Hybrid solar energy conversion

Winterschool 2018

theoretical chemistry & spectroscopy

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Outline

1) Photovoltaic energy conversion

2) Organic solar cells
   - Charge separation
   - Charge transport
   - State of the art and open questions

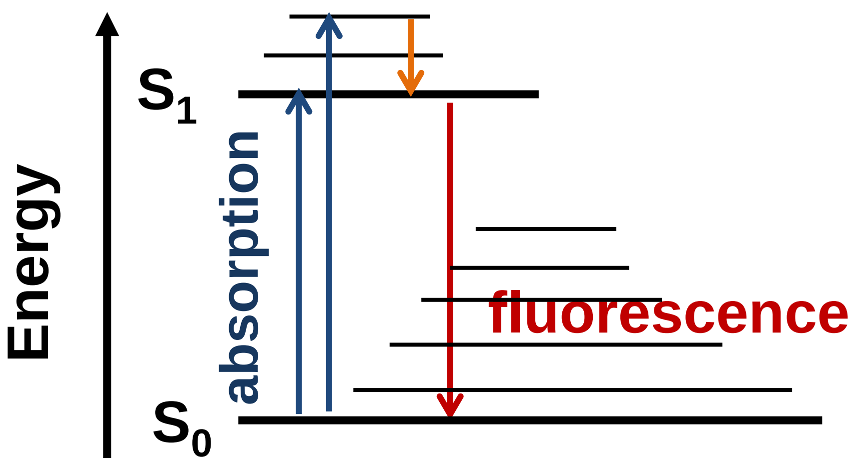
3) Perovskite solar cells

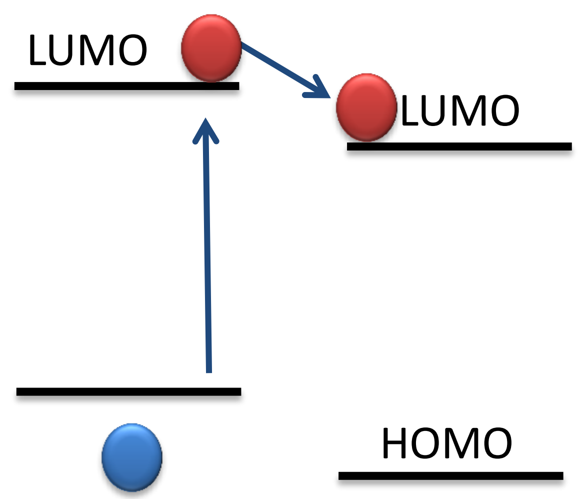
Charge separation in organic solar cells

- Charge separation in OPV: Molecular donor-acceptor systems
    - Example: Saraciftci et al, Science, 1992
- Weak versus strong donor-acceptor systems: The charge transfer exciton (CTE)
    - Measuring CTE strength: Hallermann et al, APL 2008
- What factors influence charge separation?
    - Energetics
    - Vibrational modes
    - Morphology

Charge separation in organic solar cells

- Molecular excitations are neutral
- Tightly bound excitons (0.1 – 1 eV) → **not thermally dissociated!**
- $S_1 \rightarrow S_o \sim 10^{-9} – 10^{-6}$ (s)
- Use an electron acceptor to induce electron transfer





Charge separation in organic solar cells

Charge separation between donor and acceptor

- Photoexcitation of donor
- Electron transfer from Donor LUMO to Acceptor LUMO
- Ionised Donor (cation) and ionised Acceptor (anion)
- Free charge carriers

Charge separation in organic solar cells

Charge transfer complexes

$$D + A = (D^{\delta+} + A^{\delta-})$$

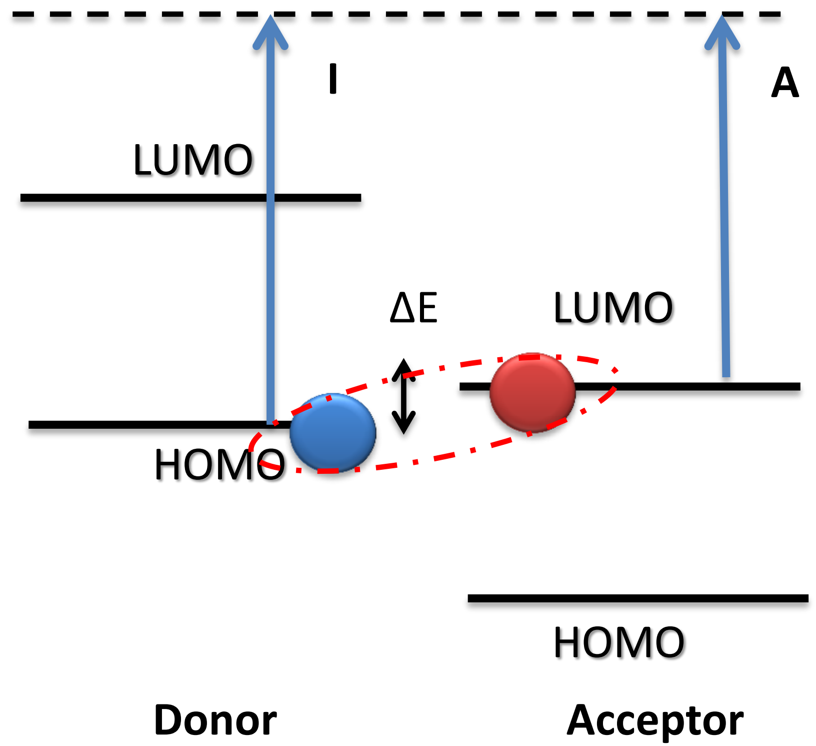
$$0 \geq \delta \geq 1$$

Strong DA complexes

$$0.5 \geq \delta \geq 1$$

Weak DA complexes

$$0 \geq \delta \geq 0.5$$



Charge separation in organic solar cells

Organic photovoltaics

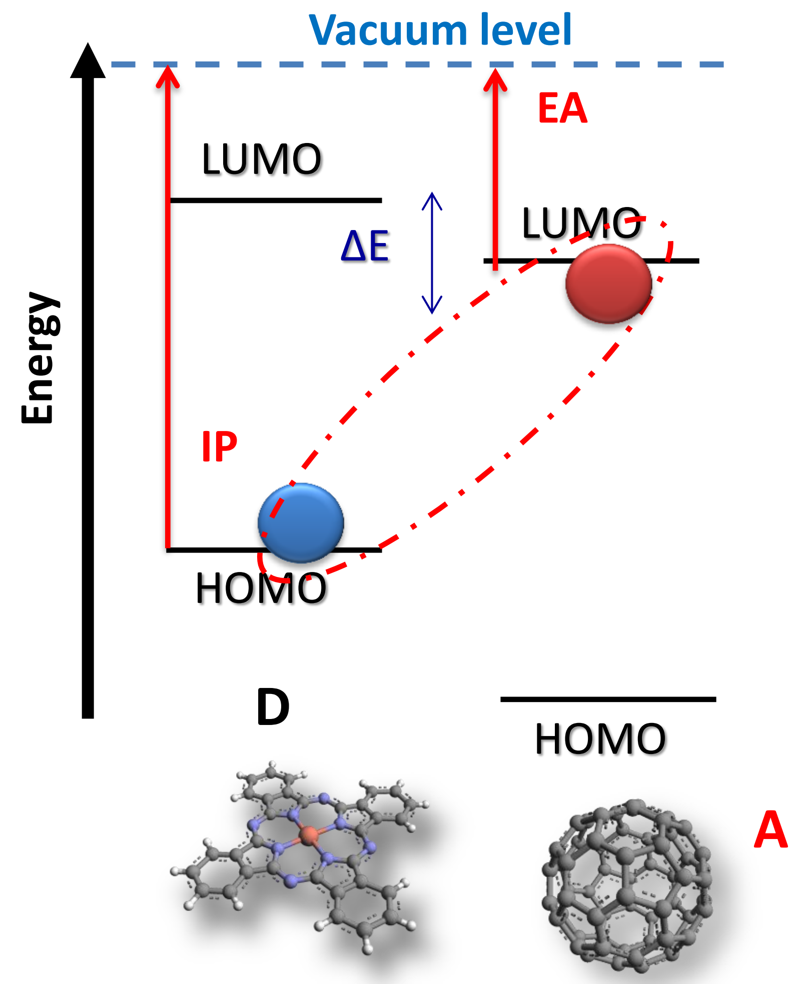
No charge transfer in the ground state

Photoinduced charge transfer from $LUMO_D$ to $LUMO_A$

Optimising ΔE

Overcoming CTE binding energy

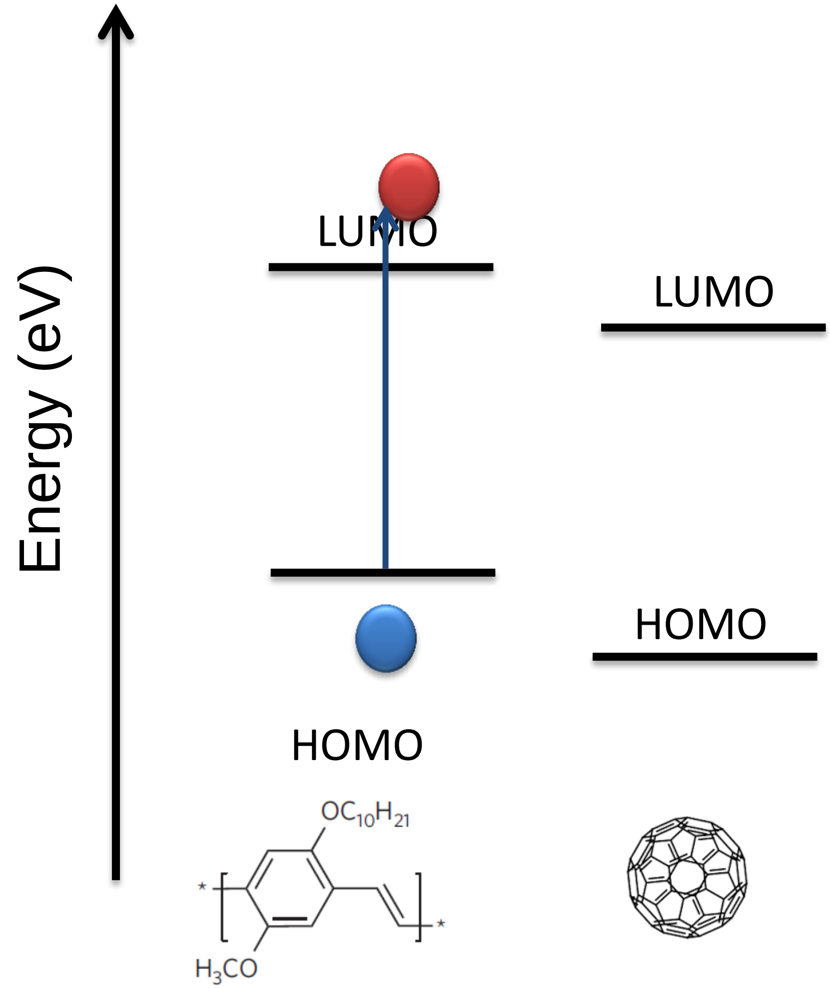
Weak charge transfer complex



Charge separation in organic solar cells

Absorption by donor

$$D + A \rightarrow {}^{1,3}(D^*) + A$$



Saraciftci Science 1992

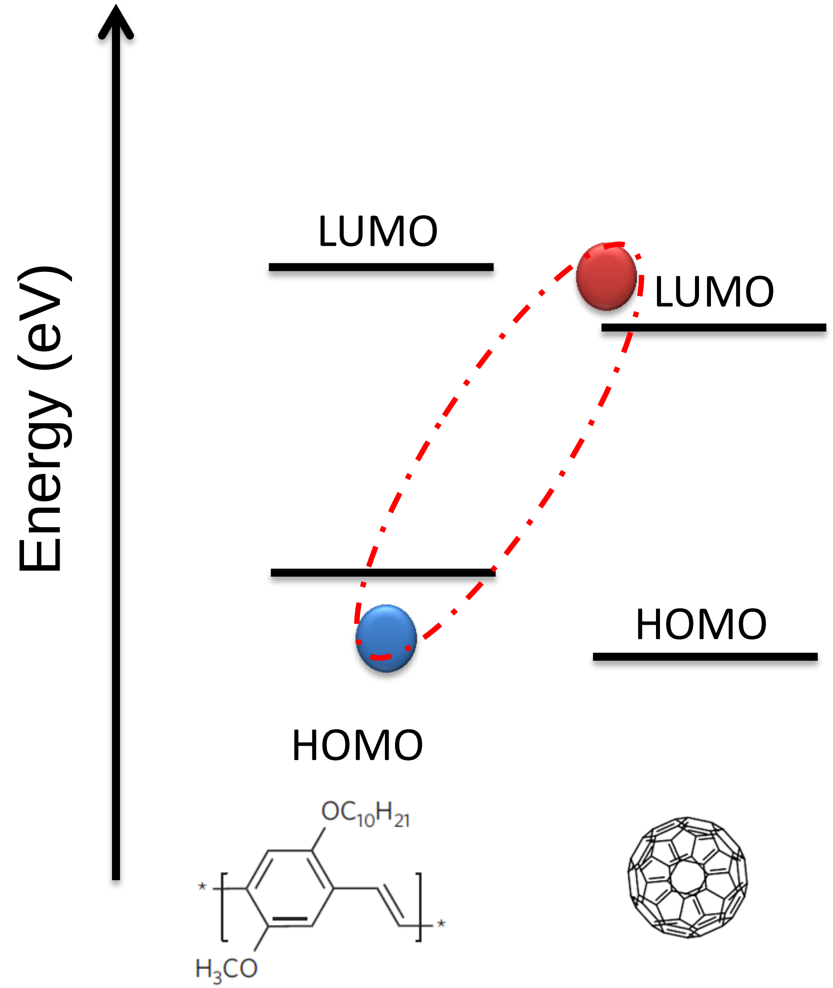
Charge separation in organic solar cells

