Georgia Tech

Charge-Transfer Electronic States: How to Describe Them Theoretically and Their Impact on the Performance of Organic Solar Cells

Jean-Luc Bredas

U. Mons
April 10, 2019

SEPOMO

- a very brief reminder of the working principle of an OSC
- how can we adequately calculate the geometric structure and optical absorption in extended conjugated polymer chains with alternating electron-rich and electron-poor moieties
- interfacial charge-transfer electronic states at donor-acceptor interfaces
    - description via the 2-state model
    - the need for a 3-state model
    - design rules to minimize voltage losses

brief reminder of the working principle of an organic solar cell

inorganic

- high dielectric constant
- creation of free carriers

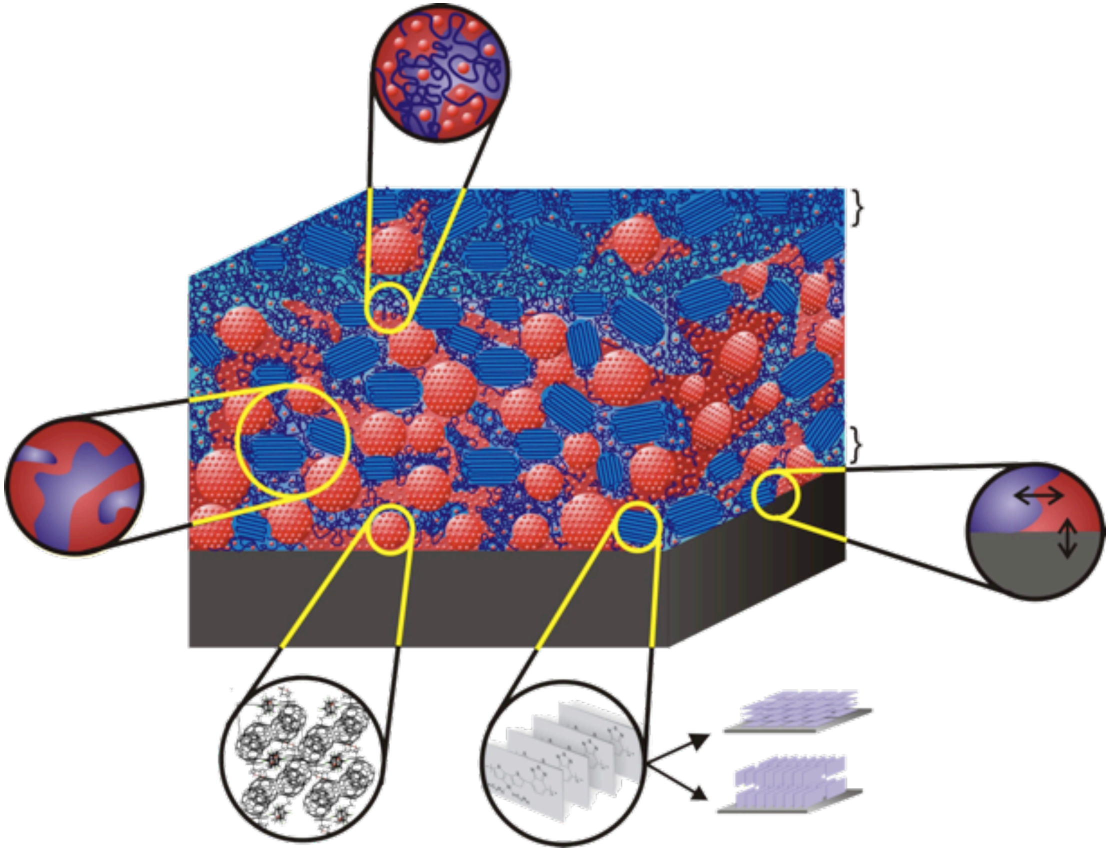
organic

- low dielectric constant; strong electron-electron and electron-vibration interactions
- creation of bound e-h pairs: *excitons*

→ need for an electron <u>donor</u> component (often a π-conjugated polymer) and an electron <u>acceptor</u> component (often a “small” molecule):

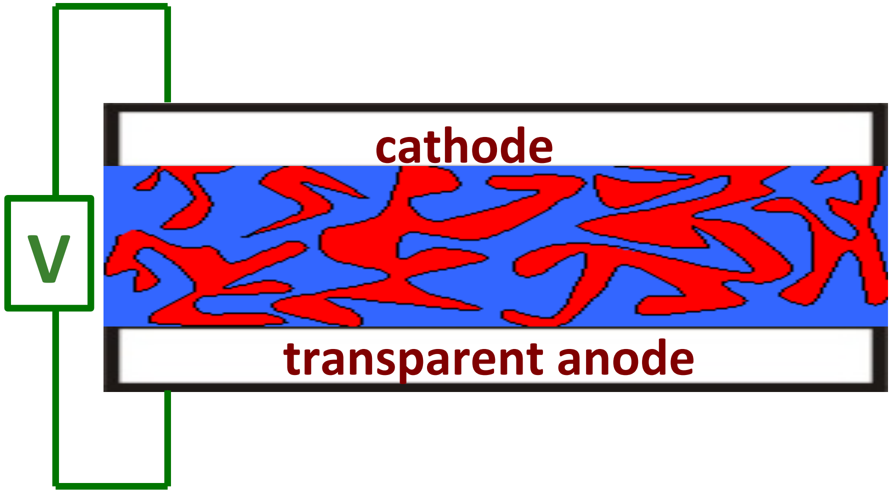
exciton dissociation occurs at their interface

bulk hetero-junctions (BHJ) architecture to maximize interfacial area



McGehee & Toney, Darling, Stingelin, Ade,…

electronic processes in an organic solar cell

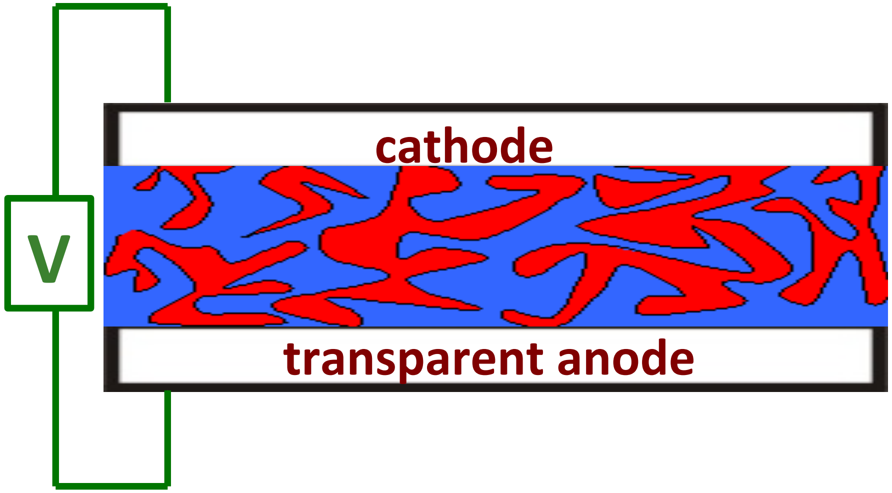


1. photon absorption and exciton formation
2. interfacial exciton dissociation and charge separation
3. charge transport to electrodes
4. charge collection at electrodes

B. Kippelen & JLB, Energy & Environmental Science 2, 251 (2009)

JLB, J. Norton, J. Cornil, & V. Coropceanu, Acc. Chem. Res. 42, 1691 (2009)

electronic processes in an organic solar cell



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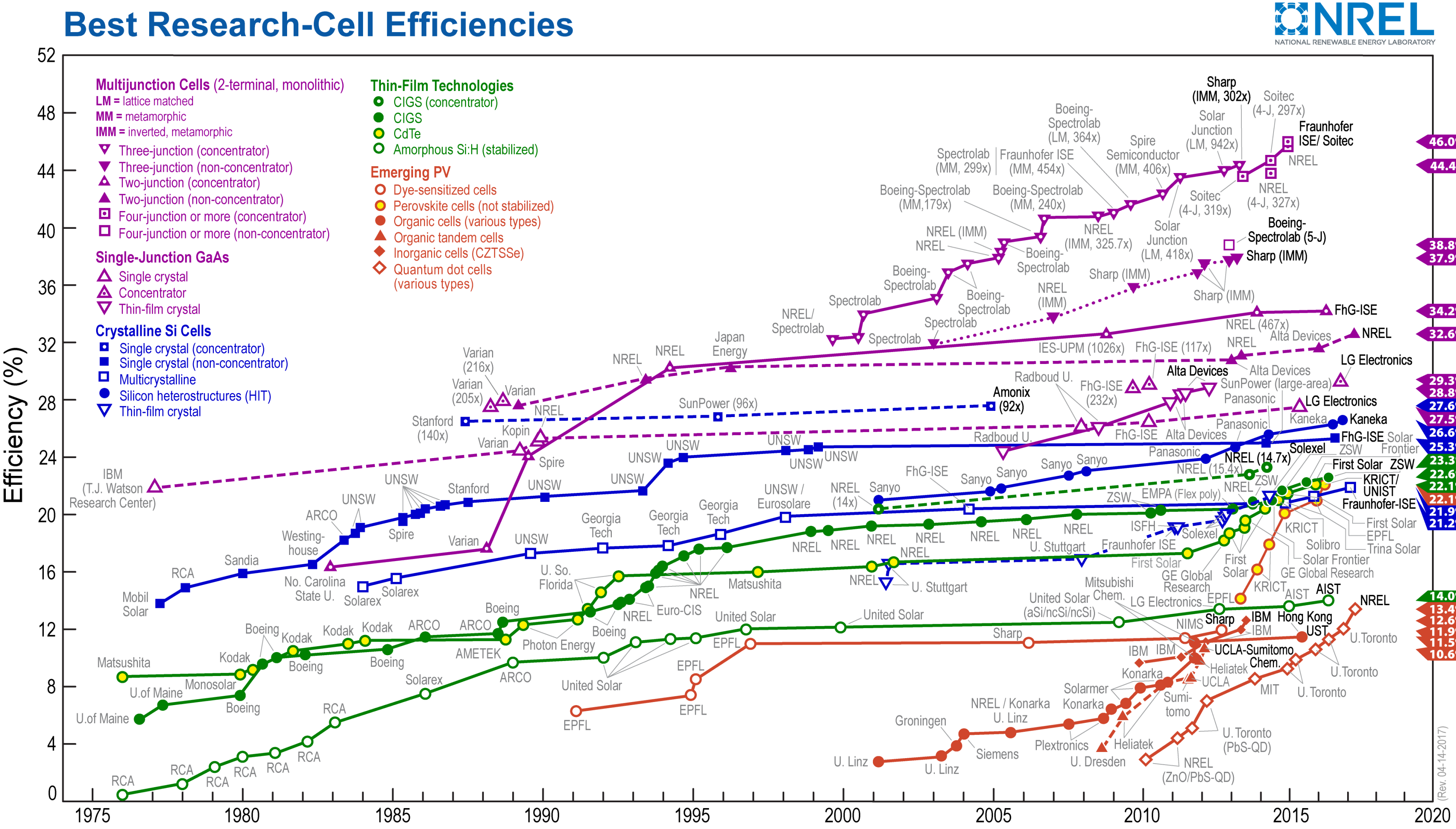
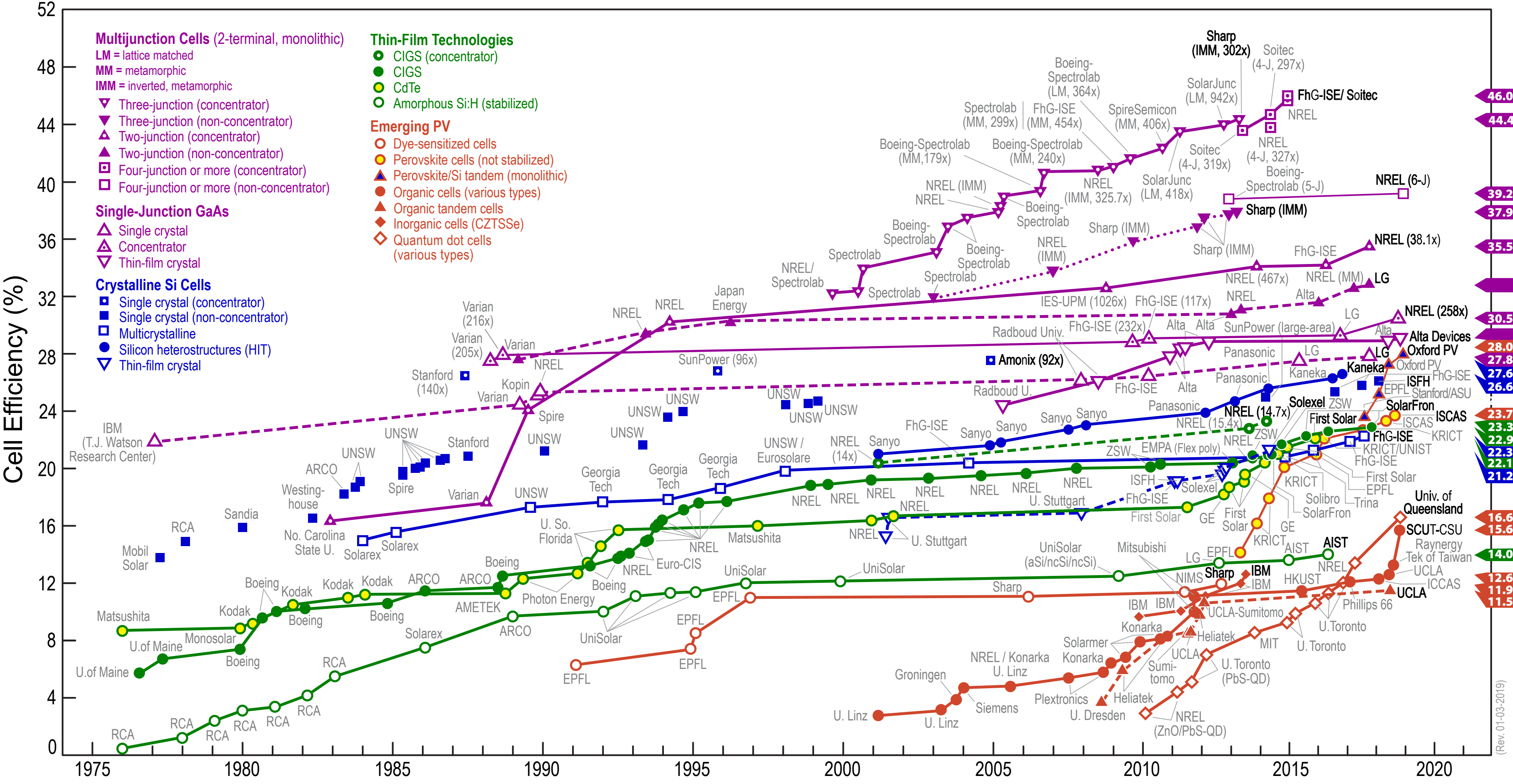
2016



● = organic solar cells

2019

Best Research-Cell Efficiencies



● = organic solar cells

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

DOI: 10.1021/jacs.6b09110
J. Am. Chem. Soc. 2016, 138, 15011−15018

Side-Chain Isomerization on an n-type Organic Semiconductor ITIC Acceptor Makes 11.77% High Efficiency Polymer Solar Cells

Yankang Yang,[†,§] Zhi-Guo Zhang,[*,†] Haijun Bin,[†,§] Shanshan Chen,[‡] Liang Gao,[†,§] Lingwei Xue,[†] Changduk Yang,[‡] and Yongfang Li[*,†,§,∥]

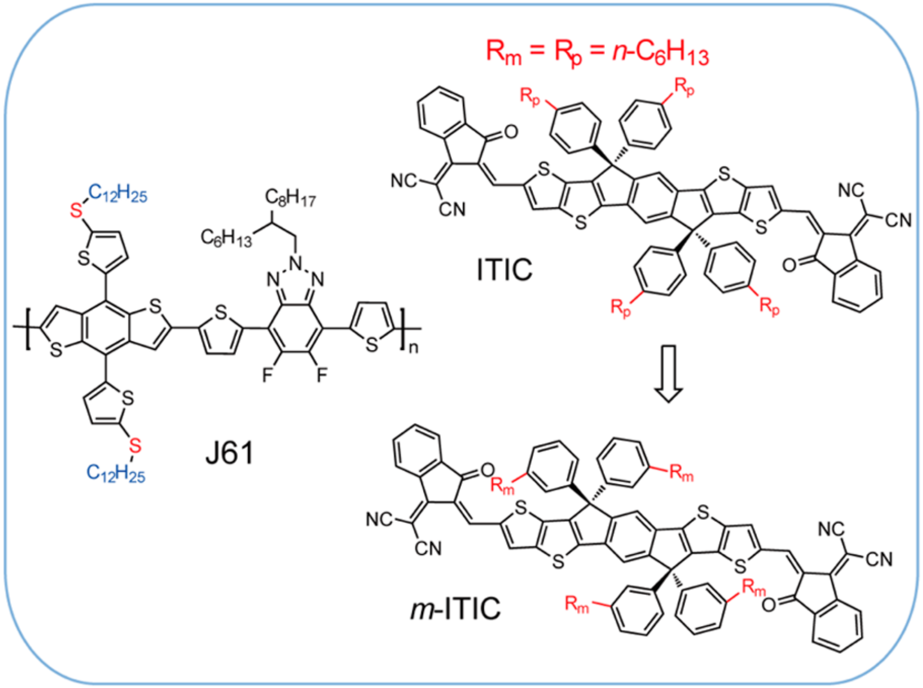
[†]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]Department of Energy Engineering, School of Energy and Chemical Engineering, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, South Korea

