Understanding the high device efficiency of a class of solution-processed small-molecule solar cells

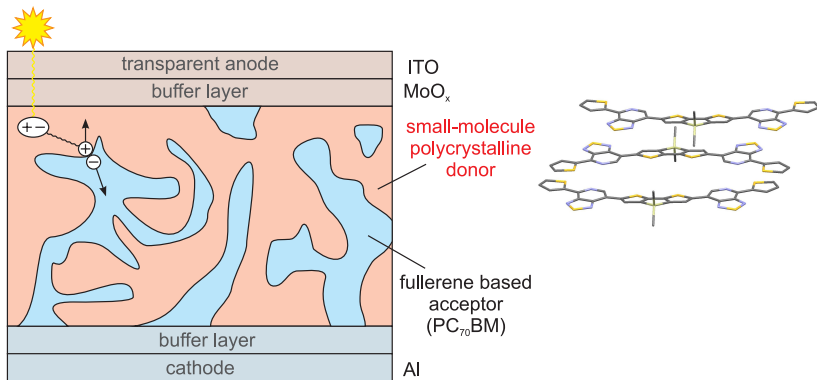Andriy Zhugayevych[1], Olena Postupna[1], Sergei Tretiak[1], Guillermo Bazan[2]

[1] *Theoretical Division, Los Alamos National Laboratory*
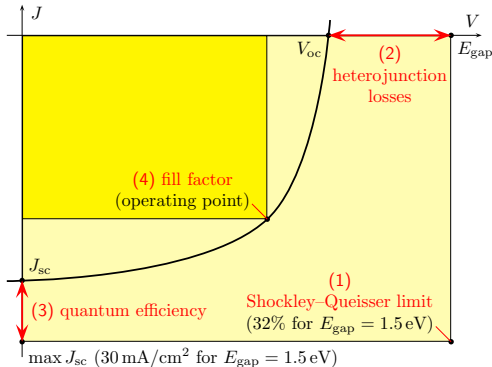[2] *Department of Chemistry and Biochemistry, University of California, Santa Barbara*

Small-molecule based bulk-heterojunction solar cells

transparent anode — ITO
buffer layer — MoO$_x$

small-molecule polycrystalline donor

fullerene based acceptor (PC$_{70}$BM)

buffer layer
cathode — Al

Power conversion efficiency: main factors

Shockley–Queisser limit for $E_{gap} = 1.5$ eV		32%	▶
Heterojunction losses, V_{oc}/E_{gap}	×	0.6	▶
Quantum efficiency, $J_{sc}/\max J_{sc}$	×	0.7	▶
Fill Factor	×	0.7	▶
Power conversion efficiency	=	10%	

V_{oc} = open-circuit voltage, J_{sc} = short-circuit current

Our goal

Perform first-principles investigations to:

- study performance on a microscopic (single-crystallite) scale

- determine the bottleneck for power conversion efficiency

- understand the dependence on chemical composition

Methods and challenges

- small-polaron/Frenkel-exciton hopping within Holstein Hamiltonian ▸

- parameters by ab-initio density functional theory (DFT): B3LYP and CAM-B3LYP

- intermolecular geometries: semiempirical PM6, force field MM3, and dispersion-corrected DFT

- at the limits of "standard" computational chemistry tools ▸

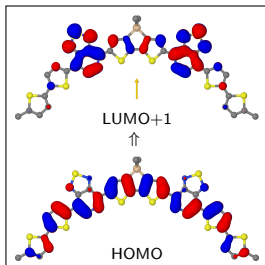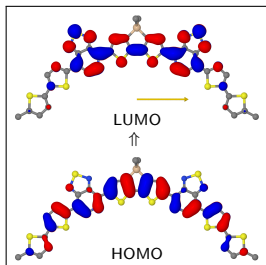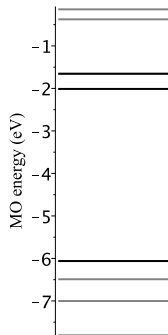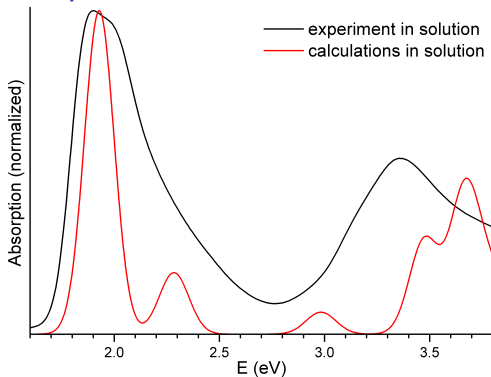- too many uncontrolled approximations ▸