Absorption by donor

$$D + A \rightarrow {}^{1,3}(D^{*}) + A$$

CTE formation

$${}^{1,3}(D^{*}) + A \rightarrow {}^{1,3}(D + A)^{*}$$



Saraciftci Science 1992

Charge separation in organic solar cells

Absorption by donor

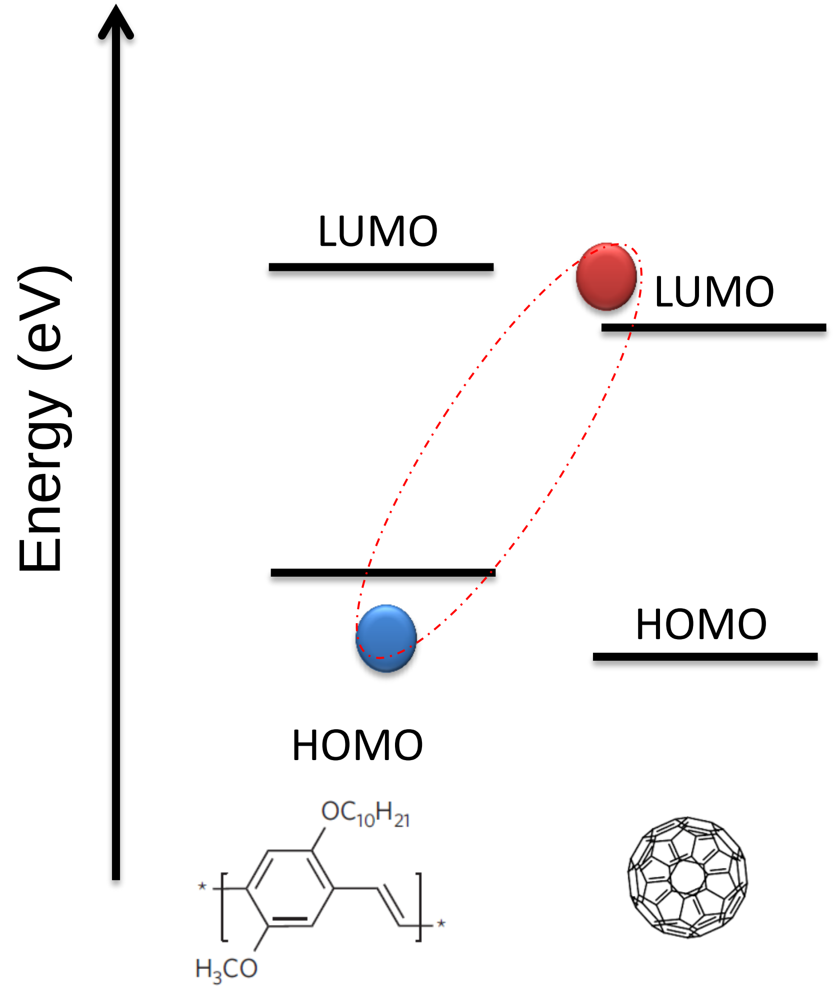
$$D + A \rightarrow {}^{1,3}(D^{*}) + A$$

CTE formation

$${}^{1,3}(D^{*}) + A \rightarrow {}^{1,3}(D + A)^{*}$$

Charge transfer

$${}^{1,3}(D + A) \rightarrow {}^{1,3}\left(D^{\delta+} + A^{\delta-}\right)^{*}$$



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Charge separation in organic solar cells

Absorption by donor

$$D + A \rightarrow {}^{1,3}(D^*) + A$$

CTE formation

$${}^{1,3}(D^*) + A \rightarrow {}^{1,3}(D + A)^*$$

Charge transfer

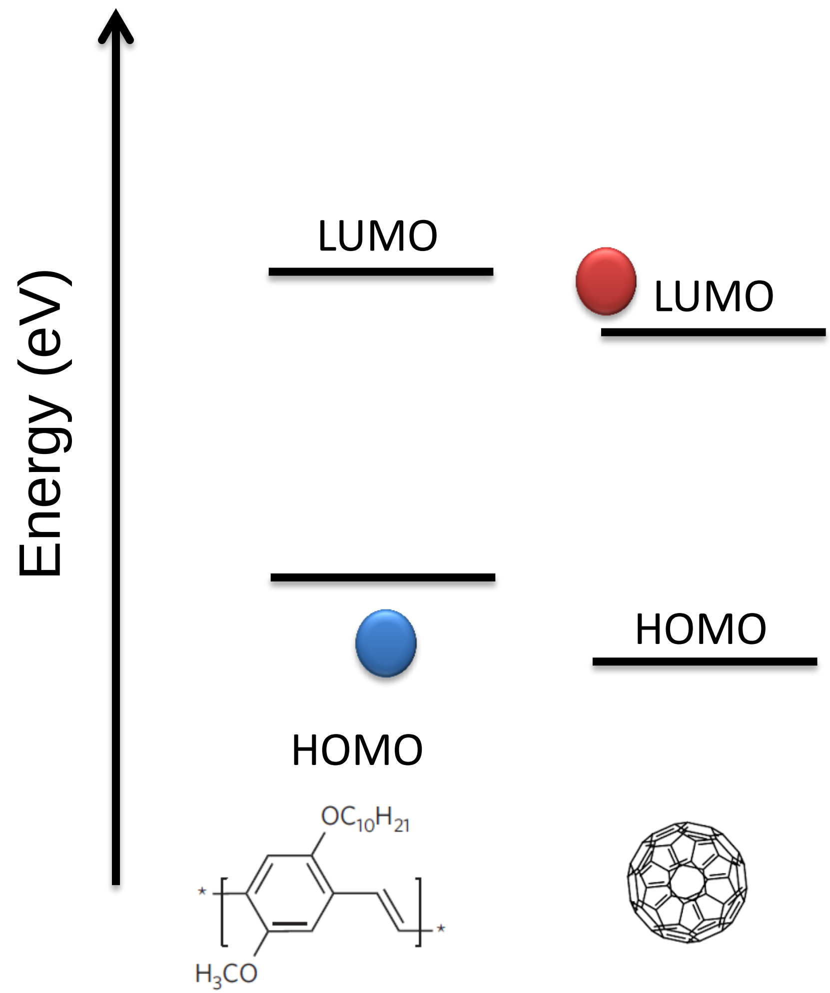
$${}^{1,3}(D + A) \rightarrow {}^{1,3}\left(D^{\delta+} + A^{\delta-}\right)^*$$

Ion pair formation

$${}^{1,3}\left(D^{\delta+} + A^{\delta-}\right)^* \rightarrow {}^{1,3}(D^{+\cdot} + A^{-\cdot})^*$$

Charge separation

$${}^{1,3}(D^{+\cdot} + A^{-\cdot})^* \rightarrow D^{+\cdot} + A^{-\cdot}$$



Saraciftci Science 1992

Charge separation in organic solar cells

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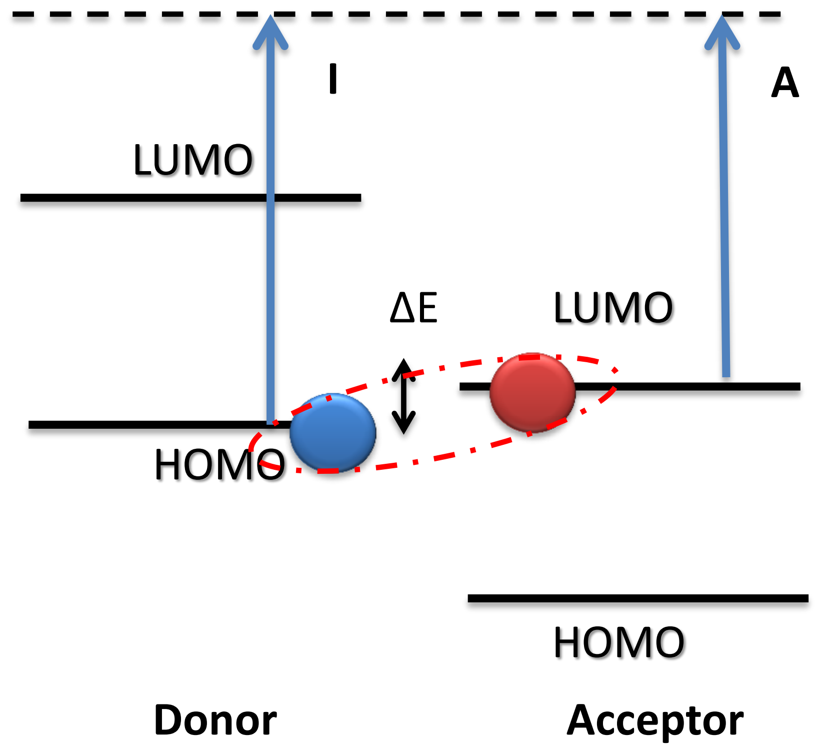
Charge transfer exciton

Energetic picture

Charge separation is driven by the gain in electrostatic potential from free charge