[§]University of Chinese Academy of Sciences, Beijing 100049, China

[∥]Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China

major push towards non-fullerene acceptors



DOI: 10.1021/jacs.7b02677
J. Am. Chem. Soc. 2017, 139, 7148−7151

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

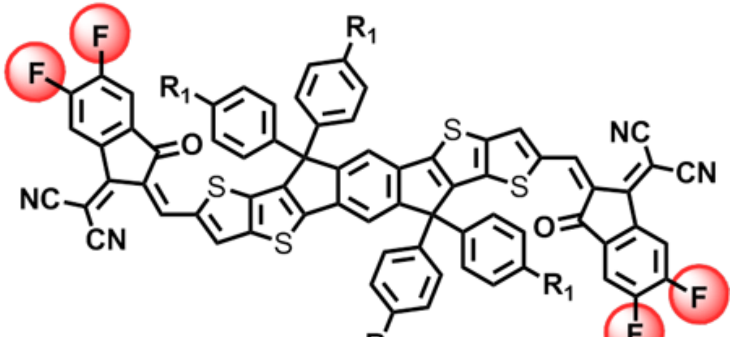
pubs.acs.org/JACS

Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells

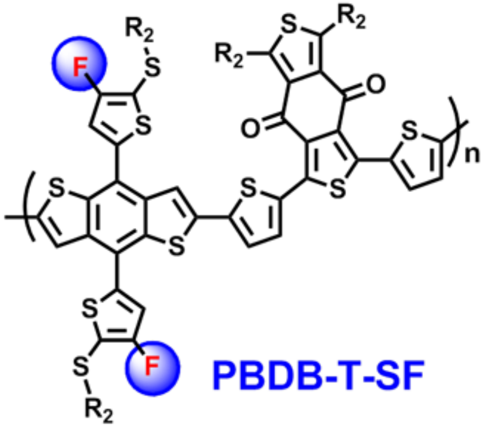
Wenchao Zhao,[†,‡] Sunsun Li,[†,‡] Huifeng Yao,*[,†,‡] Shaoqing Zhang,[†,‡] Yun Zhang,[†,‡] Bei Yang,[†,‡] and Jianhui Hou*[,†,‡]

[†]Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Polymer Physics and Chemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, China



IT-4F



PBDB-T-SF

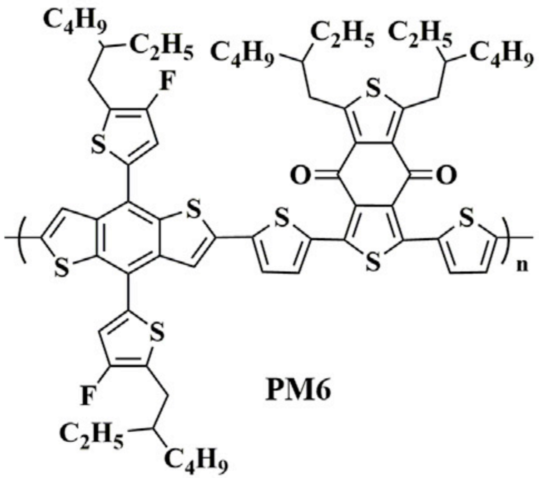
Joule

Article

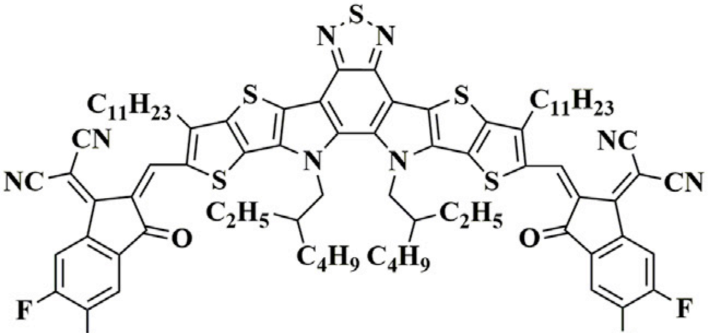
Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core

Jun Yuan,[1] Yunqiang Zhang,[1] Liuyang Zhou,[1,2] Guichuan Zhang,[3] Hin-Lap Yip,[3] Tsz-Ki Lau,[4] Xinhui Lu,[4]
Can Zhu,[1,2] Hongjian Peng,[1] Paul A. Johnson,[5] Mario Leclerc,[5] Yong Cao,[3] Jacek Ulanski,[6]
Yongfang Li,[2] and Yingping Zou[1,7,*]

Joule 3, 1-12 (2019)



PM6



Y6

theoretical characterization of geometric structure and optical absorption in *extended conjugated polymer chains* with alternating electron-rich and electron-poor moieties

how can we *reliably* describe the electronic structure of extended π-conjugated chains at the quantum-chemical level?

- quantum-chemical methods of high accuracy, such as CC-SD(T), are not applicable to the extended systems of interest

- commonly used density functionals, such as B3LYP, suffer from a delocalization error, which can be traced back to electron self-interaction (as a consequence, B3LYP favors coplanar systems for which wavefunction delocalization can be maximized)

- *ab initio* Hartree-Fock methods suffer from too much localization

long-range corrected (LCR) hybrid functionals

combine short-range (SR) DFT exchange with long-range (LR) Hartree-Fock exchange in order to reduce electron self-interaction error and thus the localization/delocalization error

$$\frac{1}{r} = \underbrace{\frac{erfc(\omega r)}{r}}_{\text{SR}} + \underbrace{\frac{erf(\omega r)}{r}}_{\text{LR}}$$

ω = range-separation parameter

short range:

semilocal/hybrid DFT

long range:

semilocal/hybrid DFT for correlation; HF for exchange

H. Iikura, T. Tsuneda, T. Yanai, and K. Hirao, J. Chem. Phys. 115, 3540 (2001)

in π-conjugated systems:

the range-separation parameter ω depends on:

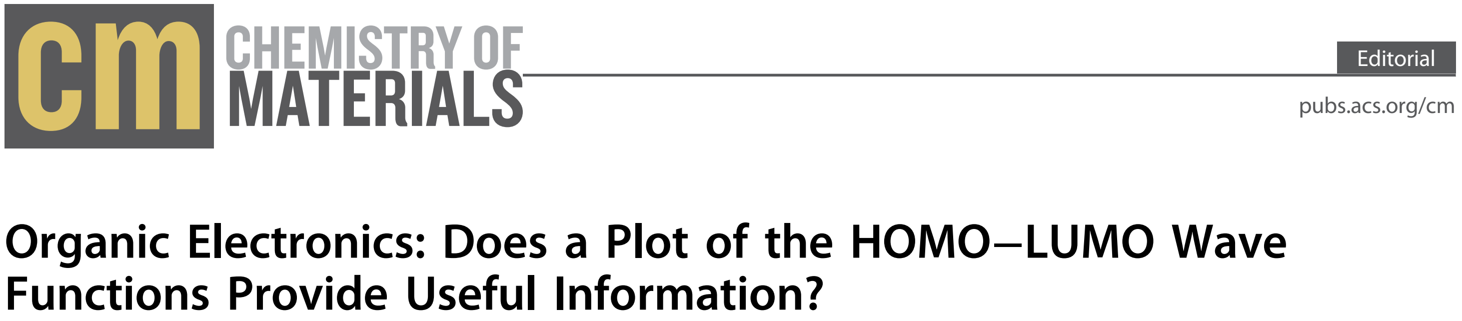
- **molecular size and**
- **degree of conjugation**

LRC functionals need to be optimized for each system *separately*

T. Körzdörfer, J. Sears, C. Sutton, & JLB
J. Chem. Phys. 135, 204107 (2011)

T. Körzdörfer, J. Sears, C. Sutton, & JLB
J. Chem. Phys. 135, 204107 (2011)

T. Körzdörfer & JLB
Acc. Chem. Res. 47, 3284 (2014)



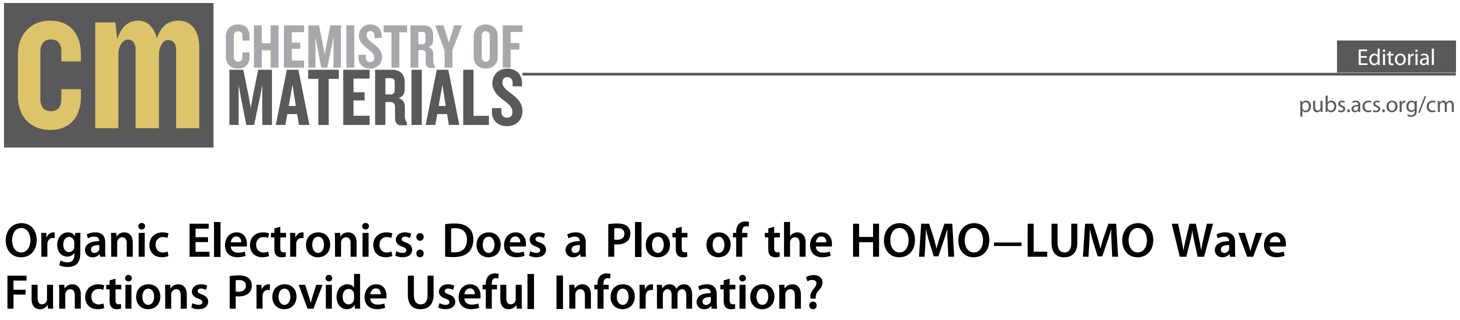
CHEMISTRY OF MATERIALS

Editorial

pubs.acs.org/cm

Organic Electronics: Does a Plot of the HOMO−LUMO Wave Functions Provide Useful Information?

DOI: 10.1021/acs.chemmater.6b04947
Chem. Mater. 2017, 29, 477−478



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Chem. Mater. 2017, 29, 477−478

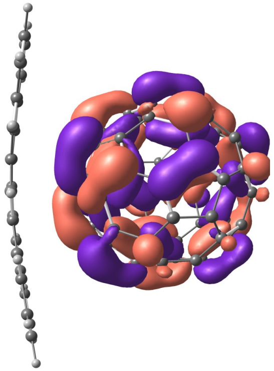
the answer is usually: NO!

going beyond simplistic HOMO-LUMO plots: Natural Transition Orbitals (NTOs)

Richard L. Martin. J. Chem. Phys. 118, 4775 (2003)

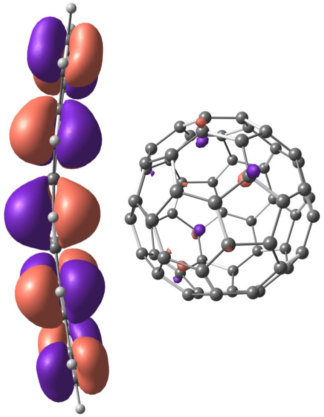
model pentacene-C_{60} complex

TD/DFT tuned ωB97XD/6-31G(d)
ω=0.137 bohr^{-1}



electron

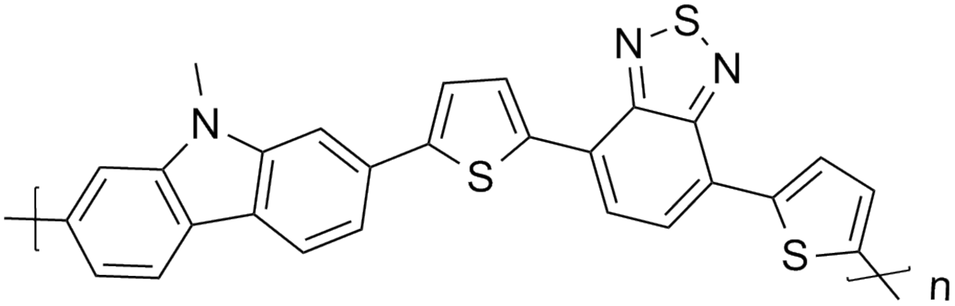
CT_1 state



hole

PCDTBT

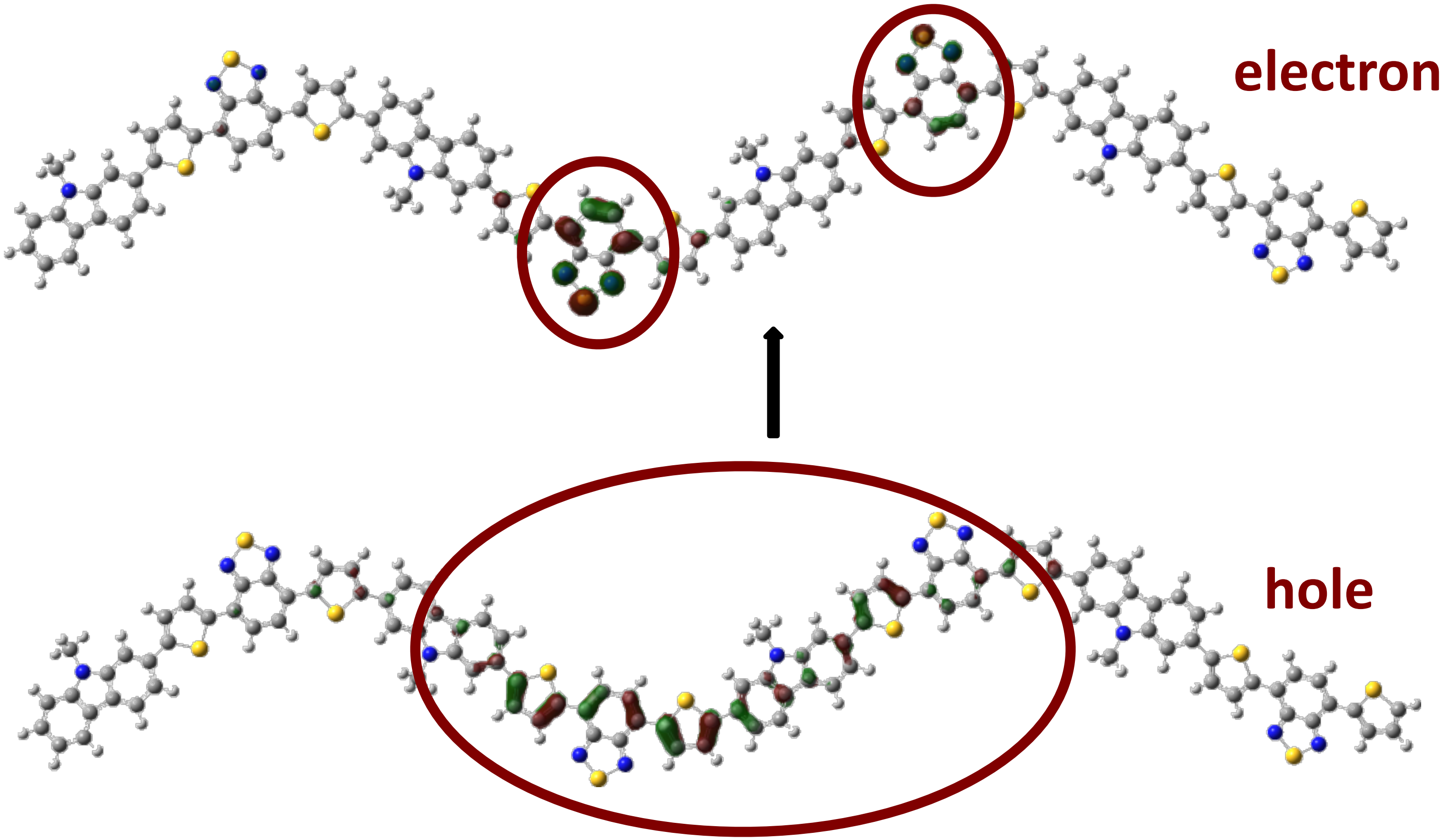
poly-carbazole-dithiophene-benzothiadiazole



optimization of the range-separation parameter ω:
PCDTBT as conjugated as polythiophene

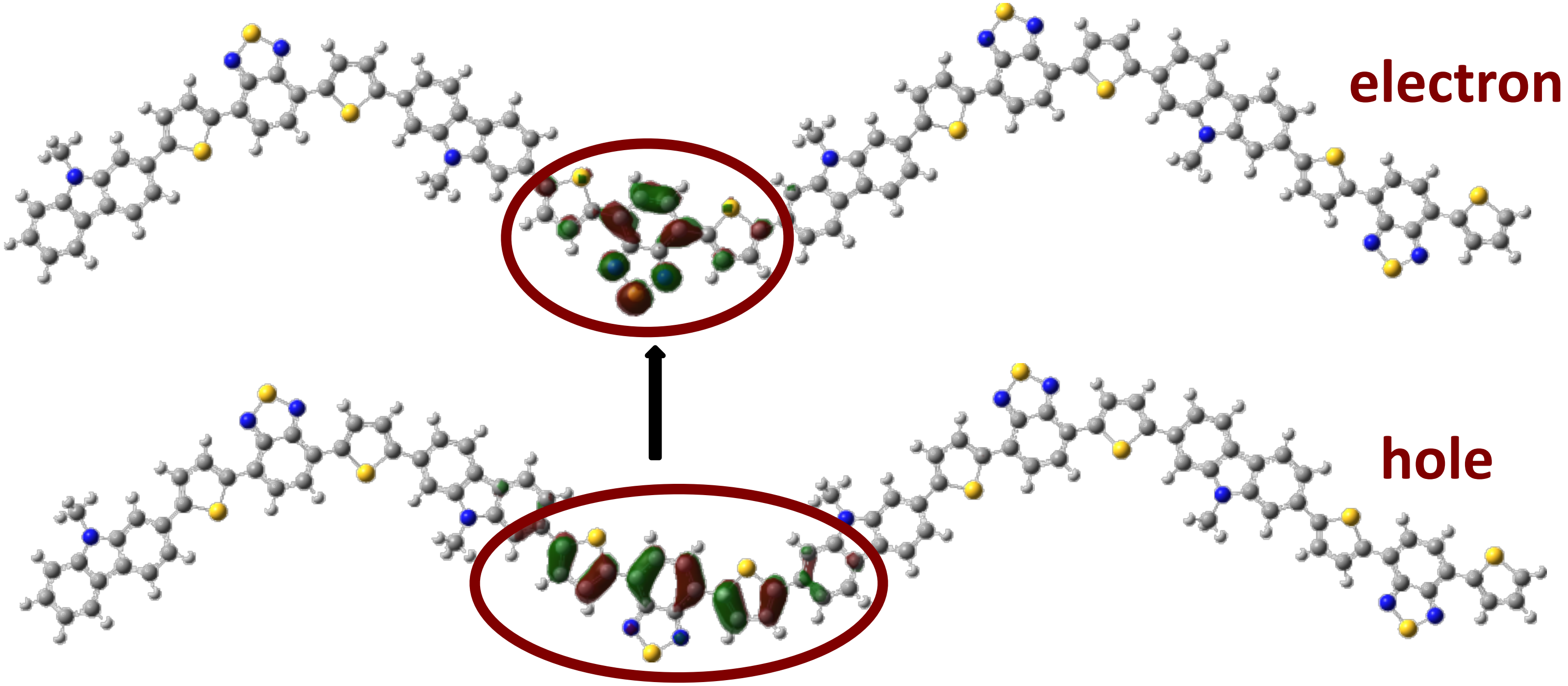
L. Pandey, C. Doiron, J.S. Sears, & JLB, PCCP 14, 14243 (2012)

