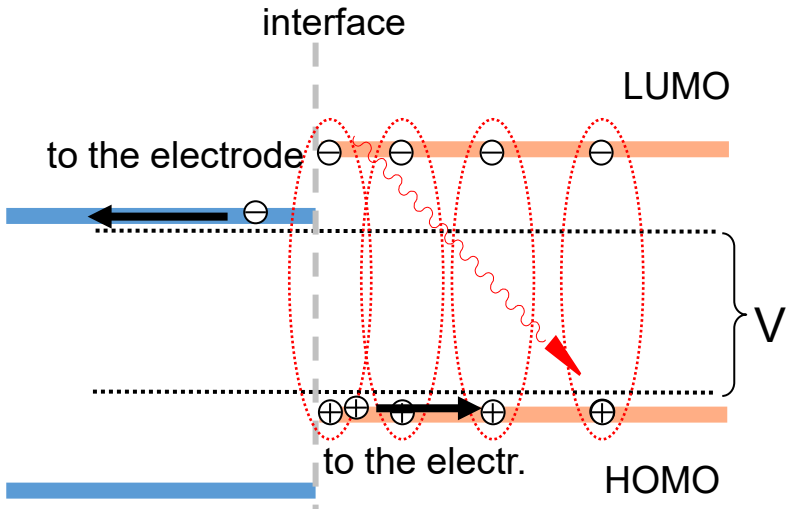
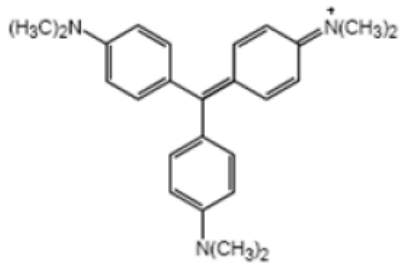
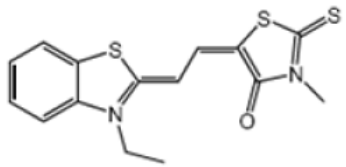
Organic photovoltaic devices (OPVs)

First report on organic donor-acceptor solar cells





crystal violet



merocyanine

HANS MEIER und *A. HAUS*, Bamberg: *Zum Problem organischer Photodioden* (vorgetr. von *H. Meier*).

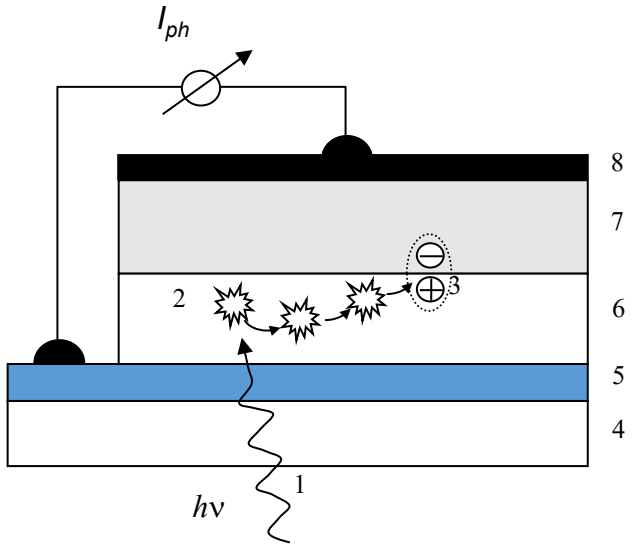
Die Einteilung der photoelektrisch aktiven organischen Farbstoffe in p- und n-Leiter, deren Stromübertragung (wie Messungen der Gasabhängigkeit von Photo- und Dunkelstrom, Thermokraft, Kristallphotoeffekt u. a. beweisen) in der Hauptsache durch Defektelektronen oder Elektronen erfolgt, führte zur Prüfung des organischen pn-Übergangs. In Übereinstimmung zur anorganischen pn-Struktur besitzt ein aus einem p- und n-leitenden Farbstoff zusammengesetztes System (z. B. Merocyanine/Triphenylmethan-Farbstoffe) die Eigenschaft einer Photodiode, die bei Belichtung mit sichtbarer Strahlung einen Kurzschlußstrom I_0 und eine Leerlaufspannung E_{00} ohne äußere Hilfsspannung ergibt. Charakteristische Merkmale dieser Photoelemente sind: Reversibilität von I_0

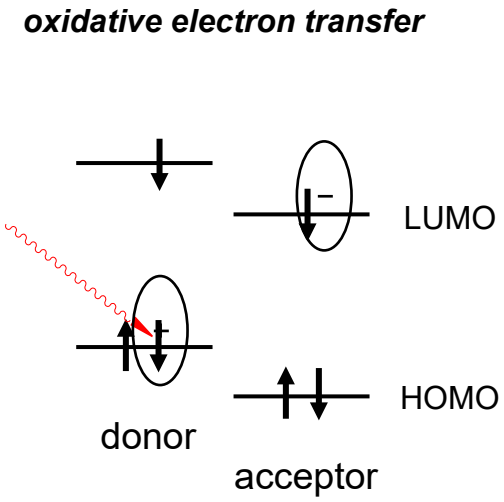
Hans Meier, Bamberg
1960, Zeitschrift für Elektrochemie

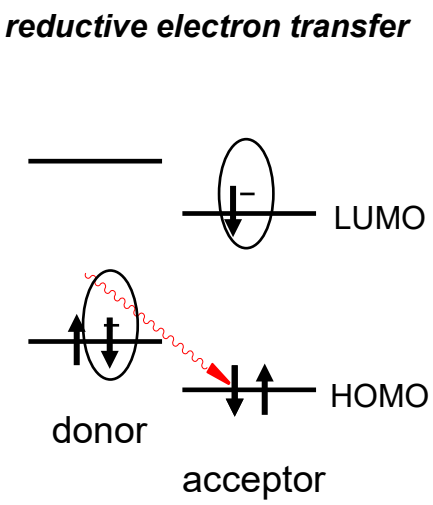
Working principle of organic solar cells

Working principle of a bilayer organic solar cell composed of a transparent substrate (4), a transparent conductive anode (5), an electron donor (6), an electron acceptor (7), and a cathode (8). Upon light absorption (1), excitons (2) diffuse until they recombine or reach the organic heterointerface where charge generation into free electron and holes takes place (3). Due to the short exciton diffusion length (short exciton lifetime) in organic solar cells, only excitons that are formed in close vicinity (about 10 nm) of the organic heterointerface can be separated into positive and negative charge carriers.

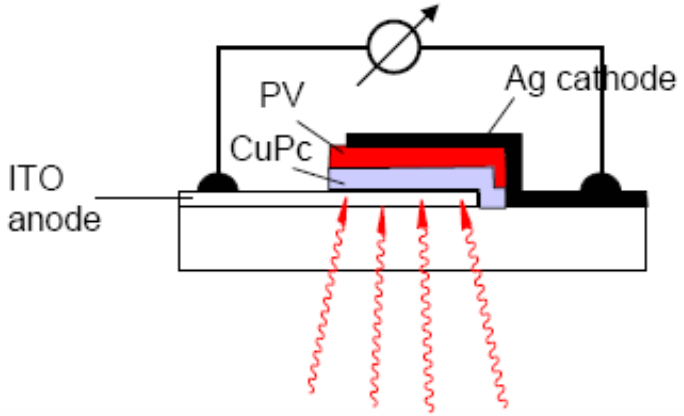
Depending on whether the electron donor or electron acceptor is photoexcited, reductive or oxidative charge transfer processes can occur if the frontier orbital levels are aligned in a favorable way.

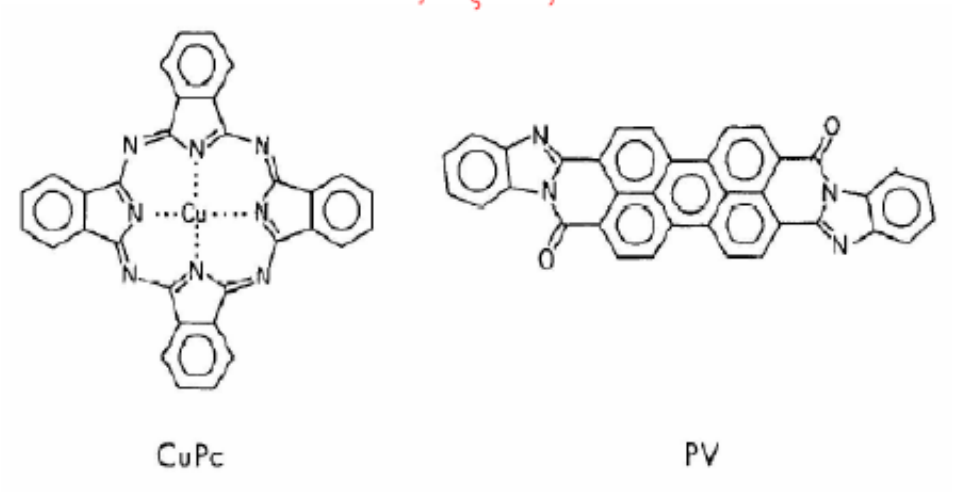






Milestone I: Bilayer solar cells reach 1%





efficiency: 1%
fill factor: 0.65

The spectral response comprises the spectral response of the chromophores of both donor and acceptor.