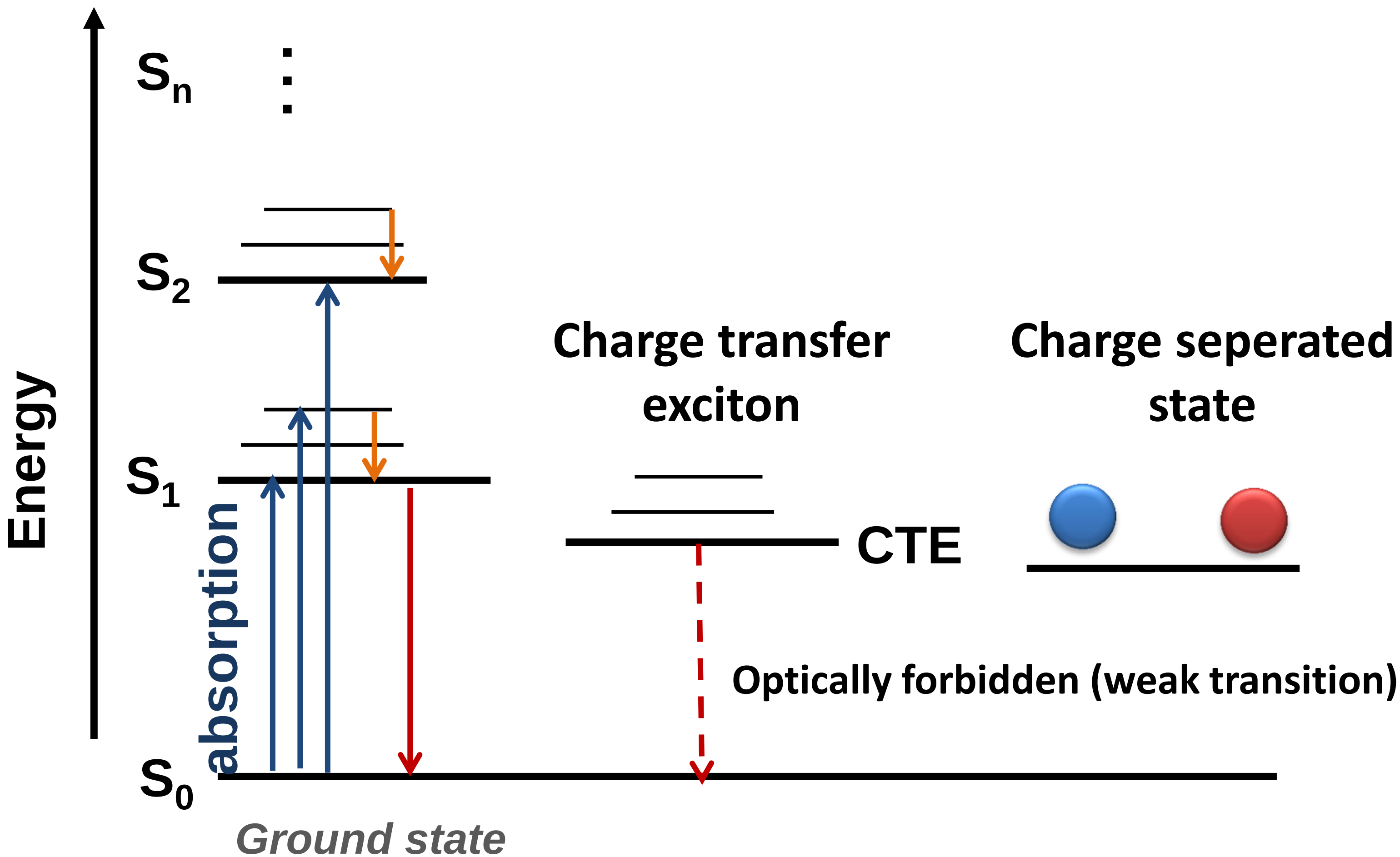
$$E_{CT} = E_{A,Acc} - E_{I,Don} + J$$

A = electron affinity
I = Ionisation potential
J = electrostatic potential



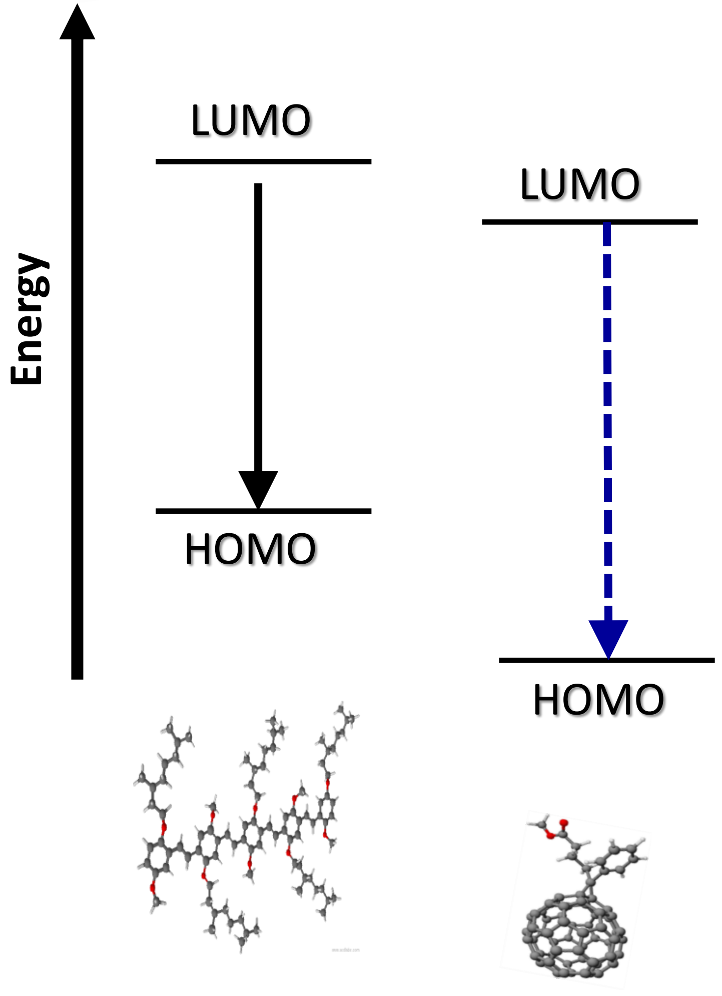
Charge transfer exciton

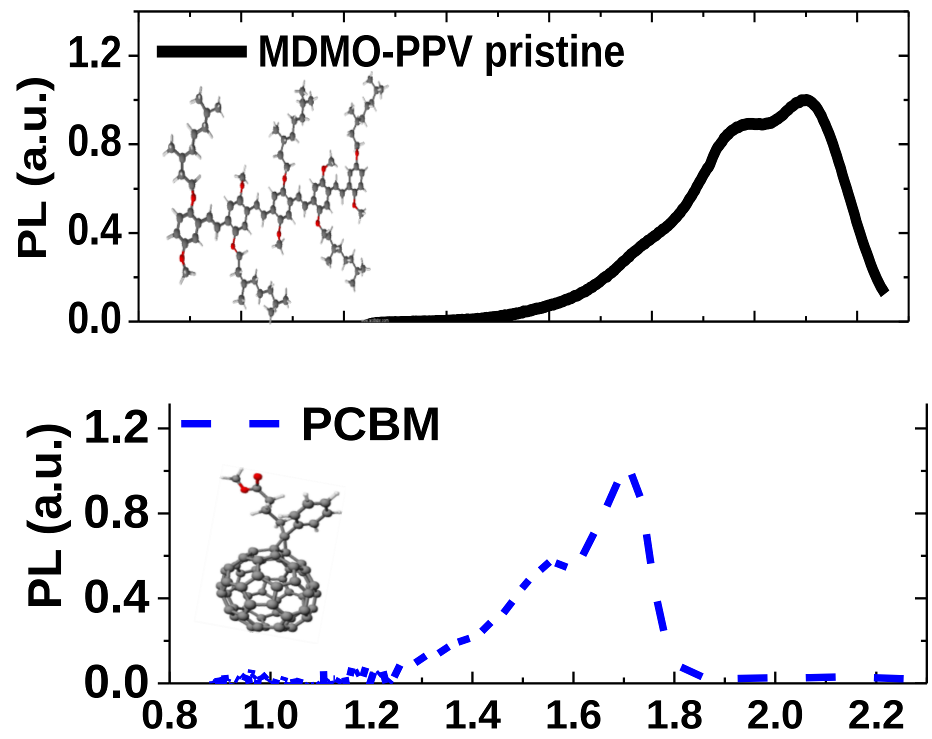
Molecular excitation



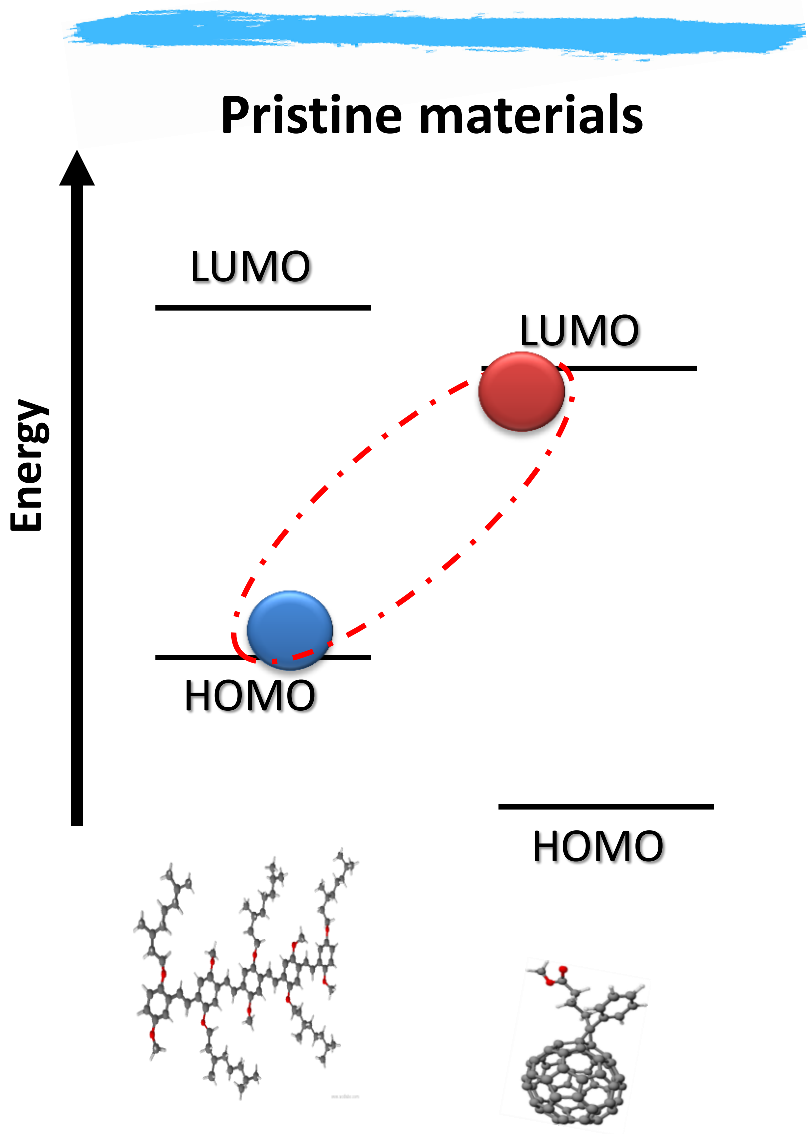
Charge transfer exciton

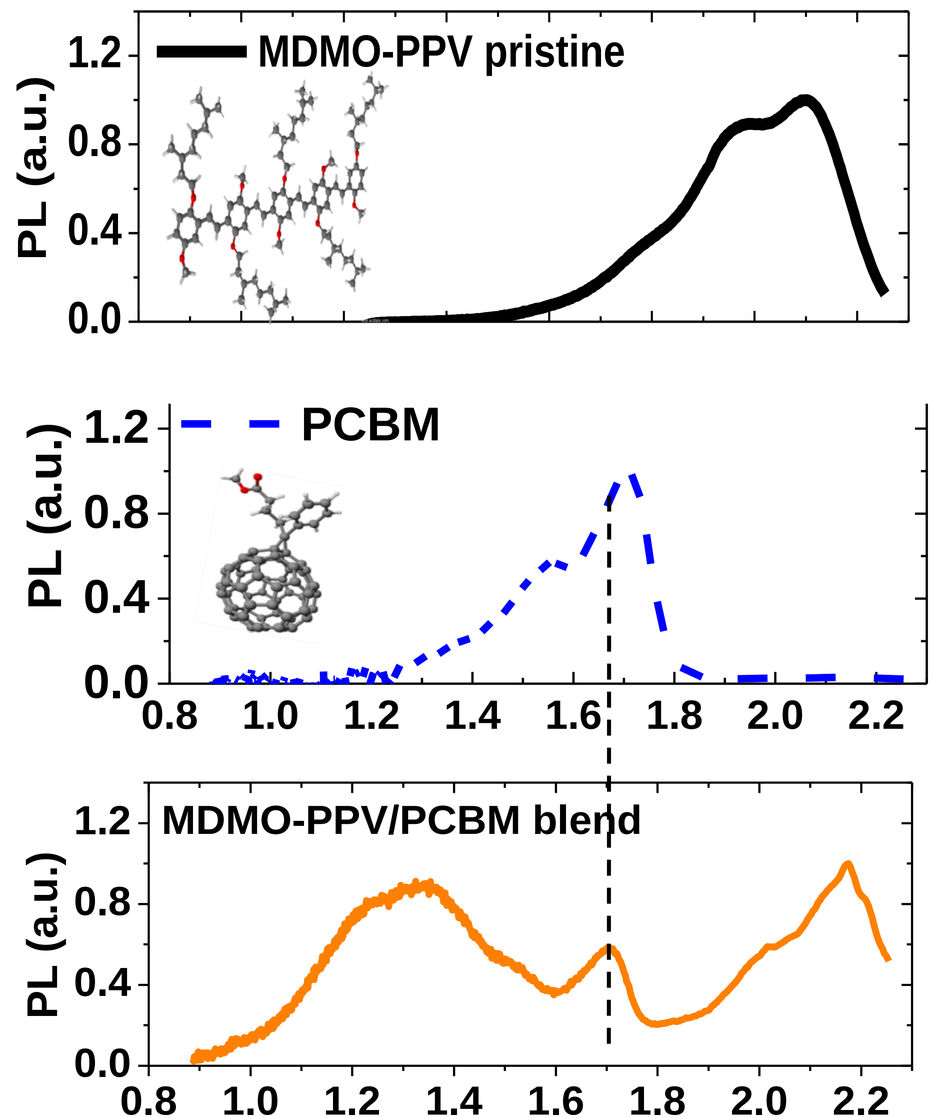
Pristine materials



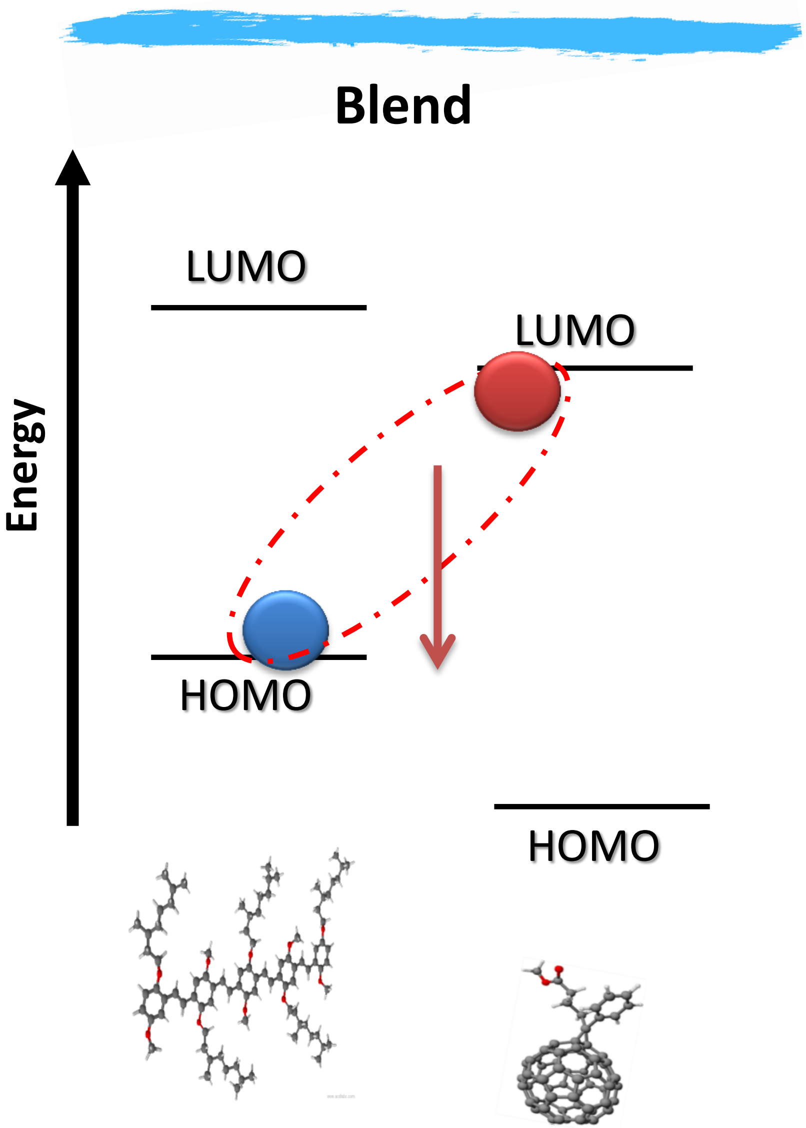


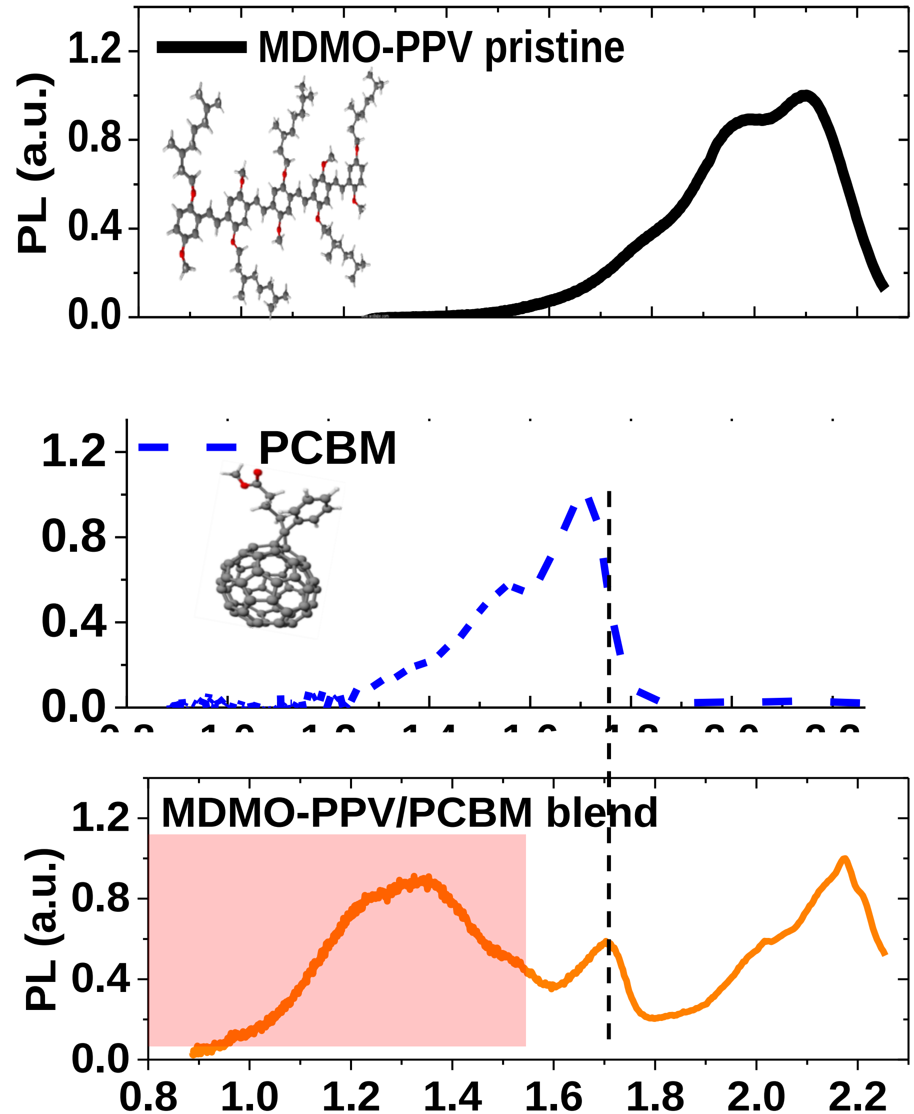
Charge transfer exciton



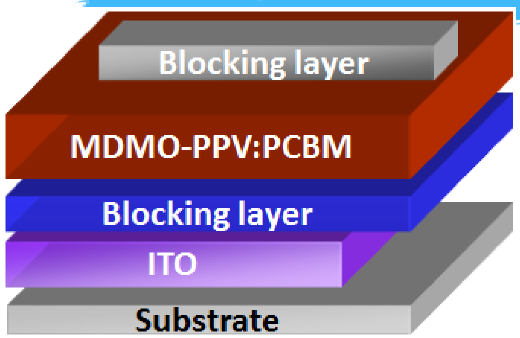


Charge transfer exciton



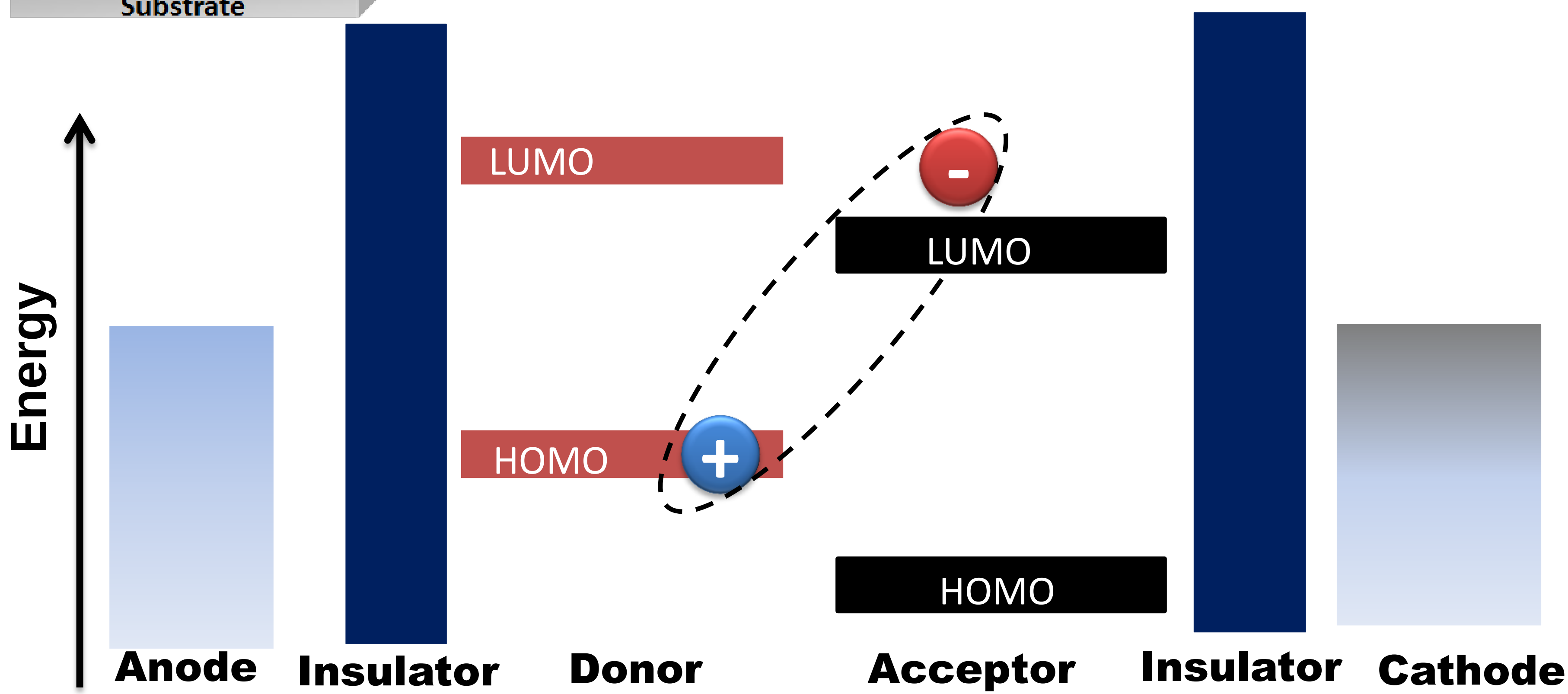