Molecules considered
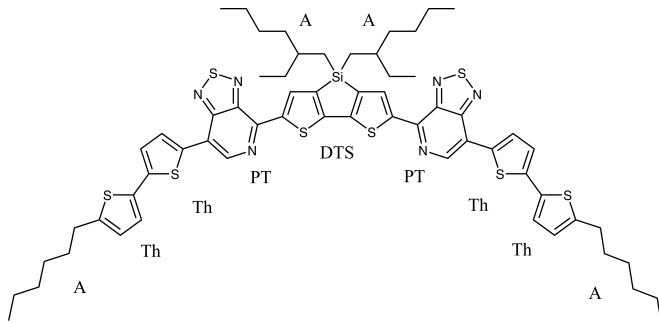
DTS(PTTh₂)₂
up to 7% efficiency
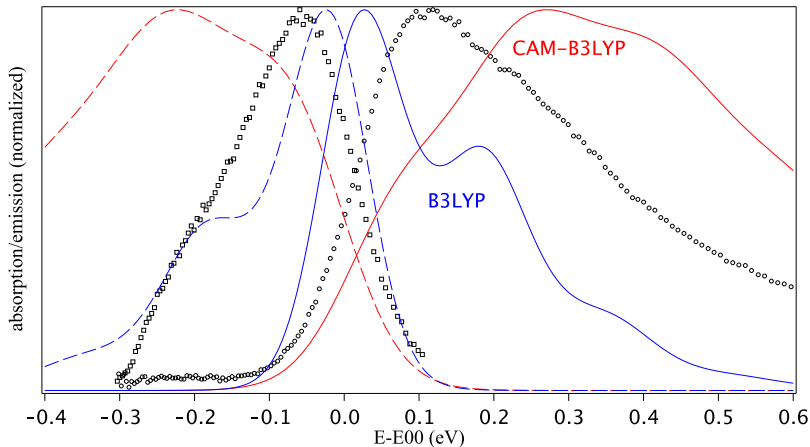[Y Sun *et al.* Nature Mater 11, 44 (2012)]

A – aliphatic chain, DTS – dithienosilole, PT – pyridalthiadiazole, Th – thiophene
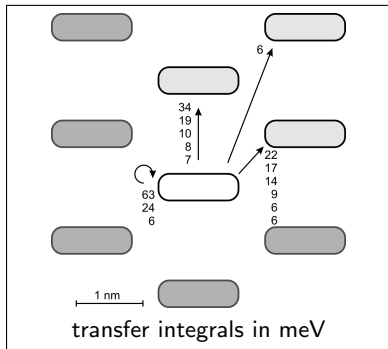
Light absorption: molecules in solution

absorption in
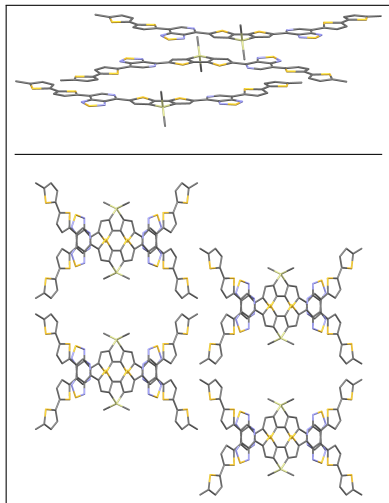crystal see [here]

Vibrationally resolved spectra

- B3LYP underestimates vibronic couplings for low-ω modes
- CAM-B3LYP overestimates vib. couplings for high-ω modes

Exciton transport

transfer integrals in meV

- transfer rates $1\,\mathrm{ps}^{-1}$
- diffusion length $50\,\mathrm{nm}$

$\implies$ Excitons are "delocalized" over crystallites of size $< 100\,\mathrm{nm}$

Hole transport

transfer integrals in meV
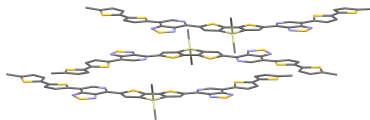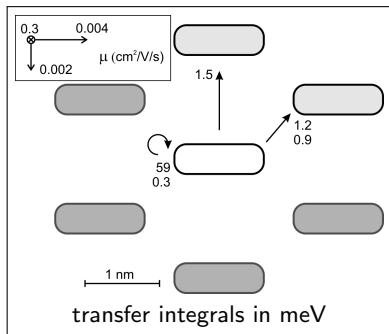
Transport goes along π-stacks

- transfer rates $1\,\mathrm{ps}^{-1}$
- mobility $0.3\,\mathrm{cm}^2/\mathrm{V/s}$
- diffusion coef. $1\,\mathrm{nm}^2/\mathrm{ps}$
- disorder-resistant

