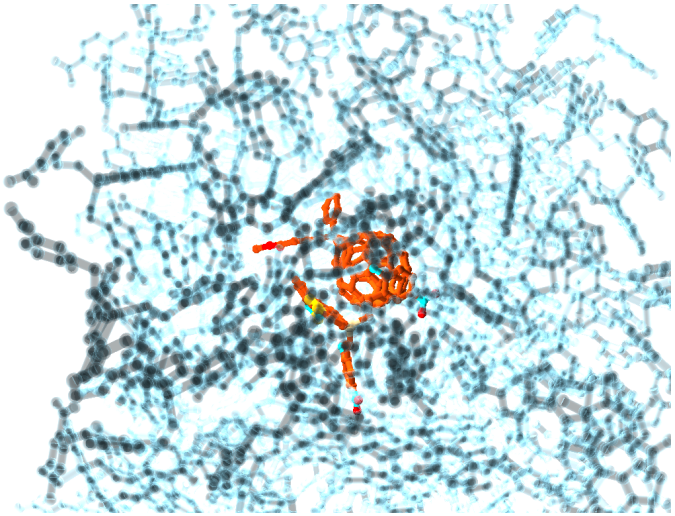
OPV research with ADF

Remco W. A. Havenith



Theoretical Chemistry,
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Ghent Quantum Chemistry Group, Ghent University, Belgium

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Theoretical Chemistry Group

Mission:

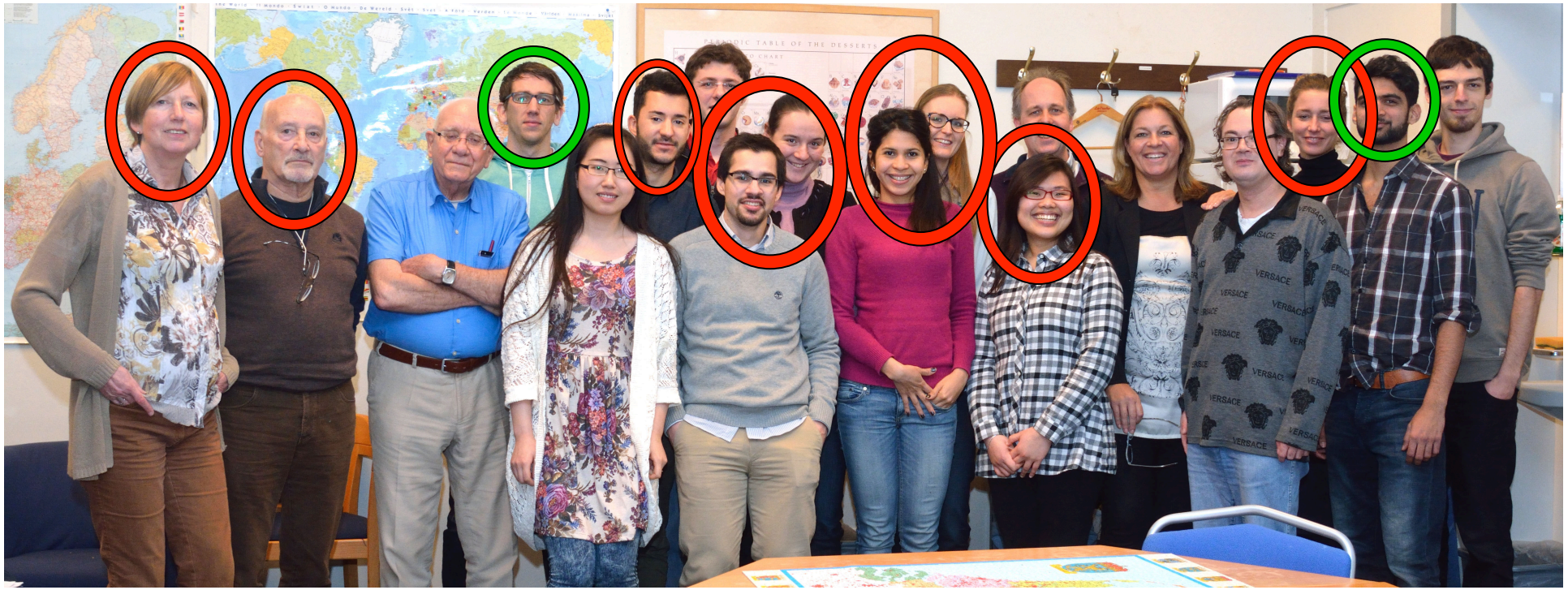
Provide independent knowledge on structures, properties and their relation, with interpretation in terms of chemical concepts

- Emphasis on
  - Molecular properties
    - Photo-physical properties
      - Spectra and excited states
    - Magnetic and electric properties
  - Non-orthogonal methods

- Application driven method development (GAMESS-UK/ADF)
- Computational experiments

The OPV gang

Theoretical Chemistry Group



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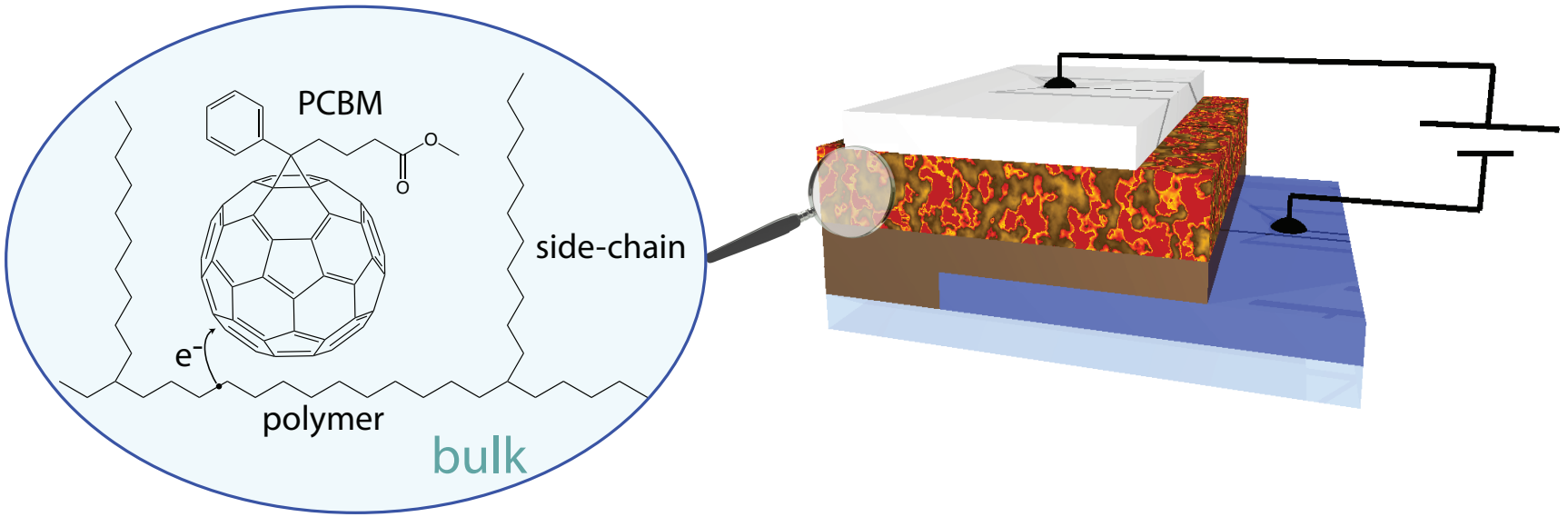
Theoretical Chemistry

FOM Focus Group Groningen 'Next Generation Organic Photovoltaics'

- Aim:
  - Deliver the science for highly efficient, long-lived, and low-cost organic photovoltaic devices
- Challenge:
  - Charge separation at the donor/acceptor interface
- Approach:
  - Multi-disciplinary:
    - Material development
    - Physical characterisation (OPV device physics)
    - *Theoretical modelling*

Organic photovoltaics



Theoretical Chemistry gives access to the fundamental processes that lead to photocurrent generation

G. Yu *et al.*, *Science* **270** (1995), 1789

What happens in an organic solar cell?

- Organic solar cell:
  - Nowadays bulkheterojunction
    - Blend of (DA) polymer and PCBM derivatives

- Light is absorbed
- Exciton diffusion to the interface
- Charge transfer from donor to acceptor
- Electron/hole diffusion to the electrodes

