Structure-property insights from fragment-based analysis of interfacial charge-transfer excitons

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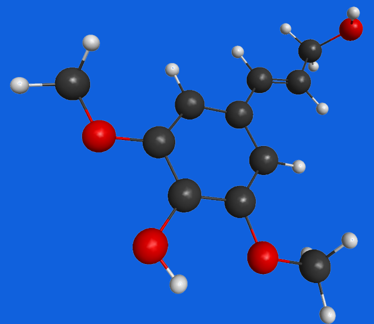
April 14th 2021



Molecular Physics

electrons positrons photons

http://fig.if.usp.br/~mvarella/

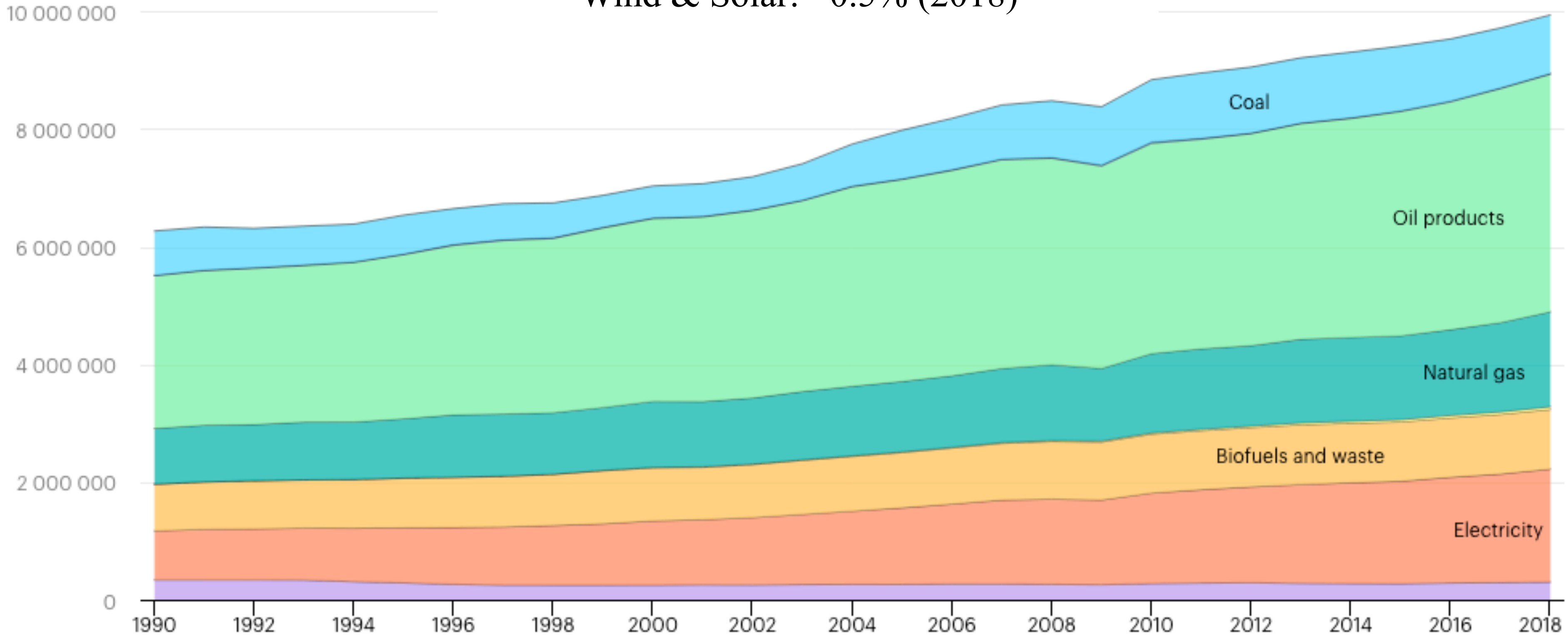
Global Energy Consumption

1 toe (tonne oil equivalent) = 42 GJ

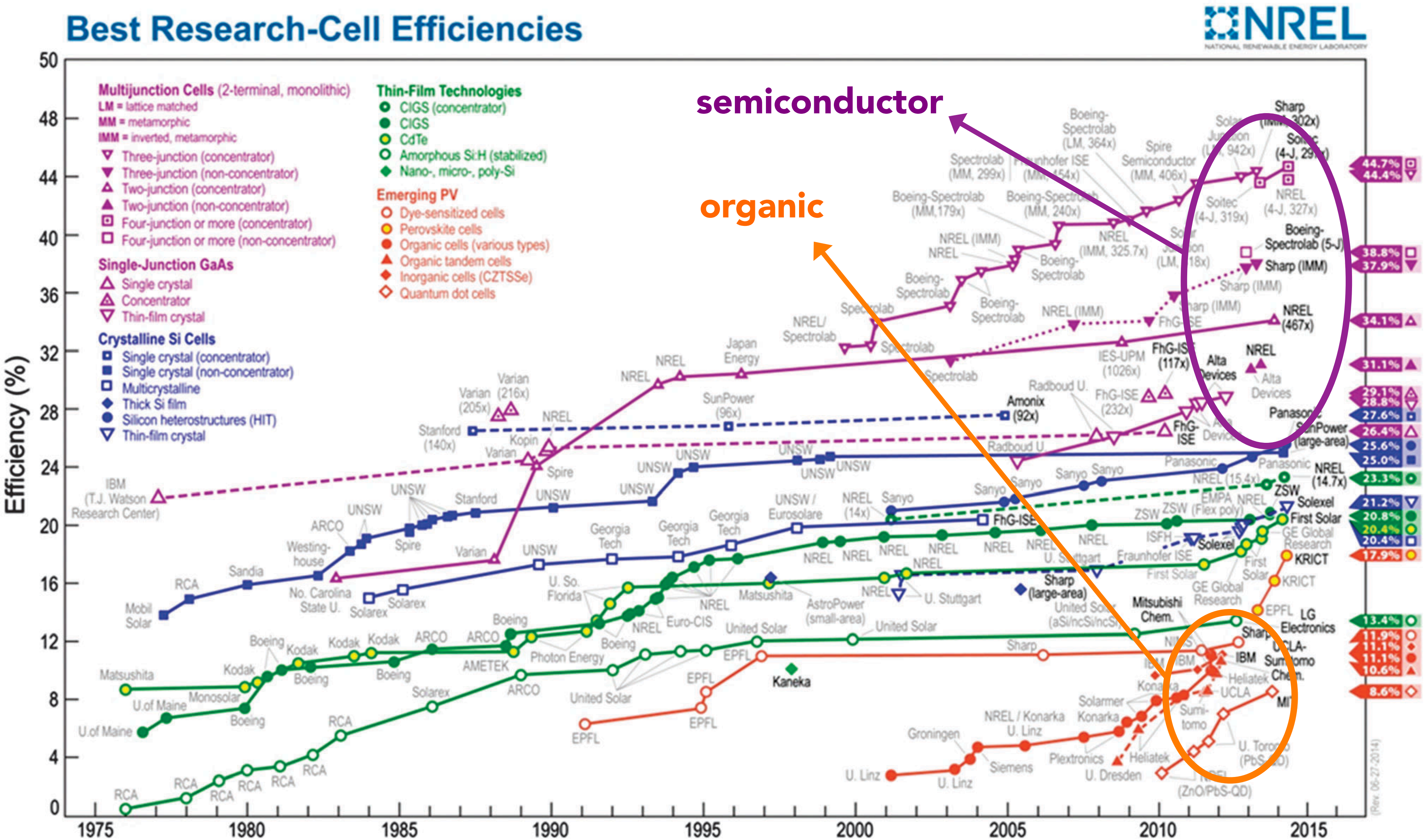
1.0×10^7 toe = 4.2×10^{17} J = 1.8 = 116 TW-h

Wind & Solar: ~0.5% (2018)

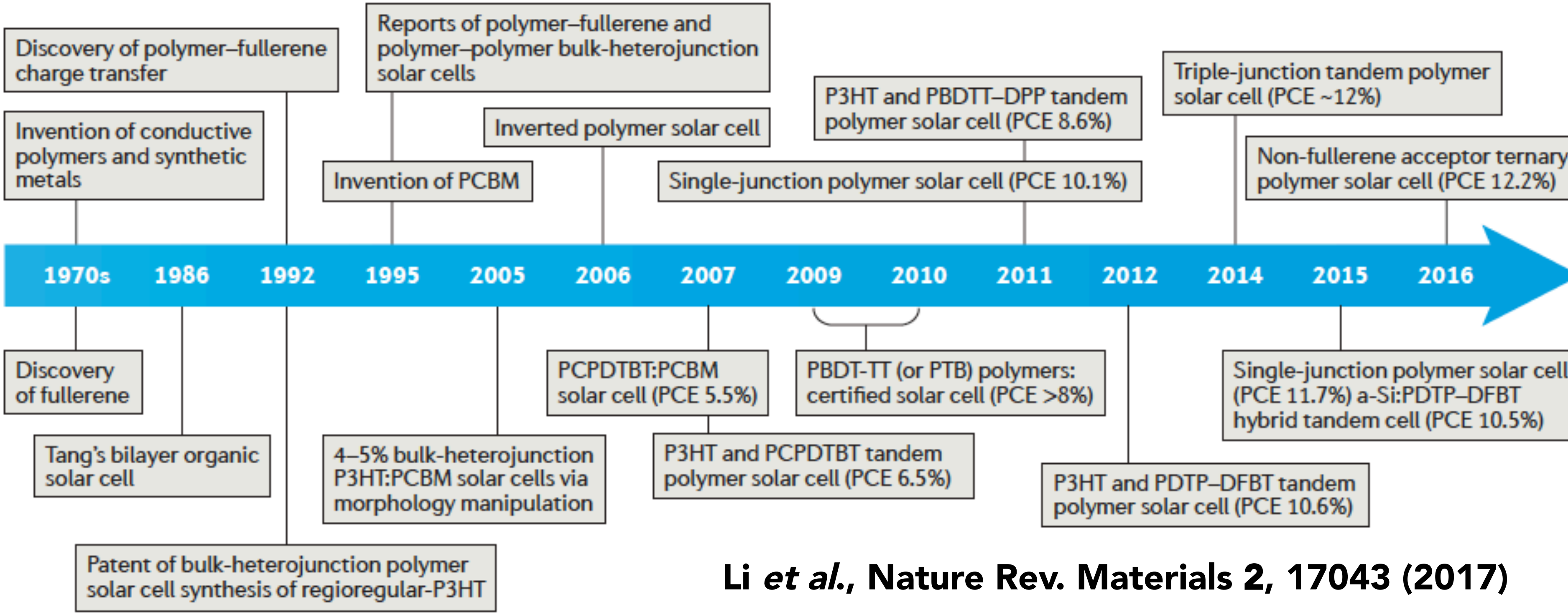
toe



World Energy Outlook 2020
https://www.iea.org/reports/world-energy-outlook-2020



National Renewable Energy Laboratory (NREL) – USA
https://www.nrel.gov



Li *et al.*, Nature Rev. Materials 2, 17043 (2017)