TDDFT **B3LYP**/6-31G**: Natural Transition Orbital analysis



would imply excitation has strong charge-transfer character

TDDFT tuned LRC ωB97/6-31G**: Natural Transition Orbital analysis

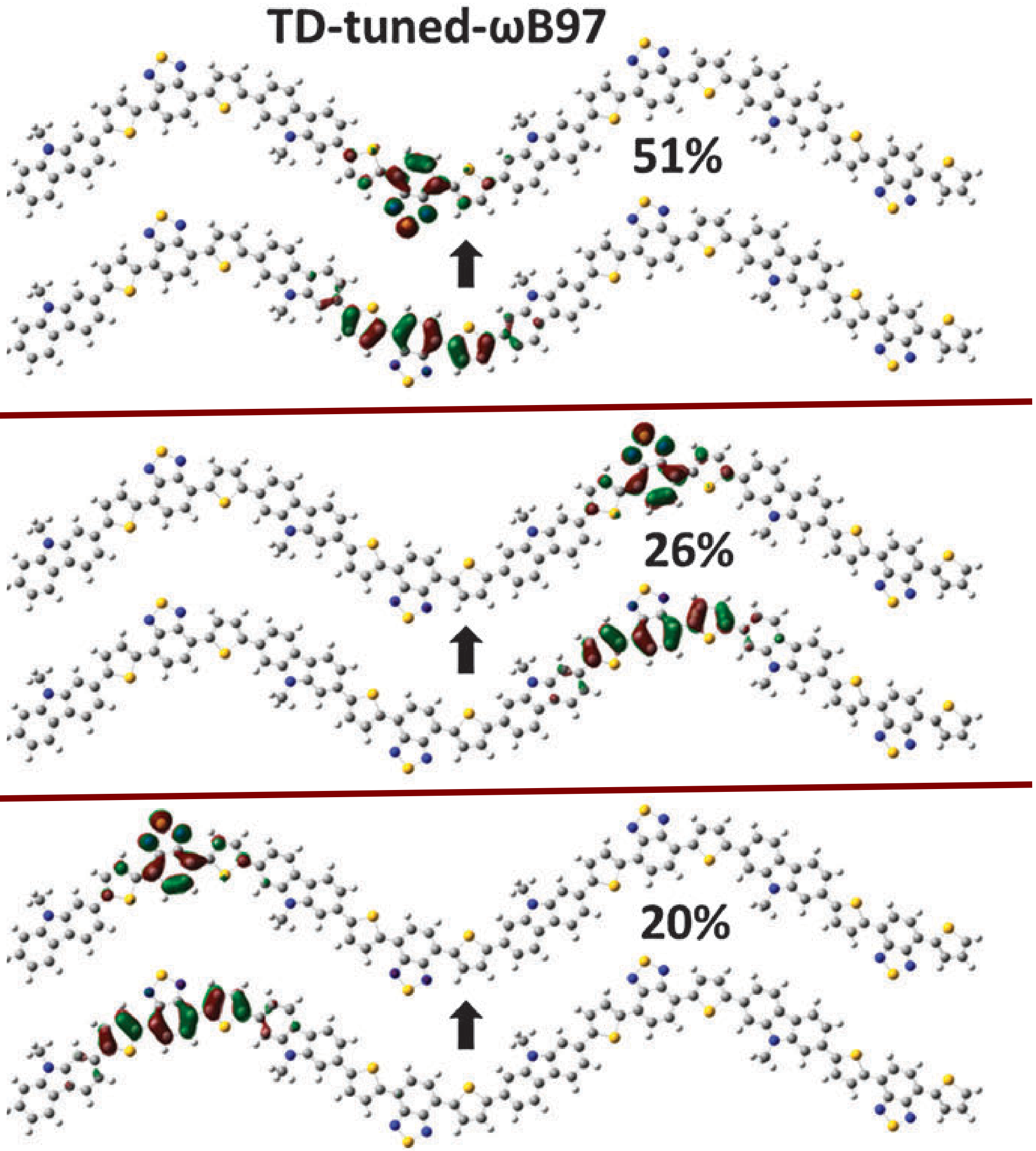


in fact, the chromophoric unit has a

much more local nature

TDDFT tuned LRC ωB97/6-31G**

coupled-oscillator picture



- optimization of range-separation parameter in LRC functionals provides an improved description of the nature of the lowest optical absorptions
  - which is due to an *improved balanced description of local and CT excitations*
  (B3LYP would overstabilize CT-state energies and exaggerate the CT character of the lowest excited states)

- LRC and similar methodologies thus prove essential for a reliable description of the excited states at the interface between donor and acceptor components in organic solar cells

charge-transfer electronic states at donor-acceptor interfaces

Computational Methodologies for Developing Structure–Morphology–Performance Relationships in Organic Solar Cells: A Protocol Review

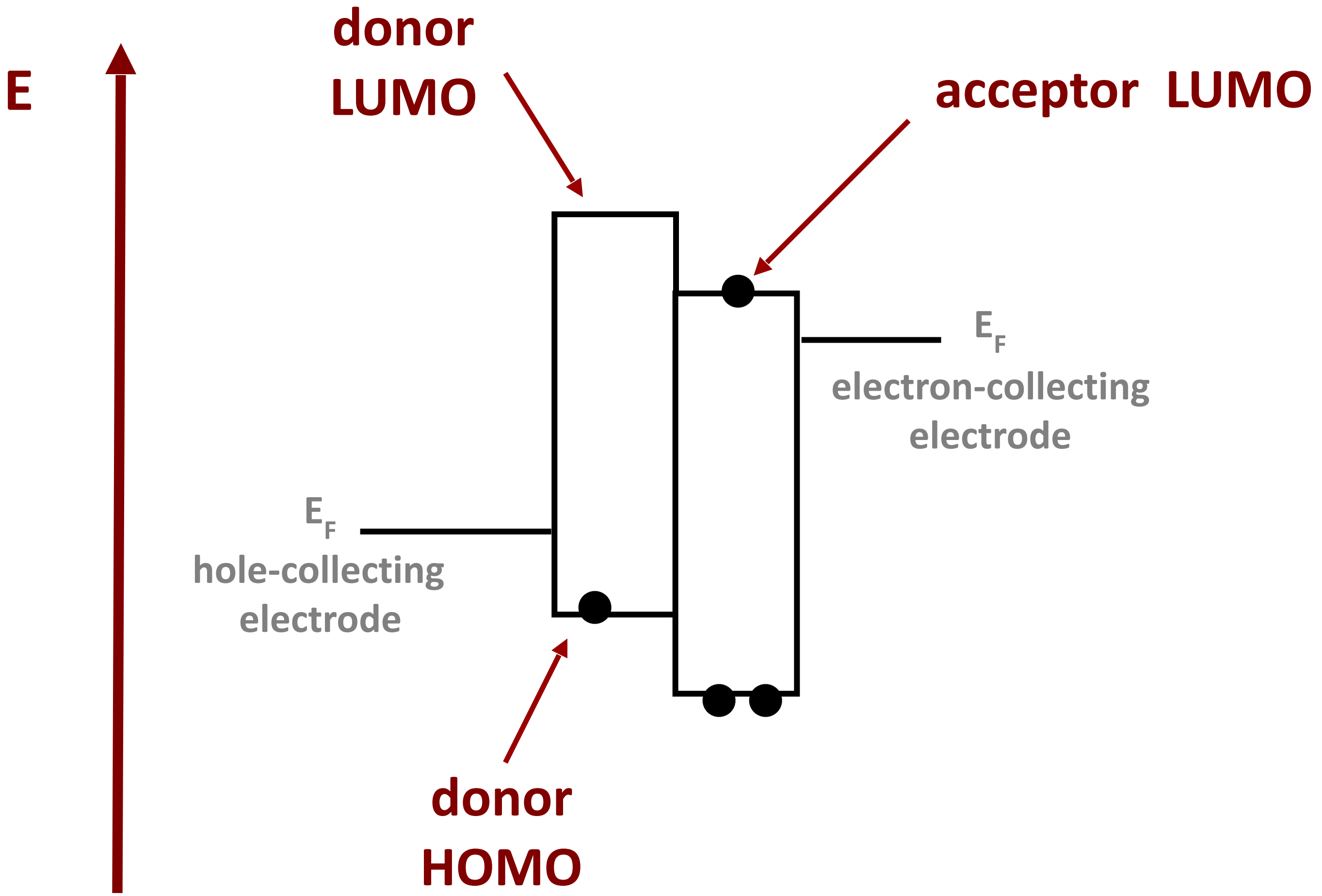
Khanh Do,[‡] Mahesh Kumar Ravva, Tonghui Wang, and Jean-Luc Brédas*

DOI: 10.1021/acs.chemmater.6b03111
Chem. Mater. 2017, 29, 346–354

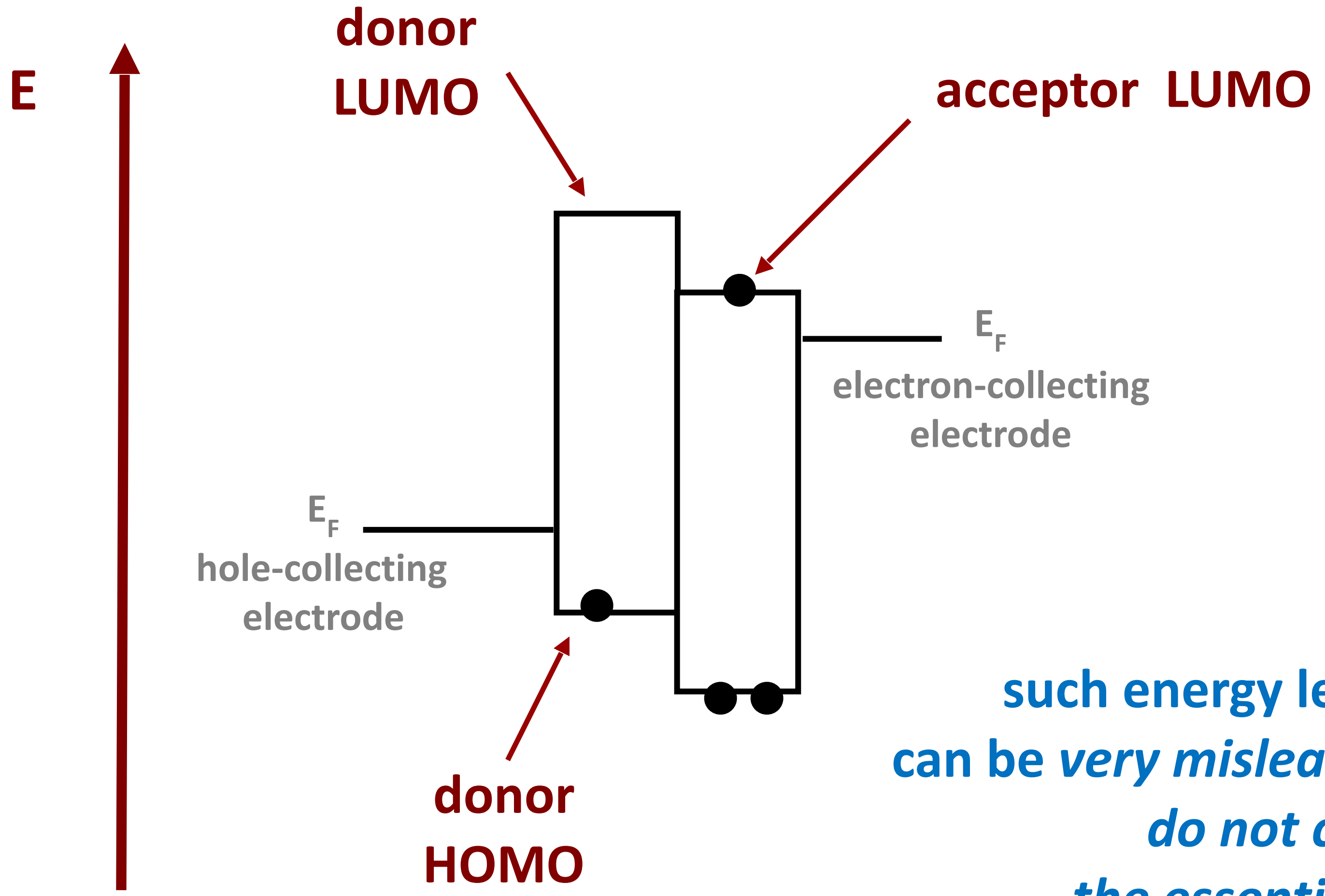
cm CHEMISTRY OF MATERIALS

Georgia Institute of Technology

HOMO-LUMO energy level diagrams

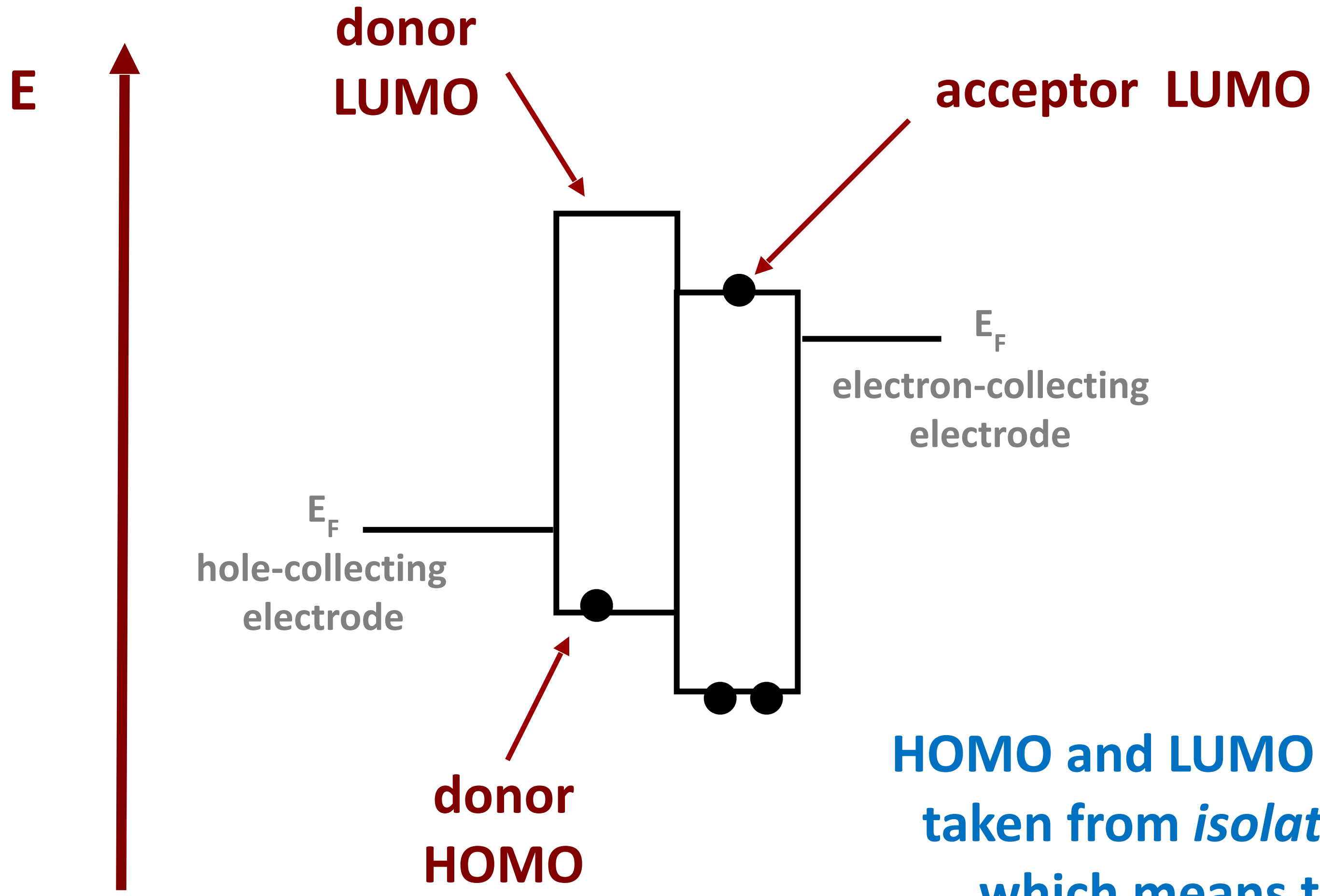


HOMO-LUMO energy level diagrams



such energy level diagrams
can be *very misleading* as they often
do not capture
the essential physics!