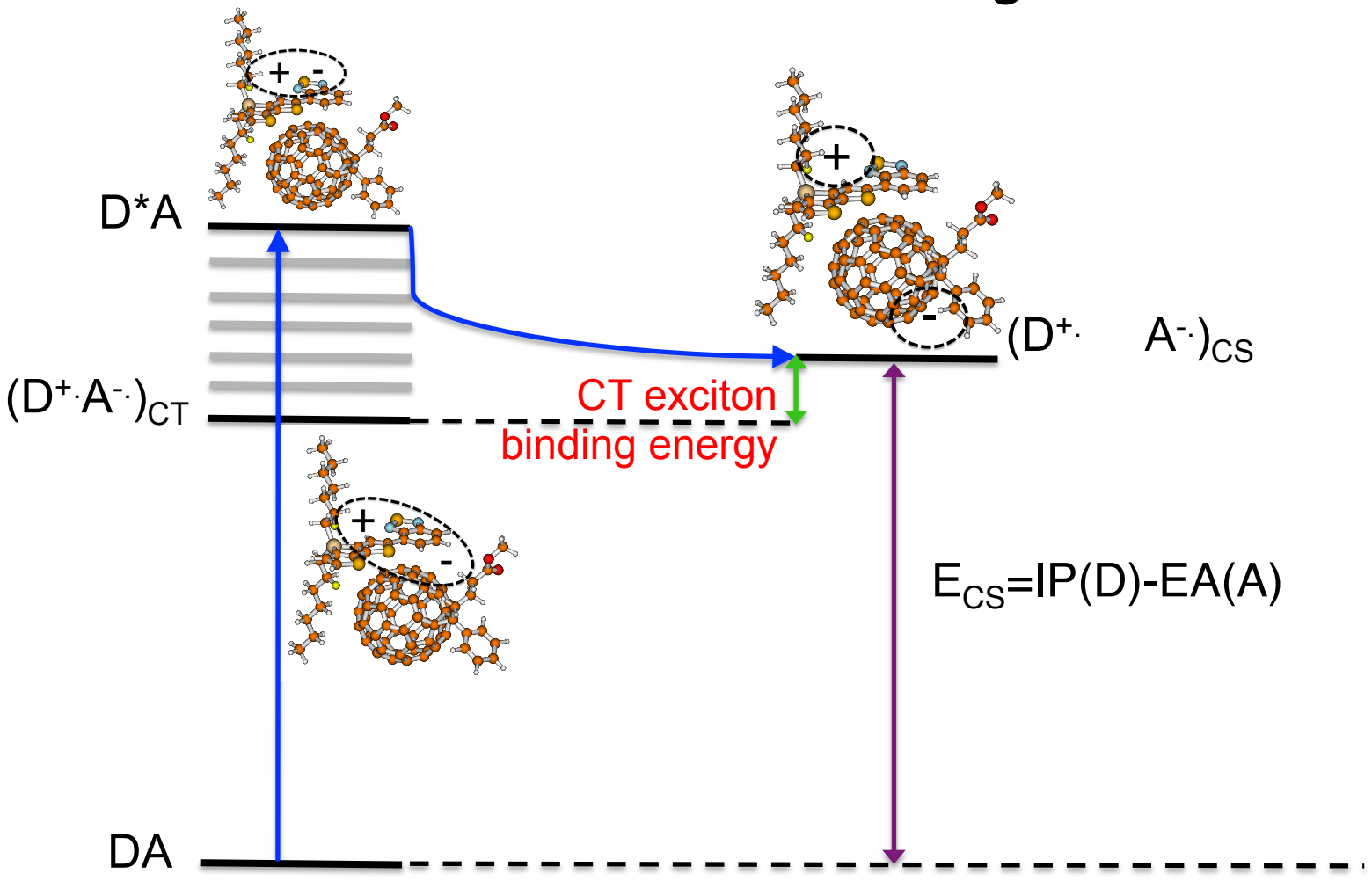
- While exciton/electron/hole diffuses through the material anything can happen

Theoretical challenges

- Predict molecular properties that determine the dielectric properties of the interface
  - Dipole moments
  - Polarisability
- Modelling of the donor/acceptor interface
  - Molecular Dynamics simulations
    - Time scales of molecular motion
- Calculation of the excited states
  - Theoretical methods
  - Influence of molecular structure
  - Influence of the embedding using multiscale modelling
- Approximation of the electron transfer rates

- Required:
  - Quantum chemical calculations
    - HOMO/LUMO levels
    - Polarisability
    - Dipole moment
    - Excited states
  - Molecular Dynamics calculations
    - Representative structures
    - Morphologies
    - Mobility of molecules in the blend
  - Combined QM and MD
    - Excited states and excited state dynamics

Electronic state diagram



Brédas J.-L., *et al.*, *Acc. Chem. Res.* **42**, 1691-1699 (2009)
Bakulin A.A., *et al.*, *Science* **335**, 1340-1344 (2012)
Clarke T.M., Durrant J.R., *Chem. Rev.* **110**, 6736-6767 (2010)

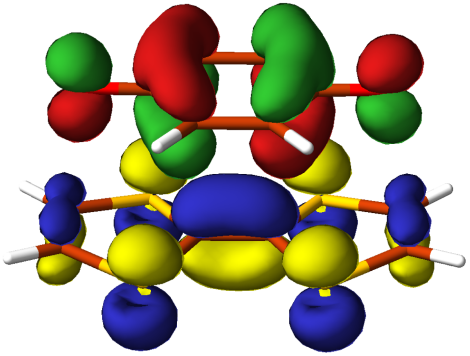
Which QM method and package to use?

- We want to describe:
  - Charge-transfer states
  - The effect of the medium
  - Electron/hole diffusion

- CT states
  - DFT?
  - HF?
  - Correlated methods?

- Medium effects
  - Explicit molecules?
  - Continuum?

Methods: Charge-transfer states with (PCM)-DFT



Method/ Functional	E_{exc} (vac) (eV)	E_{exc} (H_2O) (eV)	ΔE_{exc} (eV)
HF	3.53	3.43	0.09
B3LYP	0.91	0.77	0.14
BHandH	*1.70*	*1.57*	*0.13*
CAMB3LYP	1.66	1.55	0.11
HCTH407	0.47	0.33	0.13
PBE0	1.04	0.90	0.14
CC2	1.87	--	--

Improved methods/functionals required

Screening effect using a continuum model

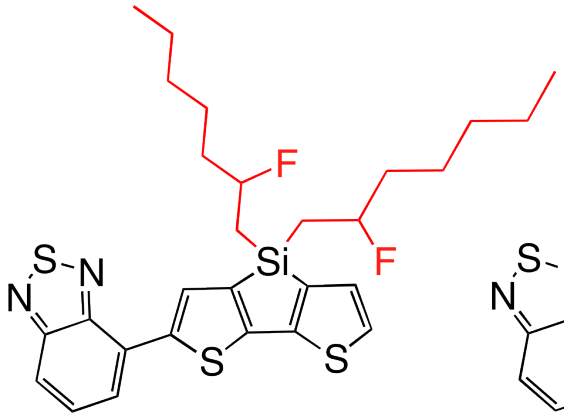
- Calculate IP(D) and EA(A)
- Determine the CS state energy in the medium: *E*(CS) = IP(D) – EA(A)

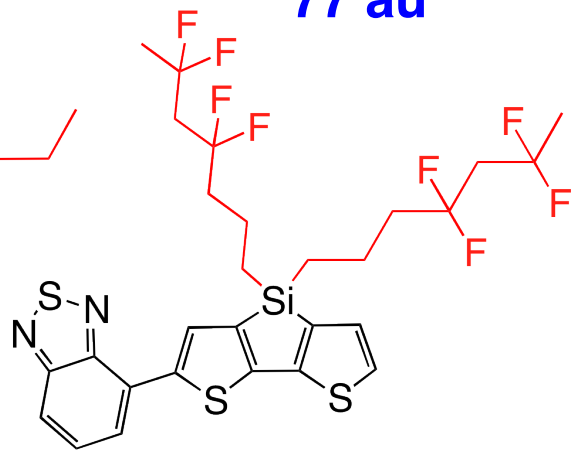
Systems under study:

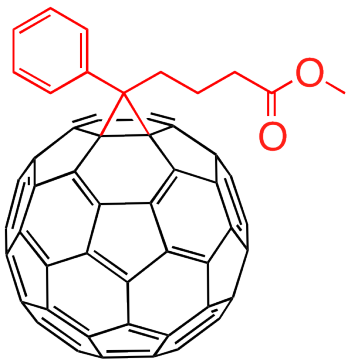
D: donor-acceptor “co-polymer” with two different side-chains (**1** and **2**)

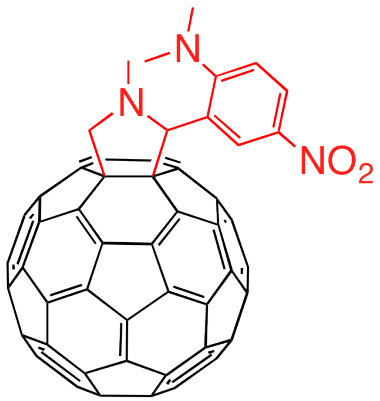
A: PCBM (**3**) and PCBM derivative (**4**)

	1	**2**	**3**	**4**
dip. mom.	**1.6 D**	**3.7 D**	**1.6 D**	**6.7 D**
polariz.	**78 au**	**77 au**	**128 au**	**148 au**