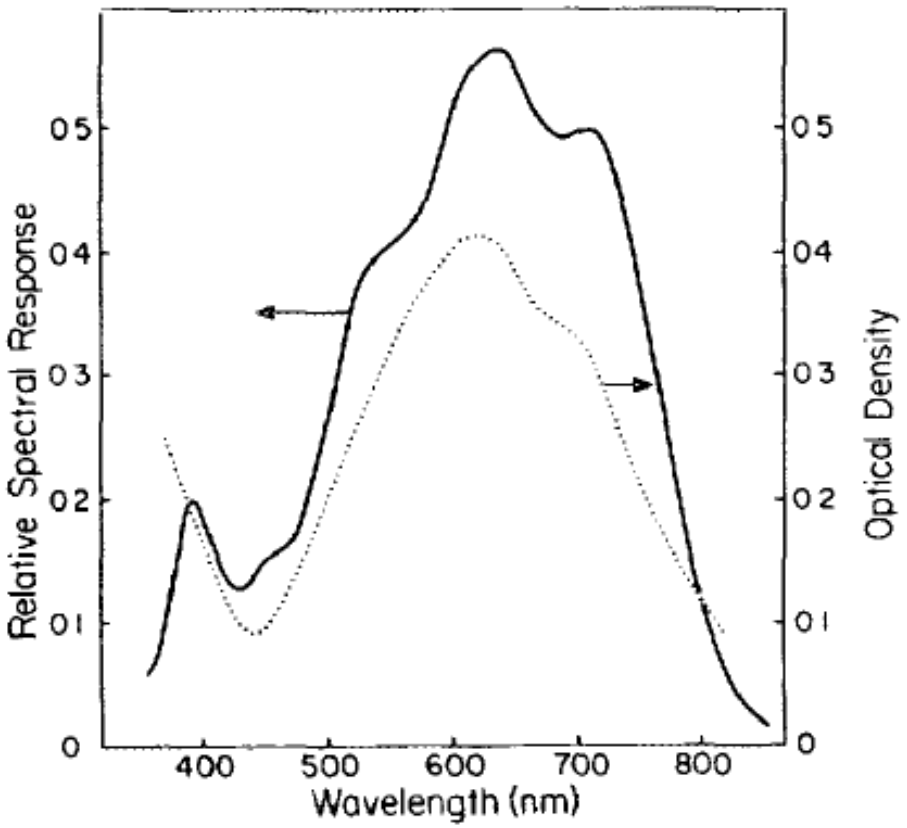
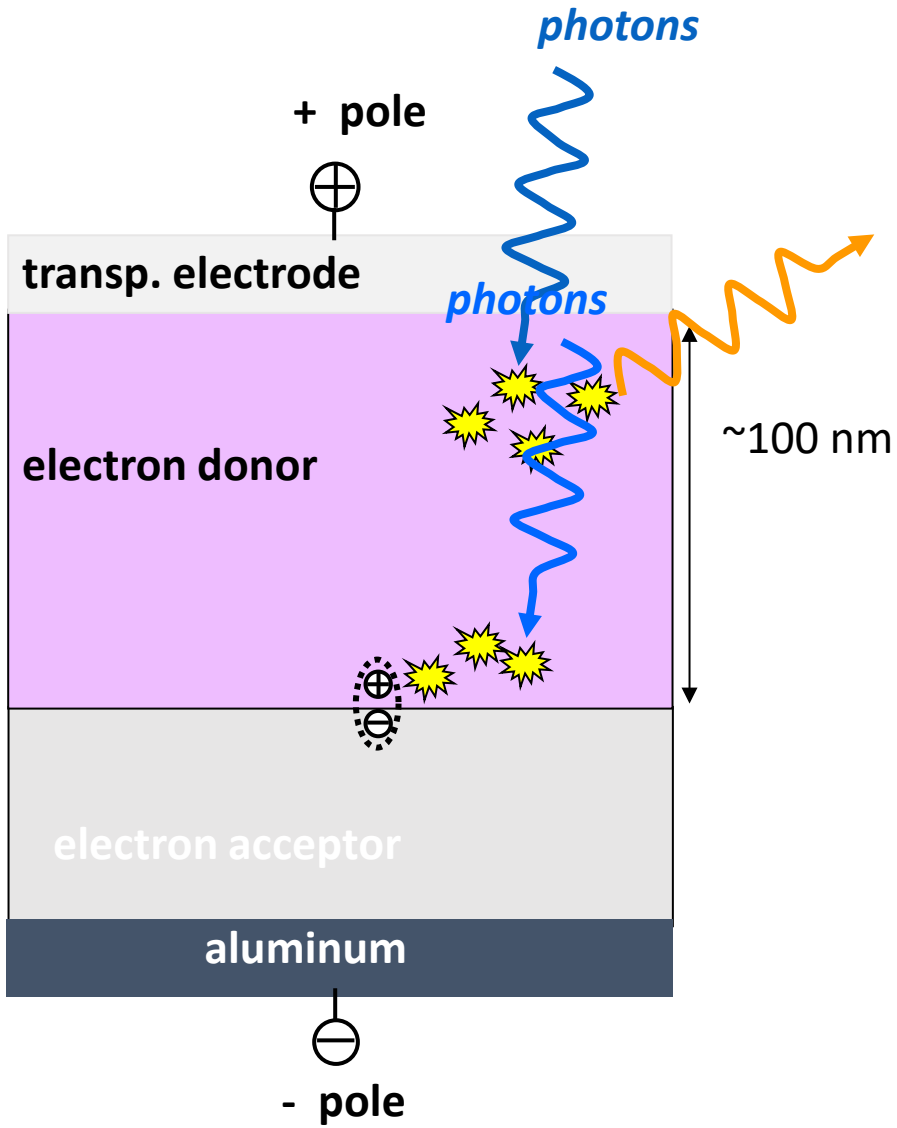


FIG. 2. Spectral response of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell and absorption spectrum of the CuPc/PV two-layer film.

C. W. Tang et al., Applied Physics Letters, 1986

Milestone II: The problem of the exciton diffusion length

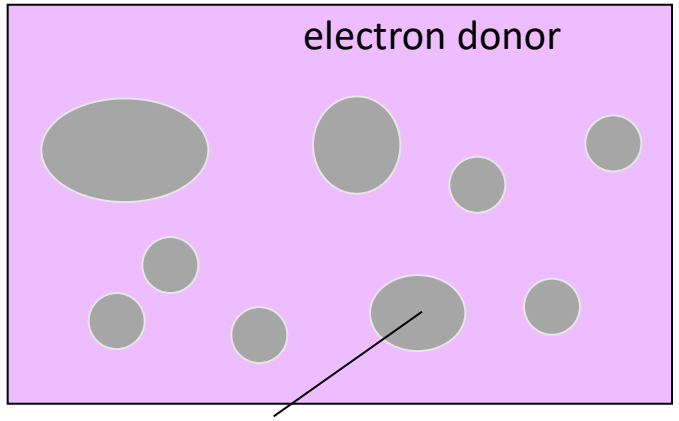


For an efficient solar cell it is primordial to absorb a large portion of the solar irradiation. Organic semiconductors benefit from very strong π-π* transitions (absorption coefficient $\alpha \approx 10^5\ \mathrm{cm}^{-1}$). As a consequence, films of 100 nm-200 nm are thick enough to harvest all the photons within the range of absorption. Advantageously, electrons and holes do not have to travel long distances and can be extracted with high efficiency.

Upon absorption, excited states are formed (excitons) which have a lifetime of about 1 ns. During this lifetime, they diffuse within the solid. Typically the diffusion length is about 5-20 nm. This condition brings a difficulty, namely that excitons that are excited far from the donor-acceptor interface will not be dissociated at the heterointerface. Ideally, a comb-like nanostructure between donor and acceptor should be fabricated.

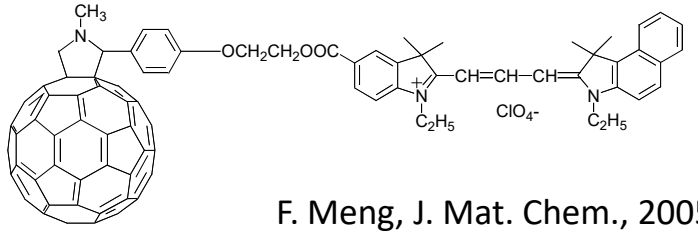
Much of the conceptual research work leading to higher efficiency devices has therefore focused on the problem of short exciton diffusion length.

What about blending of donor and acceptor?



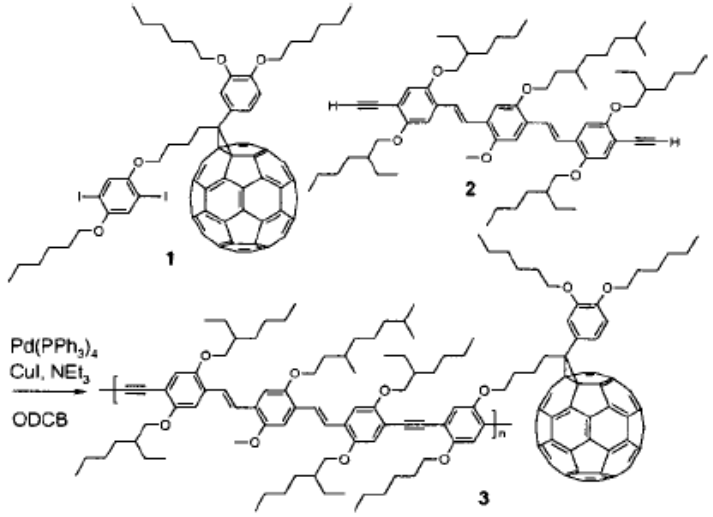
If the blend results in phase segregation, of isolated domains, charge transport of one of the species (electrons for the figure on the left) is trapped and extraction is not efficient. It has therefore been tried to synthesize tethered donor-acceptor diads such that no phase separation can occur. Such molecules are shown below for donor-acceptor dimers and polymers incorporating the donor in the main chain and the acceptor in the side chain (so-called double cable polymers).

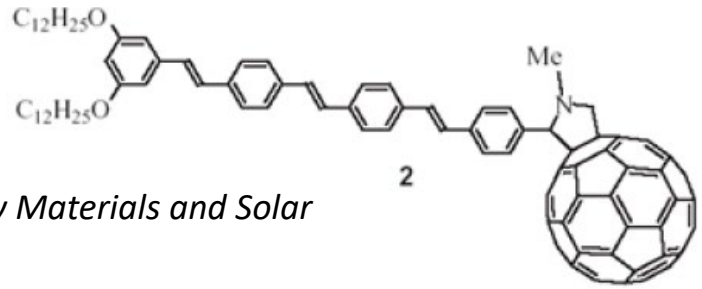
Both approaches suffer from the fact that charge recombination is enhanced in such films. The advantage is the fact that charge generation is extremely efficient.