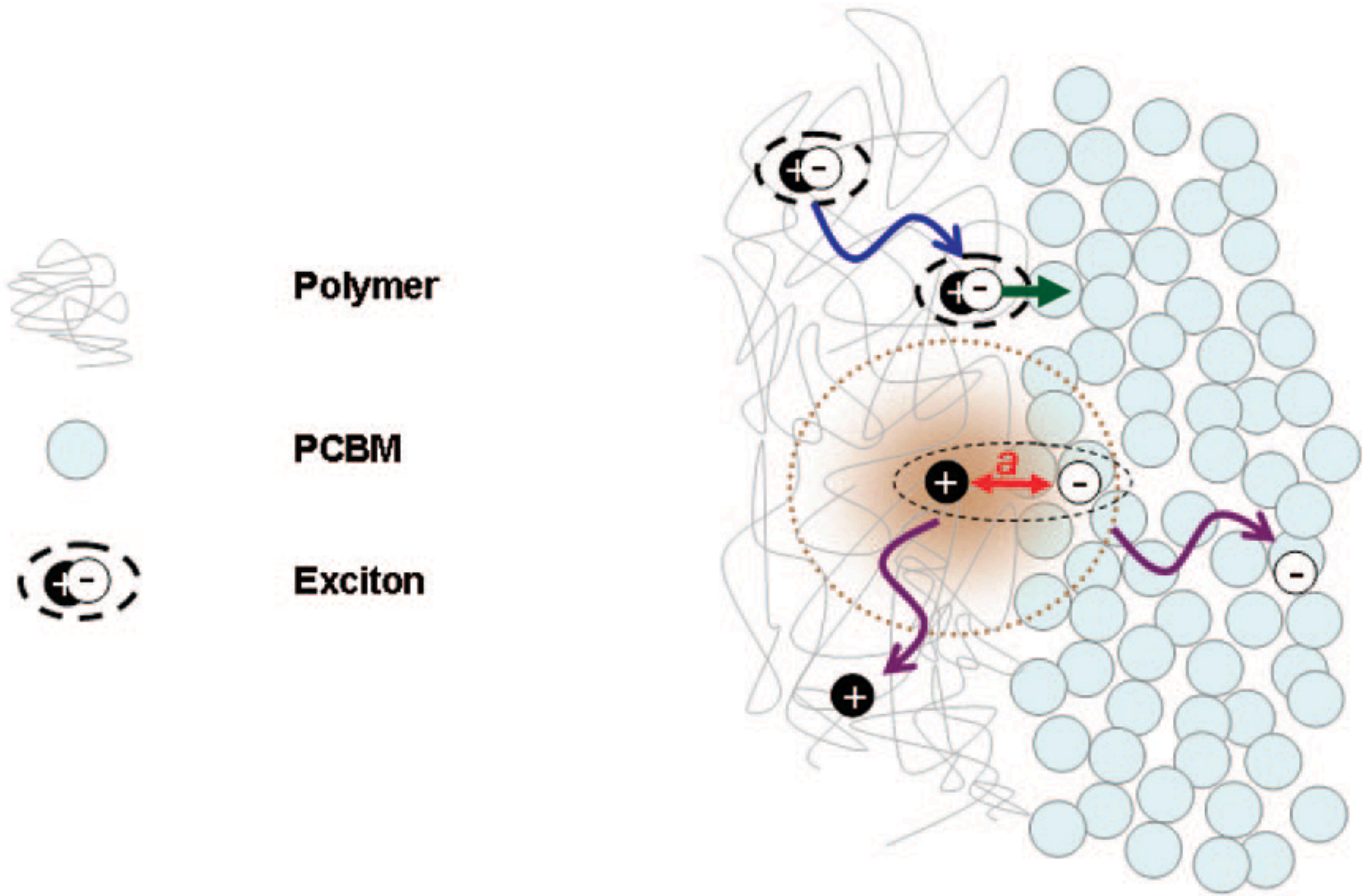
Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core

Yuan *et al.*, Joule 3, 1140 (2019)

Organic and solution-processed tandem solar cells with 17.3% efficiency

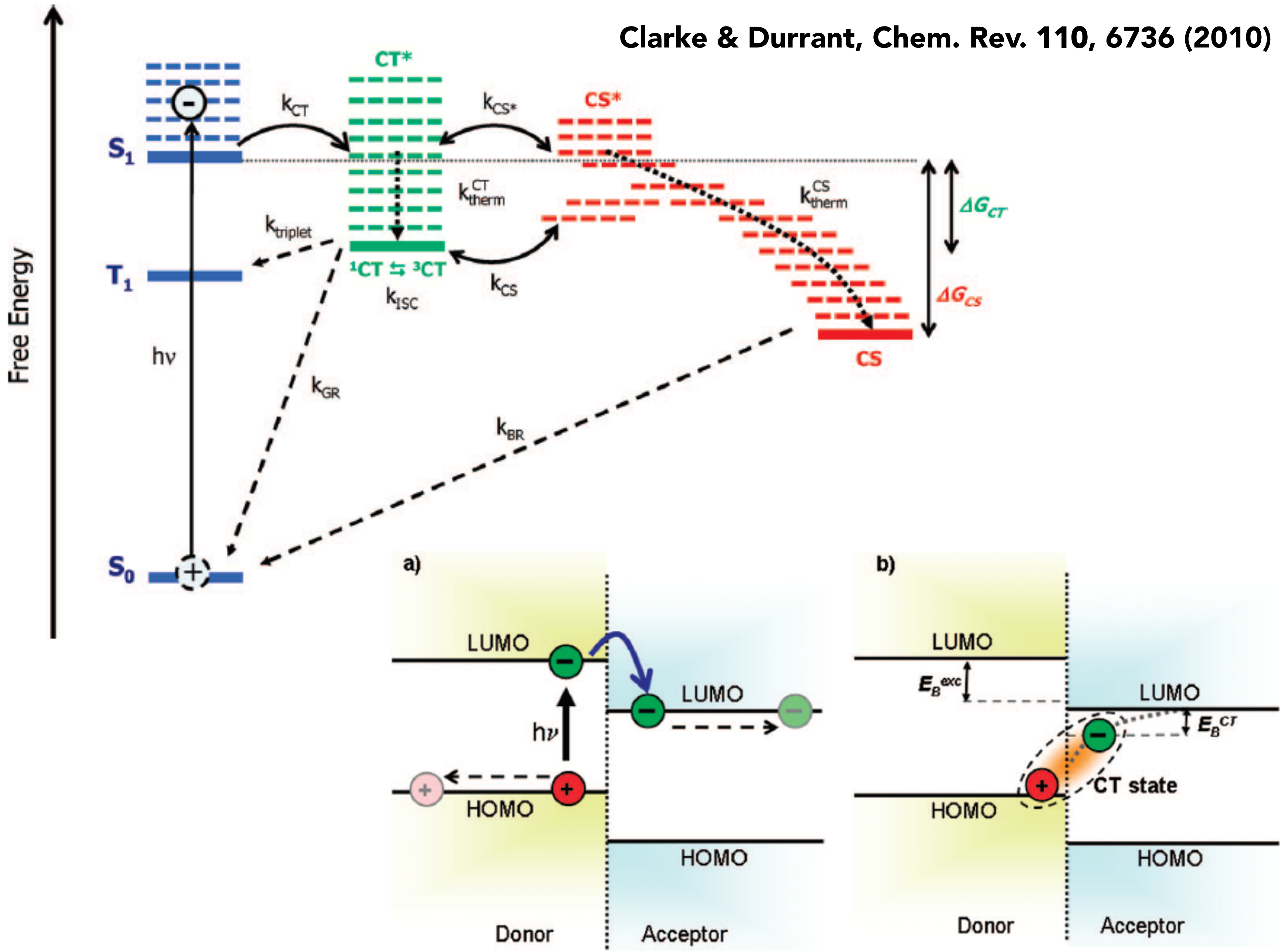
Meng *et al.*, Science 3, 1094 (2018)

Charge separation in OSCs

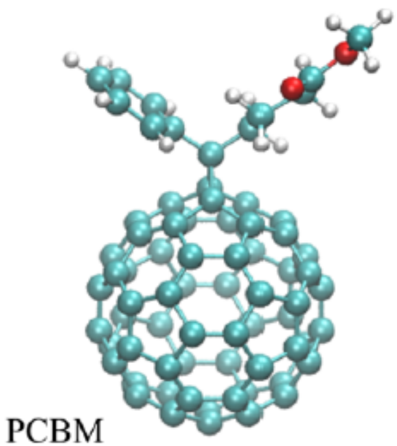


Clarke & Durrant, Chem. Rev. 110, 6736 (2010)

Clarke & Durrant, Chem. Rev. 110, 6736 (2010)

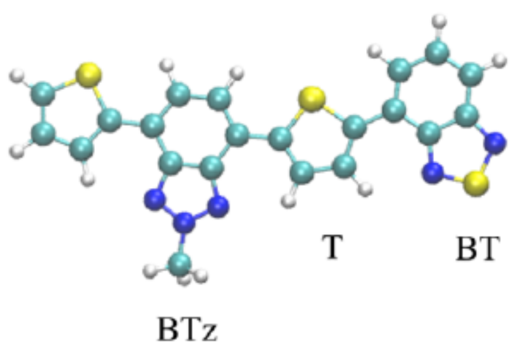


Interface Models



Acceptor: fullerene

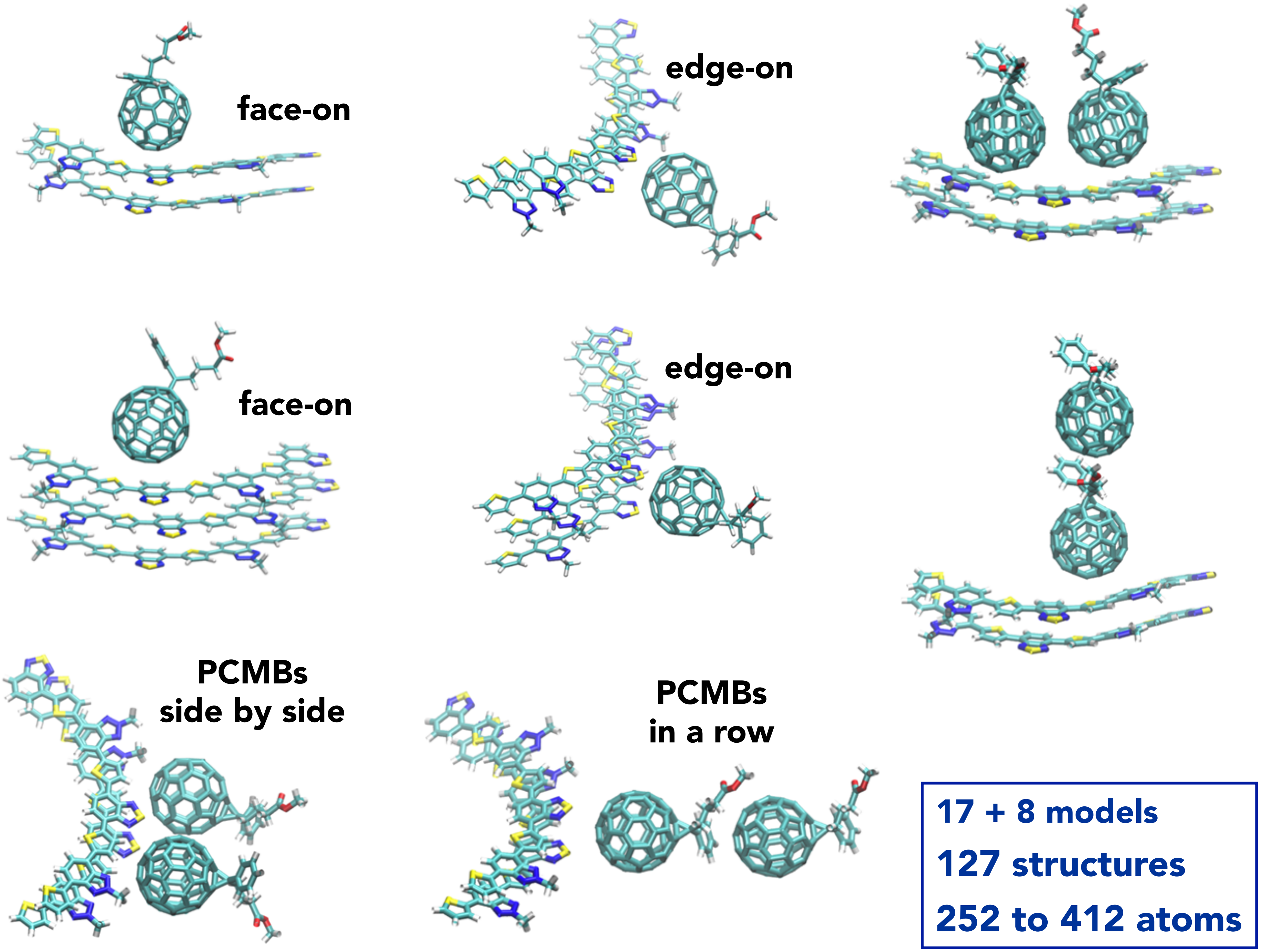
PCBM = phenyl-C61-butyric acid methyl esther