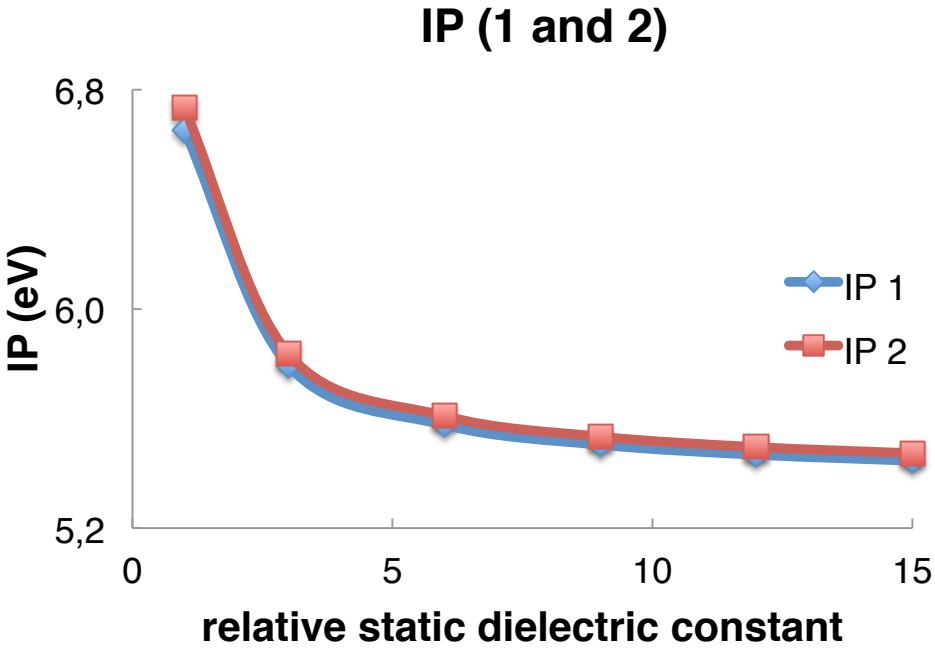


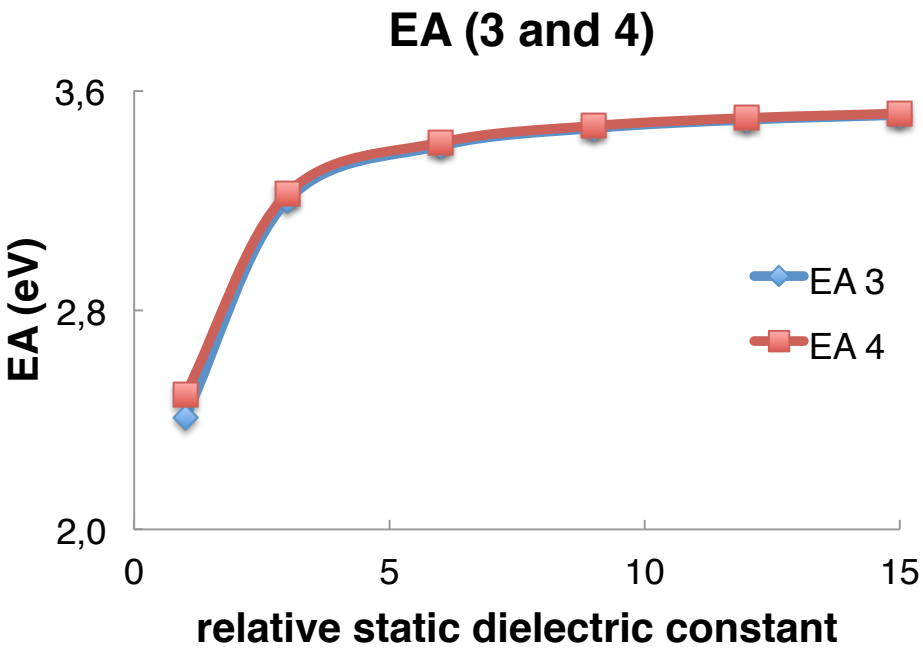


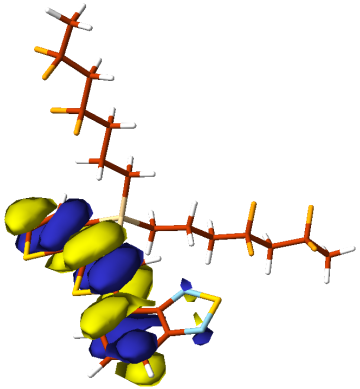




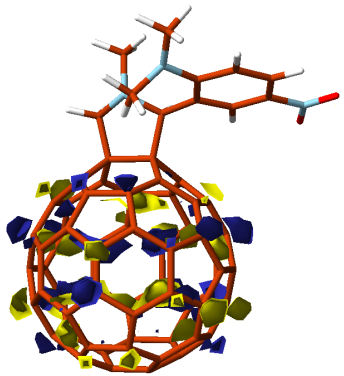
Results



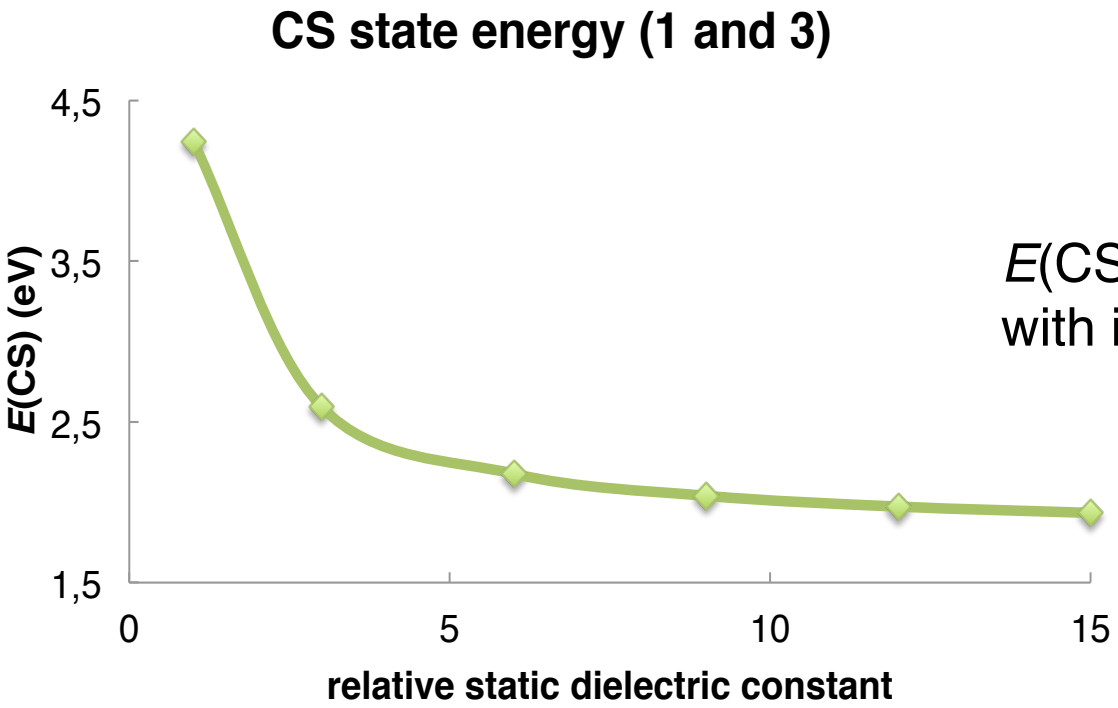




SOMO of
2 and **4**



Results



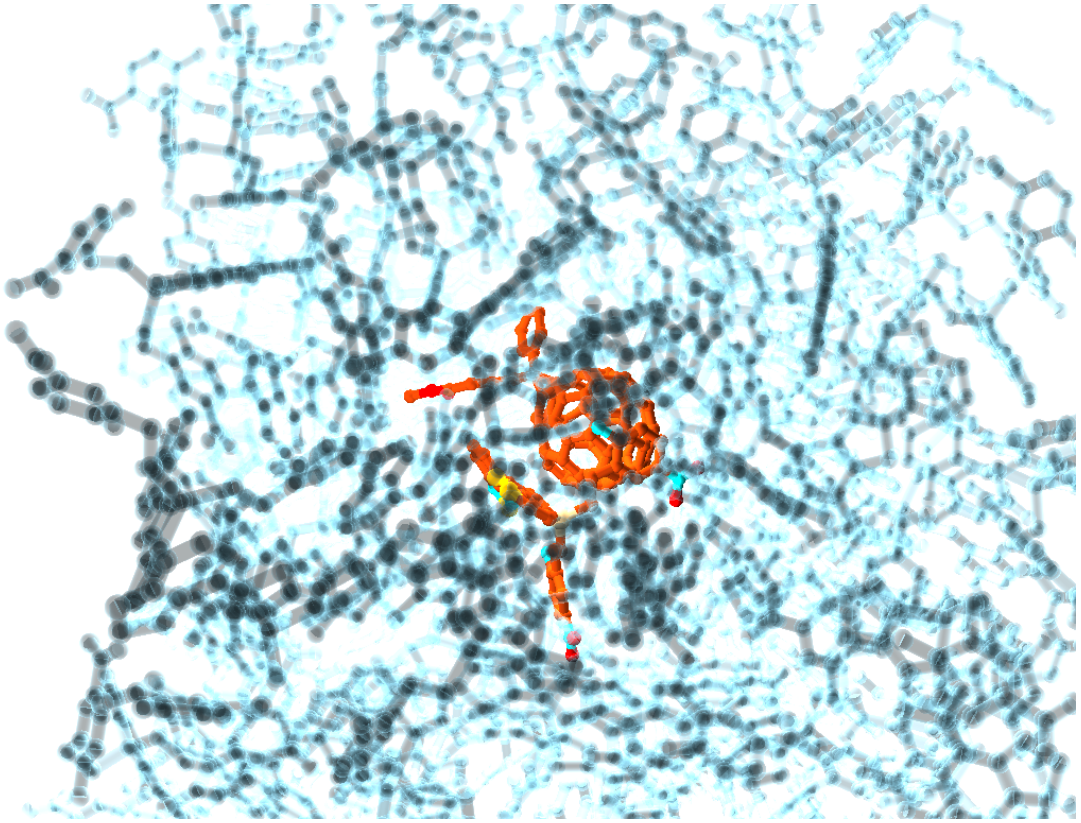
E(CS) decreases by ~ 2 eV with increasing ε

<u>But:</u>

We need to know ε

No information on relaxation effects and local field effects

Multiscale modelling: Molecular Dynamics

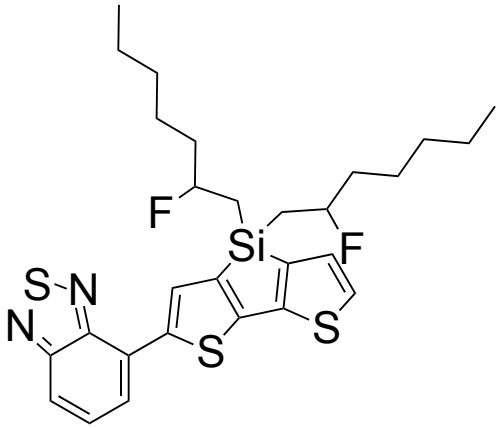


Embed the molecules in a box filled with environment

Perform (TD-)DFT calculations while treating the embedding with DRF (ADF program)

Model systems

One donor-acceptor co-monomer (**1** or **2**) and one PCBM molecule (**3**), embedded in only monomers (**1**, **2** or **4**)



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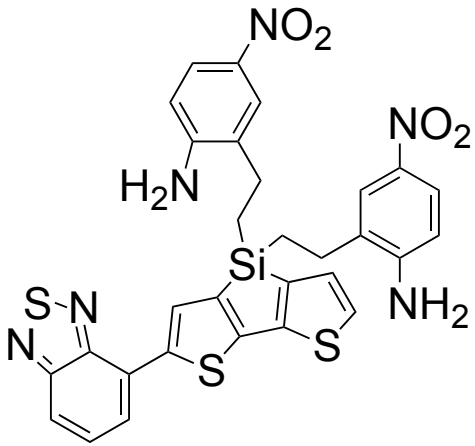

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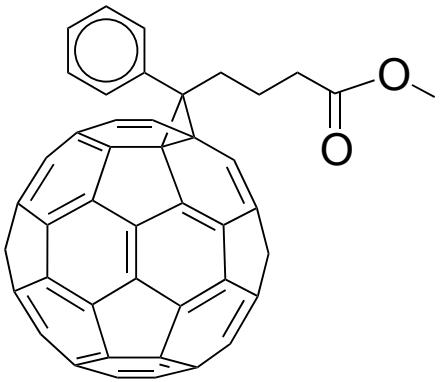

