Molecular simulation insights into morphology and charge transport characteristics of donor/acceptor systems

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cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

DRESDEN concept

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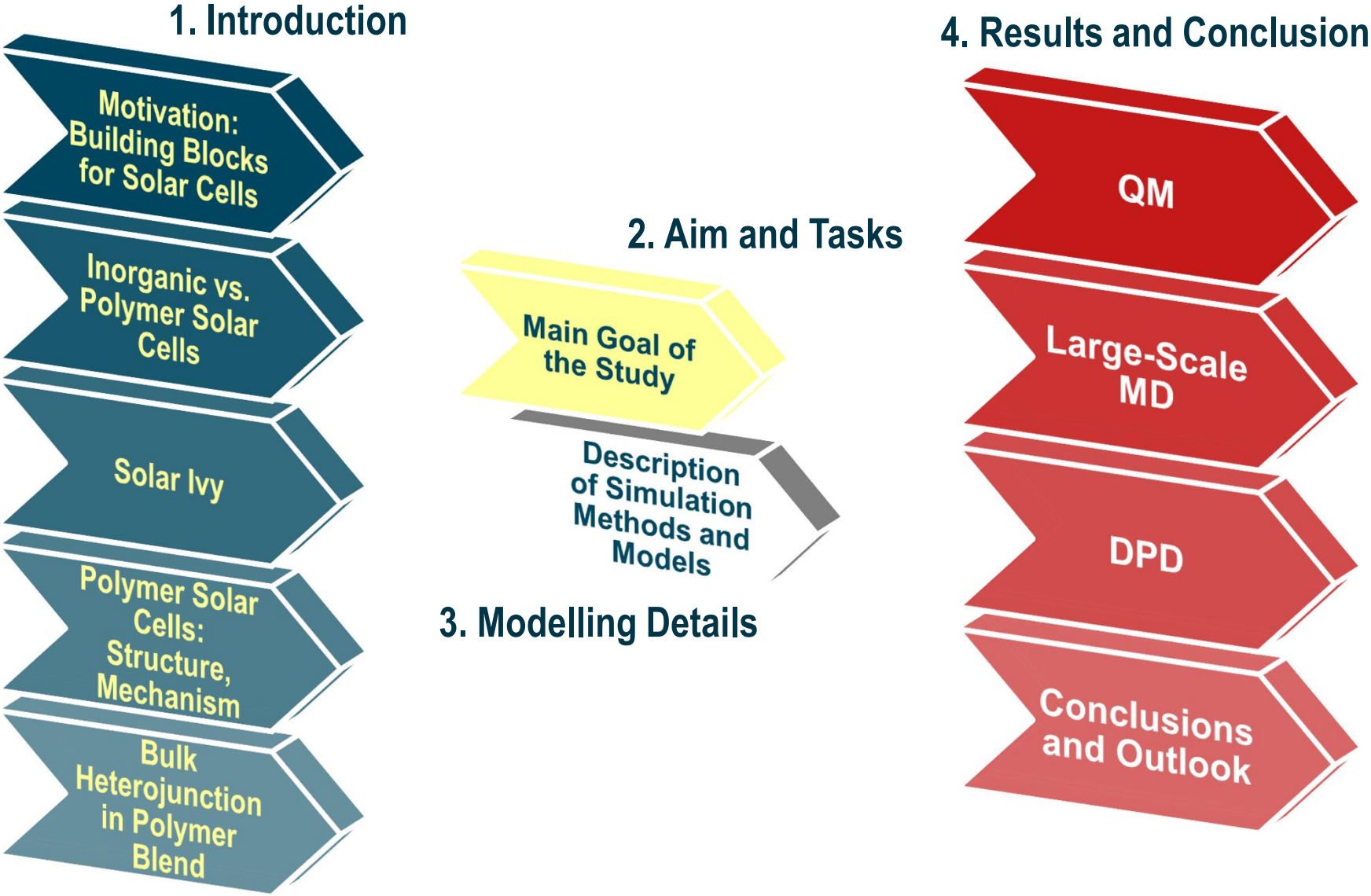
nanoSeminar, Jan., 31st, 2013

Outline


1. Introduction
Motivation: Building Blocks for Solar Cells
Inorganic vs. Polymer Solar Cells
Solar Ivy
Polymer Solar Cells: Structure, Mechanism
Bulk Heterojunction in Polymer Blend
2. Aim and Tasks
Main Goal of the Study
Description of Simulation Methods and Models
3. Modelling Details
4. Results and Conclusions
QM
Large-Scale MD
DPD
Conclusions and Outlook