Donor: dual-band polymer PTBTBTz / PT3BTBTz

T = thiophene
BT = benzothiadiazole
BTz = benzotriazole

Varella *et al.*, J. Phys. Chem. C **125**, 5448 (2021)


face-on
edge-on
face-on
edge-on
PCMBs
side by side
PCMBs
in a row
17 + 8 models
127 structures
252 to 412 atoms

Methods

– Excitation spectra obtained with the LC-TD-DFTB method [1] implemented in the DFTB+ package [2].

– Newly optimized OB2 Slater-Koster parameters for H, C, N, O, S

– Partial tuning of the range-separation parameter

– Exciton analysis with the fragment-based one-electron transition density matrix method implemented in the TheoDORE package [3].

[1]. Kranz *et al.*, JCTC **13**, 1737 (2017)

[2]. https://dftbplus.org/

[3]. Plasser, JCP 152 084108 (2020)

– **1-TDM analysis**

$$\Omega_{AB} = \int_A d\mathbf{r}_\mathrm{h} \int_B d\mathbf{r}_\mathrm{e} \gamma_{0\mathrm{I}}{}^2(\mathbf{r}_\mathrm{e}, \mathbf{r}_\mathrm{h})$$

– **Charge-transfer number**

$$\mathrm{CT} = \frac{1}{\Omega} \sum_A \sum_{B \neq A} \Omega_{AB}$$

– **Exciton position**

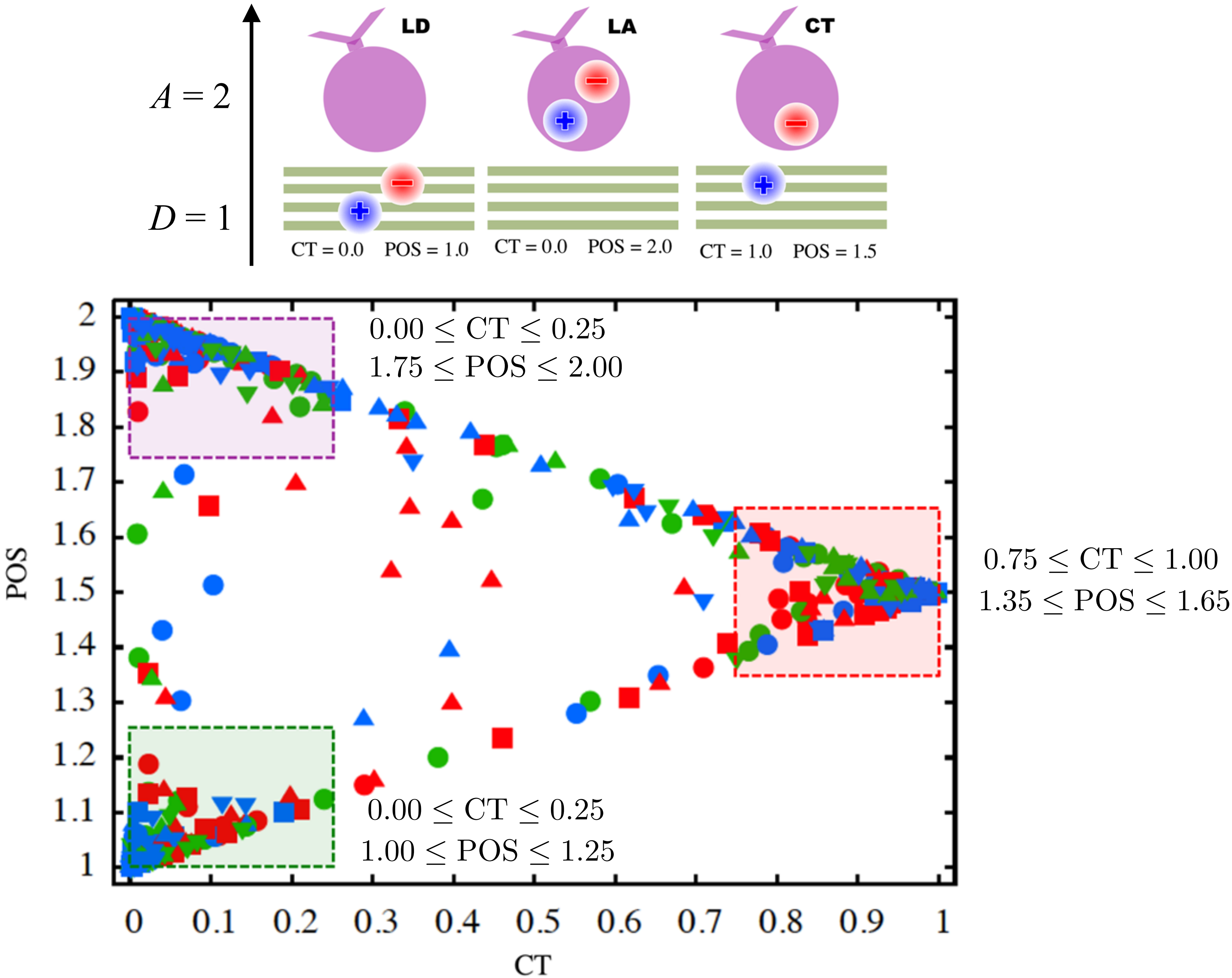
$$\mathrm{POS}_\mathrm{h} = \Omega^{-1} \sum_A A \left(\sum_B \Omega_{AB} \right)$$

$$\mathrm{POS}_\mathrm{e} = \Omega^{-1} \sum_B B \left(\sum_A \Omega_{AB} \right)$$

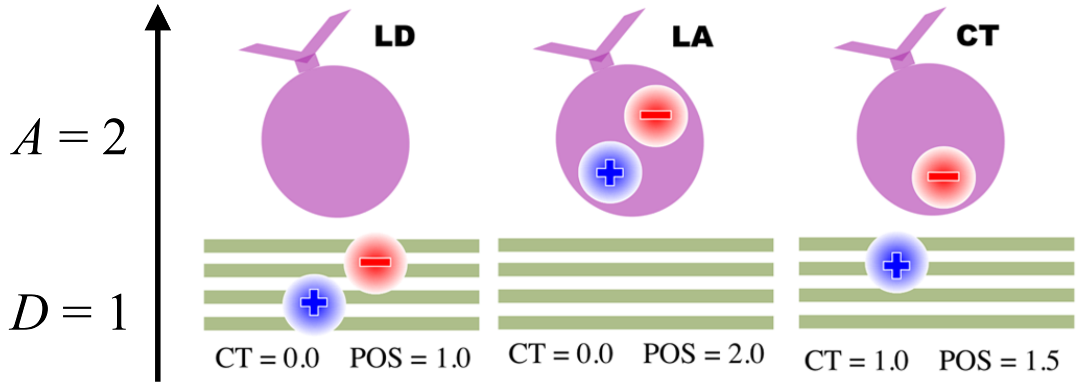
$$\mathrm{POS} = \frac{1}{2}(\mathrm{POS}_\mathrm{h} + \mathrm{POS}_\mathrm{e})$$

– **Exciton size**

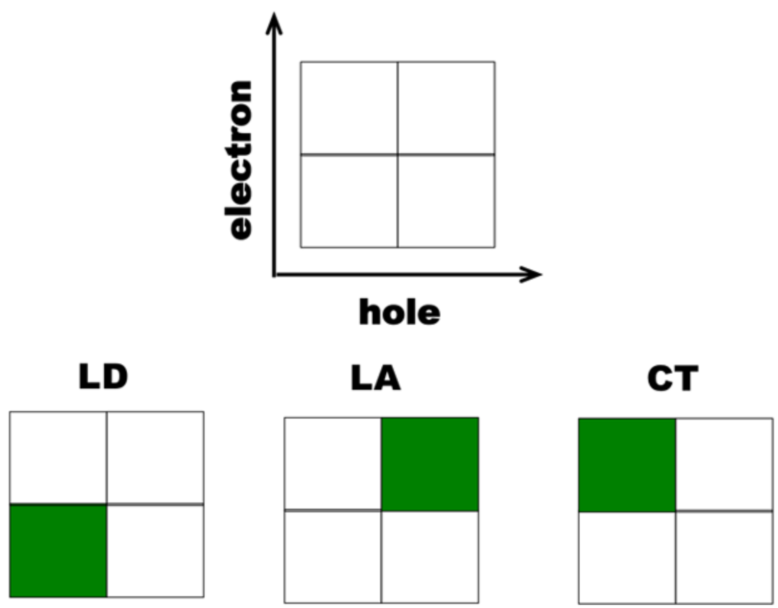
$$d_\mathrm{exc} \approx \sqrt{\frac{1}{\Omega} \sum_{M,N} \Omega_{MN} d_{MN}{}^2}$$

