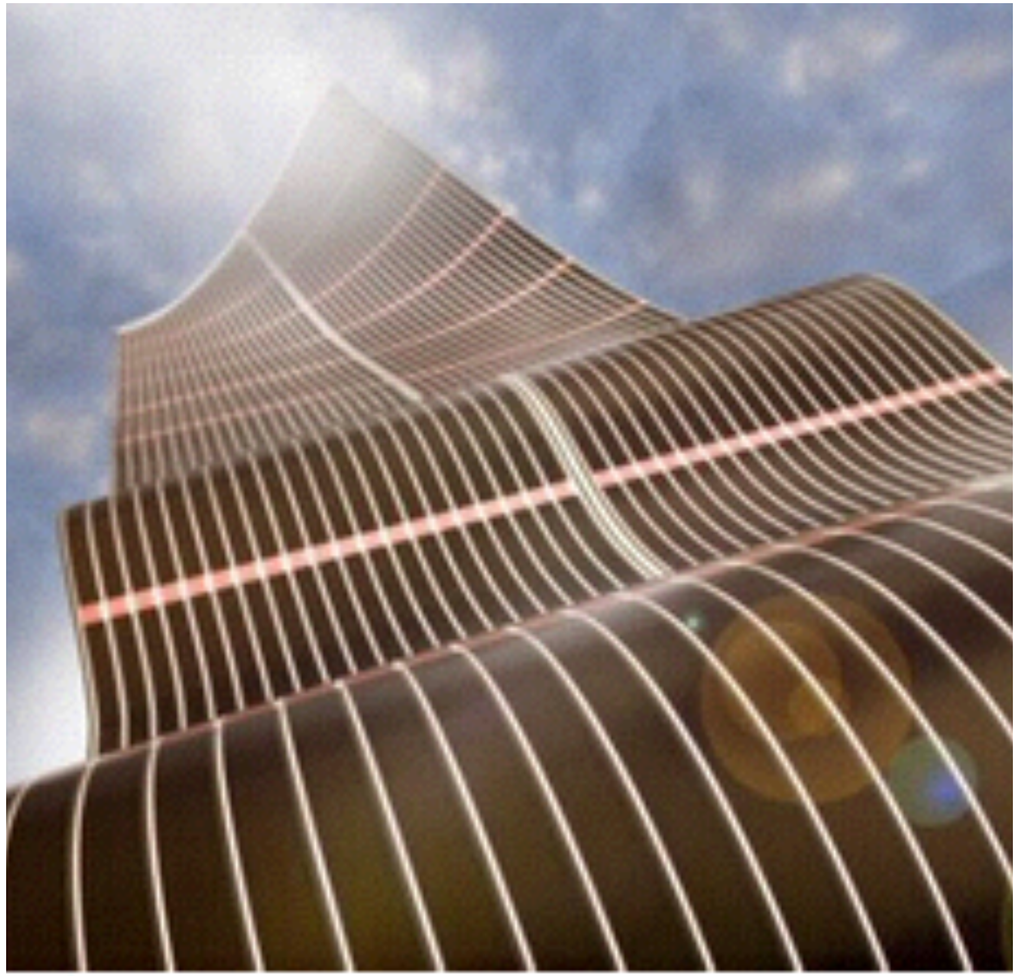




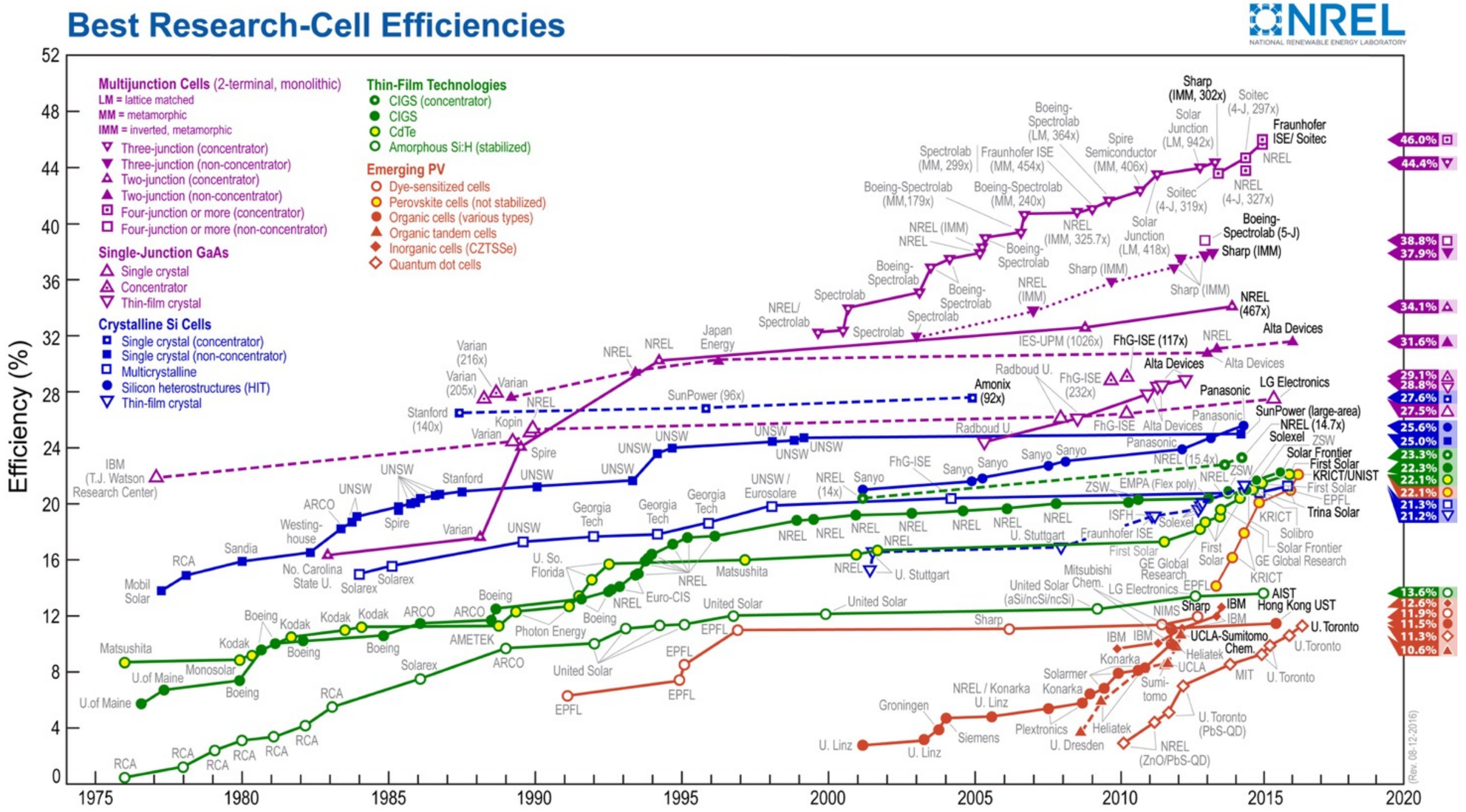


Potential Advantages of OPVs

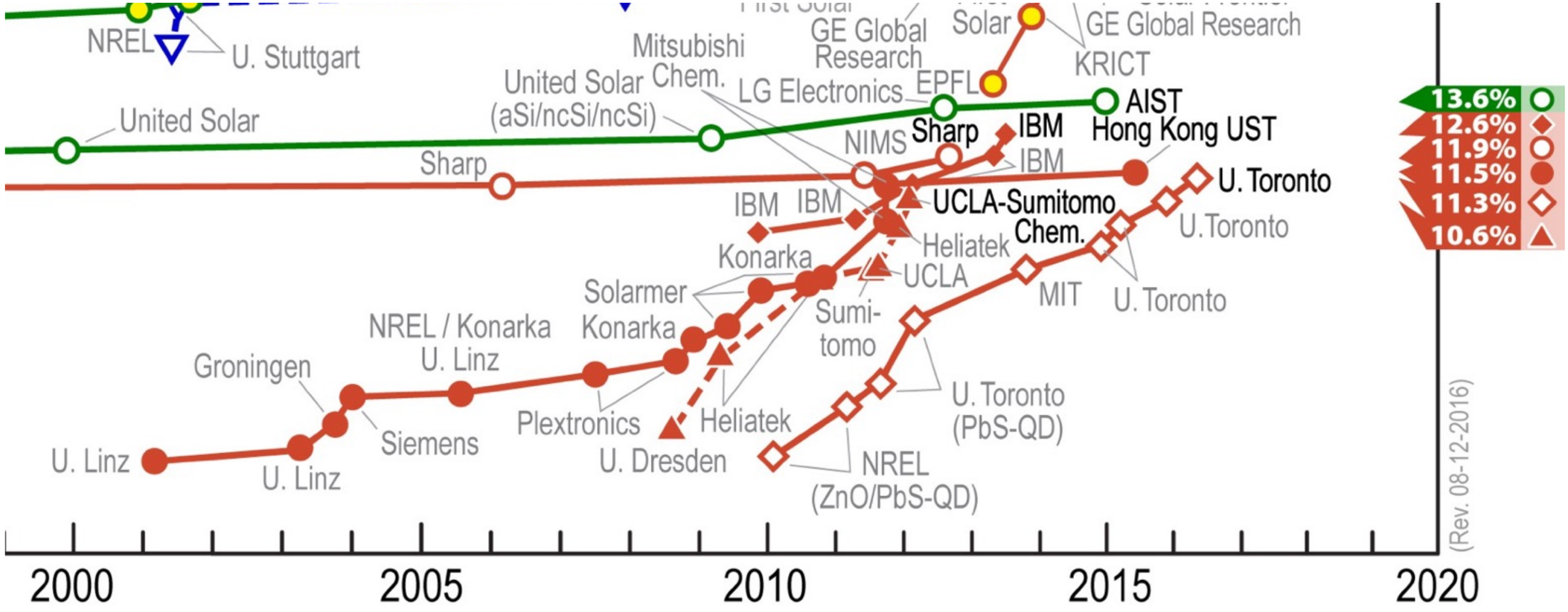
- **Cheaper**
- Sustainable
- Easy Processing ($)
- Flexible