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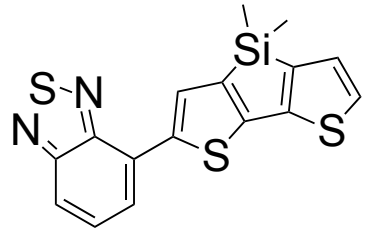
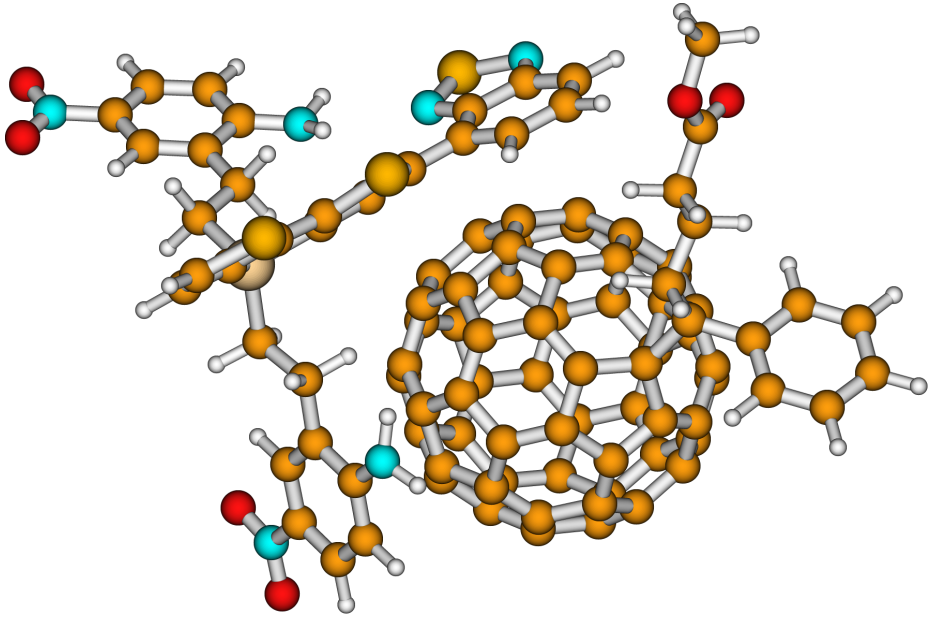
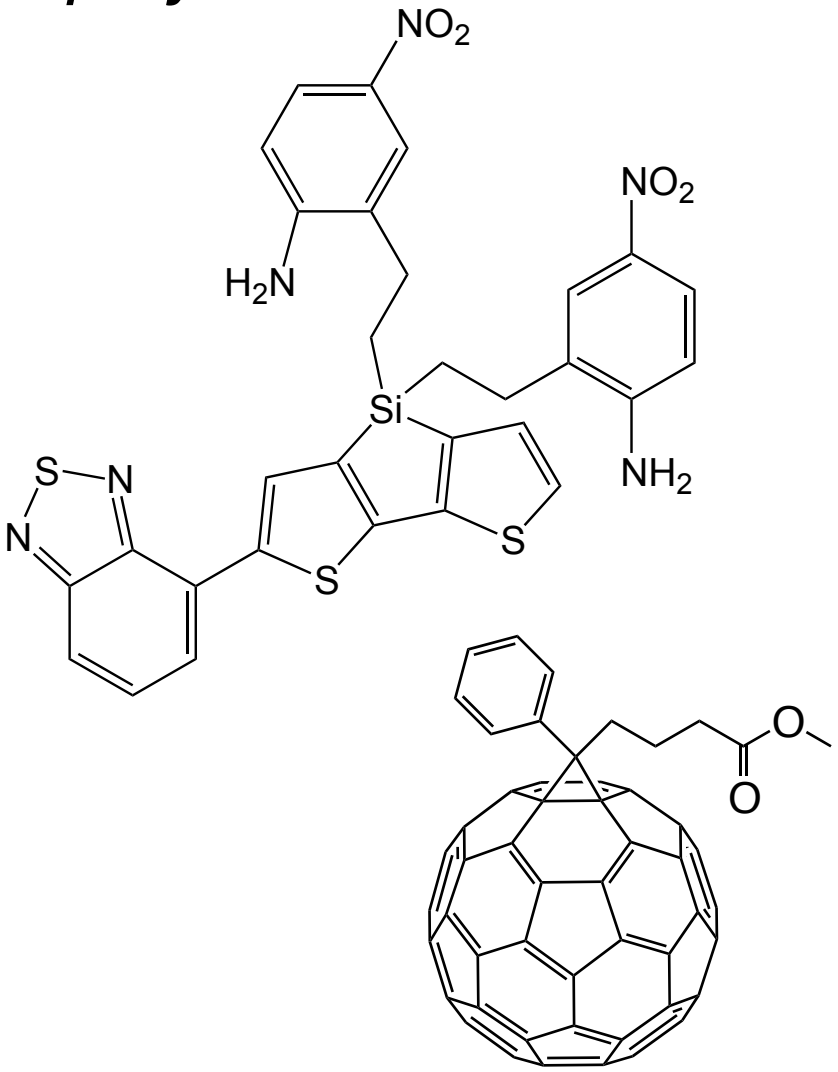


4

Embedding study: effect of polymer side-chains

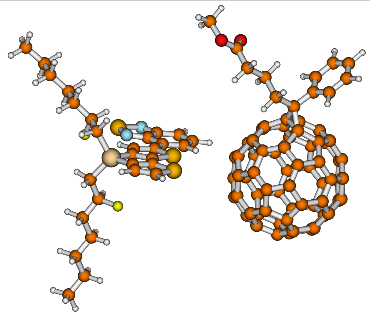
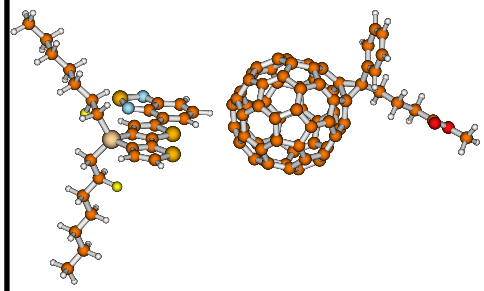
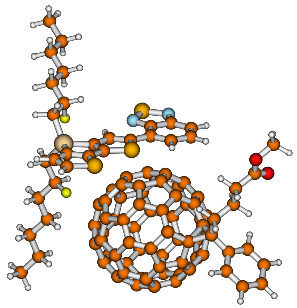
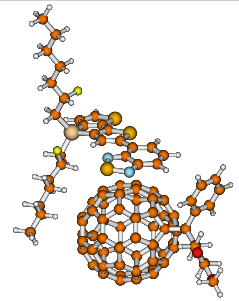
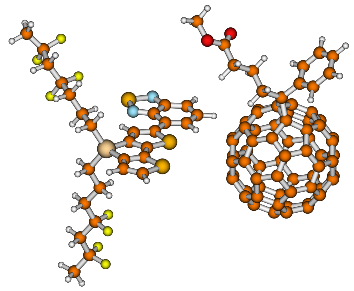
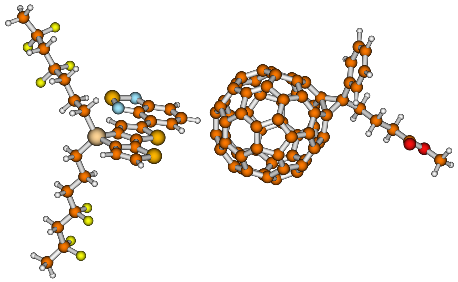
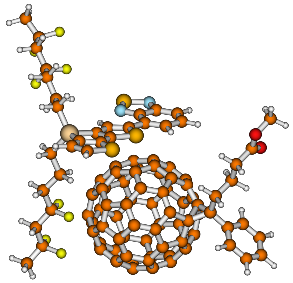
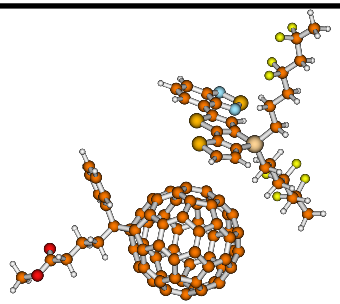
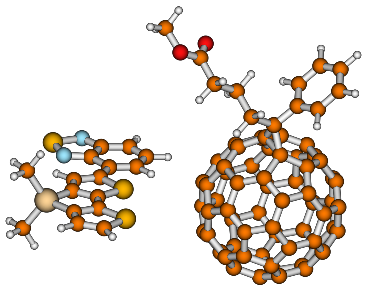
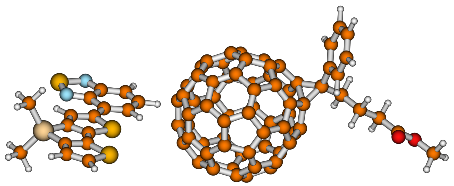
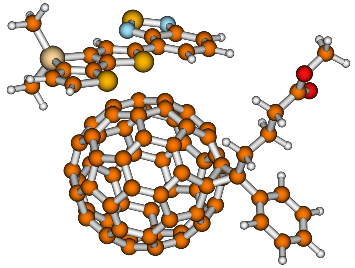
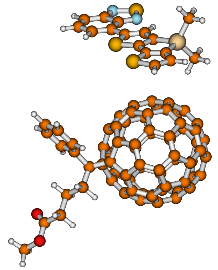


DFT geometry optimisation



Bulk effect of polymer side-chains

Winning team:

	configuration 1	*configuration 2*	*configuration 3*	*configuration 4*
1				
2				
3				