F. Meng, J. Mat. Chem., 2005, 15,979-986 979

"double cable polymers "

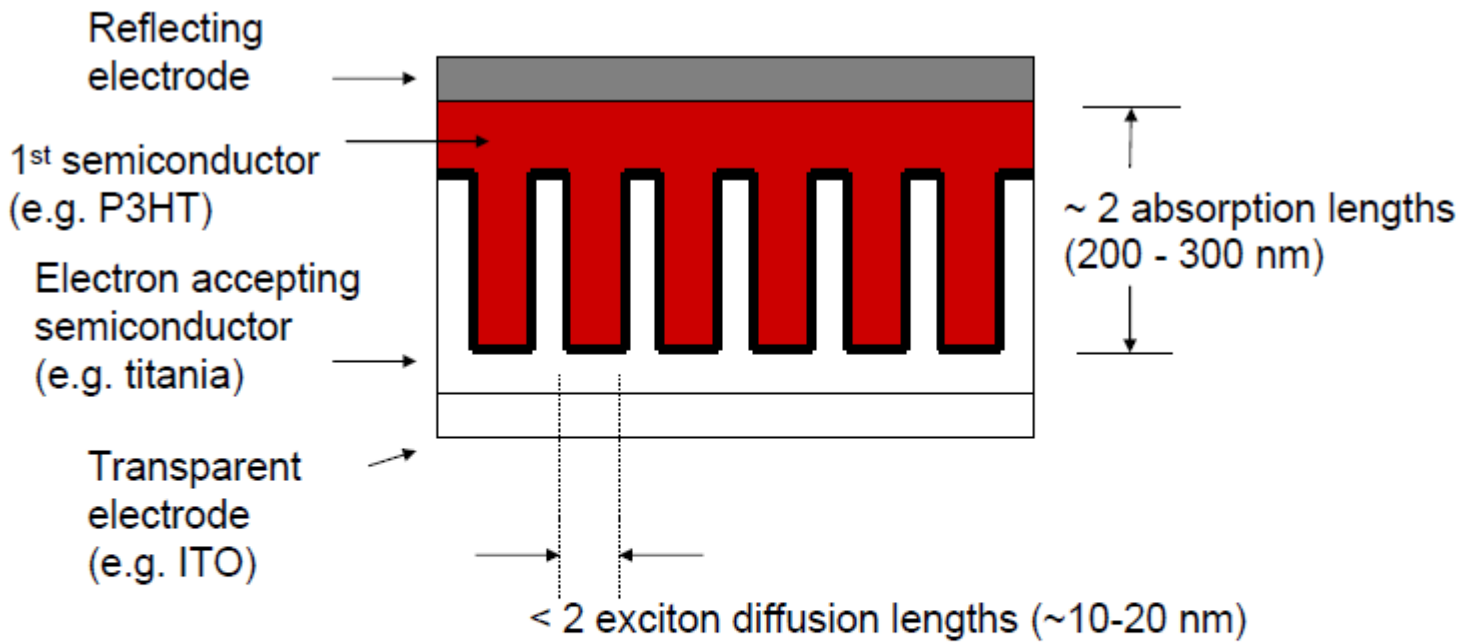




Nierengarten et al., *Solar Energy Materials and Solar Cells,* **83 (**2004), 187-199

Ramos et al., *JACS,* 123 **(**2001), 6714.

Ordered bulk heterojunction

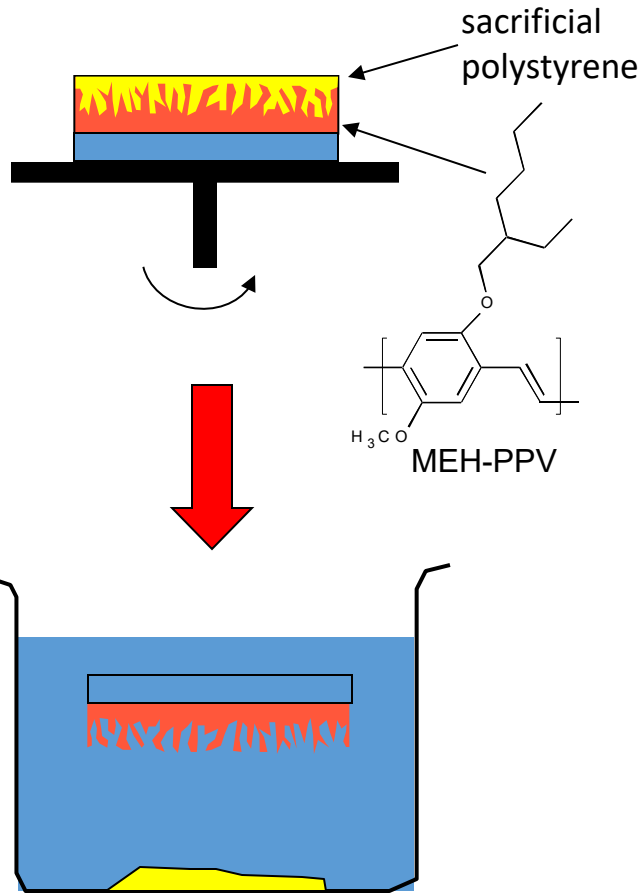


- Almost all excitons can be split
- No deadends
- Polymer chains can be aligned

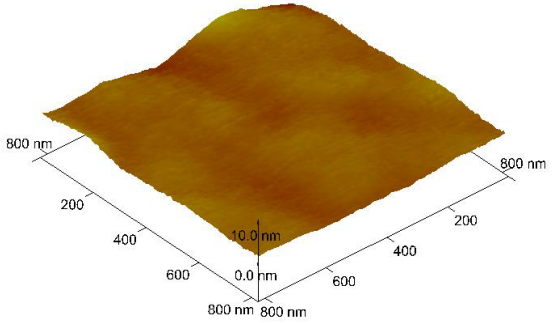
- Easy to model
- Semiconductors can be changed without changing the geometry.

Fabricating nanostructured heterojunctions

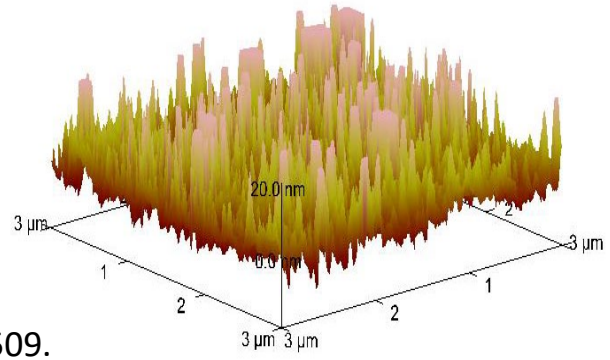
Spin coated blend

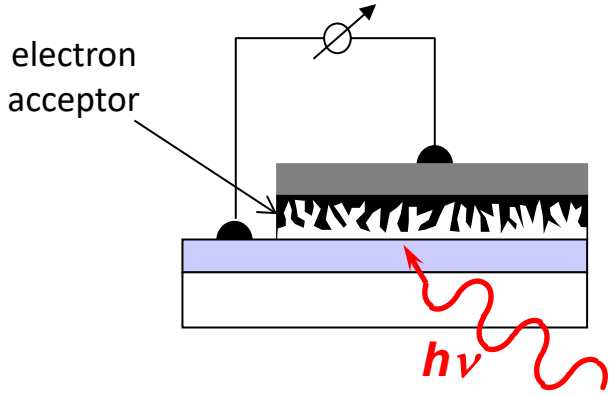


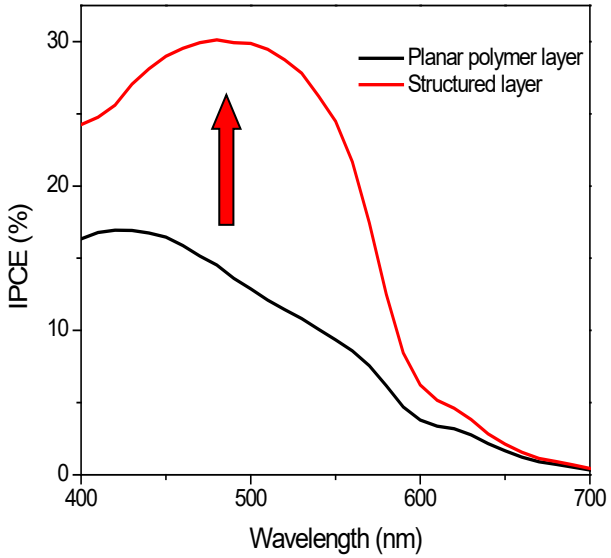
untreated film
(spin-coating)



