EXÉRCITO BRASILEIRO

I M E

INSTITUTO MILITAR DE ENGENHARIA

(REAL ACADEMIA DE ARTILHARIA, FORTIFICAÇÃO E DESENHO - 1792)

-Top engineering college in Brazil and rank as one of 25 institutions with maximum overall score (Ministry of Education)

- Founded in 1792: 1st engineering school in the American continent, 3rd in the world

- Over 50 years of Graduate programs

Teoria e Técnicas de Eletrônica – Simpósio I

CEFET-RJ

28 Novembro de 2022

Organic Photovoltaics: insights from quantum chemistry

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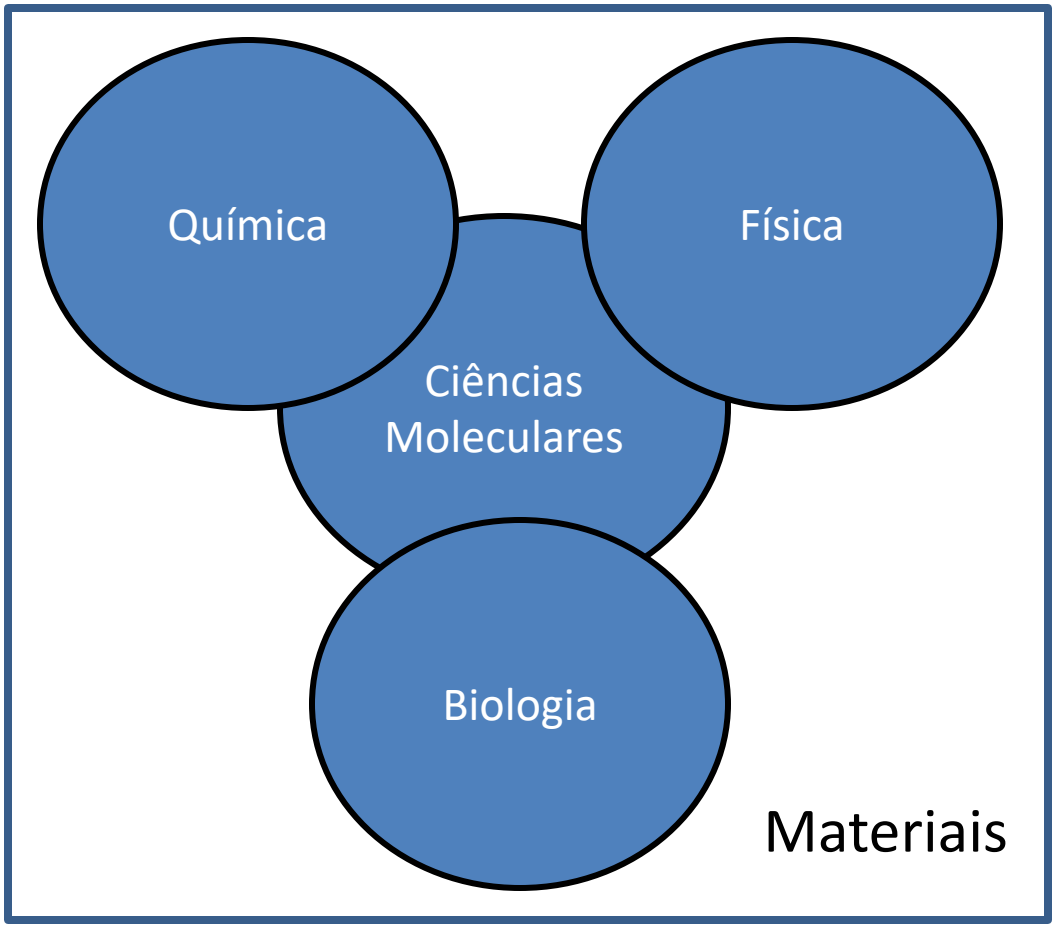


- Aplicações: Engenharia
- Entendimento
  Fenômenos
Macroscópicos

Nanotecnologia – desenvolvimento/construção de materiais em escala nanométrica (10^{-9} metros)

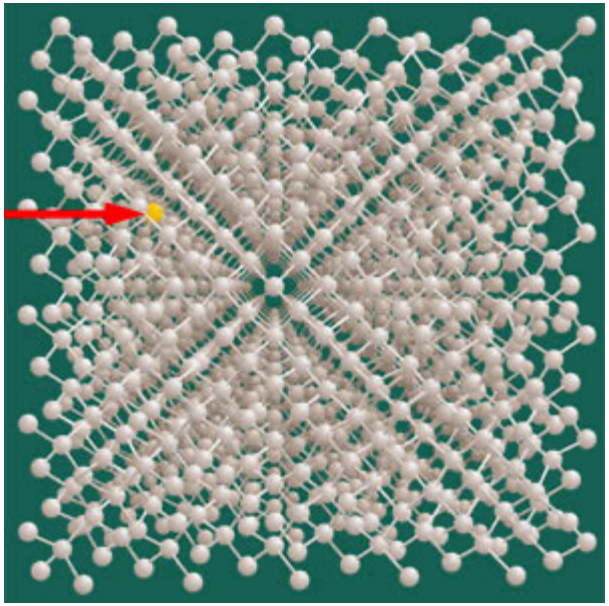
"There are plenty of space in the bottom" (R. P. Feynman, anos 50)

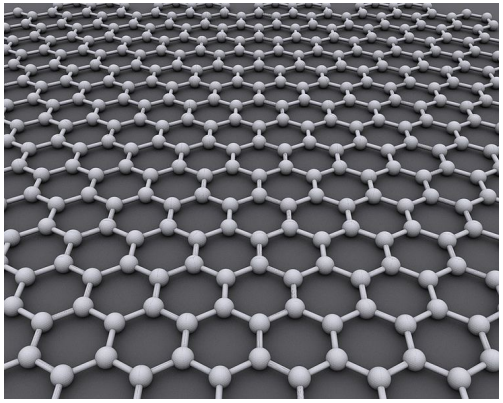
Matéria:
constituída de átomos e moléculas

Propriedades macroscópicas da matéria: *determinadas* pelos comportamento dos átomos e moléculas

impureza

Cristal de diamante





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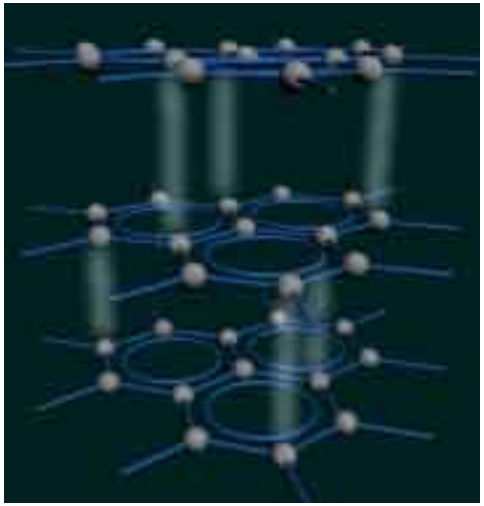

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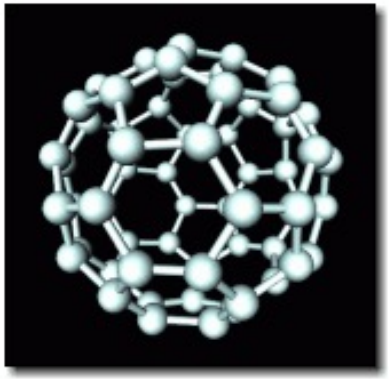


C_{60}

Química Quântica

Teoria que descreve átomos e moléculas: **Mecânica Quântica**

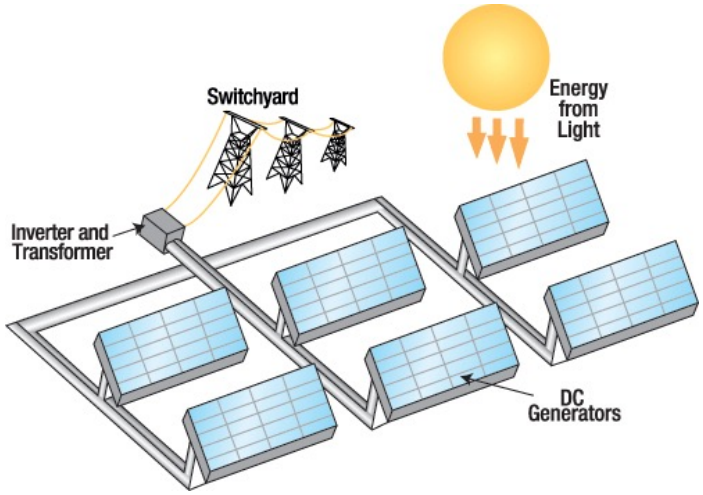
Mecânica Quântica aplicada à átomos e moléculas: **Química Quântica**

Uso de computadores: **Química Quântica Computacional**

Prêmio Nobel de Química – 1998
Walter Kohn e John Pople

ORGANIC PHOTOVOLTAICS

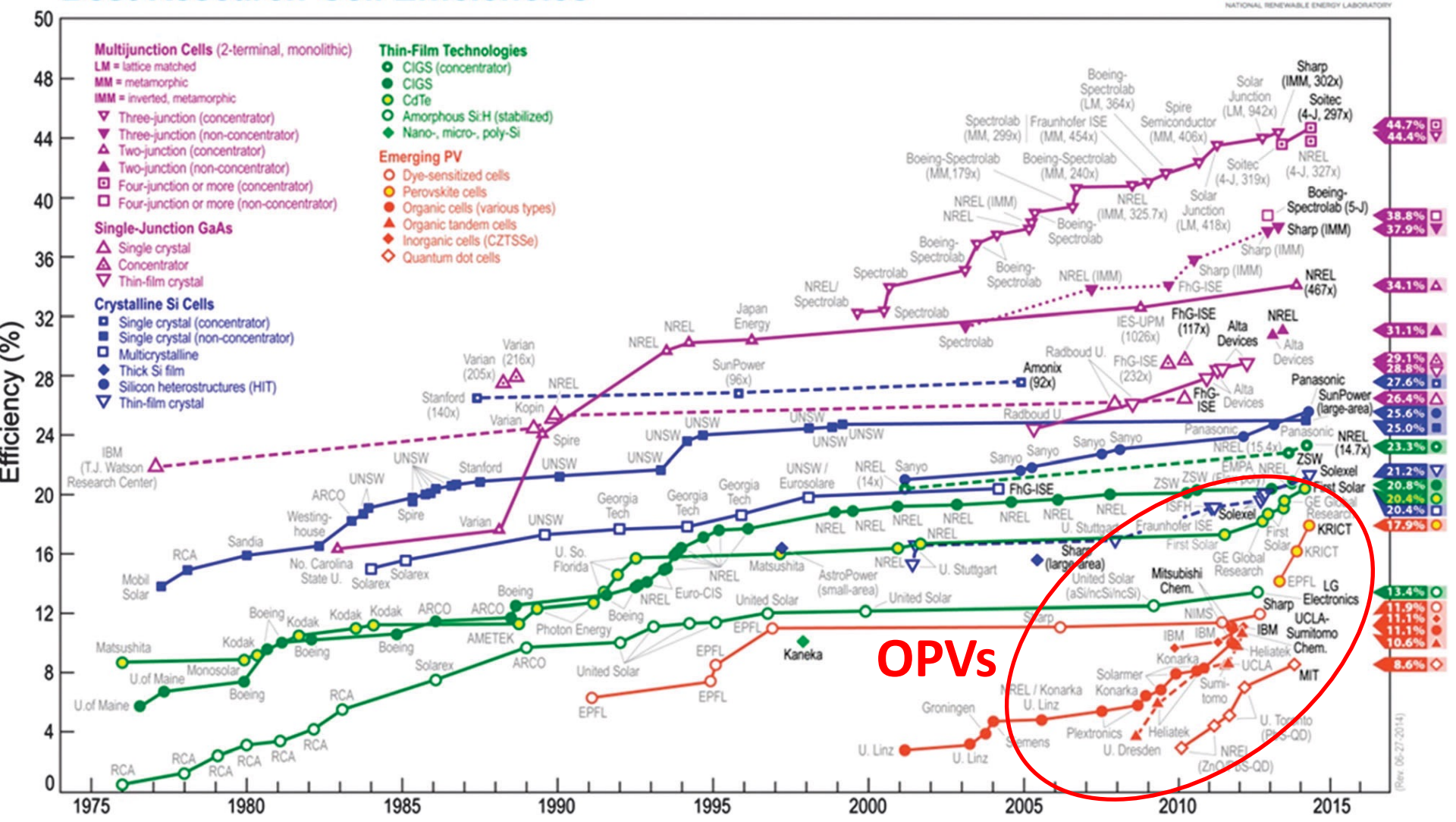
Electricity from Sunlight
Organic Photovoltaics