$\implies$ Holes are efficiently transported across crystallites

Where is the bottleneck for the power conversion efficiency

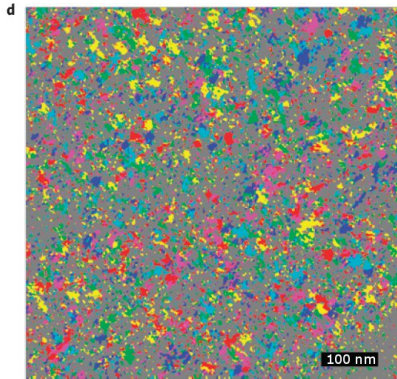No losses on single crystallite scale $\implies$ power conversion efficiency is determined at mesoscale (interfaces, grain boundaries)
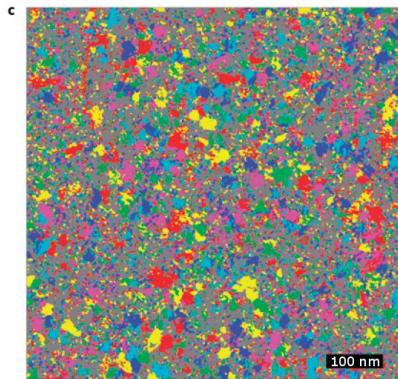
no solvent additive[1]
(color mark crystallite orientation)

optimal concentration of
solvent additive

[1]Y Sun *et al*. Nature Mater 11, 44 (2012)

Dependence of the efficiency on molecular composition
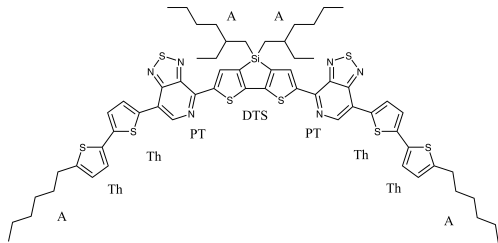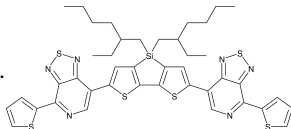
HOMO level	-5.3 eV	-5.4 eV
Light absorption peak	1.9 eV	2.1 eV
Transition dipole	6.1 Au	5.0 Au
Exciton diffusion length	70 nm	50 nm
Hole mobility	0.3 cm^2/V/s	0.2 cm^2/V/s
Binding in crystal (PM6)	0.4 eV	0.25 eV
(MM3)	4 eV	2.5 eV

Conclusions

- For high-efficiency small-molecule polycrystalline bulk-heterojunction (SMBHJ) solar cells the efficiency is limited by the mesoscale design (interfaces, morphology of the active layer).

- There are no "losses" on a single-crystallite scale due to the disorder-resistant and relatively fast charge carrier transport along π-stacks and exciton "delocalization" over crystallites.

- Two materials having similar molecular structure and electronic properties on a single-crystallite scale may show different performance as donors in SMBHJ solar cells.

Shockley–Queisser limit
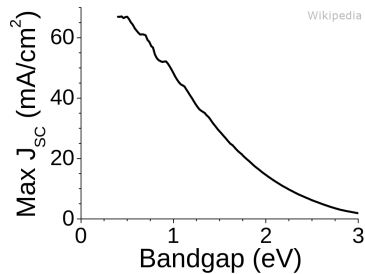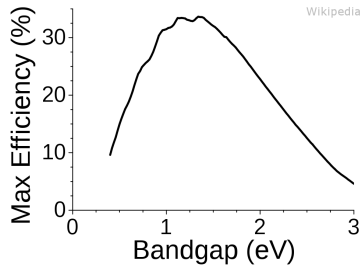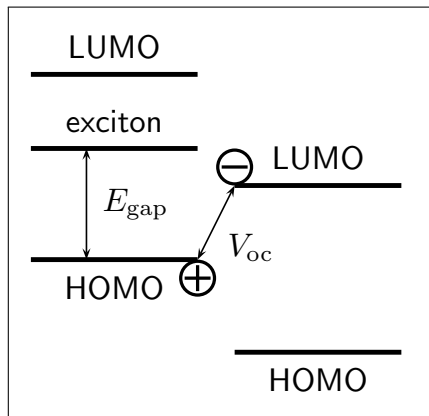
- fullerene-based acceptor: $E_{\mathsf{LUMO}} \approx -4.3\,\mathrm{eV}$
- π-conjugated donor: $E_{\mathsf{gap}} \gtrsim 1.5\,\mathrm{eV}$ for $E_{\mathsf{HOMO}} \lesssim -5.3\,\mathrm{eV}$