nanostructured film



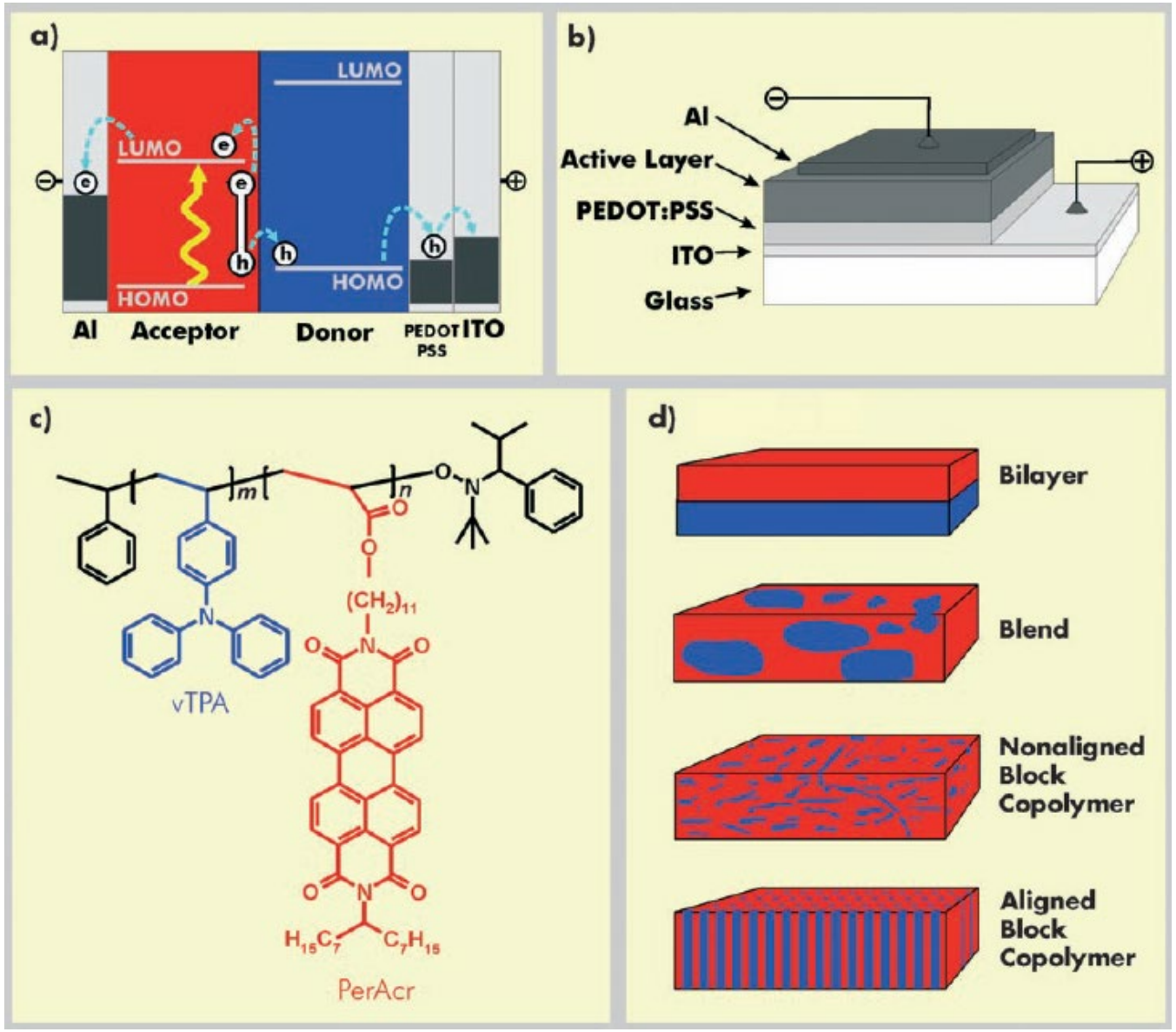




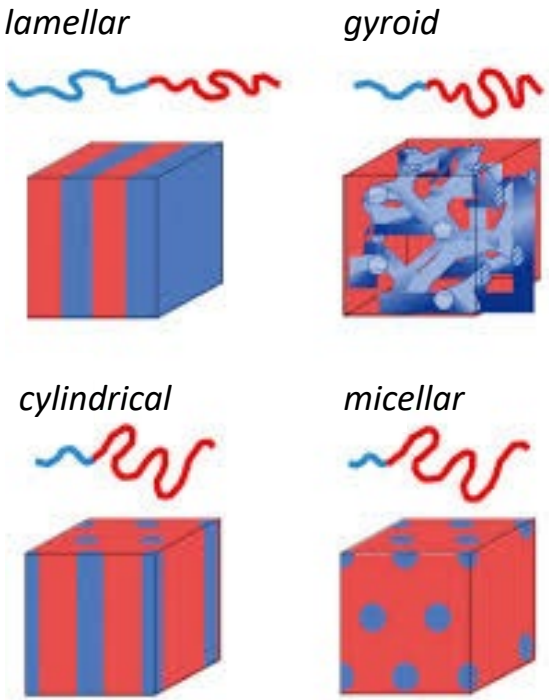
F.A. Castro, et al., *Chem. Mat.* 2006, (18), 5504-5509.

F.A. Castro, C.F.O. Graeff, J. Heier, R. Hany, *Polymer*, 48, (2007), 2380-2386

Designing film morphology at the molecular level: block copolymers

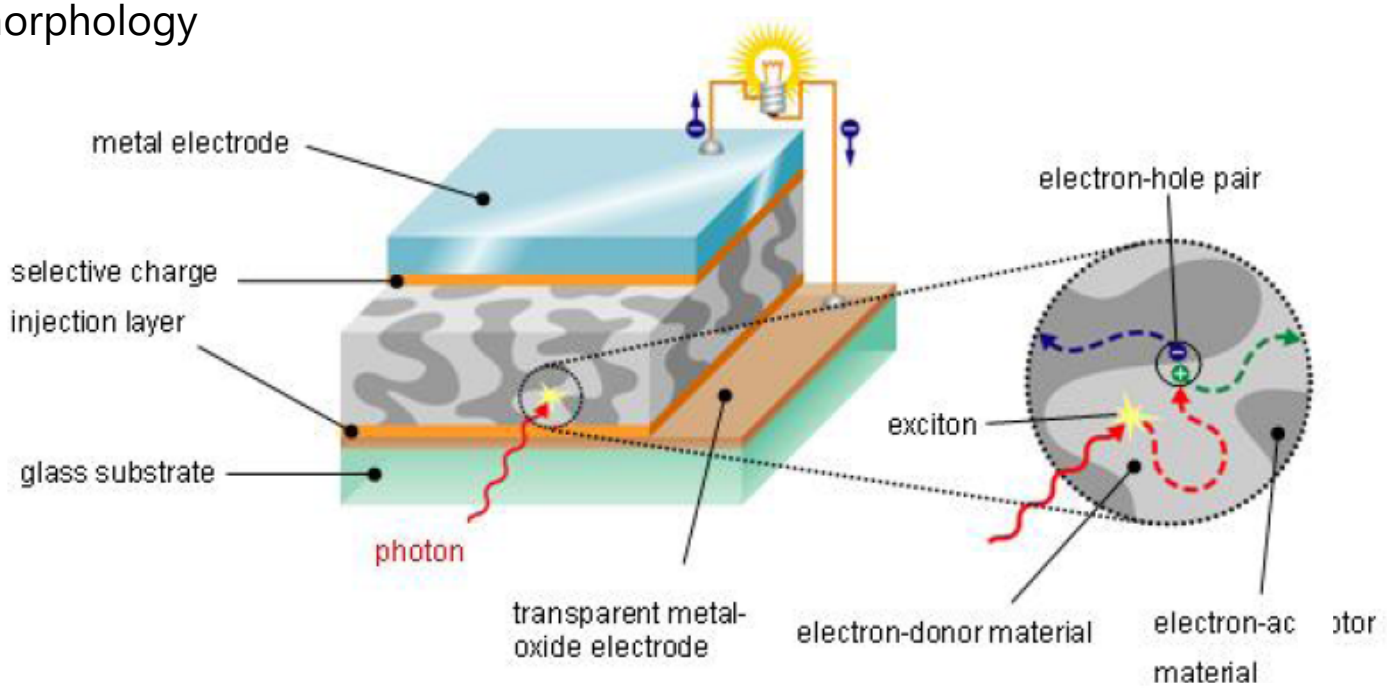


Albeit very appealing, the concept of block copolymers has so far provided power conversion efficiencies below 10%. The reason is not very clear, but it could be related to the difficulty to produce well aligned structures. Also the possibility to use gyroid structures has so far been difficult to achieve.

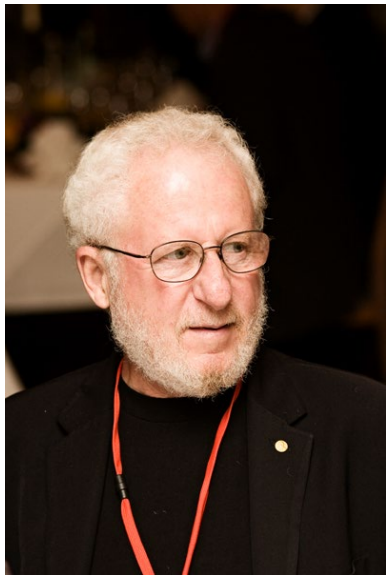


S. M. Lindner et al., Angew. Chem. Int. Ed. 2006, 45, 3364 –3368

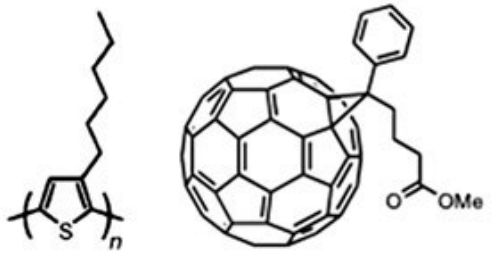
Bulk heterojunction solar cells by blending donor and acceptors: the art of fine-tuning morphology



Allan Heeger, UCSB bulk-heterojunction using conjug. polym.

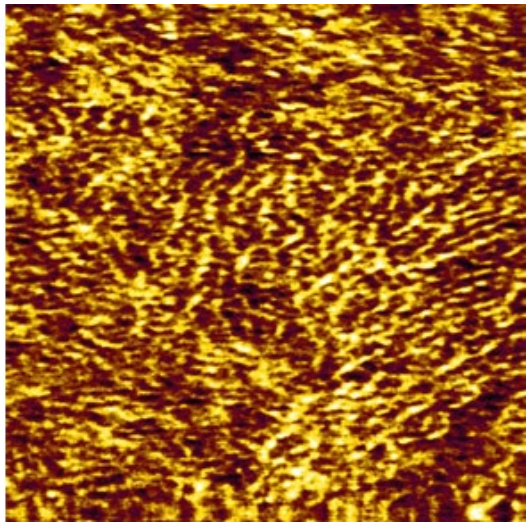


P3HT and PCBM today are reference donor-acceptor materials for organic solar cells deposited from solution. Power conversion **efficiency of 4%** in this system is limited by the limited width of the absorption spectrum of P3HT (onset at about 630 nm). Therefore much effort has been spent on “pushing” absorption to the NIR domain. Some other strategies have employed plasmonic light scattering by metallic nanoparticles.