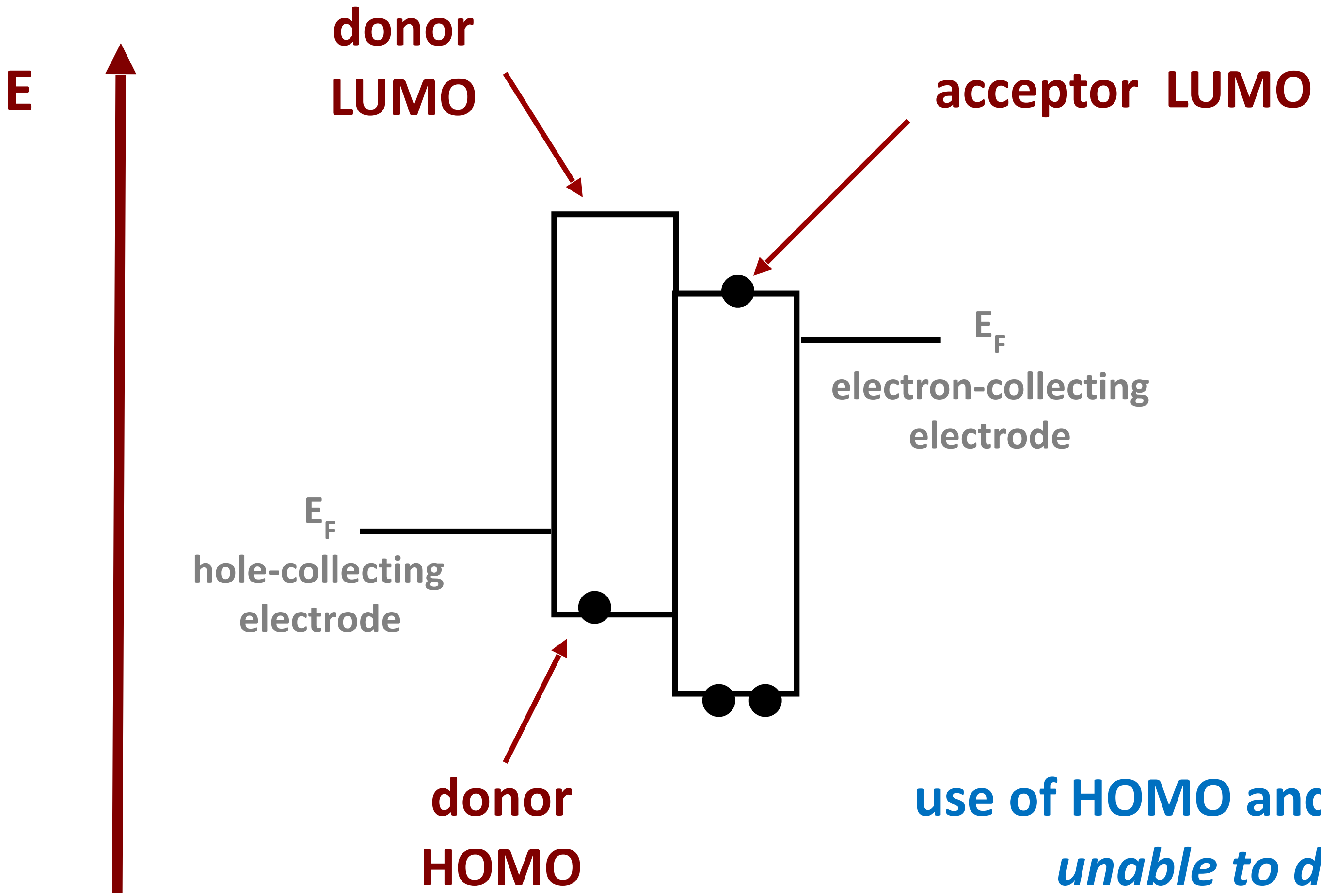
HOMO-LUMO energy level diagrams



HOMO and LUMO levels are usually taken from *isolated* components, which means the neglect of:

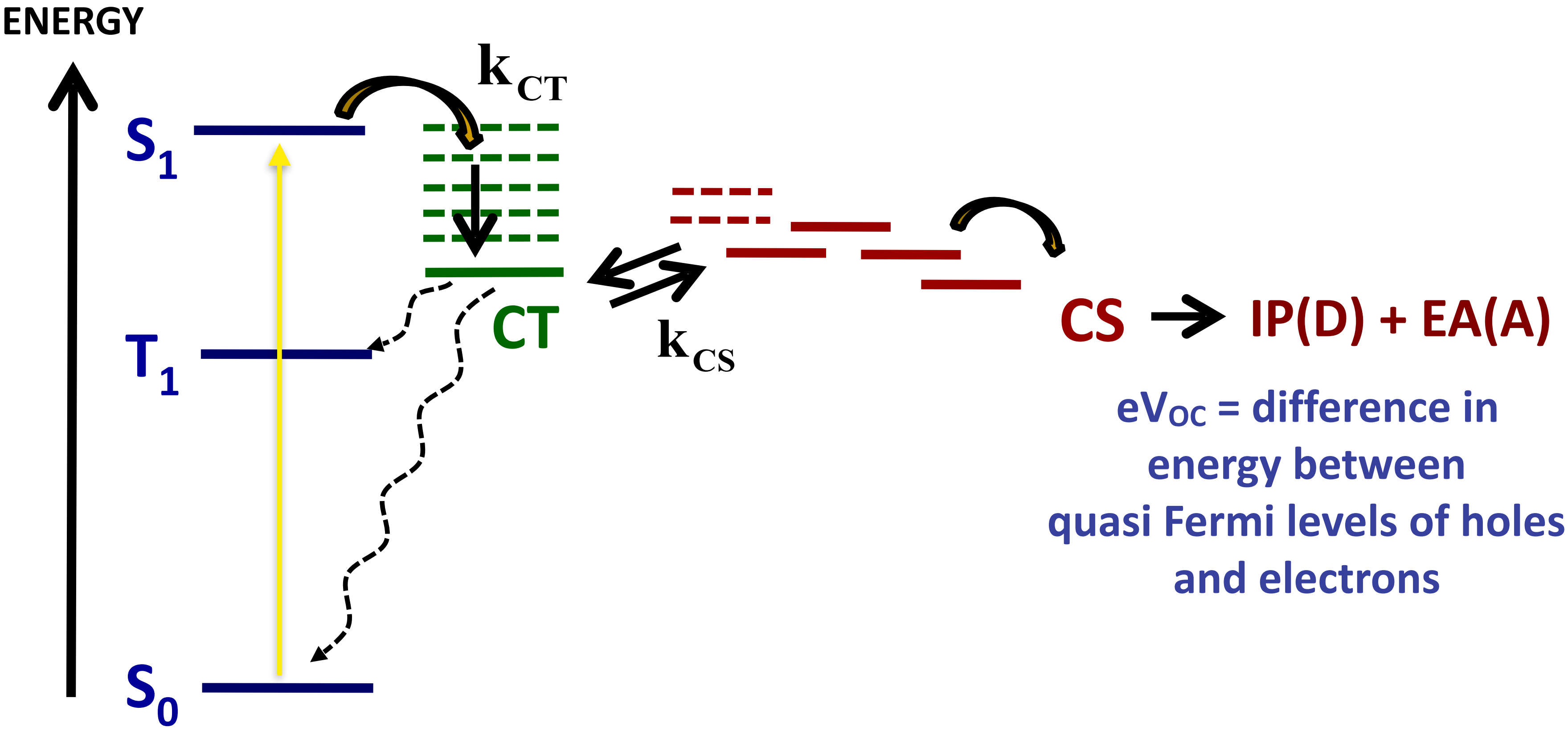
interfacial - polarization effects

HOMO-LUMO energy level diagrams



use of HOMO and LUMO levels is
unable to distinguish
singlet and triplet excitons

electronic-state diagrams



CS → IP(D) + EA(A)

eV_{OC} = difference in energy between quasi Fermi levels of holes and electrons

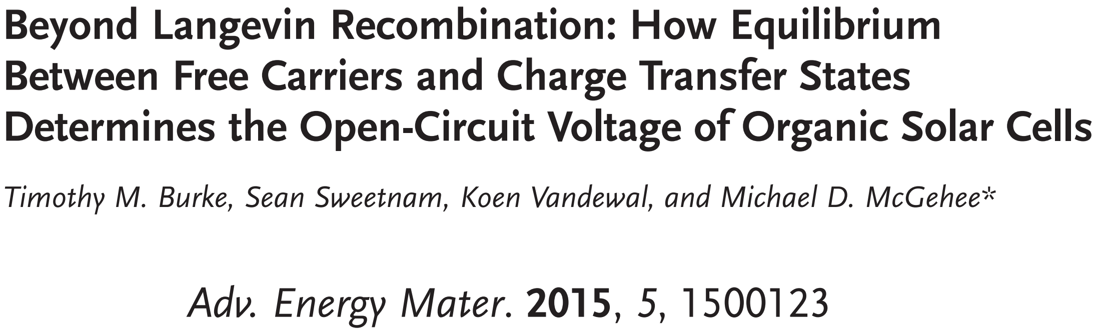
exciton ➡ charge transfer ➡ charge separation

the donor/acceptor interfacial CT states mediate charge generation, separation, and recombination

JLB, J. Norton, J. Cornil, & V. Coropceanu, *Acc. Chem. Res.* 42, 1691 (2009)

to minimize energy losses and maximize V_{OC}:

- the CT-state energy distribution should be narrow
- the CT-state energy should be as close as possible to S_1
- the non-radiative recombination paths should be reduced



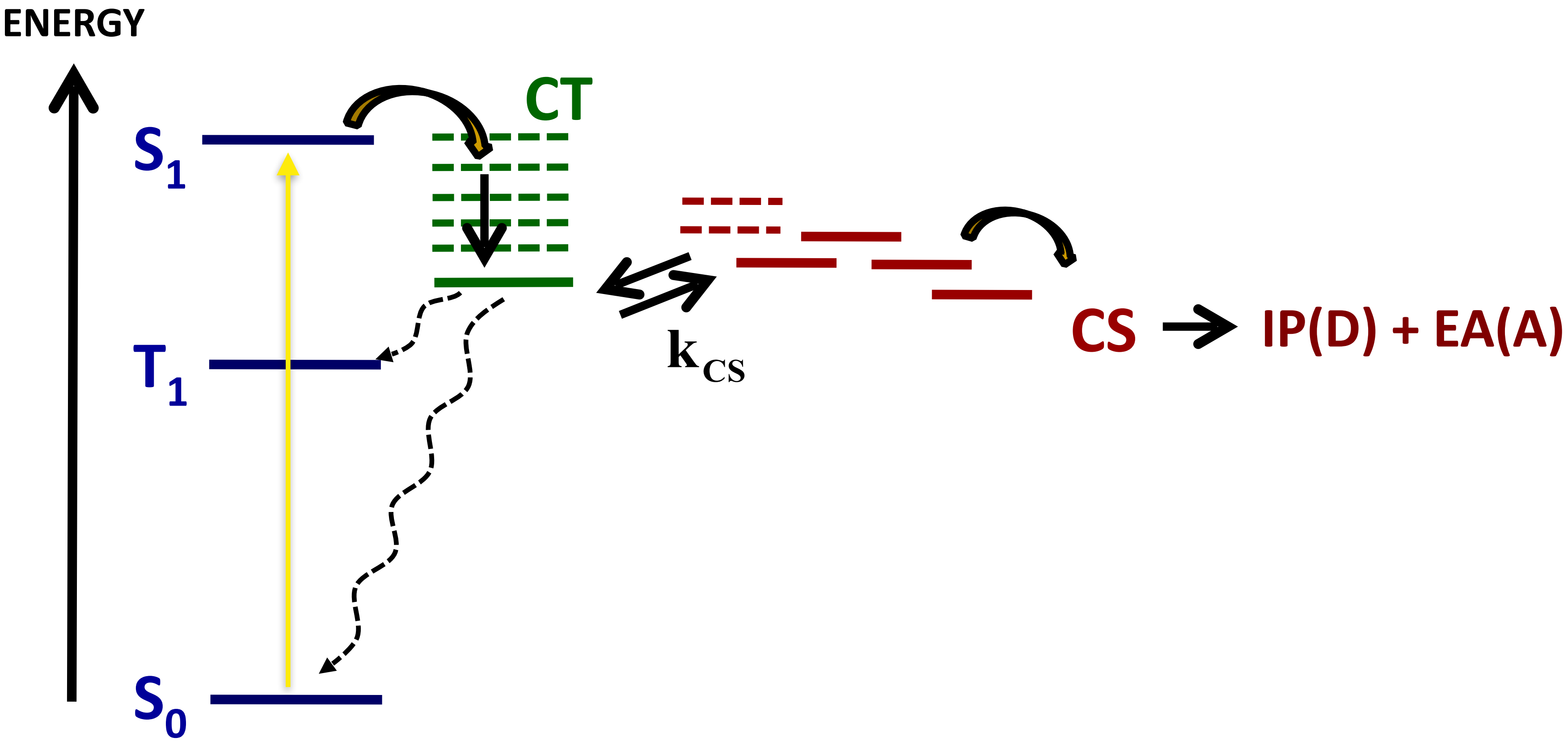
Beyond Langevin Recombination: How Equilibrium Between Free Carriers and Charge Transfer States Determines the Open-Circuit Voltage of Organic Solar Cells

*Timothy M. Burke, Sean Sweetnam, Koen Vandewal, and Michael D. McGehee**

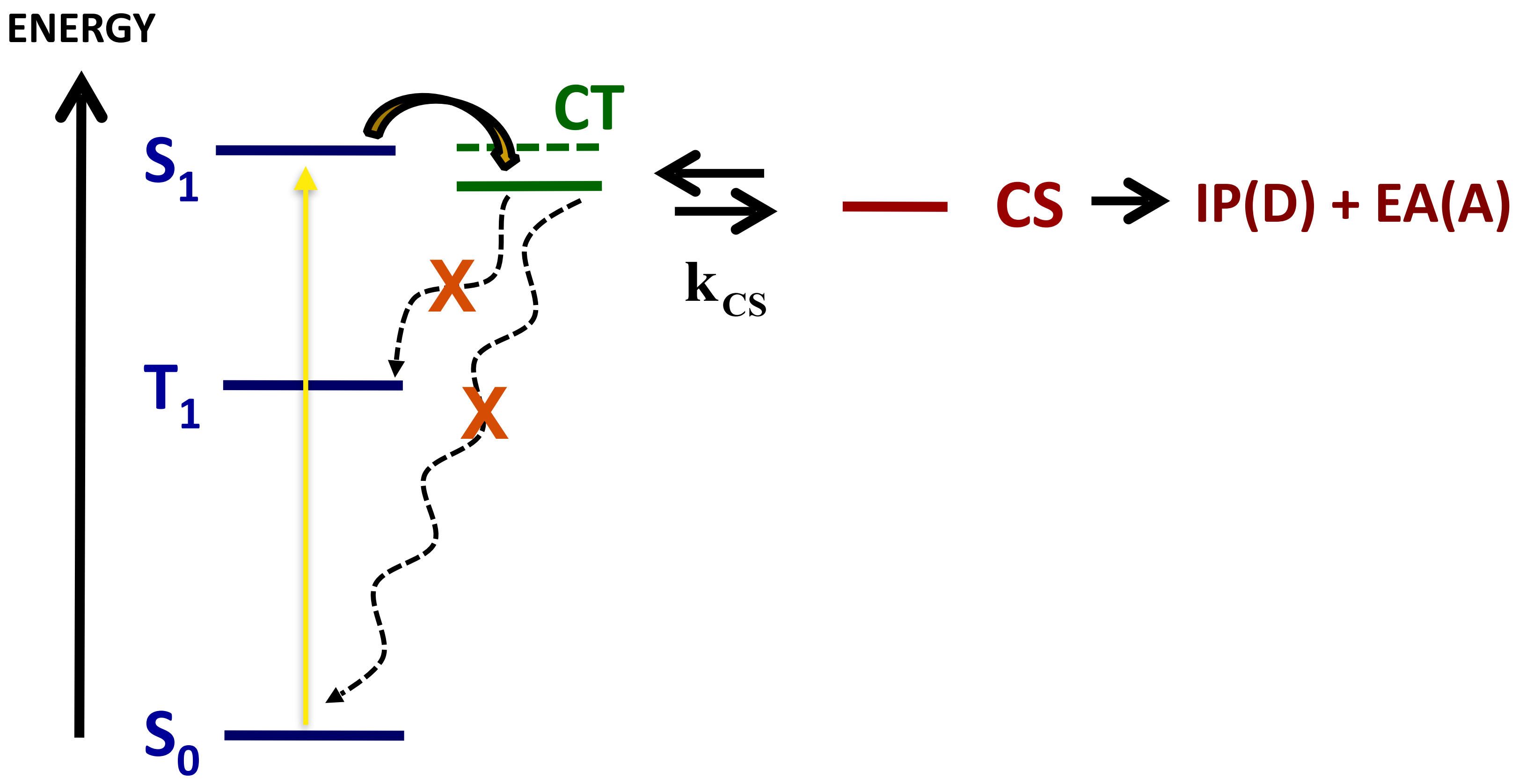
Adv. Energy Mater. **2015**, *5*, 1500123

see also: S.M. Menke, N.A. Ran, G.C. Bazan, and R.H. Friend,
Joule 2, 25-35 (2018)

electronic-state diagrams



electronic-state diagrams



characterization of the charge-transfer (CT) electronic states

how are the CT states characterized experimentally?

generally, their characterization is conducted in the framework of the two-state Mulliken-Hush model, which includes *only* the CT and G states:

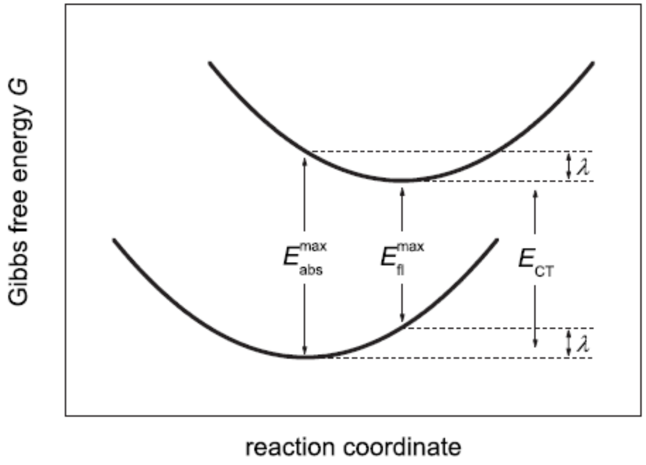
K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, and J.V. Manca, *PRB* 81, 125204 (2010)