Charge transfer exciton – binding energy

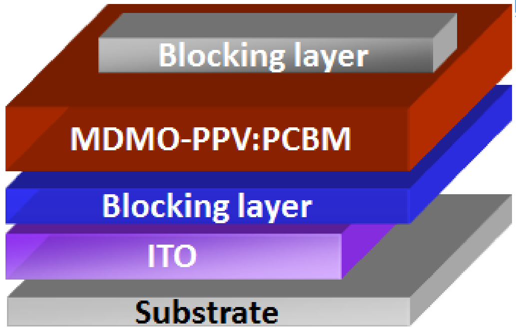


Electroluminescence measurements

Diode with ***blocking contacts*** (no charge injection or extraction)



Charge transfer exciton – binding energy

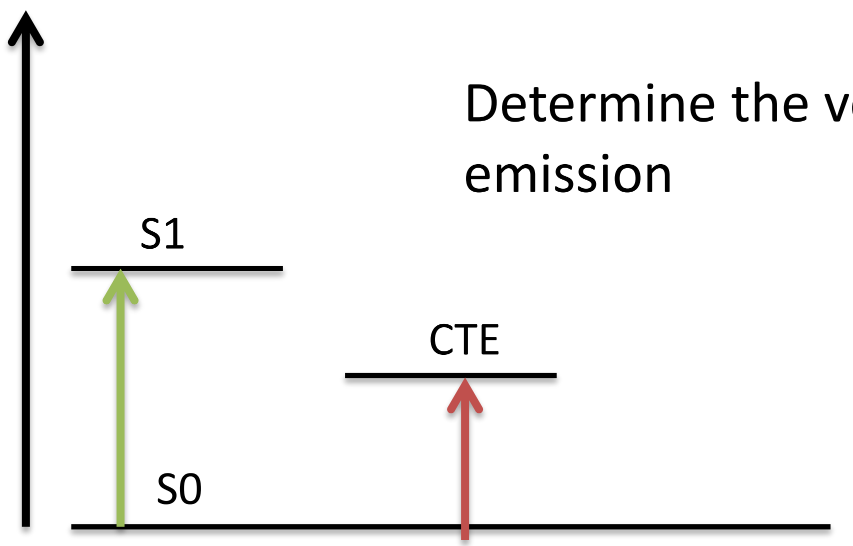


Electroluminescence measurements

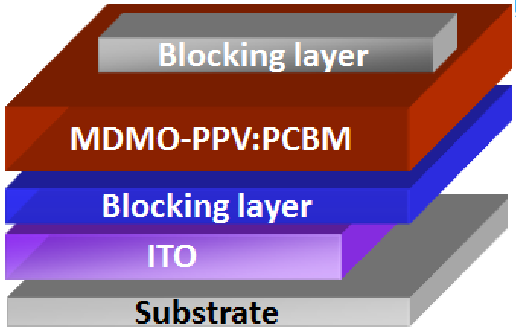
Diode with ***blocking contacts*** (no charge injection or extraction)

Photoexcite the polymer:fullerene blend with ***sub-bandgap light*** (800 nm)

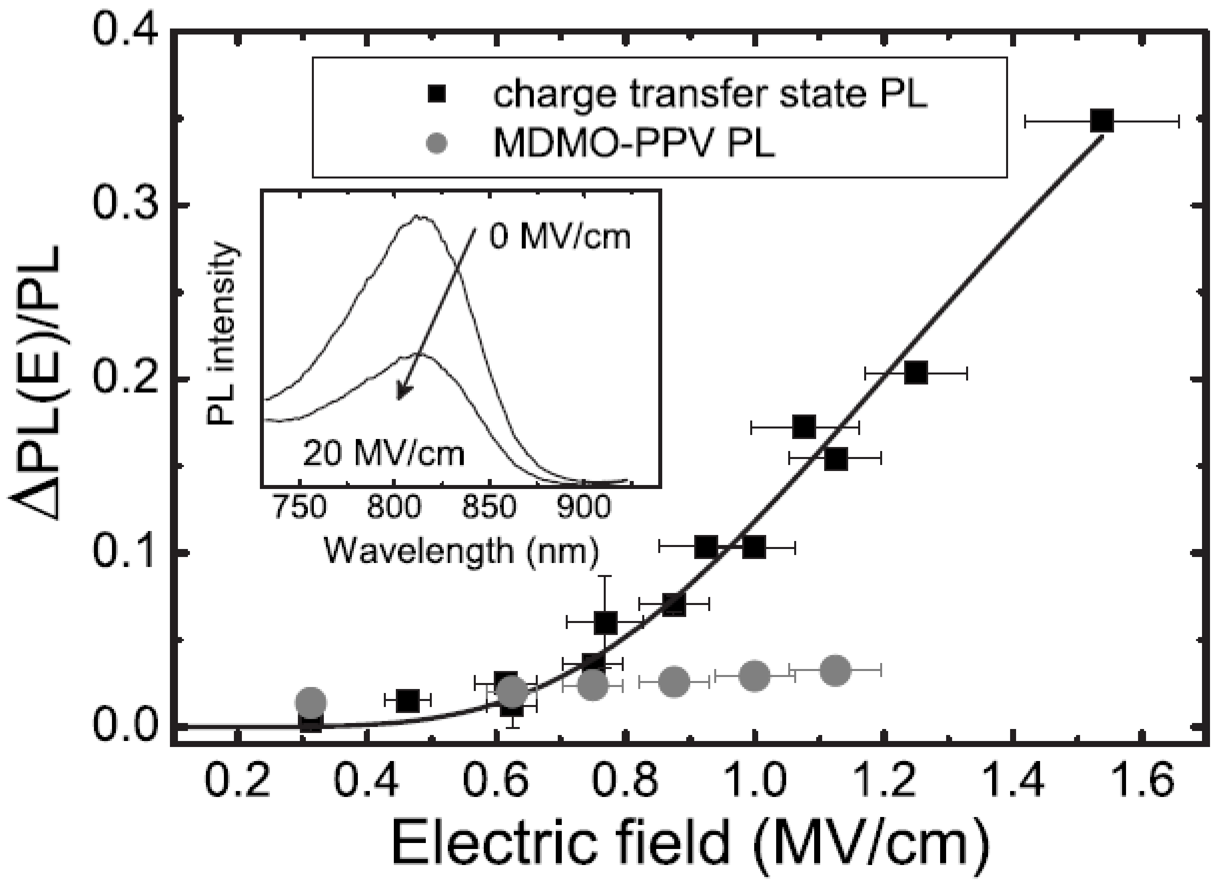
Determine the voltage-dependence of the CTE emission