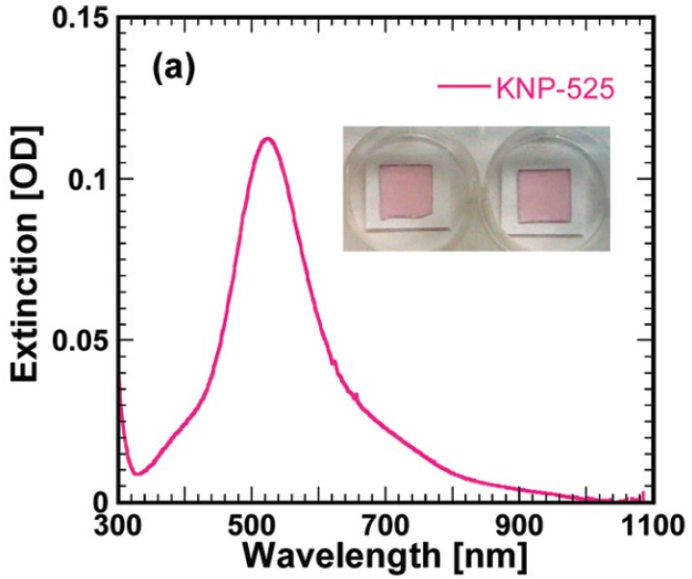
P3HT
donor

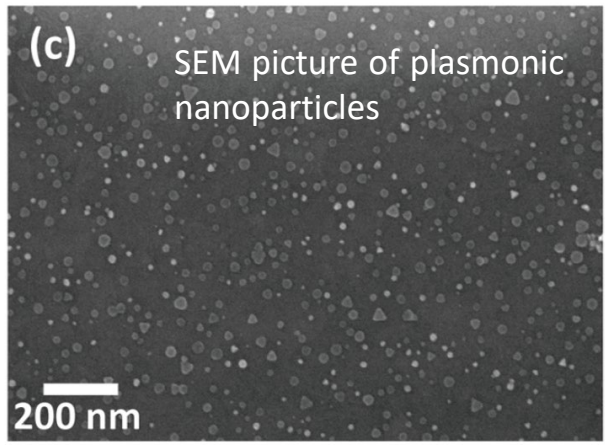
PCBM
acceptor

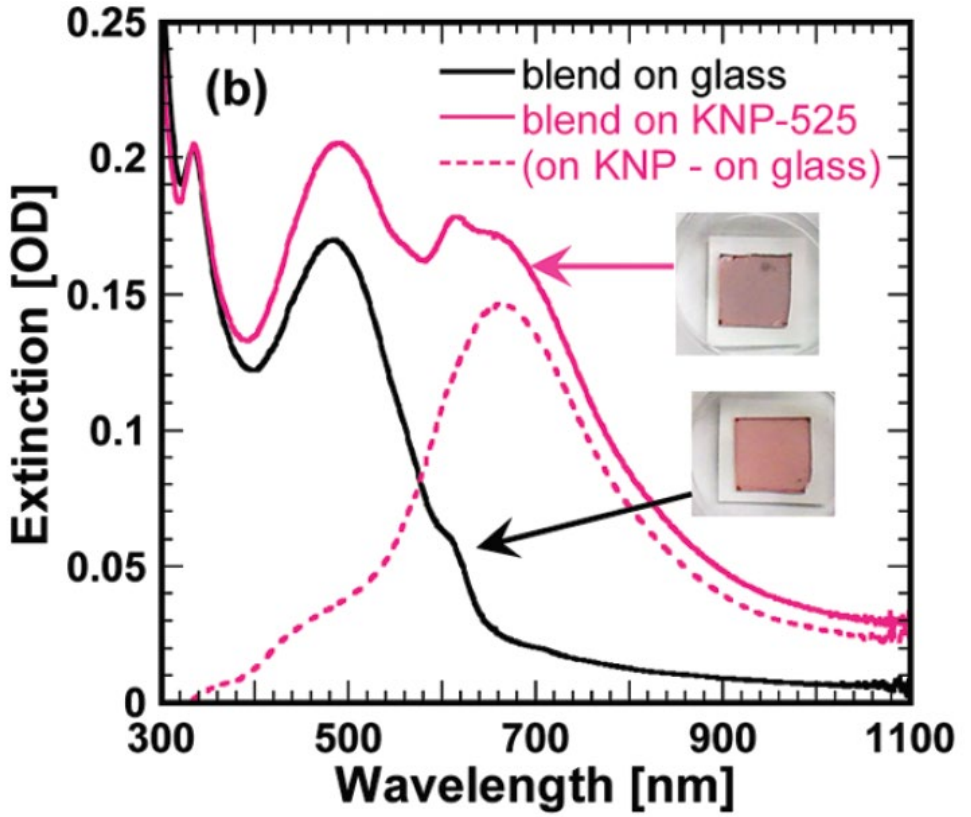


Absorption enhancement using plasmonic nanoparticles

Extinction coefficient of nano-prism particles on glass slides (top)





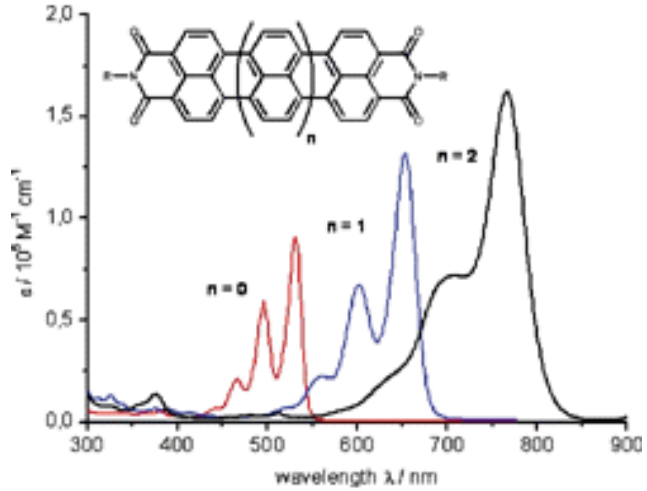


Extinction spectra of 35 nm thick P3HT/PCBM blend film on glass (solid black line) and on silver nano-prisms (solid pink line). The dotted pink line is the difference between the extinction spectra of the polymer blend on bare glass and the polymer blend on the nano-prisms.
With the polymer coating, the nano-prism LSPR resonances red shift by ~140 nm. This red shift is primarily attributed to the change in refractive index sensed by the nano-prisms in going from air (n = 1) to polymer film on top (n ~ 1.7).

A.P. Kulkarni et. al., DOI: 10.1021/nl100615e, *Nano Lett.* **2010,** *10*, 1501–1505

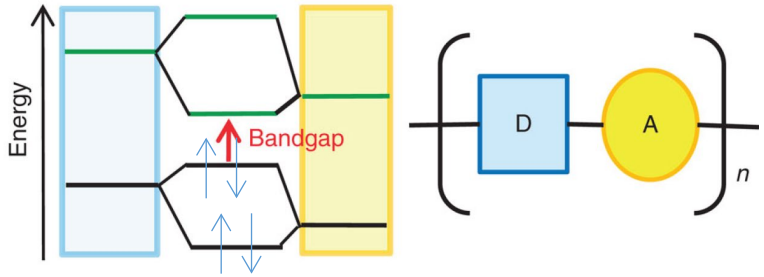
Milestone III: Developing molecules absorbing in the near infrared (NIR)

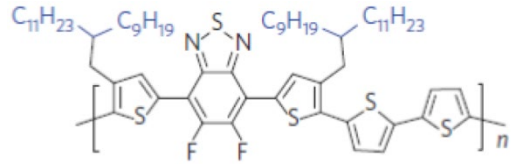
Large p-conjugated systems (graphene, rylene dyes etc.)



Herrmann et al., Chemistry Letters Vol.35, No.9 (2006)

Donor-acceptor CT motives

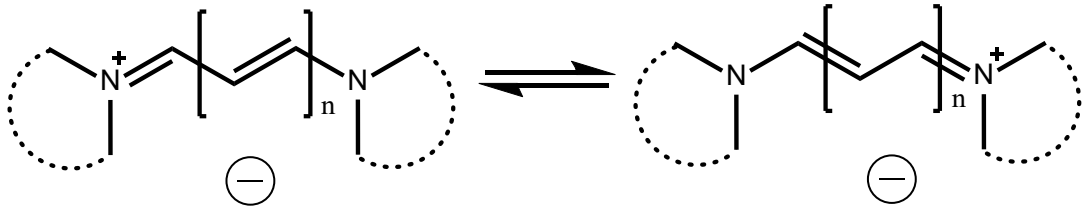




J. Zhao et al., Nature Materials, 2016

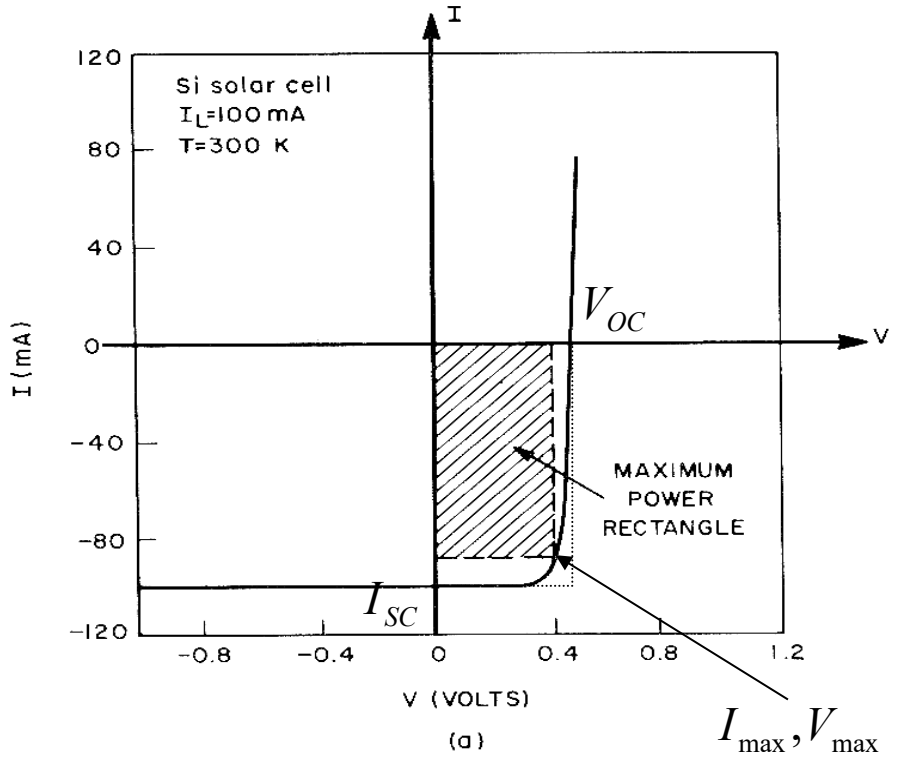
PffBT4T-C_9C_{13} (donor)