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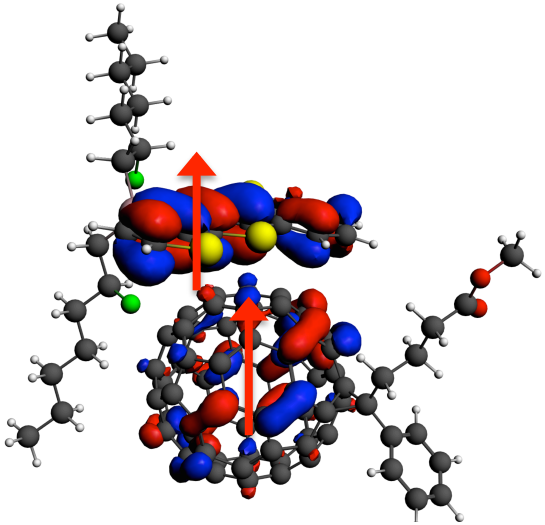
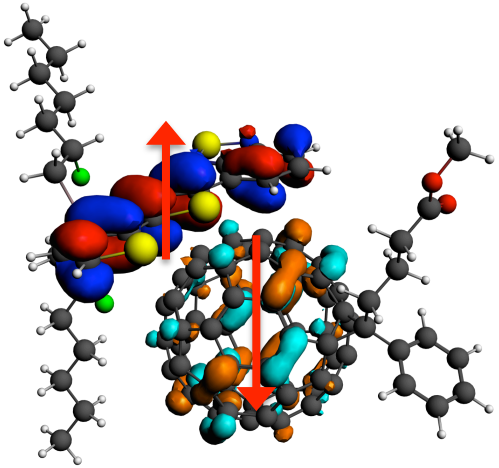
Theoretical Chemistry

Lowest triplet excited state: energy and geometry

$E(T_1)_{relaxed}$ = 1.9 eV

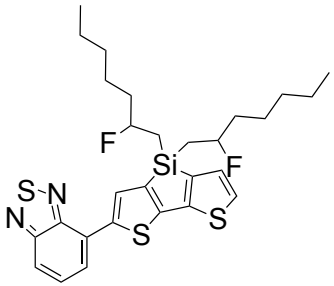


$E(CT_1)_{T1} = E(CT_1)_{relaxed}$
= 2.1 eV

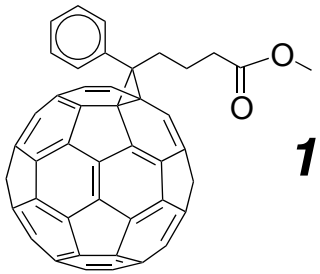


Results

1-3 *in vacuum, in* ***4*** *and in* ***1***



1



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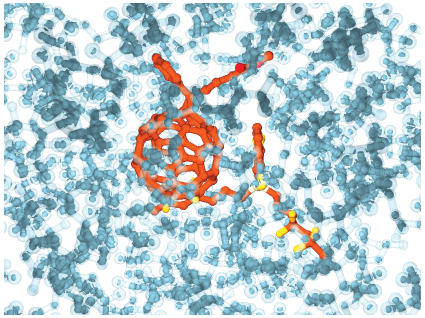

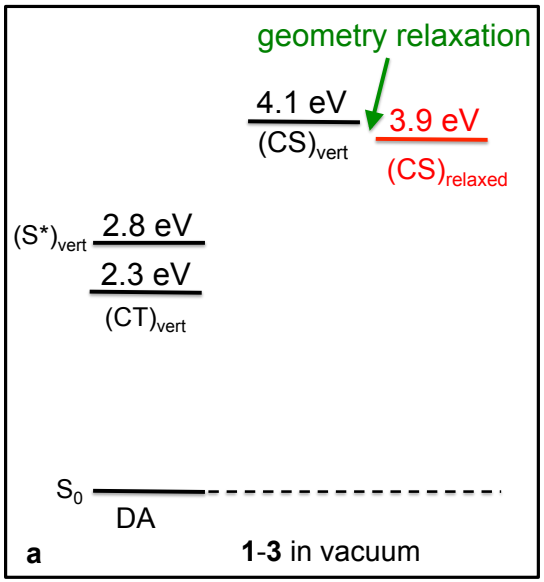

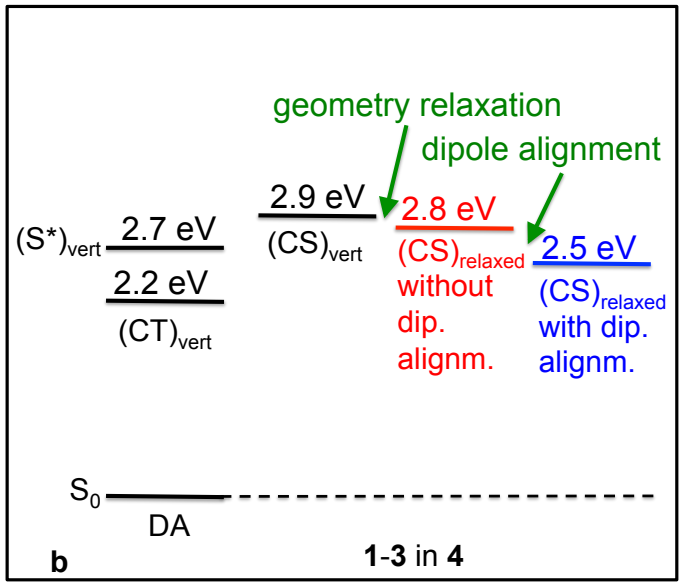

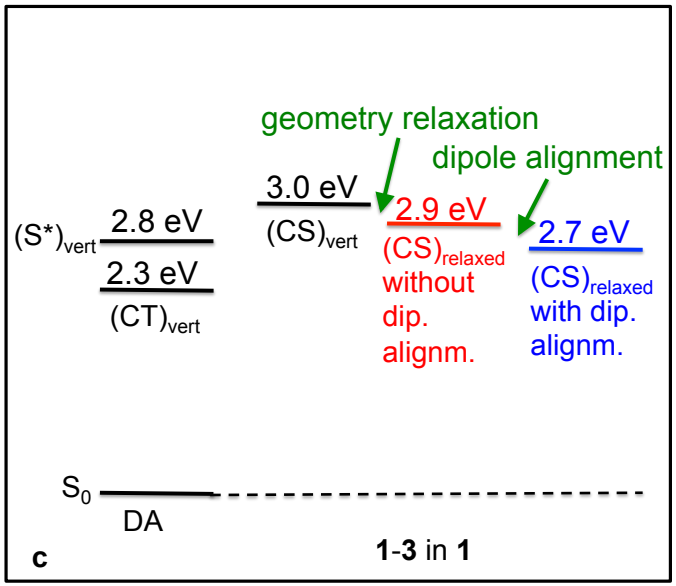

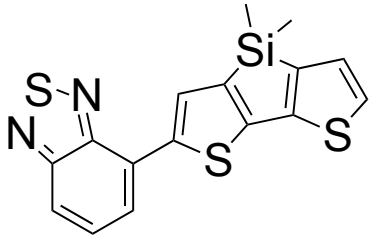

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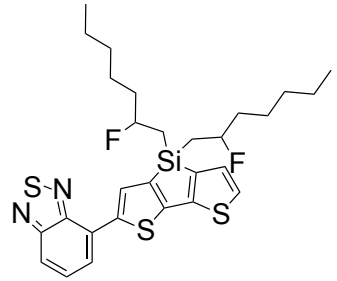

1

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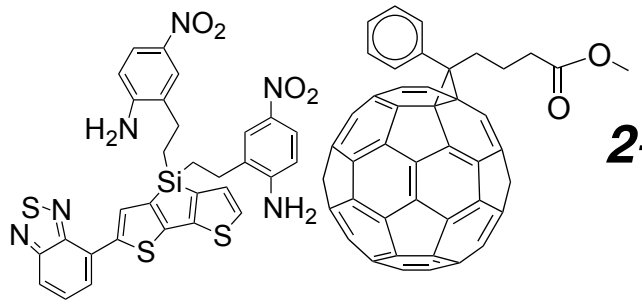
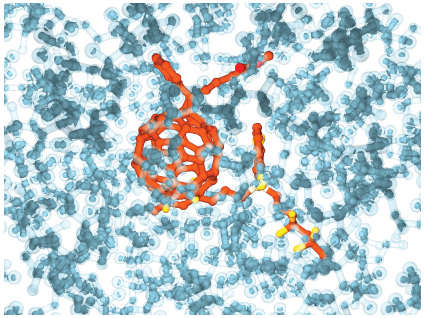
Theoretical Chemistry

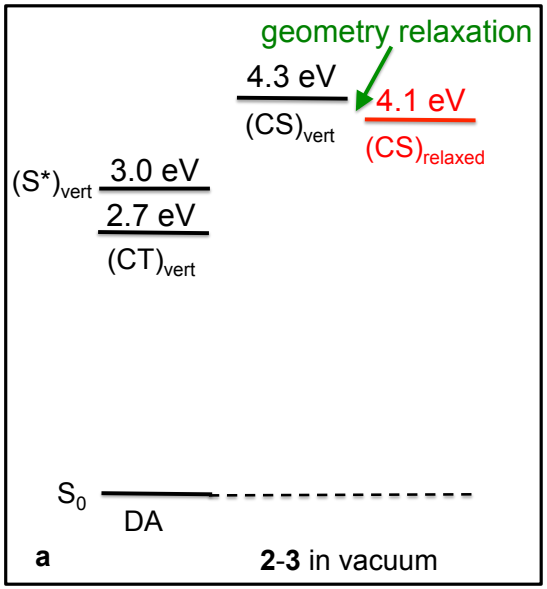
Results

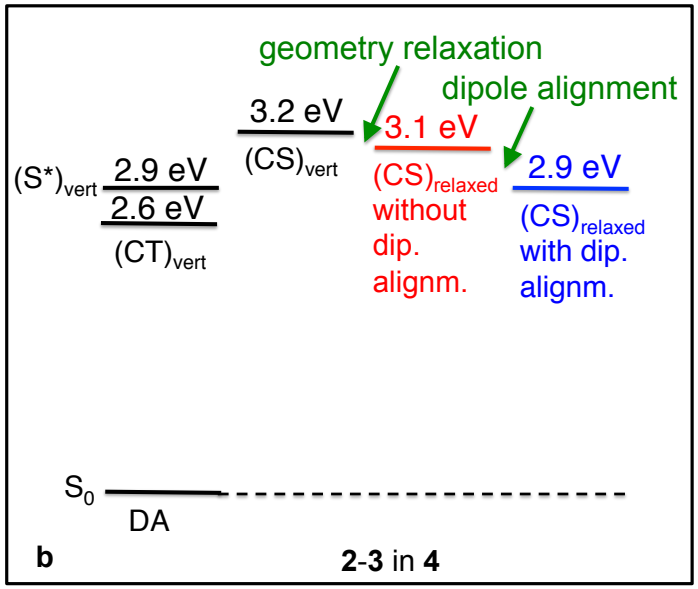
2-3 *in vacuum, in* ***4*** *and in* ***2***