Charge transfer exciton – binding energy



CTE binding in MDMO-PPV:PCBM 130 meV



Hallermann et al, APL, 2008

Charge separation in organic solar cells

- Charge separation in OPV: Molecular donor-acceptor systems
    - Example: Saraciftci et al, Science, 1992
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- What factors influence charge separation?
    - → Energetics
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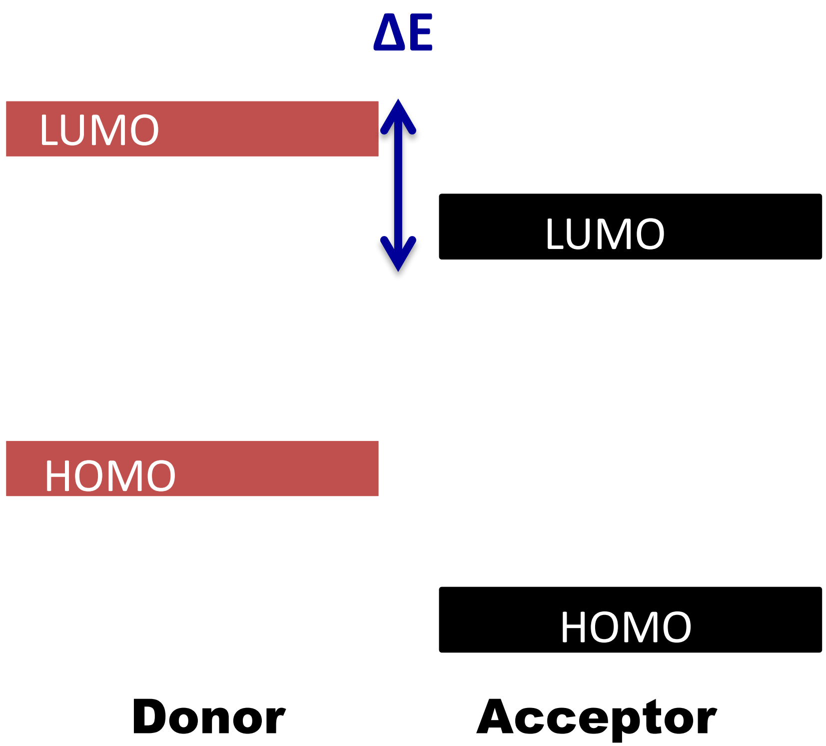
Charge separation in organic solar cells

CTE binding energy versus ΔE

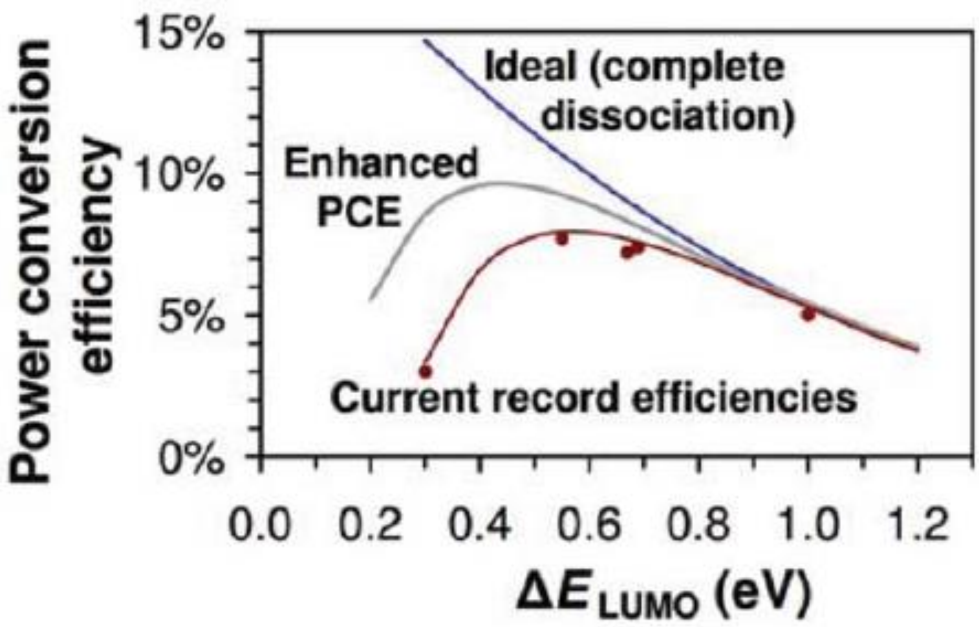
Large ΔE – increase in photocurrent, loss in photovoltage

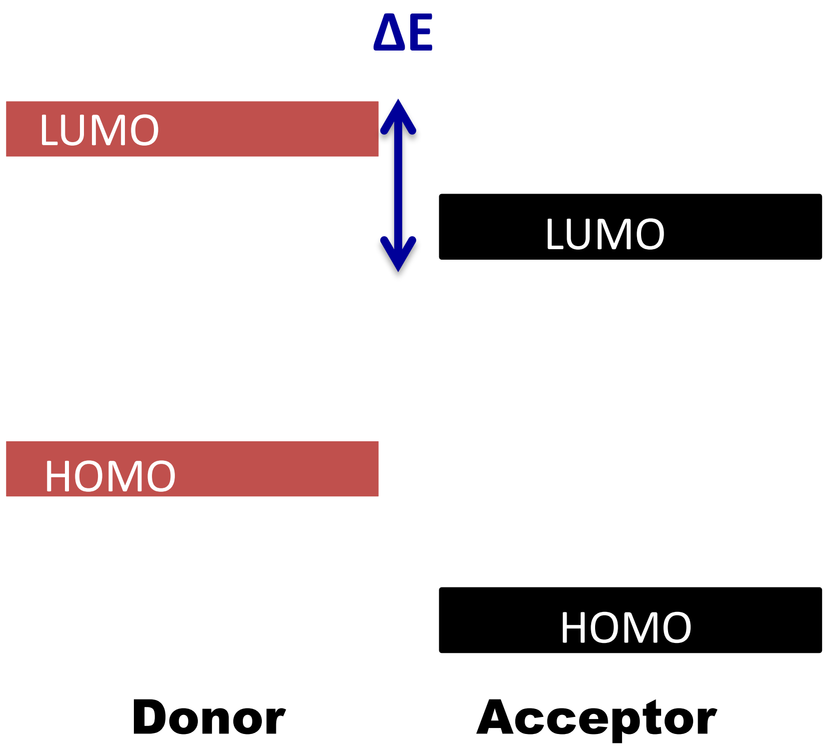
Small ΔE – increase in photovoltage, loss in photocurrent

ΔE – driving force or driving energy



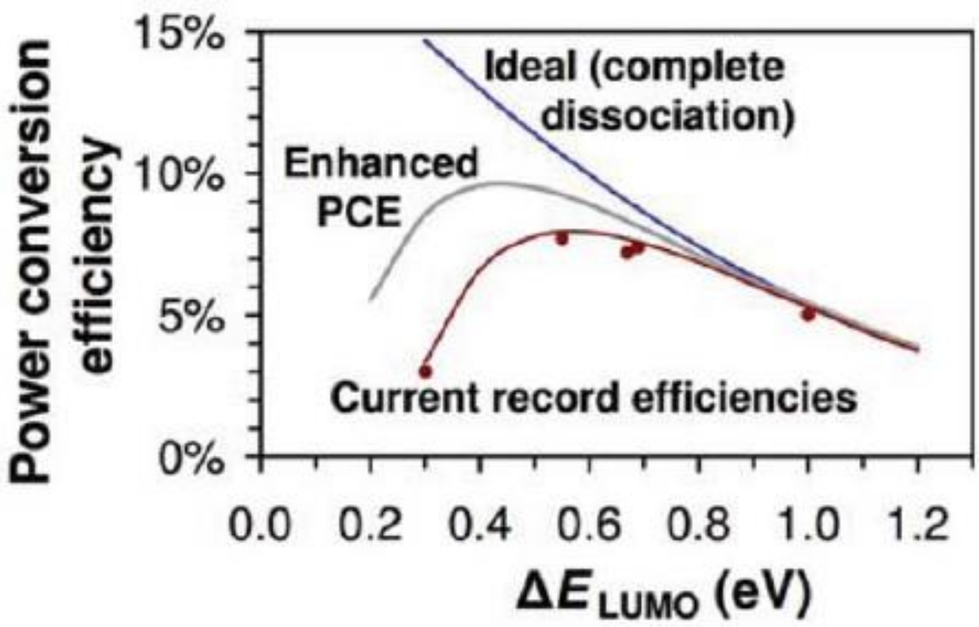
Charge separation in organic solar cells

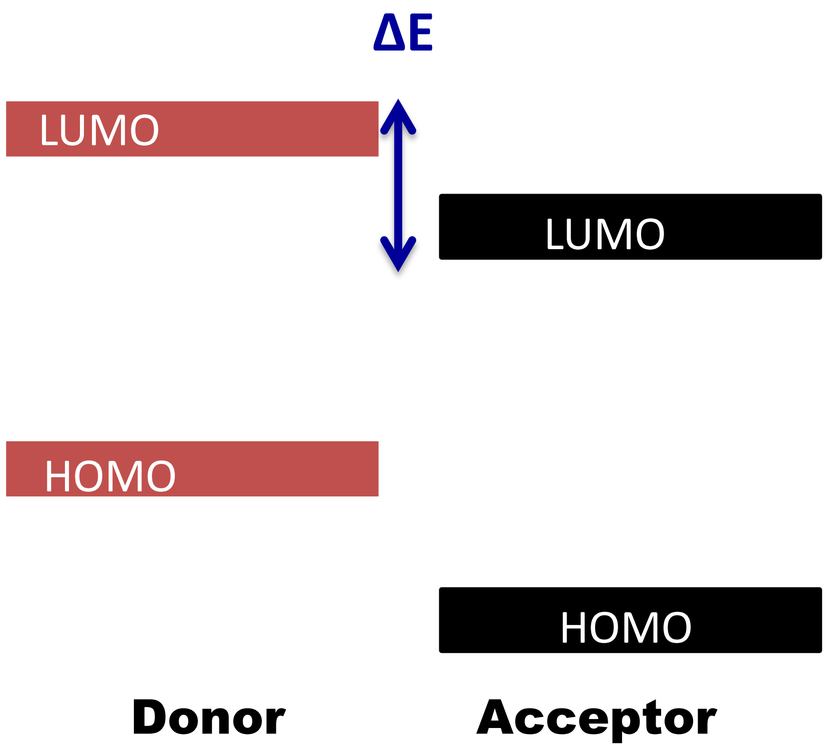




Ideal: charge separation efficiency not dependent on ΔE

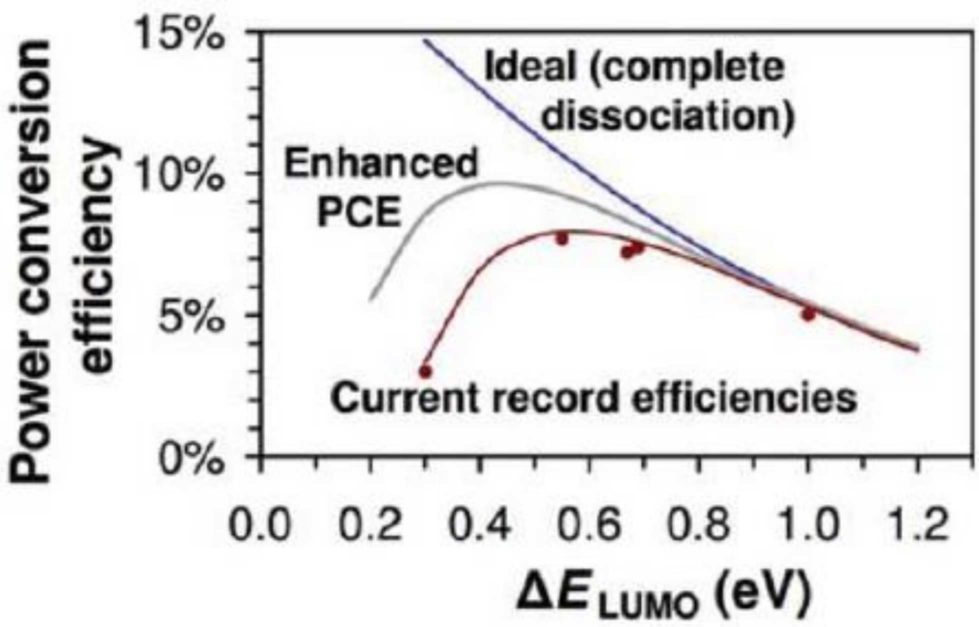
Charge separation in organic solar cells

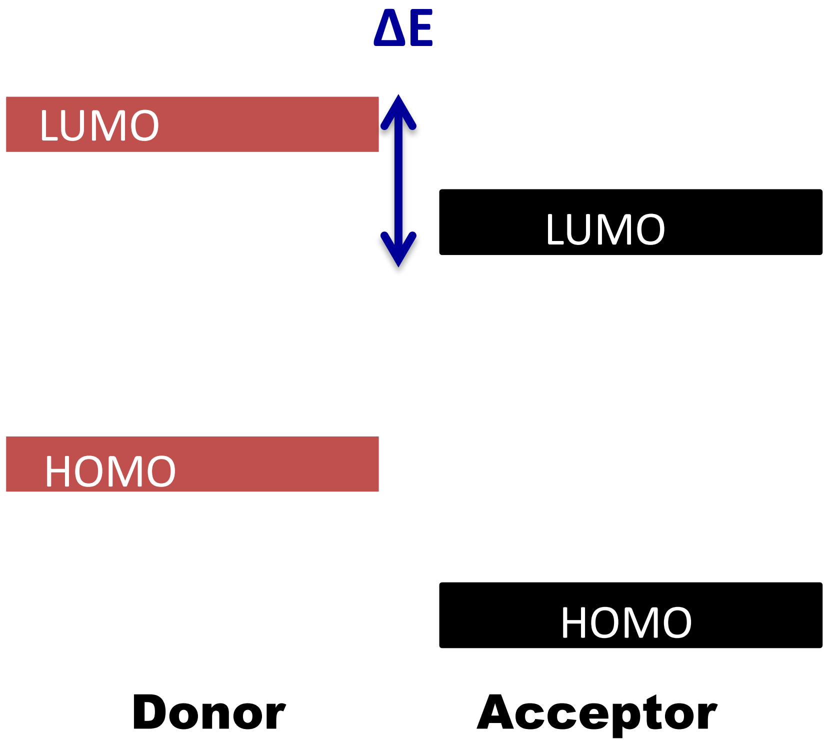




Current measured efficiencies (dots) in 2011

Charge separation in organic solar cells





Predicted theoretical limit

Charge separation in organic solar cells

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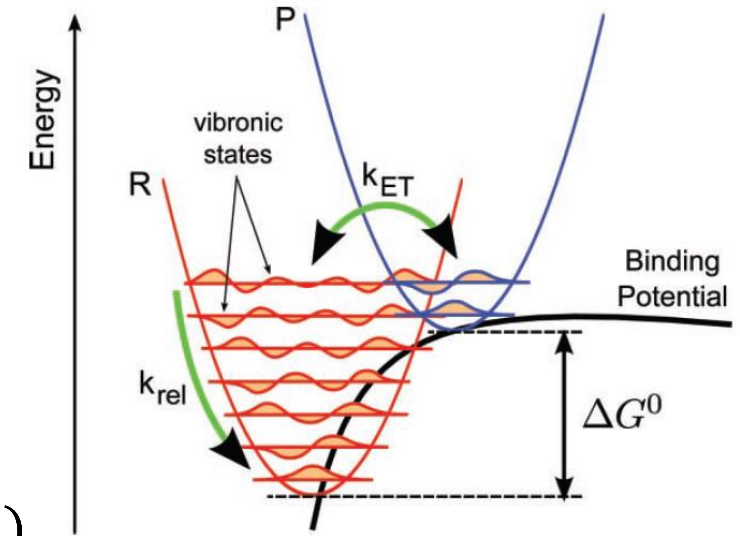
- ❑ What factors influence charge separation?
    - Energetics
    - → Vibrational modes
    - Morphology