Cyanine dyes (Brooker cations)

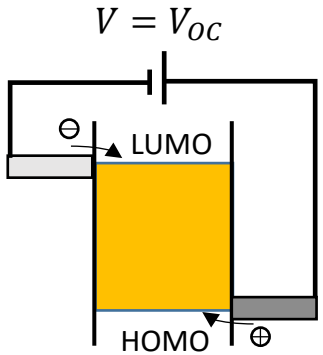


- odd number of linear vinylene units, fully conjugated system flanked by N atoms
- "cyanine limit" : 100 nm red shift per vinylene unit
- counterion for tuning material properties

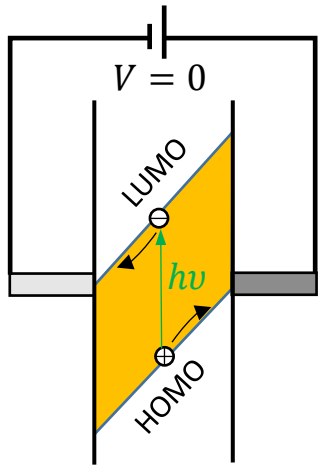
Short circuit current J_{SC}, open circuit voltage V_{OC}, power conversion efficiency η_{PCE}, and external quantum efficiency *EQE* (sometimes also called incident photon to converted electron or IPCE) are defined below:



Open circuit condition:



Short circuit condition: (the current is negative, i.e. is opposite to the forward direction of the diode):



Power conversion efficiency (η_{PCE}):

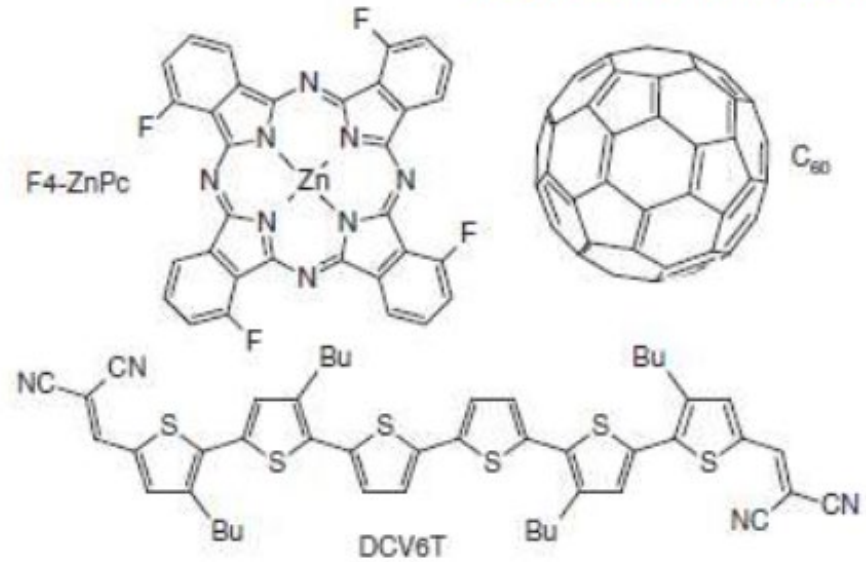
$$\eta_{PCE} = \frac{P^{out}_{electric}}{P^{in}_{photons}} = \frac{V_{\max} I_{\max}}{P^{in}_{photons}} = \frac{FF \cdot V_{OC} I_{SC}}{P^{in}_{photons}}$$

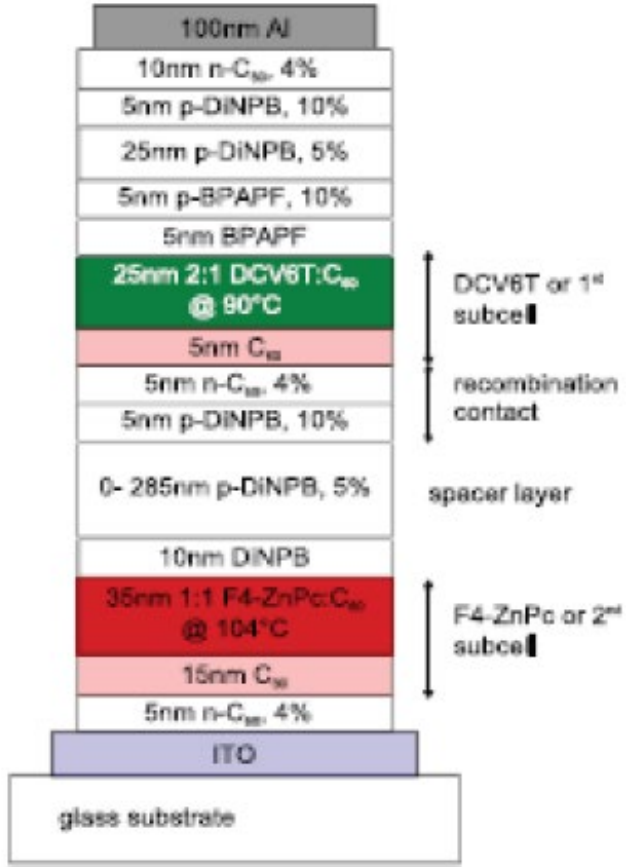
External quantum efficiency *EQE*:

$$EQE = \frac{\text{number of generated electrons}}{\text{number of incident photons}} = \frac{I_{SC}(\lambda) / |e|}{P^{in}_{photons}(\lambda) \lambda / hc} = \frac{I_{SC}(\lambda) \cdot hc}{P^{in}_{photons}(\lambda) \cdot \lambda \cdot e}$$

13.2 % 2016 world record for small molecule multi-junction solar cells (Heliatek press release)