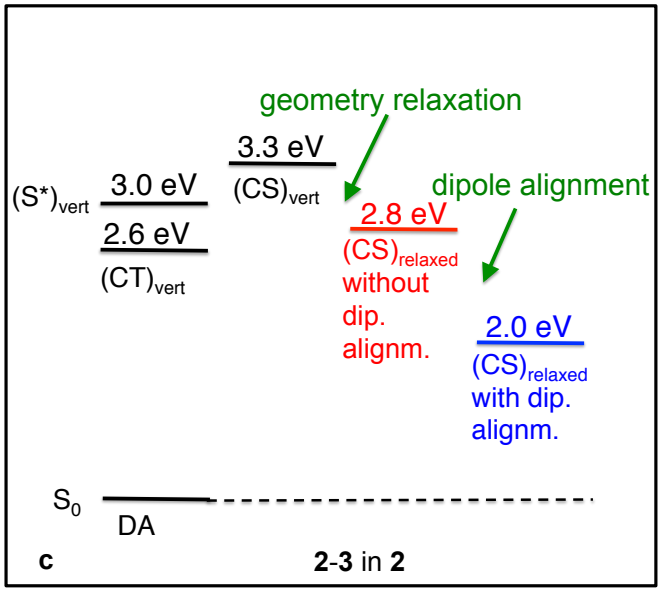


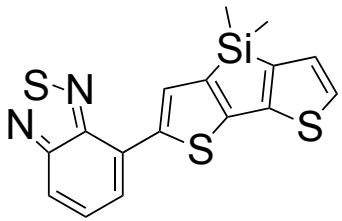
2 **3**











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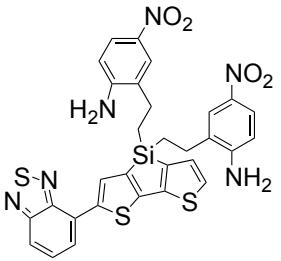

2

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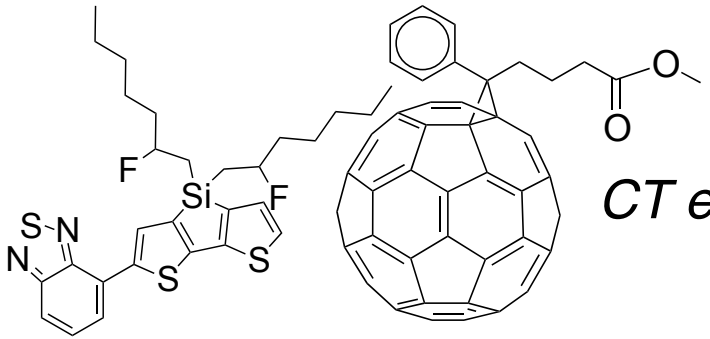
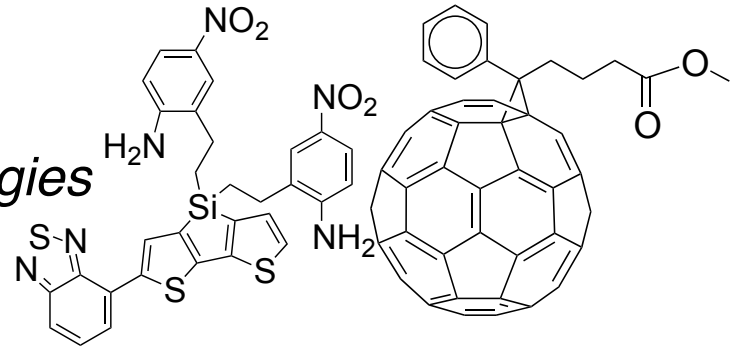
Theoretical Chemistry

Results



1 3

CT exciton binding energies

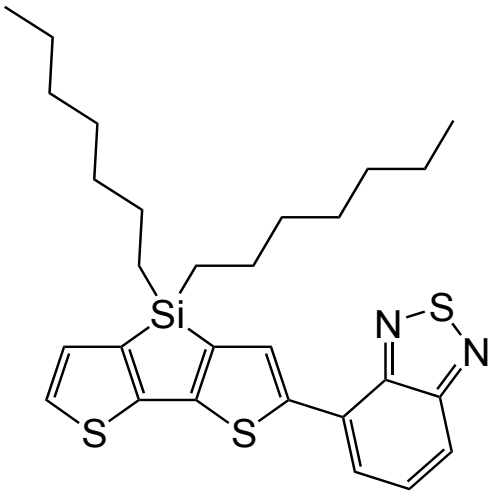


2 3

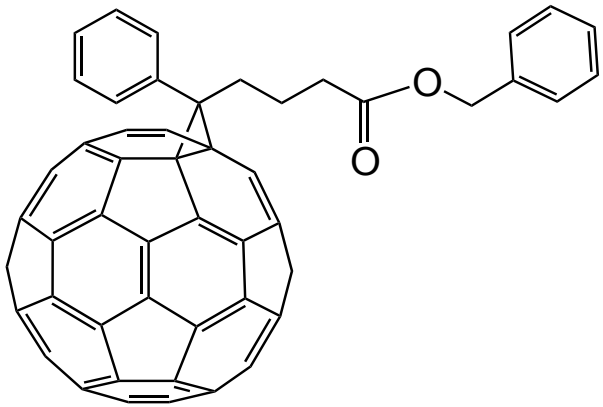
	1-3 in vac.	**1-3** in **4**	**1-3** in **1**
E_b no dip. alignm. (eV)	1.6	0.6	0.6
E_b with dip. alignm. (eV)	1.6	0.3	0.4
	2-3 in vac.	**2-3** in **4**	**2-3** in **2**
E_b no dip. alignm. (eV)	1.4	0.5	0.2
E_b with dip. alignm. (eV)	1.4	0.3	-0.6

PCBM environment: Model systems

One donor-acceptor co-monomer (**1**) and one PCBM molecule (**3**), embedded in only PCBM molecules (**2** or **3**)



1



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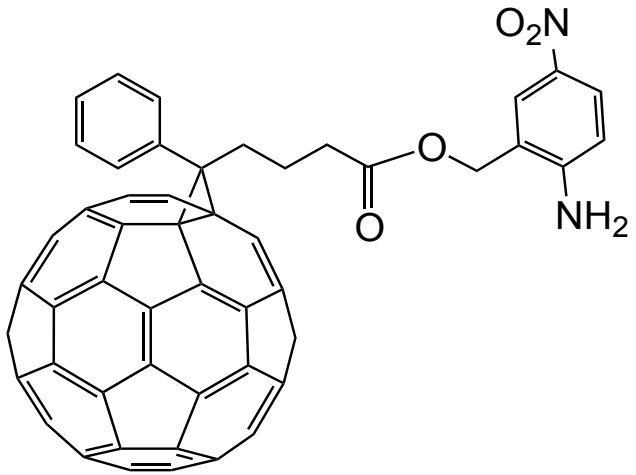
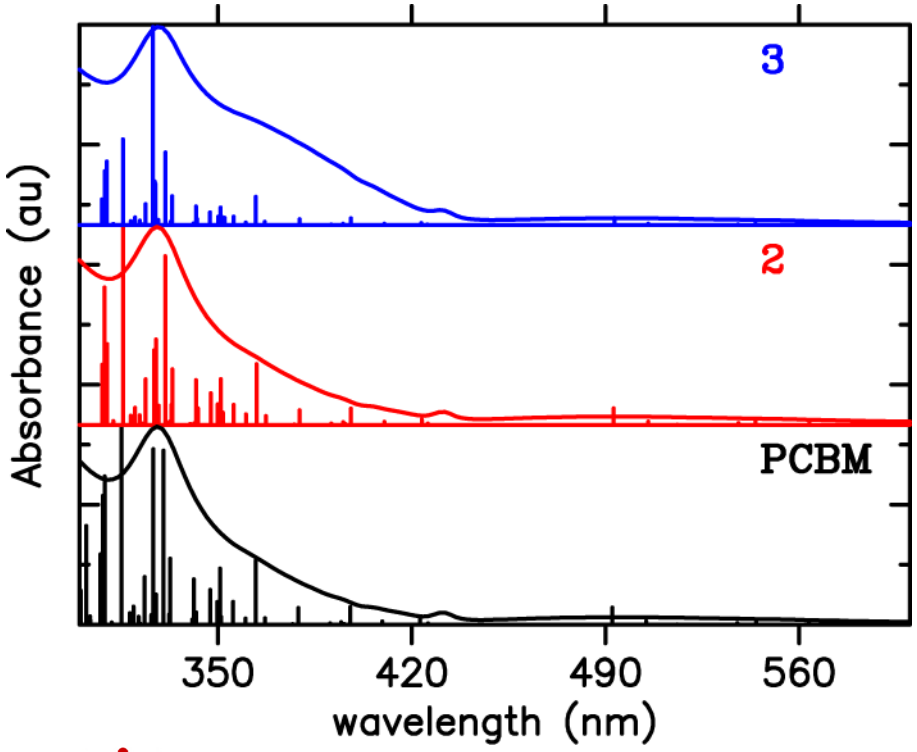


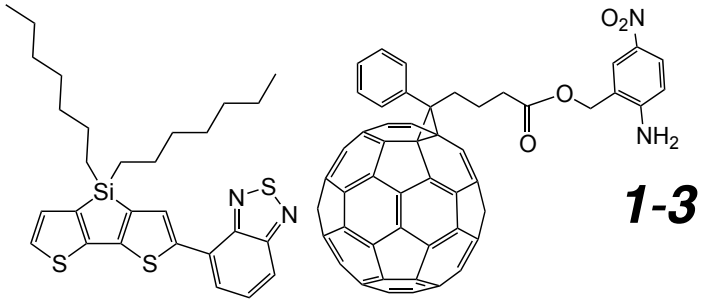
3

Electronic properties

	$E_{1/2}$-1,red (V)	$E_{1/2}$-2,red (V)	ε_{HOMO} (eV)	ε_{LUMO} (eV)	α/e^- (au)	μ (Deb)
PCBM	-1.089	-1.482	-7.92	-3.88		
2	-1.095	-1.489	-7.90	-3.86	1.56	2.35
3	-1.097	-1.487	-7.87	-3.83	1.53	5.97