Silicon technology: crystalline material

Alternative: organic semiconductors - π-conjugated polymers

Best Research-Cell Efficiencies



March 2015

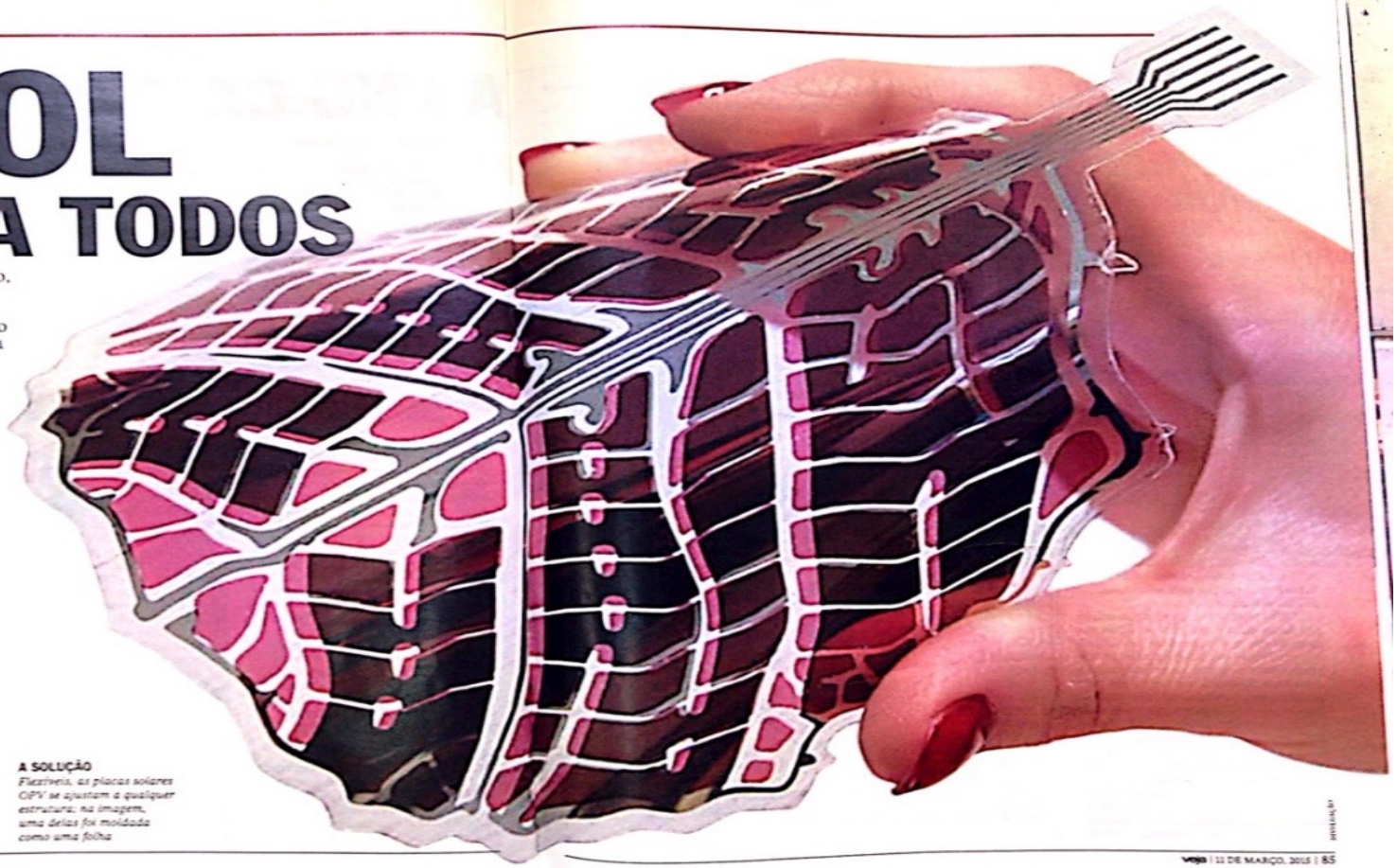
Tecnologia

O SOL É PARA TODOS

Placas feitas de material orgânico, maleáveis, leves e delgadas, podem finalmente popularizar uma fonte de energia ainda muito cara, mas destinada a substituir a era dos combustíveis fósseis

RAQUEL BEER

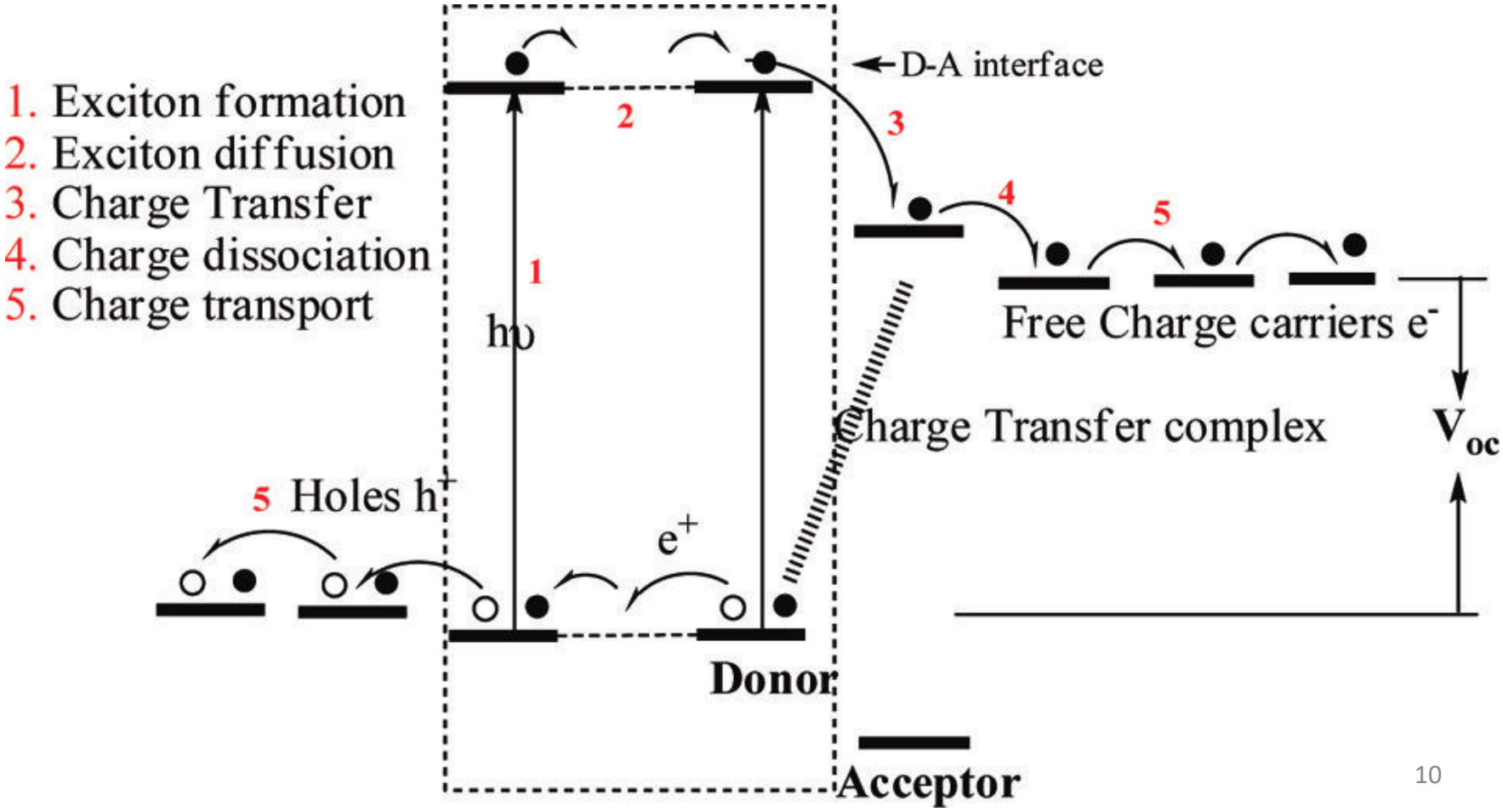
Se toda a radiação que atinge a Terra em um único dia, vinda do Sol, virasse eletricidade, seria possível sustentar o consumo da humanidade ao longo de 27 anos. A energia solar, limpa e renovável, funcionaria como perfeito substituto do petróleo, finito e refém da gangorra dos preços. Representaria ainda o mais magnífico processo de troca de matriz energética, no aveso da poluição provocada pela queima de combustíveis fósseis, o mais rápido e barato atalho para o aquecimento global. E, no entanto, por que a energia solar ainda é pouco usada, quase sempre mais promessa que realidade? As placas de silício necessárias para captá-la por meio de painéis são caras, pesadas e grossas. Apesar de úteis em grandes espaços, como campos, são inúteis para substituir o petróleo na vida urbana. Nos últimos cinco anos, porém, surgiu uma nova tecnologia afeita a vencer esses desafios. Construídas com material não tóxico, as placas OPV (sigla em inglês para painéis fotovoltaicos orgânicos) têm a finura de uma cartolina e a flexibilidade do plástico. Podem ser coladas no teto de um carro, nas janelas de prédios ou mesmo em mochilas.



A SOLUÇÃO
Flexíveis, as placas solares OPV se ajustam a qualquer estrutura; na imagem, uma delas foi moldada como uma folha

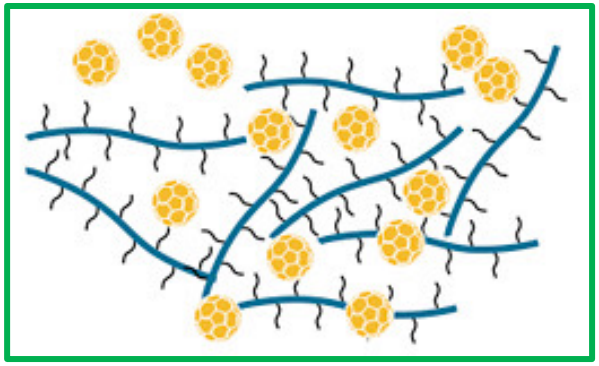
Organic Photovoltaics Fundamental Processes

EXCITON: **electron – hole pair** formed upon **light absorption**

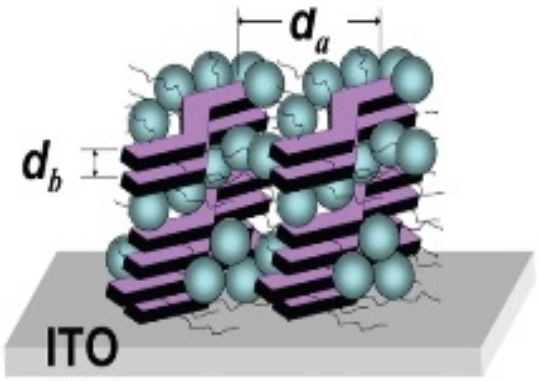


Inorganic vs Organic photovoltaics

- ✓ Light absorption creates excited states – electron-hole pair (exciton)
- ✓ In contrast with inorganic, organic semiconductor:
  - ✓ localized excitations
  - ✓ low dielectric constant
  - ✓ exciton binding energy is rather large (***~0.5 eV***)
  - ✓ dissociation is not straightforward

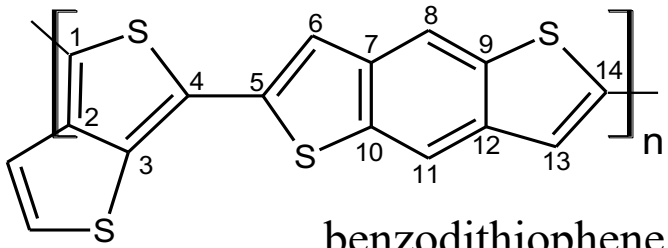


- ✓ Bulk heterojunction (BHJ) – workhorse and state-of-art of organic photovoltaics;
- ✓ PTB1/PCBM (alternating poly(thieno[3,4-*b*]thiophene benzodithiophene)/[6,6]-phenyl-C_{61}- acid methyl ester)



Liang et al. *J. Am. Chem. Soc.* **2009,** *131* (1), 56-57

PTB1



thienothiophene
electron-deficient

benzodithiophene
electron-rich

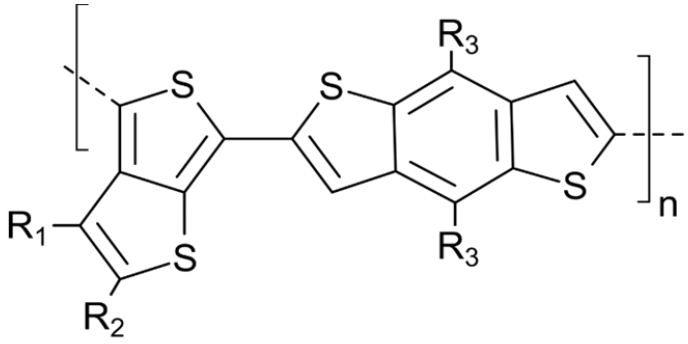
Challenge

Understand thoroughly and accurately electronic processes in organic photovoltaics (OPVs)

Compute properties of the OPVs

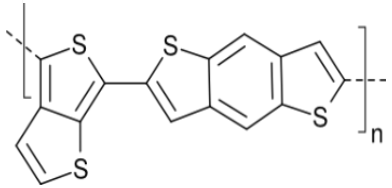
PTB family of donor polymers properties

- ✓ Support quinoidal structure leading to a narrow band gap;
- ✓ Unique zig-zag structure favors parallel orientation to the substrate;
- ✓ Low band gap for eficient absorption
- ✓ Proper **level matching** of HOMO (donor) – LUMO (acceptor) to overcome binding energy of exciton (~ 0.1 – 0.5 eV)
- ✓ Effective π–π overlap between polymers favor charge transport
- ✓ PTB7 is the first polymer in an organic photovoltaic to have power conversion efficency (PCE) > 7%

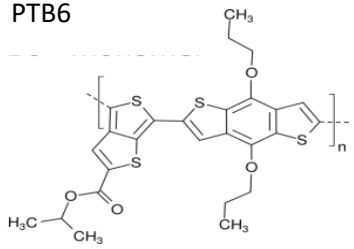


	PTB1	PTB6	PTB7
R_1	H	H	F
R_2	H	Isopropyl acetate	Isopropyl acetate
R_3	H	O-n-propyl	O-iso-propyl

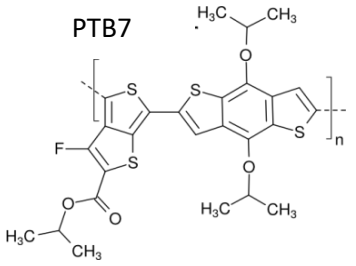
PTB1



PTB6



PTB7



Results

Quantum chemical modeling:

- PTB1/PCBM heterojunction
- PTB1
- PTB6 and PTB7

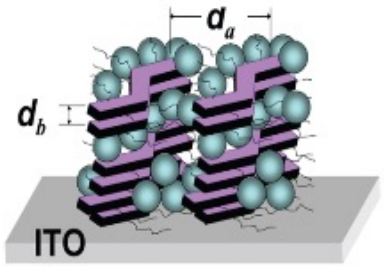
METHODS

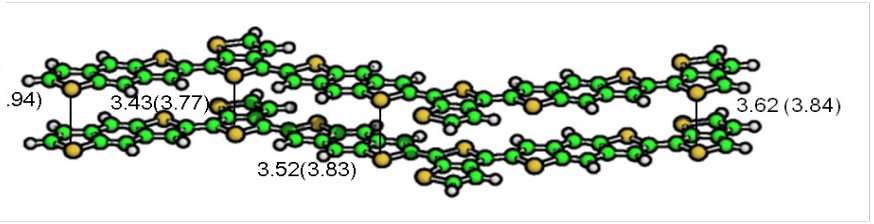
Theoretical approach

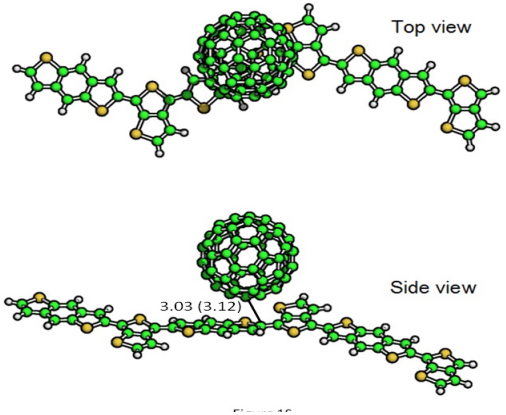
- ✓ Algebraic diagrammatic construction method to second order - ADC(2) – *ab initio* wave function-base polarization propagator method with judicious freezing of occupied and virtual orbitals
- ✓ MP2 for electronic ground state
- ✓ Grimme dispersion correction
- ✓ DFT: Five exchange-correlation functionals PBE, B3LYP, BhandHYLYP, CAM-B3LYP and LC-wPBE, in order of increasing degree of Hartree-Fock exchange
- ✓ SV/SVP basis set (SVP for S, SV for C and H)

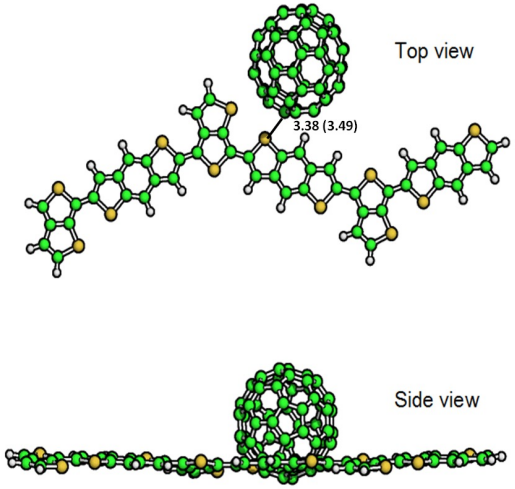
RESULTS

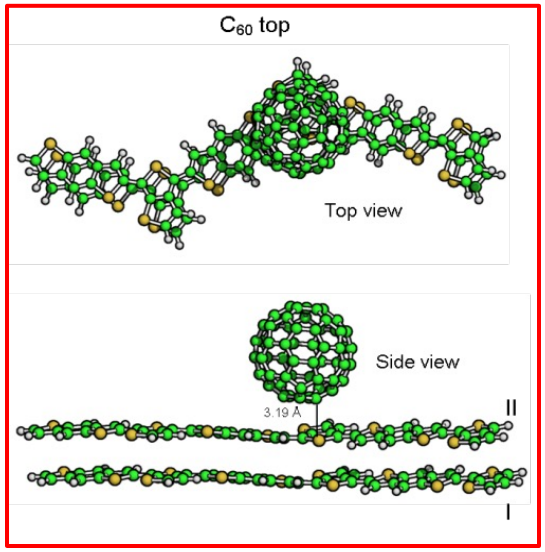
PTB1/PCBM - models

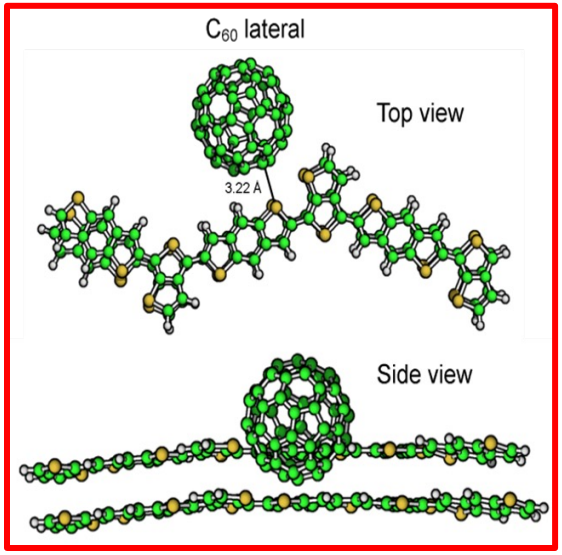






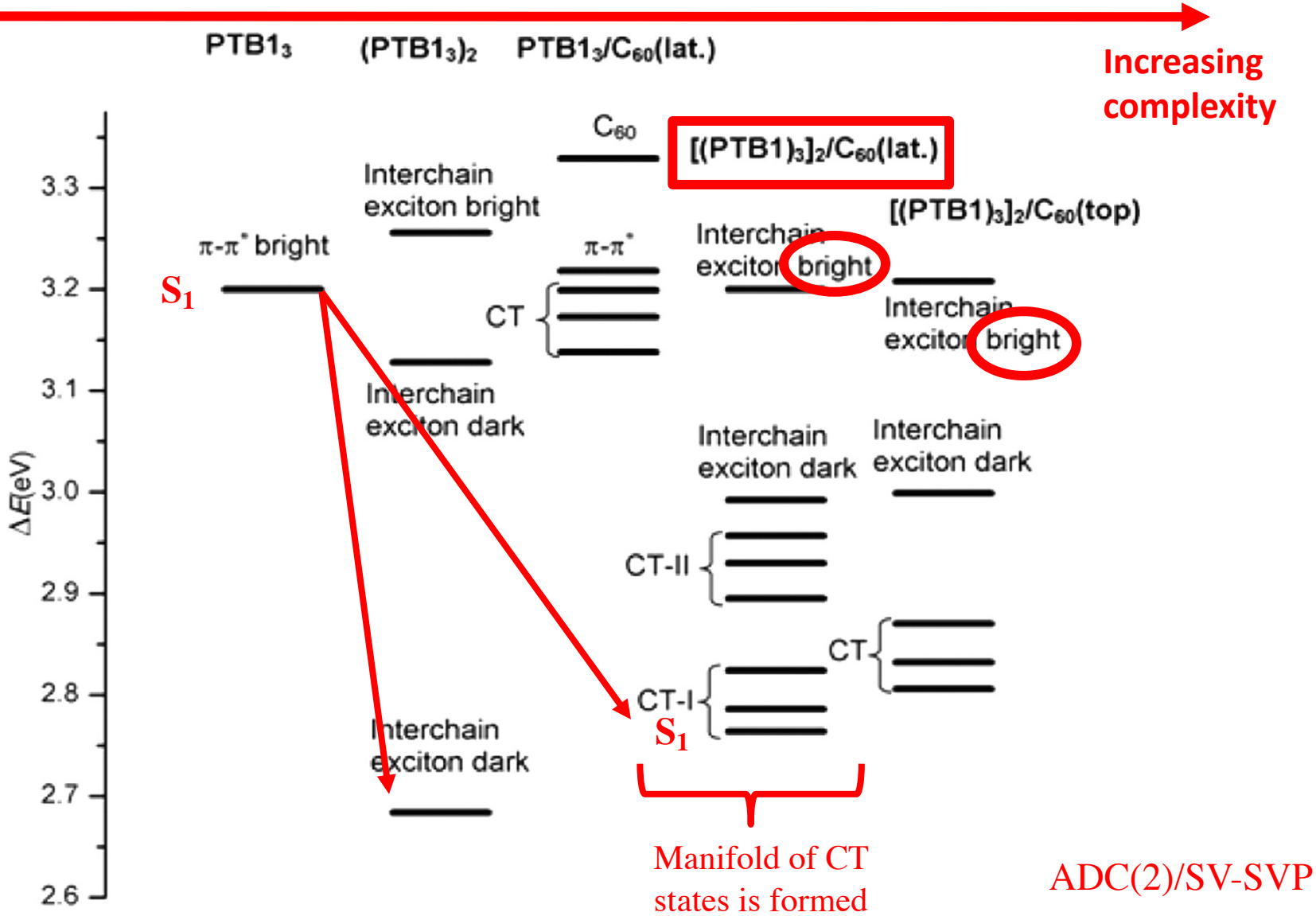






5 **fully optimized geometries**: PBE(D)/SV-SVP with BSSE counterpoise correction and dispersio

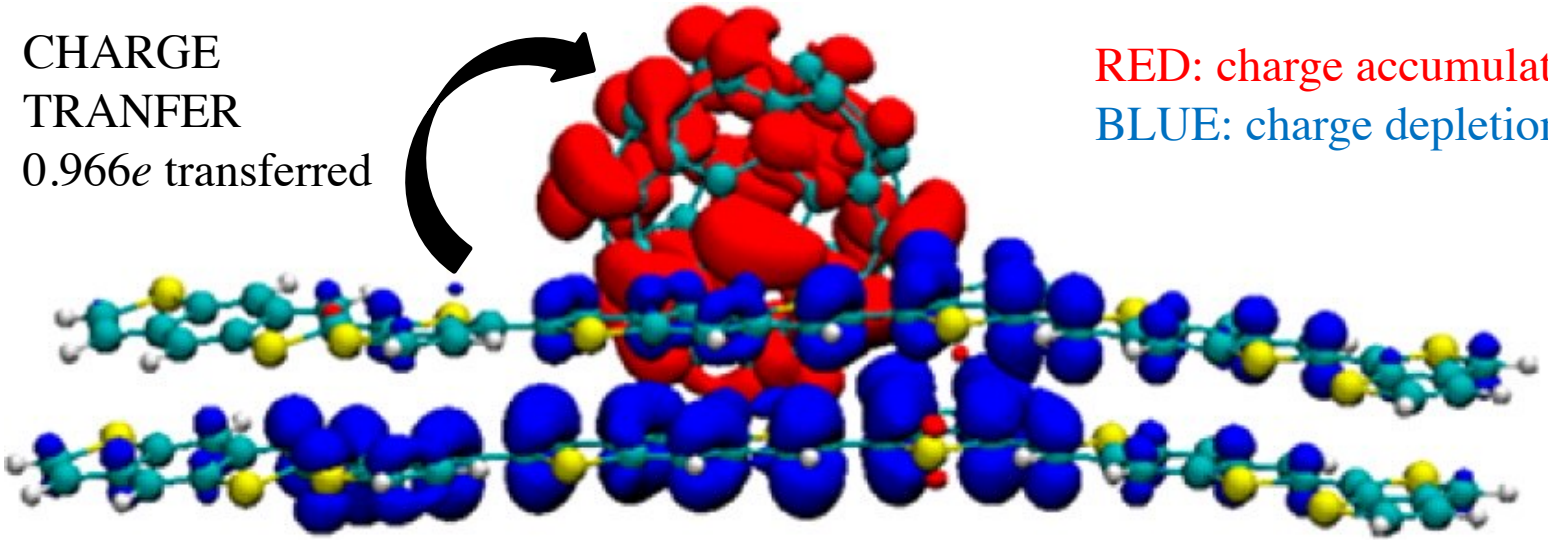
PTB1/C_{60} – energy levels



PTB1/C_{60} - electron density difference

Most efficient: **$(PTB1)_3$/ $(PTB1)_3$ / C_{60} (lat): $S_0 \rightarrow S_1$ (CT)**

CHARGE
TRANFER
0.966*e* transferred



RED: charge accumulation
BLUE: charge depletion

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Ab Initio Modeling of Excitonic and Charge-Transfer States in Organic Semiconductors: The PTB1/PCBM Low Band Gap System

Itamar Borges, Jr.,*[§,†] Adélia J. A. Aquino,[§] Andreas Köhn,[∥] Reed Nieman,[§] William L. Hase,[§] Lin X. Chen,[⊥] and Hans Lischka*[§,#]

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[†]Departamento de Química, Instituto Militar de Engenharia, 22290-270 Rio de Janeiro, Brazil
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[#]Institute for Theoretical Chemistry, University of Vienna, 1090 Vienna, Austria

Bechmark of electronic properties of PTB1

- Use ADC(2) to benchmark data for for excited state energies, oscillator strengths, and bond length alternation (BLA) analysis

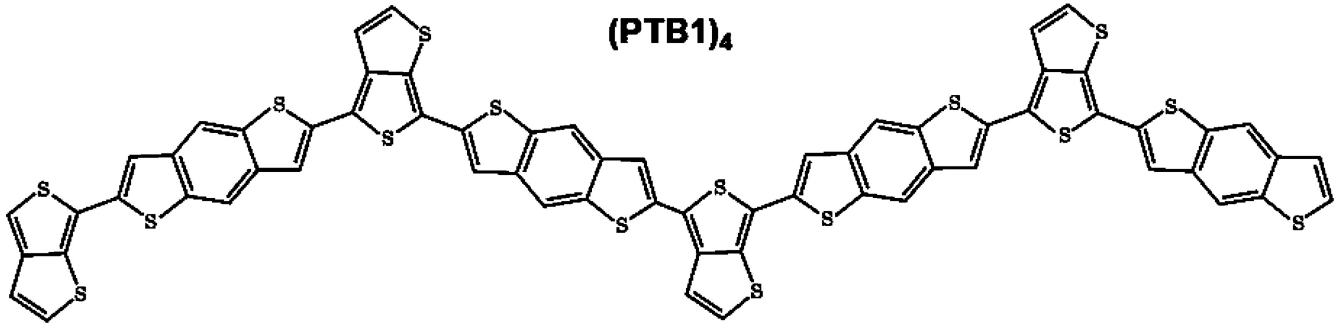
- Hierarchy of DFT exchange-correlation funcionals ranging from pure GGA to long-range hybrids with different percentages (a) of HF exchange E_X^{HF} according to

$$E_{\mathrm{XC}} = aE_{\mathrm{X}}^{\mathrm{HF}} + (1-a)E_{\mathrm{X}}^{\mathrm{GGA}} + E_{\mathrm{C}}^{\mathrm{GGA}}$$

Why HF exchange E_X^{HF} ?