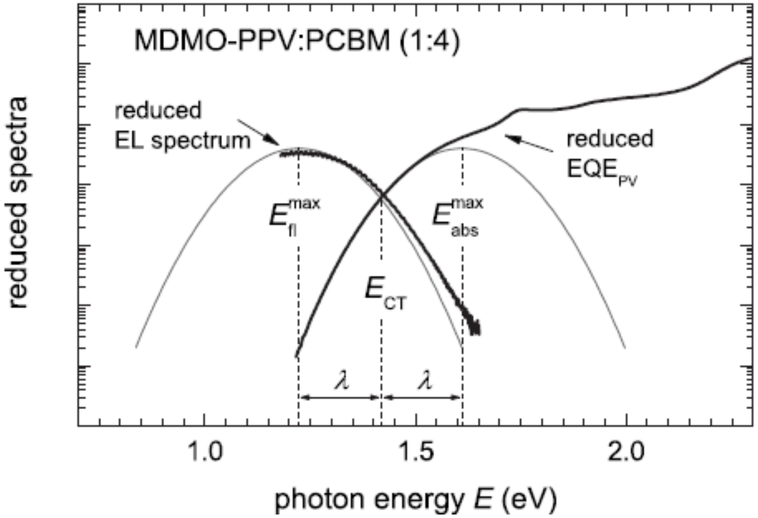
absorption spectra

$$\sigma(E)E = \frac{f_\sigma}{\sqrt{4\pi\lambda kT}}\exp\left(\frac{-(E_{CT}+\lambda-E)^2}{4\lambda kT}\right)$$

emission spectra

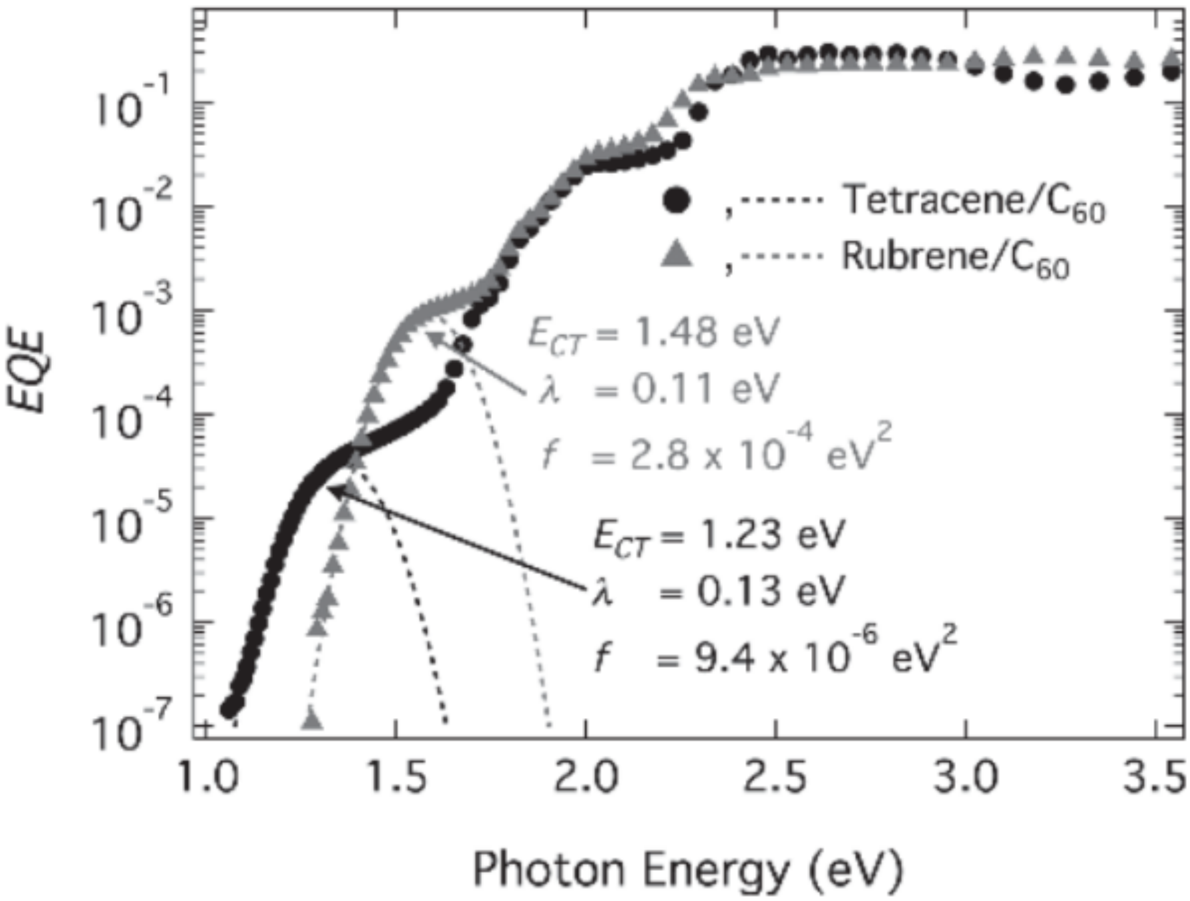
$$\frac{I_f}{E} = \frac{f_{I_f}}{\sqrt{4\pi\lambda kT}}\exp\left(\frac{-(E_{CT}-\lambda-E)^2}{4\lambda kT}\right)$$

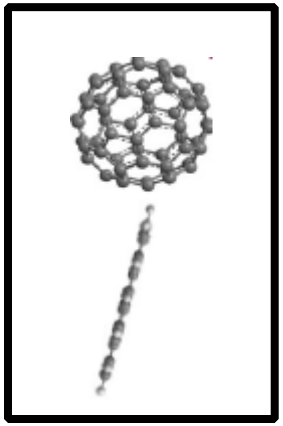


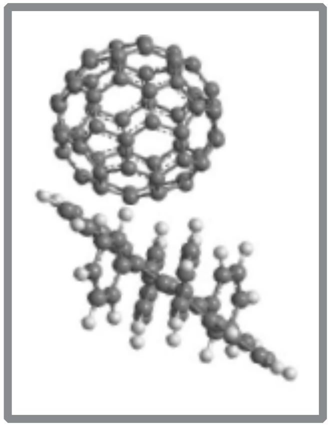


optical absorption in tetracene/C_{60} and rubrene/C_{60} bilayer

such a two-state model has been used to fit the absorption spectra in systems with low-energy absorption shoulders





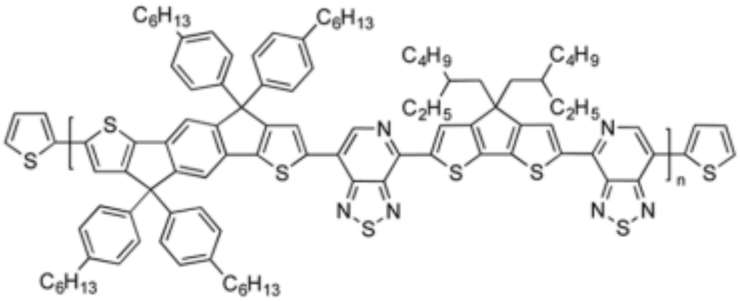


K.R. Graham, M.D. McGehee, A. Amassian, *et al.*,
Adv. Mater. 25, 6076 (2013)

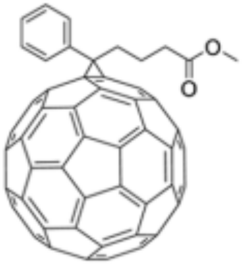
optical absorption in the PIPCP/PCBM blend

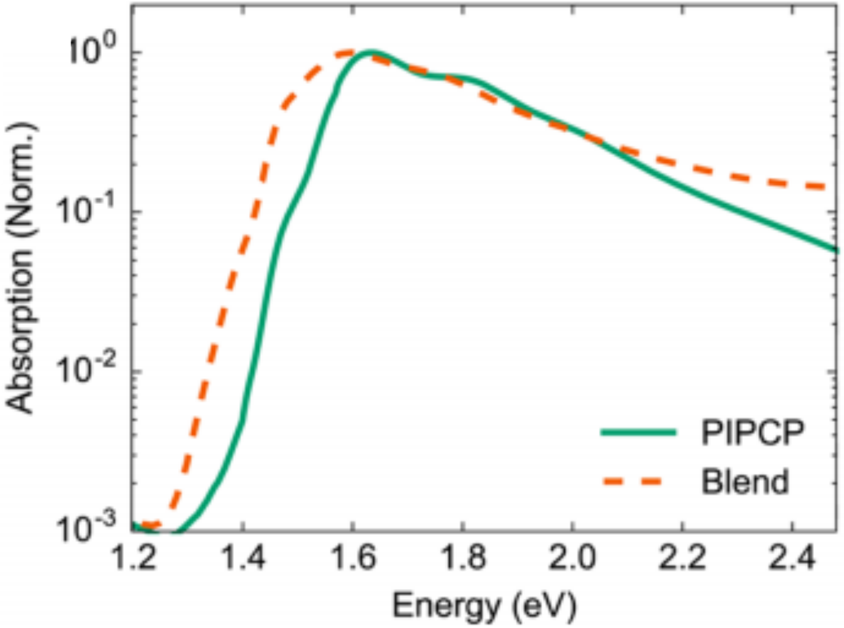
more recent experimental investigations have found that, in a number of systems, low-energy absorption shoulders are *not* observed

PIPCP



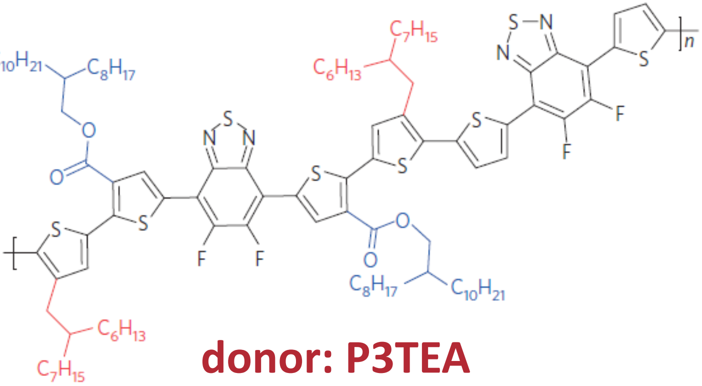
PCBM



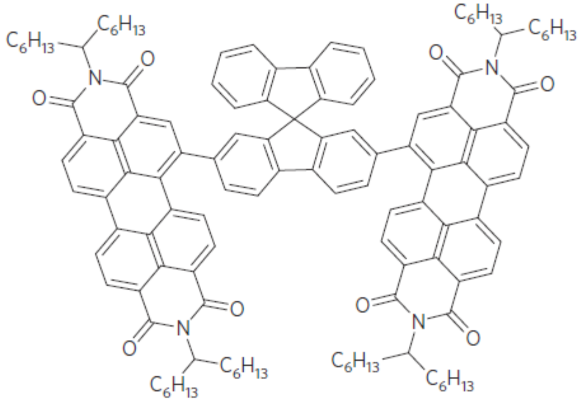


N.A. Ran, G.C. Bazan, T.Q. Nguyen, *et al.*, *Adv. Mater.* 28, 1482 (2016)

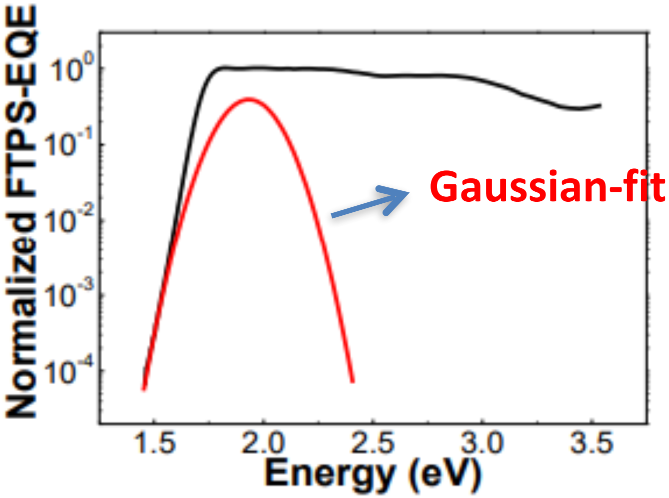
this is especially the case in efficient *non-fullerene acceptor/polymer* systems such as the P3TEA/SF-PDI2 blend:



donor: P3TEA



acceptor: SF-PDI$_2$



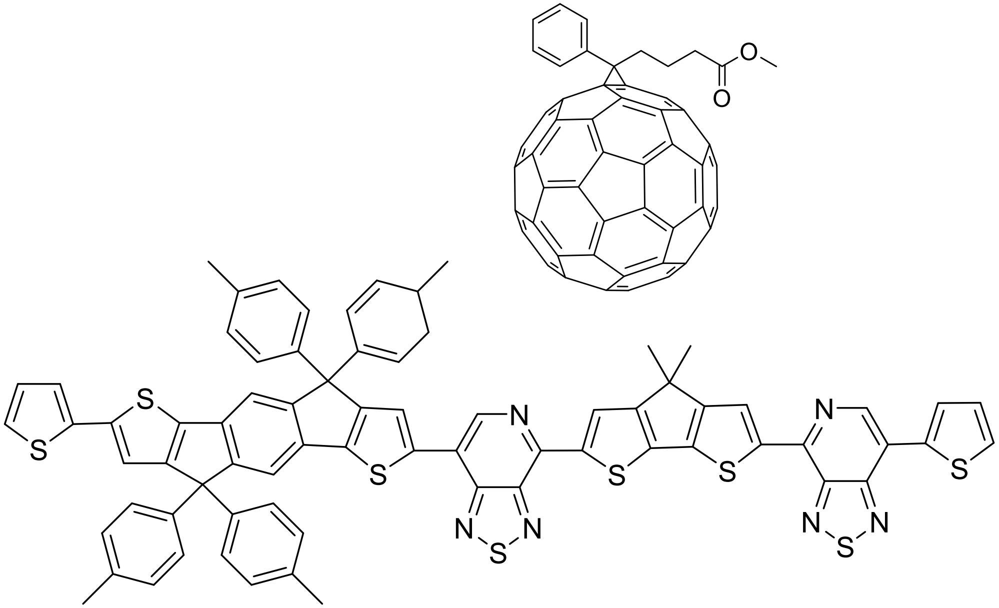
J. Zhao, H. Yan, *et al.*, *Nature Energy* 1, 15027 (2016)

the case of PIPCP / PCBM

Limits for Recombination in a Low Energy Loss Organic Heterojunction

S. Matthew Menke,[†] Aditya Sadhanala,[†] Mark Nikolka,[†] Niva A. Ran,[‡] Mahesh Kumar Ravva,[§] Safwat Abdel-Azeim,[§] Hannah L. Stern,[†] Ming Wang,[‡] Henning Sirringhaus,[†] Thuc-Quyen Nguyen,[‡] Jean-Luc Brédas,[§] Guillermo C. Bazan,[‡] and Richard H. Friend*,[†]

ACS NANO <u>10</u>, 10736-10744 (2016)



long-range corrected ωB97X-D/6-31G(d,p) DFT calculations of:

- **S_1 states of the isolated PIPCP oligomer**
- **CT states of the complex (8 configurations)**

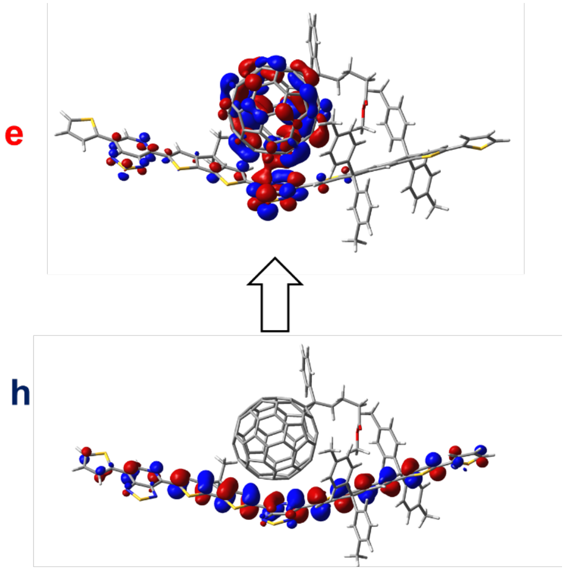
Configuration	E_{CT} (eV)	S_1 (eV)
Isolated PIPCP		1.62 (1.835)
1	1.52 (0.396)	1.66 (1.135)
2	1.59 (0.025)	1.67 (1.466)
3	1.55 (0.597)	1.61 (0.526)
4	1.57 (0.679)	1.59 (0.548)
5	1.51 (0.172)	1.66 (1.056)
6	1.67 (0.168)	1.58 (1.246)
7	1.73 (0.148)	1.68 (1.322)
8	1.73 (0.367)	1.64 (1.142)

lowest CT state:

- **generally *ca*. 0.1 eV below S_1**
- **significant oscillator strength**

NTO’s
(natural transition orbitals)

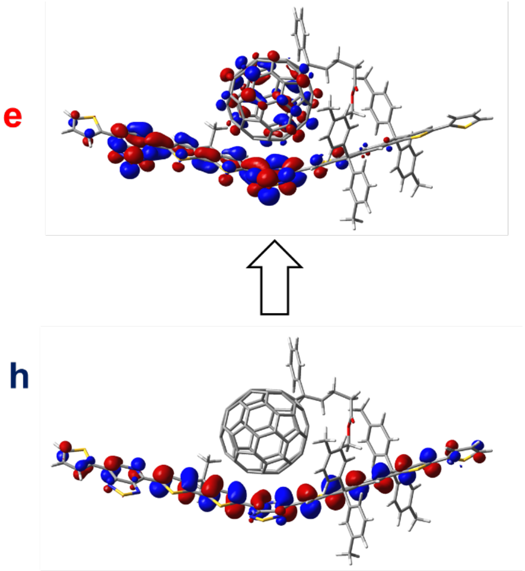
lowest excited state
“CT”
1.52 eV



second lowest excited state

“LE–S$_1$”

1.66 eV



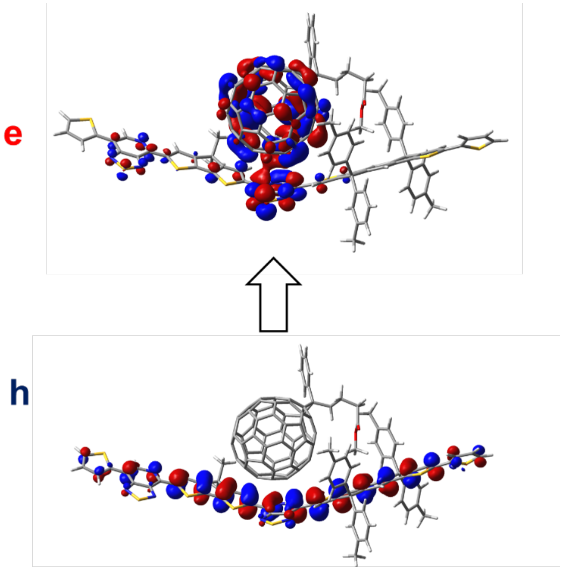
NTO’s

(natural transition orbitals)

lowest excited state

“CT”