1. Introduction

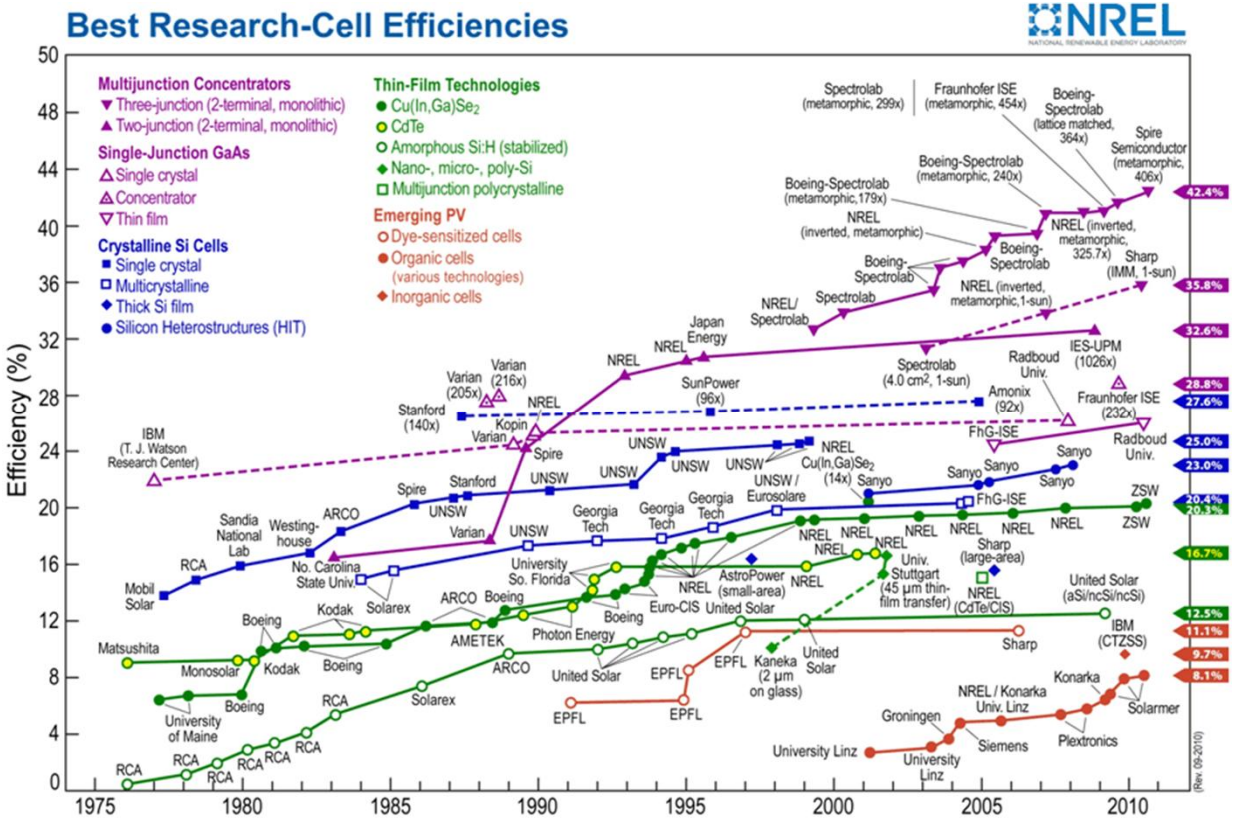
The generations of solar cells

I. Single crystal silicon wafers

II: Polycrystalline silicon or Amorphous silicon

III: Nanocrystal solar cells or **Polymer solar cells**

IV: Hybrid - inorganic crystals within a polymer matrix or Tandem Solar Cells

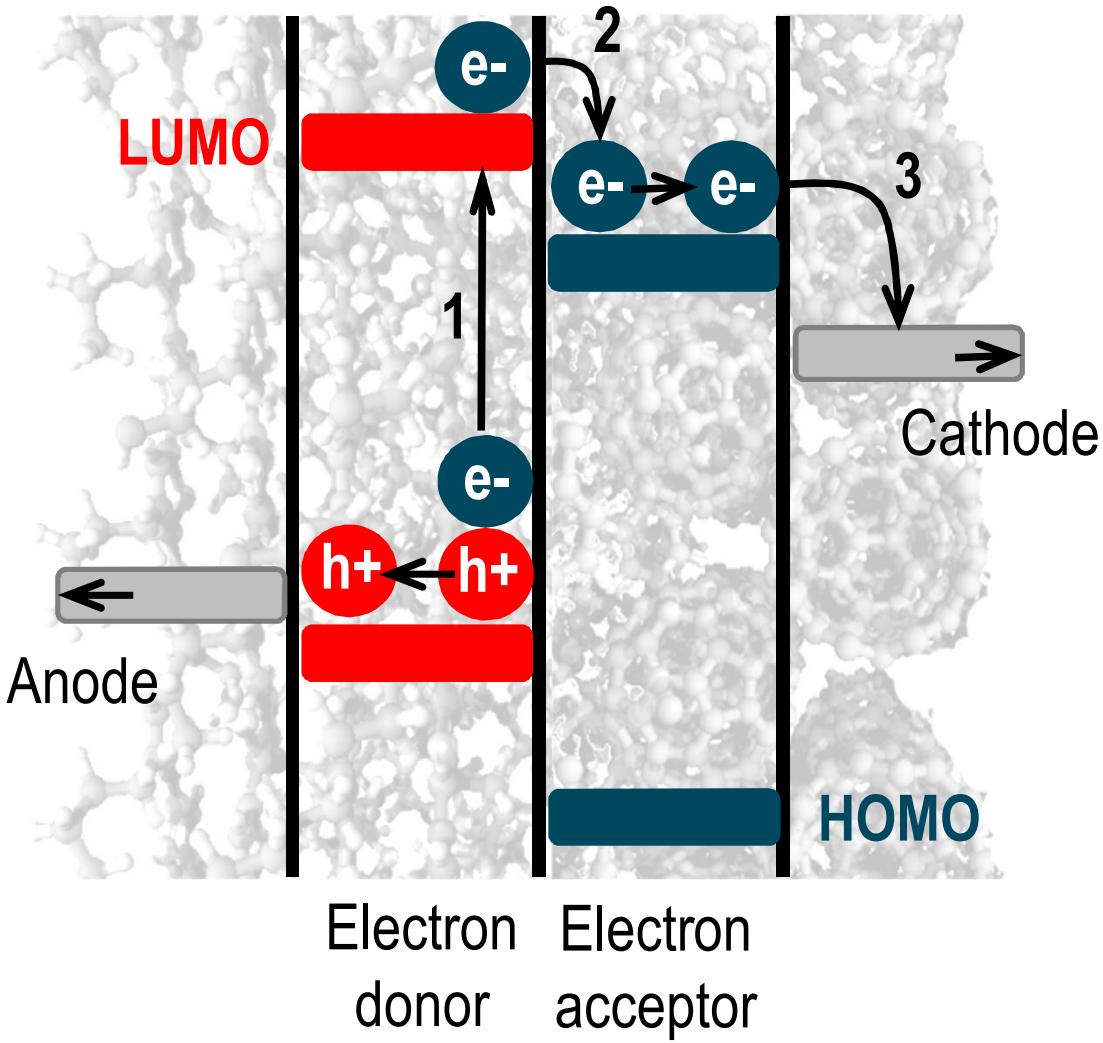


Efficiency of inorganic solar cells: ~10–45%

- **Current Polymer Solar Cell: ~12%[1]**
- **Max Inorganic: ~45%**

[1] http://www.heliatek.com/wp-content/uploads/2013/01/130116_PM_Heliatek-erzielt-Weltrekordeffizienz-fuer-OPV.pdf

Polymer Solar Cells: Structure, Mechanism



Advantages:

- No clean room or high temperature steps needed (large-area, low cost)
- Flexible panels (form factor)
- Versatility of polymer structures and properties via synthesis
- Nanostructural tailoring

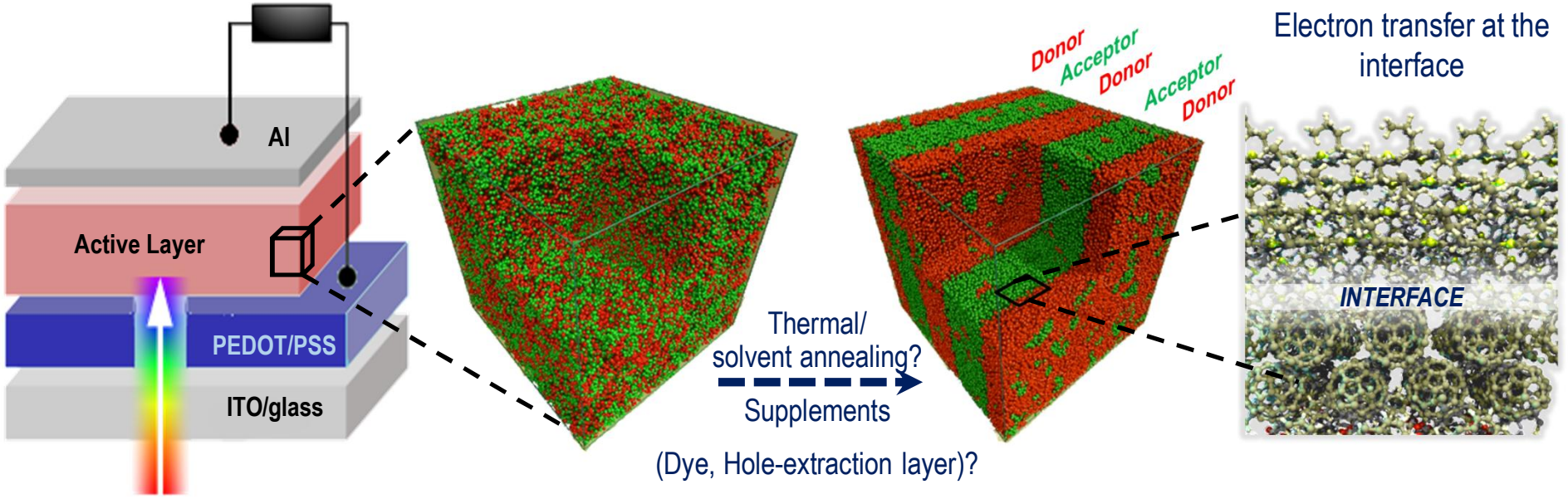
Main Factors Limiting the Efficiency:

- Low absorption
- Short Exciton Lifetime (Diff. Length)

Solution → Bulk heterojunction in Polymer Blend

Bulk Heterojunction in polymer blends

Nanophase-segregated systems

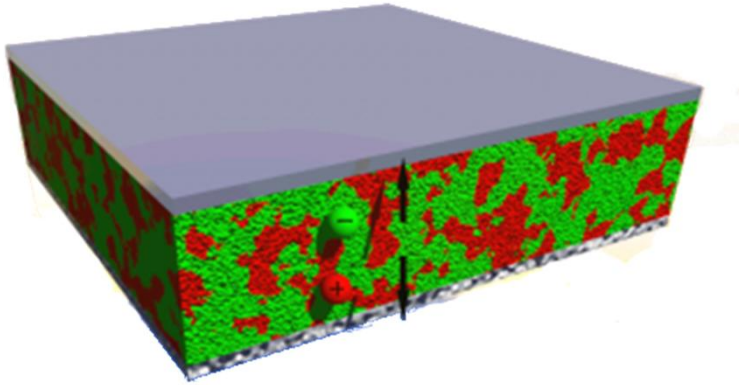


Morphology control & Interface control

new strategy of **synthesis** (rational design)+ **physics** of self-organization

Bulk Heterojunction in polymer blends

Active Layers in Polymer Solar Cells – Donor/Acceptor Mixture



Methods to improve efficiency:

-BHJ instead of Planar HJ

-Thermal/solvent annealing

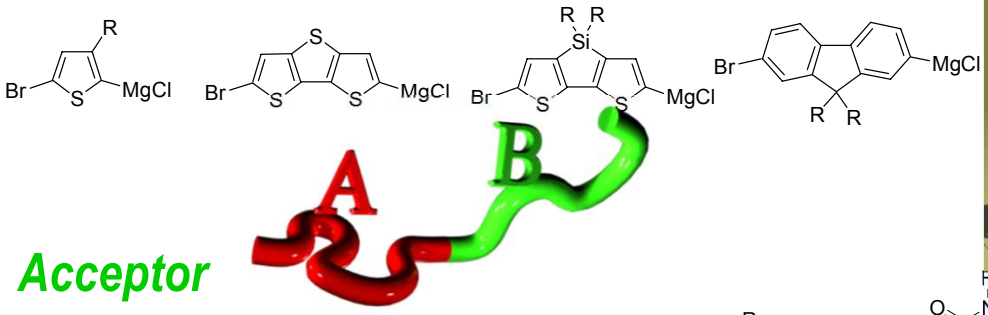
-Supplements (Dye, Hole-extraction layer)

-Rational design of conjugated polymers (functional, side chains, new monomers)

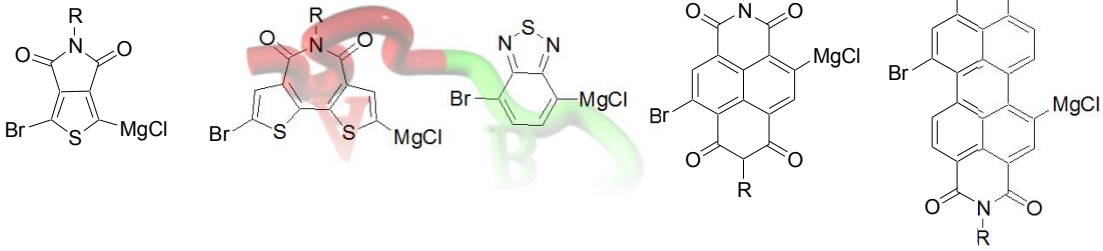
-Donor/Acceptor block copolymers vs. D/A blend