Charge separation in organic solar cells

K_{ET} proportional to

- overlap between vibrational states of R and P and energy difference between vibrational states of R and P

$$k_{ET} = \frac{2\pi}{\hbar} |\langle R|H|P\rangle|^2 \, |\langle R_{vib}|P_{vib}\rangle|^2 \, \delta(E_R - E_P)$$



K_{ET} – probability for electron transfer
R – reactant
P – product
ΔG – change in Gibbs free energy

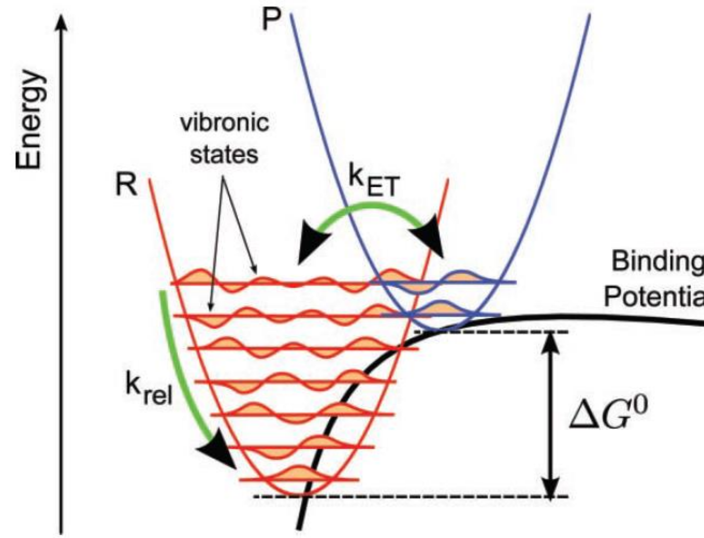
Deibel Adv Mater 2010

Charge separation in organic solar cells

$$k_{ET} = \frac{2\pi}{\hbar} |\langle R|H|P\rangle|^2 \, |\langle R_{vib}|P_{vib}\rangle|^2 \, \delta(E_R - E_P)$$

Becomes

$$k_{ET} = \frac{2\pi}{\hbar} H_{RP}{}^2 \left(\frac{1}{4\pi\lambda kT}\right)^2 (FC)$$



- H_{RP} – coupling matrix between states
- λ – reorganisation energy upon electron transfer
- FC – Franck-Condon factor –all overlap integrals between R ground state and P states
- $FC \sim \left(\frac{\Delta G^o}{\lambda kT}\right)$

K_{ET} – probability for electron transfer
R – reactant
P – product
ΔG – change in Gibbs free energy

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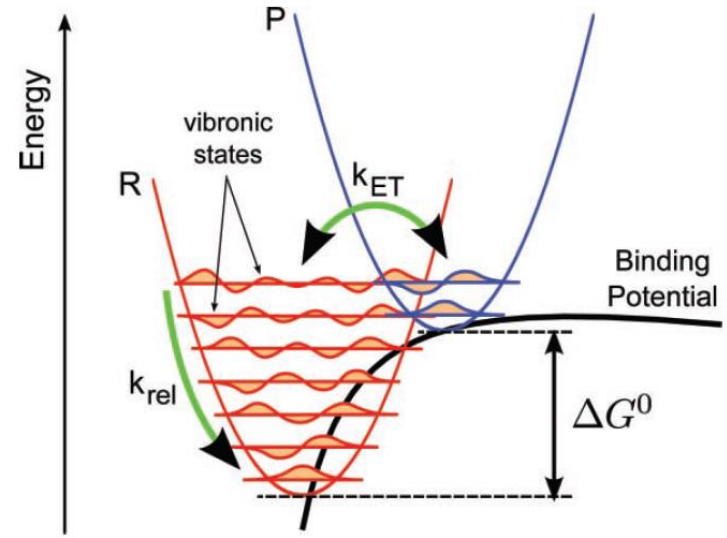
Charge separation in organic solar cells

"HOT" CTE versus "COLD" CTE states

Excess energy (hot CTE) can help electron transfer by

- Overcoming Coulombic binding of charge
- Overcoming reorganisation energy λ

Experimental evidence that hot CTE states dissociate more efficiently than cold (thermally relaxed) CTE



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Charge separation in organic solar cells

The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors

Artem A. Bakulin,[1]* Akshay Rao,[1] Vlad G. Pavelyev,[2] Paul H. M. van Loosdrecht,[2] Maxim S. Pshenichnikov,[2] Dorota Niedzialek,[3] Jérôme Cornil,[3] David Beljonne,[3] Richard H. Friend[1]†

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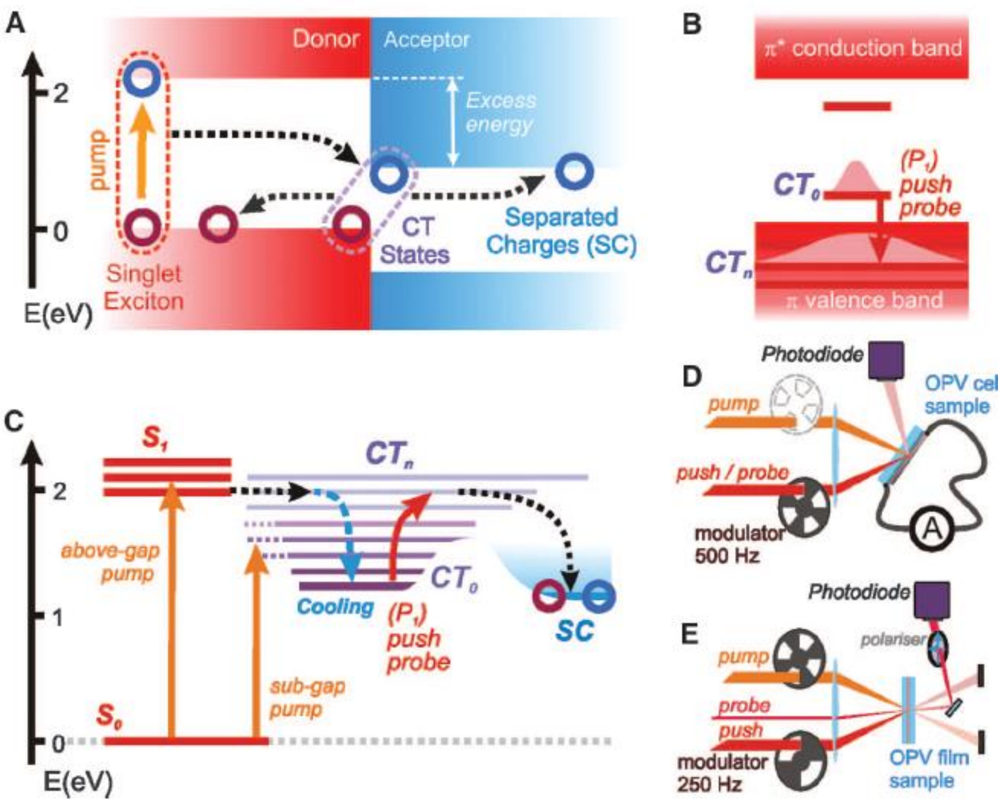

Compare commonly used donor-acceptor systems

Photo-excite donor

Monitor photocurrent
- With IR push = “hot” CTE
- Without IR push = “cold” CTE

Charge separation in organic solar cells

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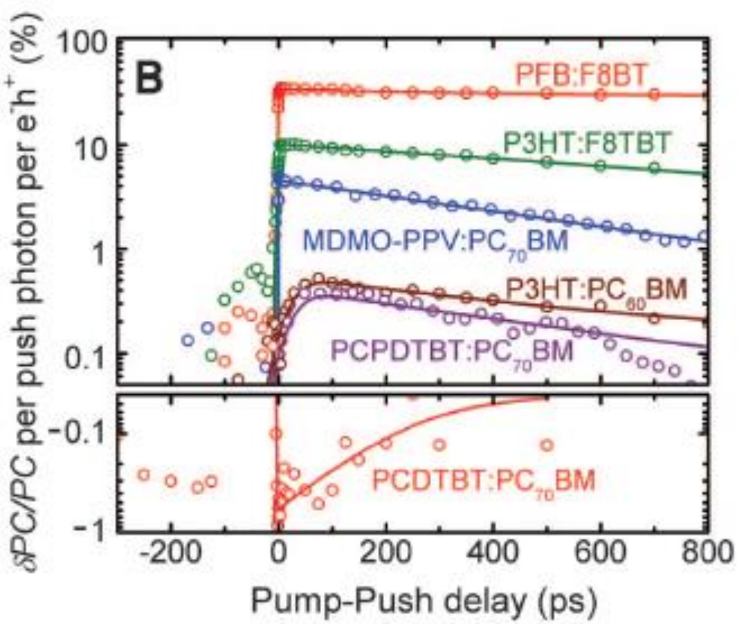

← No influence of IR push

← Influence of IR push

Process of charge separation is dependent on system!

Charge separation in organic solar cells

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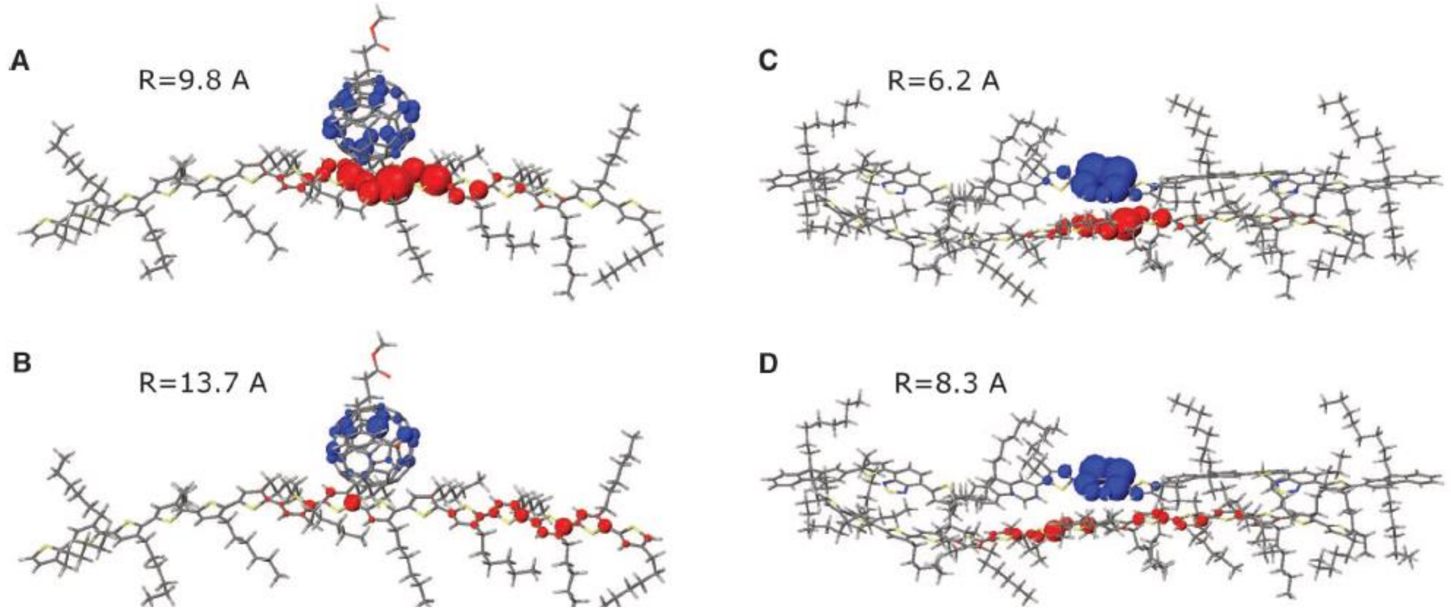