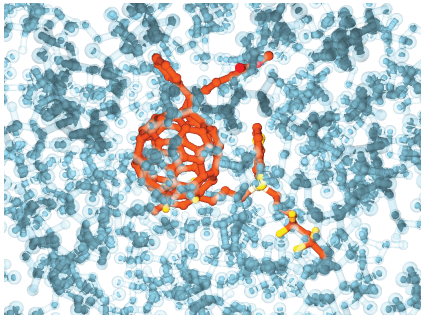
- All compounds have similar electronic properties, except for the dipole moment

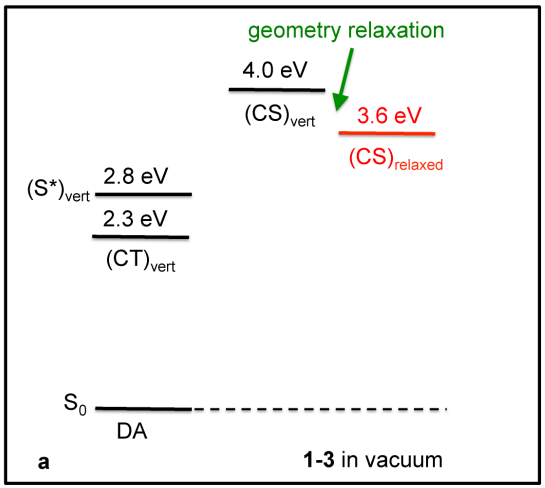


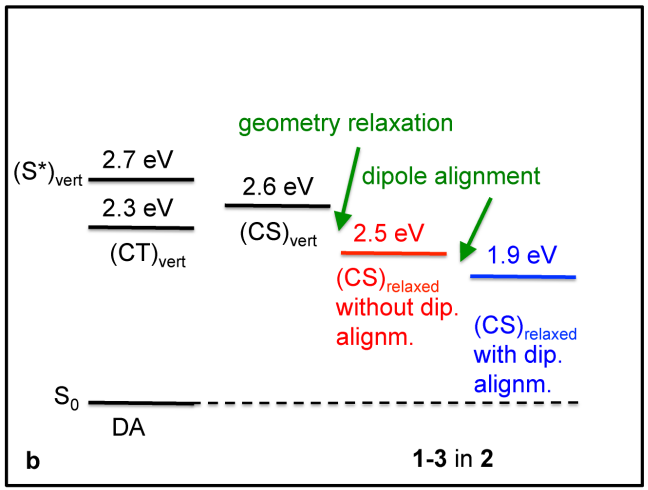
1 3

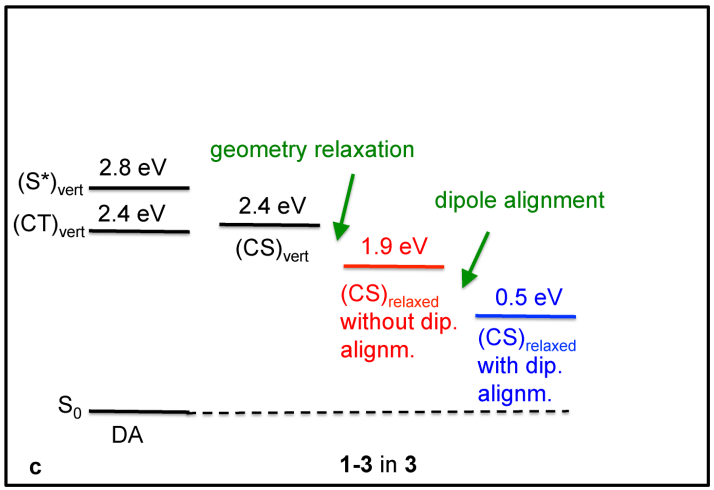
Results

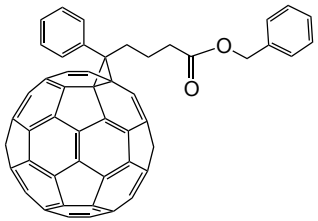
1-3 in vacuum, in 2 and in 3











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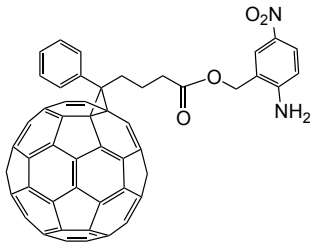
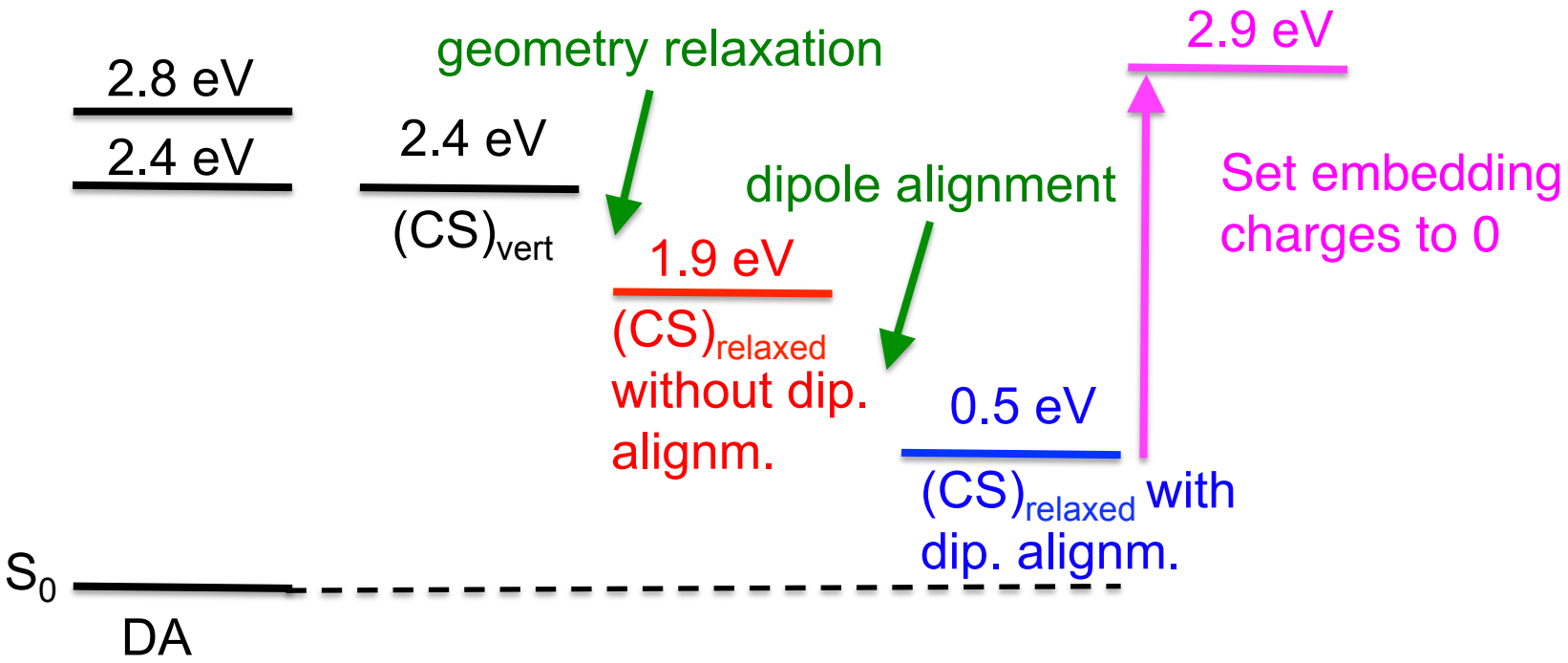


3

university of groningen
faculty of mathematics and natural sciences
zernike institute for advanced materials
Theoretical Chemistry

Effect of dipoles?



1-3 in **3**

- If embedding dipoles are set to 0, CS goes up again

What is still missing?

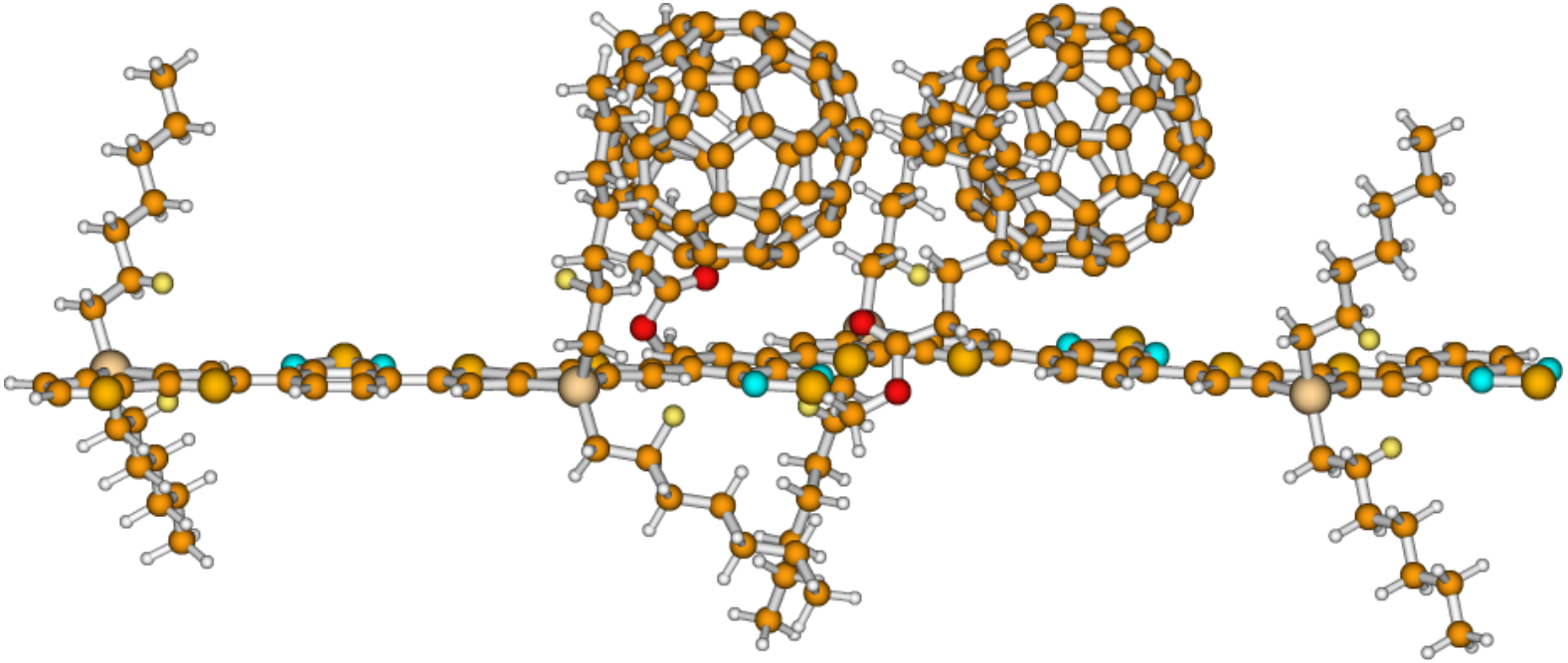
- A lot!
  - Geometry optimisation within the environment
  - Geometry relaxation of CT states
  - Entropy contributions
  - Energy transfer rates
    - Couplings between excited states
  - Role of vibrations?
  - Role of delocalisation?