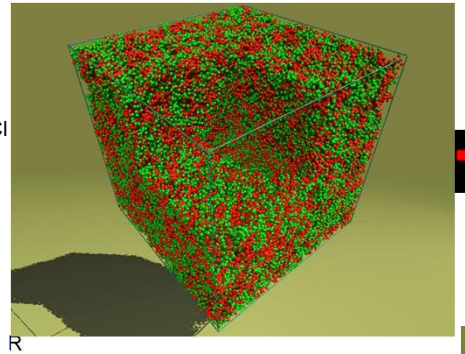
-Suitable mediator for D/A interface

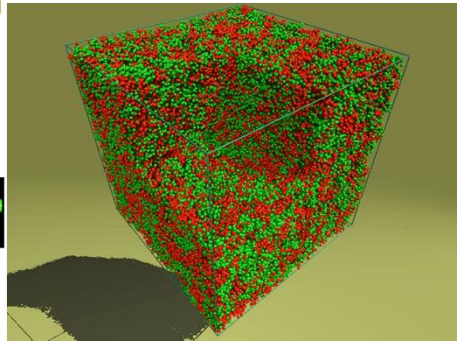
Donor



Acceptor







2. Goal and Tasks

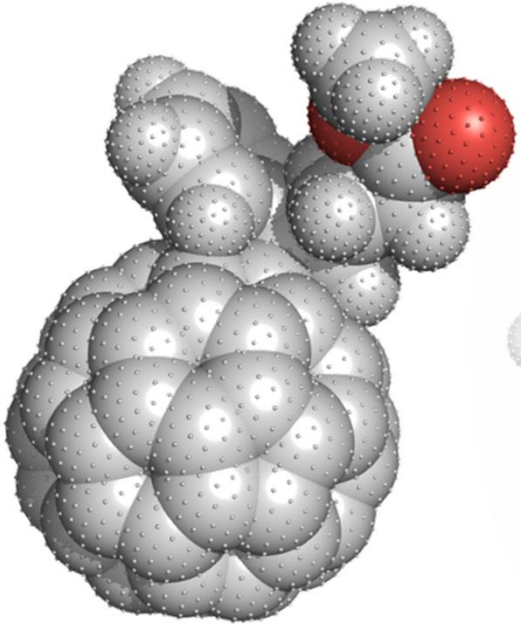
General Goal of the Study

The aim of this study is to develop

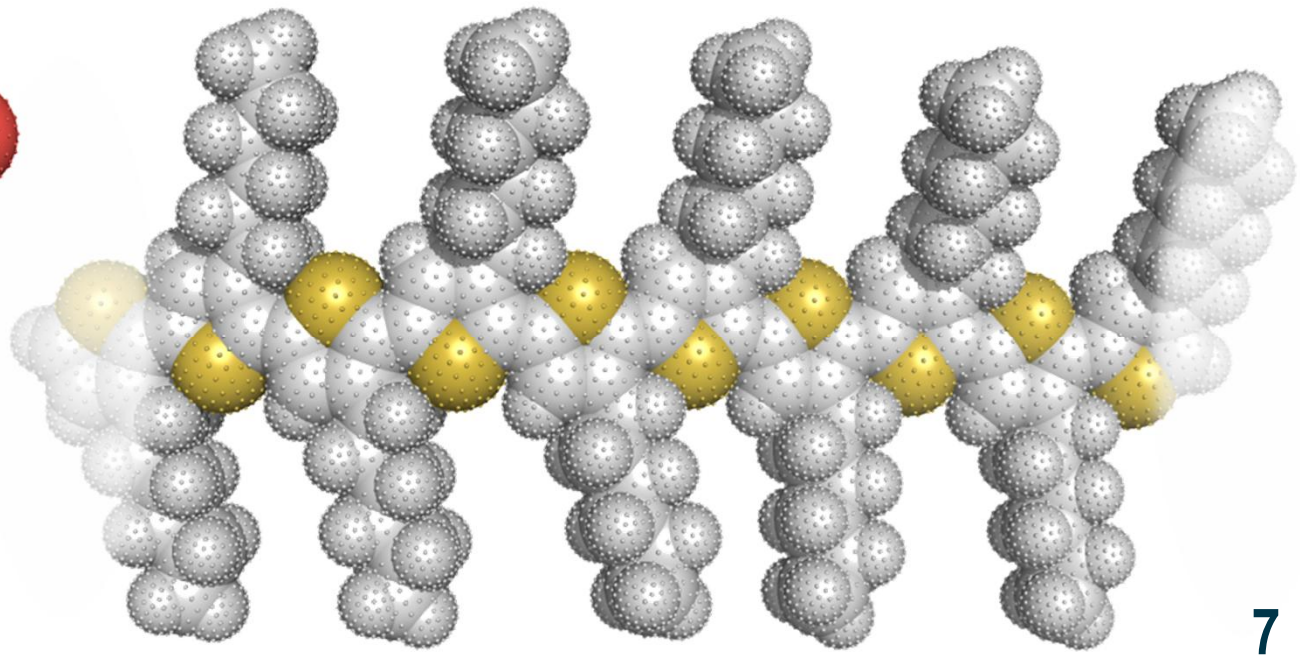
- a multiscale molecular simulation framework including QM, large-scale MD and CG,
- reverse mapping,
- and morphology evaluation scheme

to investigate the structure of BHJ blend films comprising donor and acceptor

Methanofullerene derivative PCBM (A)

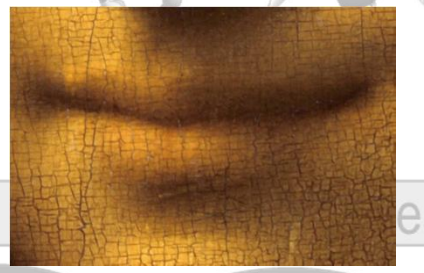


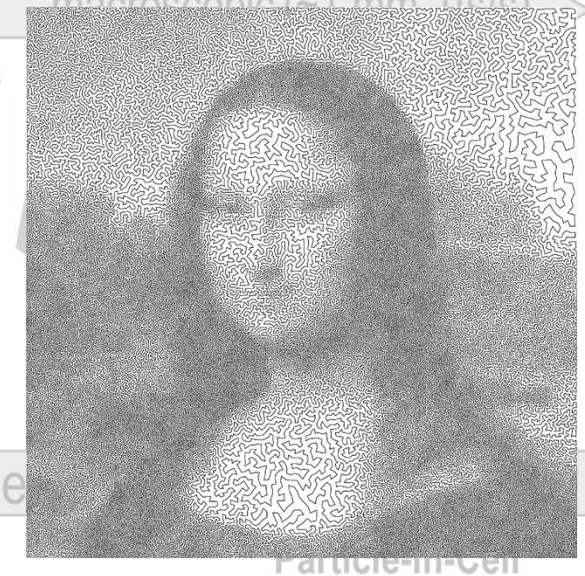
Polythiophene P3HT (D)



3. Models. Methods

Research strategy – Multiscale approach – simulation on different time and length scales





Length/Time Scale: 1-10 nm, fs/ps
Methods: DFT, QM, CPMD
Atomic resolution:
- electronic states
- atomic charge calculation
- parameterization of potentials

Length/Time Scale: 10-1000 nm, ns/μs
Methods: Full Atomistic MD
Molecular resolution:
- microstructure formation
- properties of molecular crystals
- properties of interfaces