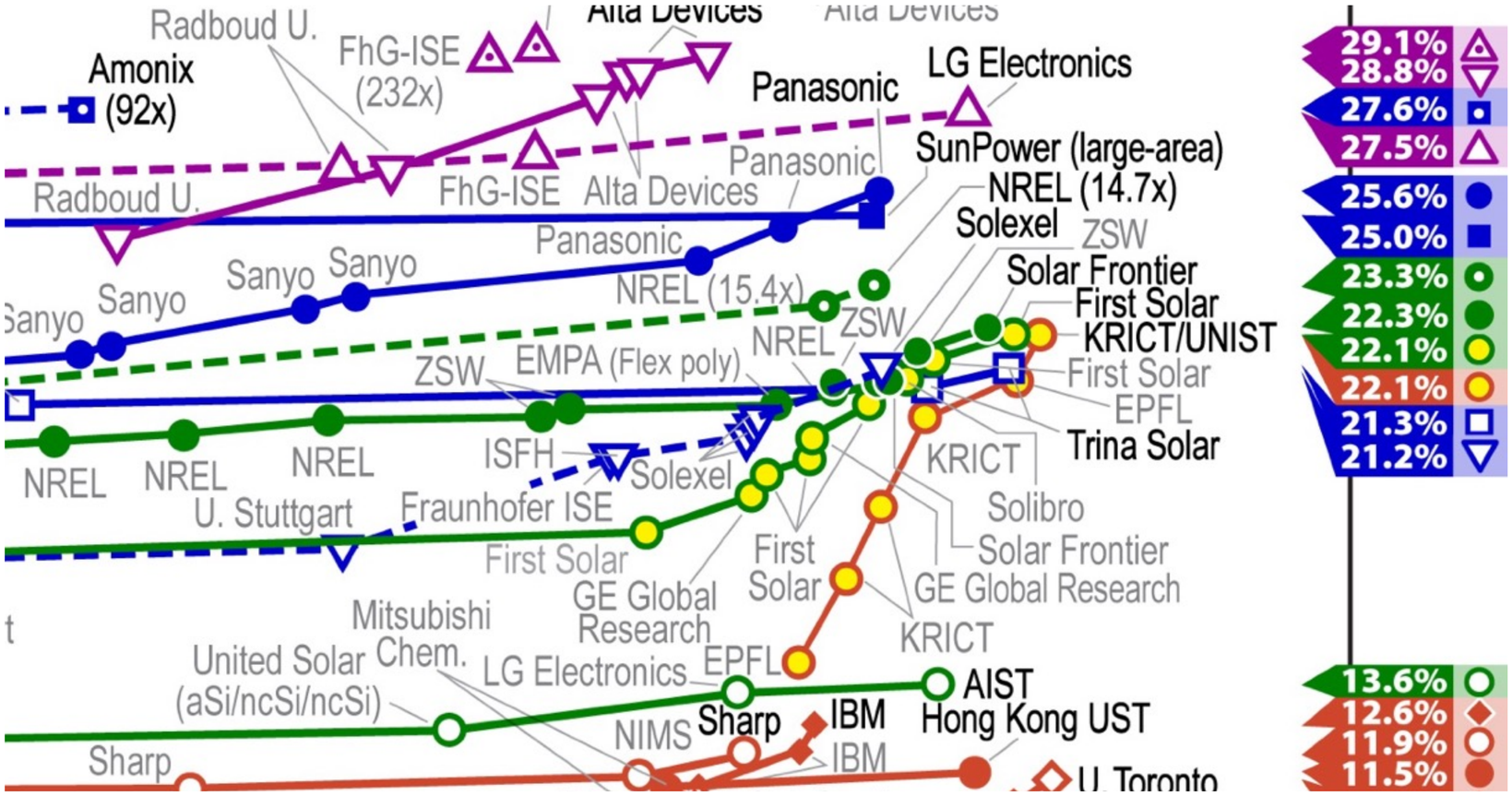
Efficiency Trends



Efficiency Trends



Efficiency Trends



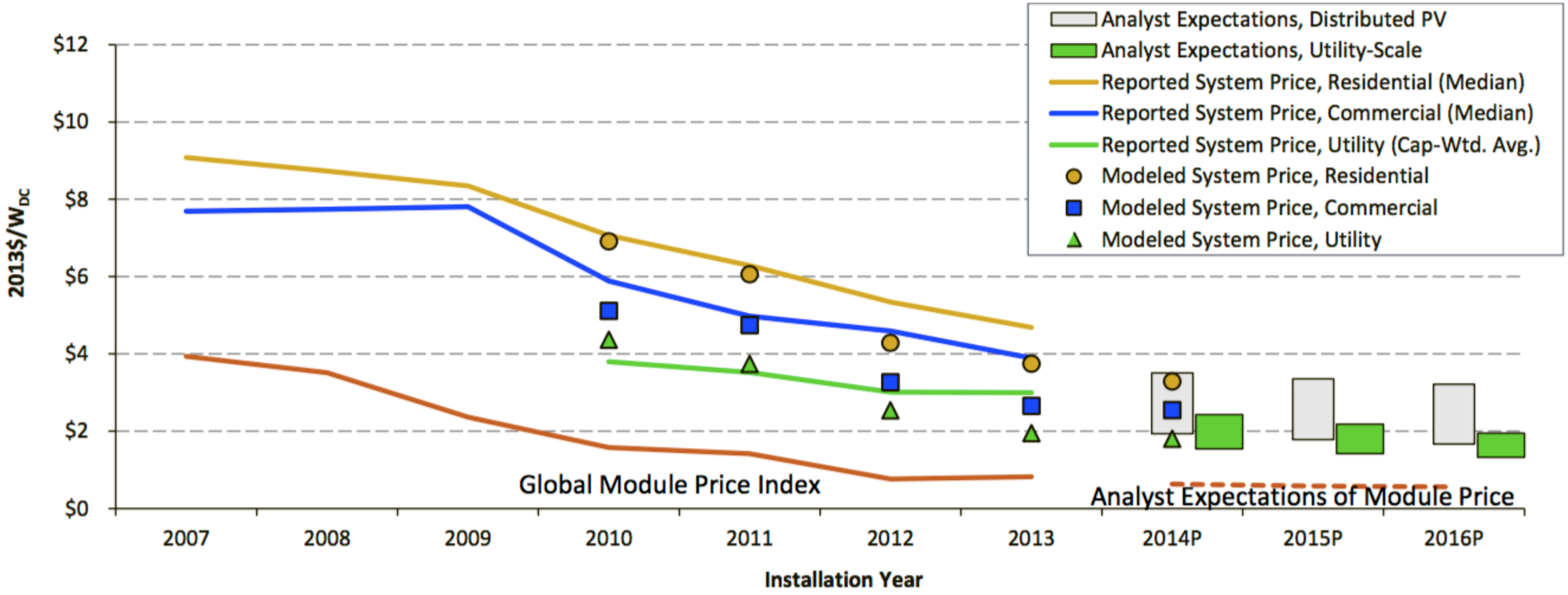
Silicon

Thin Film

Perovskite

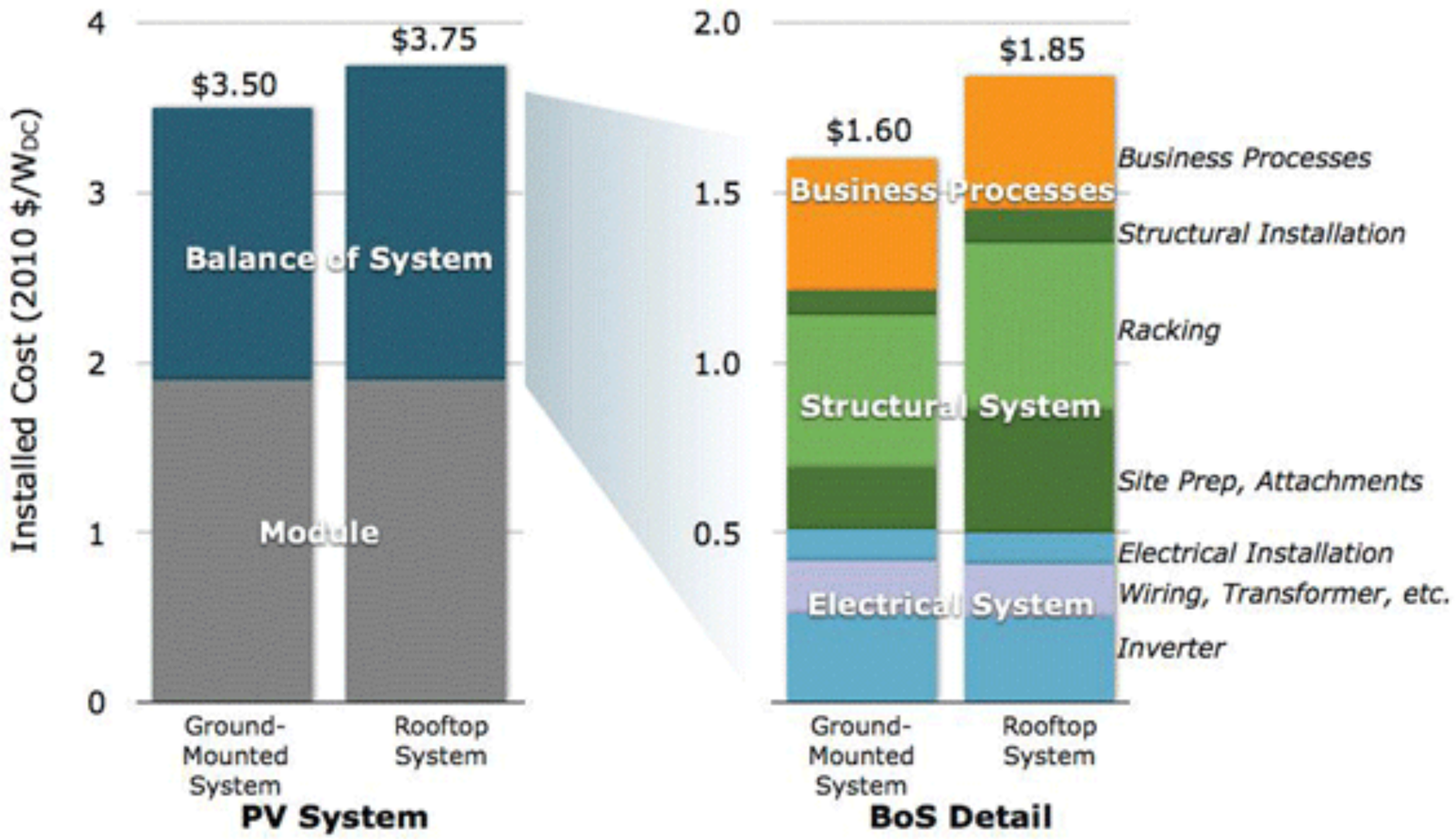
OPV

Ever dropping cost of Si-PV



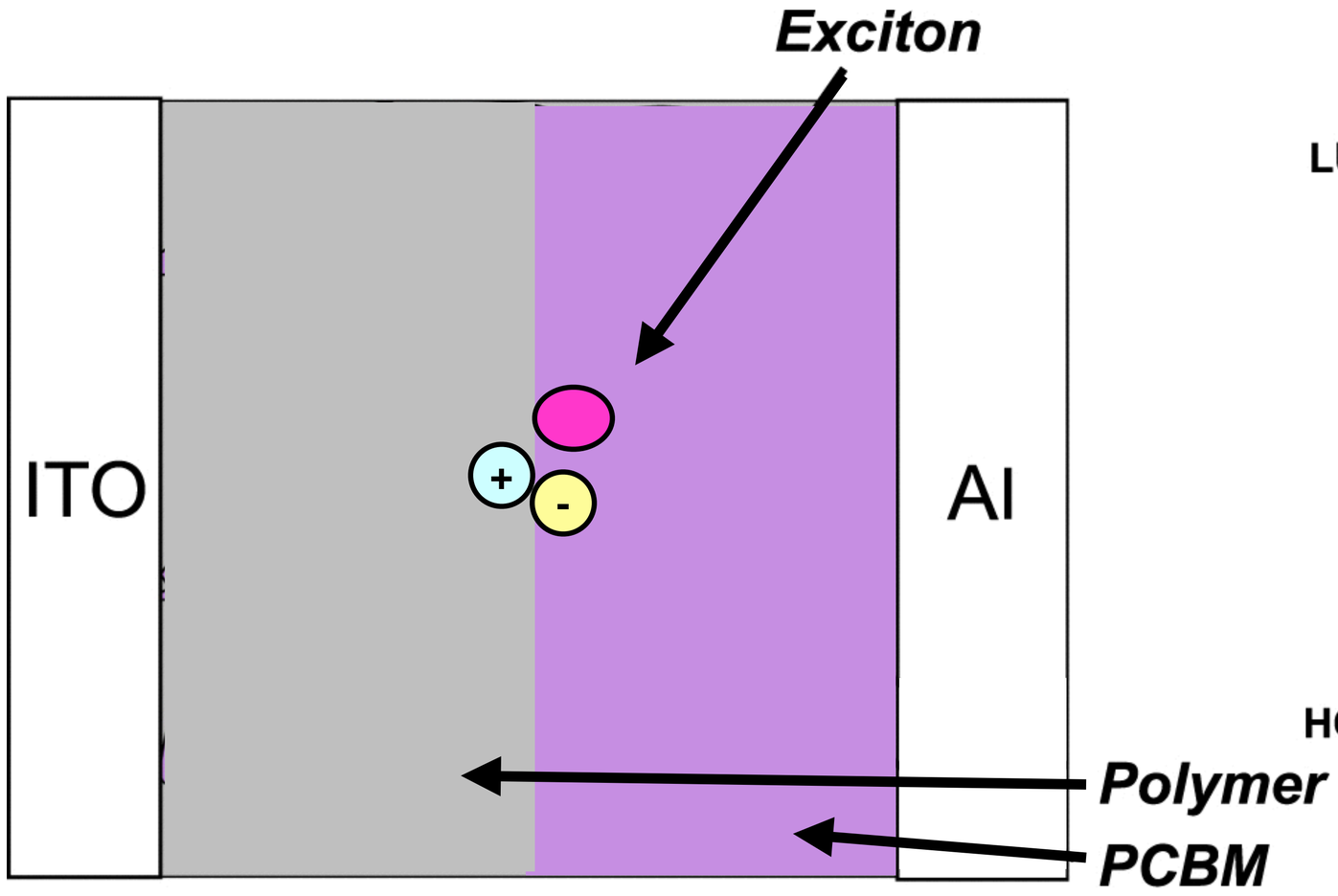
NREL SunShot Report NREL/PR-6A20-62558

Balance of Systems

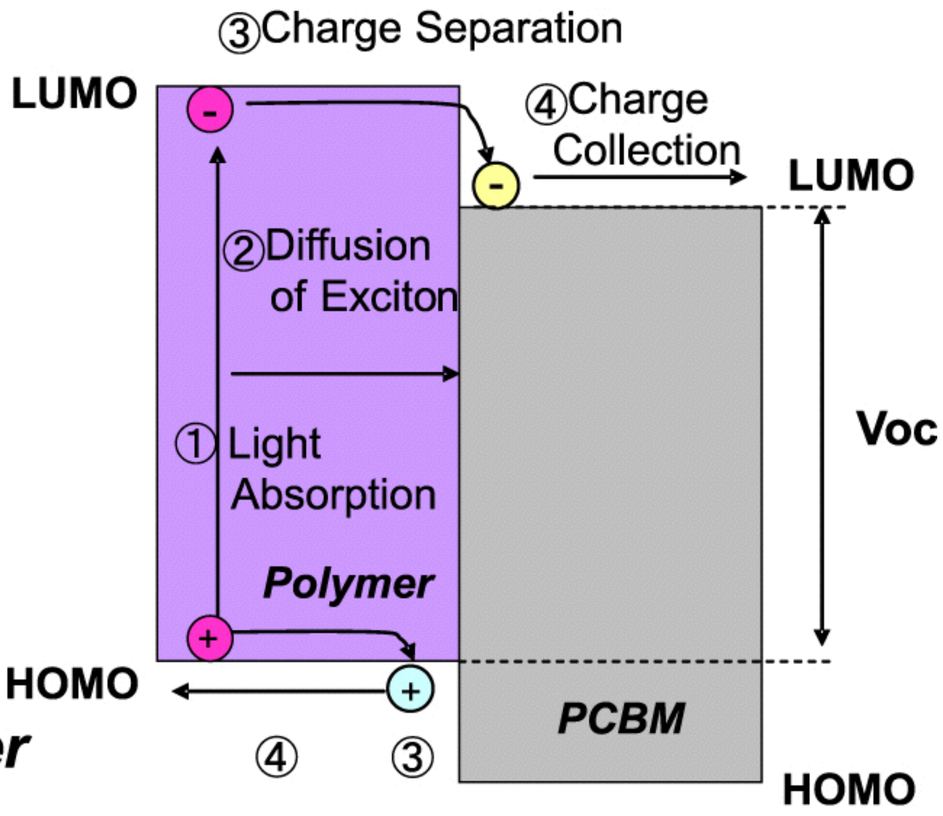


Source: NREL Renewable Energy Project Finance
https://financere.nrel.gov/finance/content/solar-pv-module-price-reductions-balance-system-costs-trends

Bilayer Device

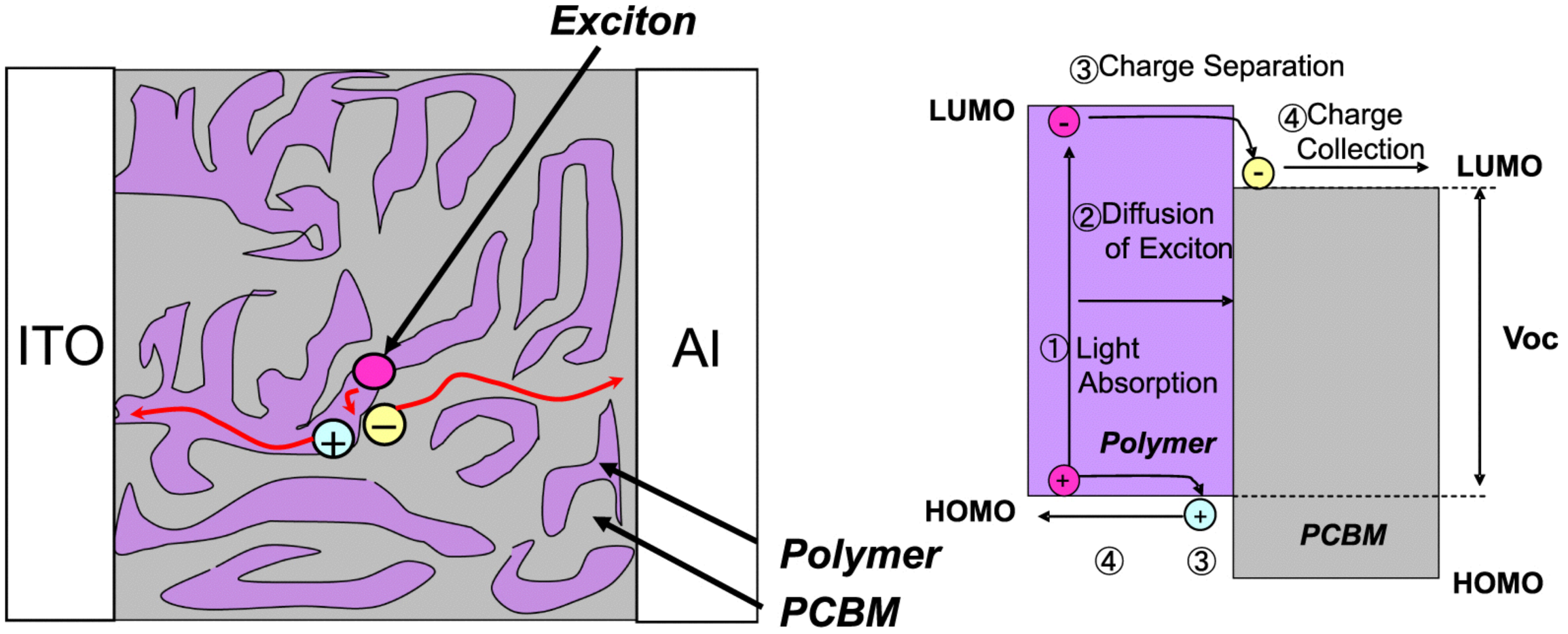


Charge separation mechanism in bulk hetero



adapted from
Sci. Technol. Adv. Mater. 15 (2014) 034203 (15pp)
doi:10.1088/1468-6996/15/3/034203

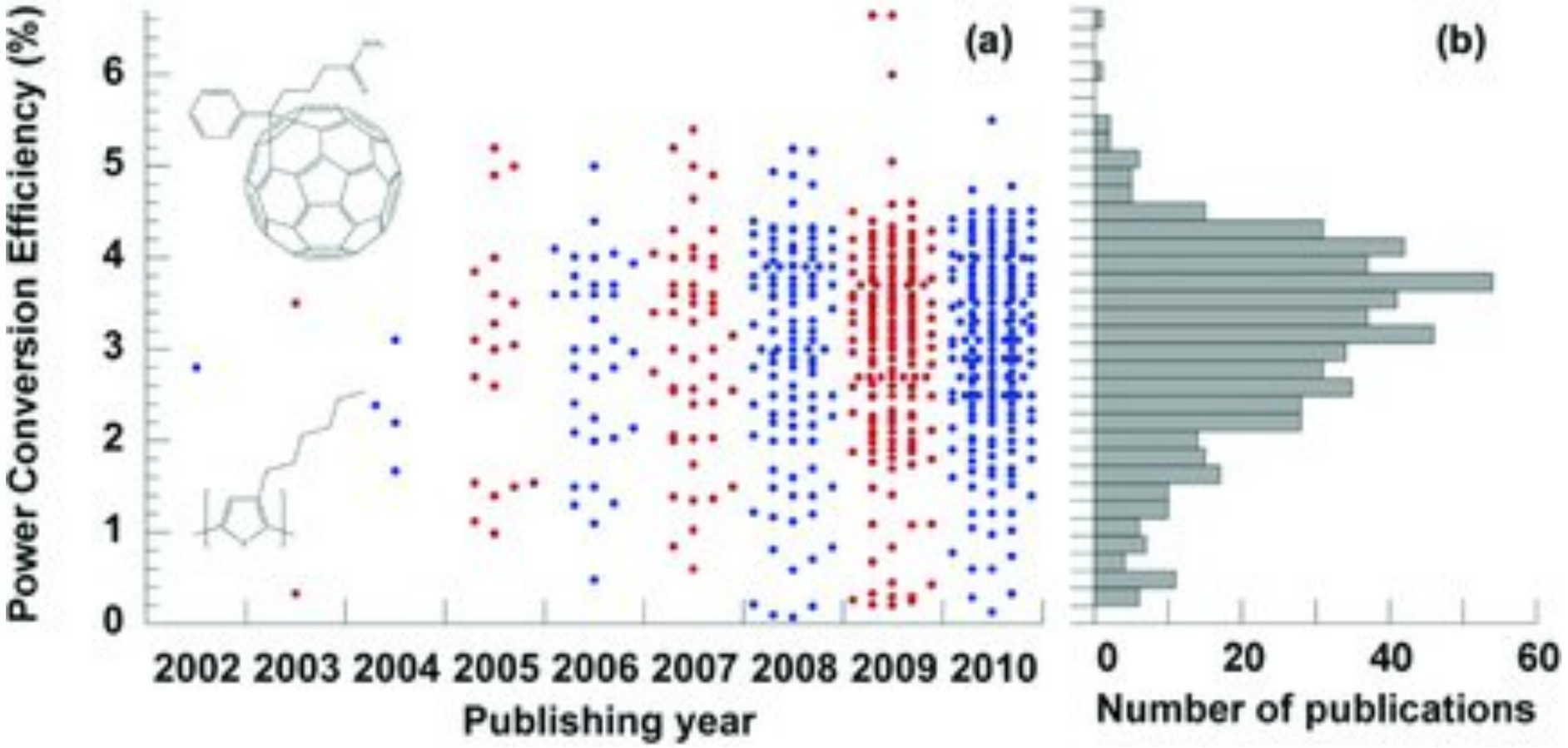
Bulk Heterojunction Device



Charge separation mechanism in bulk hetero

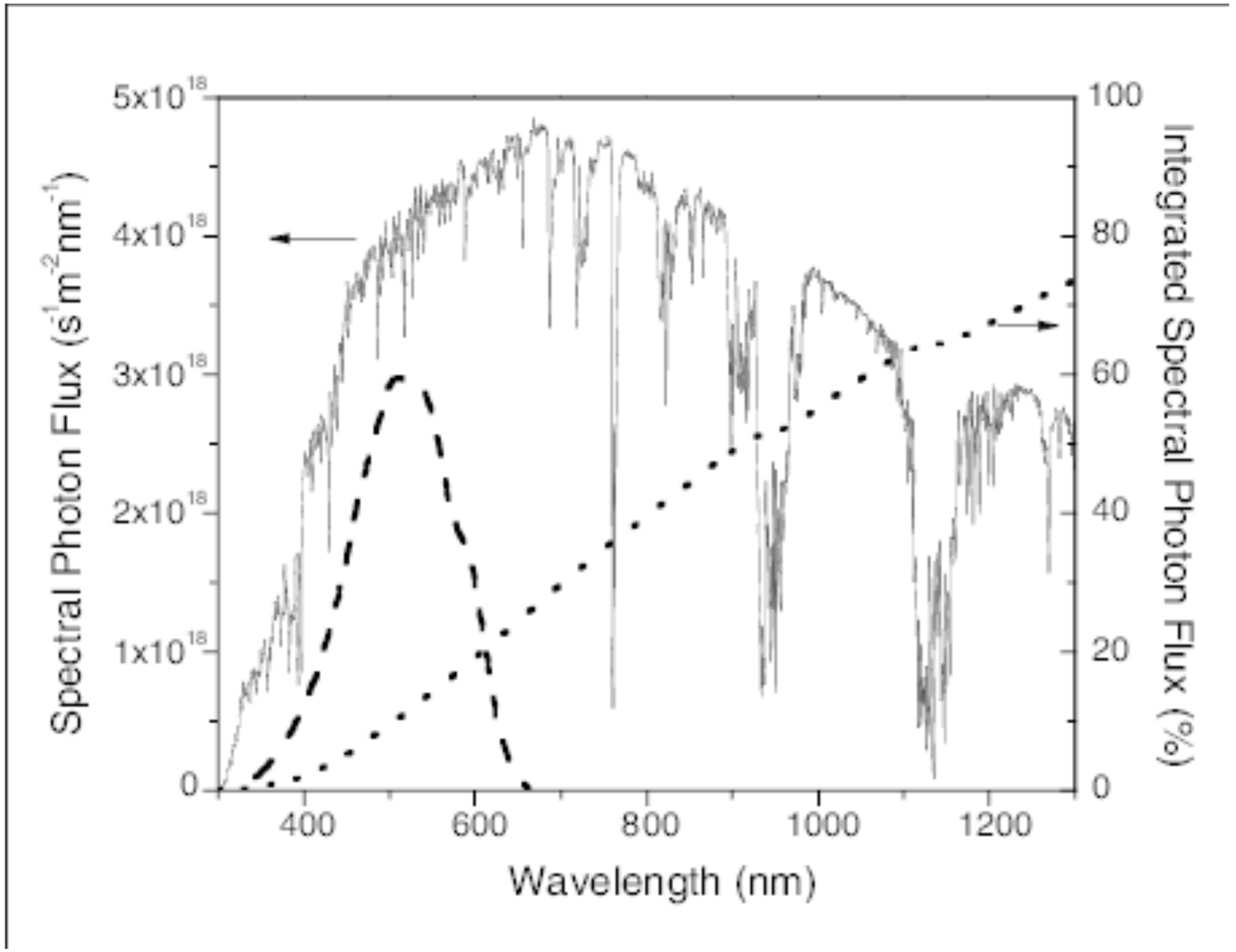
Sci. Technol. Adv. Mater. 15 (2014) 034203 (15pp)
doi:10.1088/1468-6996/15/3/034203

P3HT/PCBM



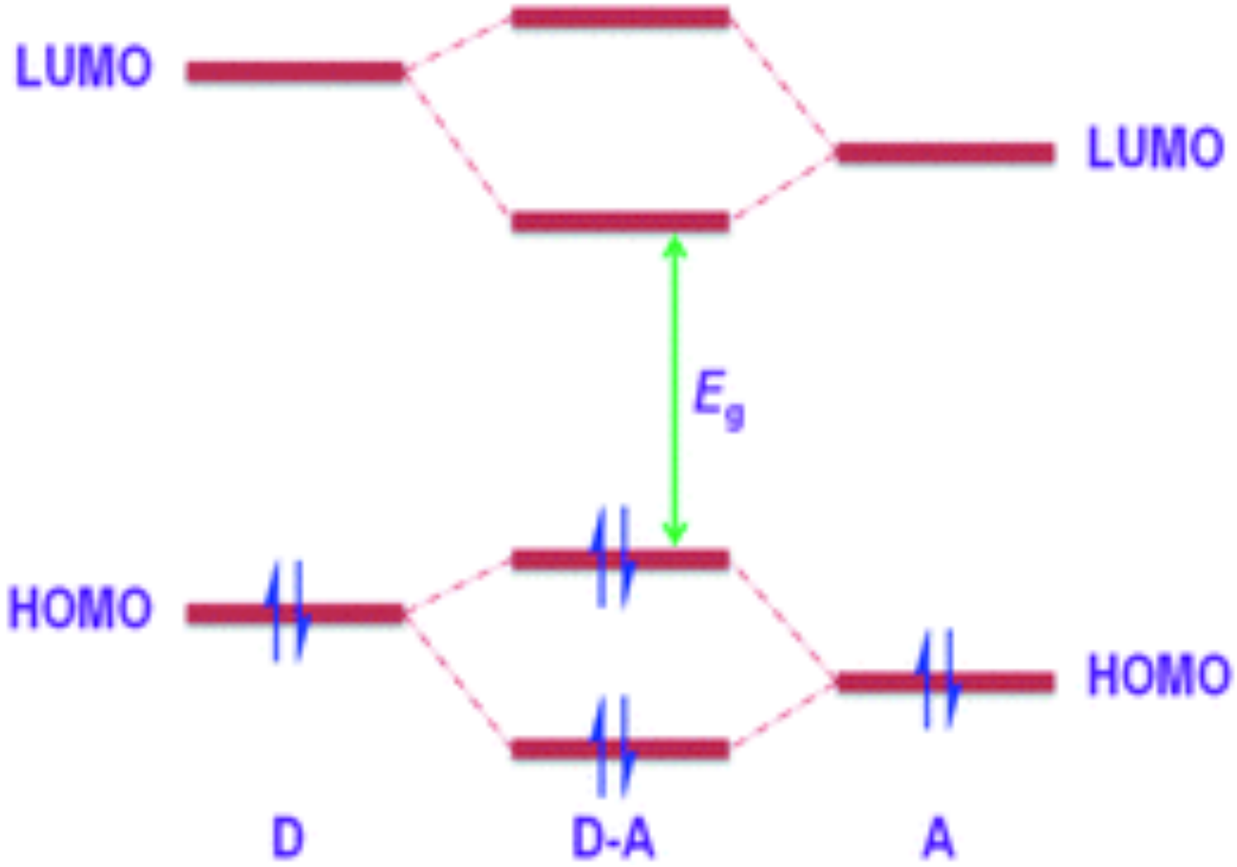
Adv. Mater. **23**(31), 2011, 3597-3602

Better Capturing the Solar Spectrum



Push Pull Polymers

Donor-Acceptor energy levels lower the “band gap” and push the absorption spectrum into the red