Because charge transfer (CT) properties, crucial and defining characteristic of organic photovoltaics, are very sensitive to the degree of HF exchange in the functional

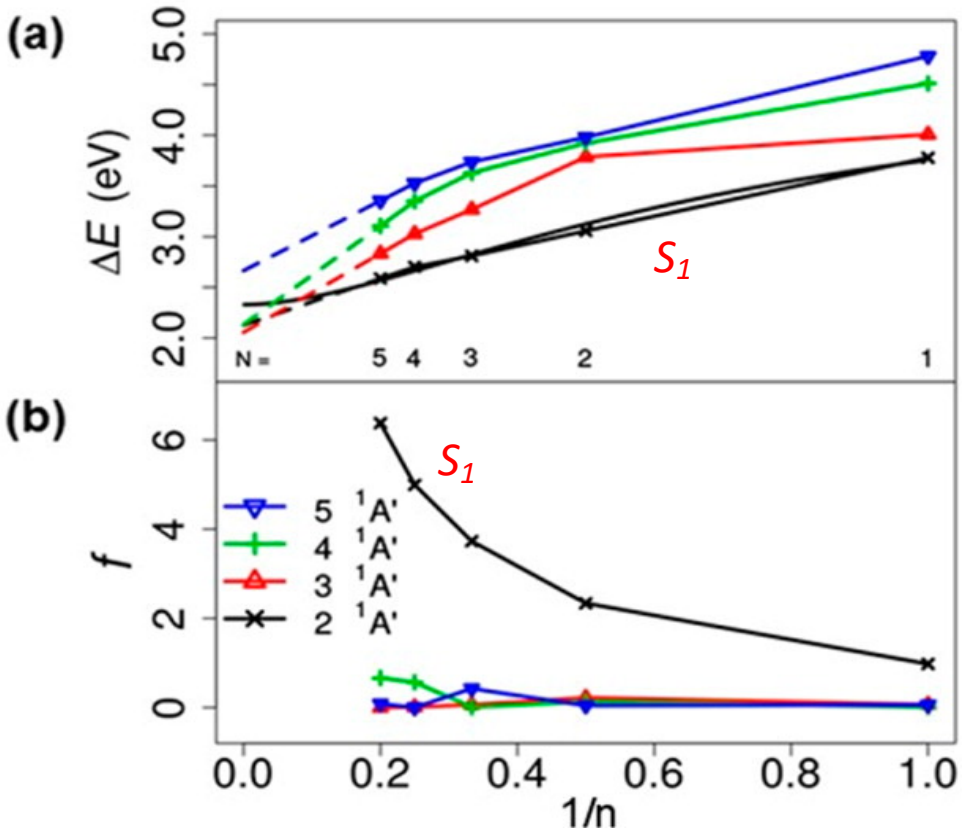
PTB1 model polymer



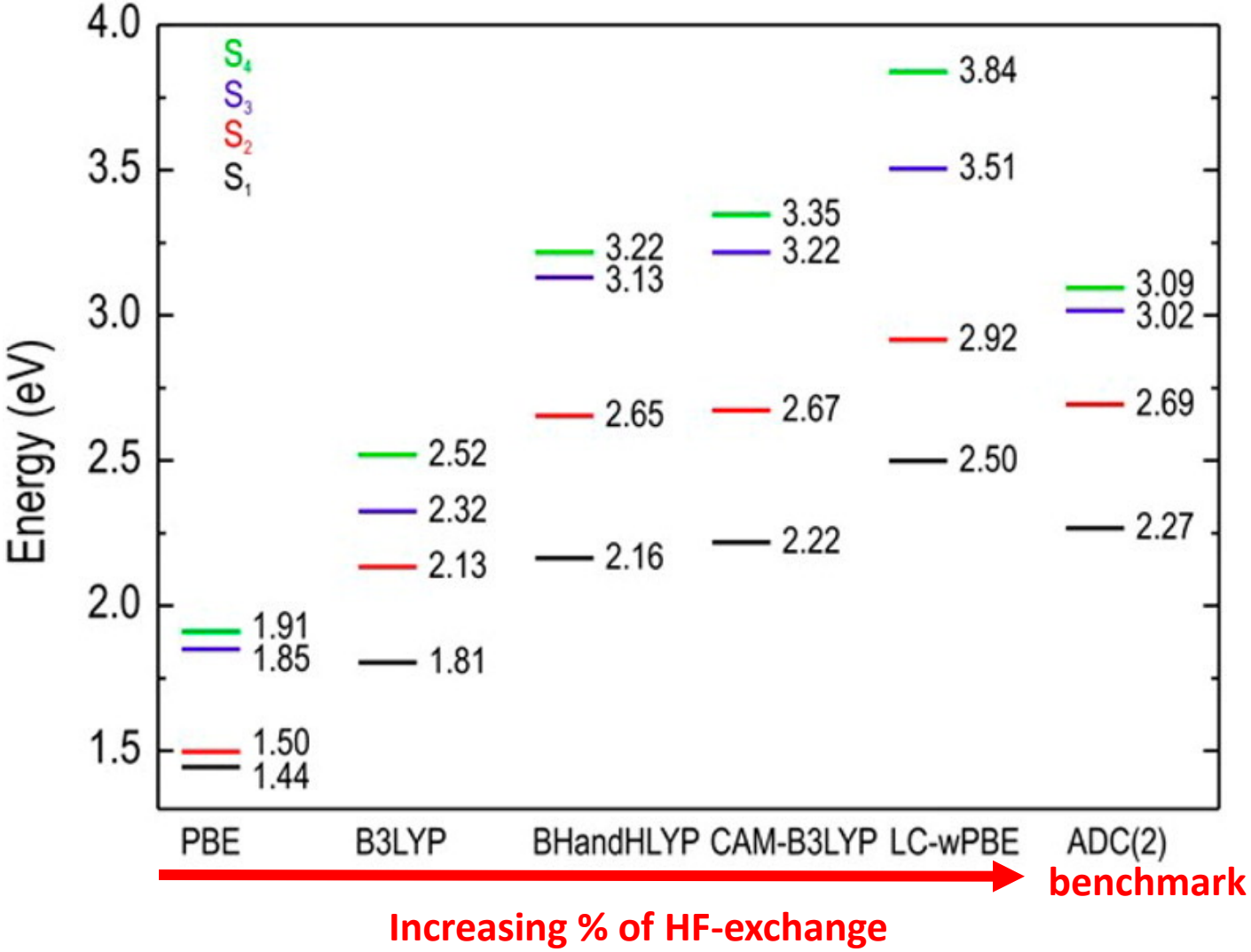
Vertical transitions

S_1 bright state

$\pi - \pi^*$ HOMO-LUMO transition



ADC(2)/SV-SVP (a) transition energies Δ*E* (eV) and (b) optical oscillator strengths (*f*) as function of 1/*n*, *n* being the number of units of the oligomer. Dashed lines are linear extrapolated values of the transition energies. The continuous line is the Kuhn extrapolation of the PTB1 *S*1 transition energy.



$(PTB1)_3$ TDDFT and ADC(2) vertical transition energies using the def2-TZVP basis set. The PBE/SV-SVP optimized geometry was used in all cases.

Table 1. ADC(2)/SV-SVP Lowest Excited State (S_1) Adiabatic and Vertical Transition Energies (eV) of the $(PTB1)_1$ to $(PTB1)_4$ Oligomers

state	$\Delta E_{adiabatic}$	$\Delta E_{vertical}$	difference
$(PTB1)_1$	3.308	3.779	0.471
$(PTB1)_2$	2.501	3.057	0.556
$(PTB1)_3$	2.348	2.810	0.462
$(PTB1)_4$	2.279	2.702	0.423

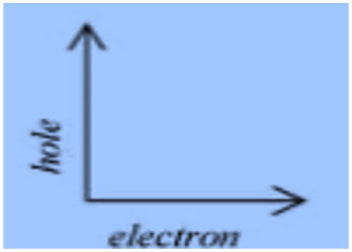
Table 2. $(PTB1)_4$ Lowest Excited State (S_1) Adiabatic and Vertical Transition Energies (eV) Using the Five Exchange–Correlation Functionals in Order of Increasing Percentage of HF Exchange and the SV-SVP Basis Set

method	$\Delta E_{vertical}$	$\Delta E_{adiabatic}$	difference
PBE	1.322	1.224	0.098
B3LYP	1.850	1.637	0.213
BHandHLYP	2.457	2.103	0.354
CAM-B3LYP	2.522	2.181	0.341
LC-wPBE	2.992	2.578	0.414

Charge transfer effects

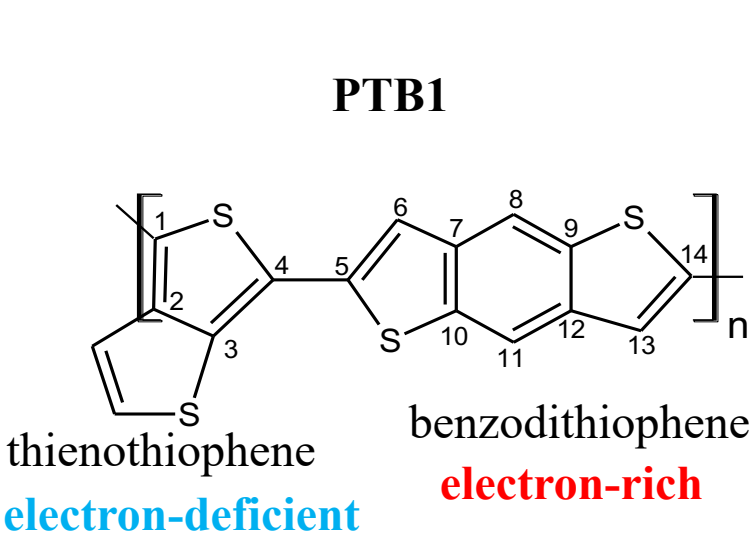
Plot of the Ω (charge transfer number) matrix

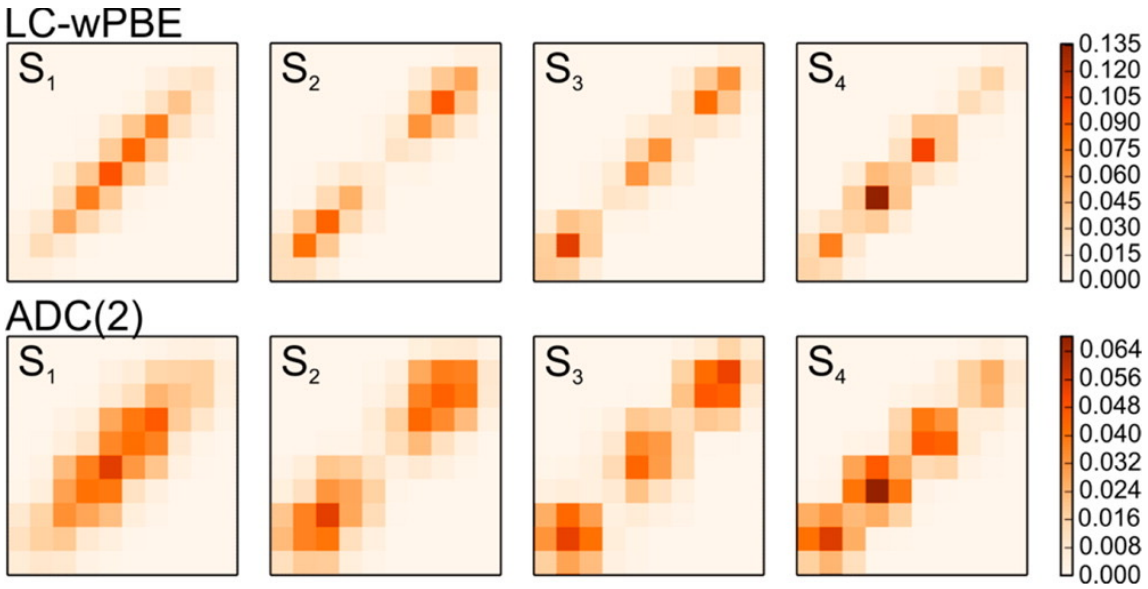
- Diagonal length represents the **spatial extent of the excitons**
- Off-diagonal elements, corrresponding to CT configurations, mark coherences between the fragments (**electron-hole separation – CT character**)
- Position in the diagram:



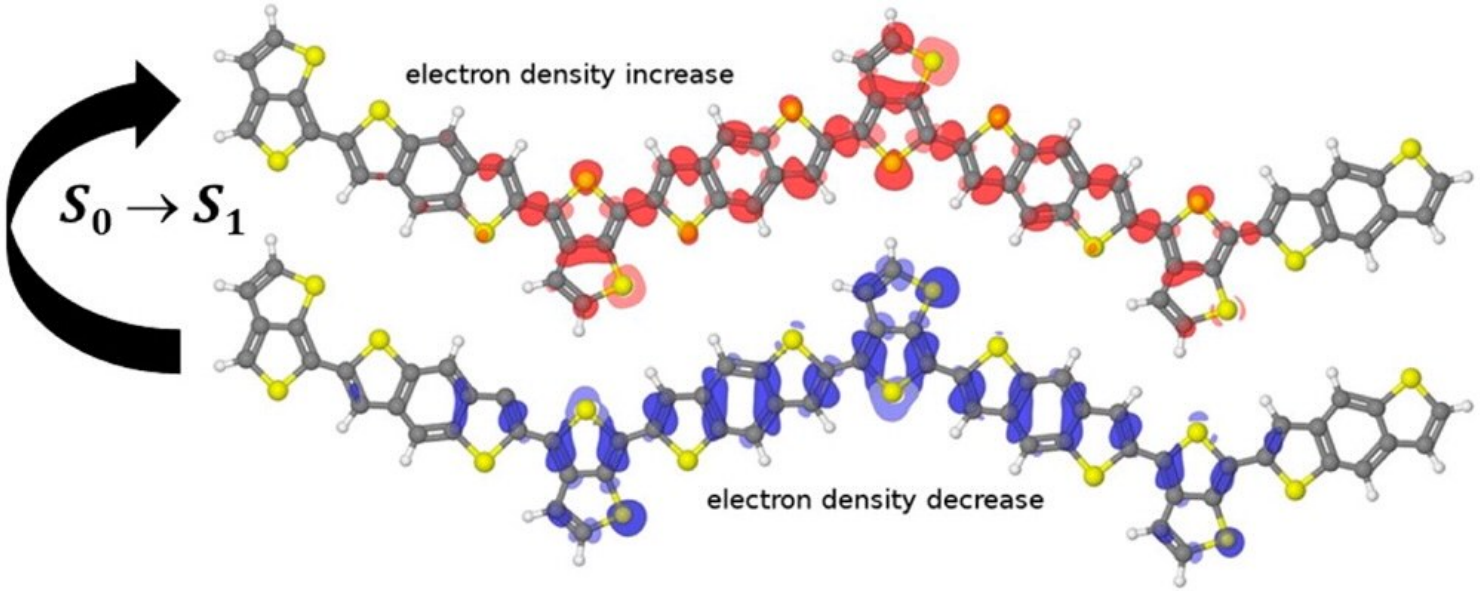
- Each box → value of Ω^{α}_{AB} (charge transfer number):**probability** of simultaneoulsy finding the hole on fragment A and the electron on fragment B

Plot of CT matrix





$(PTB1)_5$ Ω_{AB} plots of the first four electronic transitions (S_1 to S_4) employing ADC(2), LC-wPBE, and the SV-SVP basis set. The vertical axis indicates the position of a hole and the horizontal axis the position of the electron. Each square of the plot represents either a benzodithiophene or a thienothiophene subunit. The square in the lowest leftmost corner corresponds to the electron rich benzodithiophene moiety and in the highest rightmost corner to the electron deficient thienothiophene. The shades represent the probability values according to the scale on the right of each panel.



THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
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Insight into the Excited State Electronic and Structural Properties of the Organic Photovoltaic Donor Polymer Poly(thieno[3,4-*b*]thiophene benzodithiophene) by Means of *ab Initio* and Density Functional Theory

DOI: 10.1021/acs.jpcc.6b07689
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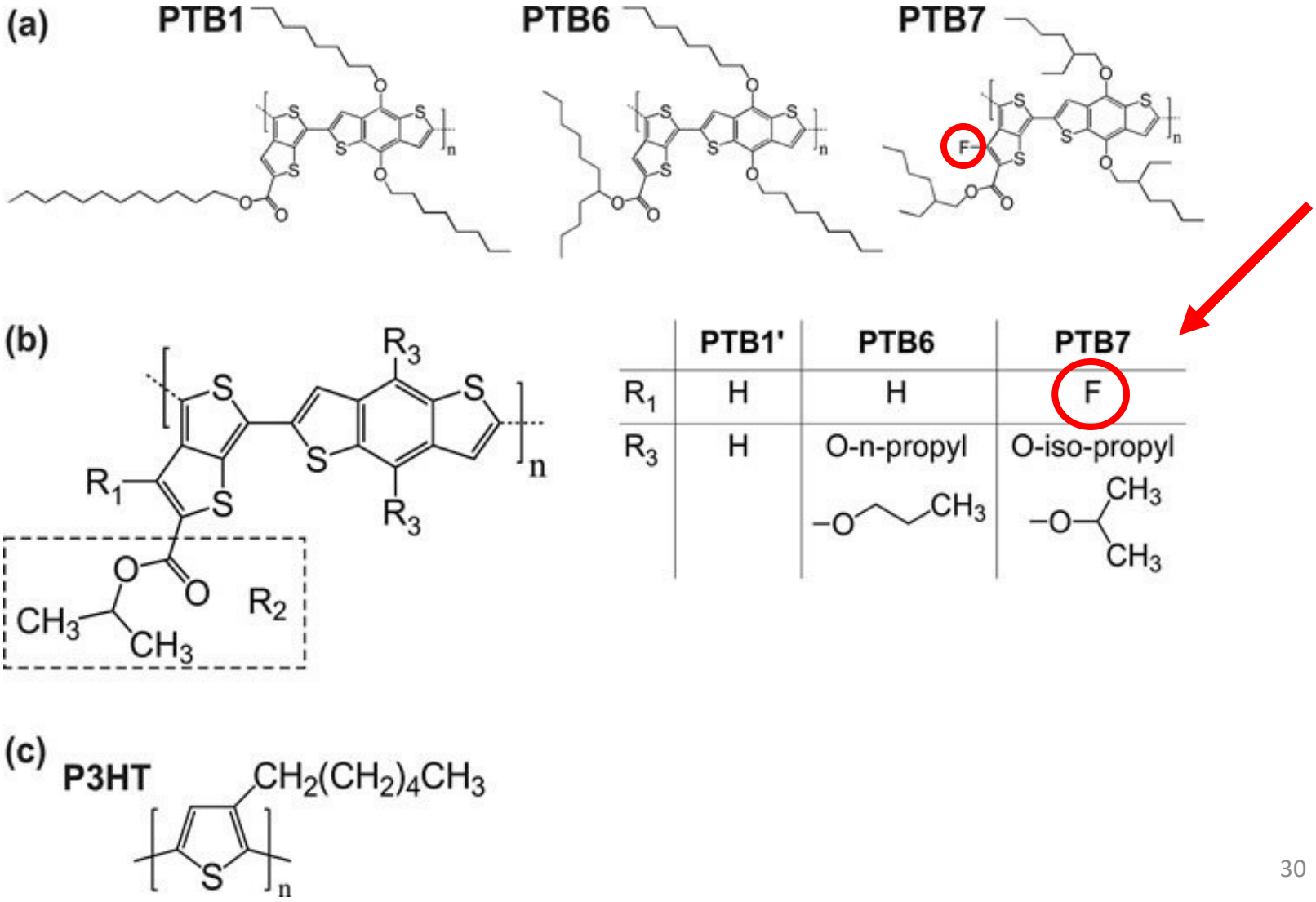
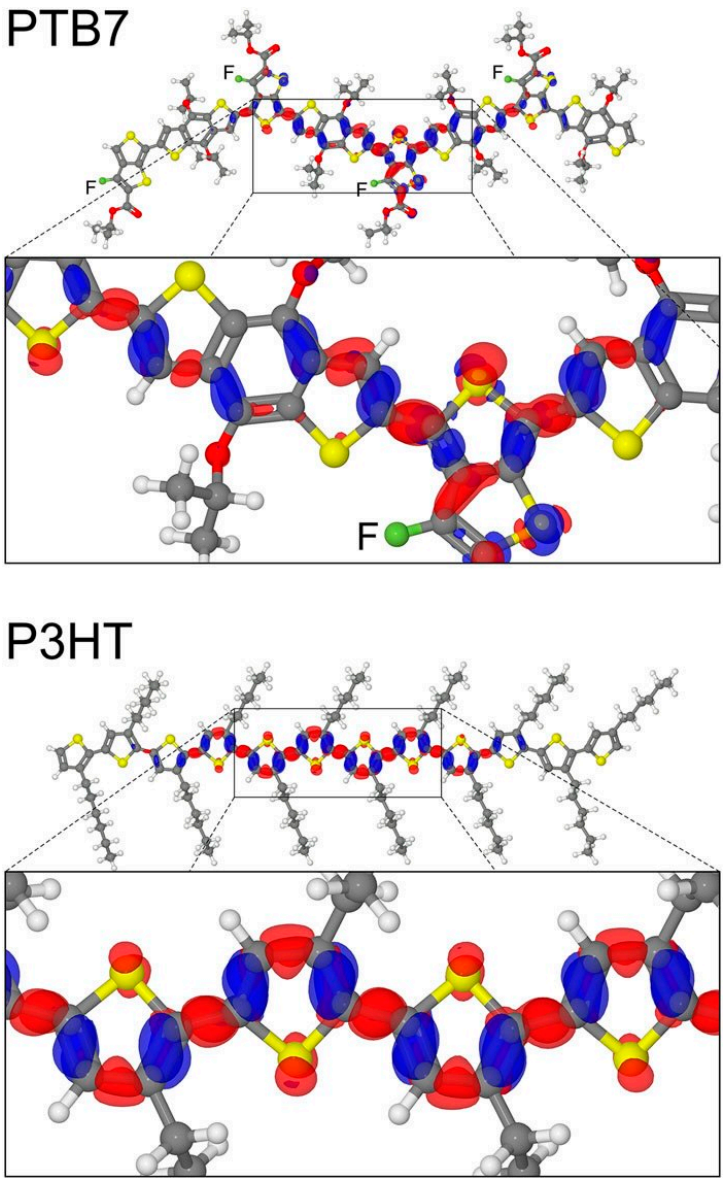
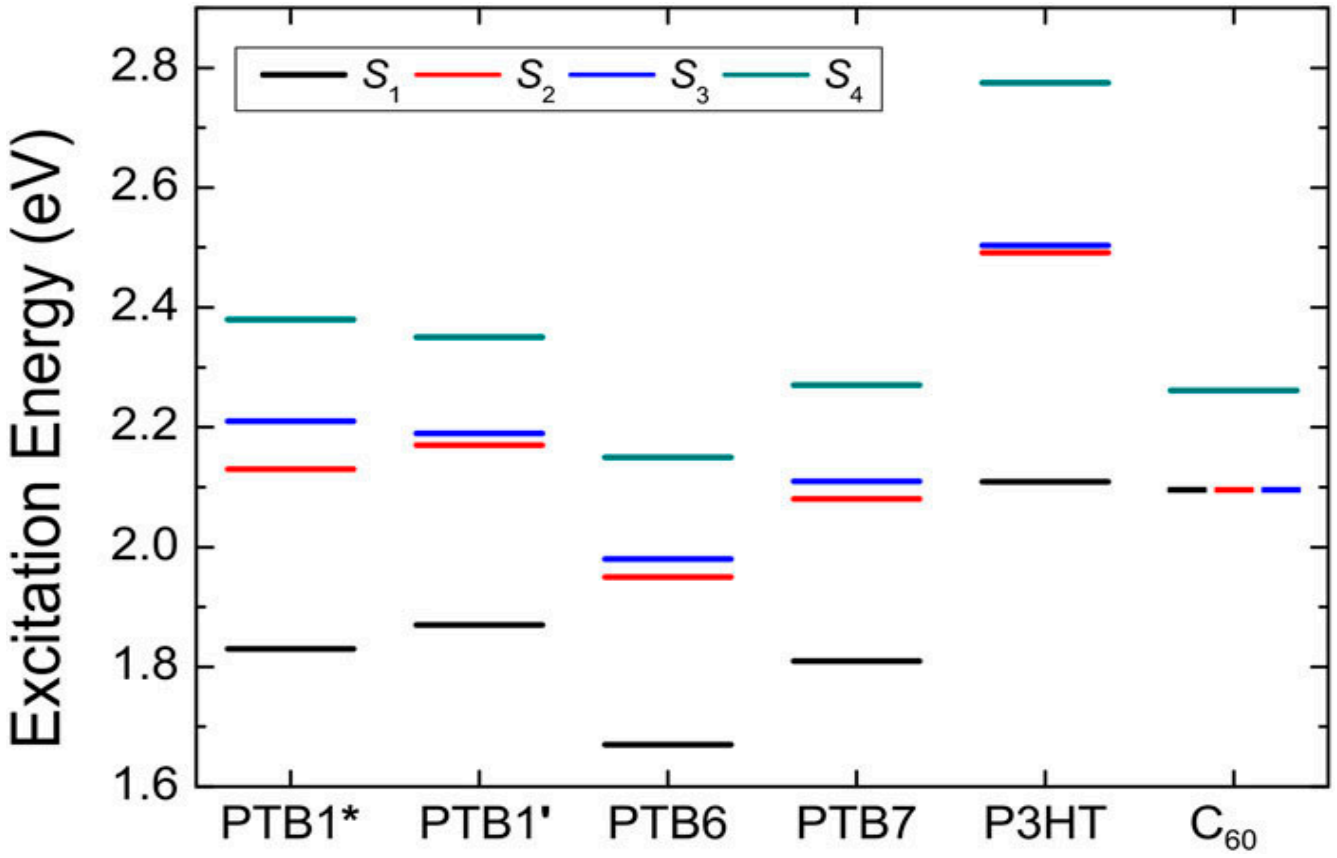
Itamar Borges, Jr.,[*,†,‡,§] Elmar Uhl,[§] Lucas Modesto-Costa,[‡] Adélia J. A. Aquino,[†] and Hans Lischka[*,†,∥]

Why PTB series polymers are more efficient than prototypical P3HT?





TDDFT/B3LYP//TZVP electronic density difference plots for the $S_0 \rightarrow S_1$ bright transition in the PTB7 and P3HT oligomers of similar lengths. Red: electron accumulation (+0.0007e/bohr^3). Blue: electron depletion (−0.0007e/bohr^3). The fluorine atom in PTB7 is depicted in green and by the letter F.



Computed TDDFT S_1–S_4 excitation energies of PTB1, PTB1', PTB6, PTB7, P3HT, and C_{60}. PTB1* corresponds to the PTB1' oligomer without any side chains.*

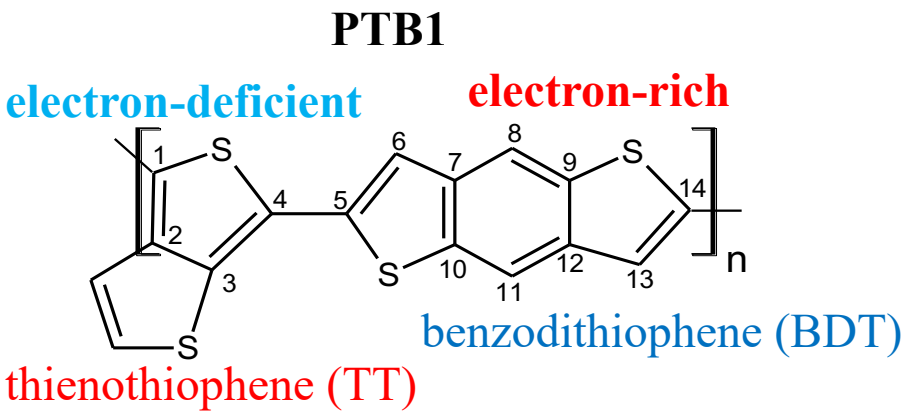
The dipolar effect – why PTBs are more efficient in OPVs