Cold CTE

Hot CTE

IR push can be used to increase distance between electron and hole

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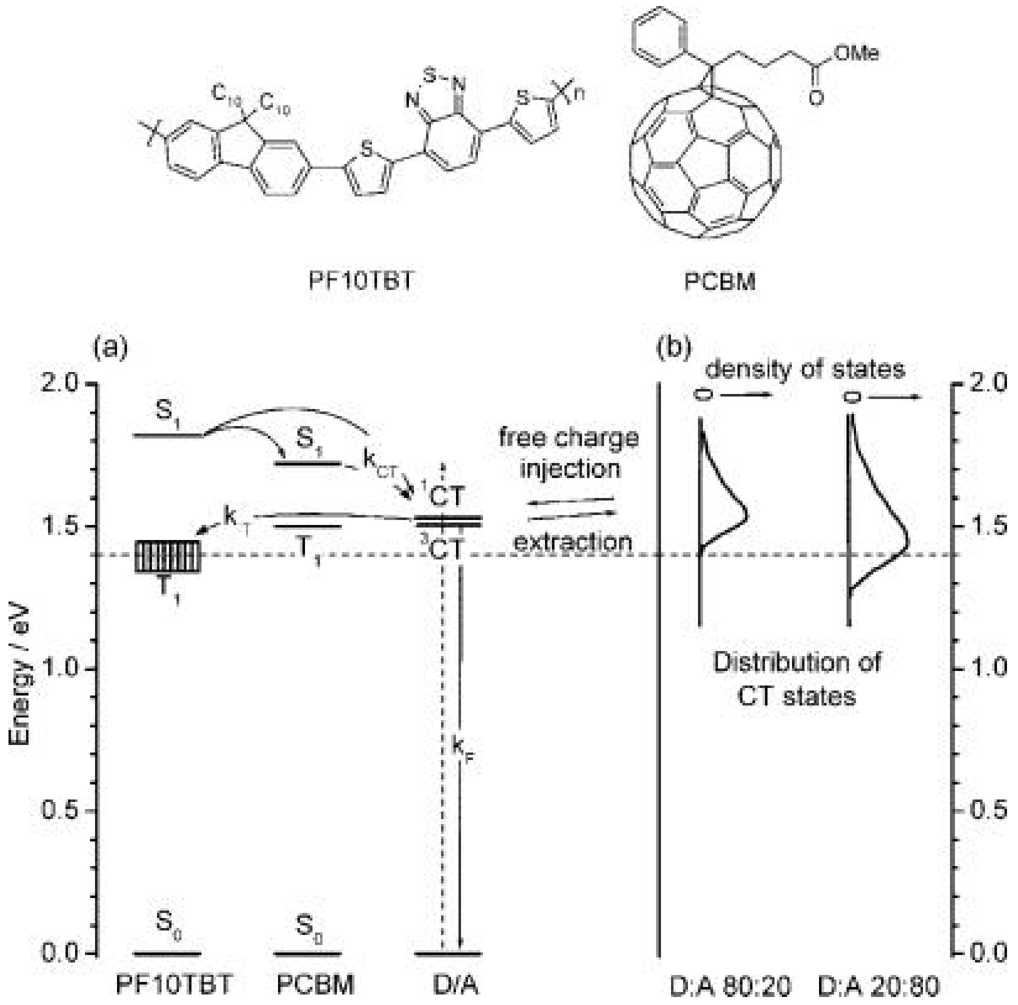
Charge separation in organic solar cells

DoS at the donor-acceptor interface

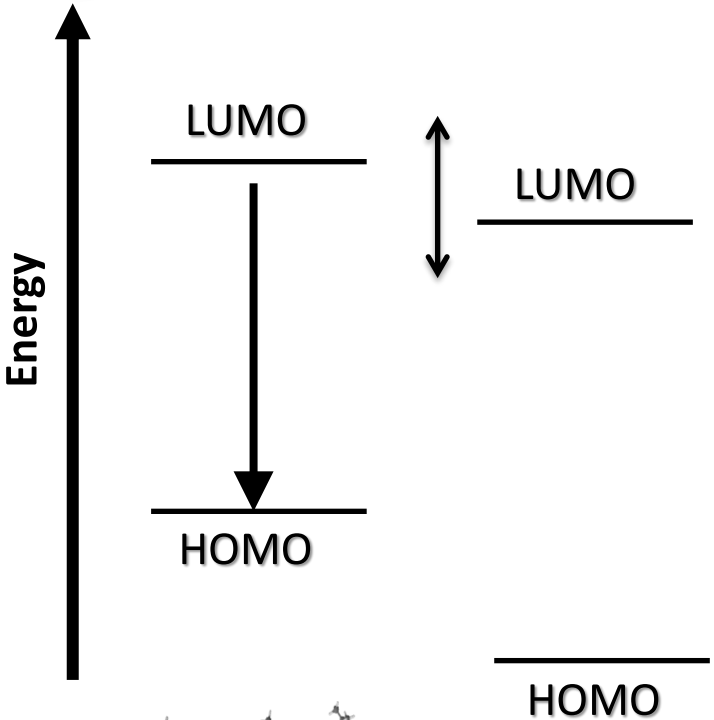
Delocalisation of charge reduces CTE recombination

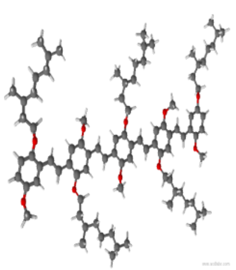
Thin film properties influence molecular charge transfer!

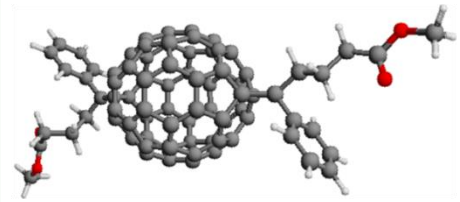


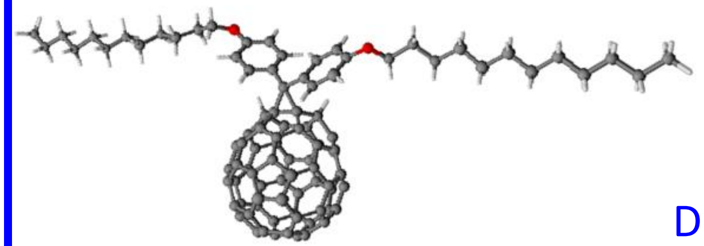
Veldman et al., JACS 2008

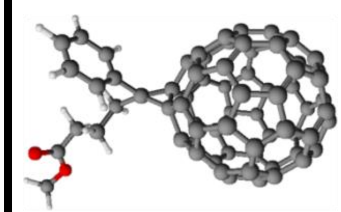
Charge separation in organic solar cells