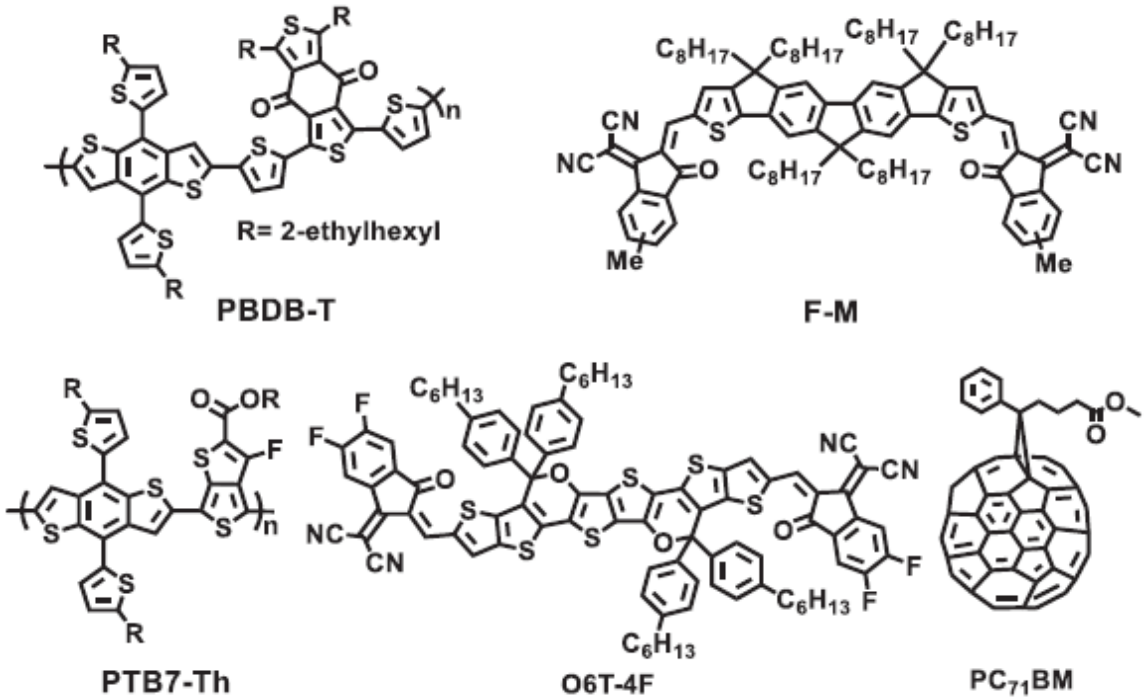
Closest Published Info. – 6.1%

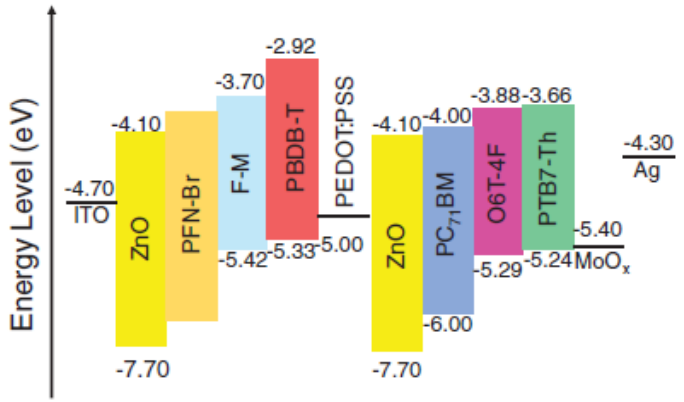


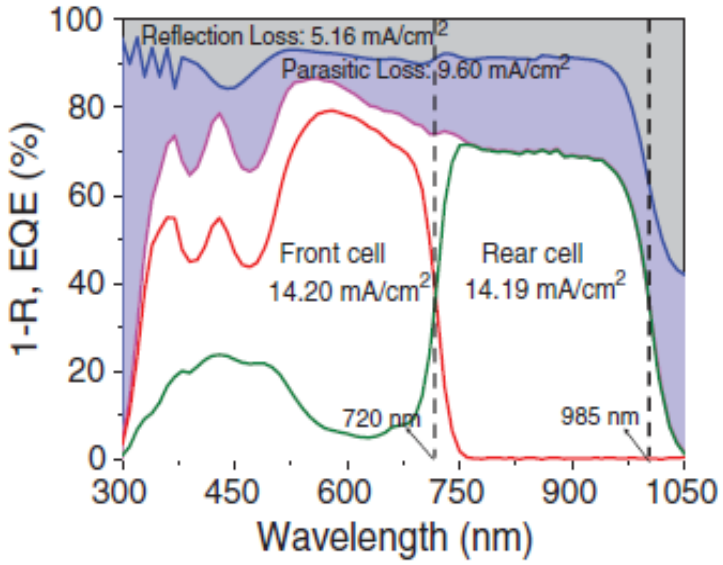


Adv. Funct. Mater. **2011**, *21*, 3019

Organic and solution-processed tandem solar cells with 17.3% record efficiency using non-fullerene acceptors



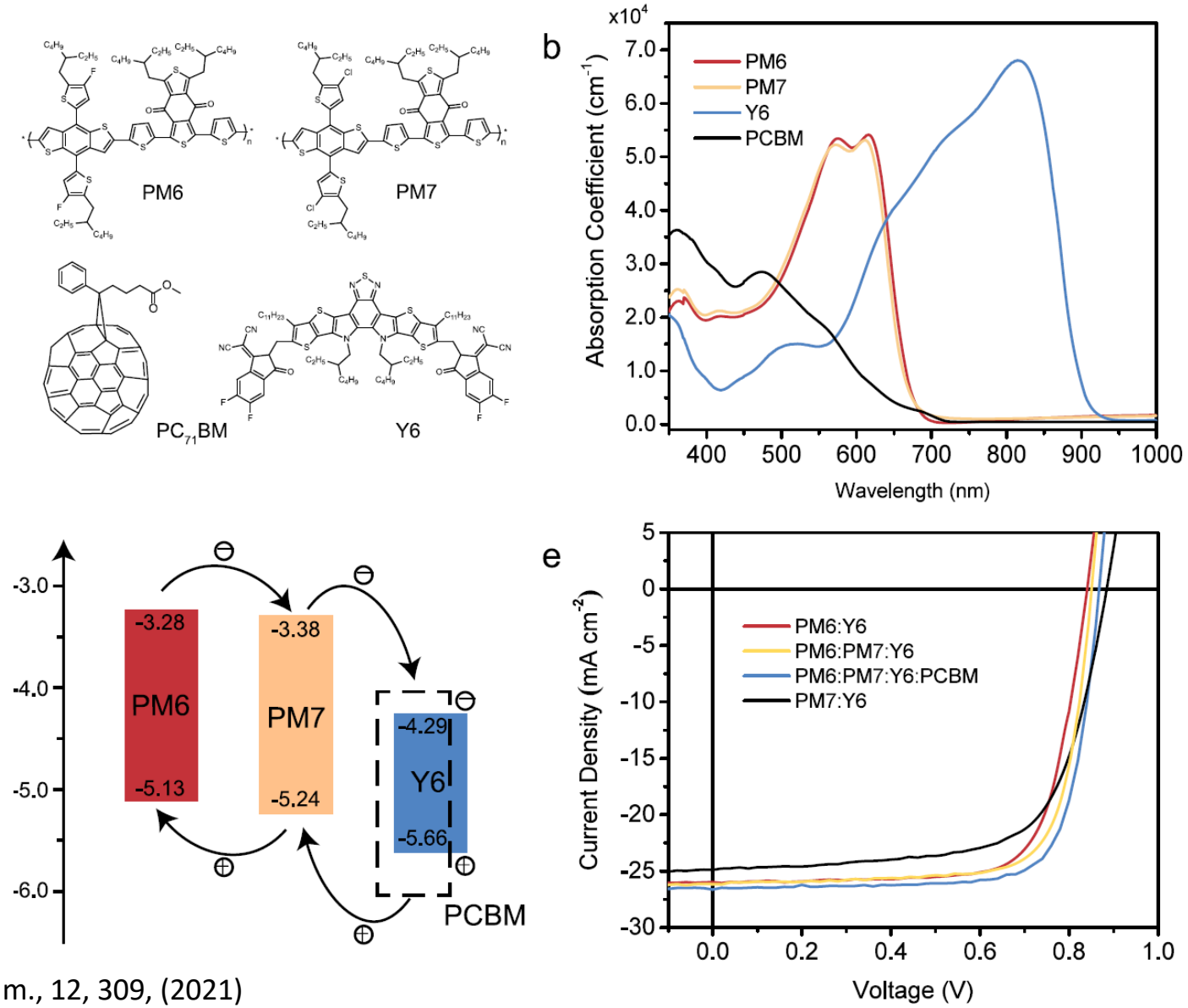




- Broad band absorption
- Perfect current matching
- Optical optimization

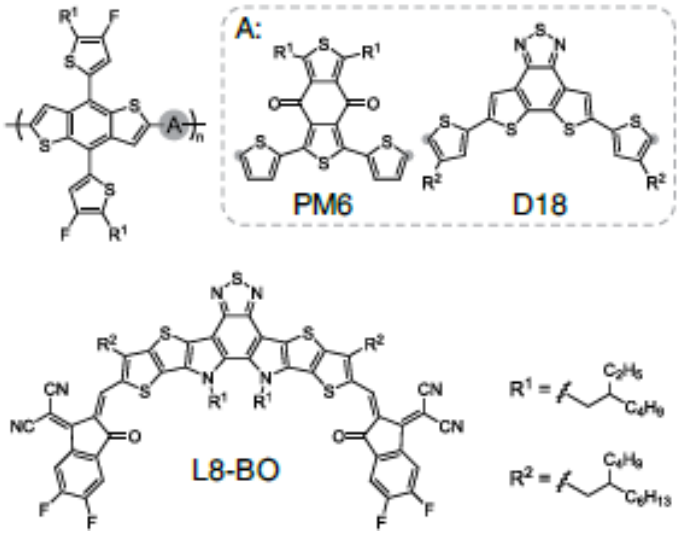
L. Meng et al., Science 361, 1094–1098 (2018)

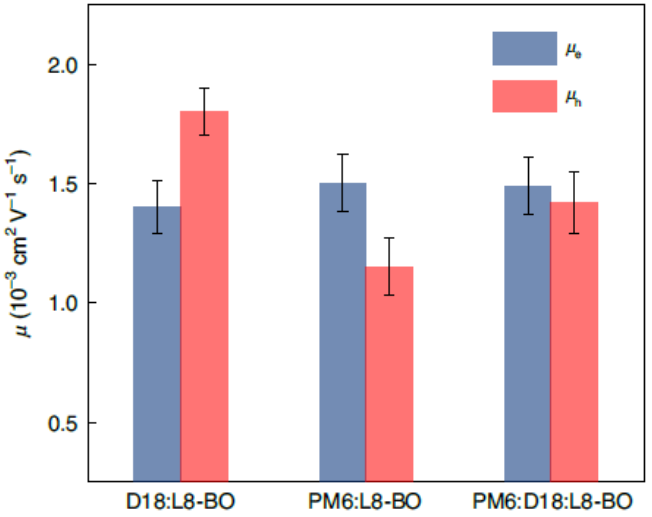
18% efficiency record using quaternary blends for the donor-acceptor heterostructure

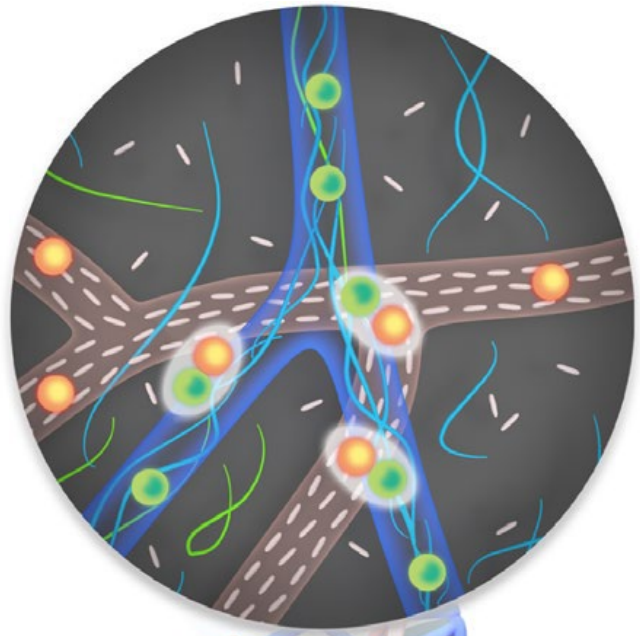


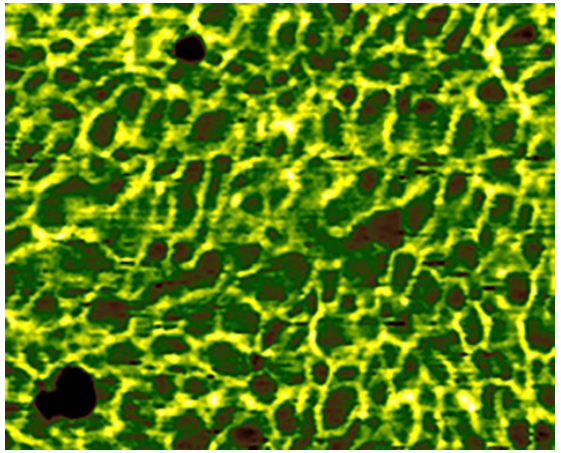
M. Zhang et al, Nature Comm., 12, 309, (2021)