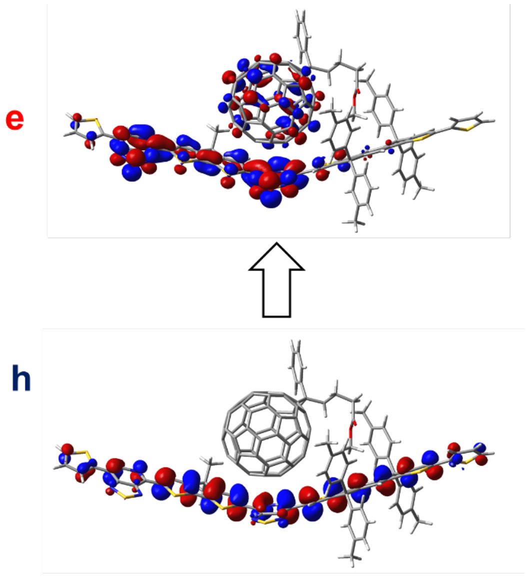
1.52 eV



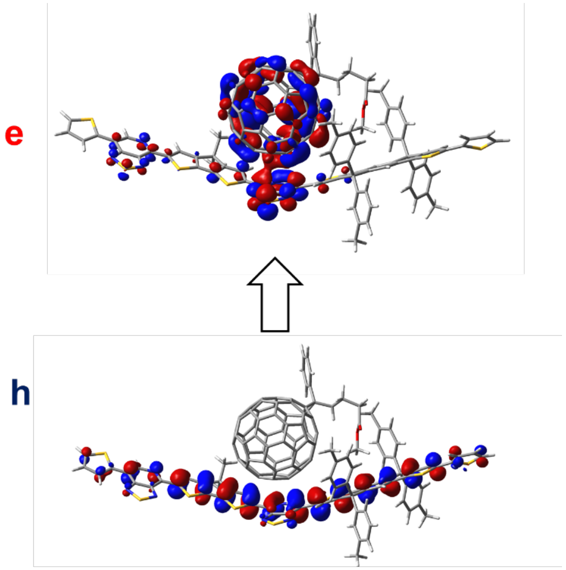
second lowest excited state

“LE–S$_1$”

1.66 eV



hybrid Frenkel-CT character!



lowest excited state

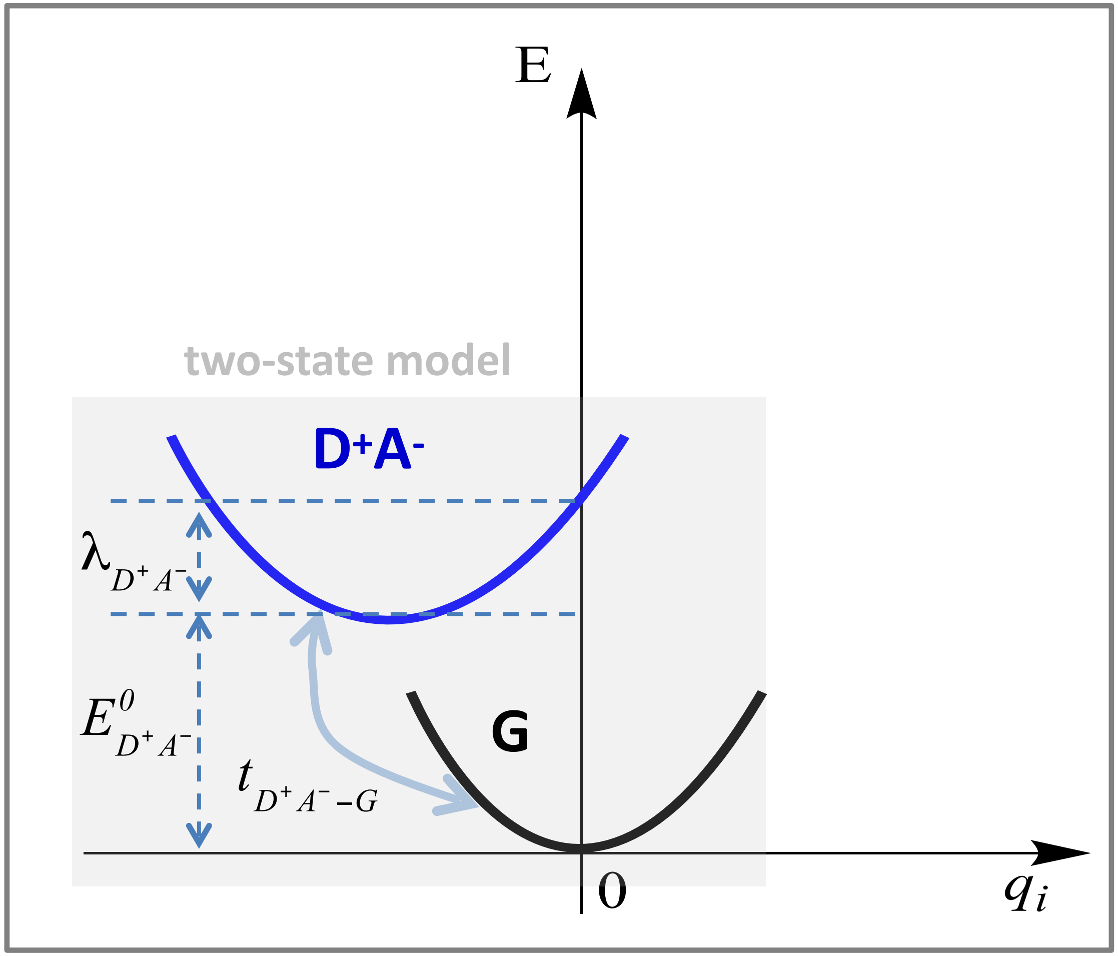
“CT”

1.52 eV

- long-range corrected DFT calculations confirm that the lowest CT state energies in PIPCP-PCBM complexes are only some 0.1 eV below the S_1 energy of PIPCP

- the lowest excitations of the PIPCP-PCBM complexes have *hybrid* charge-transfer / local excitation (Frenkel) character, consistent with the red shift of absorption in going from PIPCP thin film to PIPCP-PCBM blend

limitations of the two-state model



limitations of the two-state model

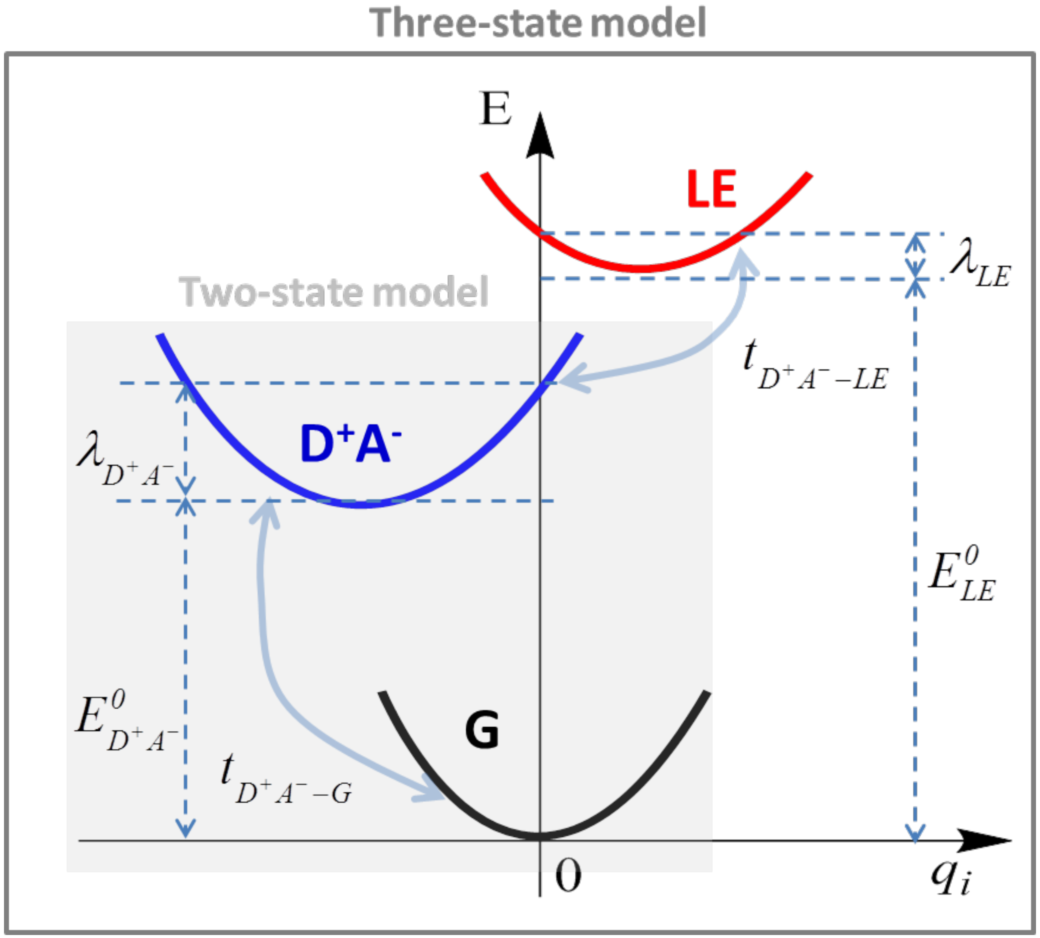
- only two states, the CT (D^+-A^-) state and the ground (G) state, are considered
- perturbation theory
- semi-classical treatment of high-frequency vibrations
- assumption of Gaussian line shapes

a 3-state approach

X.K. Chen, V. Coropceanu, & JLB, *Nature Commun.*
DOI: 10.1038/s41467-018-07707-8 (2018)

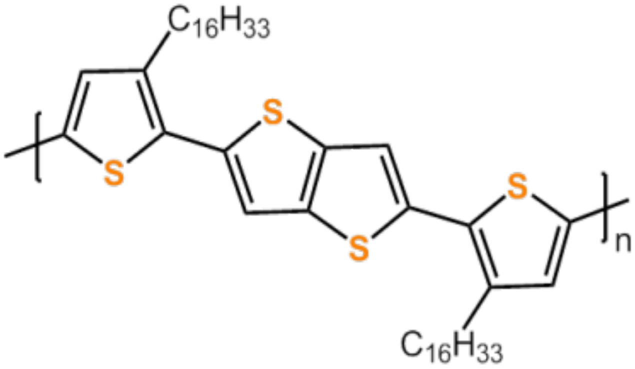
the three-state model

we have developed a *three-state model* that includes
the local-excitation (LE) state (= S_1 state of the absorbing material)
in addition to the charge-transfer (D^+A^-) state and the ground (G) state
and accounts quantum-mechanically for their vibronic couplings

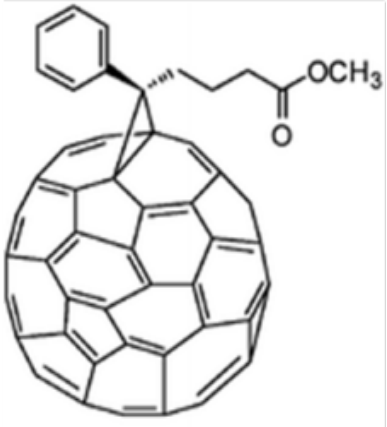


applications of the 3-state methodology

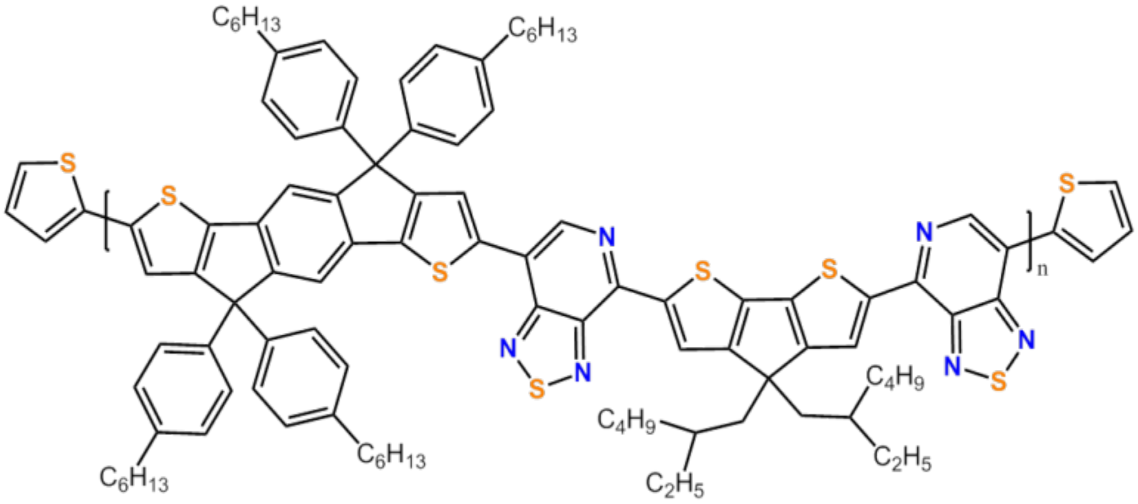
PBTTT



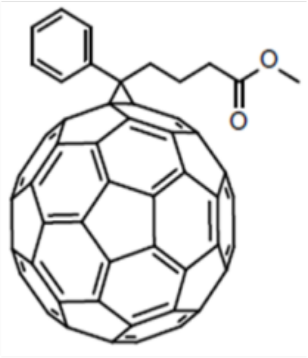
PC$_{70}$BM



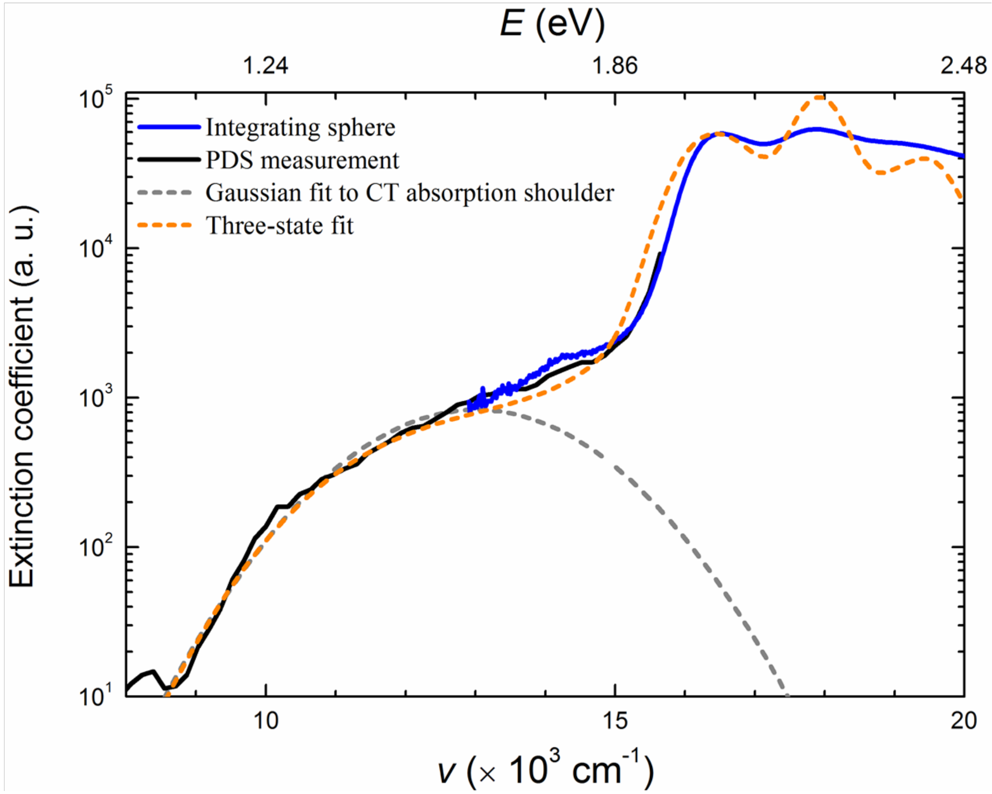
PIPCP



PC$_{60}$BM



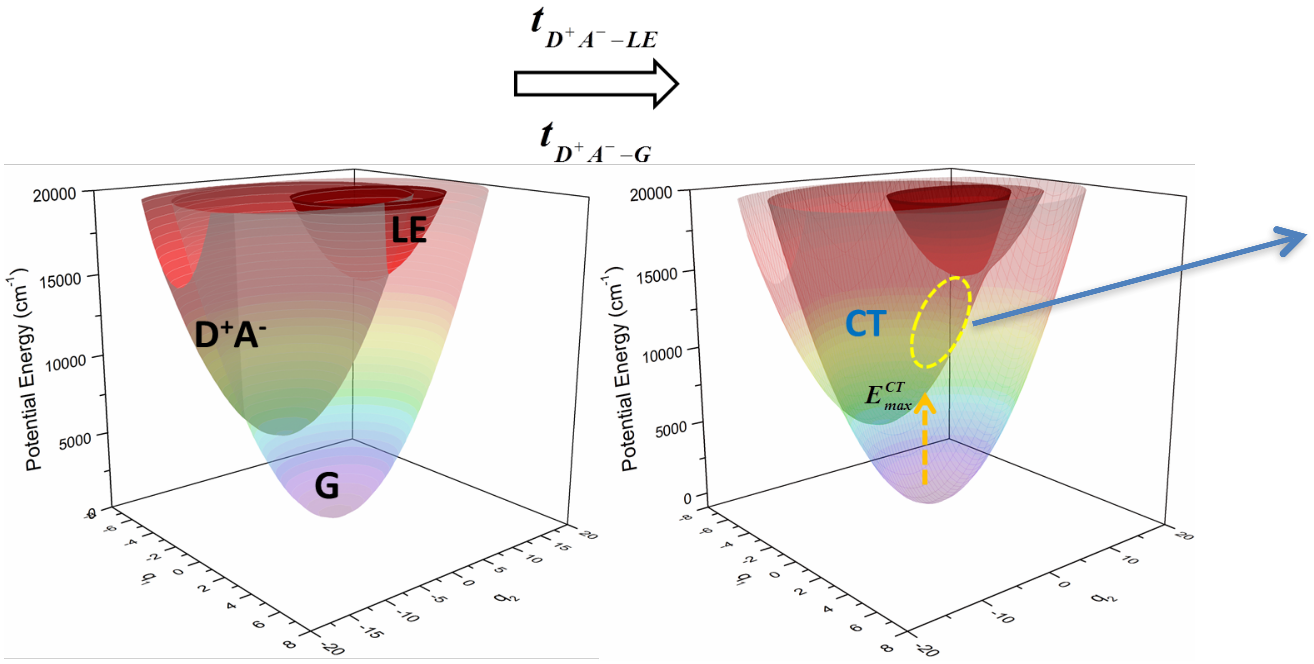
optical absorption of the PBTTT/PCBM blend