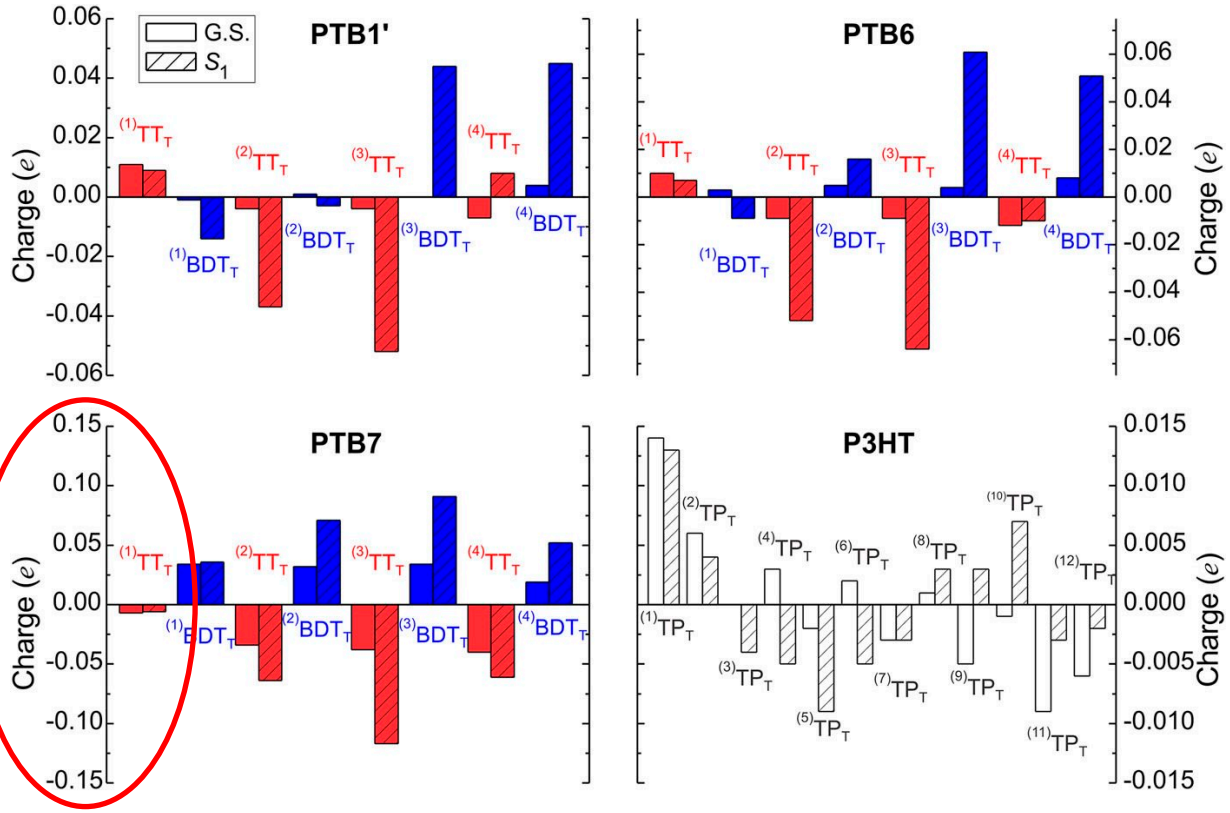
- ✓ Experimental evidences from different sources including ultrafast transient absorption spectroscopic results show that local charges and dipole values in different repeating subunits play a crucial role in organic photovoltaic properties

- ✓ The term dipolar effect in PTBn stems from the hypothesis that the exciton, just before it converts into the charge transfer state, is polarized with opposite partial charges on neighboring TT and BDT subunits

- ✓ The better balanced and larger this polarization are, the better power conversion efficiency should be

NPA charges





Ground (G.S.) and first excited (S_1) states charges. Thienothiophene (TT) and benzodithiophene (BDT) moieties in PTB and thiophene (TP) unit in P3HT. The subscript "T" is to indicate total charge values. Left superscript indicates the monomer number. Different colors are to highlight alternation of the TT and BDT type of charges.

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Electronic structure theory gives insights into the higher efficiency of the PTB electron-donor polymers for organic photovoltaics in comparison with prototypical P3HT

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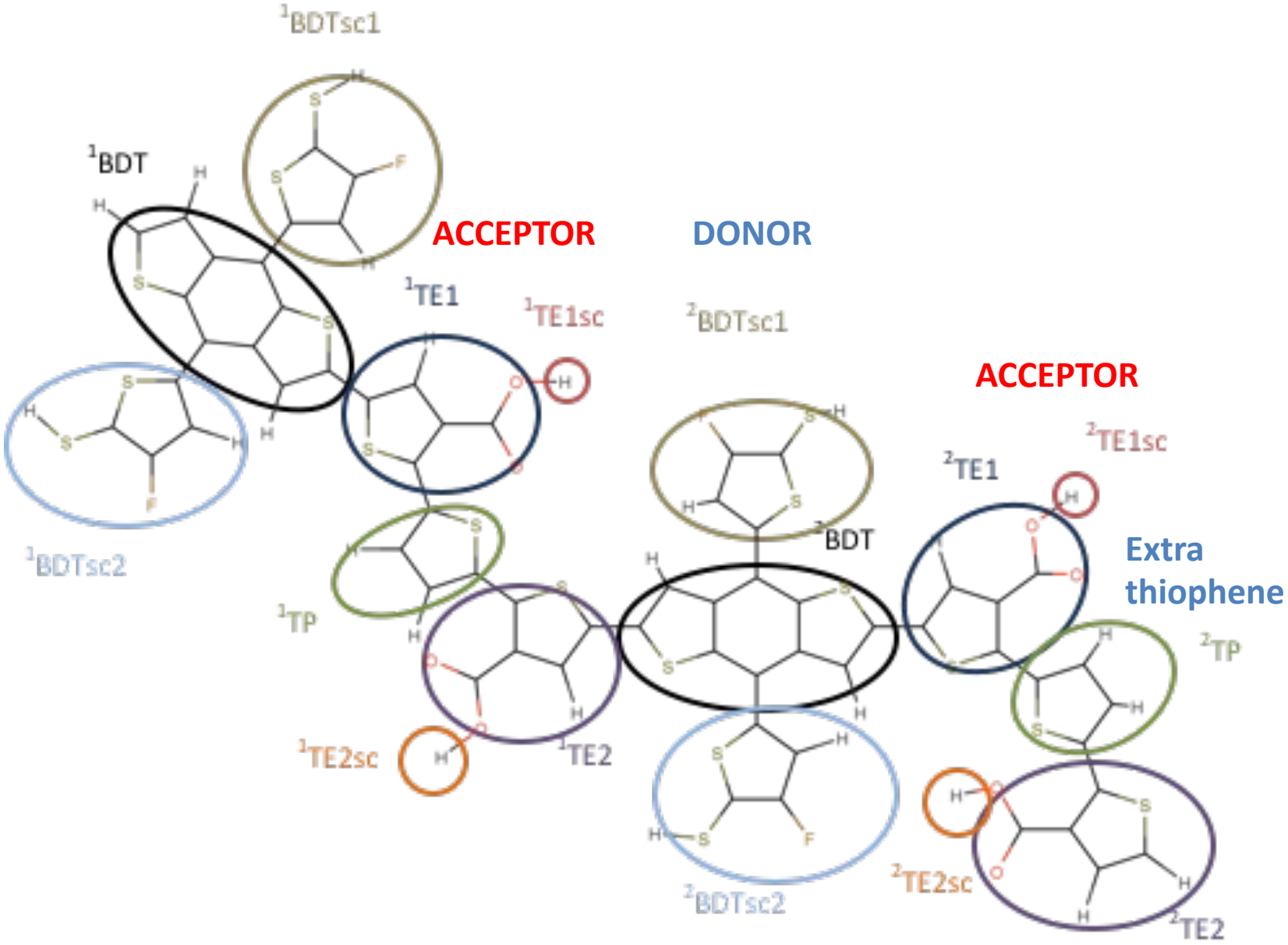
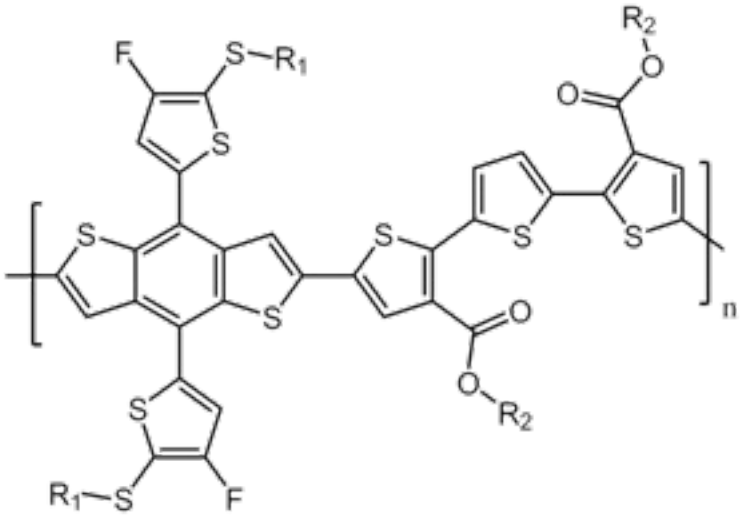
A NEW PATH FOR ORGANIC PHOTOVOLTAICS – FULLERENE-FREE PHOTOVOLTAICS

- ✓ Conventional OPVs based on C_{60} derivatives – Power Conversion Efficiencies (PCE) reached 11-12% in lab scale
- ✓ However, below the 15% commercialization benchmark (also problems with stabilitity)
- ✓ Best alternative today: substitute C_{60} for fluorinated small molecule acceptor IT-4F polymer in a bulk heterojunction
- ✓ In 2018, a wide gap donor polymer based on a new benzodithiophene (BDT) unit (DTBDT-EF) has reached a breakthrough efficiency of 14.2% in a single-junction fullerene-free polymer solar cell based on a bulk heterojunction structure

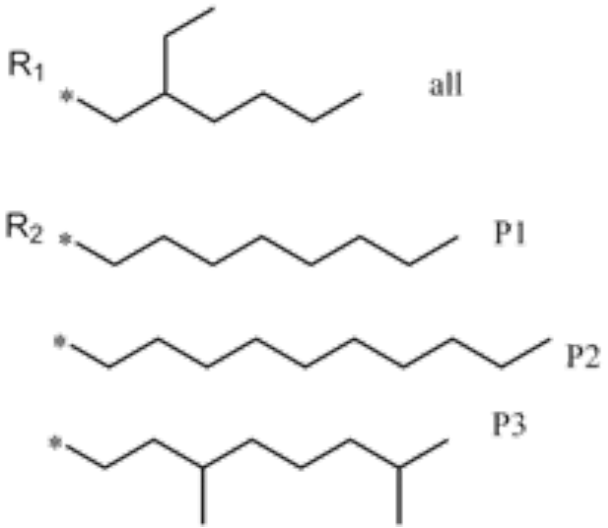
DTBDT-EF unit



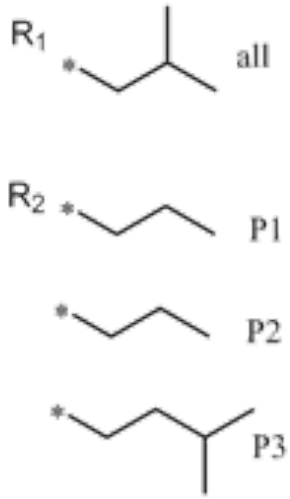
Model polymer – reduced side chains



ORIGINAL



MODEL

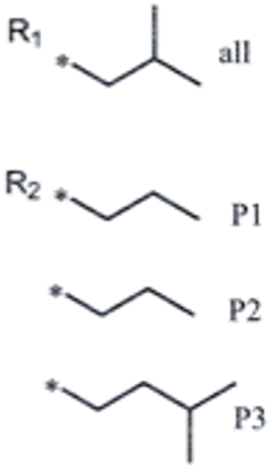


Methods

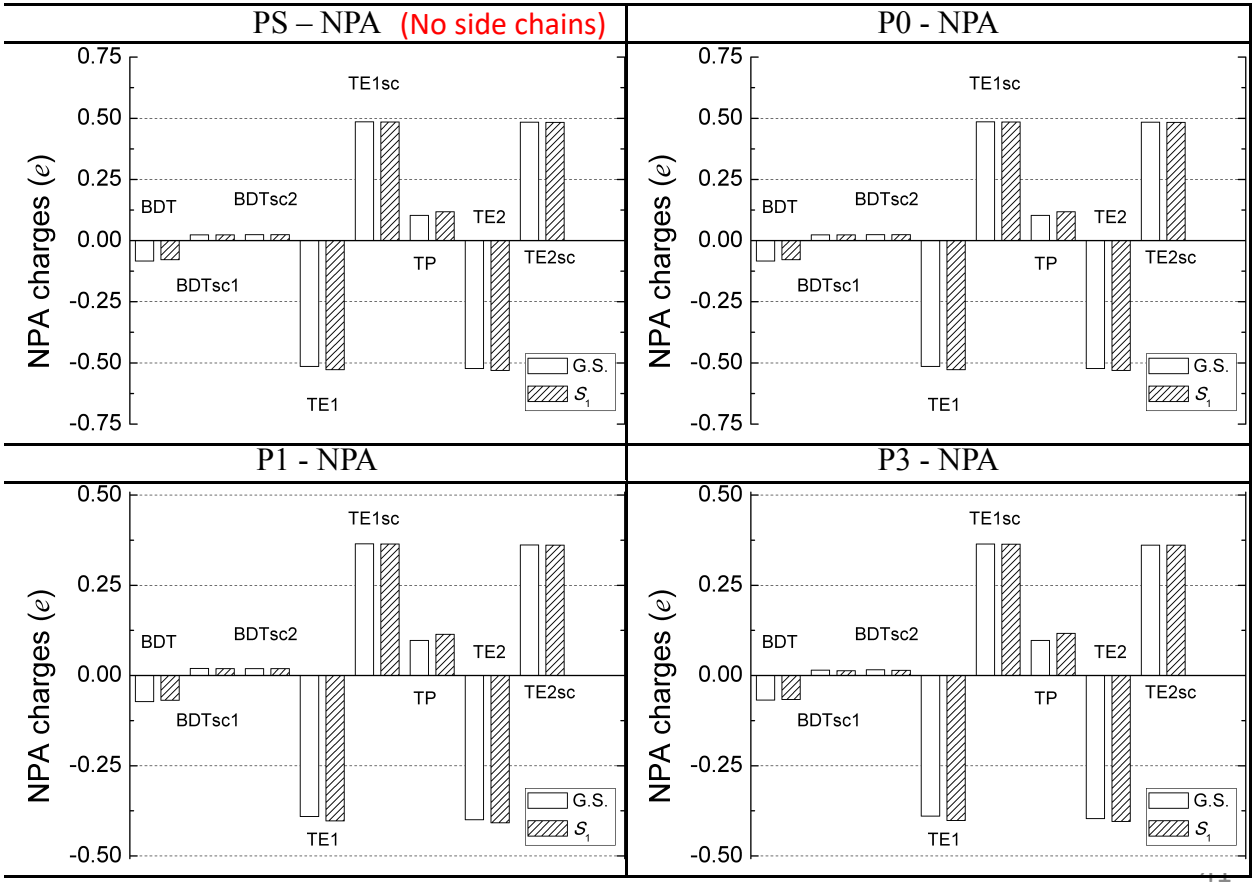
- ✓ Electronic spectra: CAM-B3LYP TD-DFT
- ✓ Geometries: RI/PBE
- ✓ Tetramer model polymer
- ✓ Stacking up of DTBDT-E donor polymers: dimers and trimers , D3 dispersion correction

Prominent dipole effect in DTBDT-EF

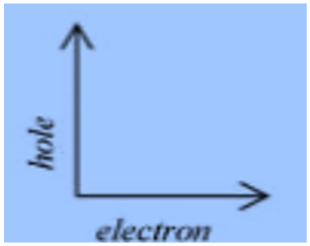
Magnitude of dipolar effect in DTBDT-EF ~ 30 times larger than in the PTB7 !