Wide-array of push-pull polymers

CHEMICAL REVIEWS

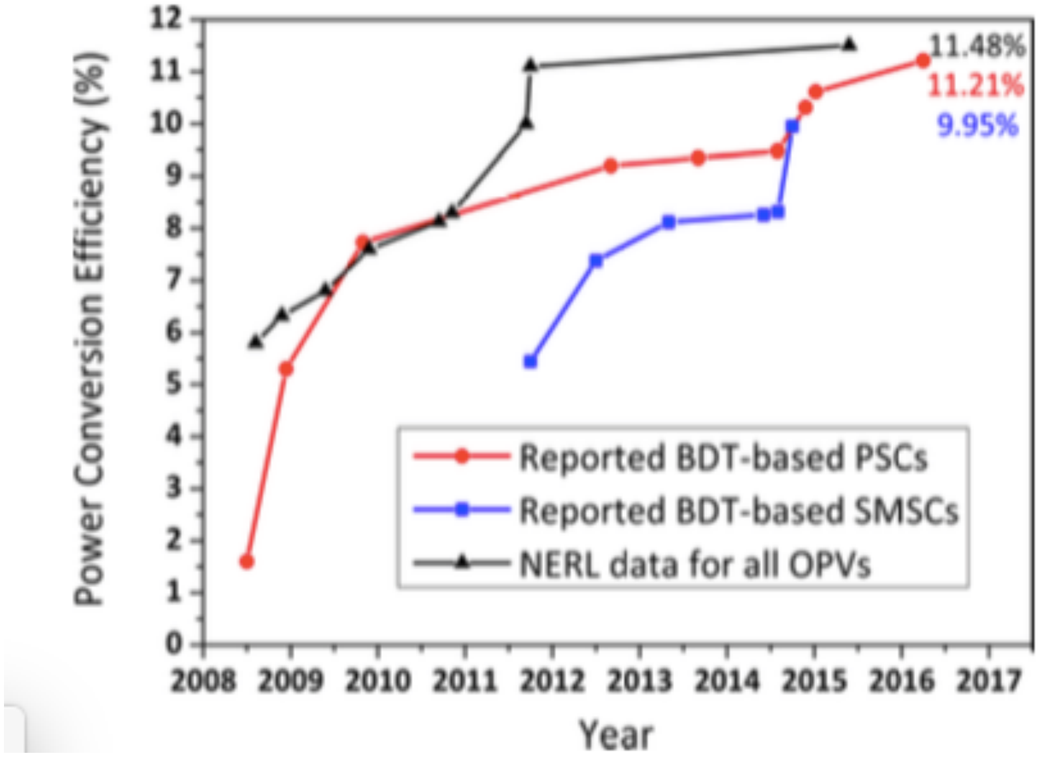
Review

pubs.acs.org/CR

Molecular Design of Benzodithiophene-Based Organic Photovoltaic Materials

Huifeng Yao,[†,‡] Long Ye,[†,‡] Hao Zhang,[†,‡] Sunsun Li,[†,‡] Shaoqing Zhang,[†] and Jianhui Hou*[,†,‡]

Review of more than 300 different donor polymers with OPV performance



All hydrocarbon processed OPV

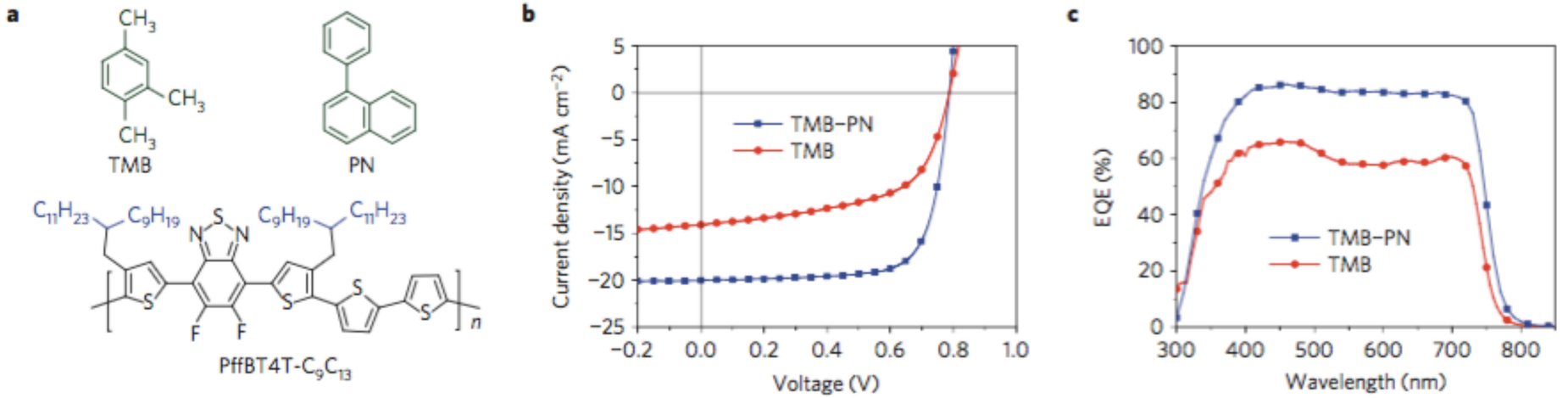
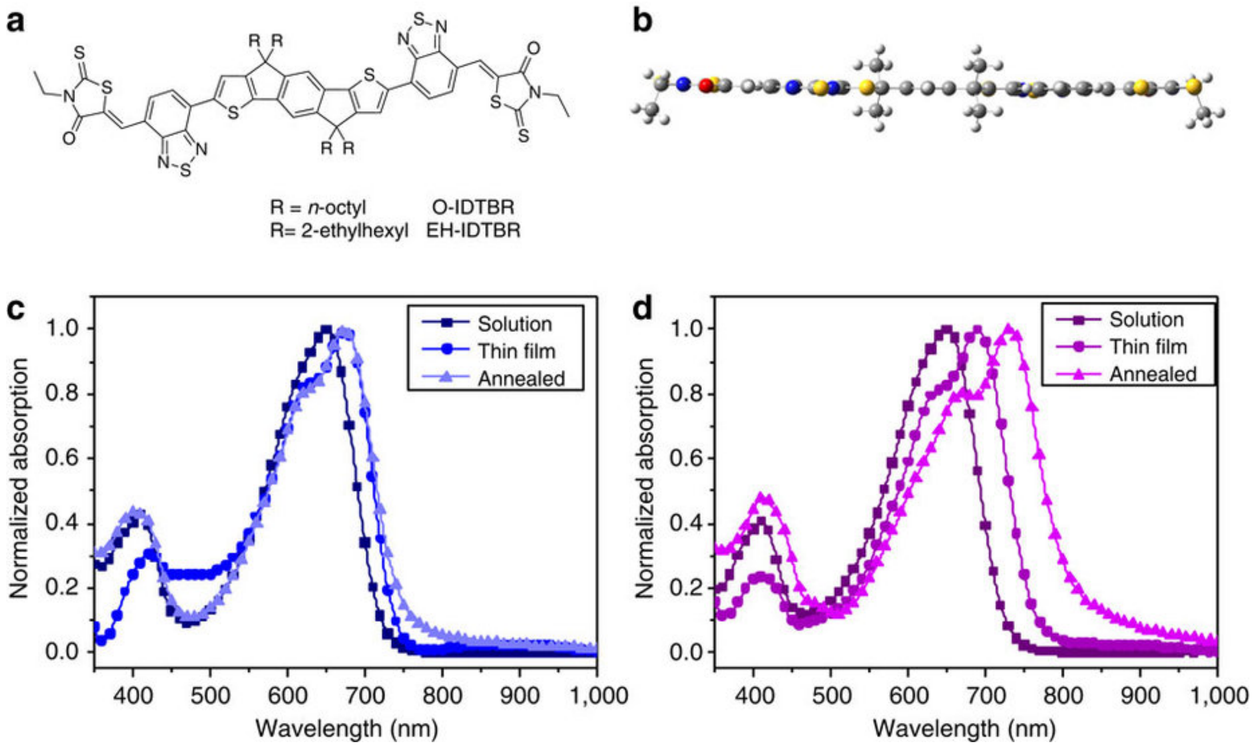


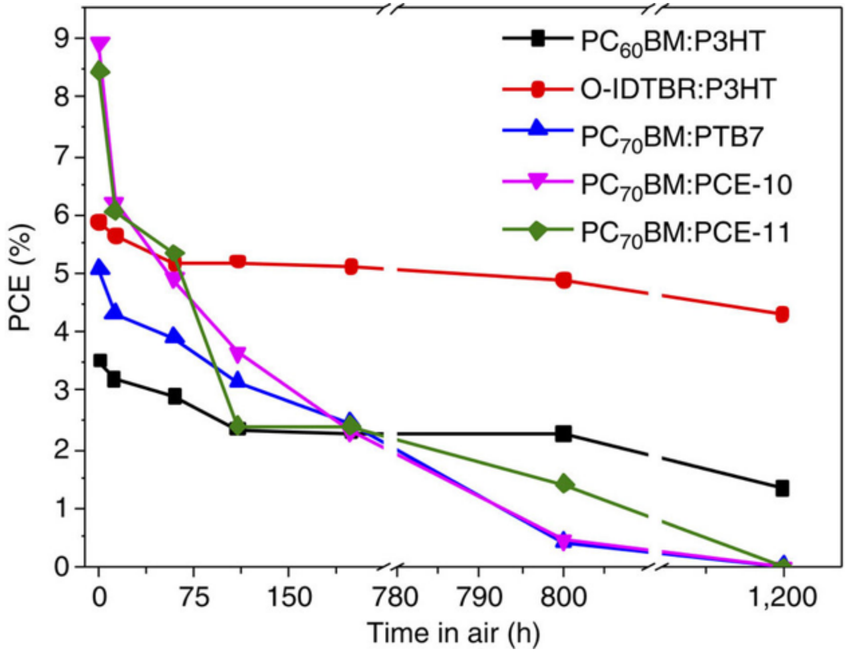
Table 1 | Solar cell and RSoXS characteristics of PffBT4T-C_9C_{13}:$PC_{71}BM$ processed from different solvents.

	V_{OC} (mV)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	Domain spacing (nm)	Domain purity	Anisotropy parameter
TMB-PN	784 ± 4	19.8 ± 0.4	73 ± 1	11.3 ± 0.1 (11.7)	38	1.00	0.26
TMB	773 ± 14	13.2 ± 1.4	55 ± 4	5.6 ± 0.5 (6.4)	56	0.74	0.29
CB-DIO	767 ± 6	18.3 ± 0.5	66 ± 2	9.3 ± 0.1 (9.6)	40	0.90	0.14

The values in the parentheses are from the best devices. The statistics are from 50 devices.

A comeback for P3HT?





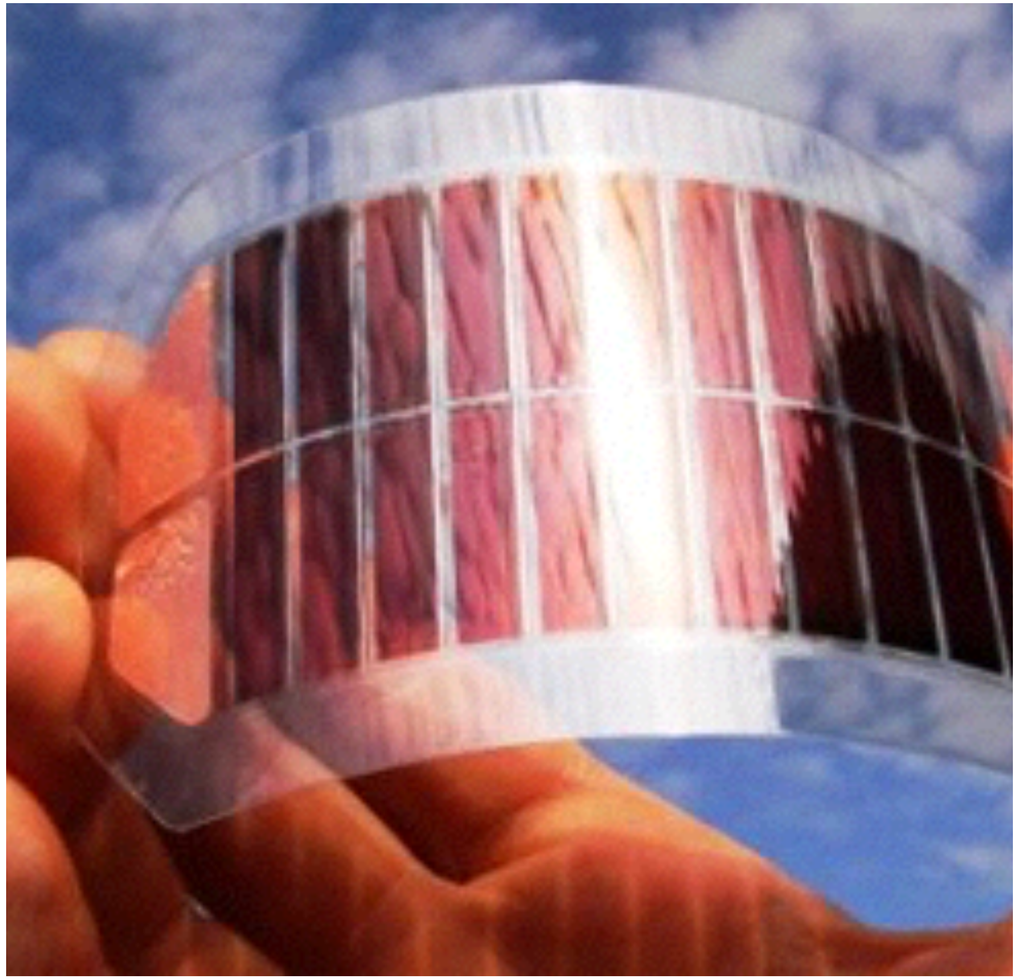
Replace fullerenes with small molecule acceptors

Nature Communications **7**, Article number: 11585 (2016)
doi:10.1038/ncomms11585

Problems that remain

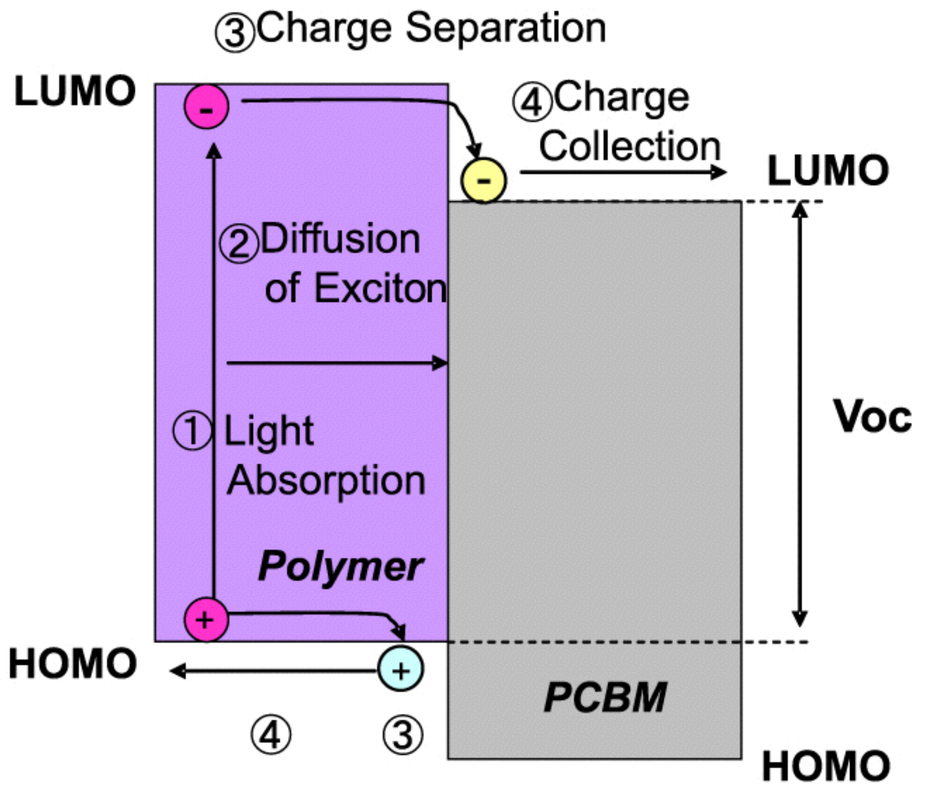
- Efficiencies still too low
- Stability needs to be improved
- Morphology poorly controlled

- **Fundamental understanding**

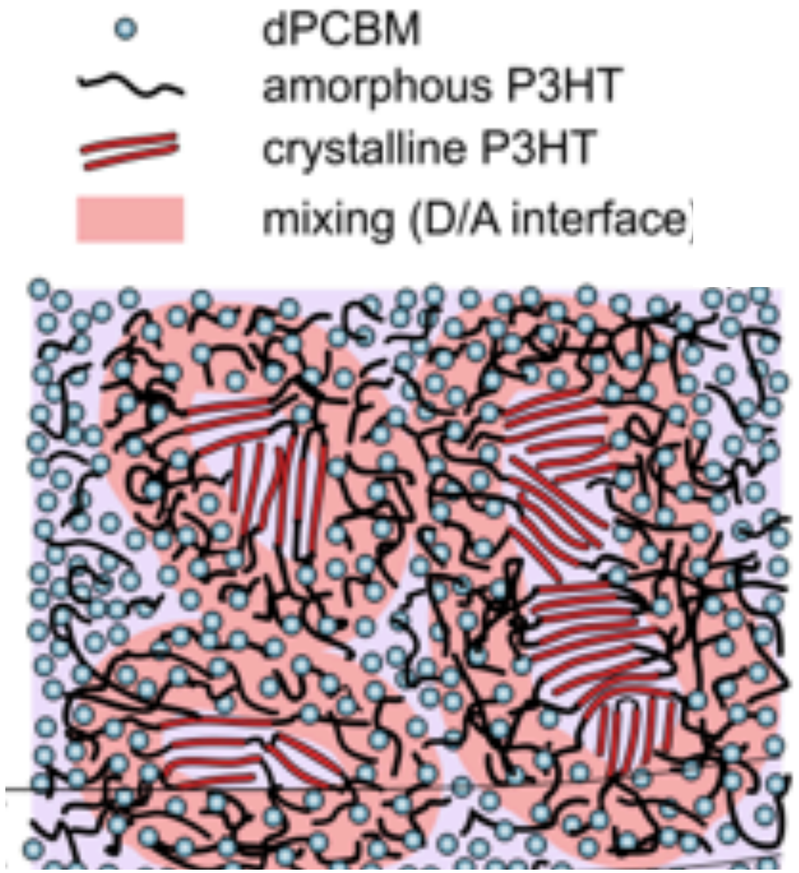


Is this picture correct?

- 1. Light Absorption
- 2. Exciton Diffusion
- 3. Charge Separation
- 4. Charge Collection



Complex Morphology



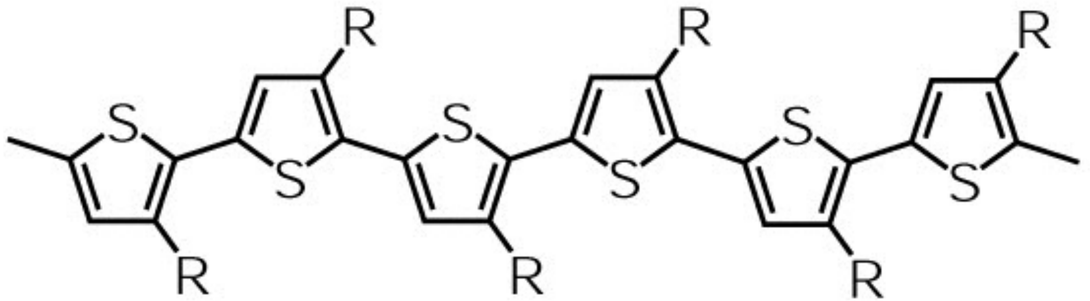
Amorphous Polymer
Crystalline Polymer
Intermixed polymer/fullerene
Amorphous fullerene
Crystalline fullerene
…..