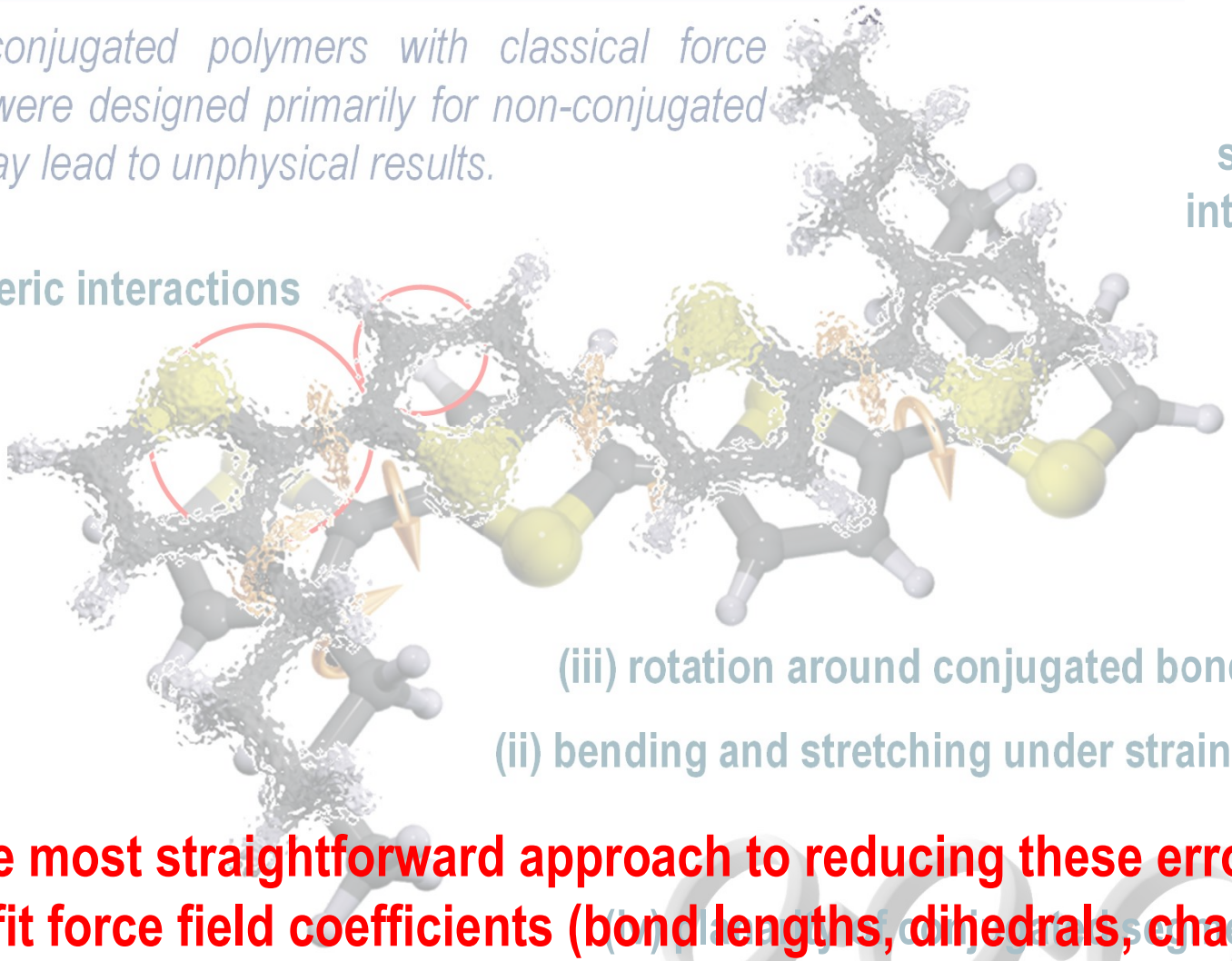
Length/Time Scale: ~100 μm, μs-s
Methods: DPD
Molecular ensembles:
- self-organization processes
- microphase separation
- properties of interfaces

4. Results

Modelling conjugated polymers with classical force fields (that were designed primarily for non-conjugated systems) may lead to unphysical results.

(v) π-π stacking interactions

(i) close steric interactions



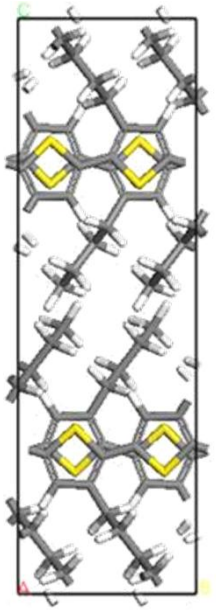
(iii) rotation around conjugated bonds

(ii) bending and stretching under strain

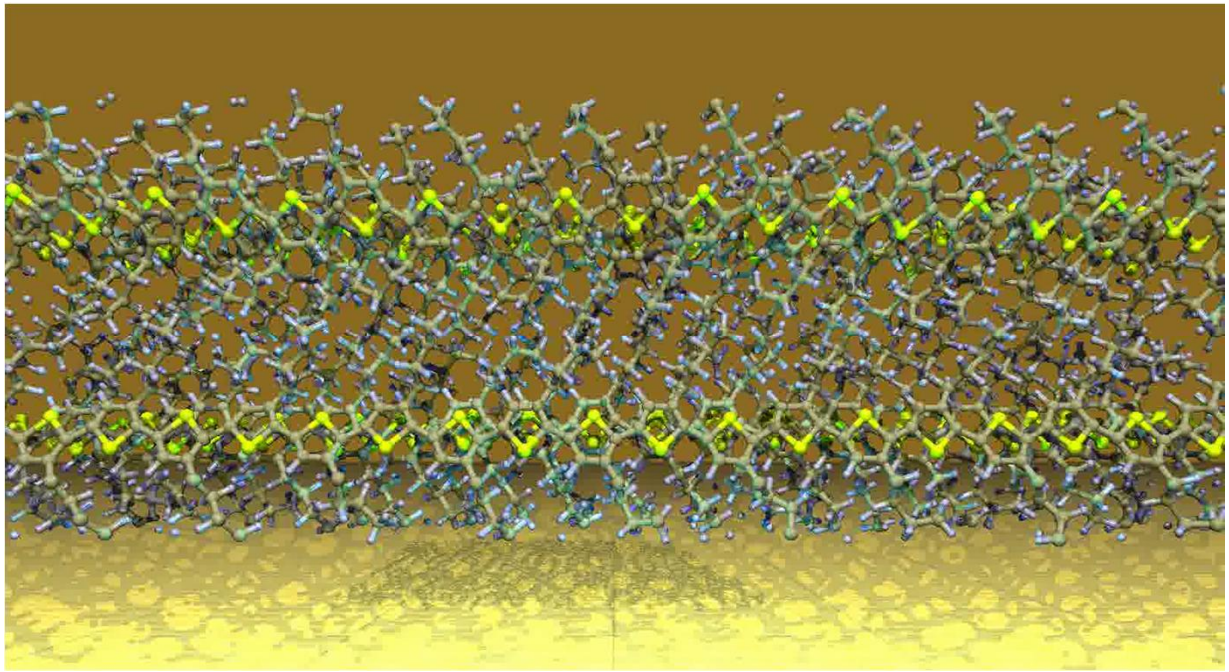
The most straightforward approach to reducing these errors is to fit force field coefficients (bond lengths, dihedrals, charges) to an accurate quantum chemical potential surface.

4. Results: Full-atomistic MD simulations

MD: Donor P3HT



Unit cell parameters
a=7.64Å,
b=7.75Å,
c=24.97Å
α=β=γ=90°



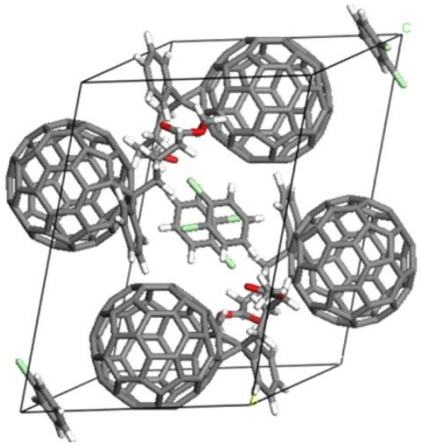
150 Å

YZ-projection of P3AT crystal (2a×10b×1c), MD (NVT), *T*=300K (thermostat Nose), dynamics time 6ns ($t=6\cdot10^6$ steps, Δt=1fs), calculated charges, calculated interring potential

- Crystal structure is stable at room temperature.
- Even in the absence of chain folding, thermal motions can produce significant disordering of the side chains
- The distance between thiophene backbones 3.6-3.9Å (the π-π stacking).
- The twisting of polythiophene chains corresponds to $\pm15^0$ (not-so-stiff π-conjugated backbone).

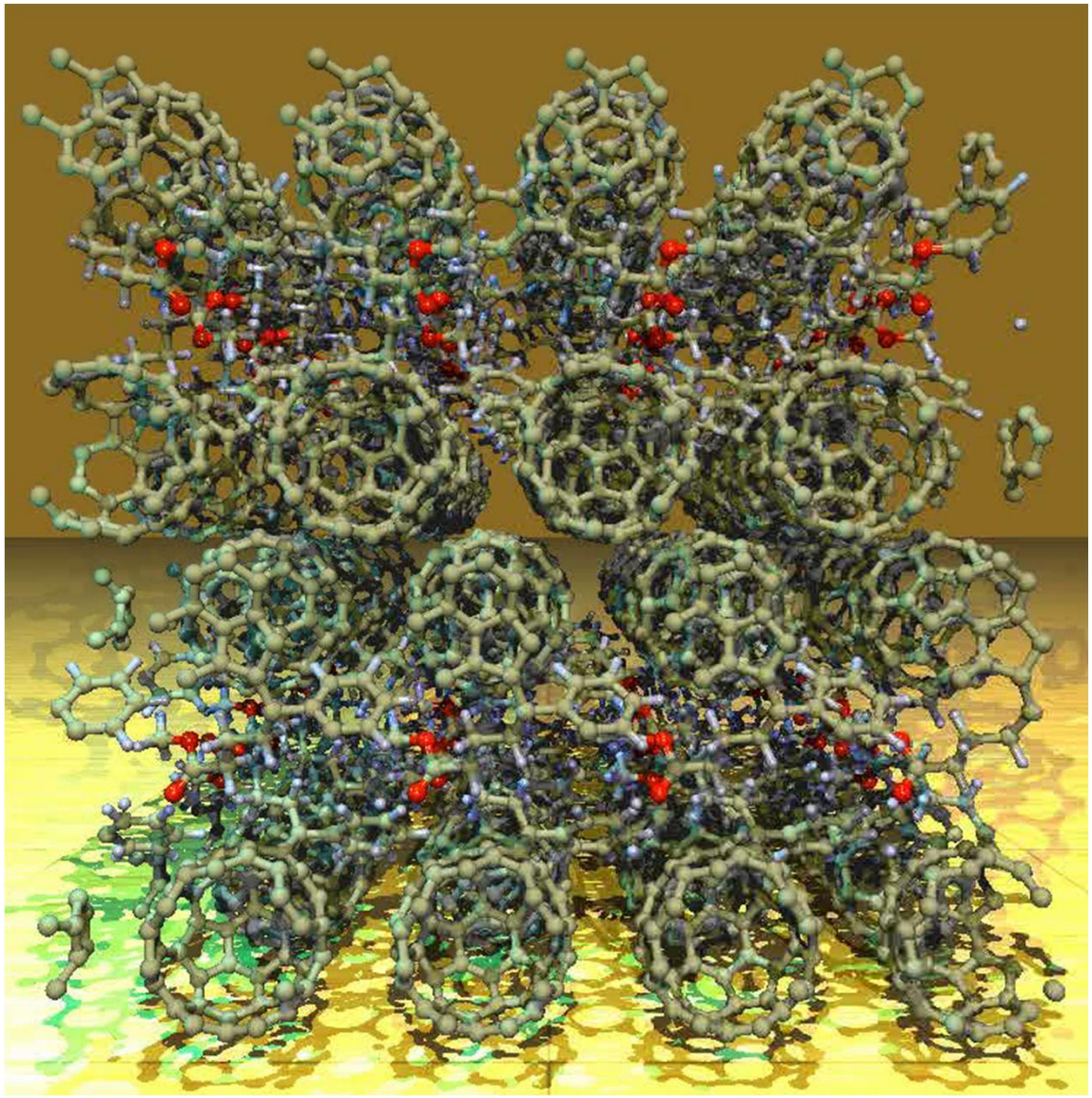
4. Results: Full-atomistic MD simulations