S. Sweetnam, M.D. McGehee,
JLB, *et al.*,
Chem. Mater., 28, 1446 (2016)

application of the two-state model leads to:

- an overestimation of the electronic coupling between the D^+A^- state and the ground state by ca. 270 cm^{-1}
- an underestimation of the relaxed D^+A^--state energy by 1000 cm^{-1}
- an overestimation of the D^+A^- state relaxation energy by ca. 500 cm^{-1}

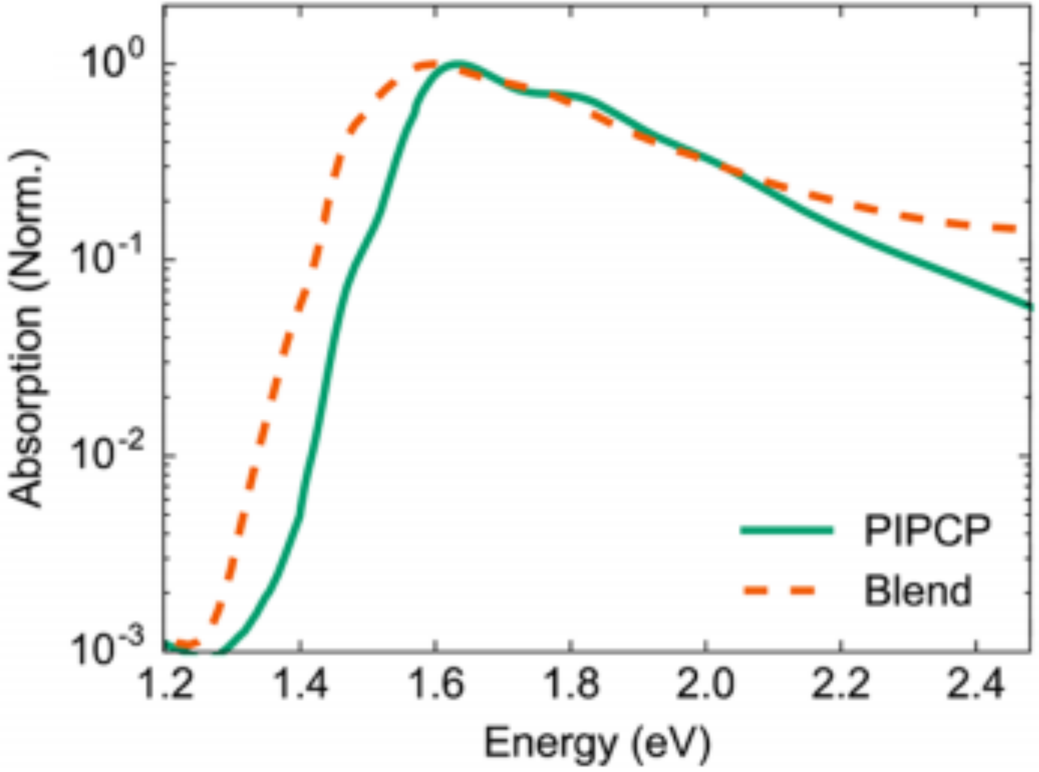


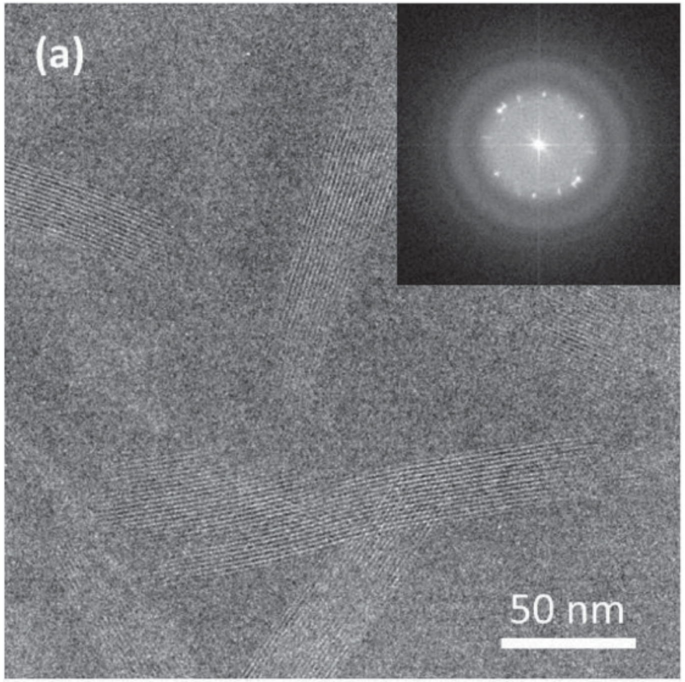
“hot” vibronic states

general consequence of the coupling between the D^+A^- and LE states:

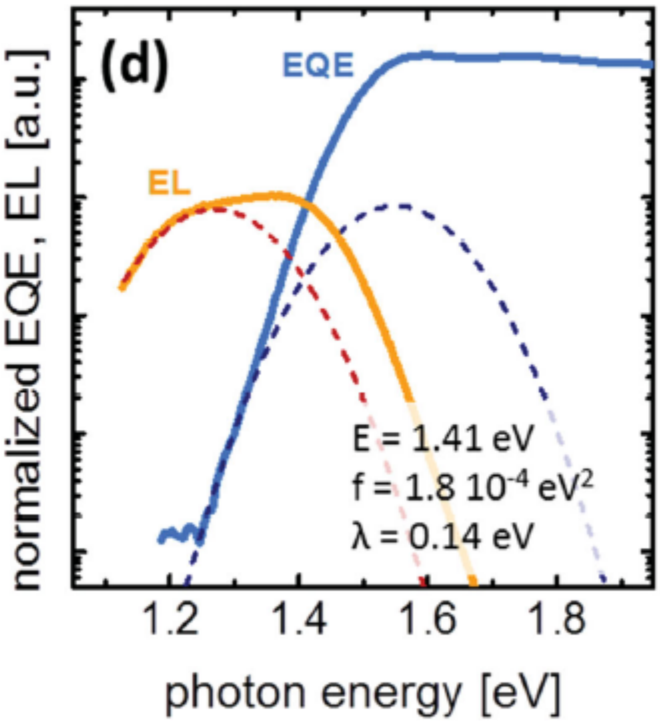
- “hot” CT vibronic states represent hybrid D^+A^--LE states and are therefore characterized by a significant transition dipole moment
- these can thus be efficiently directly accessed via optical excitation and could open a direct pathway to dissociation into free charge carriers, as soon as their energies are located above the charge-separated states, or below them but within thermal excitation energy

optical absorption of the PIPCP/PCBM blend

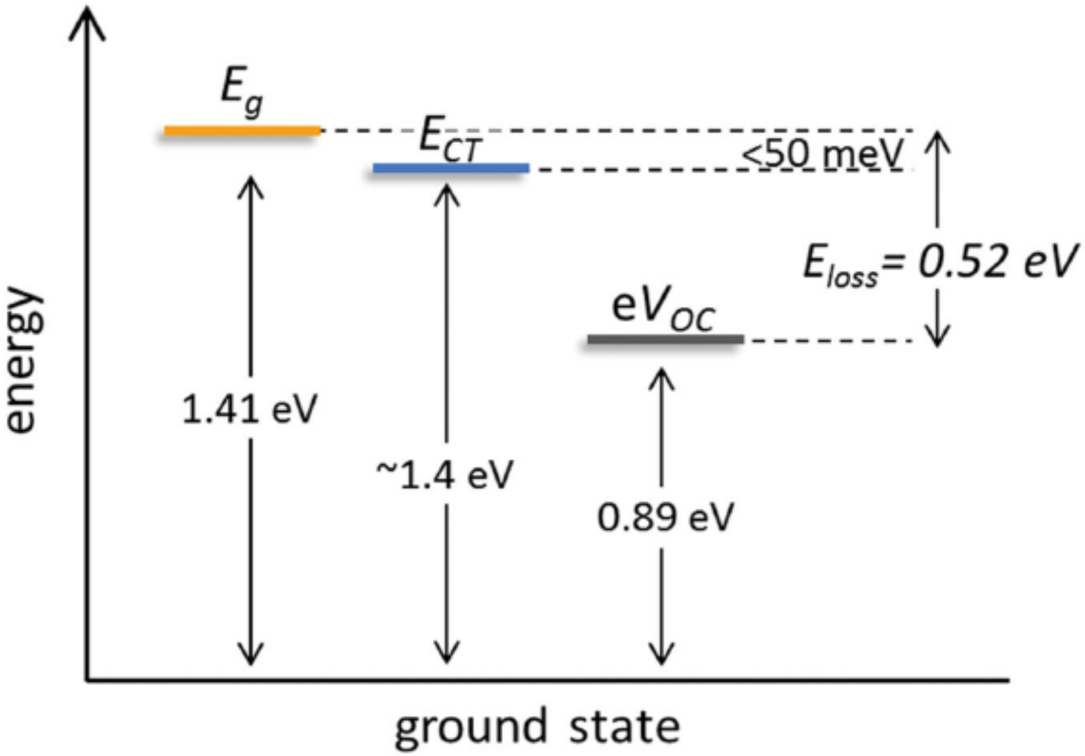




N.A. Ran, G.C. Bazan, T.Q. Nguyen, and co-workers
Adv. Mater. 28, 1482 (2016)



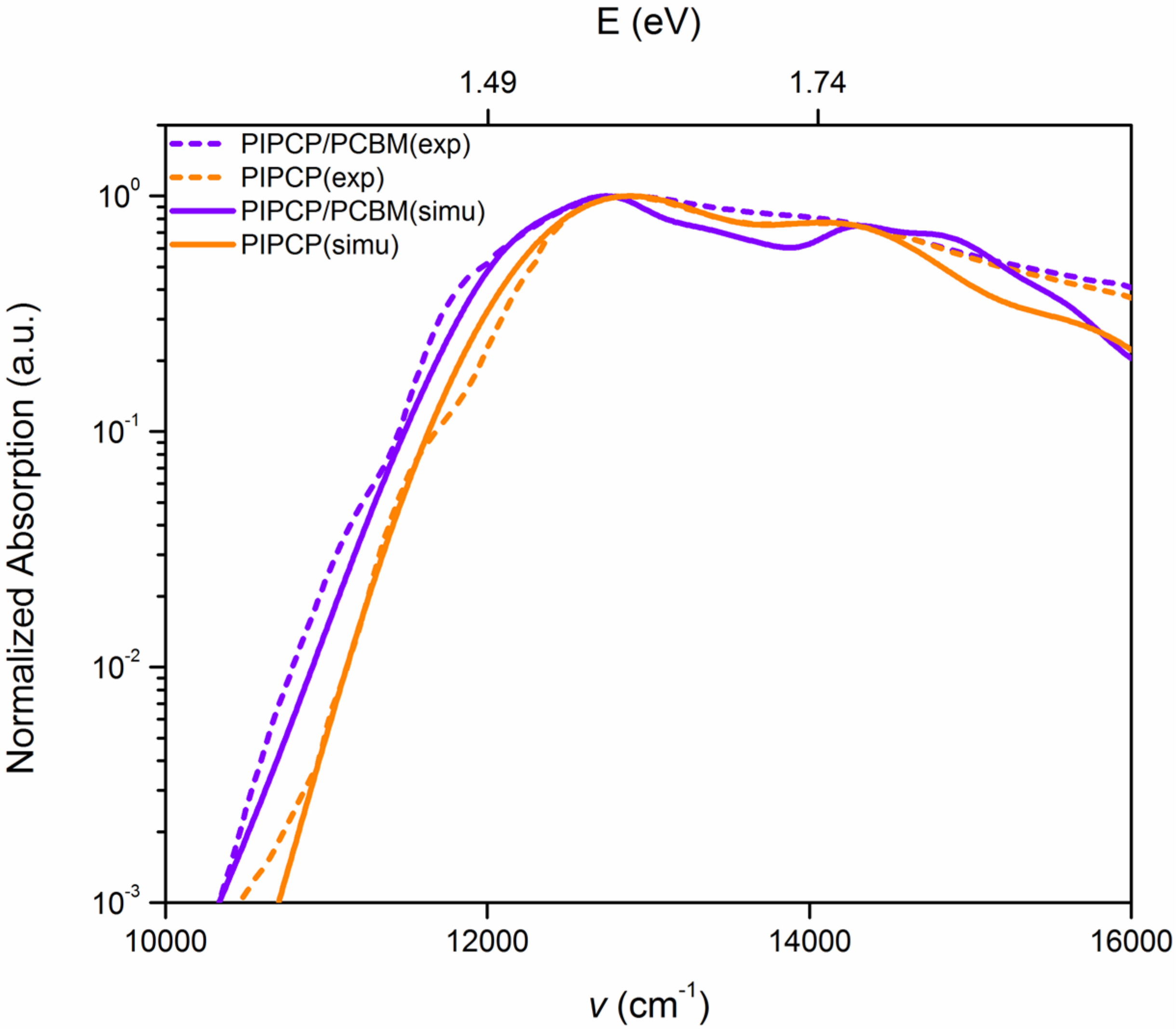
when the low-energy shoulder of the *electroluminescence* spectrum of PIPCP/PCBM is fitted by a Gaussian in the context of the 2-state model:
the procedure leads to a mere 0.05 eV difference between the polymer LE state and the D^+A^- state



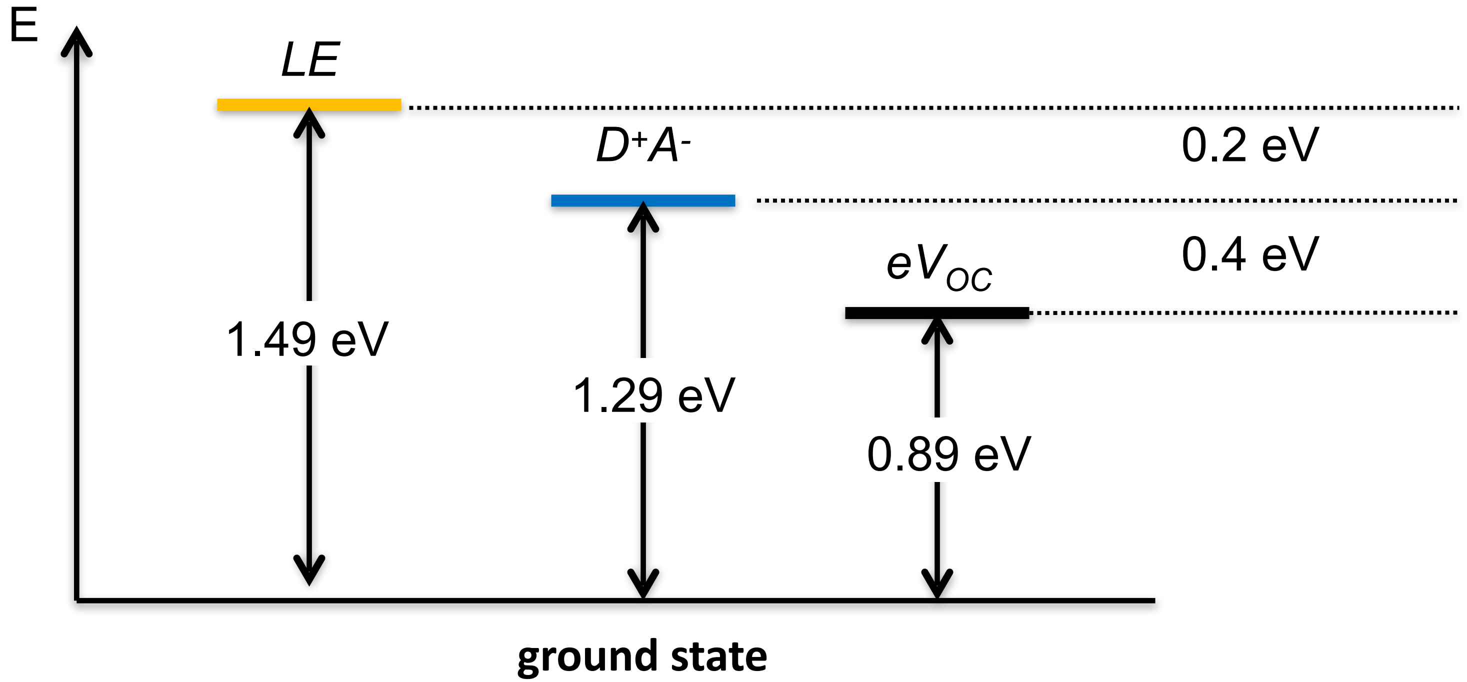
N.A. Ran, G.C. Bazan, T.Q. Nguyen, and co-workers
Adv. Mater. 28, 1482 (2016)

our best fit to the *absorption* data in the context of the 3-state model leads to:

- a 0.2 eV difference between the polymer LE state and the D^+A^- state
- a $LE-D^+A^-$ electronic coupling of 400 cm^{-1}
- a D^+A^--G electronic coupling of 100 cm^{-1}



through our three-state fit:



- **in the case of a large energy offset between the D^+A^- and LE states:**

the electronic coupling between the D^+A^- and LE states can make the shape and intensity of the low-energy shoulder substantially different from those that the semi-classical two-state Mulliken-Hush model would predict

hot CT vibronic states resulting from D^+A^--LE coupling gain a more substantial transition dipole moment

these hot CT vibronic states, which are directly optically accessible, have energies that can allow them overcome, entirely or at least in part, the electron-hole Coulomb barrier and dissociate easily into free charge carriers