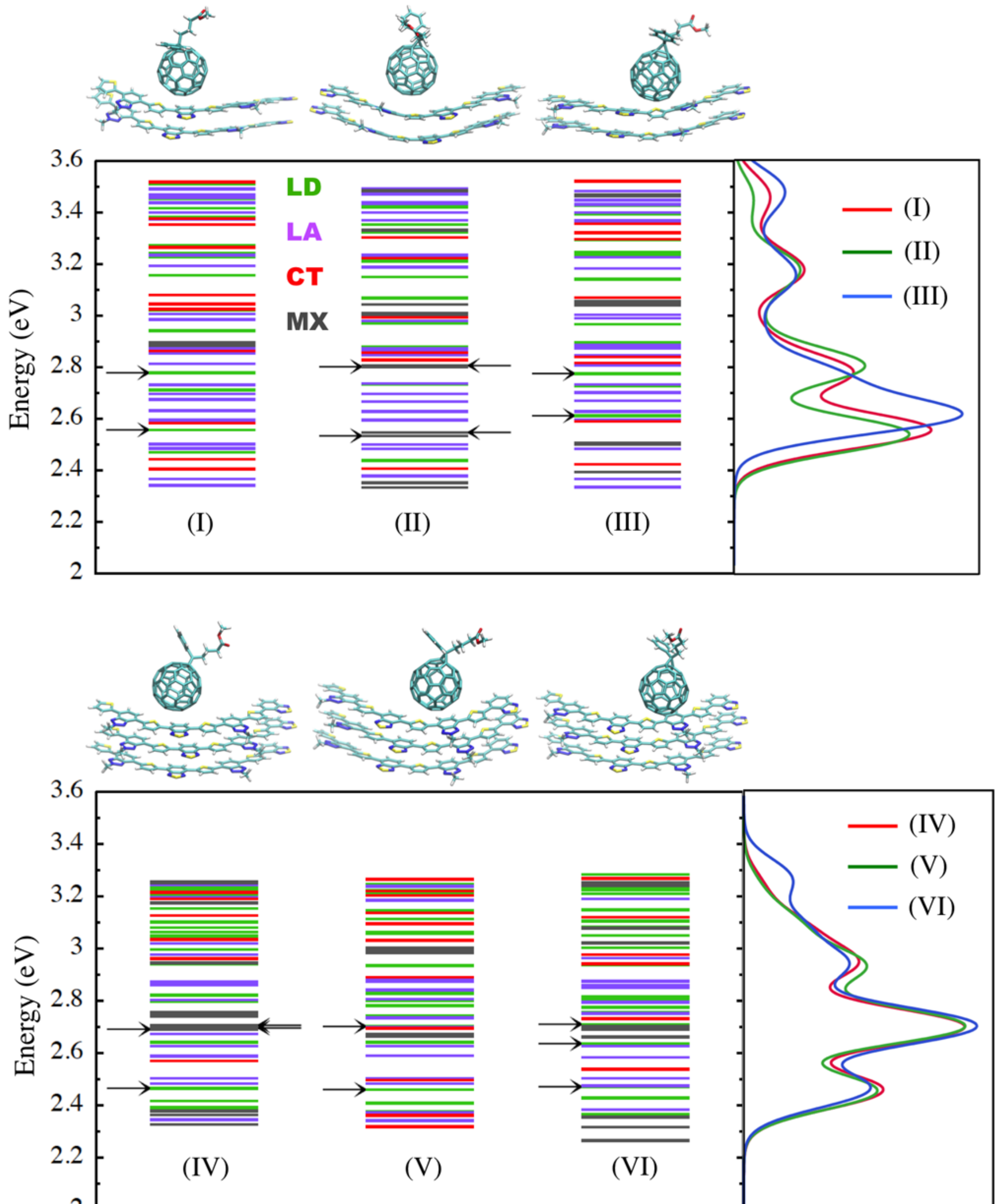


LD
LA
CT
A = 2
D = 1
CT = 0.0 POS = 1.0
CT = 0.0 POS = 2.0
CT = 1.0 POS = 1.5
0.00 ≤ CT ≤ 0.25
1.75 ≤ POS ≤ 2.00
0.75 ≤ CT ≤ 1.00
1.35 ≤ POS ≤ 1.65
0.00 ≤ CT ≤ 0.25
1.00 ≤ POS ≤ 1.25
POS
CT
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

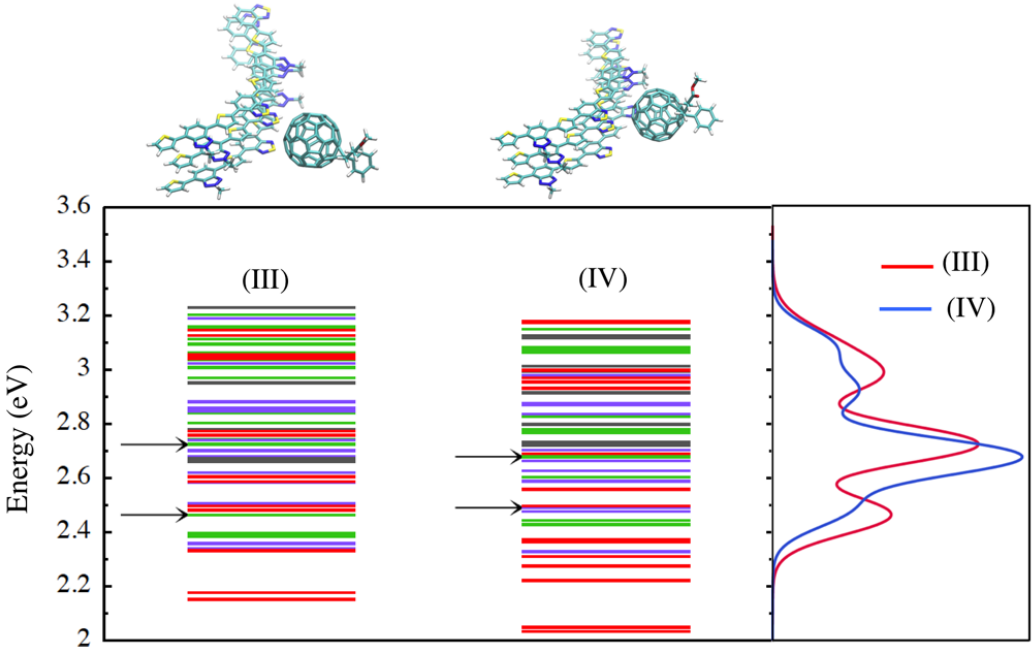


$$\Omega_{AB} = \int_A \mathrm{d}\mathbf{r}_\mathrm{h} \int_B \mathrm{d}\mathbf{r}_\mathrm{e} {\gamma_{0\mathrm{I}}}^2(\mathbf{r}_\mathrm{e}, \mathbf{r}_\mathrm{h})$$

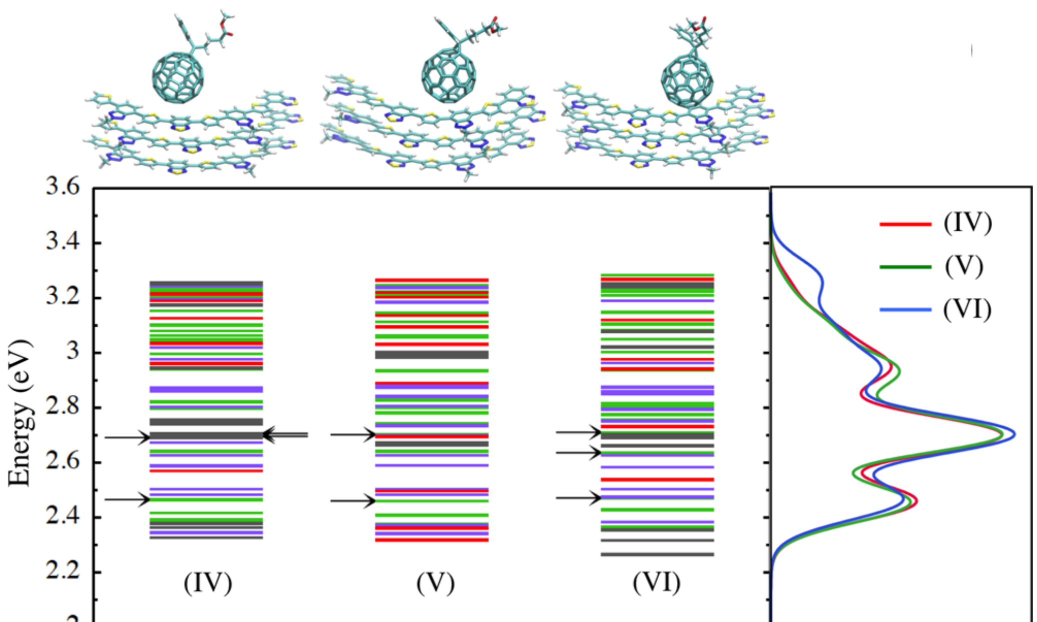




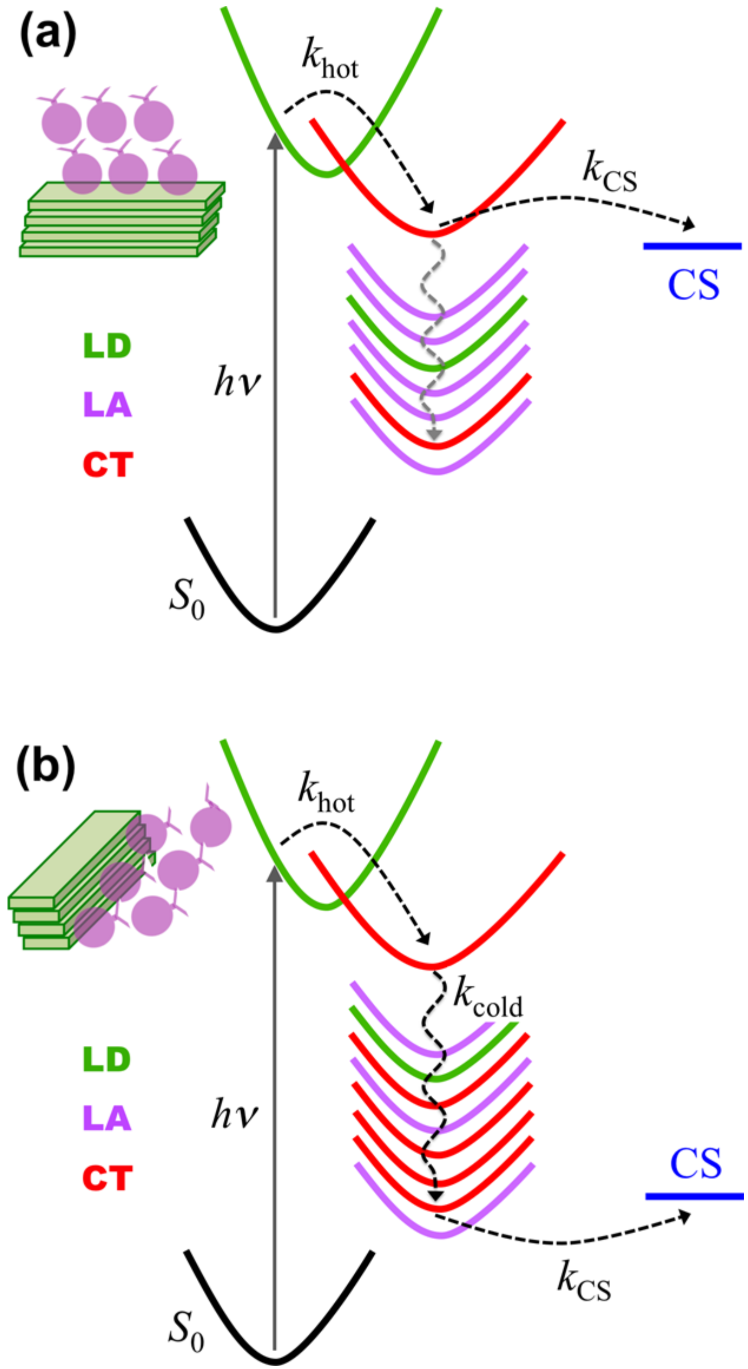
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
Energy (eV)
LD
LA
CT
MX
(I)
(II)
(III)
(IV)
(V)
(VI)



$$\langle n_{\mathrm{CT}}^{\mathrm{low}} \rangle = (8.0 \pm 2.2)$$
$$\langle n_{\mathrm{CT}}^{\mathrm{cold}} \rangle = (2.6 \pm 1.3)$$
$$\langle \mathrm{CT}_{\mathrm{cold}} \rangle = (0.995 \pm 0.009)$$



$$\langle n_{\mathrm{CT}}^{\mathrm{low}} \rangle = (1.9 \pm 1.1)$$
$$\langle n_{\mathrm{CT}}^{\mathrm{cold}} \rangle = (1.3 \pm 0.5)$$
$$\langle \mathrm{CT}_{\mathrm{cold}} \rangle = (0.89 \pm 0.05)$$