MD: Acceptor PCBM



Unit cell parameters [5]
a=13.75Å,
b=16.63Å,
c=19.077Å
α=γ=90°,β=105.2°

PCBM crystal (2a×2b×2c)
MD (NVT)
T=300K (thermostat Nose)
t=6ns (*t*=6·10^6 steps, Δ*t*=1fs)

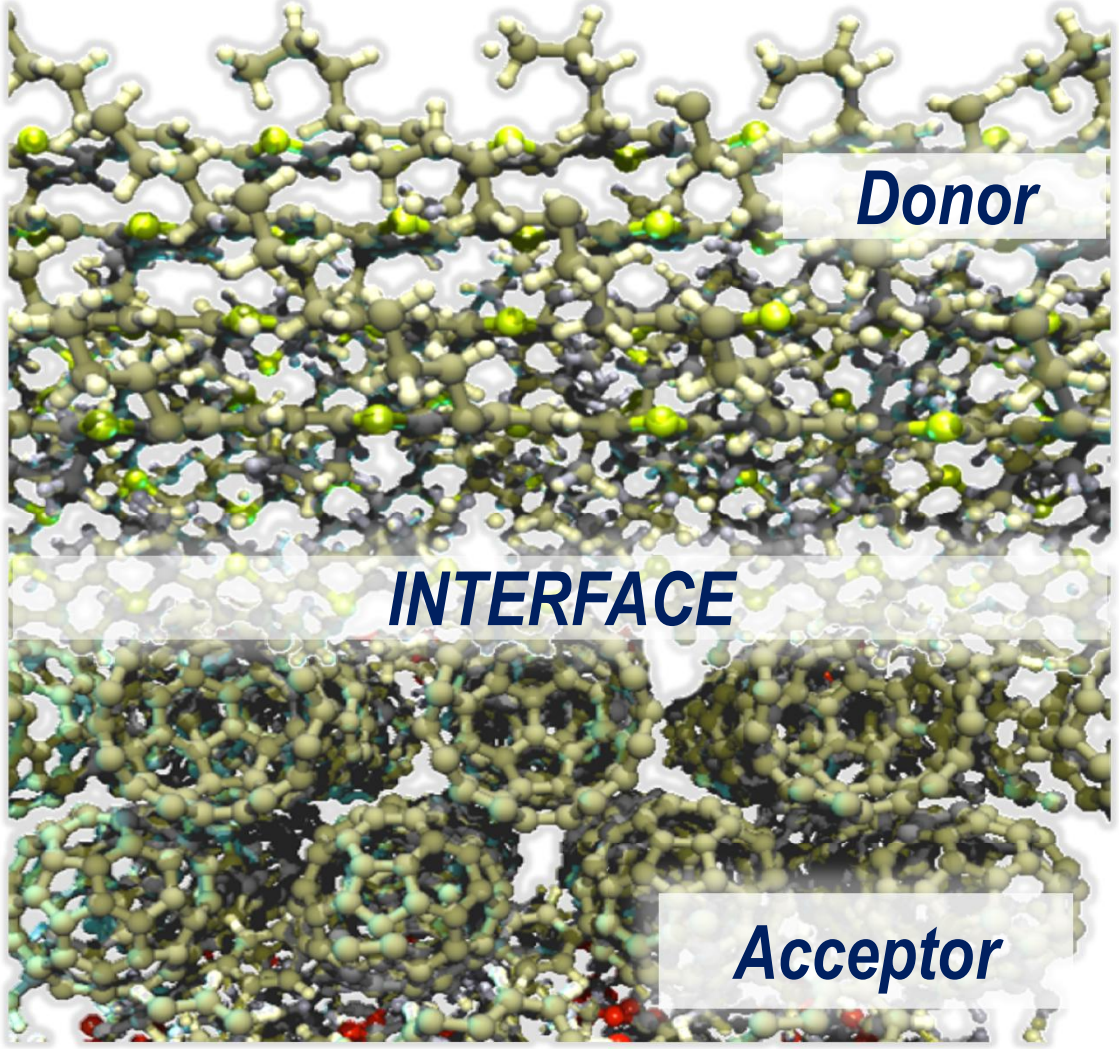


[5] Rispens M.T. et al // Chem. Commun. 2003. V. 17. P. 2116.

4. Results: Full-atomistic MD simulations

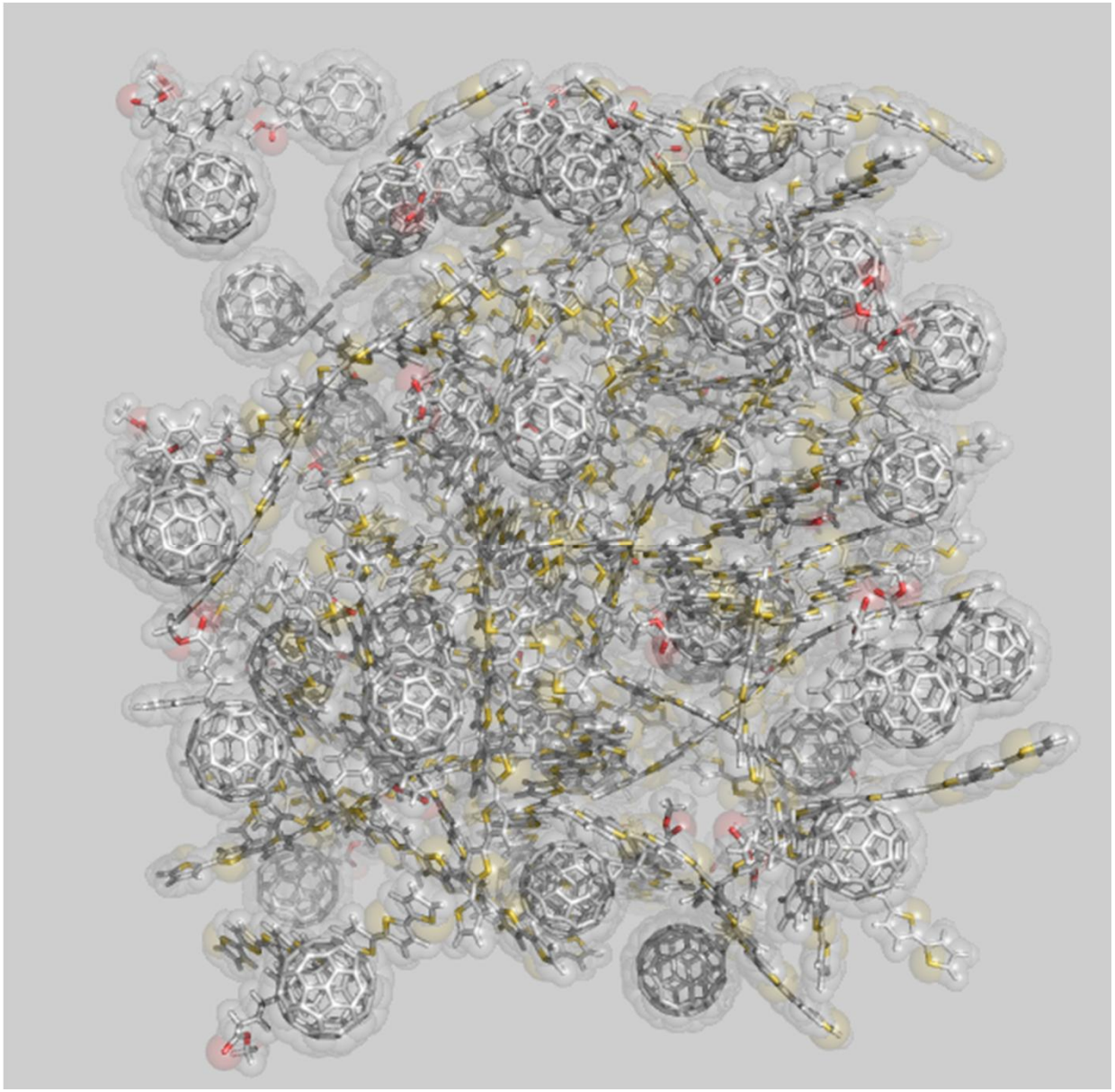
MD: Donor/Acceptor interface

Electron transfer at the interface



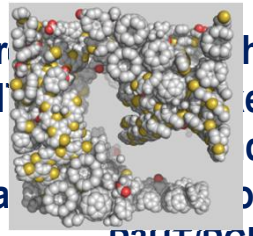
4. Results: Full-atomistic MD simulations