- **in the case of a small energy offset between the D^+A^- and LE states:**

the absorption spectra hardly show any low-energy absorption feature instead, the D^+A^--LE coupling leads to a red-shift of the whole low-energy absorption edge

in such instances, a three-state model is *mandatory* in order to extract reliable information on the CT states from the absorption spectra

X.K. Chen, V. Coropceanu, & JLB, *Nature Commun.*
DOI: 10.1038/s41467-018-07707-8 (2018)

design rules to limit energy losses

nature materials

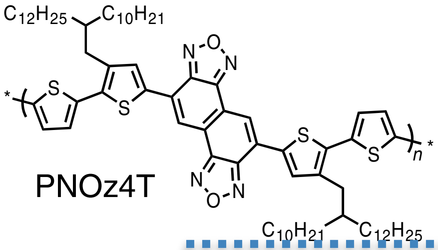
ARTICLES

https://doi.org/10.1038/s41563-018-0128-z

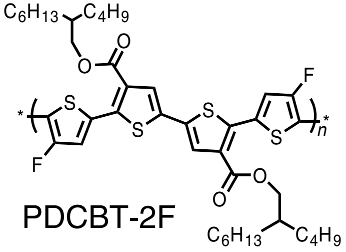
Design rules for minimizing voltage losses in high-efficiency organic solar cells

Deping Qian[1], Zilong Zheng[2], Huifeng Yao[3], Wolfgang Tress[4], Thomas R. Hopper[5], Shula Chen[1], Sunsun Li[3], Jing Liu[6], Shangshang Chen[6], Jiangbin Zhang[5,7], Xiao-Ke Liu[1], Bowei Gao[3], Liangqi Ouyang[1], Yingzhi Jin[1], Galia Pozina[1], Irina A. Buyanova[1], Weimin M. Chen[1], Olle Inganäs[1], Veaceslav Coropceanu[2]*, Jean-Luc Bredas[2], He Yan[6], Jianhui Hou[3], Fengling Zhang[1], Artem A. Bakulin[5]* and Feng Gao[1]*

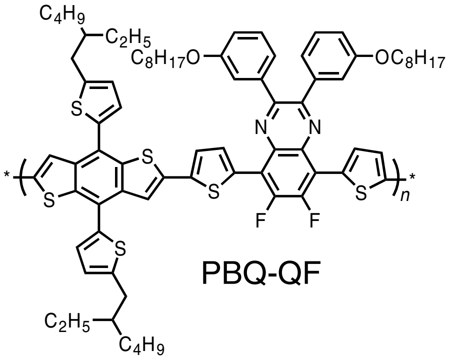
The open-circuit voltage of organic solar cells is usually lower than the values achieved in inorganic or perovskite photovoltaic devices with comparable bandgaps. Energy losses during charge separation at the donor–acceptor interface and non-radiative recombination are among the main causes of such voltage losses. Here we combine spectroscopic and quantum-chemistry approaches to identify key rules for minimizing voltage losses: (1) a low energy offset between donor and acceptor molecular states and (2) high photoluminescence yield of the low-gap material in the blend. Following these rules, we present a range of existing and new donor–acceptor systems that combine efficient photocurrent generation with electroluminescence yield up to 0.03%, leading to non-radiative voltage losses as small as 0.21 V. This study provides a rationale to explain and further improve the performance of recently demonstrated high-open-circuit-voltage organic solar cells.



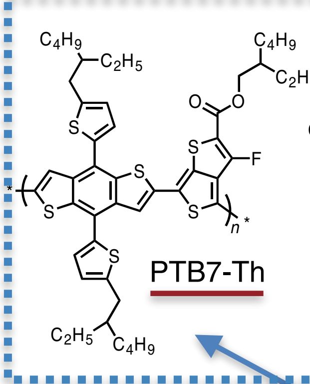
PNOz4T



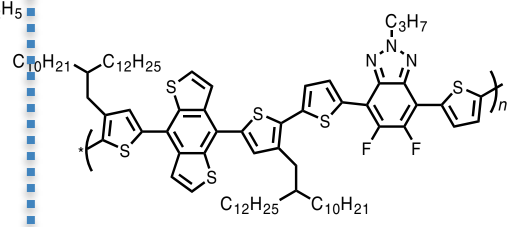
PDCBT-2F



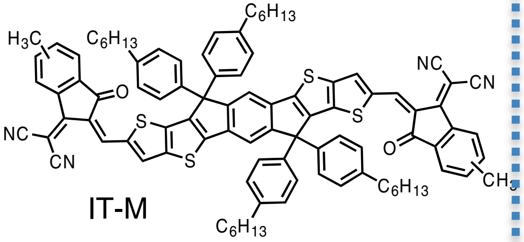
PBQ-QF



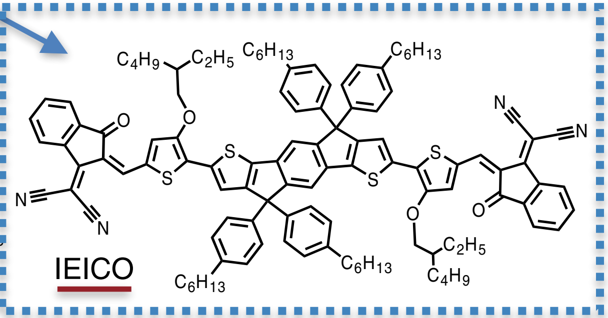
PTB7-Th



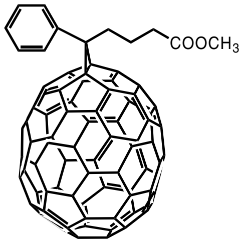
PvBDTTAZ



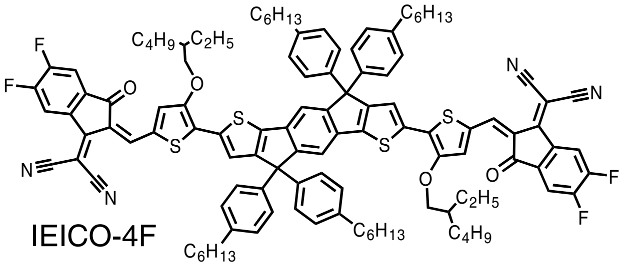
IT-M



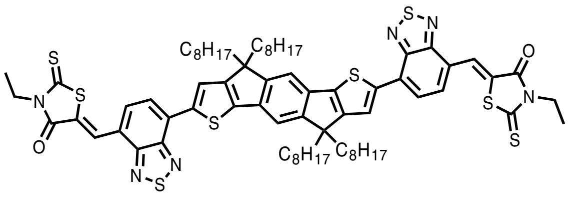
IEICO



$PC_{71}BM$

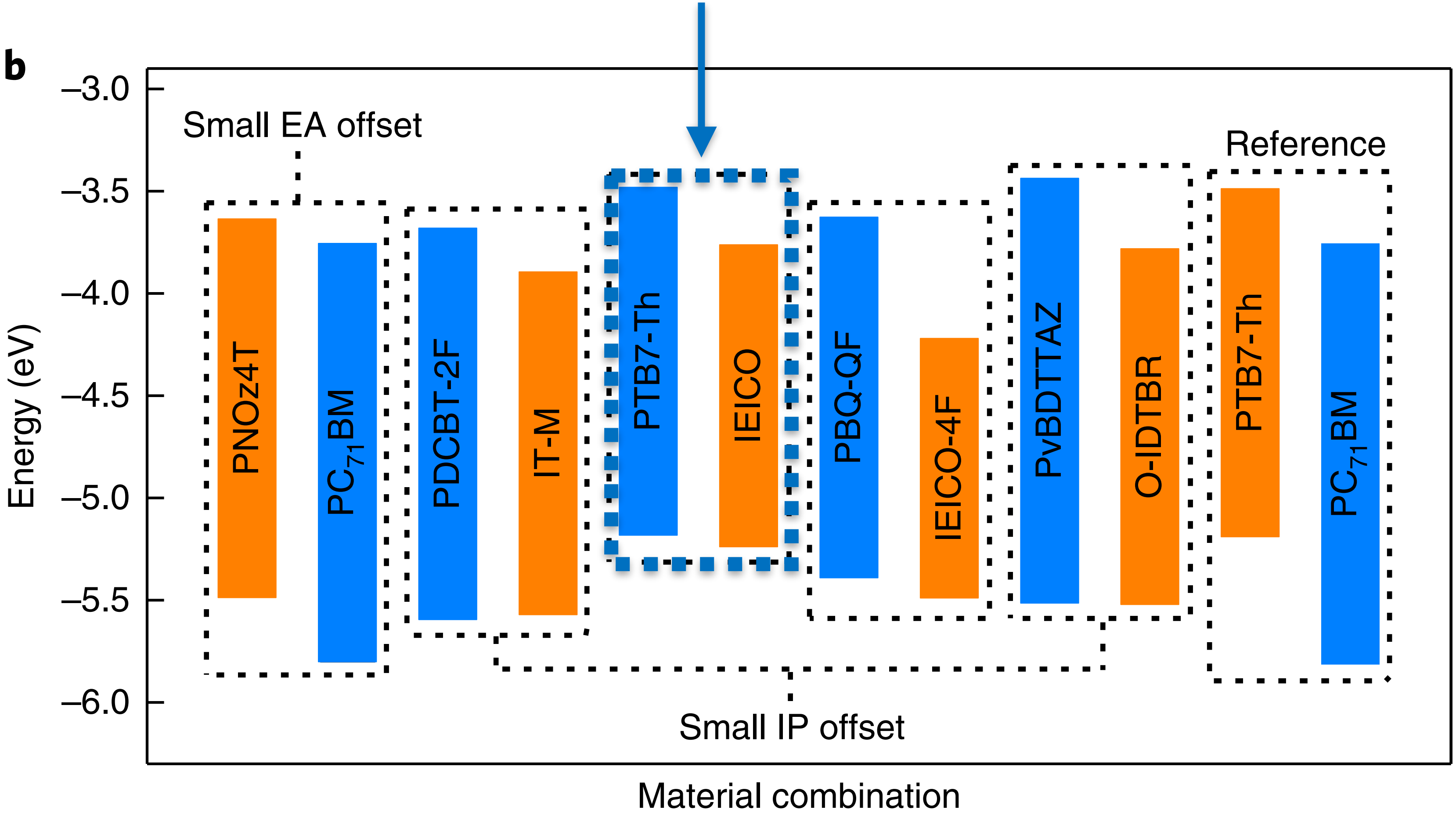


IEICO-4F



O-IDTBR

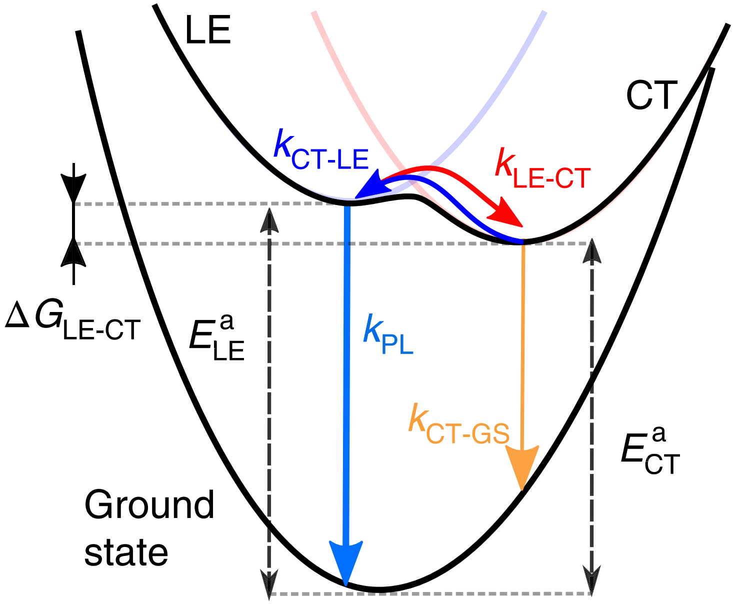
looking for either small IP or small EA offset:



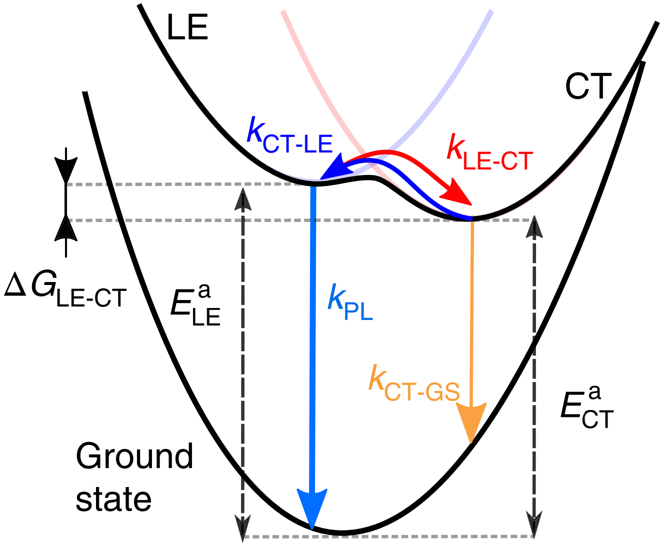
Marcus theory for the non-radiative recombination rate of the CT states

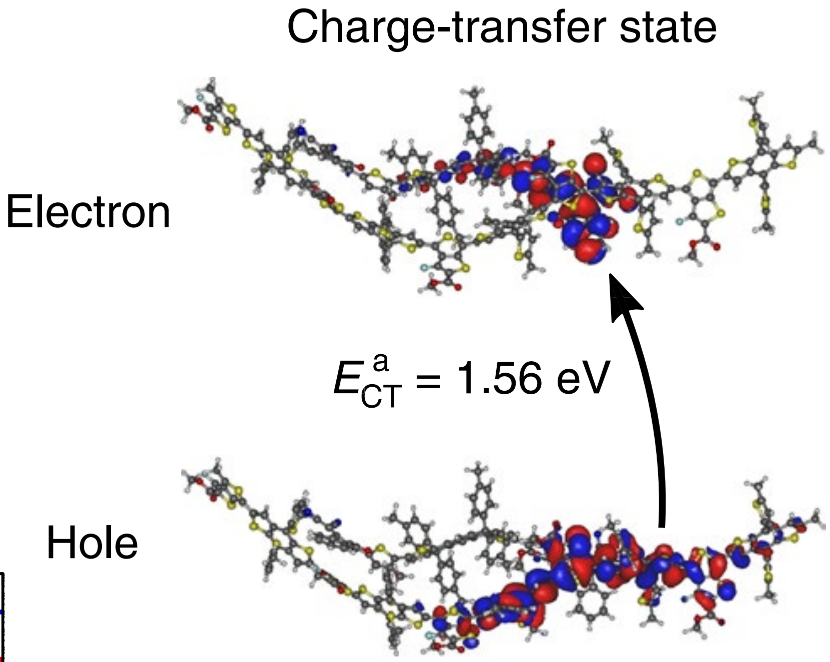
based on the parameters extracted either from the CT absorption spectra *within the 3-state model* or from direct DFT calculations, the non-radiative recombination rate of the CT states can be evaluated via Marcus theory:

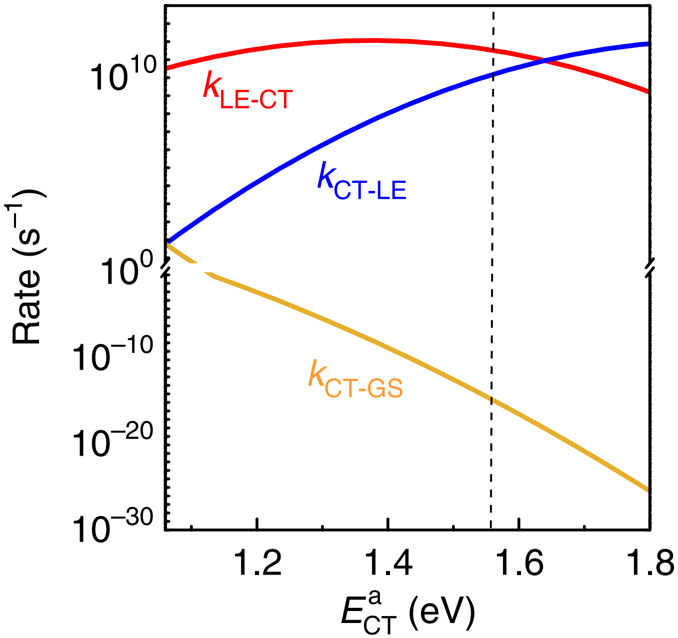
$$\boxed{k_{nr} = \frac{2\pi}{\hbar}\frac{\left|t_{D^+A^- - G}\right|^2}{\sqrt{4\pi\lambda_{D^+A^-}k_BT}}\,exp\left[-\frac{\left(-E^0_{D^+A^-}+\lambda_{D^+A^-}\right)^2}{4\lambda_{D^+A^-}k_BT}\right]}$$



PBT7-Th/IEICO







electron-transfer rates from LE to CT and from CT to LE states, and non-radiative recombination rate computed for the PTB7-Th:IEICO complex

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we have identified key rules for minimizing voltage losses:

(1) a low energy offset between donor and acceptor molecular states

(2) high photoluminescence yield of the low-gap material in the blend

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can such a design also ensure that:

there could be no additional intrinsic limitation with respect to the Shockley-Queisser limit

in terms of V_{OC} and efficiency of organic solar cells compared to other photovoltaic technologies

“Nature and Role of the Charge-Transfer Electronic States in Organic Solar Cells”
V. Coropceanu, X.K. Chen, T. Wang, Z. Zheng, and JLB
***Nature Reviews Materials*, invited review, submitted (2019)**

Veaceslav Coropceanu, Xiankai Chen, Zilong Zheng,
Hong Li, Tonghui Wang, Ajith Ashokan
– Georgia Tech

Mahesh Kumar Ravva – SRM University, India
Artem Bakulin – Imperial
Feng Gao – Linköping
Henry Yan – HKUST
Matt Menke, Richard Friend – Cambridge

Thank you!