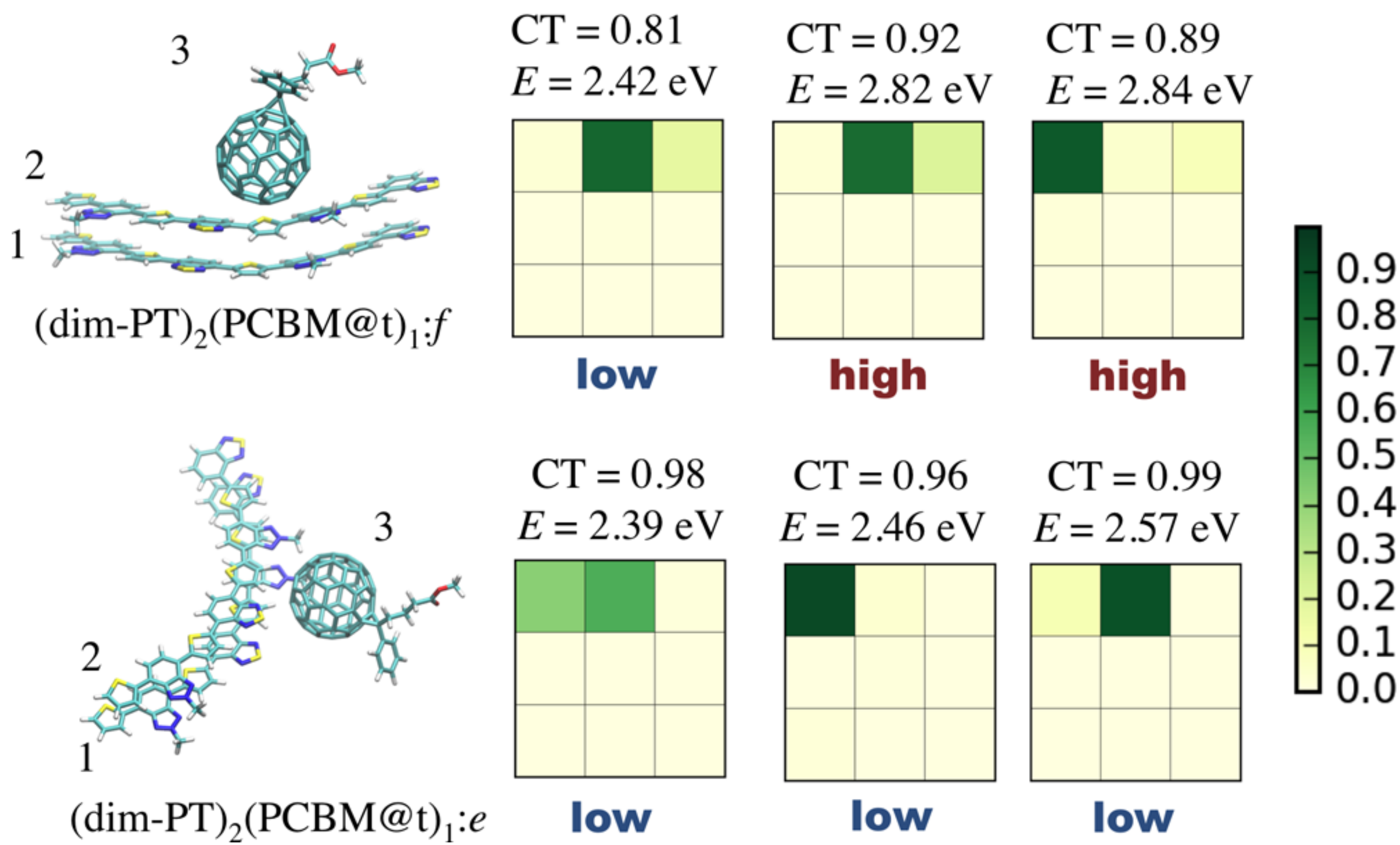
Conclusions in line with TD-DFT studies:

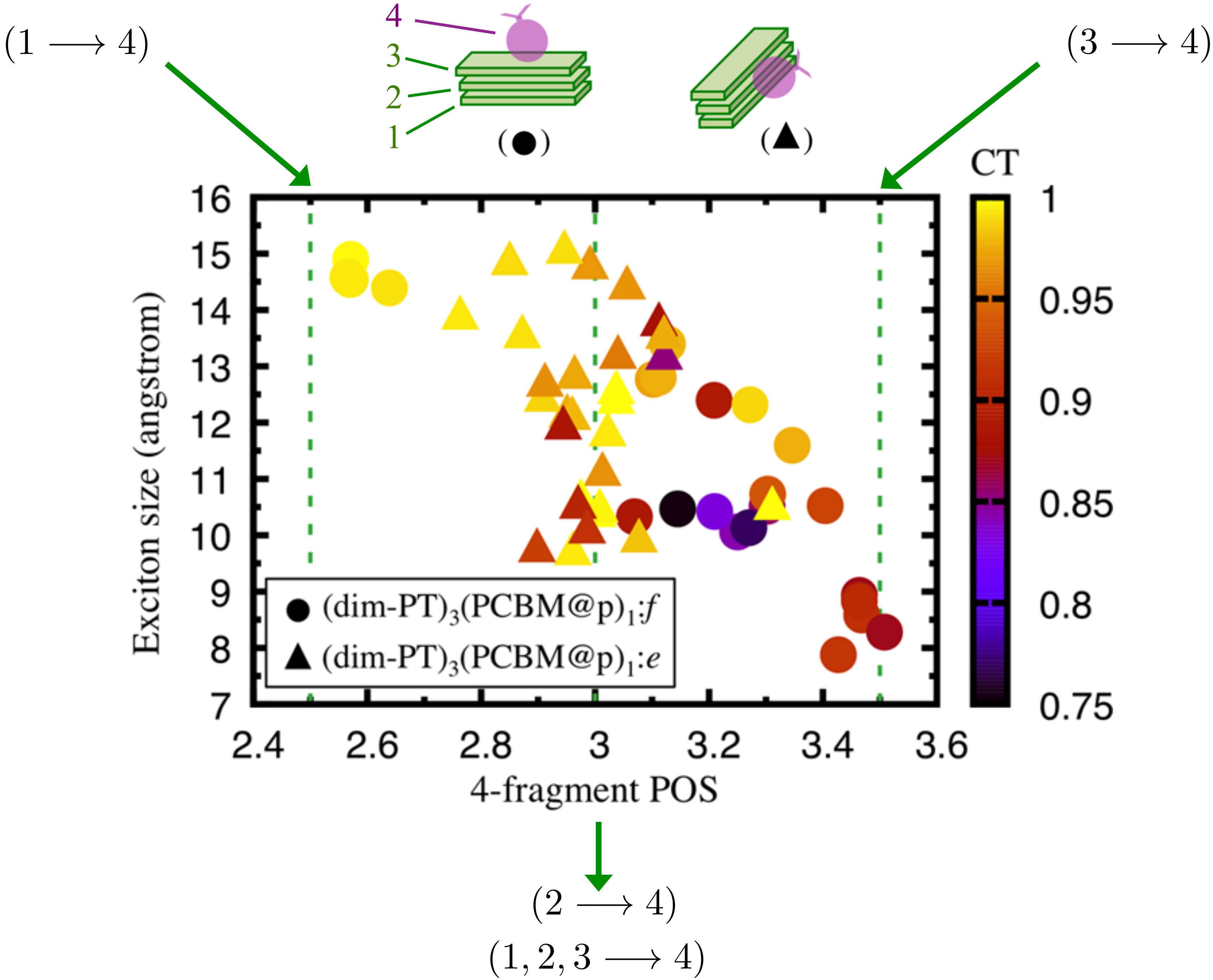
Chen *et al.*, Adv. Energy Mater. 6, 1601325 (2016)

Ran *et al.*, Nat. Commun., 8, 79 (2017)

Fazzi *et al.*, J. Phys. Chem. Lett. 8, 4727 (2017)