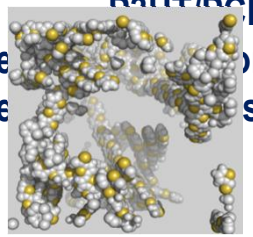
MD: Donor/Acceptor blends

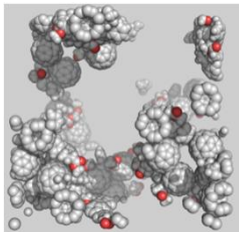


P3HT/PCBM-blends
(density ρ=0.7g/cm^3):
Self-aggregation→
(a) 90 D-100 A
(b) 100 D-90 A
(c) mixture1:1

Thr hology :
1. P3H e domains,
d
3. a orphous
BM)
inste ominately
be se one



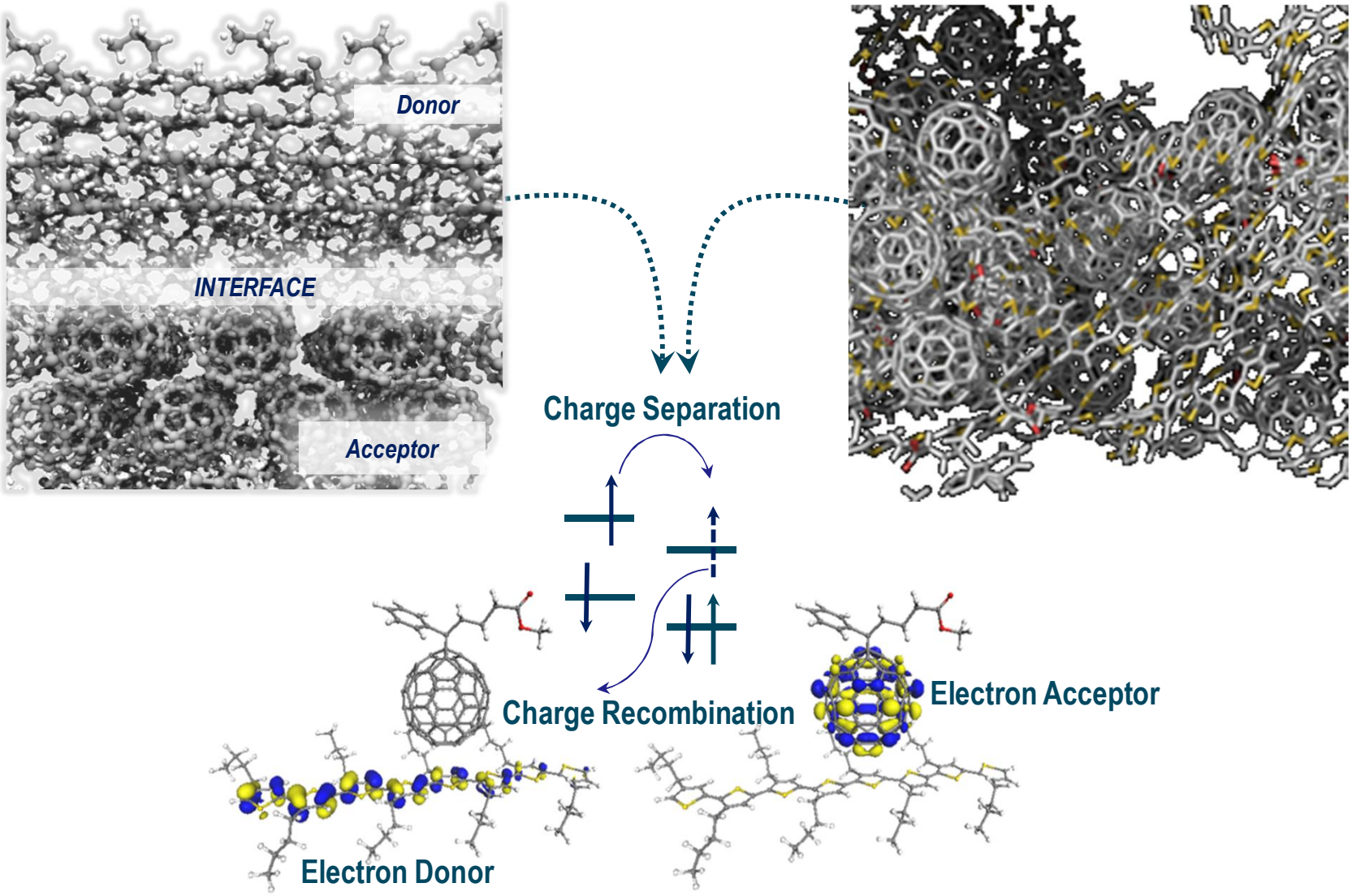




4. Results. Back to Micro: QM

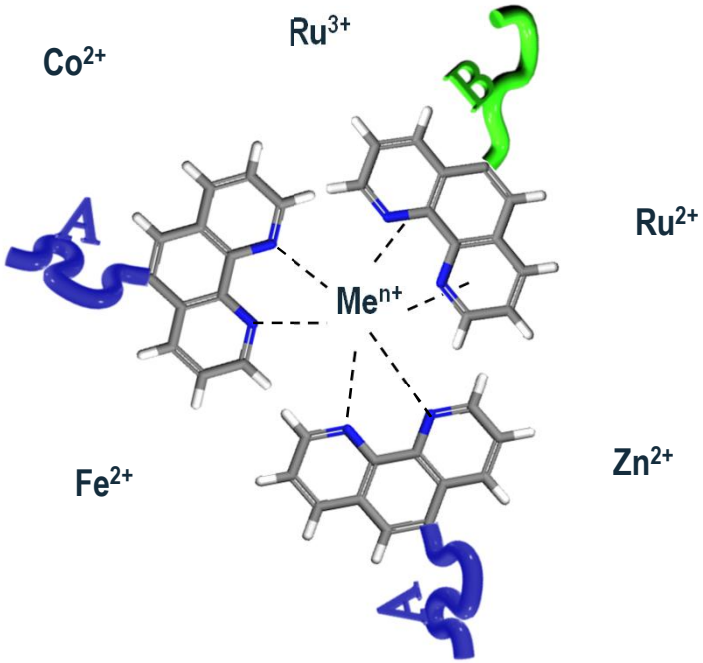
QM: Donor/Acceptor blends

Electron transfer at the interface



4. Results. Supramolecular D/A BCPs

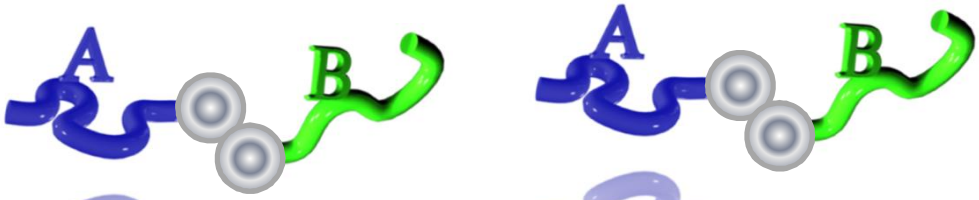
DPD: Supramolecular D/A block copolymers



End-functionalized conjugated polymers

Interfacial groups (IG) – control electronic and/or self-assembly processes at interface (complexation with metal ions – *1,10-phenanthroline* – chelate formation or interfacial mediator – *porphyrin derivative*):

- facilitate charge-separation
- suppress charge recombination



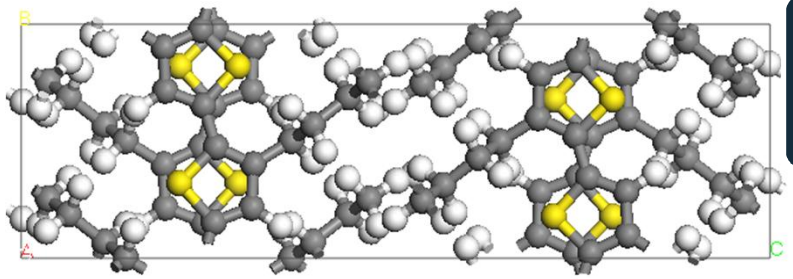
Interaction parameters: a_{ij}, k_BT/r_c