Complex Electronic Structure

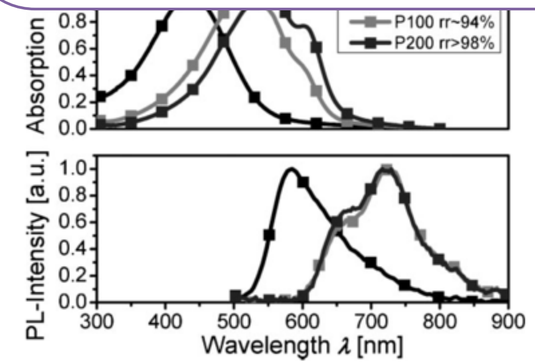
Solvent quality solution

Solvent spin-casting

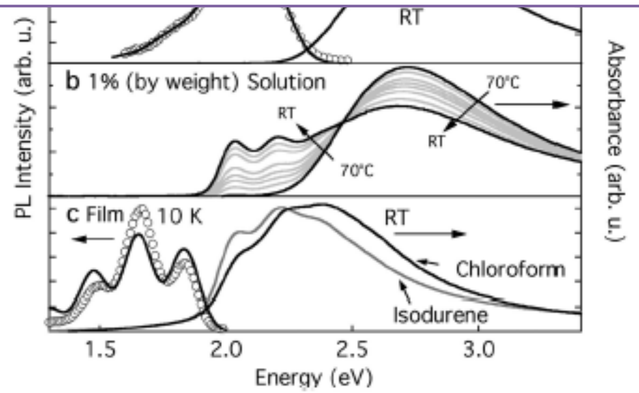
Poly-3-Hexyl Thiophene (P3HT)



sting…

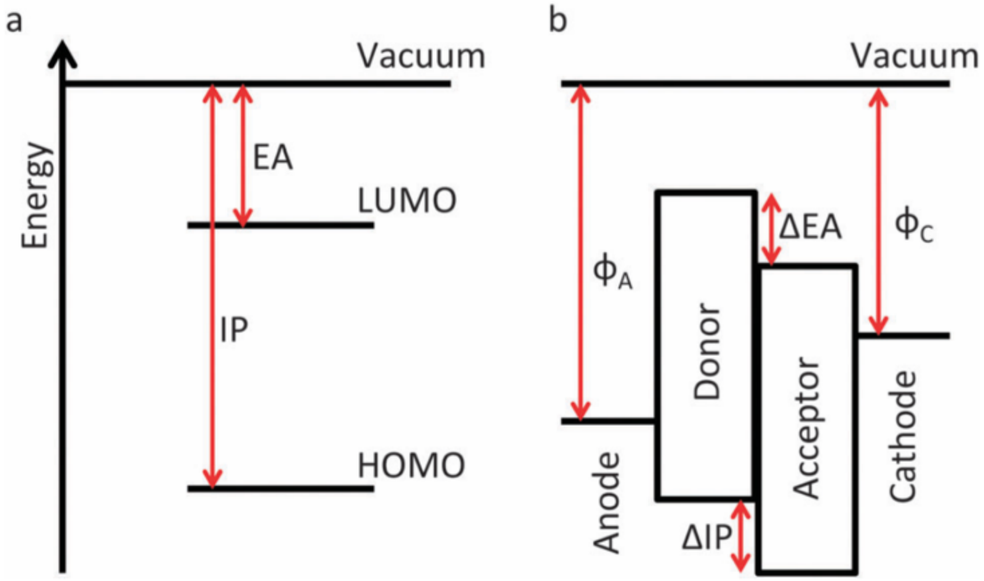


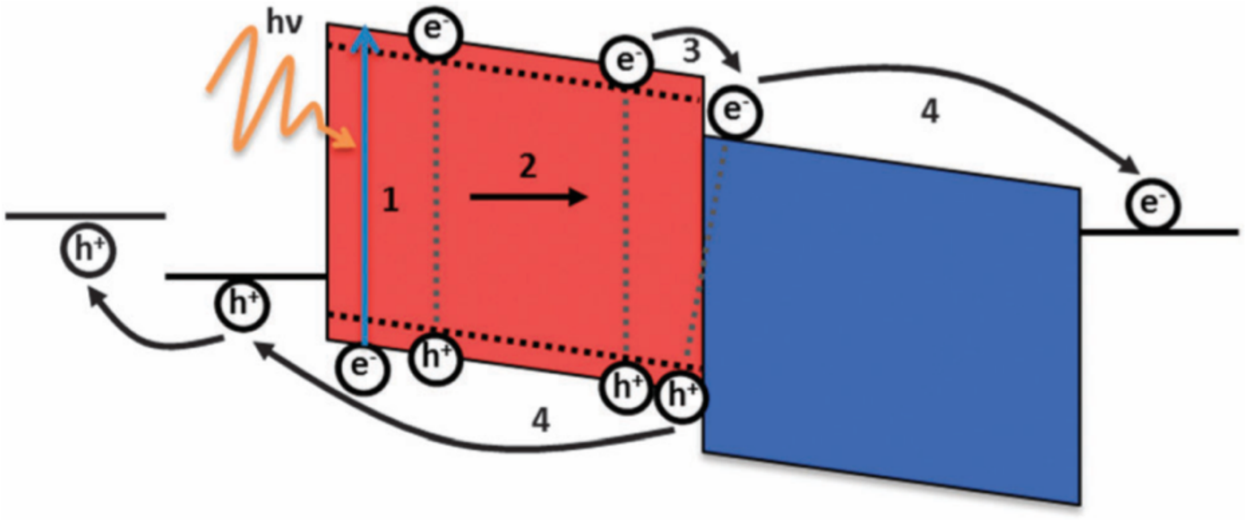
Mauer et.al. Adv. Funct. Mater. 2010, 20, 2085



Jenny Clark et al., Phys. Rev. Lett. 98, 206406 (2007)

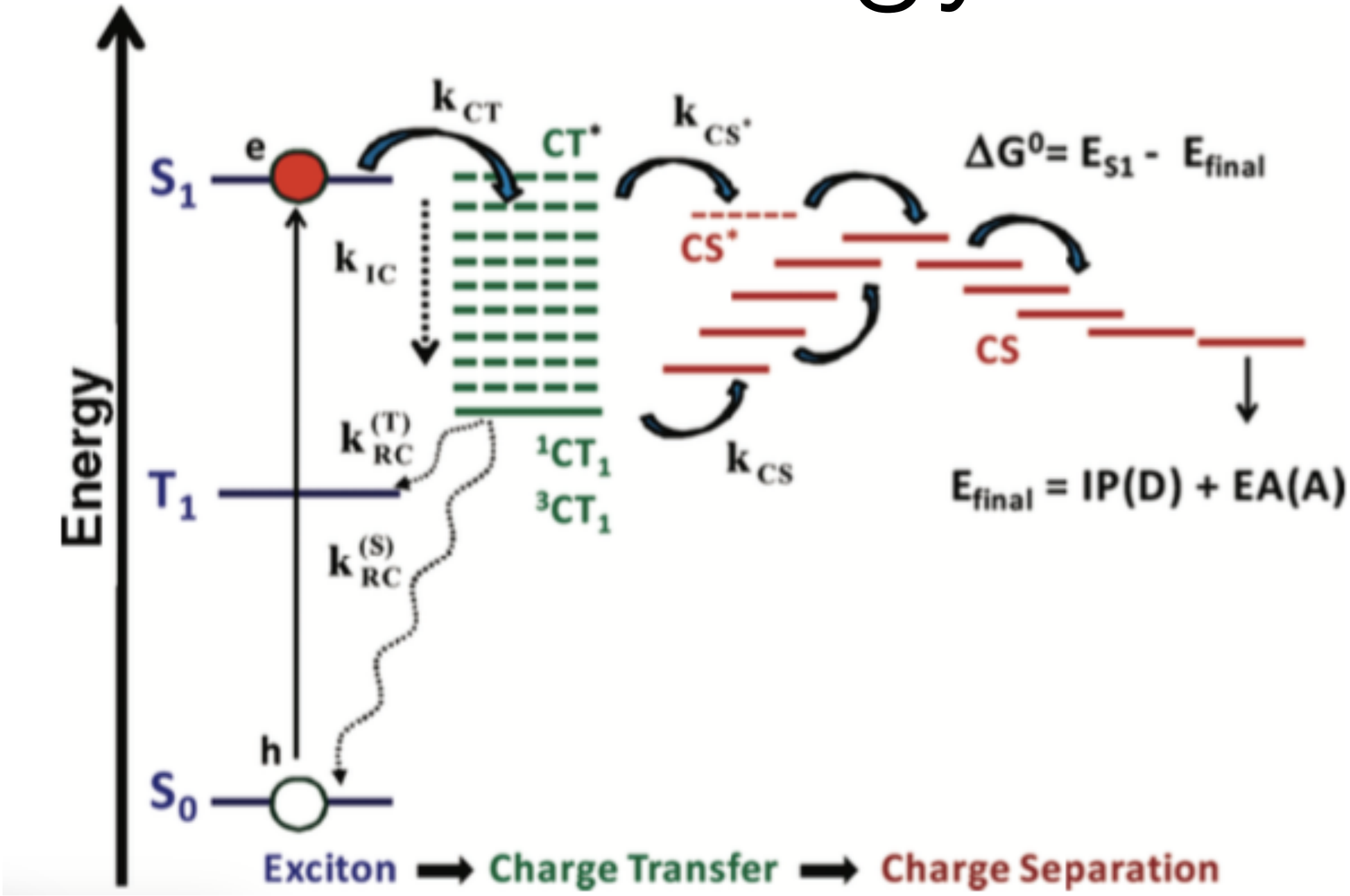
States vs Energy Levels





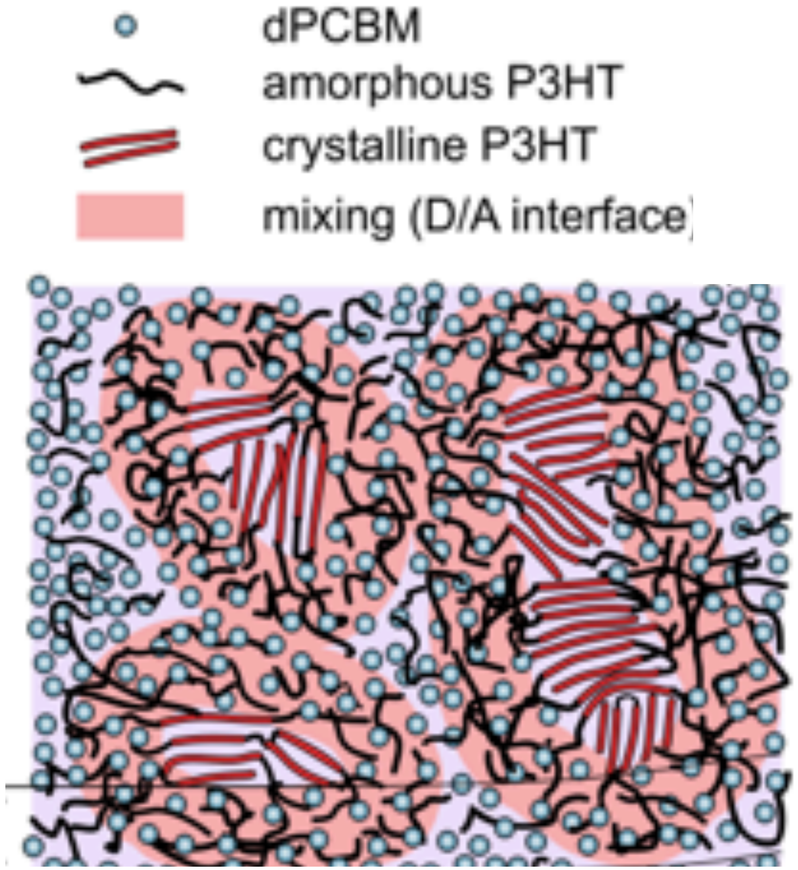
Chem. Soc. Rev., 2015, 44, 78
DOI: 10.1039/c4cs00227j

States vs Energy Levels



Molecular Understanding of Organic Solar Cells, Brédas et al., Acc. Chem. Res. **42**, 2009, 1691-1699

Complex Morphology

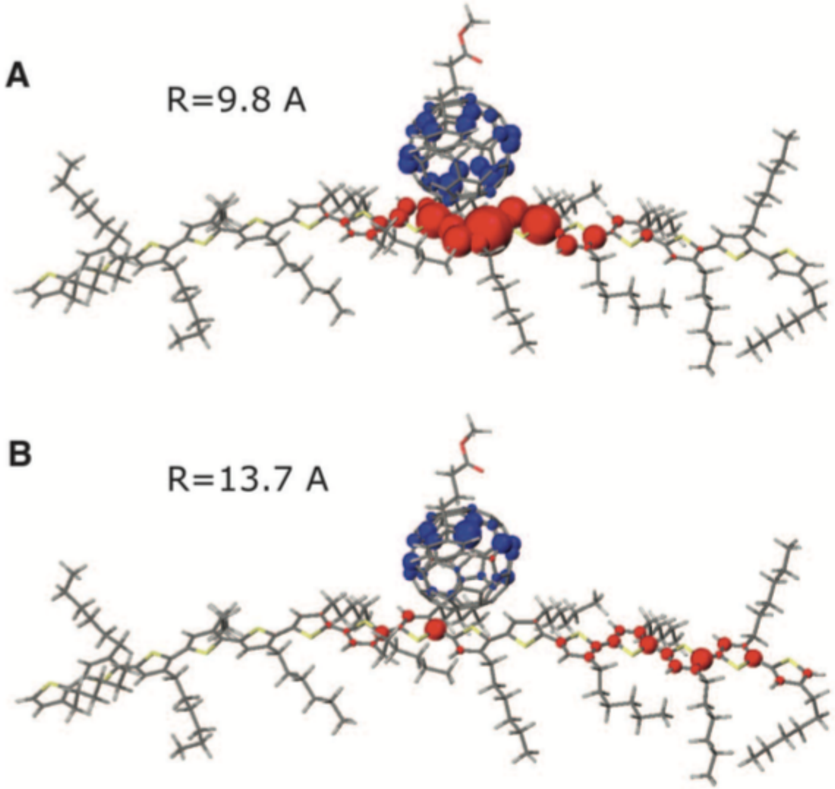


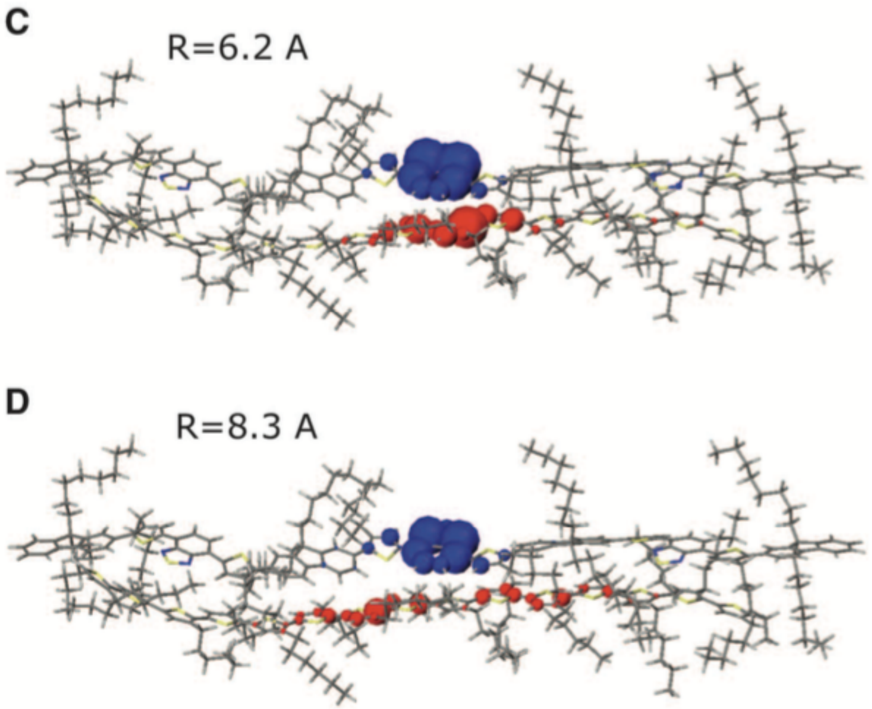
Need to think about potential for delocalization of electronic states in aggregated domains

Can we control the microstructure?

What structure do we even want?

Delocalized States





Lowest CT State

delocalized
CT State

P3HT/PCBM

P3HT/F8BT

Bakulin et al, DOI: 10.1126/science.1217745

Delocalized States

Delocalized states can greatly affect performance

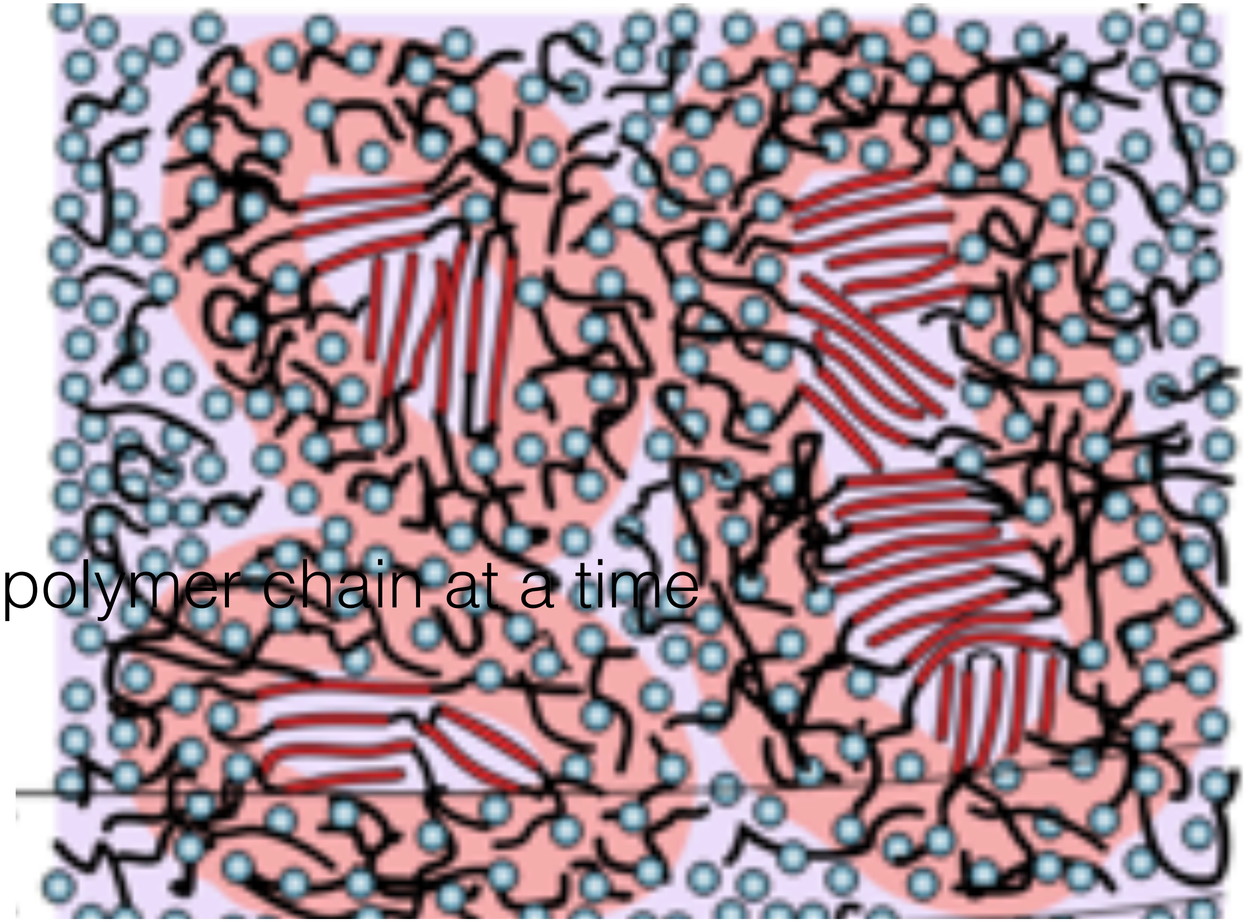
May be critical for charge separation
- allow for physical separation of charges
- greatly increases DOS