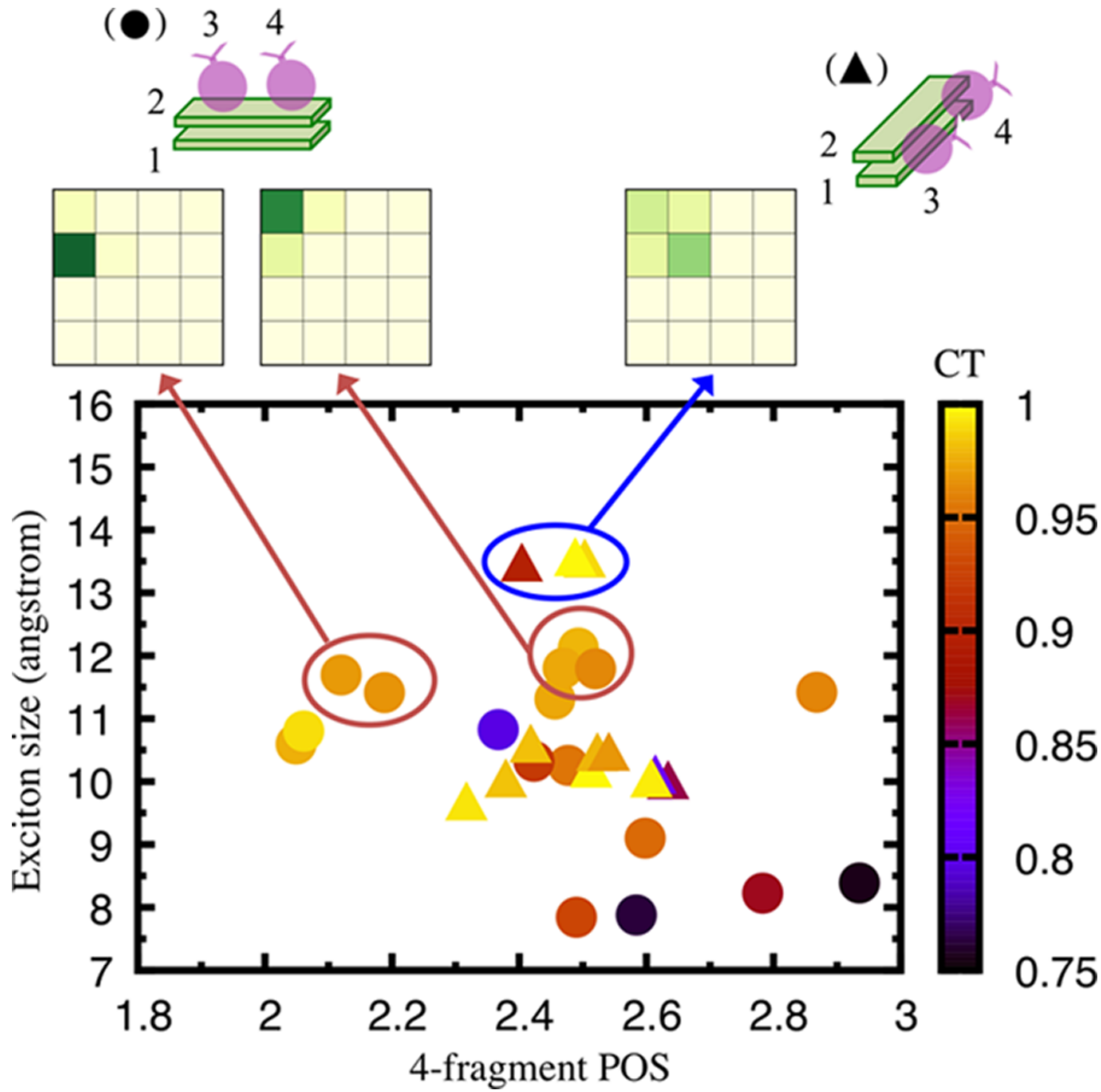
Hole delocalization



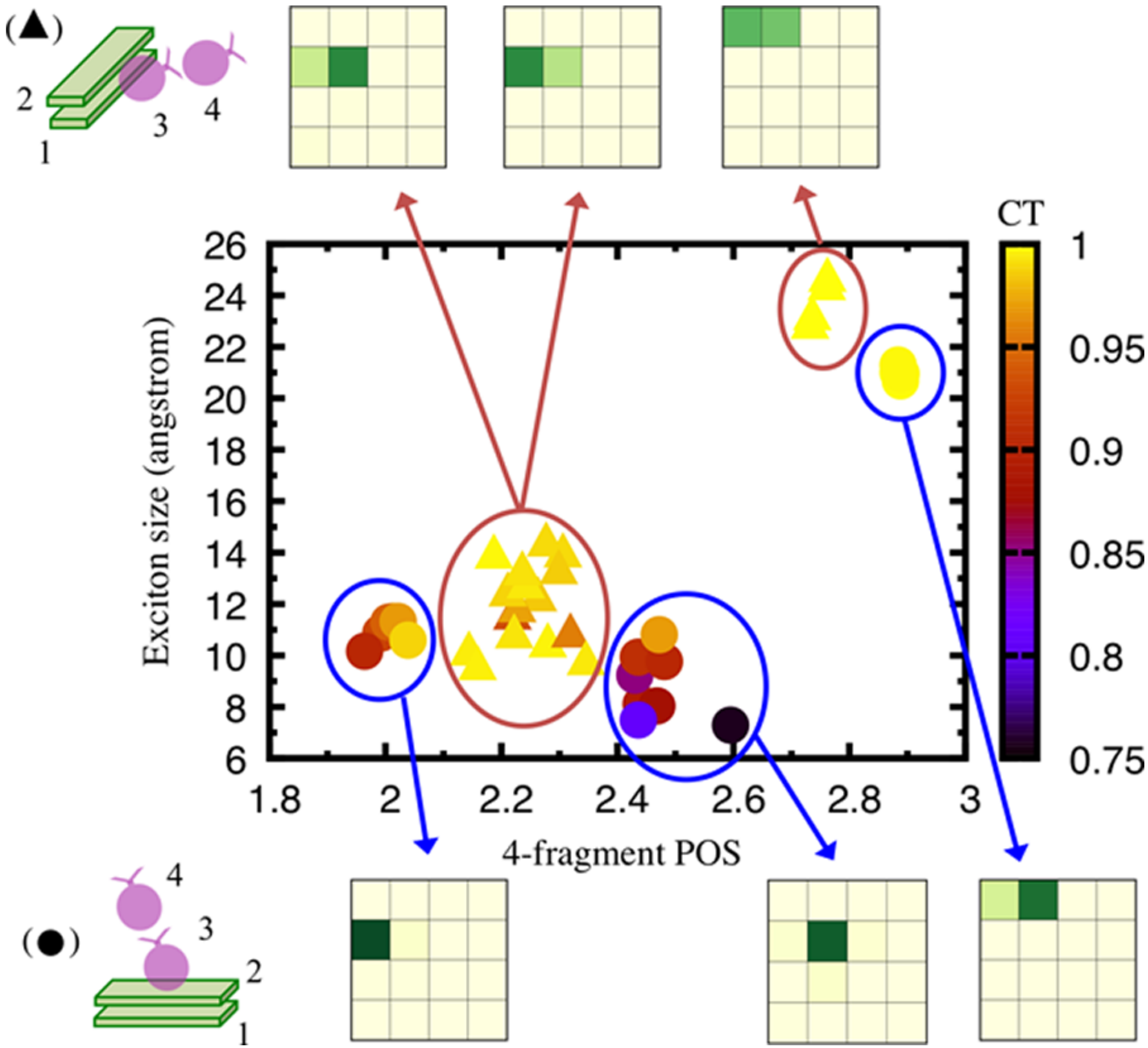


(1 ⟶ 4)
(3 ⟶ 4)
4
3
2
1
(●)
(▲)
CT
1
0.95
0.9
0.85
0.8
0.75
16
15
14
13
12
11
10
9
8
7
Exciton size (angstrom)
2.4
2.6
2.8
3
3.2
3.4
3.6
4-fragment POS
● (dim-PT)$_3$(PCBM@p)$_1$:*f*
▲ (dim-PT)$_3$(PCBM@p)$_1$:*e*
(2 ⟶ 4)
(1, 2, 3 ⟶ 4)

Electron delocalization



Electron delocalization

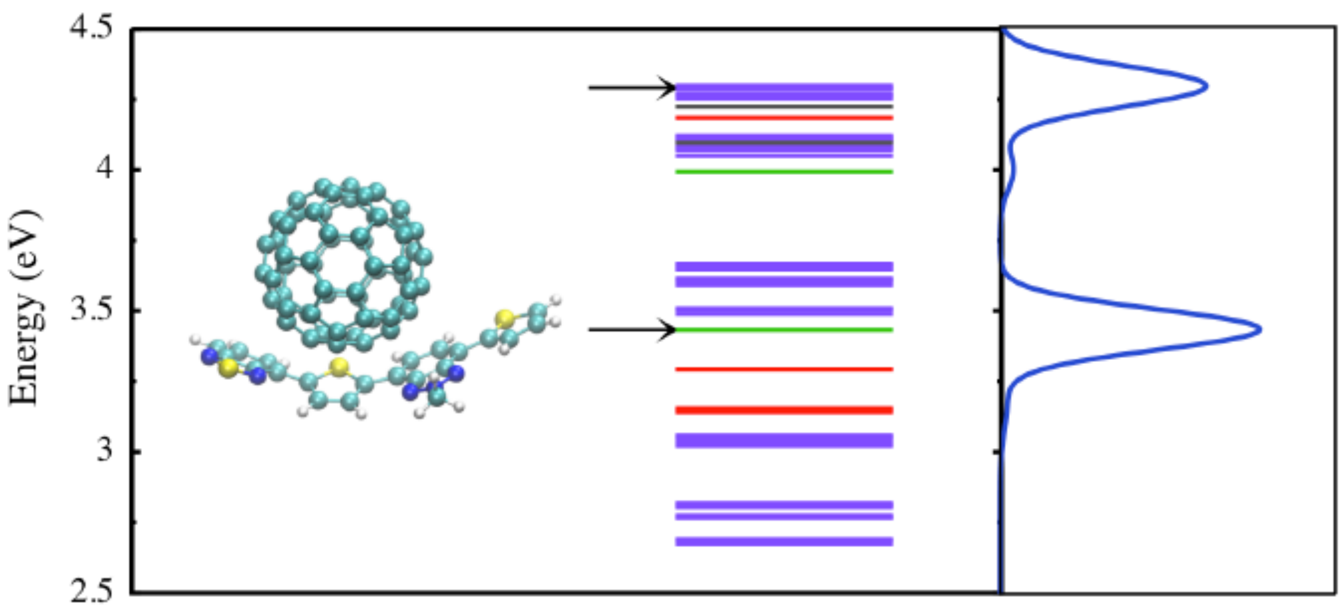


Insights Into Exciton Sizes

– Face-on models: exciton size increases as the hole lies farthest from the electron

– Edge-on models: exciton size increases as the hole delocalizes over the stacked donor chains.

– Electron delocatization perpendicularly to the interface produces larger excitons.



Ongoing :
FSSH dynamics

Many thanks to

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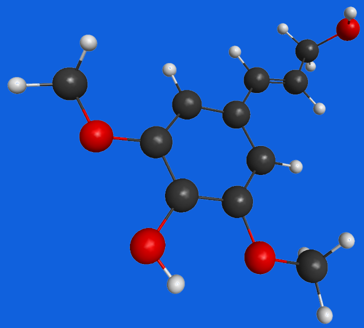
Stepahn Irle
Thomas Niehaus