Bead Type	A	B	IG
A	25	-	-
B	40	25	-
IG	40	40	25

- 3 different types of soft beads: polymer donor and acceptor (A, B) and interfacial group IG, r_c =1;
- Periodic boundary conditions, 3D slab geometry
- Polymer chains, a_{AB}=40 (θ-point a_{PS}=27.3)
- Functional groups – 1,2,3 and 9 beads interconnected (harmonic potential), almost spherical IG, diameter D=2.42 r_c (9 beads)
- 50:50 mixture, L_{box}=25 r_c, N=46875 DPD beads
- polymer chain length 5-9 DPD beads

Conclusions & Outlook

Multiscale simulation of conjugated polymer/methanofullerene blends



Step 4.
CG Level, DPD Model

TAKE HOME MESSAGE:

This universal scheme goes much beyond specific materials described here.
Applicable to:
(a) different D/A pairs
(b) D/A copolymers

Step 2.
Mesoscopic Level

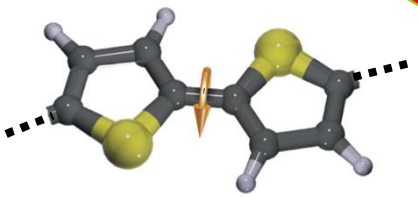
- 10-10^3 nm, ns/μs
- *Full Atomistic MD*
- Properties of the molecular crystals, microstructure formation in P3BT/PCBM mixture, detailed analysis of donor-acceptor interface

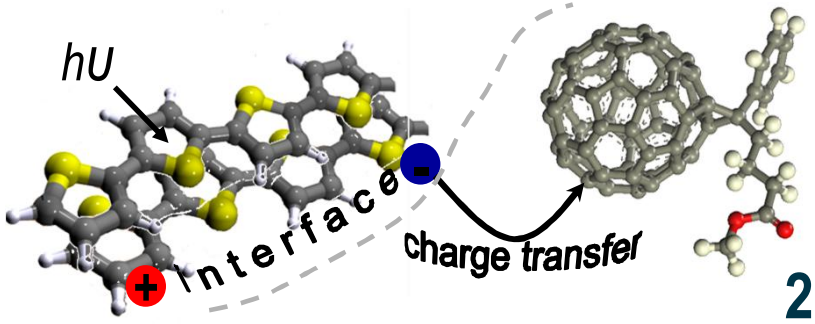
- 1-10 nm, fs/ps
- *DFT, QM, CPMD*
- Molecular geometry optimization, atomic charge calculation, parameterization of interring torsion potential of P3HT

Step 1.
Microscopic Level

- 1-10 nm, fs/ps
- *TDDFT, QM*
- calculation of charge separation and charge recombination rates

Step 3.
Back to Microscopic Level





Conclusions & Outlook

Tasks for the Future

1. MD simulation of D/A dyads, D/A block copolymers (rational design of monomer units for all-conjugated polymers);

2. Kinetics of charge transfer processes in organic solar cells (time dependent density functional theory);

3. Covalently-bonded donor-acceptor units vs. face-to-face oriented donor acceptor pairs;

4. Structural control of solubilizing side groups in fullerene-based electron acceptor;

5. DPD simulation of supramolecular assembly in mixtures of D/A polymers decorated with interfacial groups.

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Leibniz-Institut
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Thank you for your kind attention!

3. Methods. QM and CPMD

Static and dynamic ab initio calculations

G09 A.1, 0K

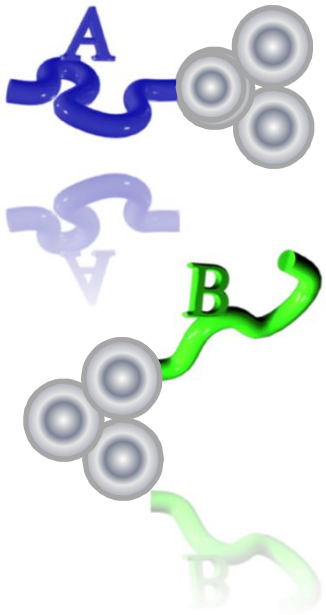
- Geometry optimization at B3LYP/(6-31G(d)) or HF /(6-31G(d)), each corresponding energy minimum, confirmed by frequency calculations
- Calculation of partial charges: Mulliken population analysis, NBO charges
- TDDFT scheme for calculation of excited states

CPMD

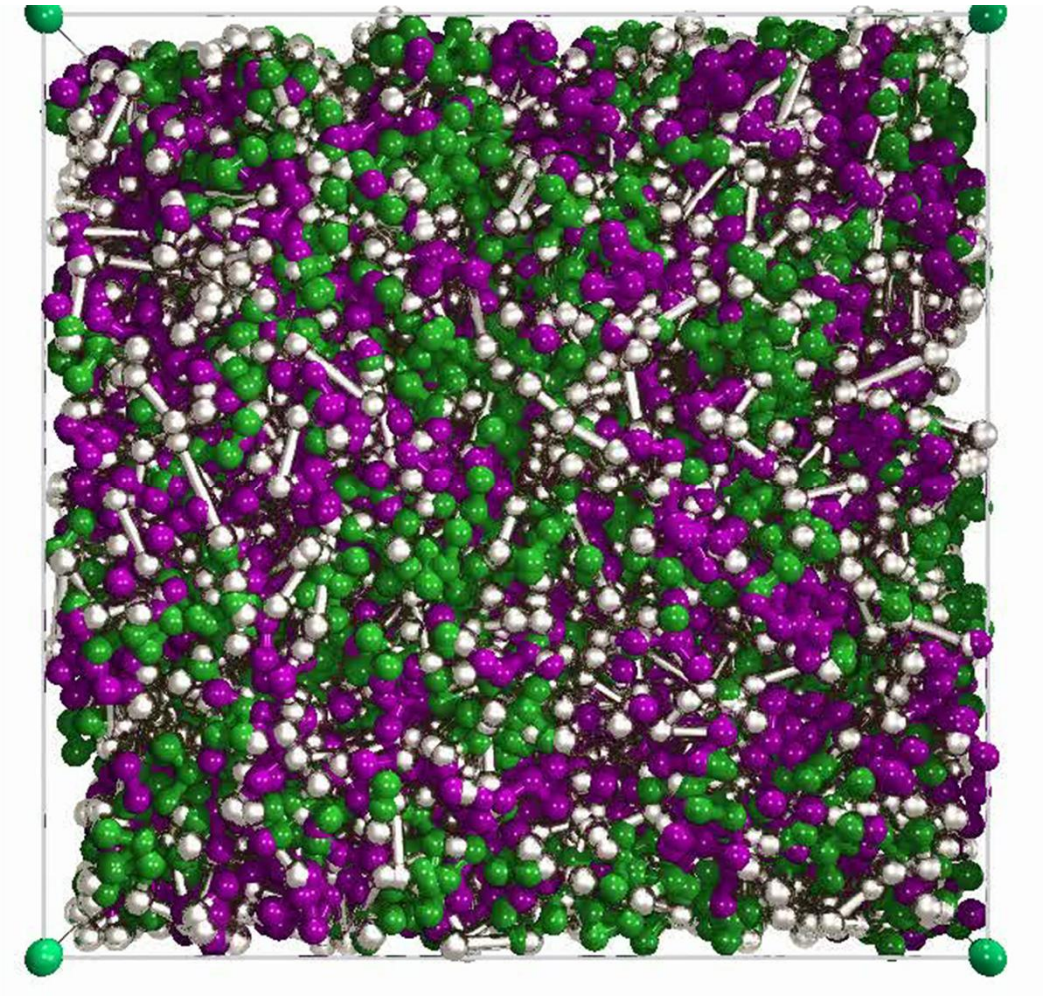
- NVE Ensemble, Nosé-Hoover chain thermostat
- Pseudopotentials for core electrons (Troullier-Martins)
- PBE functional in conjunction with plane wave basis for valence electrons and electron correlation energy
- 1 bithiophene molecule
- Box (cubic) – corresponds to system size, ~40Å
- Periodical Boundary Conditions
- Fictitious Electron Mass = 400 m_e
- dt = 0.1 fs
- t = 5.0 ps
- Kinetic energy cutoff for the plane wave basis set is 85 Ry.

4. Supramolecular D/A BCPs

Tail length 5



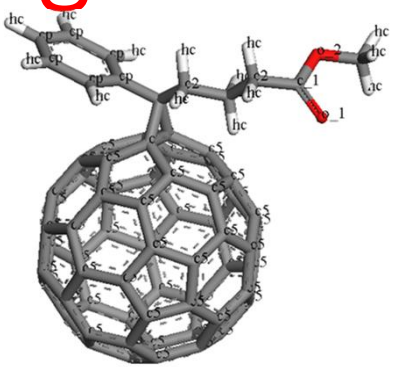
IG size 3



100 000 steps to equilibrate the system, 1000 000 DPD steps after equilibration, Δt=0.04

4. Results: partial charges of PCBM

QM: Acceptor PCBM

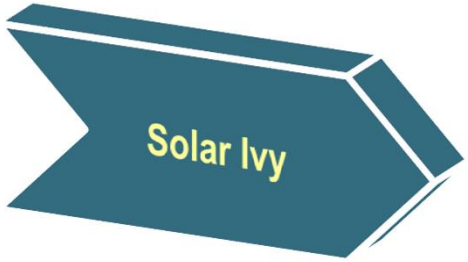


Structure of PCBM, showing definitions of PCFF atom types.