Enhance Exciton Diffusion

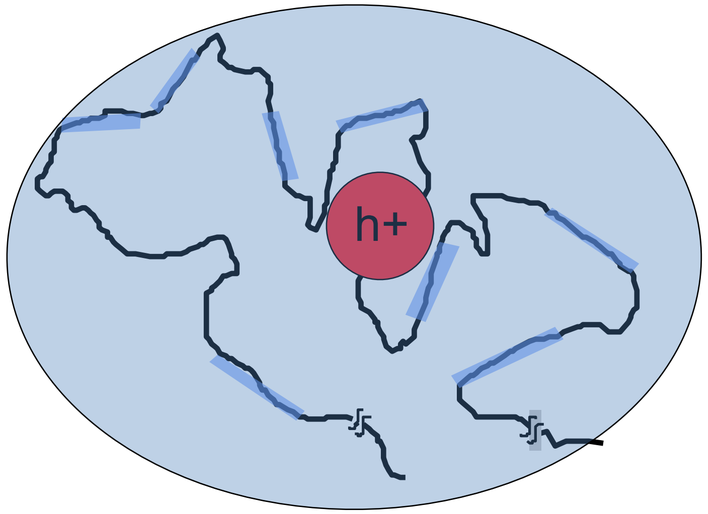
Enhance Charge Transport

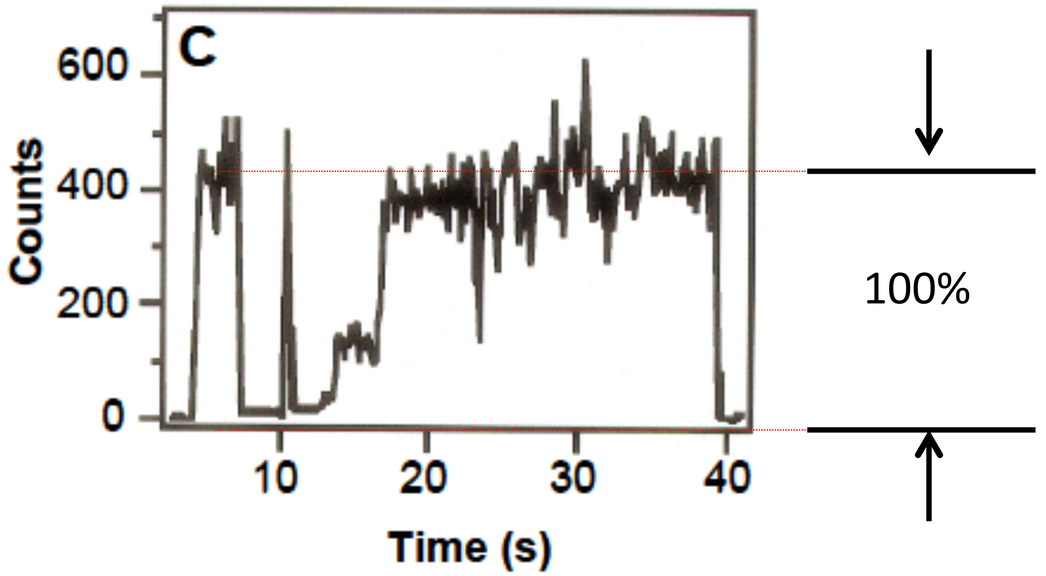
Strip Everything Away

Look at one polymer chain at a time



Blinking in Single Chains

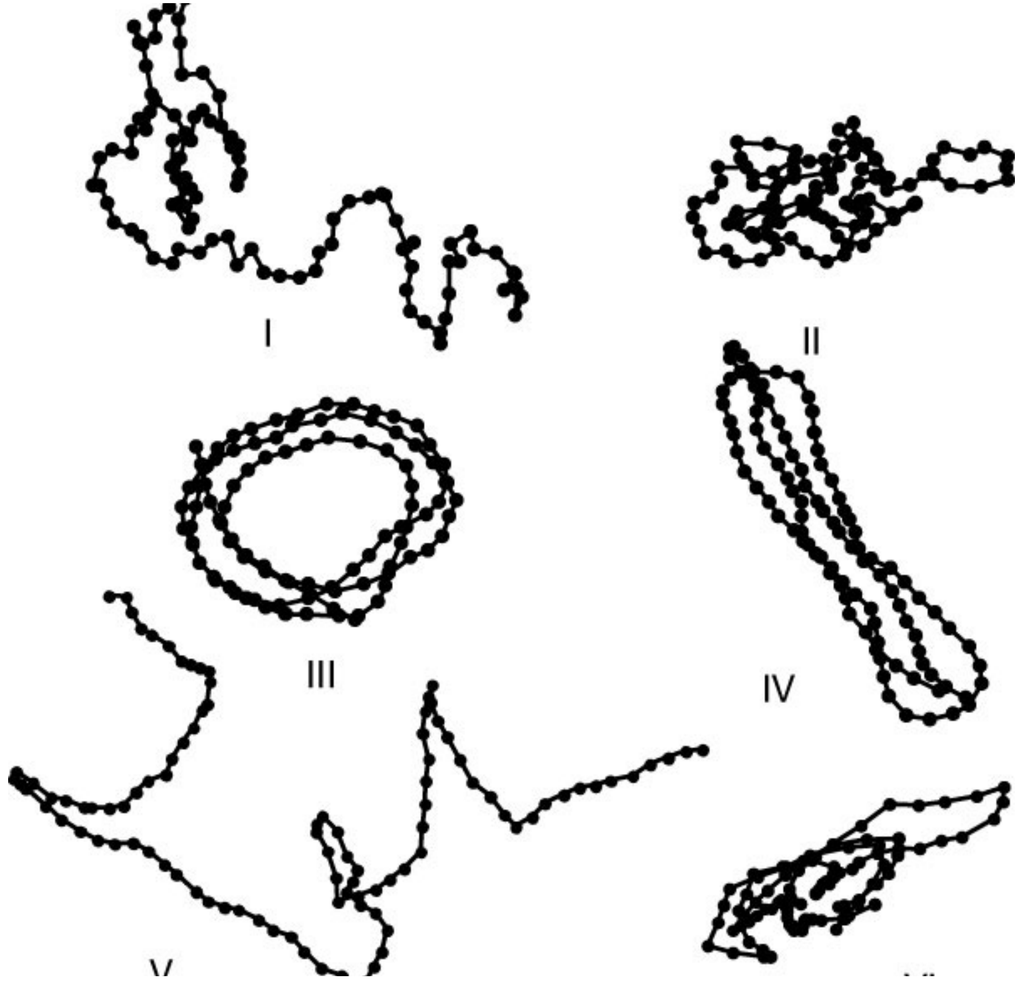




Science **277**, 1074 (1997)

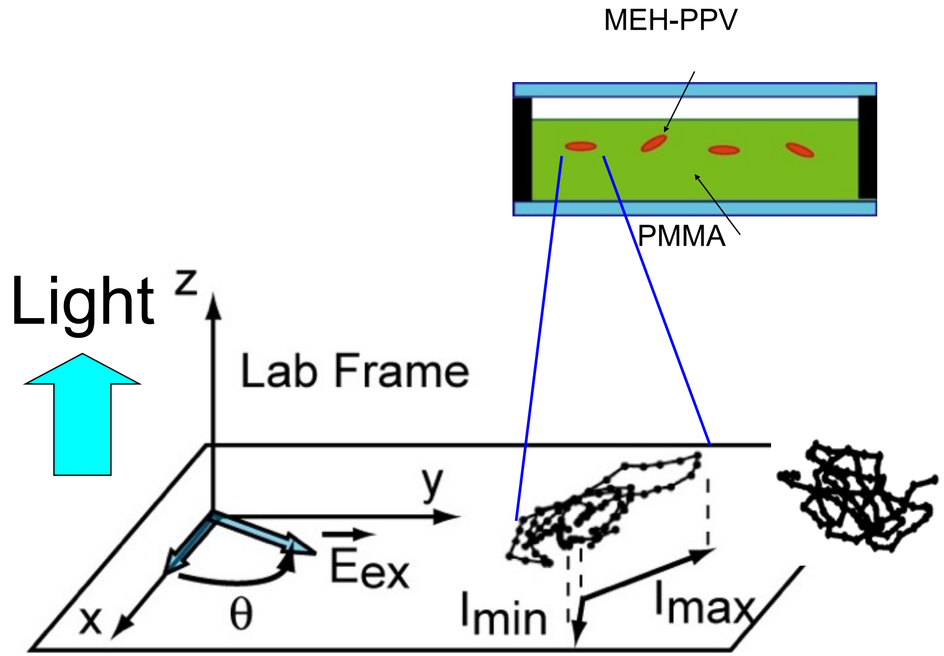
Chain Conformation

What is the conformation of the individual chains?

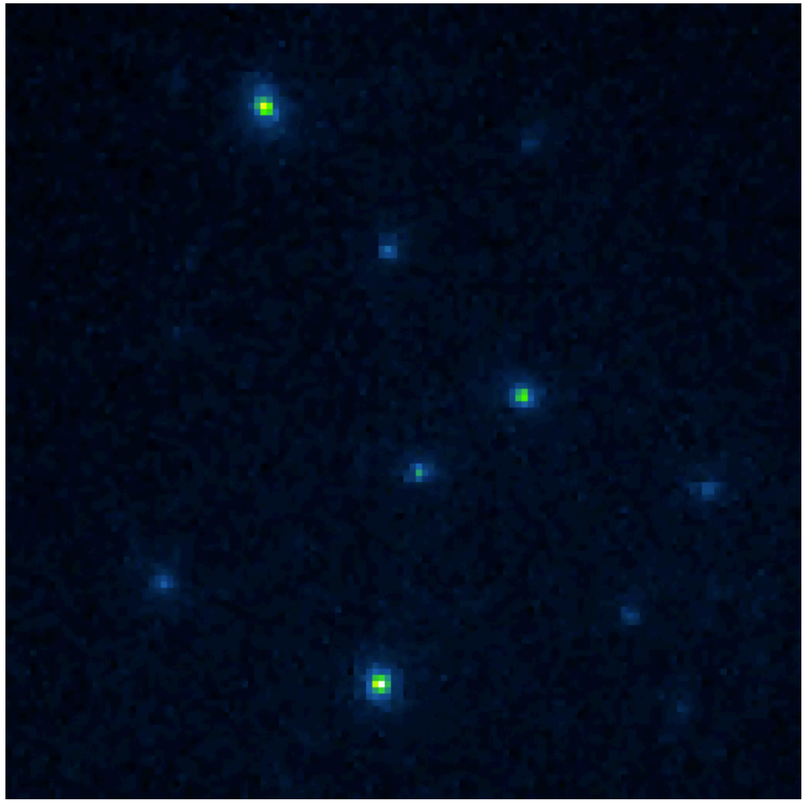


Rossky and Barbara
Nature 405, 1030-1033 (2000)

Probing single chain conformation



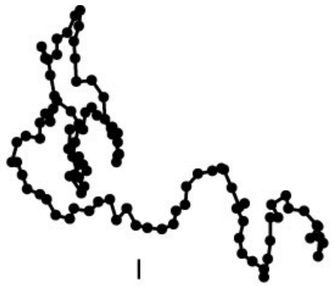
rotate linearly polarized excitation light

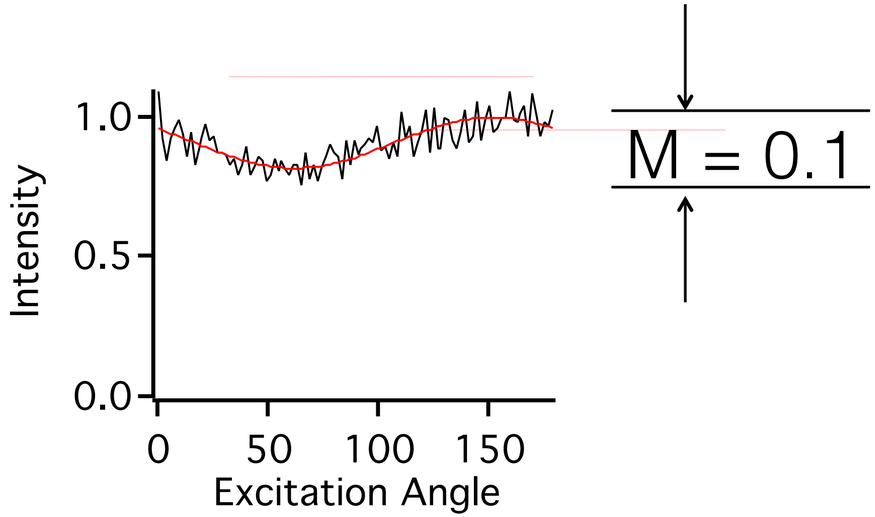


Modulation depth (M) represents the morphological order

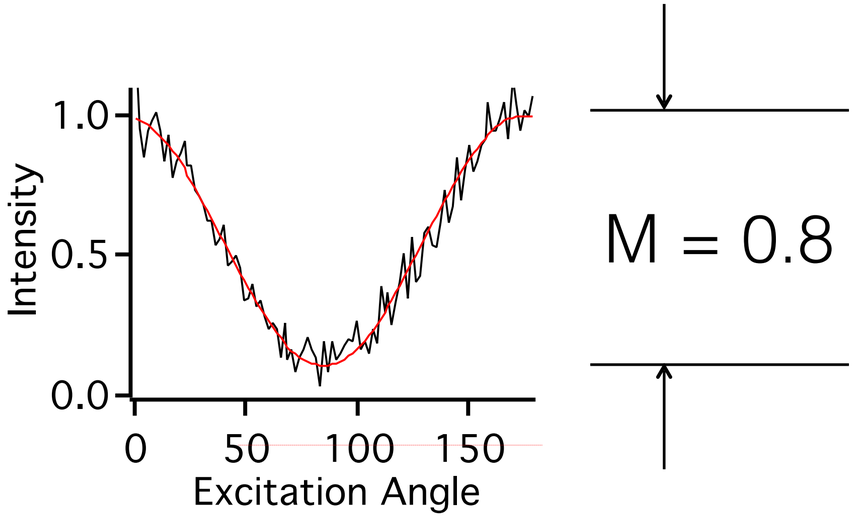
Chain Conformations

Isotropic

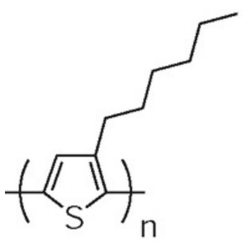




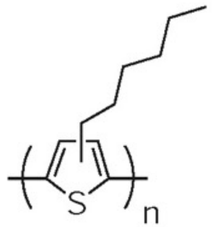
Anisotropic



Look at single chains for a variety of thiophenes

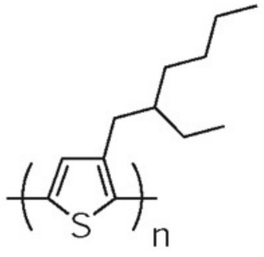


rr-P3HT

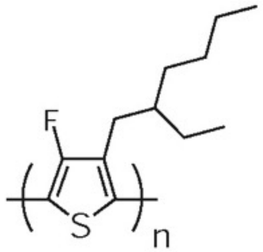


rra-P3HT

Arrangement of side-chain

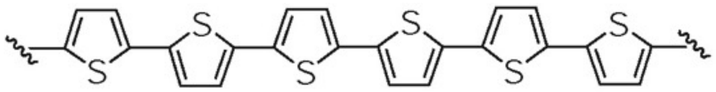


P3EHT

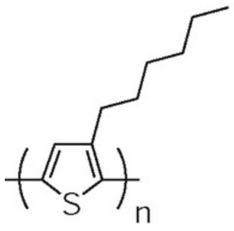


F-P3EHT

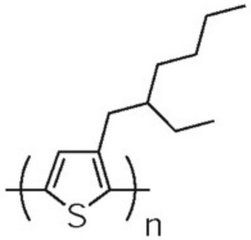
Backbone



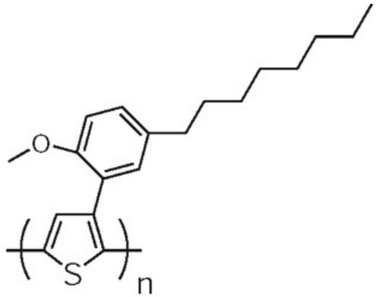
Size of side-chain



P3HT



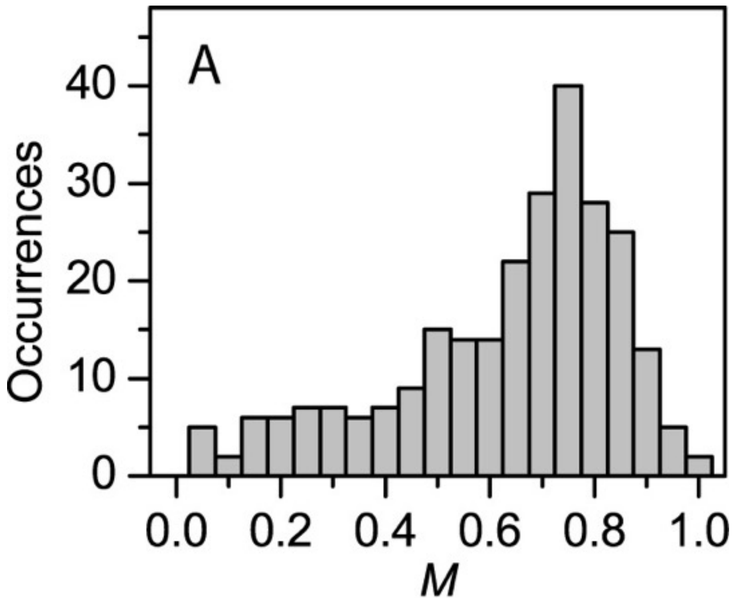
P3EHT



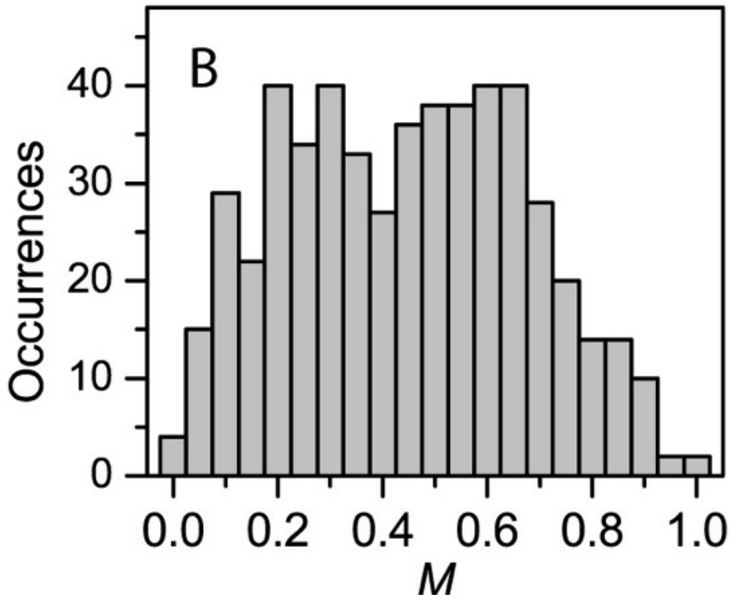
POMeOPT

Effect of regioregularity on P3HT

rr-P3HT (Mn: 148 kDa, PDI: 1.35, HT-HT 97%)



rra-P3HT (Mn: 191 kDa, PDI: 1.33 HT-HT 64%)



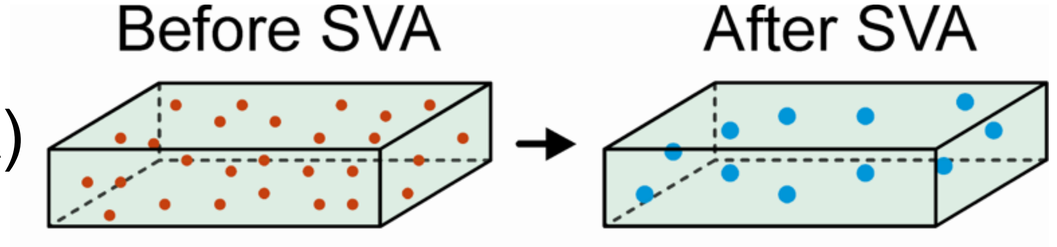
Most of rr-P3HT chains fold into highly ordered conformation while rra-P3HT assumes a wide variety of conformations from isotropic to even anisotropic.

Side-chains do affect P3HT conformation even at single chain level

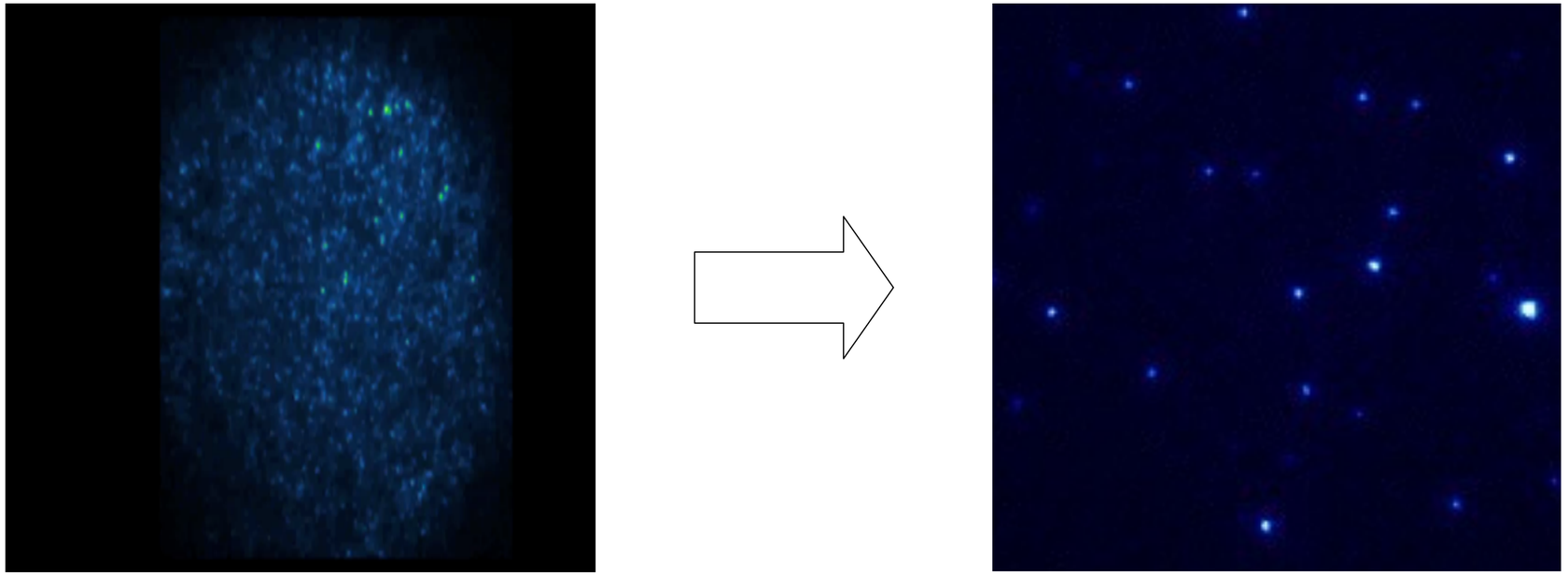
Adachi et al, J. Phys. Chem. Letters, 2, 1400-1404 (2011)

Forming aggregates with solvent vapor annealing

(MEH-PVV in PMMA)



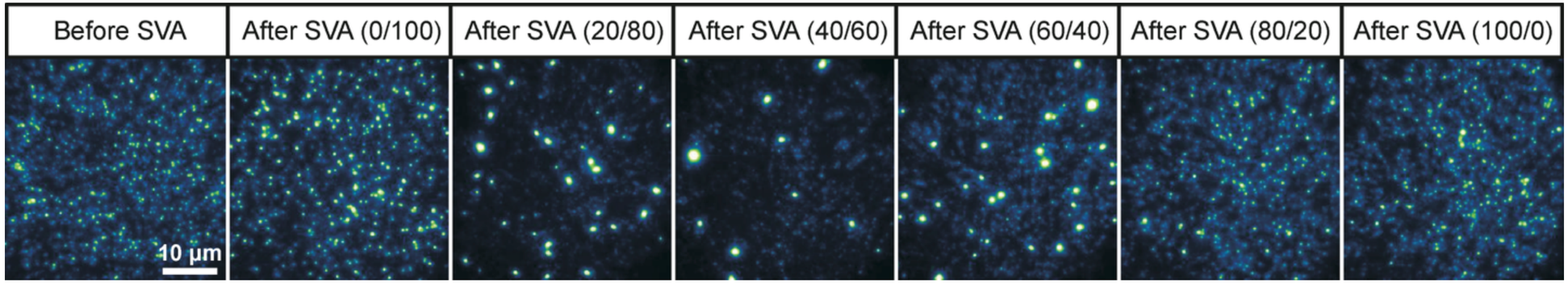
Careful choice of solvent makes molecules aggregate slowly
Solvent has to be good solvent for host matrix (PMMA) and bad solvent for MEH-PPV



Vogelsang, et al, Nature Materials, 10, 942–946 (2011).