Support

FAPESP

USP
PRÓ-REITORIA
DE PESQUISA

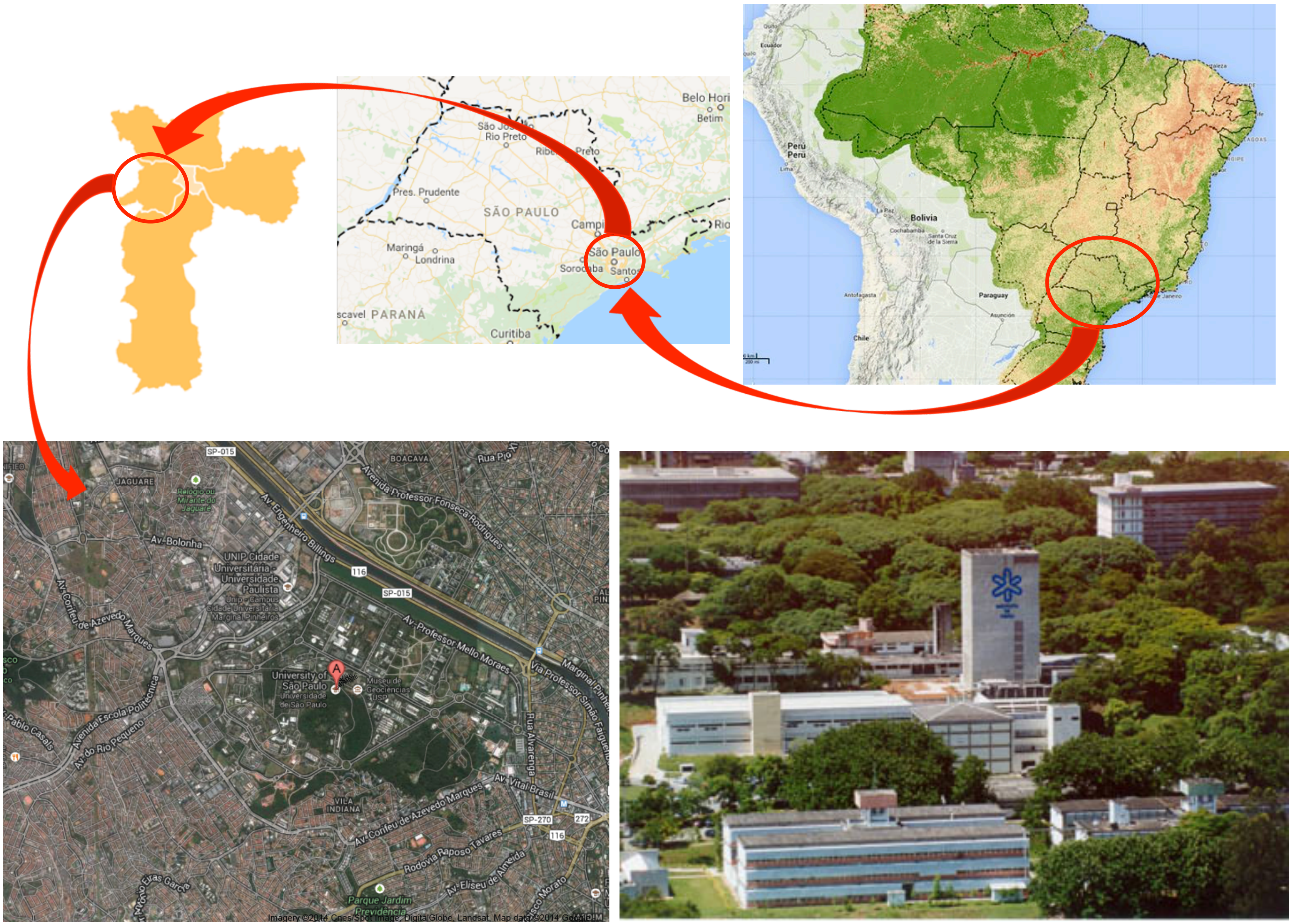
Thanks for your attention!