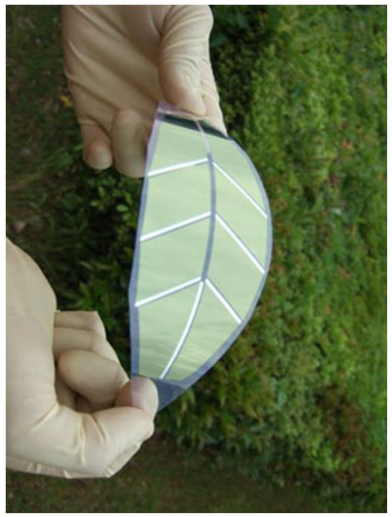
OPLS		*PCFF (calculation)*	
Atom type	Charge	Atom type	Charge
cf (fullerene)	0	c5, c (methano-bridge)	0
ca (aromatic carbon)	-0.115	cp	-0.127
ca (aromatic bonded to aliphatic)	0	cp	0
c (carbonyl)	0.7	c_1	0.702
ct (aliphatic)	-0.12	c2	-0.106
ct (aliphatic CH_3)	-0.18	c3	0.066
ct (aliphatic bonded to C60)	-0.03	c3m	0
o (carbonyl)	-0.5	o_1	-0.531
os (ester)	-0.17	o_2	-0.396
ha (aromatic)	0.115	hc	0.127
hc (aliphatic)	0.060	hc	0.053

CPMD (ESP Charges)	
Atom type	Charge
c5, c (methano-bridge)	≈0
cp	-0.153
cp	0.219
c_1	0.485
c2	-0.106
c3	0.018
c3m	-0.168
o_1	-0.514
o_2	-0.321
hc	0.126
hc	0.096

1. Introduction



is a solar energy delivery device that draws inspiration from ivy growing on a building (solar cells printed with conductive ink)[2,3].



[2] www.solarivy.com
[3] www.zedomax.com/blog/2008/06/04/organic-thin-film-solar-cells-leaves/

1. Introduction

Computer simulation of self-assembling nanowires from thiophene-peptide diblock oligomers ("molecular chimeras")

Theoretical analysis workflow:

1. **Propose various consistent repetitive patterns**
2. **Find optimal conformation in periodic arrangement**
3. **Construct aggregates and perform simulations**

Macromol. Theory. Simul. **2009**, *18*, 219

Pol. Sci. A **2009**, *51*, 430

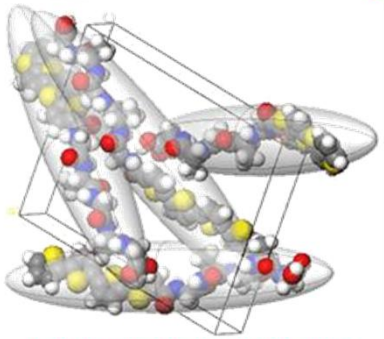
Nanotechnologies in Russia **2008**, *3*, 481

Chem. Phys. Lett. **2008**, *461*, 64

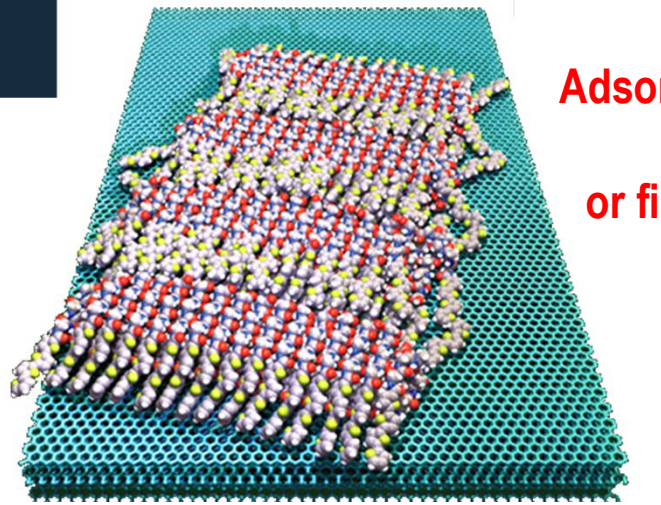
Pol. Sci. A **2007**, *48*, 939

J. Phys. Chem. C **2007**, *111*, 7165

α-helix or β-sheets

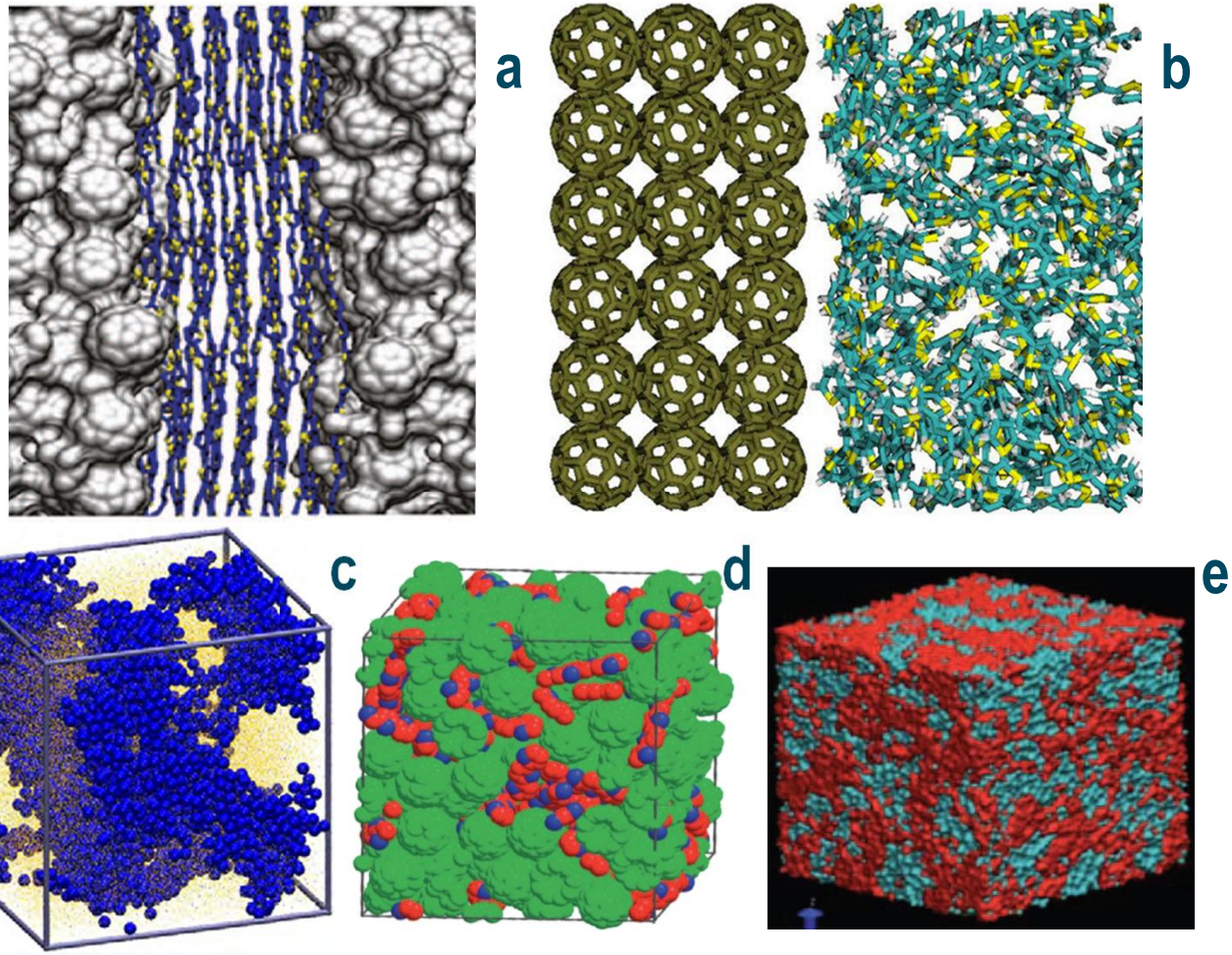


Crystal structure prediction (atomistic MM model)



Adsorption layers on graphite or fibers in solution (MD)

3. State-of-the-art



Full-atomistic representation:
Two ideal crystals, one interface P3MT/PCBM (a[1]) and fcc polymorph of fullerene/physisorbed quaterthiophene (b[2])

Coarse-grained simulation of blends:
P3HT:C60=1.27:1(w/w) C60 cluster formation (c[3])
P3HT amorphous phase showing substantial fullerene concentration (d[4])
P3HT:PCBM, blend ratio of 1:1 (w/w): highest interface-to-volume ratio and an adequately percolated network (e[5])

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3. Methods. MD: Force fields

Σ Force fields ⟶ Conformational energy (potential energy)

Definition by:

- Atom type
- Atomic charges
- Constant of force, equilibrium values
- Energy equations