bis-PCBM

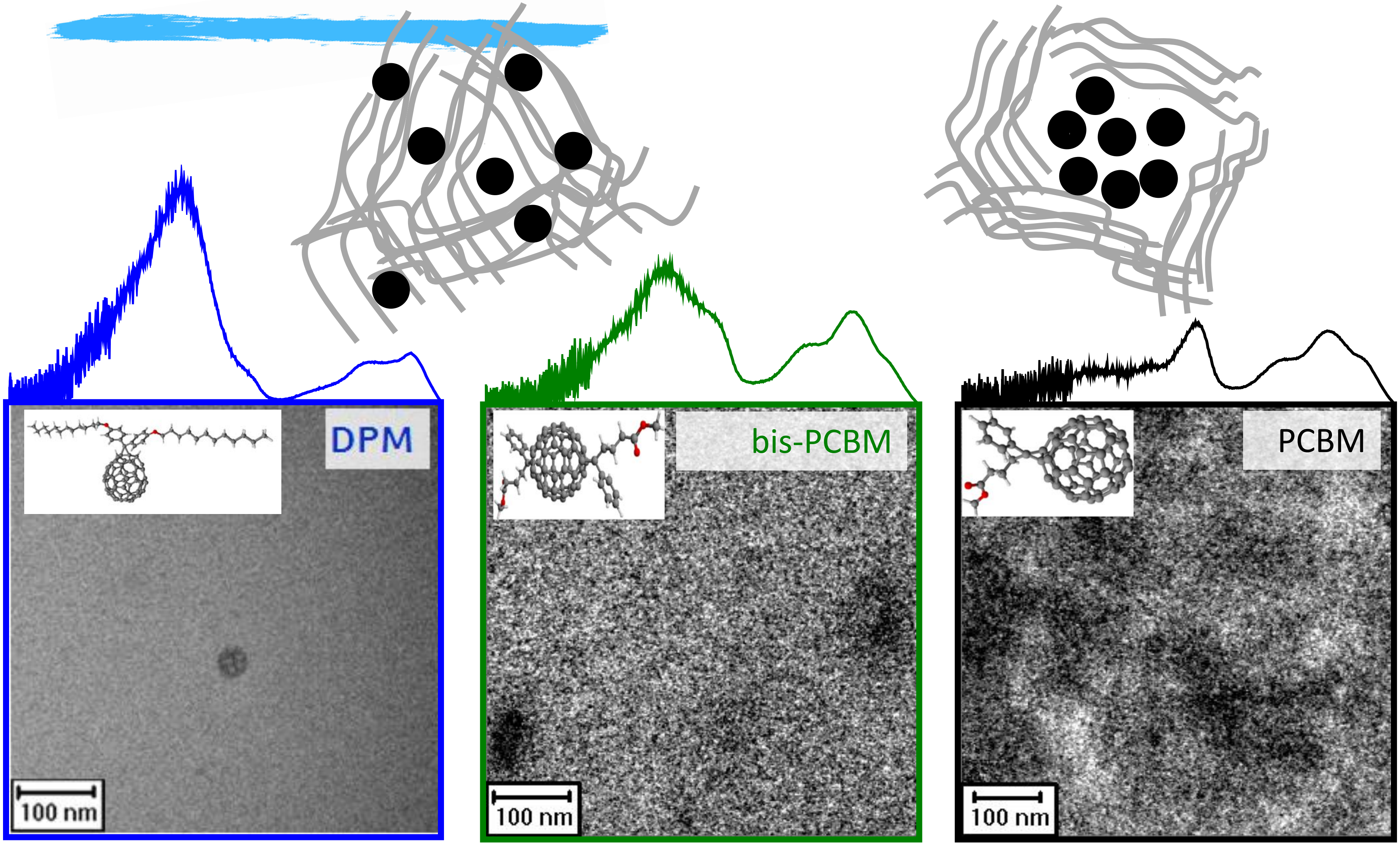

DPM


PCBM

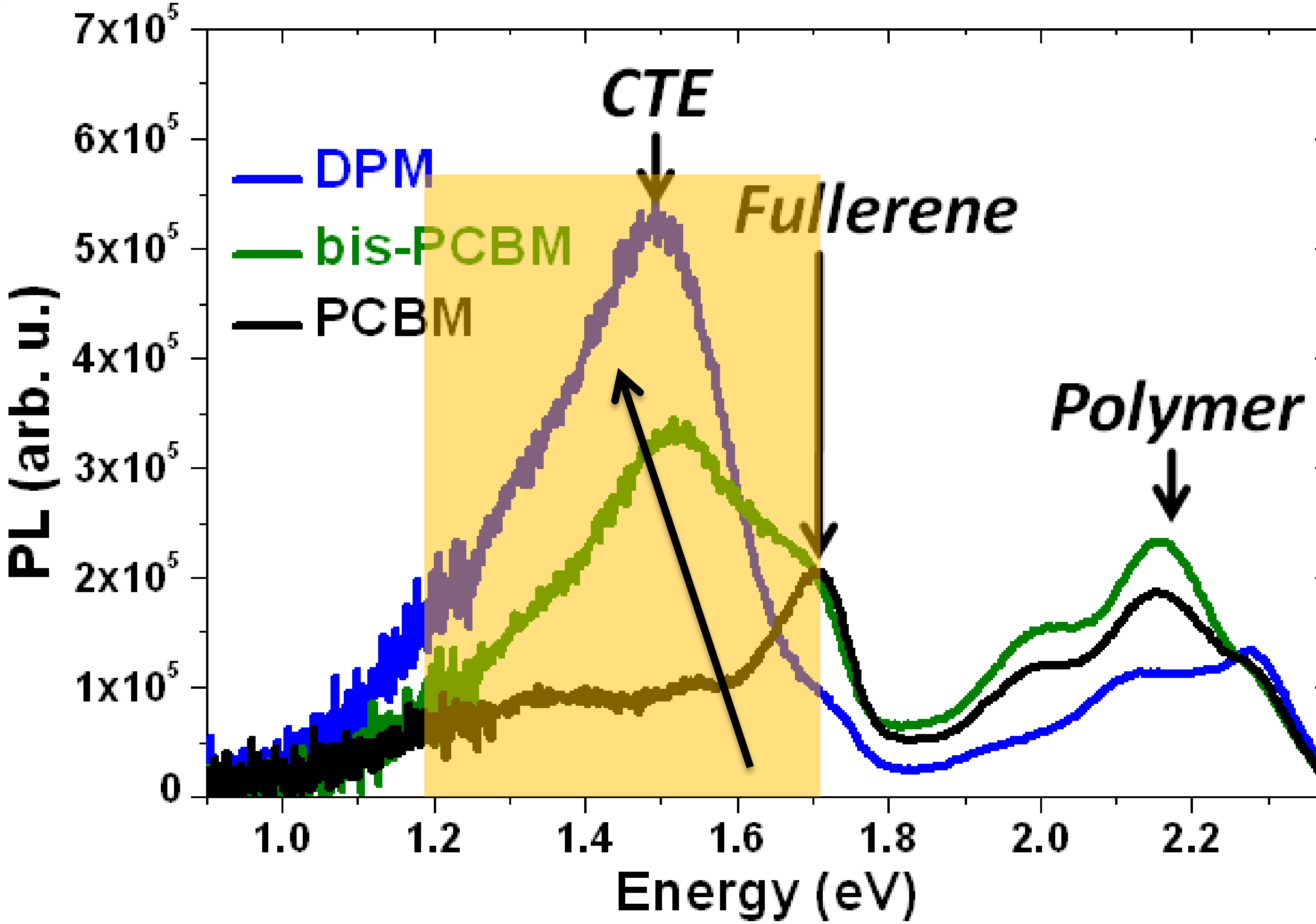
Fullerene

MDMO-PPV

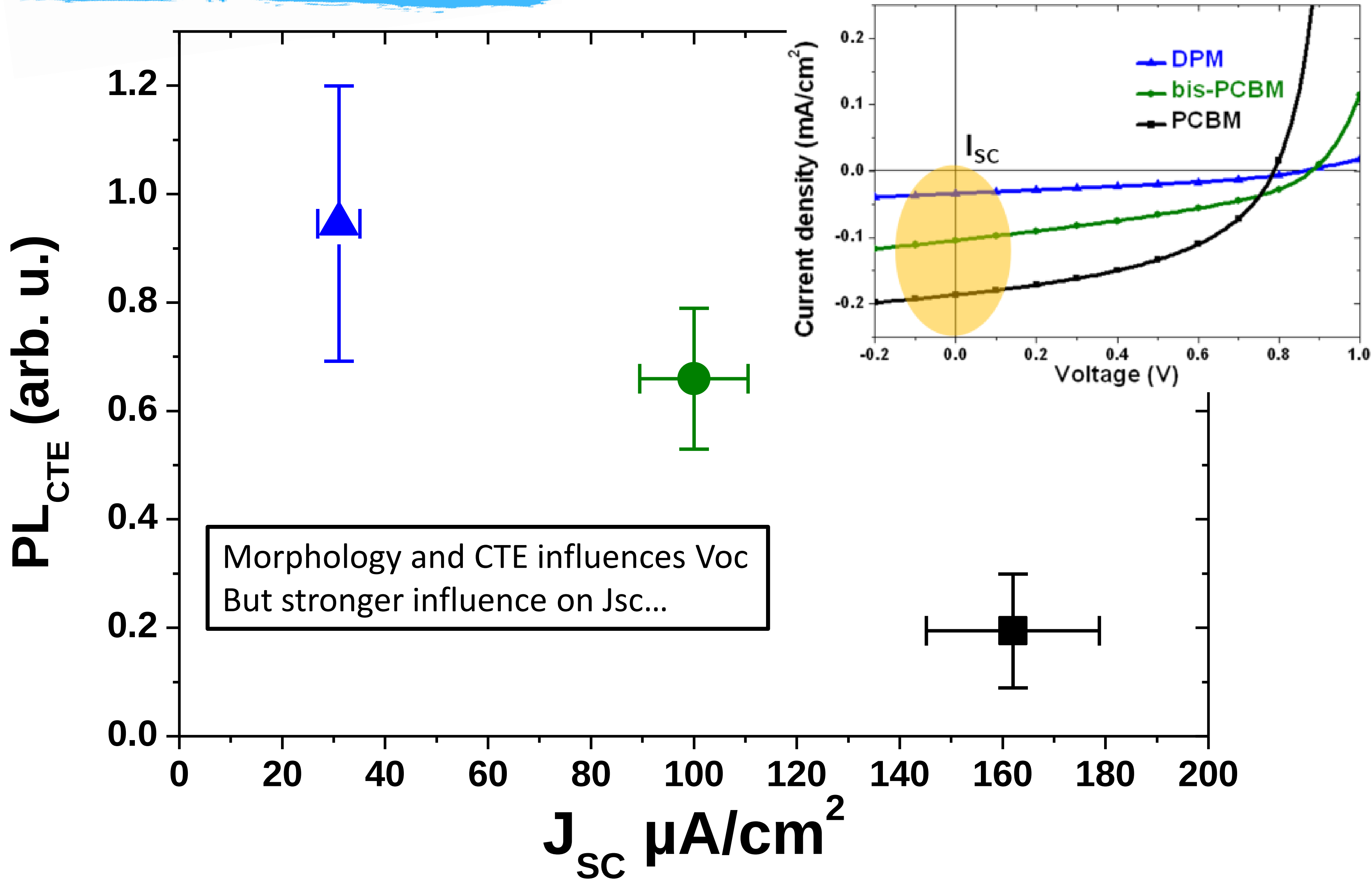
Charge separation in organic solar cells



Charge separation in organic solar cells



Charge separation in organic solar cells



Morphology and CTE influences Voc
But stronger influence on Jsc…

Charge separation in organic solar cells

nature energy
ARTICLES
PUBLISHED: 27 JUNE 2016 | ARTICLE NUMBER: 16089 | DOI: 10.1038/NENERGY.2016.89

Fast charge separation in a non-fullerene organic solar cell with a small driving force

Jing Liu[1†], Shangshang Chen[1†], Deping Qian[2], Bhoj Gautam[3], Guofang Yang[1,4], Jingbo Zhao[1], Jonas Bergqvist[2], Fengling Zhang[2], Wei Ma[4], Harald Ade[3], Olle Inganäs[2], Kenan Gundogdu[3*], Feng Gao[2*] and He Yan[1,5*]

- Driving energy ΔE is negligible
- Singlet energy S1 in donor has same energy as CTE
- These blends show efficient charge transfer and high efficiency
- Why?

Charge separation in organic solar cells

Low driving energy ΔE means higher open circuit voltage V_{oc}

Recall from the Shockley-Queisser limit

- radiative recombination losses are ideal, non-radiative losses are non-ideal
- energy gap limits Voc and therefore efficiency

Charge separation in organic solar cells

Low driving energy ΔE means higher open circuit voltage V_{oc}

Recall from the Shockley-Queisser limit

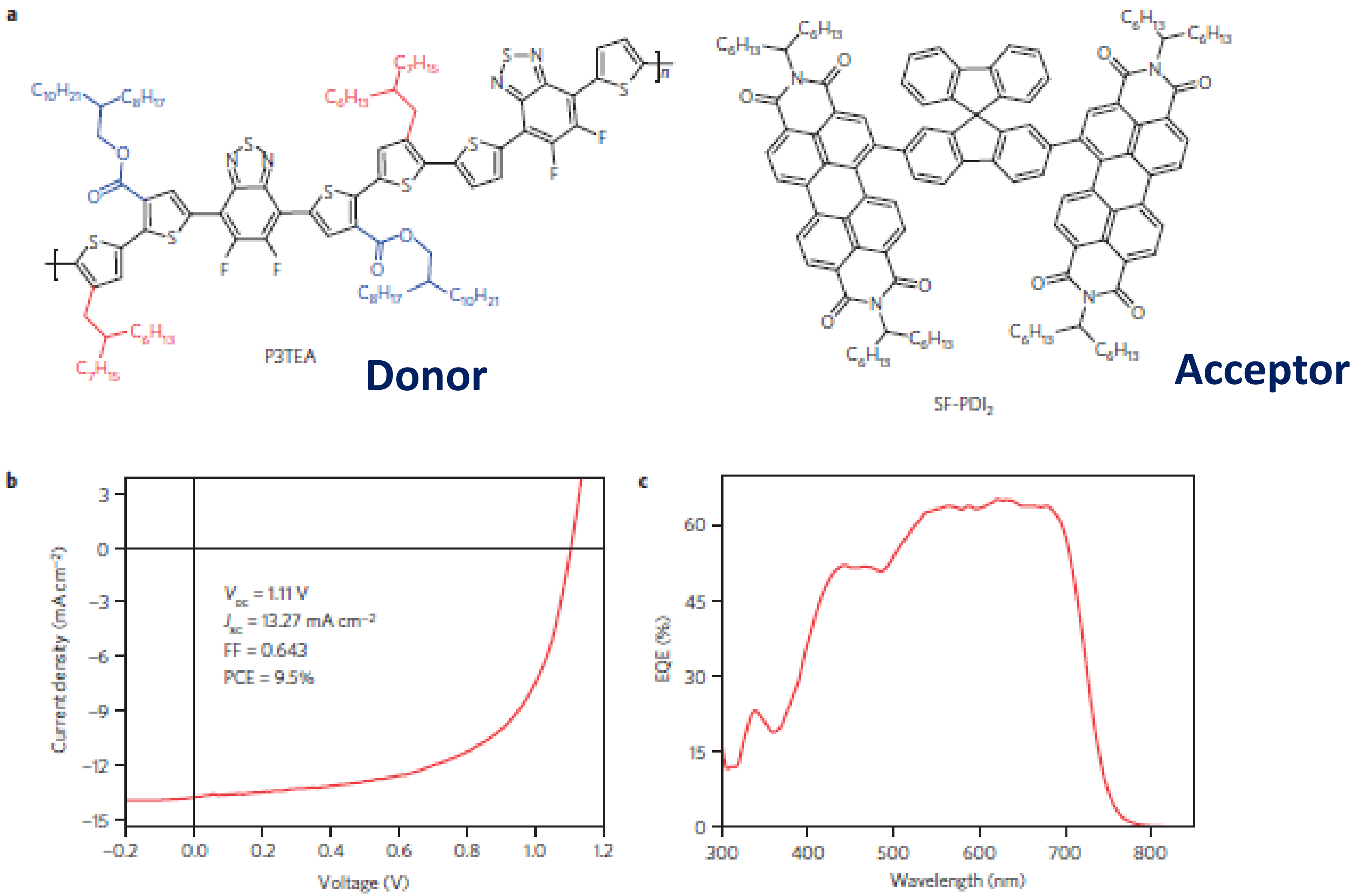
- radiative recombination losses are ideal, non-radiative losses are non-ideal
- energy gap limits Voc and therefore efficiency

voltage loss ΔV in terms of radiative loss over bandgap (V^{SQ}) and CTE (V^{rad}):

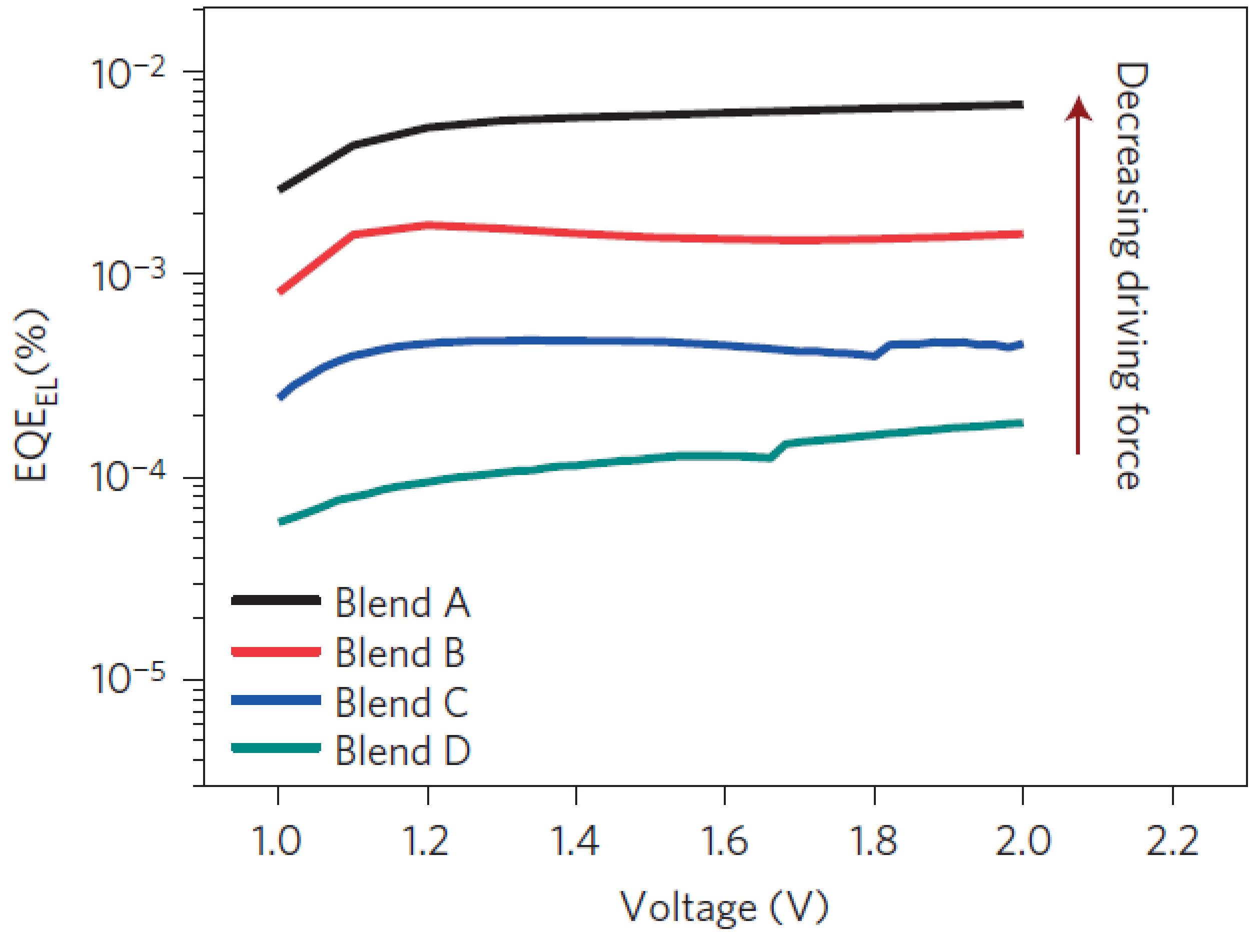
$$\begin{aligned} q\Delta V &= E_{\mathrm{gap}} - qV_{\mathrm{OC}} \\ &= \left(E_{\mathrm{gap}} - qV_{\mathrm{OC}}^{\mathrm{SQ}}\right) + \left(qV_{\mathrm{OC}}^{\mathrm{SQ}} - qV_{\mathrm{OC}}^{\mathrm{rad}}\right) + \left(qV_{\mathrm{OC}}^{\mathrm{rad}} - qV_{\mathrm{OC}}\right) \\ &= \left(E_{\mathrm{gap}} - qV_{\mathrm{OC}}^{\mathrm{SQ}}\right) + q\Delta V_{\mathrm{OC}}^{\mathrm{rad,below\ gap}} + q\Delta V_{\mathrm{OC}}^{\mathrm{non\text{-}rad}} \end{aligned}$$

Need to minimise qV_{rad} which are sub-bandgap losses over CTE state

Charge separation in organic solar cells



Charge separation in organic solar cells



These blends show very little low energy losses over CTE state

Charge separation in organic solar cells

- Donor-Acceptor systems for charge separation in OPV

- CTE recombination = geminate recombination. Key loss mechanism

- Charge separation is influenced by

  - Molecular energetics - Optimising driving energy?
  - Coupling between donor-acceptor, re-organisation energy
  - Excitation energy (HOT versus COLD CTE states)
  - Molecular structure
  - Morphology