Solvent Vapor Annealing to Control Size

Anneal with a mixture of good/bad solvent to change the saturation solubility



Increasing Size → Full solublbe

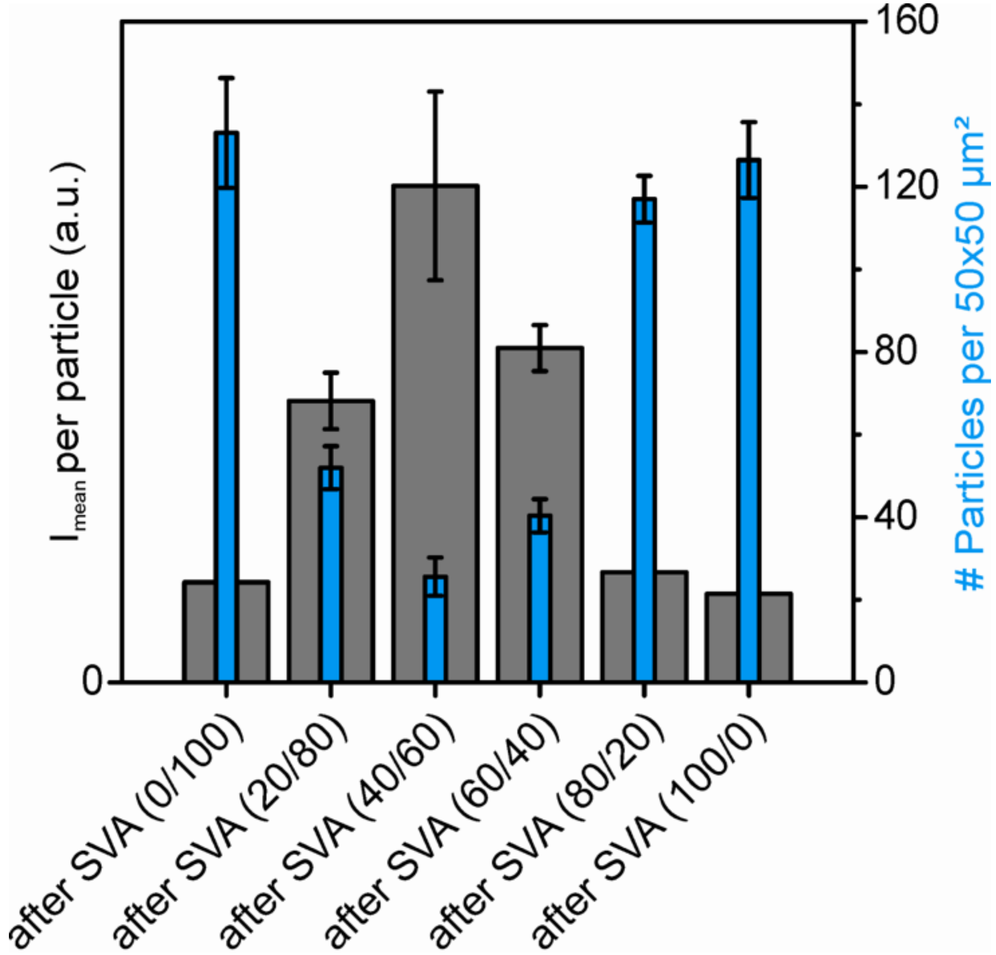
$$R_C = \left(\frac{2\sigma}{kT}\right) v \frac{C_\infty}{C - C_\infty} \quad \text{for} \quad C > C_\infty$$

Nature Materials, 10, 942–946 (2011).

Self-assembly of aggregates via SVA

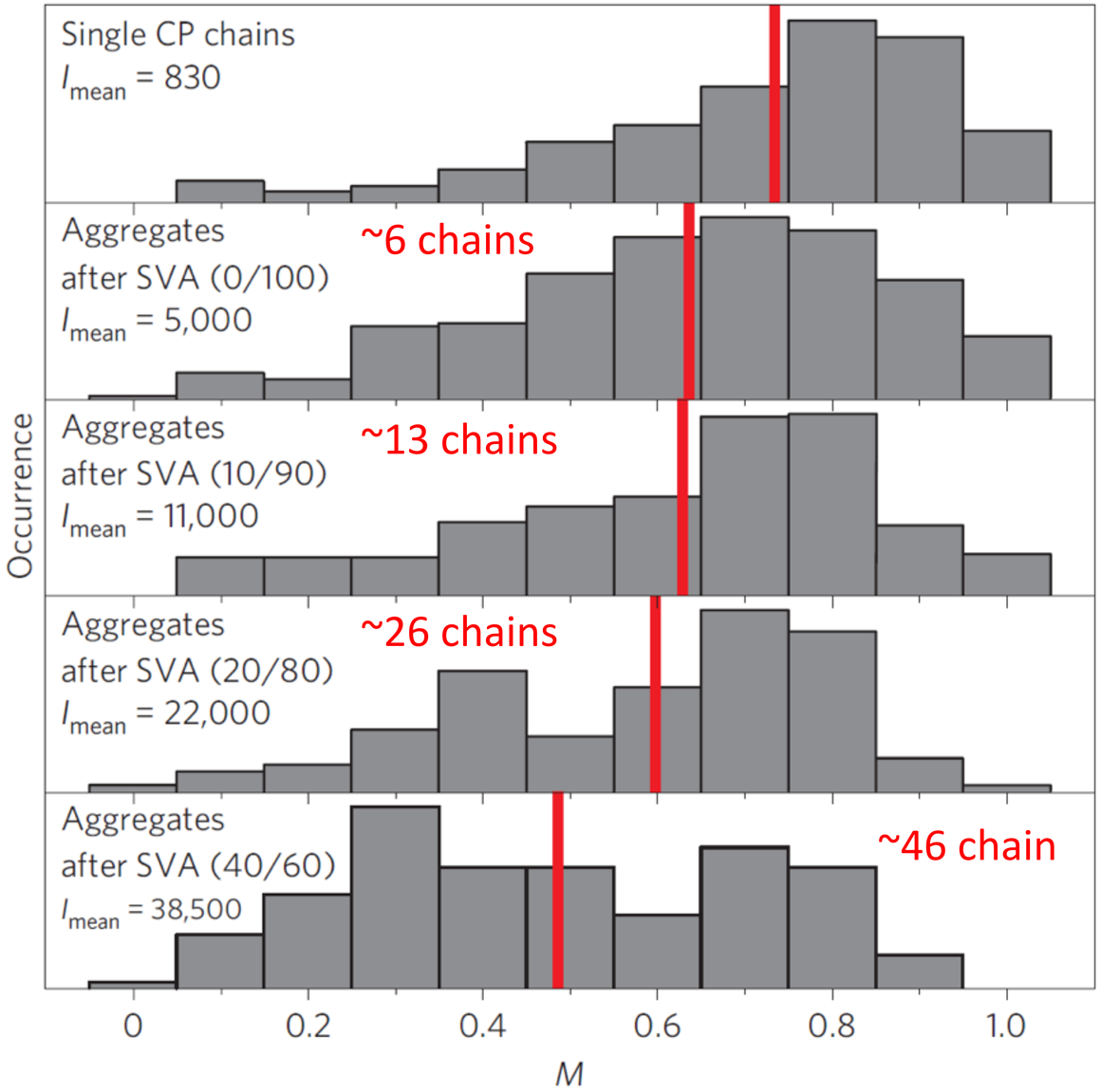
Aggregates are still diffraction limited!

⇒ Particle analysis with an intensity threshold above single CP chains



- stable aggregates up to 40/60 chloroform/acetone
- anti-correlation between # particles and brightness

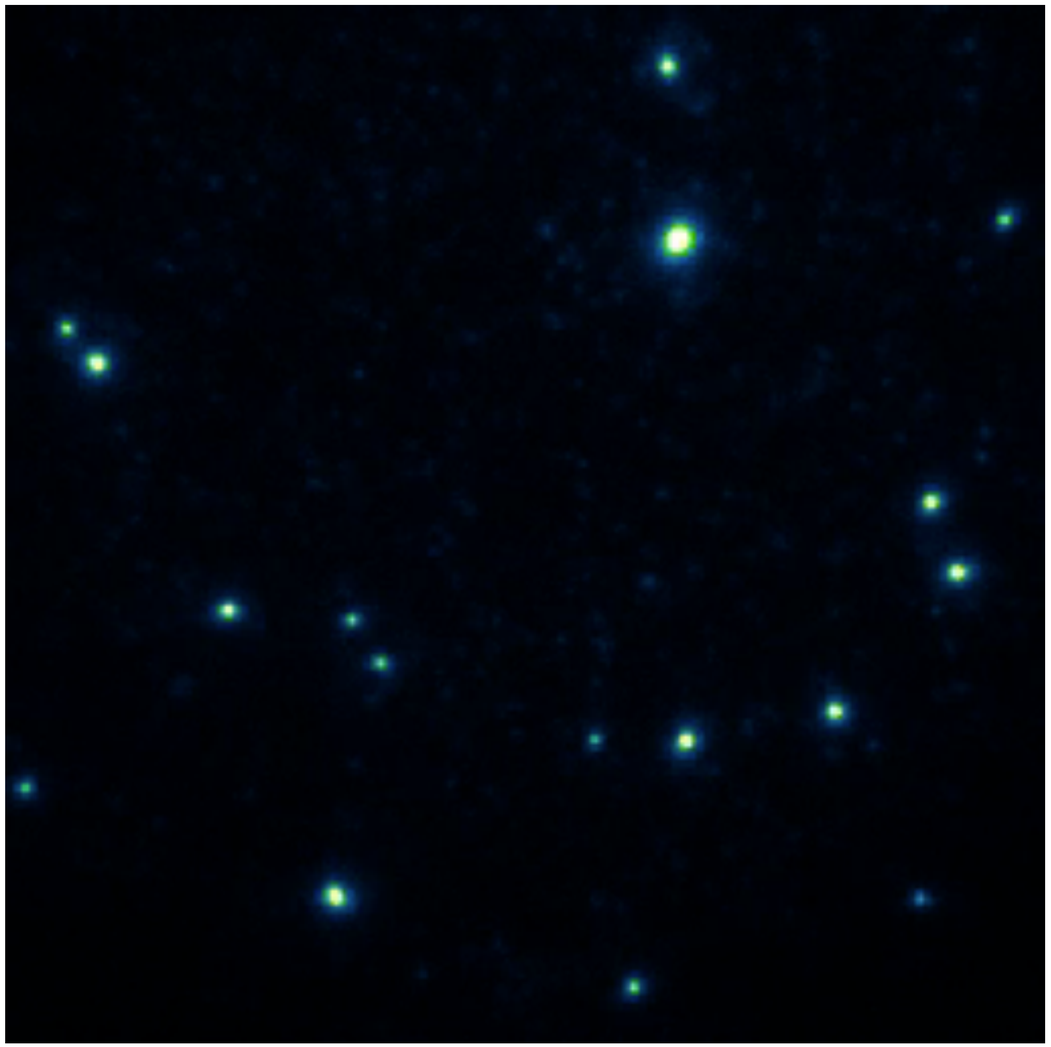
Modulation depth histogram of aggregates



Bad -> Good Solvent
After 30 min SVA

26x brighter compared to single chain (830 kDa)
⇛ 22 MDa
⇛ 45,000 nm³ ordered domains

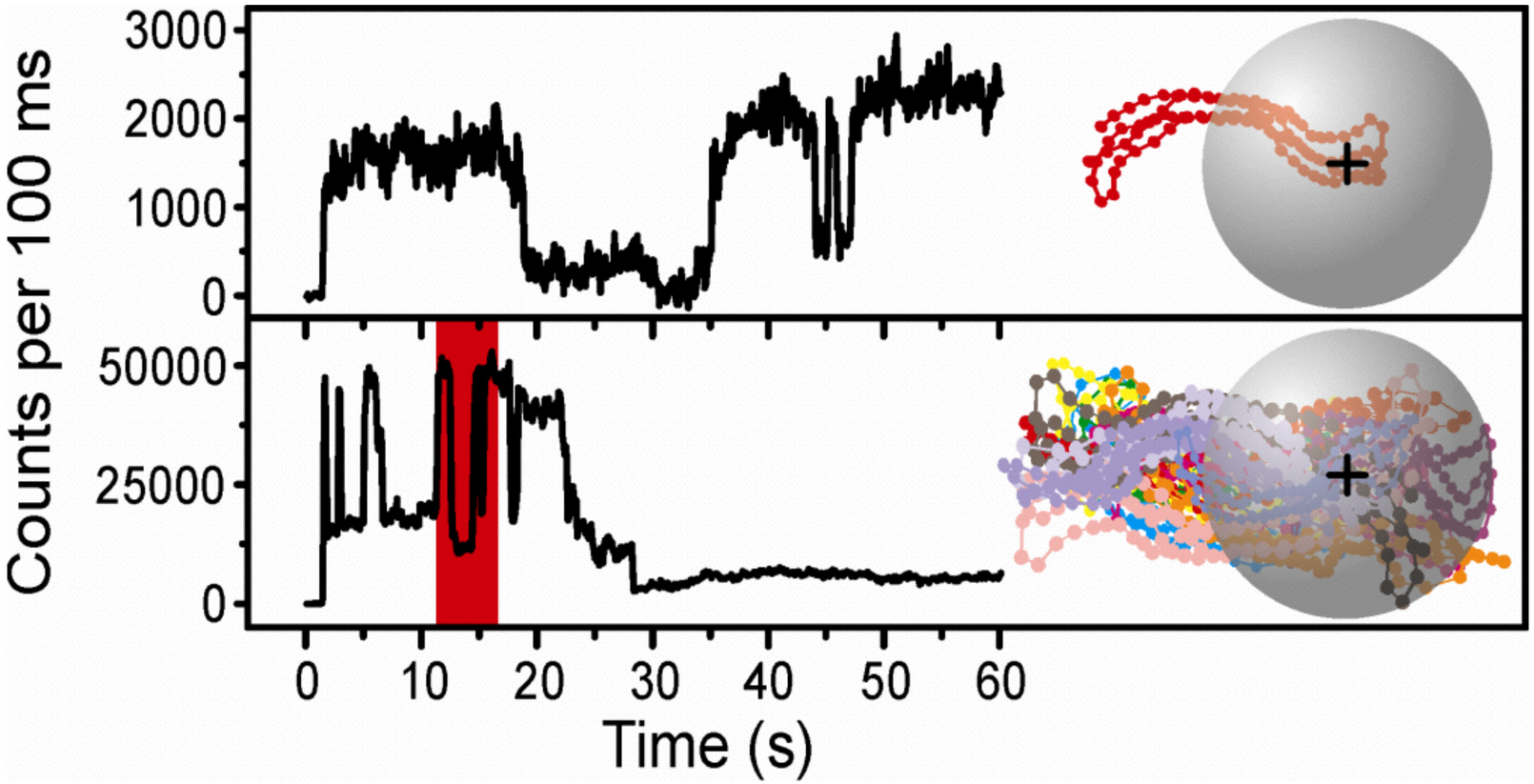
Observation of fluorescence blinking from Aggregates



After SVA (40/60)

~46 chains

Observation of fluorescence blinking from Aggregates



Intensity jumps up to 33,000 counts (830 kDa single chain = 1,500 – 2,000 counts)

⇒ One quencher can quench up to many chains simultanously (here ~ 20 MDa)

Long-range energy transfer in aggregates

Excitation anisotropy

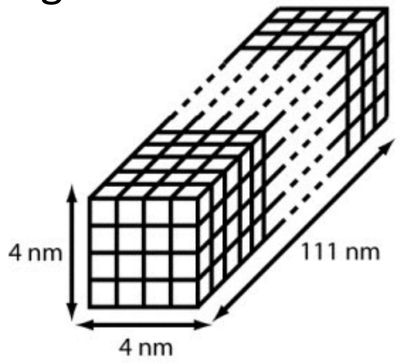
Adachi, T. et al. *J. Phys. Chem. C* **114**, 20896-20902 (2010)

+

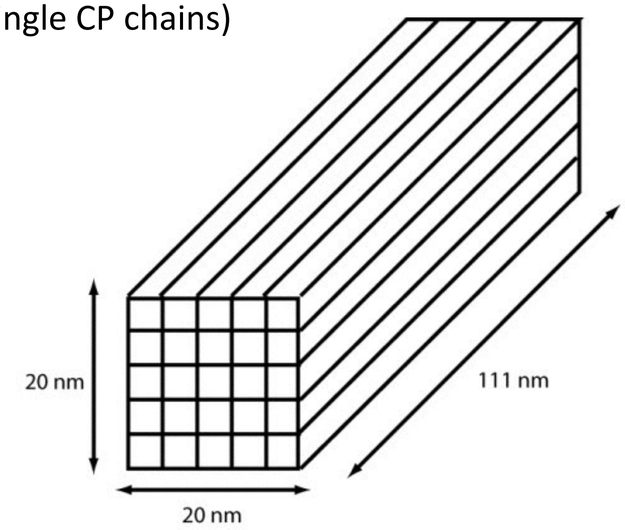
Centroid displacement

Bolinger, J.C. et al. *Science* **331**, 565-567 (2011)

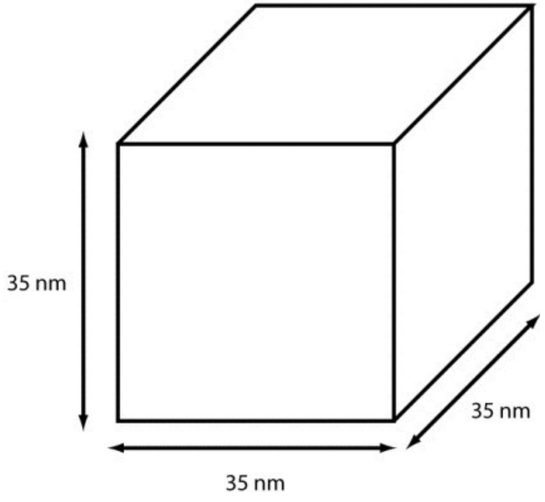
Single chain is Rod-like shape



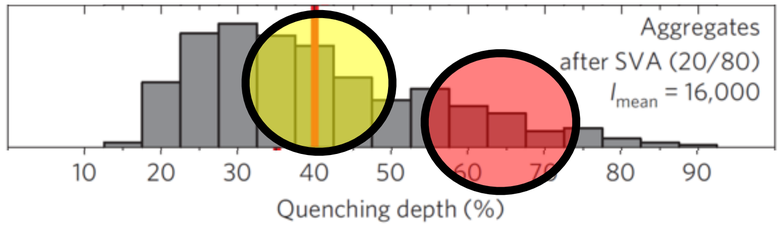
Case 1: Anisotropic aggregates
(smallest surface area without refolding of single CP chains)



Case 2: Isotropic aggregates
(smallest surface area with refolding of single CP chains)