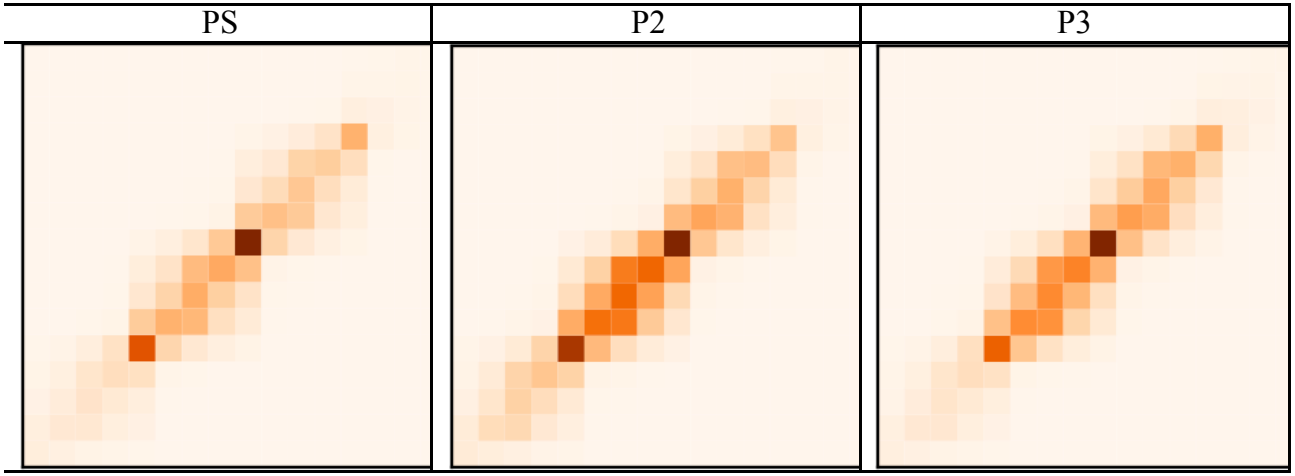


(Model P1 identical to model P2)



Charge transfer effects – S_1 state



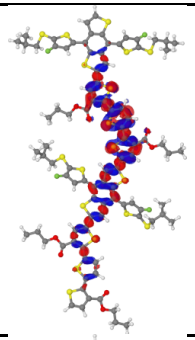
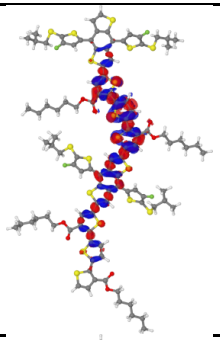
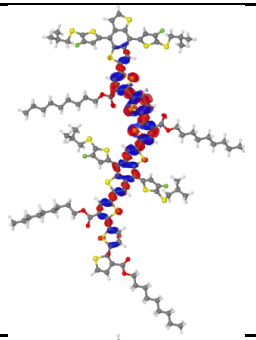
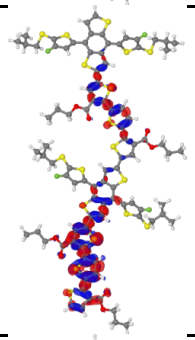
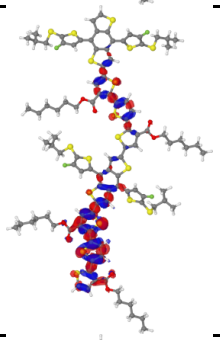
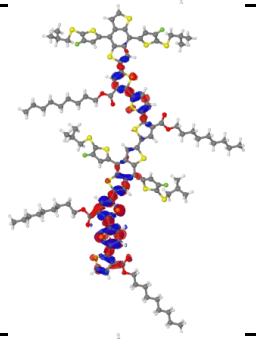
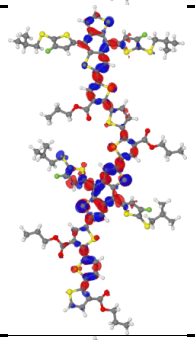
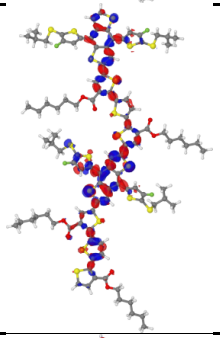
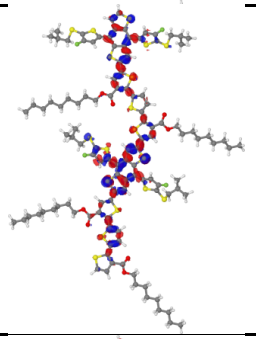
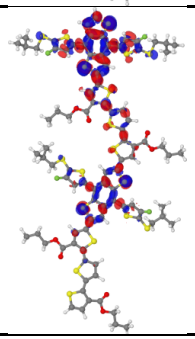
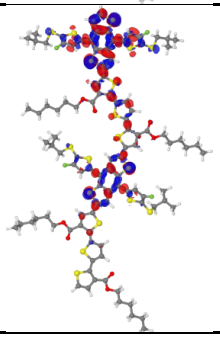
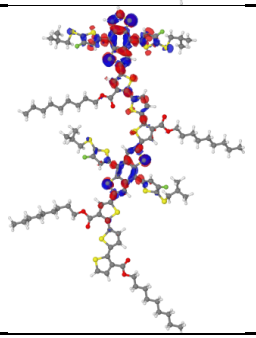


More prominent CT in P2 an P3 - inductive effect of the side-chains

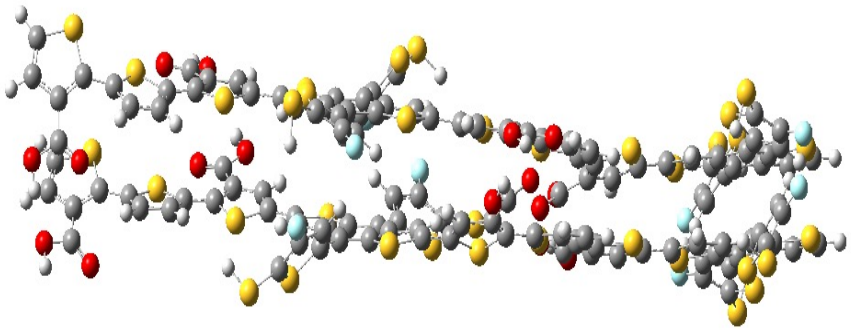
Effect of increasing side chains in charge transfer effects **Single sheet**

Upon excitation:

RED: electron density increase
BLUE: electron density depletion

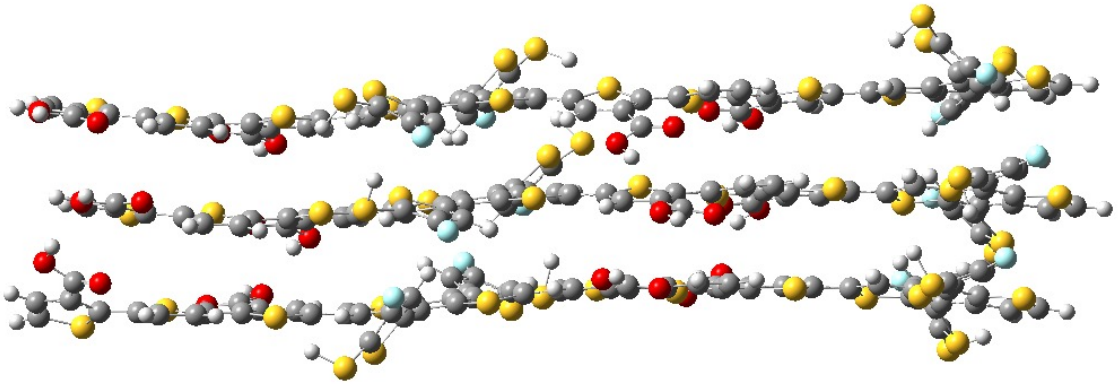
Charge Transf.	P1 – SC3	P1 –SC6	P1 – SC9
GS -> S1			
GS -> S2			
GS -> S3			
GS -> S4			

Pilling up DTBDT-EF sheets geometries



Dimer – lateral view

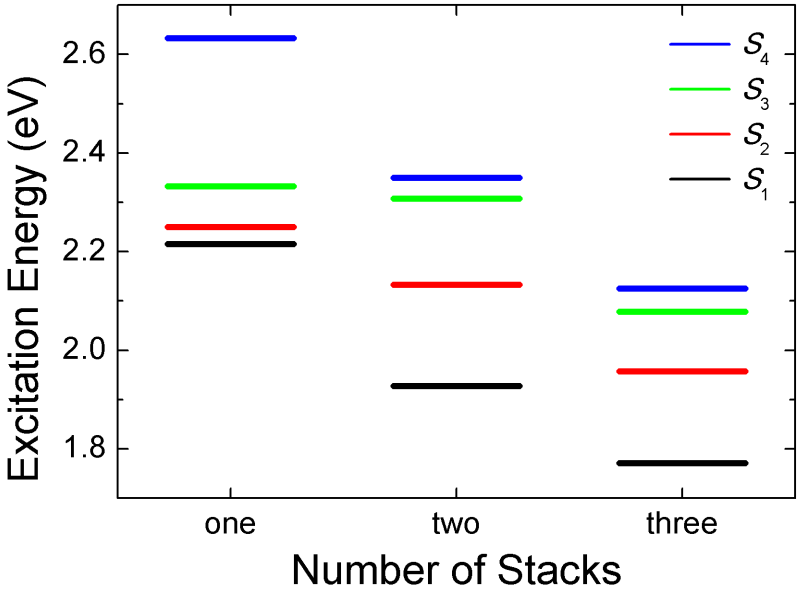
In the trimer, the sheets are more parallel ⇒ crucial for preserving the π system



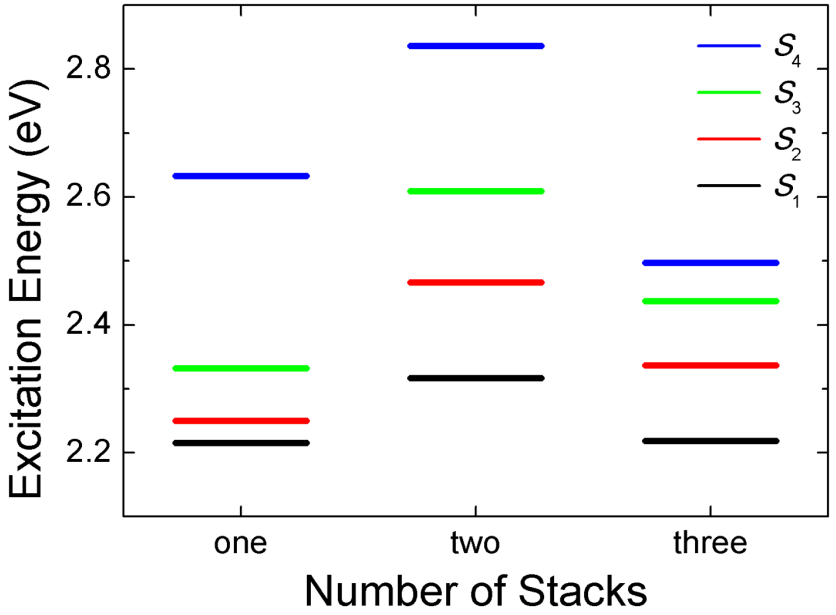
Trimer – lateral view

Spectra of DTBDT-EF

DIST – only separation distance optimized



OPT – full optimization



The energy levels in the fully optimized structures gets closer (i.e. range of energies decrease – notice the scale of the vertical axis)

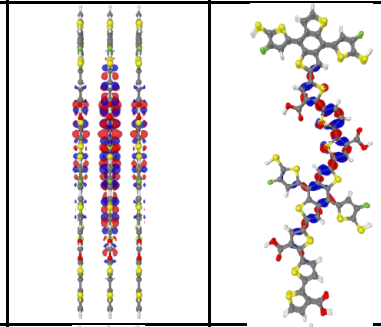
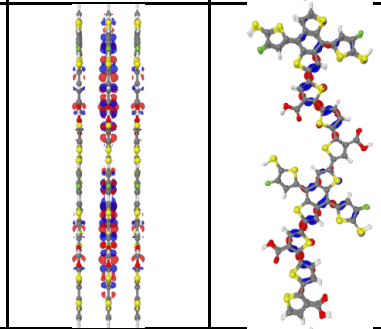
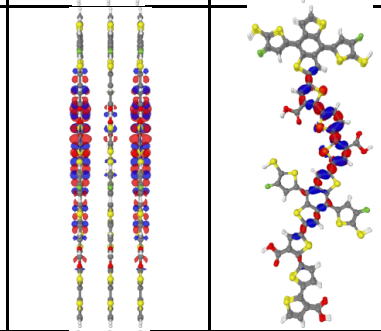
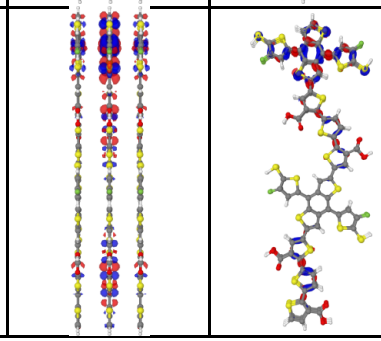
Charge transfer effects