Molecular Physics

electrons positrons photons

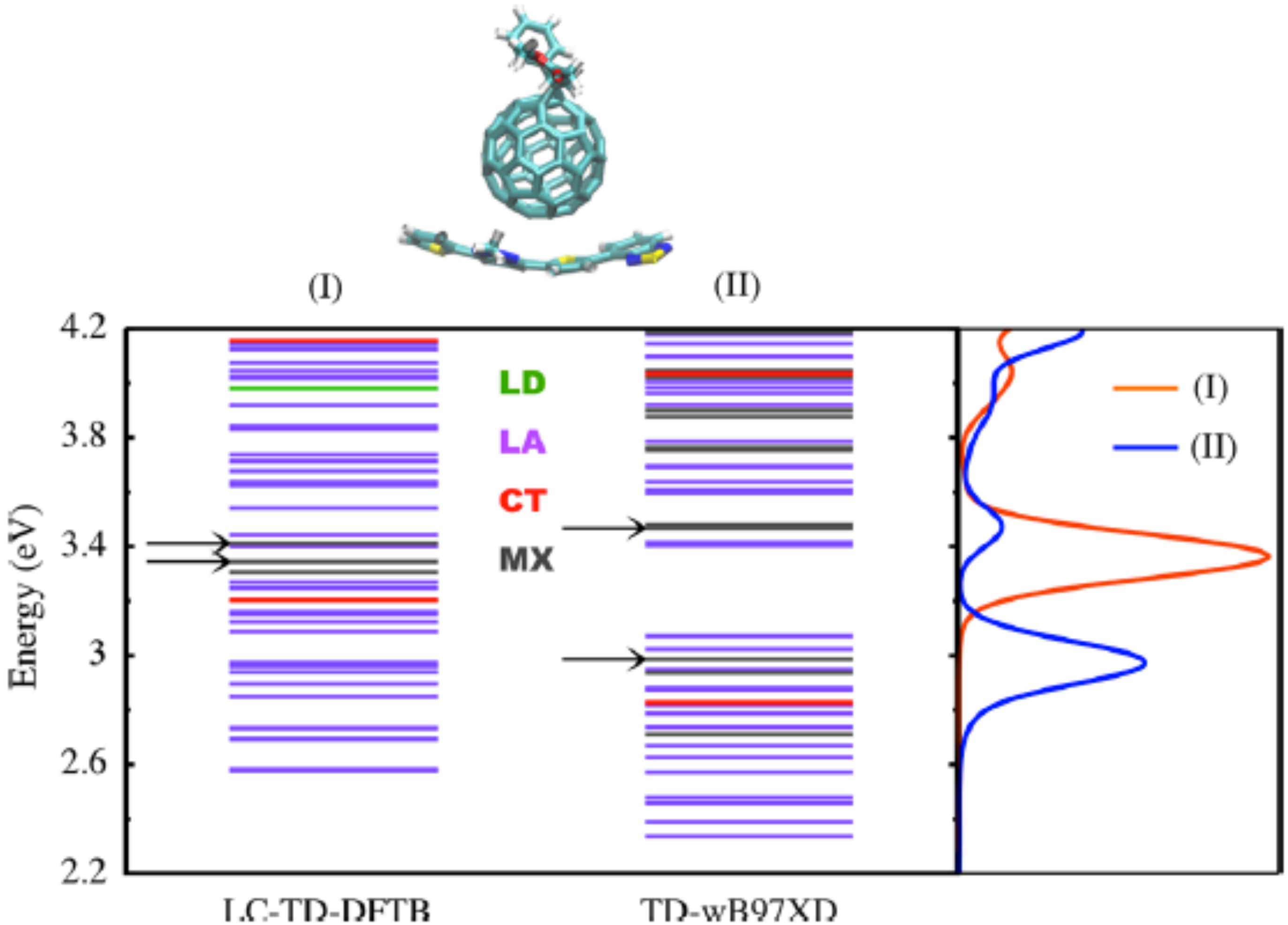
http://fig.if.usp.br/~mvarella/



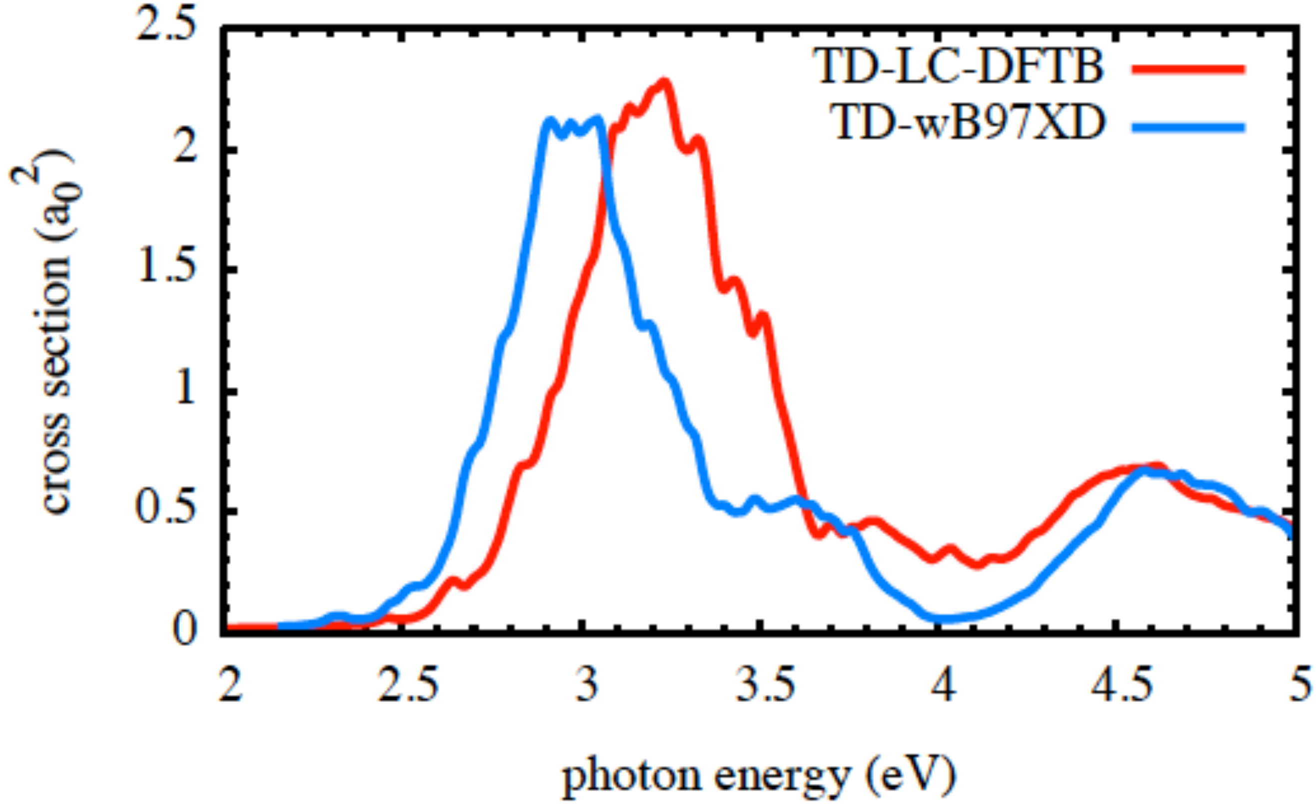
University of São Paulo Campus

Physics Institute

Benchmark

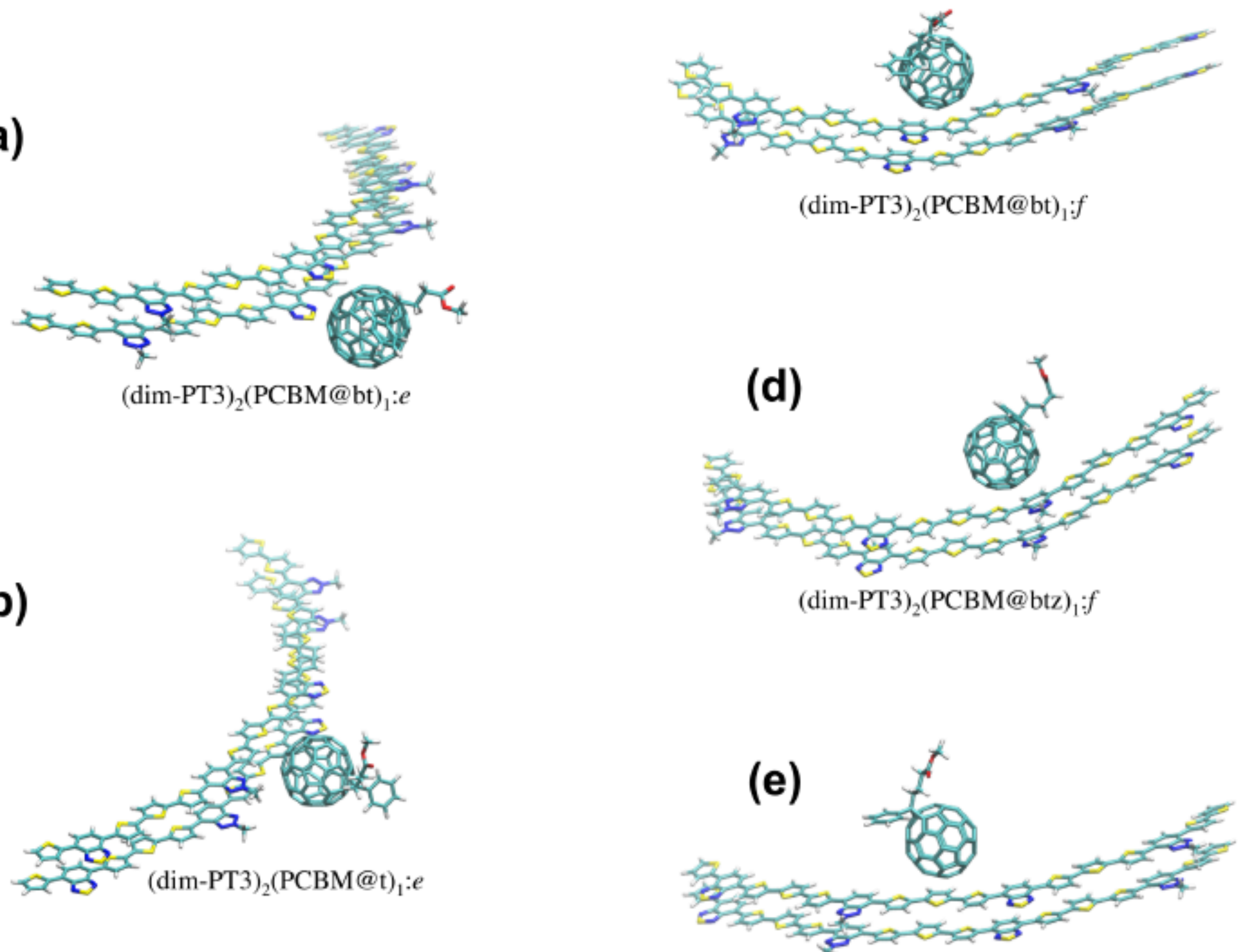


Benchmark



TD-LC-DFTB
TD-wB97XD
cross section (a_0^2)
photon energy (eV)
2.5
2
1.5
1
0.5
0
2
2.5
3
3.5
4
4.5
5

PT3BTBTz models



(a) (dim-PT3)$_2$(PCBM@bt)$_1$:*e*

(b) (dim-PT3)$_2$(PCBM@t)$_1$:*e*

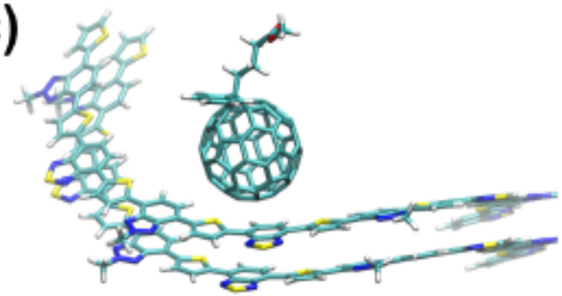
(c) (dim-PT3)$_2$(PCBM@bt)$_1$:*f*

(d) (dim-PT3)$_2$(PCBM@btz)$_1$:*f*

(e) (dim-PT3)$_2$(PCBM@t)$_1$:*f*

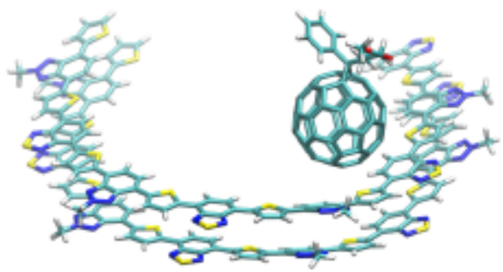
PTBTBTz tetramers

(c)



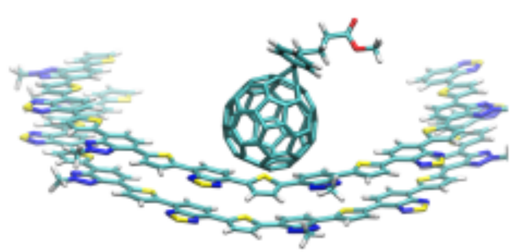
(tet-PT)$_2$(PCBM@bt)$_1$:f

(d)



(tet-PT)$_2$(PCBM@btz)$_1$:f

(e)



(tet-PT)$_2$(PCBM@t)$_1$:f

DFTB

$$\rho(\mathbf{r}) \;=\; \rho_0(\mathbf{r}) \;+\; \Delta\rho(\mathbf{r})$$

– Second-order expansion of the energy leads to

$$E = \underbrace{\sum_{i}^{\text{occ}} \sum_{\mu\nu}^{\text{basis}} c_{\mu i} c_{\nu i} H^0_{\mu\nu}(R_{\alpha\beta})}_{\text{variational coeffs + 2-center } H(\rho_0)} + \underbrace{\frac{1}{2} \sum_{\alpha\beta}^{\text{atoms}} \gamma_{\alpha\beta}(R_{\alpha\beta}) \Delta q_\alpha \Delta q_\beta}_{\text{semi-empirical + SC charges}} + \underbrace{\frac{1}{2} \sum_{\alpha\beta}^{\text{atoms}} V_{\alpha,\beta}(R_{\alpha,\beta})}_{\text{nuclear rep + } E_{xc}(\rho_0) \text{ terms}}$$

variational coeffs + 2-center $H(\rho_0)$

semi-empirical + SC charges

nuclear rep + $E_{xc}(\rho_0)$ terms

– Generalized eigenvalue problem:

$$\sum_{\nu} \left[H^0_{\mu\nu} + \frac{1}{2} S_{\mu\nu} + \sum_{\sigma}^{\text{atoms}} (\gamma_{\alpha\sigma} + \gamma_{\beta\sigma}) \Delta q_\sigma \right] c_{\nu i} \;=\; \epsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i}$$

– Compressed STOs, Slater-Koster files

Phys. Rev. B 58, 7260 (1998); JPCA 11, 5614 (2007)

TD-DFTB

– **Linear response formalism:**

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \Omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

$$A_{ia\sigma,jb\sigma'} = \delta_{ij}\delta_{ab}\delta_{\sigma\sigma'}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + (ia\sigma||jb\sigma')$$

$$B_{ia\sigma,jb\sigma'} = (ia\sigma||bj\sigma')$$

– **Generalized 2-electron integrals in terms of transition Mullken charges:**

$$\int\int' \psi_i(\mathbf{r})\psi_a(\mathbf{r})\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}[\rho](\mathbf{r},\mathbf{r}')\right)\psi_j(\mathbf{r}')\psi_b(\mathbf{r}') = \sum_{\mu\nu} q_\mu^{ia}\tilde{\gamma}_{\mu\nu}q_\nu^{jb}$$

$$q_\mu^{ia} = \frac{1}{2}\sum_\nu (c_{\mu i}c_{\nu a}S_{\mu\nu} + c_{\nu i}c_{\mu a}S_{\nu\mu})$$

J. Mol. Struct. THEOCHEM 914, 38 (2009); JCTC 13, 1737 (2017)

LC-TD-DFTB

– **Yukawa ansatz with Bauer-Neuhauser-Livshits (BNL) XC potential:**

$$v_C = v_C^{\mathrm{sr}} + v_C^{\mathrm{lr}} = \frac{\exp(-\omega r_{12})}{r_{12}} + \frac{1 - \exp(-\omega r_{12})}{r_{12}}$$

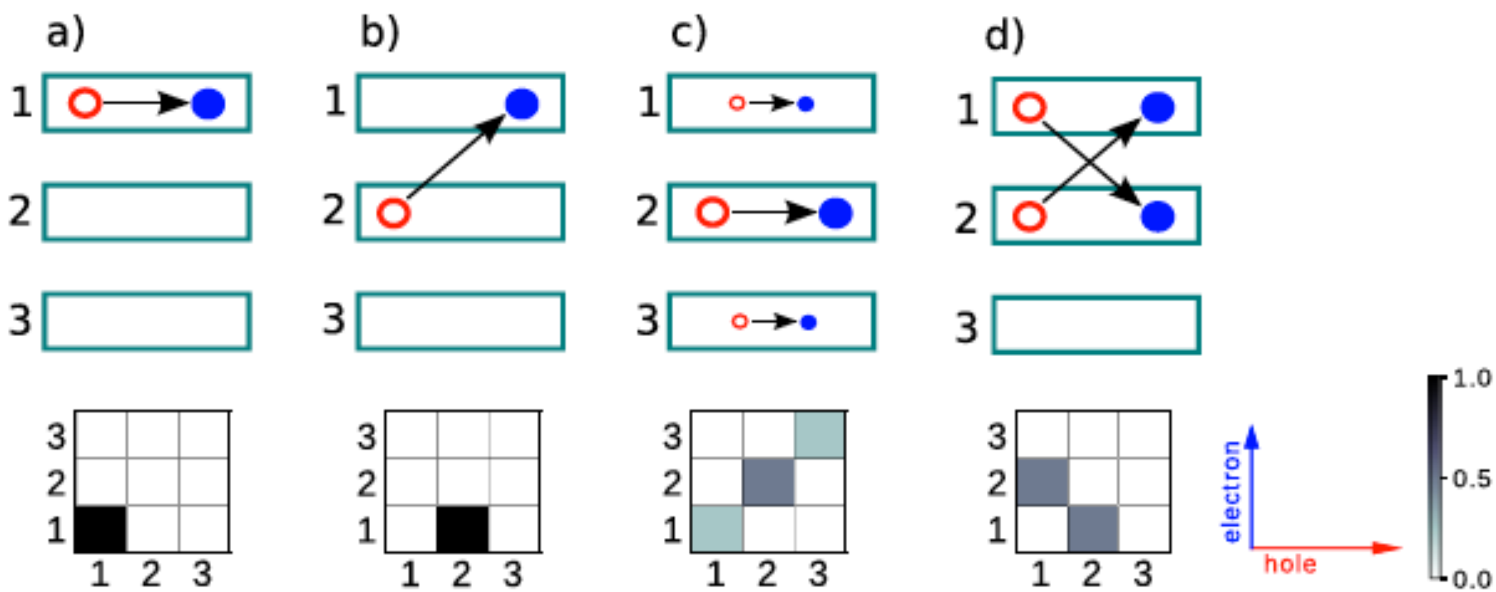
– **Modified γ integrals**

JCP 143 184107, (2015) ; JCTC 13, 1737 (2017)

1-TDM-Analysis

$$\Omega_{AB} = \int_A d\mathbf{r}_\mathrm{h} \int_B d\mathbf{r}_\mathrm{e} \gamma_{0\mathrm{I}}{}^2(\mathbf{r}_\mathrm{e}, \mathbf{r}_\mathrm{h})$$

$$\Omega^{\alpha}_{\mathrm{AB}} = \frac{1}{2} \sum_{\substack{\mathrm{a}\in \mathrm{A} \\ \mathrm{b}\in \mathrm{B}}} (\mathbf{D}^{0\alpha,[\mathrm{AO}]}\mathbf{S}^{[\mathrm{AO}]})_{\mathrm{ab}} (\mathbf{S}^{[\mathrm{AO}]}\mathbf{D}^{0\alpha,[\mathrm{AO}]})_{\mathrm{ab}}$$



JCTC 8 2777, (2012) ; JCP 152, 084108 (2020)