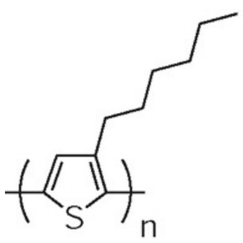


Long-range energy transfer in aggregates

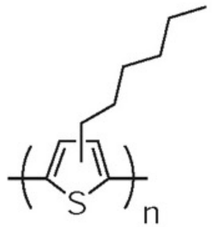


R_0 (nm)	<Quenching depth> (%) Single chain	<Quenching depth> (%) Anisotropic Aggregate	<Quenching depth> (%) Isotropic Aggregate
10	17	7	9
15	26	17	23
20	34	27	41
25	41	36	58
30	48	44	73
35	54	51	83
40	60	58	90
45	65	63	94
50	70	68	97
55	74	73	98
60	78	77	99

Look at single chains for a variety of thiophenes

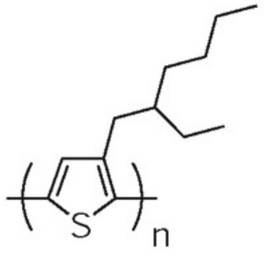


rr-P3HT

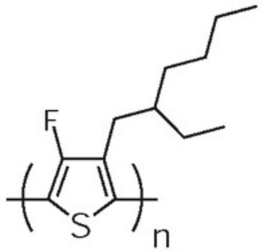


rra-P3HT

Arrangement of side-chain

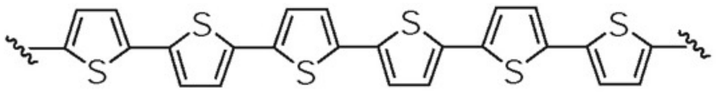


P3EHT

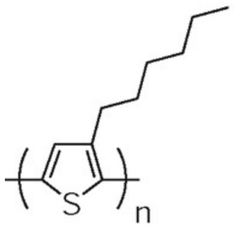


F-P3EHT

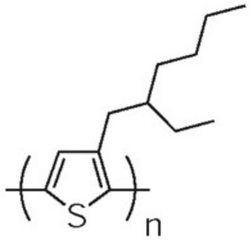
Backbone



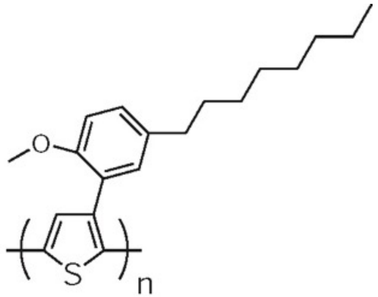
Size of side-chain



P3HT

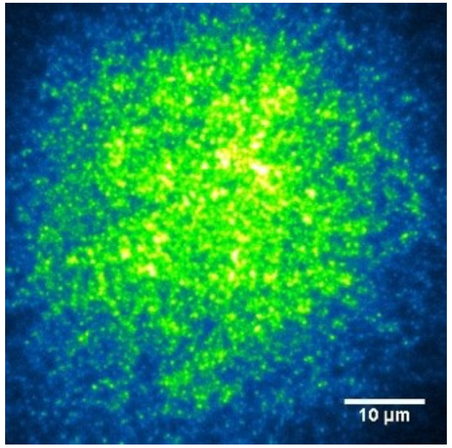


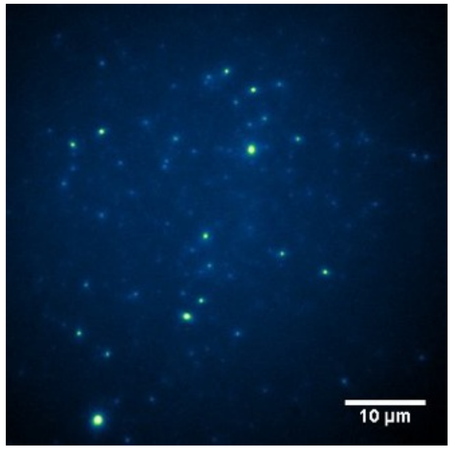
P3EHT

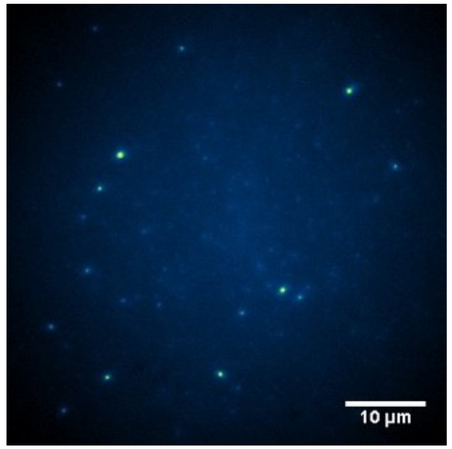


POMeOPT

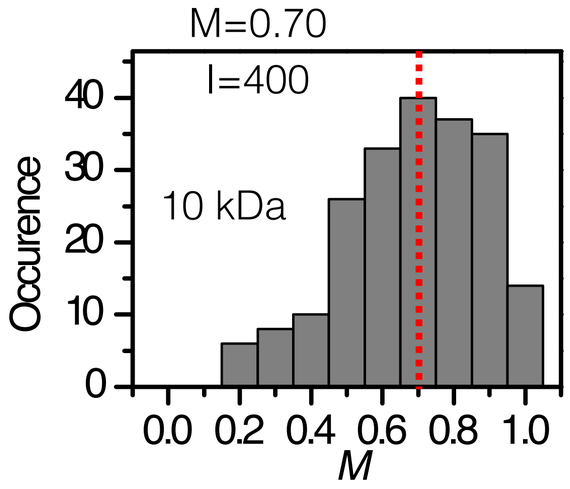
rr-P3HT aggregates

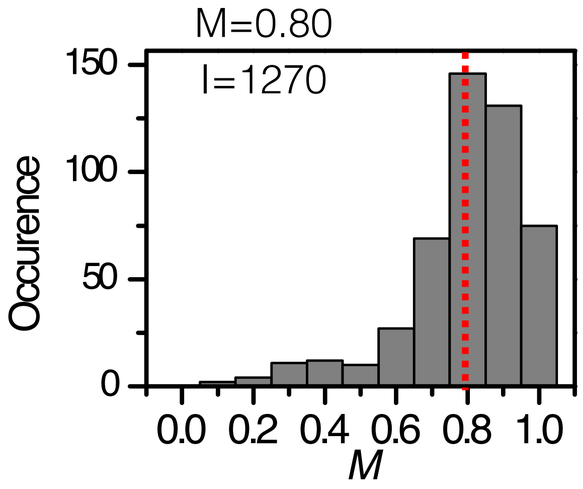


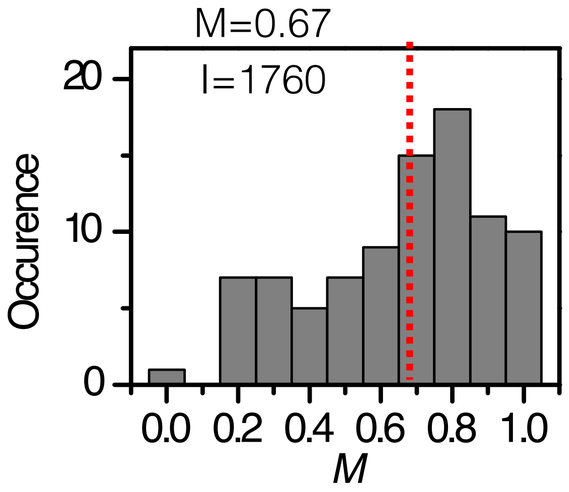




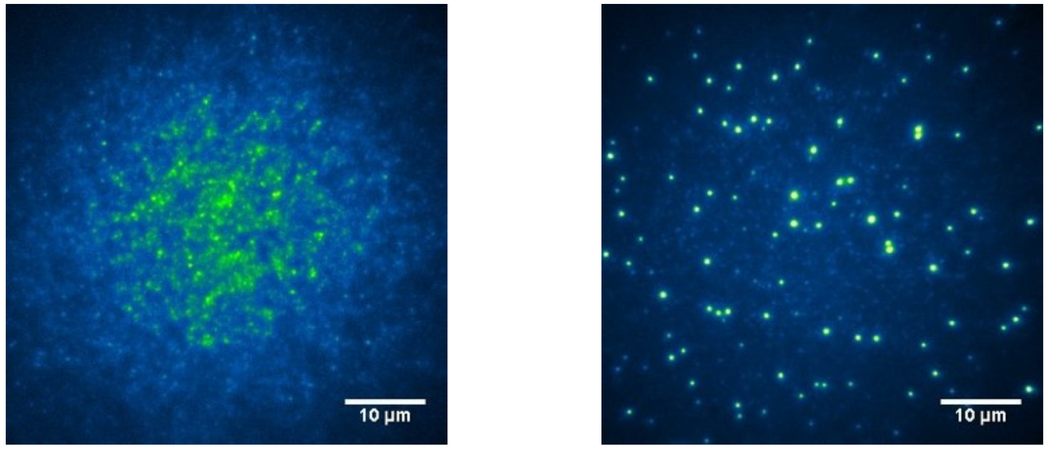
Before SVA (single chains) 100-chain 330-chain



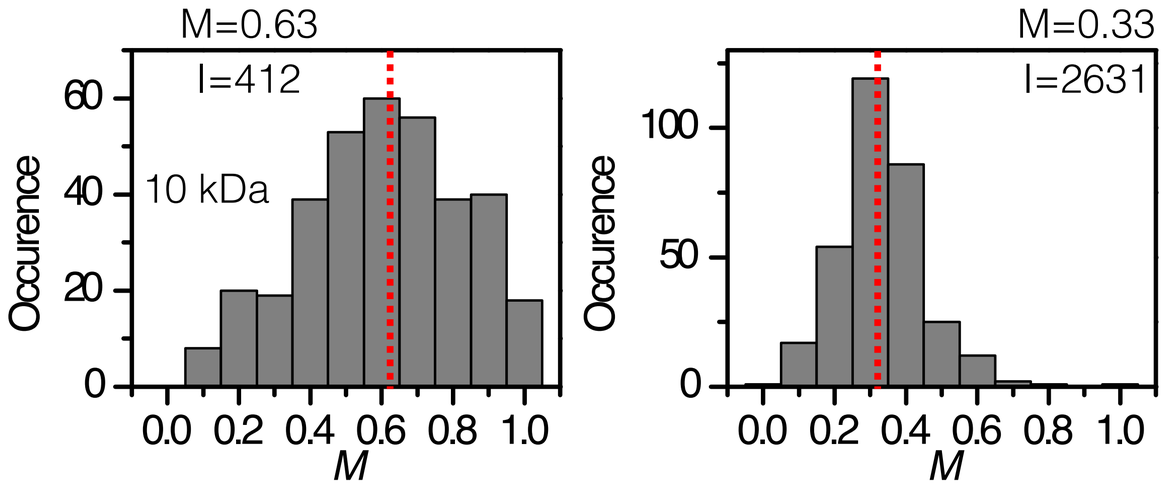


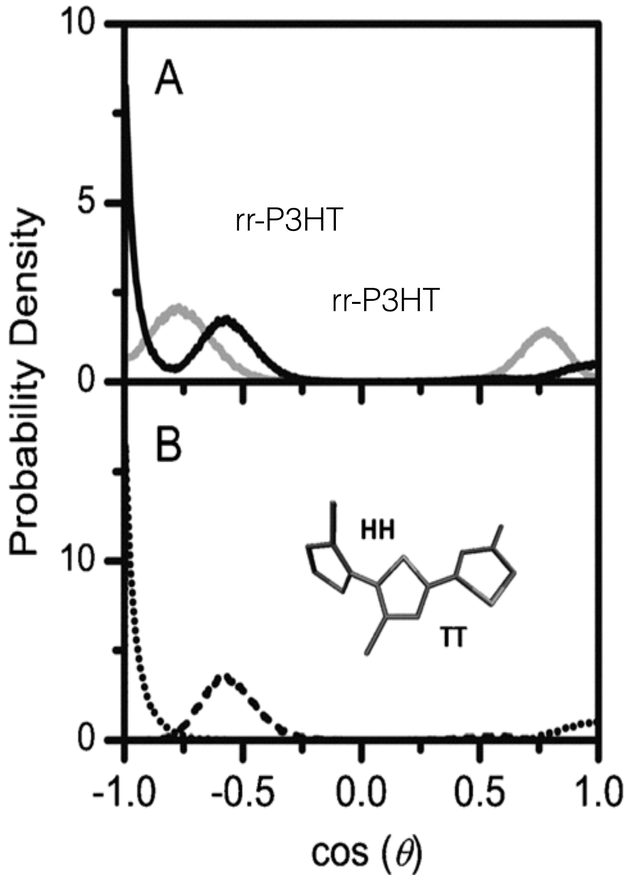


rra-P3HT aggregates



Before SVA (single chains) → 6-chain

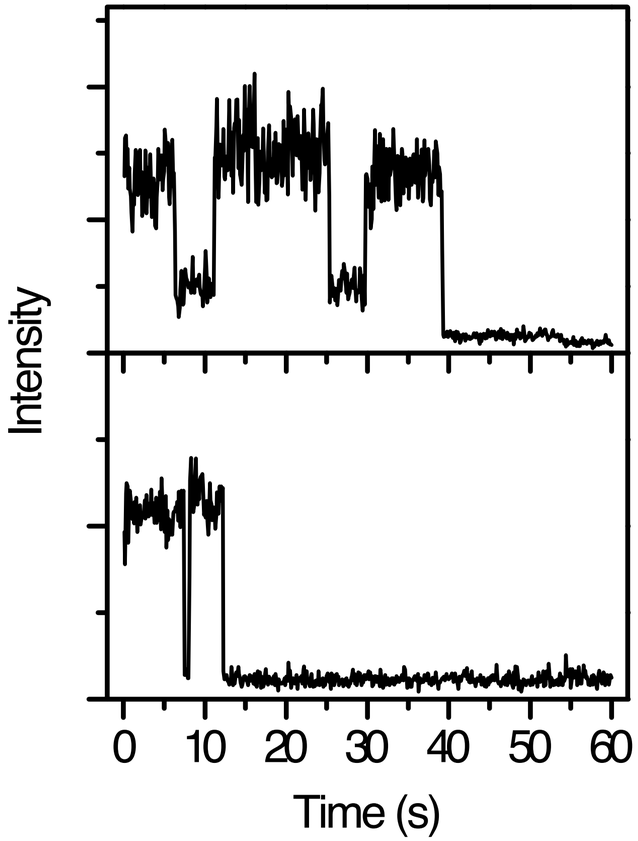




Z. Hu, et al, ChemPhysChem, 2013

Interchain order affects blinking (energy transfer)

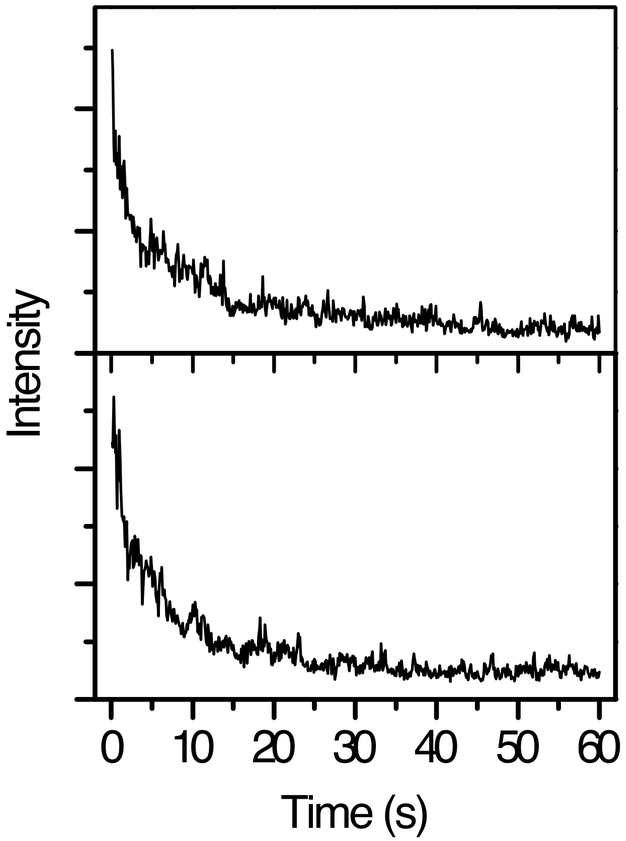
100-chain rr-P3HT aggregates



Stochastic jumps

Large fraction of intensity

6-chain rra-P3HT aggregates

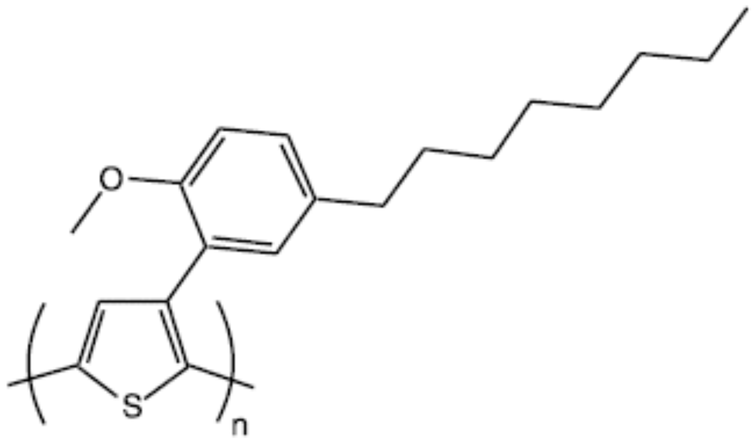


No stochastic behavior

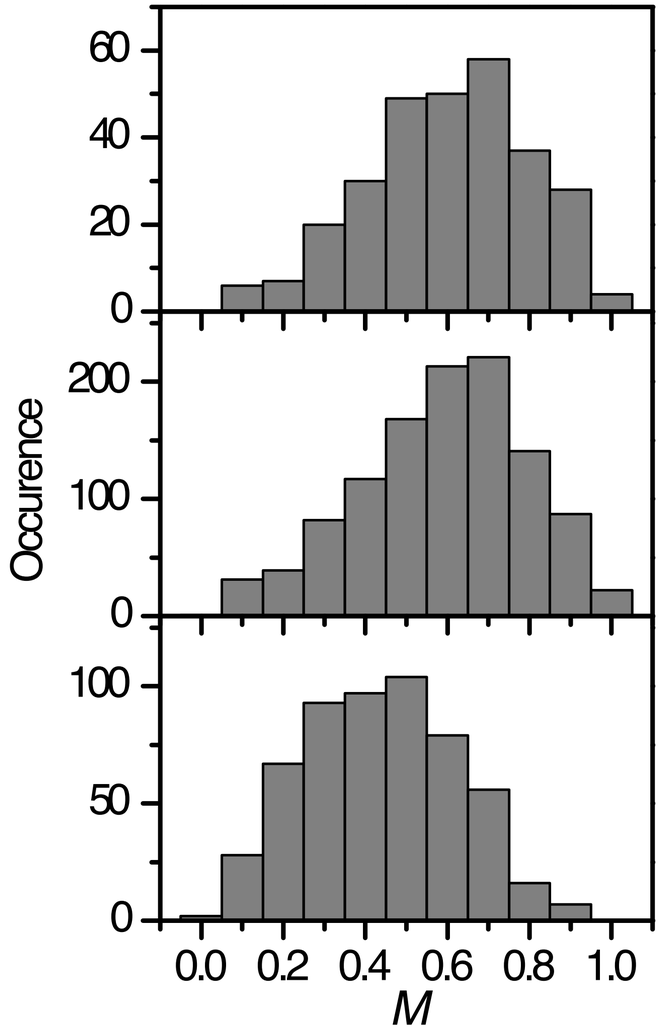
Can we maintain order but minimize energy transfer?

POMeOPT (Dπ–π= 7.0 Å)

Bulky side-chain thiophene



A longer packing distance is expected to confine the excitons within individual chains.