DIST – only separation distance optimized

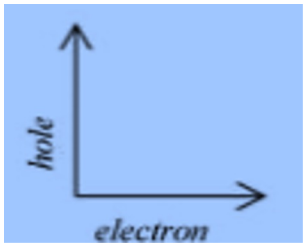
OPT – full optimization

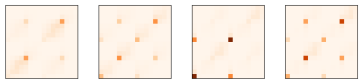
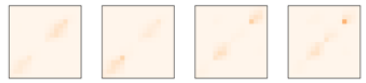
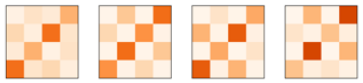
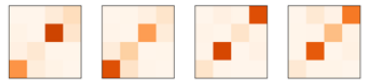
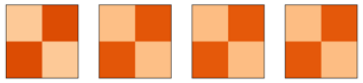
More stacked up sheets - enhanced charge transfer

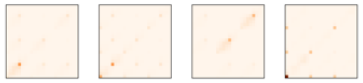
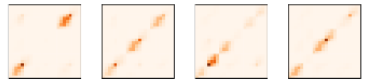
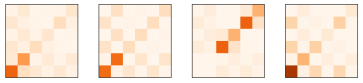
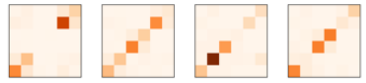
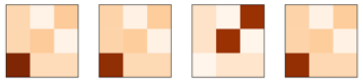
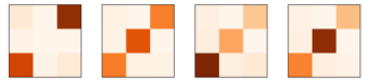
Frozen sheets – more charge transfer as compared to CT in fully optimized sheets

	Dis		OPT	
Charge Transf.	Side view	Top view	Side view	Top view
GS -> S1				
GS -> S2				
GS -> S3				
GS -> S4				

Charge transfer effects in the stacked-up piles of DTBDT-EF



	P0	DIS-TWO	OPT-TWO
Divided			
United			
Poly			

	P0	DIS-THREE	OPT-THREE
Divided			
United			
Poly			

Divided – each subunit
United – each monomer
Poly – a full dimer (intersheet CT)

DIST – only separation distance optimized

OPT – full optimization

Properties that can be computed

- Exciton binding energies
- Open circuit voltage V_{oc}
- The power conversion efficiency (PCE)

$$PCE = \frac{V_{OSC} J_{sc} FF}{P_{in}}$$

- Light harvesting efficiencies (LHE)

$$LHE = 1 - 10^{-f}$$

Work under way

- ❑ Other systems
- ❑ Computation of afrelevant properties
- ❑ Quantum Chemistry ⟹ machine learning algorithms

A recent application to molecular properties affecting the sensitivity of explosives

https://doi.org/10.26434/chemrxiv-2022-qqfbf

Summary

- Realistic model of PTB1/PCBM could be studied with ab initio wave function ADC(2) and careful use of TD-DFT
- PTB1/C60 model:
  - interchain excitonic state delocalized over PBT1 chains
  - band of CT states lies below bright state
  - Charge separation (CS) step feasible
- PTB1 and the more efficient PTB6 and PTB7 were investigated
- The electronic origin of the dipolar effect could be explained in the different donor polymers
- Compreensive study of the new DTBDT-EF donor polymer of fullerene–free OPVs
- TD-DFT can provide accurate results using long range corrected funcionals. This is crucial to describe the CT states typical of organic photovoltaics

Possibilidades

Trabalho interdisciplinar

Programa de Pós-Graduação em Engenharia de Defesa - PGED

Mestrado e doutorado

https://sites.google.com/view/imepged?pli=1

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FAPERJ

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

FULBRIGHT

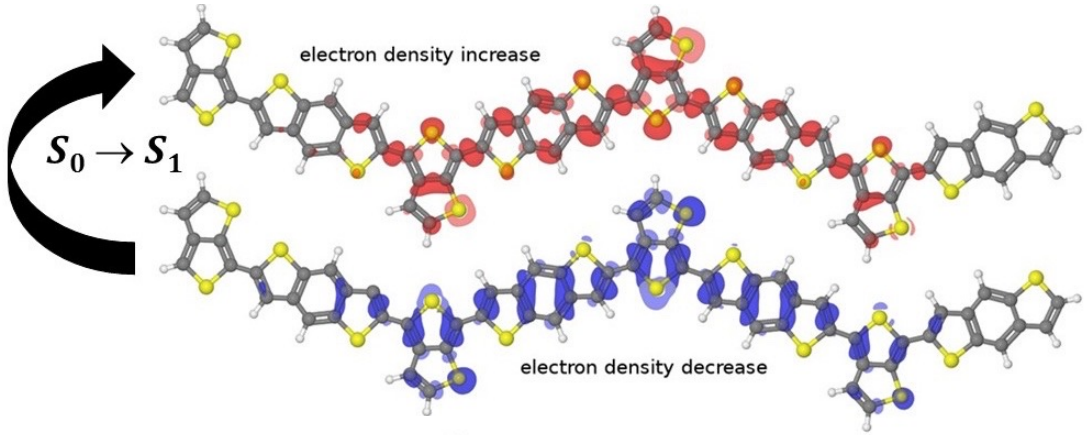
CAPES

D C T

Thanks for your attention!

EXTRA MATERIAL

Bechmark of electronic properties of PTB1



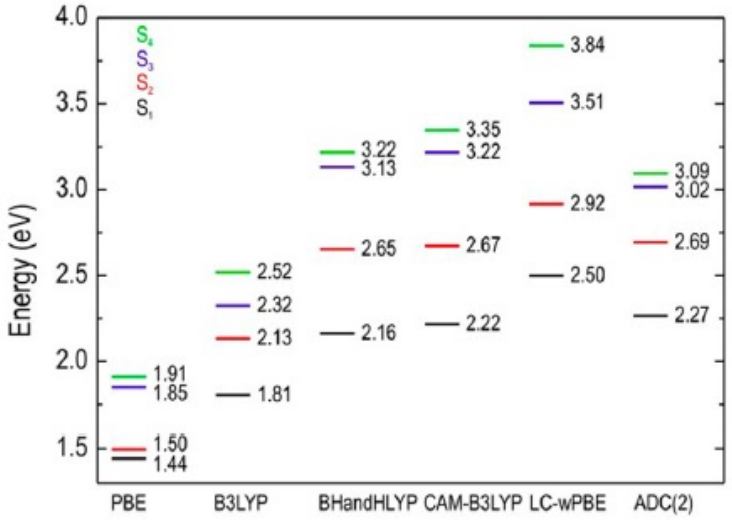


Figure 2. $(PTB1)_3$ TDDFT and ADC(2) vertical transition energies using the def2-TZVP basis set. The PBE/SV-SVP optimized geometry was used in all cases.

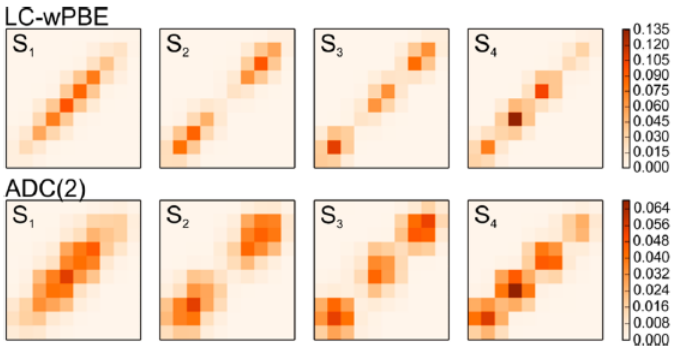
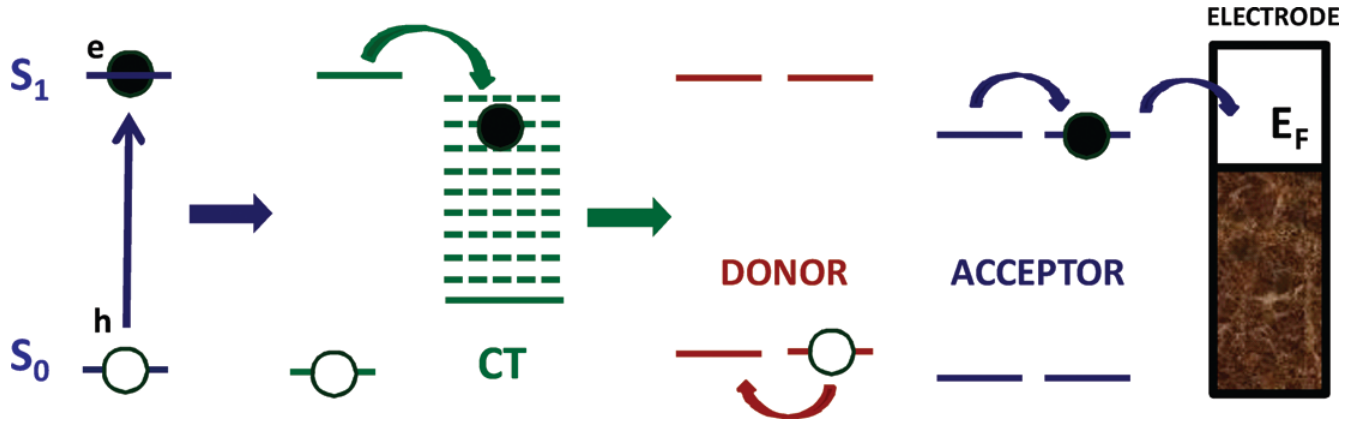


Figure 4. $(PTB1)_5$ Ω^{α}_{AB} plots of the first four electronic transitions (S_1 to S_4) employing ADC(2), LC-wPBE, and the SV-SVP basis set. The vertical axis indicates the position of a hole and the horizontal axis the position of the electron. Each square of the plot represents either a benzodithiophene or a thienothiophene subunit. The square in the lowest leftmost corner corresponds to the electron rich benzodithiophene moiety and in the highest rightmost corner to the electron deficient thienothiophene. The shades represent the probability values according to the scale on the right of each panel.

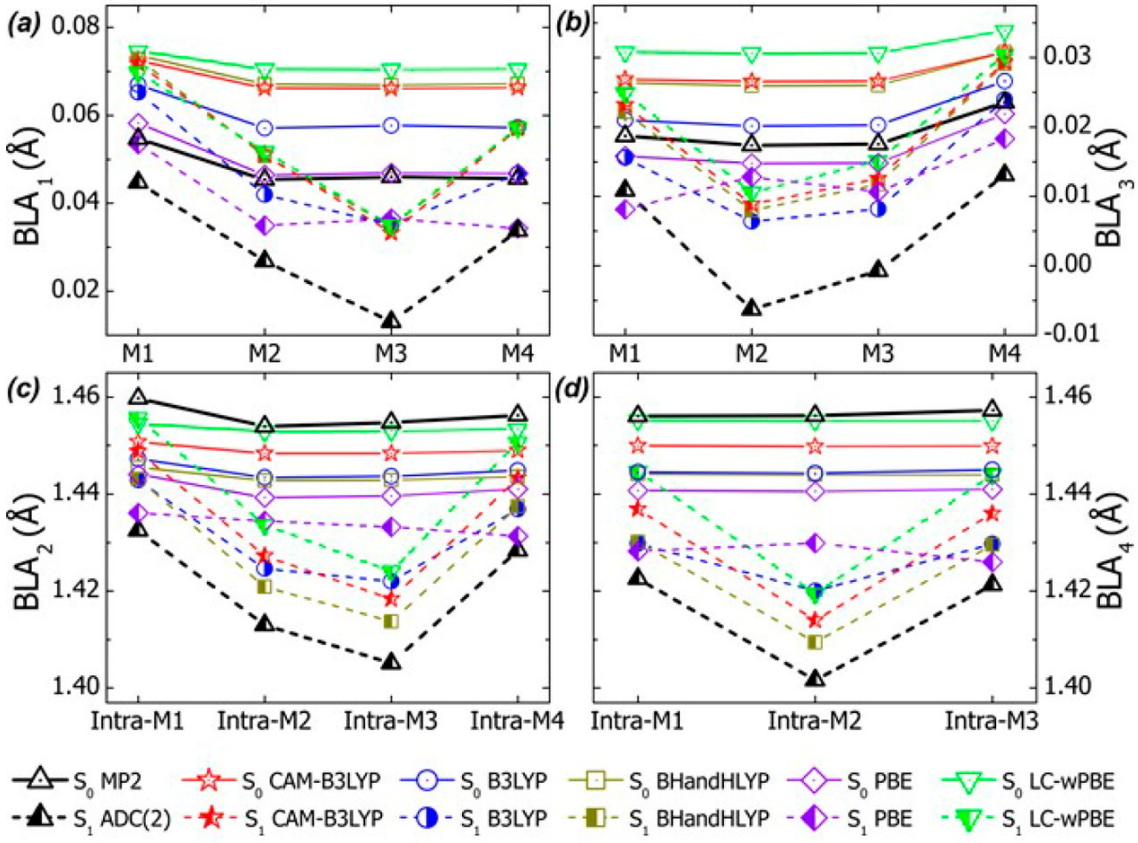
Organic Photovoltaics Fundamental Processes



Exciton formation Charge transfer(CT) Charge separation (CS)

J. L. Bredas et al. Acc. Chem. Res, 42, 1691 (2009)

Bond length alternation (BLAS)



Bond length alternation (BLA) analysis of (PTB)4 *S*0 (solid lines) and *S*1 (dashed lines) states using MP2, ADC(2), and DFT methods with different exchange-correlation functionals. MP2 *S*0 values are represented by solid black lines and ADC(2) *S*1 by the dashed black lines. (a) BLA1, (b) BLA3, (c) BLA2, and (b) BLA4. Labels M1–M4 denote the monomer number.

Acknowledgements

- Present collaborators

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FAPERJ

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CAPES

PBCT DCT

Inorganic vs Organic photovoltaics

- Light absorption creates excited states – electron-hole pair (exciton), can migrate through the material
- Inorganic semiconductor (p-n silicon junction):
  - delocalized bands
  - high dielectric constant
  - exciton binding energy is small (***few meV***)
  - thermal energy is sufficient to create free carriers
- Organic semiconductor:
  - localized excitations
  - low dielectric constant
  - exciton binding energy is rather large (***~0.5 eV***)
  - dissociation is not straightforward

PTB1/C_{60} Summary

- Electronic excitation: inter-chain excitonic delocalized state whose transition density spreads over 1-2 PTB1 units close to C_{60}
- CT states lie below bright state and form band of states possible accessible via Internal Conversion processes
- Besides low-lying CT states there are dark excitonic CT states: they either contribute to the CT processes or can trap the exciton
- Charge separation (CS) step seems energetically feasible
- CS depends on local dielectric environment and can be enhanced by introducing polarity in the material