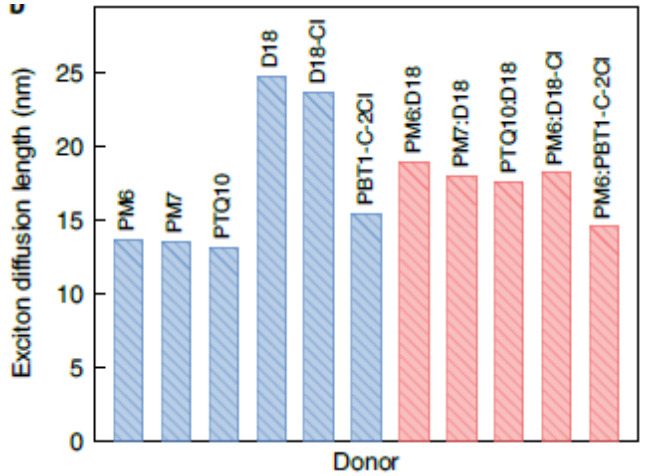
19.3 % efficiency record using ternary blends for the donor-acceptor heterostructure

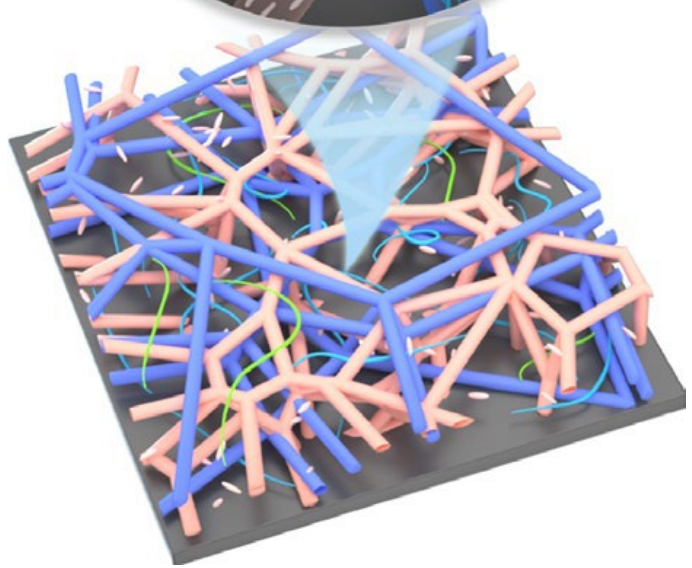






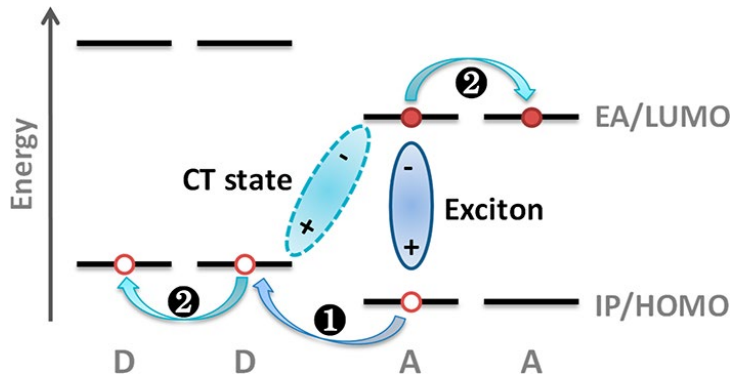


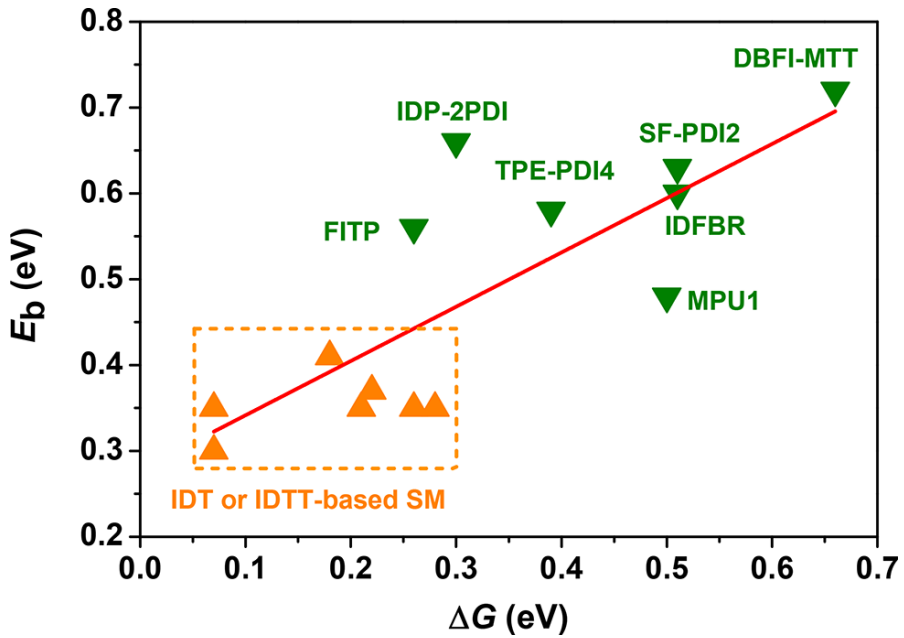


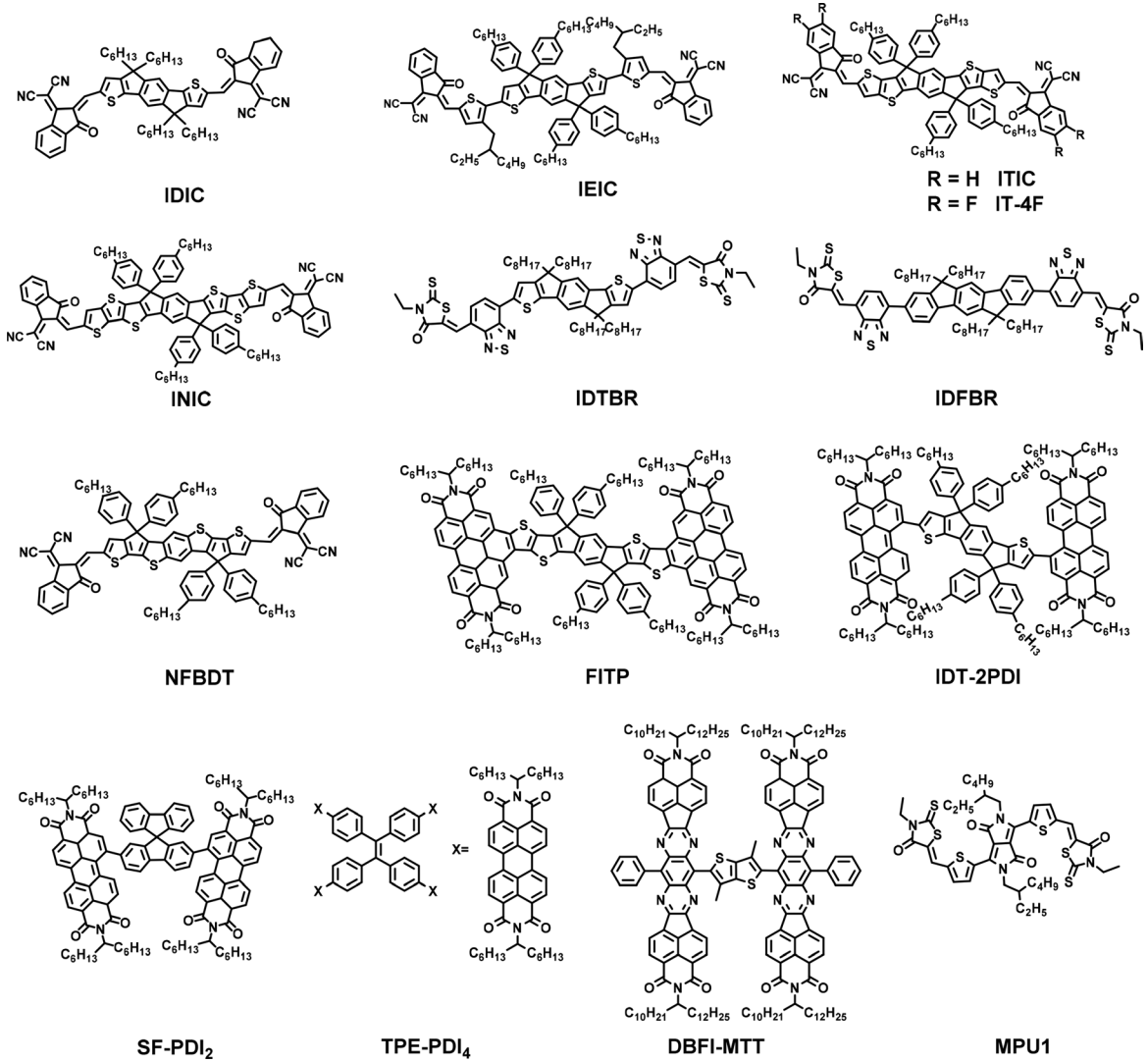


Lei Zhu et al., Nature Materials, 2022, 21(6):1-8

Exciton dissociation in non-fullerene acceptors







ΔG is the (experimental) driving force for hole transfer

E_b is the exciton binding energy

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