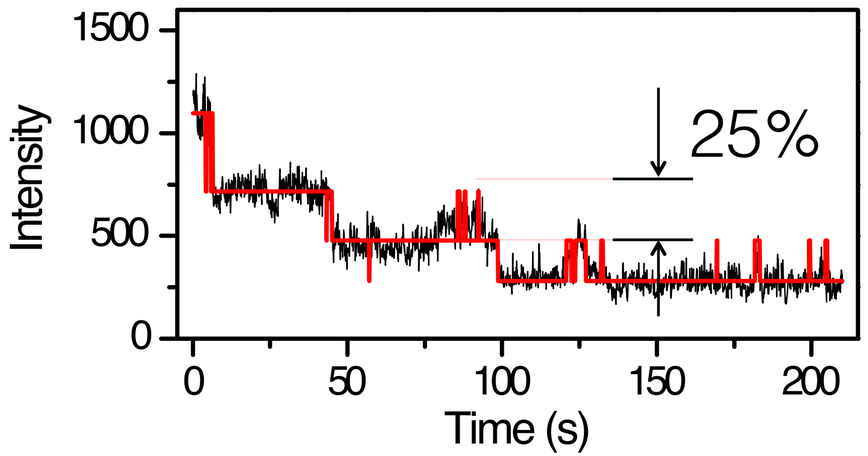
single

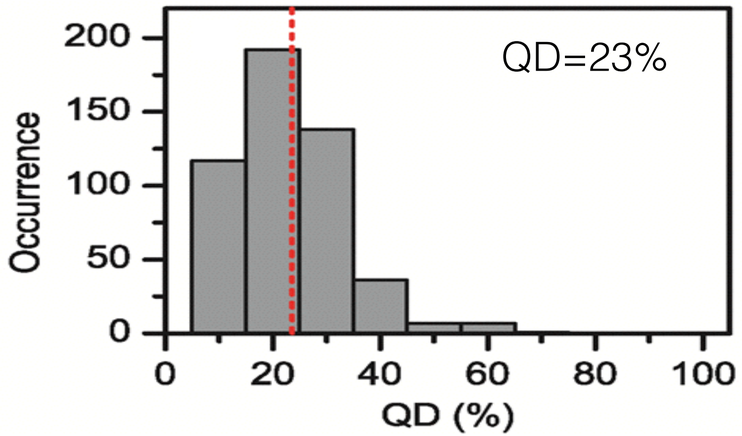
4 chain aggregate

12 chain aggregate

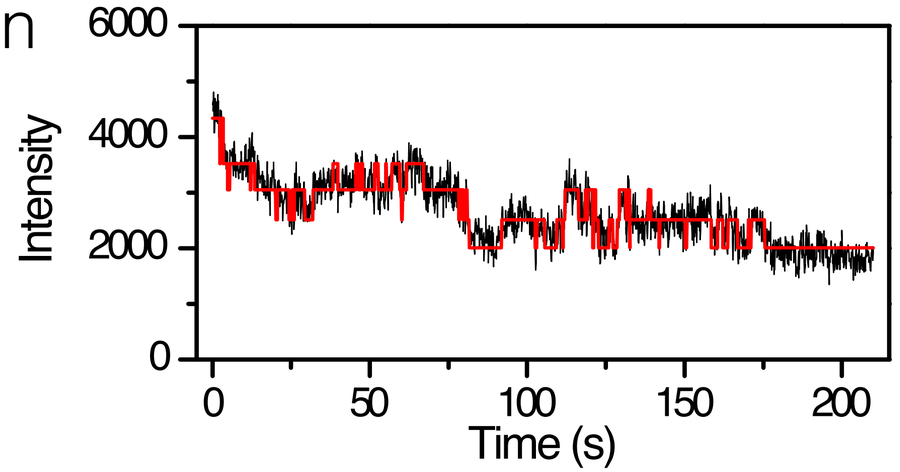
POMeOPT aggregates fluorescence transients

4-chain

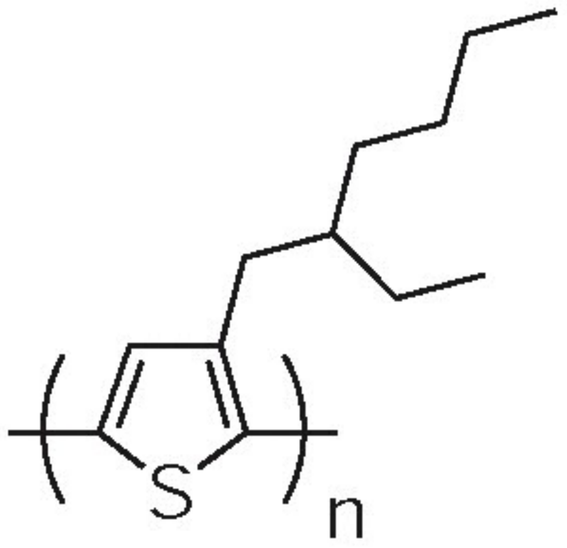




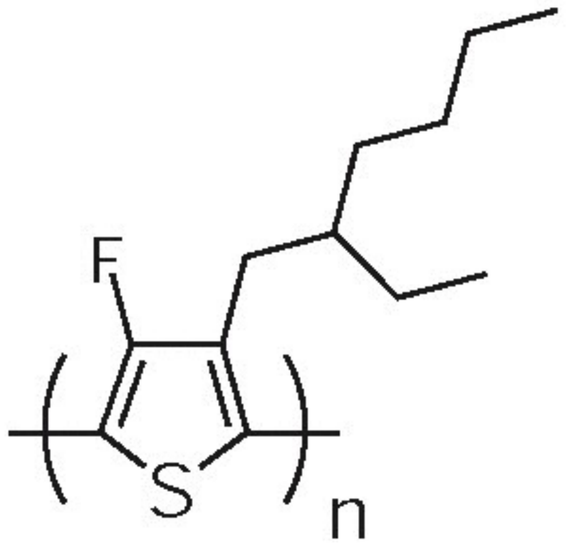
12-chain



Effect of backbone on interchain morphology and energy migration

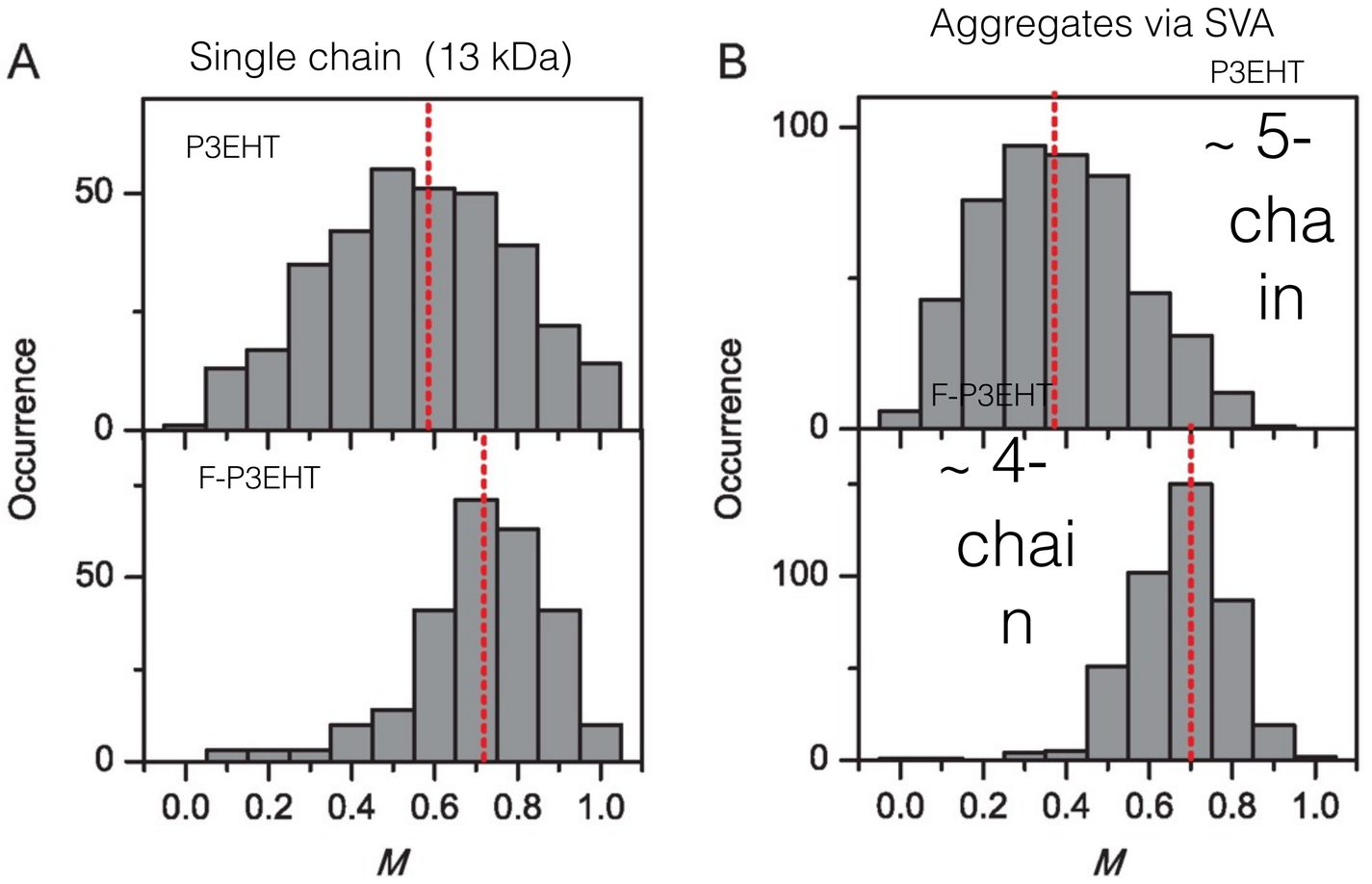


P3EHT



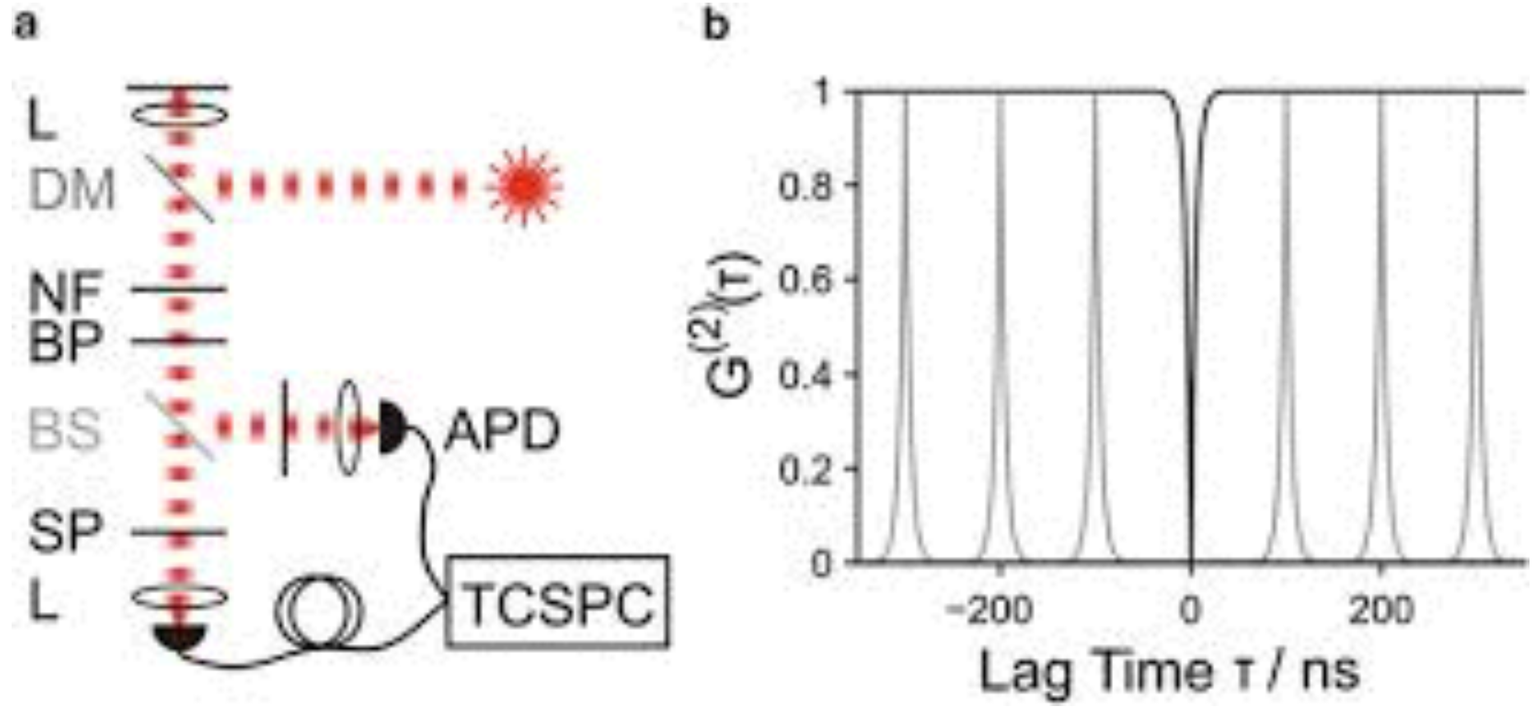
F-P3EHT

Morphology of single chains and aggregates



- F-P3EHT more anisotrpoic as single chain and aggregate

Photon Anti-Bunching

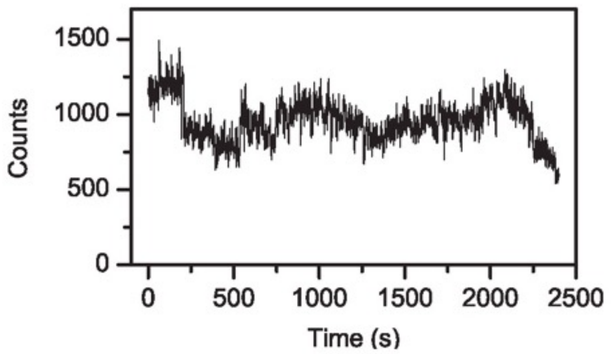


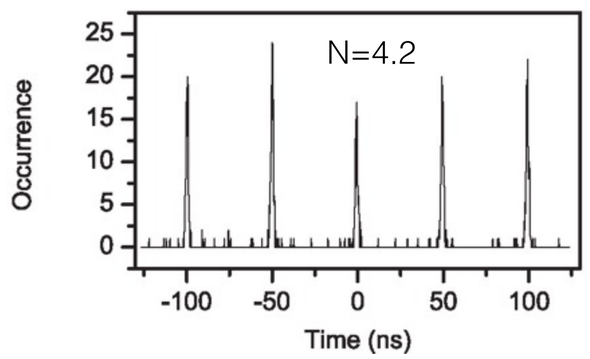
Dirk-Peter Herten,
Advances in Photon Counting: Applications Methods, Instrumentation
Springer Series in Fluorescence 15: 159-190 (2015)

Blinking in P3EHT aggregates

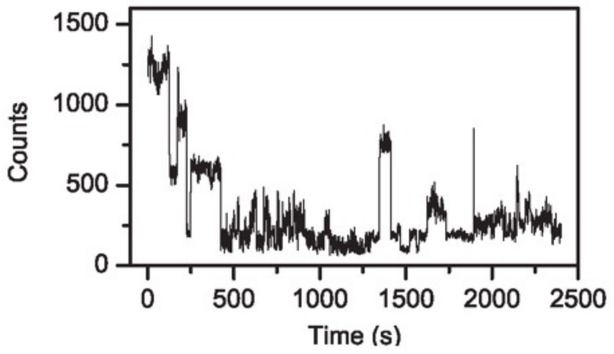
P3EHT (~ 5-chain aggregates)

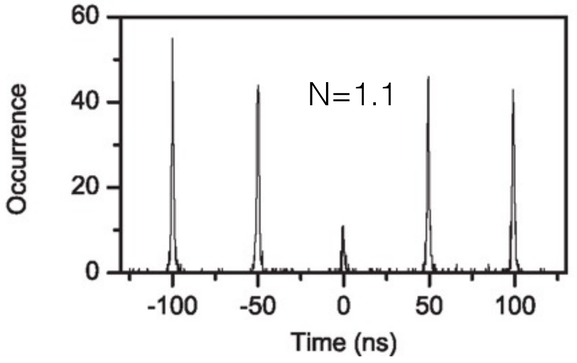
gradual or small step-wise (~65%)





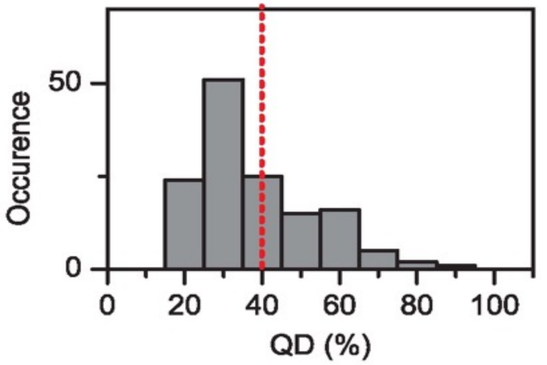
large transition(~35%)

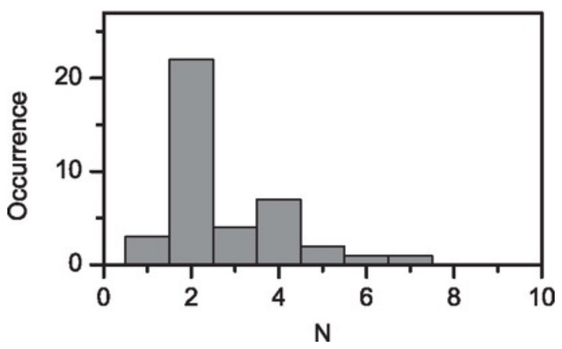




Ensemble data

Distribution of quenching-depth



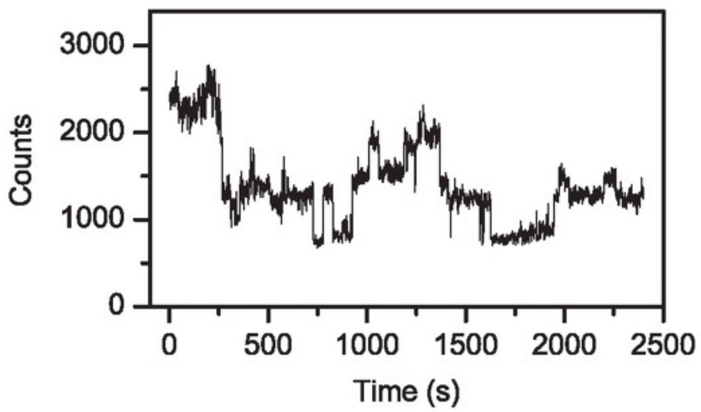


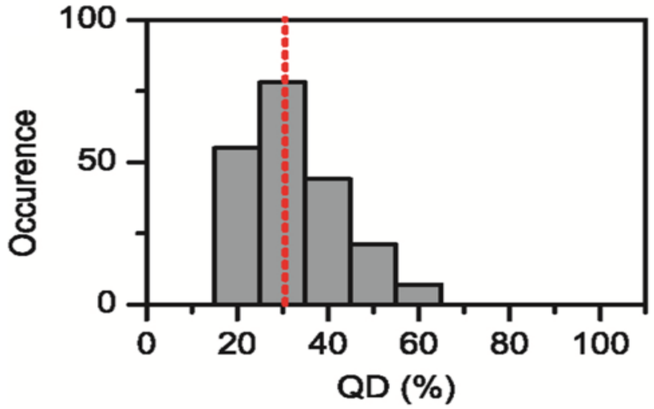
Distribution of # of emitters

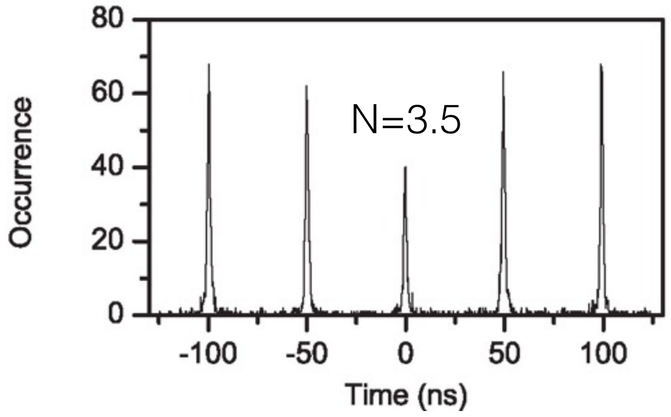
Broad distribution in EM behavior for P3EHT agg. due to variations interchain ordering.

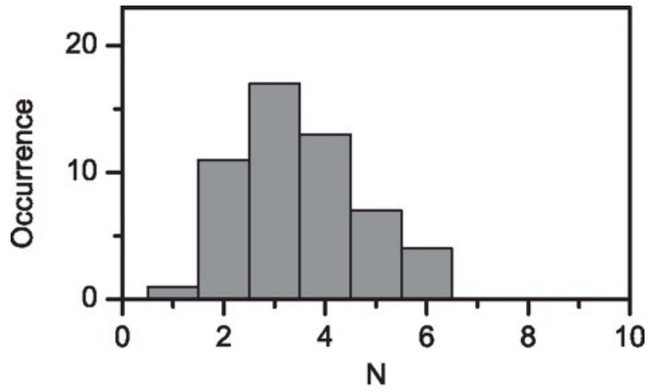
Energy migration in F-P3EHT aggregates

F-P3EHT (~ 4-chain aggregates)









- In spite of highly ordered packing, there is no efficient EM in F-P3EHT aggregates, very similar to POMeOPT

Conclusions / Questions

- Individual conjugated polymers display a wide array of spectra
- Regio-regular P3HT is highly ordered and forms ordered aggregates that behave collectively up to size of 100 chains
- Larger side-chains prevent strong interchain coupling but excitations delocalized along the chains

Acknowledgements

Single Molecule

Zhongjian Hu
Beiyue Shao
Geoff Gerberth
Jan Vogelsang
Takuji Adachi
Johanna Brazard

Synthesis

Chris Bielawski
Robert Ono

Martin Heeney
Zhuping Fei

Theory

Peter Rossky
Ryan Haws
Adam Willard
Venkat Ganessan
Ben Hanson

Christy Landes
David Cooper
Bo Shuaung

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US Department of Energy