Quantum efficiency
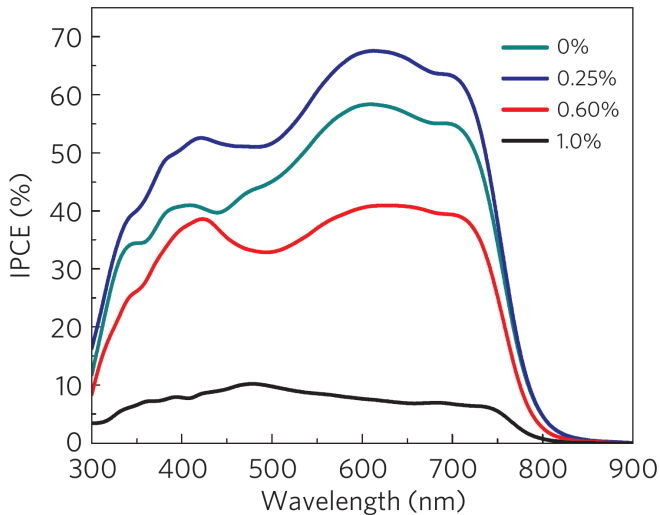
Y Sun *et al.* Nature Mater 11, 44 (2012)

Fill factor

Y Sun *et al.* Nature Mater 11, 44 (2012)
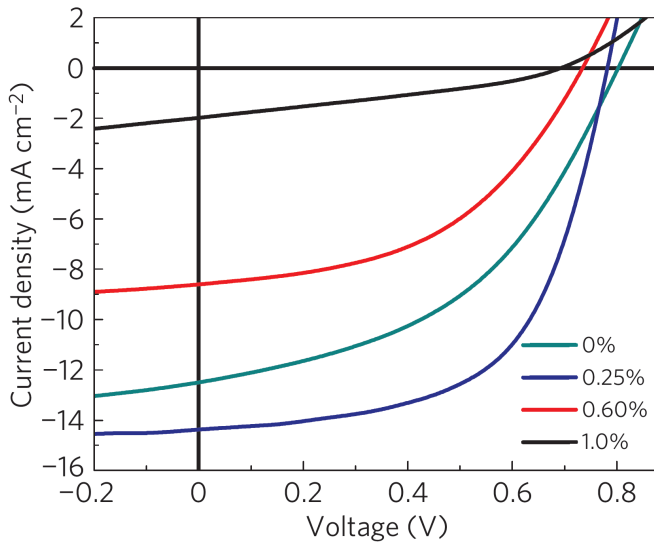
Small polaron hopping

Holstein model (local coupling) with one site per molecule:

$$\sum_i \varepsilon_i \mathsf{n}_i + \sum_{ij} t_{ij} \mathsf{c}_i^\dagger \mathsf{c}_j + \sum_\alpha \hbar\omega_\alpha \left(\mathsf{b}_\alpha^\dagger \mathsf{b}_\alpha + \frac{1}{2}\right) + \sum_{i\alpha} \hbar\omega_\alpha g_{i\alpha} \left(\mathsf{b}_\alpha^\dagger + \mathsf{b}_\alpha\right) \mathsf{n}_i$$

here c_i – excitons, holes, or electrons treated as noninteracting quasiparticles, b_α – intramolecular normal modes.

	ε	t, meV	$\hbar\omega_{\mathsf{eff}}$, meV	g_{eff}^2	E^{polaron}, meV
exciton,hole	0	60	50	4	200

For $T = 300\,\mathrm{K}$ (25 meV):

- $\hbar\omega > kT \implies$ no nonadiabatic molecular dynamics
- $t^{\mathsf{polaron}} = 0 \implies$ no polaron bands
- $t < E^{\mathsf{polaron}} \implies$ **small polaron hopping**

But transfer rates $w_{(i \to j)} = \frac{2\pi}{\hbar} |t_{ij}|^2 \int \rho_i^{\mathsf{emi}}(E) \rho_j^{\mathsf{abs}}(E)\, \mathrm{d}E \sim 1\,\mathrm{ps}^{-1}$ are comparable with intramolecular relaxation times

"Standard" computational chemistry tools

- 150 atoms per molecule, 1000 atoms per unit cell
- 8 cpu/node
- Gaussian, MOPAC
- state-of-the-art methods are not implemented
- geometry optimization fails
- PBC calculations fail
- no SCF convergence for RO-DFT
- . . .

Too many uncontrolled approximations

For small polaron hopping:

- basis set
- density functional
- oversimplified environment (dimer calculations, PCM)
- simplified potential energy surfaces
- infinitely fast on-site polaron relaxation
- thermally equilibrated vibrations
- Fermi golden rule (small constant transfer integrals)
- discrepancies in calculating transfer integrals
- hole polaron wave function $=$ HOMO
- . . .

Light absorption: crystal