- Currently we are working on several of these aspects in ADF

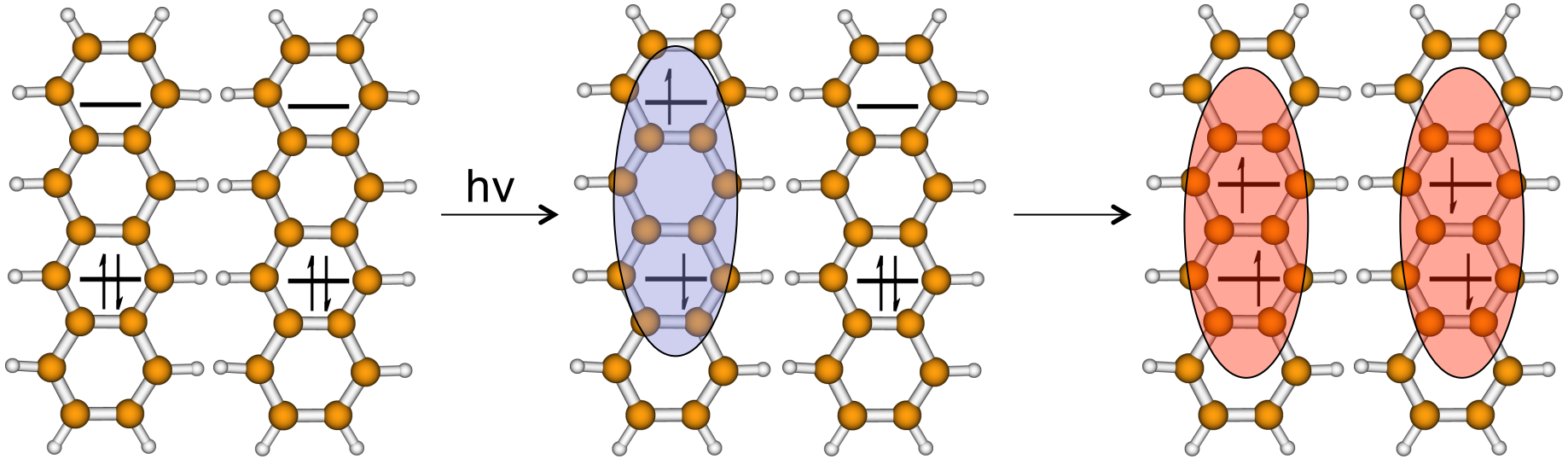
Future directions

- Improve the theoretical methods
  - CC2 (NWChem) in combination with leading supercomputers

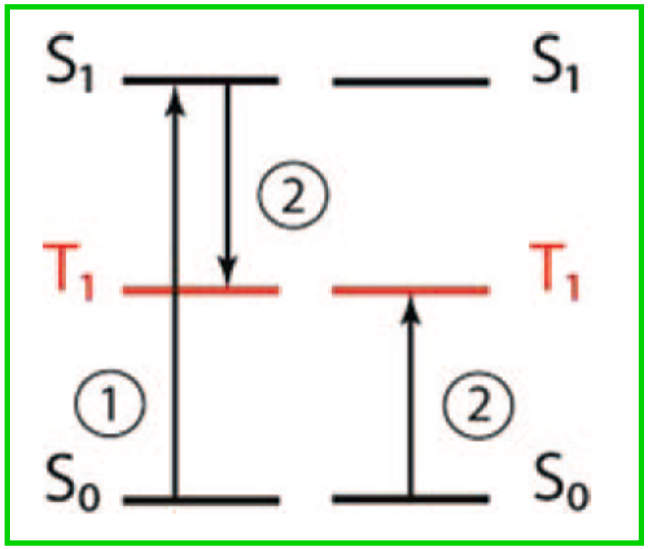
- Extend the system (10000 - 30000 bfs) to get a more realistic model of the donor-acceptor interface (DFT – ADF)



Other aspects that may improve OPV: Singlet fission

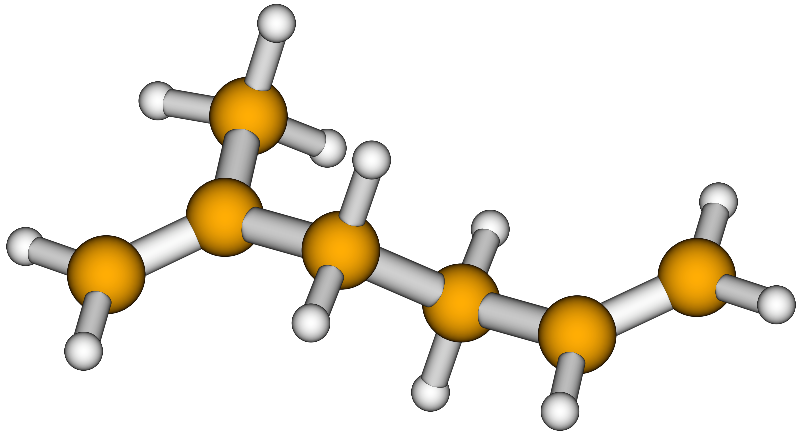


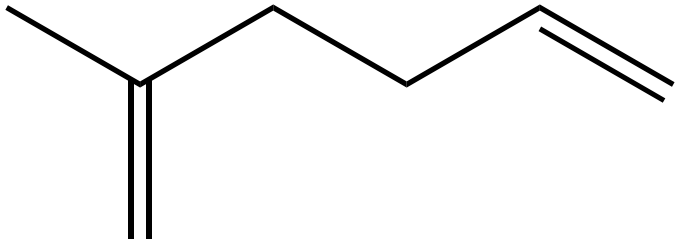
- Spin allowed
- Radiationless process



M. B. Smith, J. Michl, *Chem. Rev.* **110** (2010), 6891

Model calculations





- Two weakly coupled chromophores

Demands on Computational Techniques

^{1}TT state is a singlet state with four open-shells:

Multi determinant wavefunction

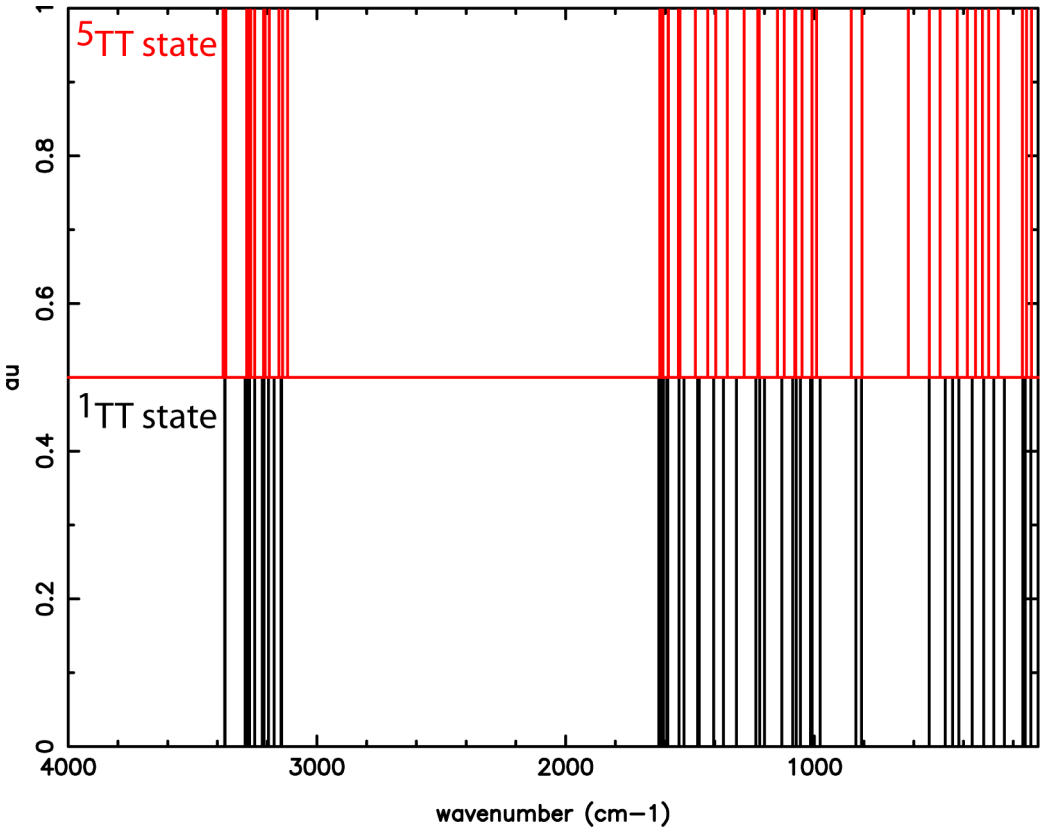
- MCSCF
  - CAS/RASPT2, MRCI
- Non orthogonal CI
  - compact wavefunctions
  - clear chemical/physical interpretation

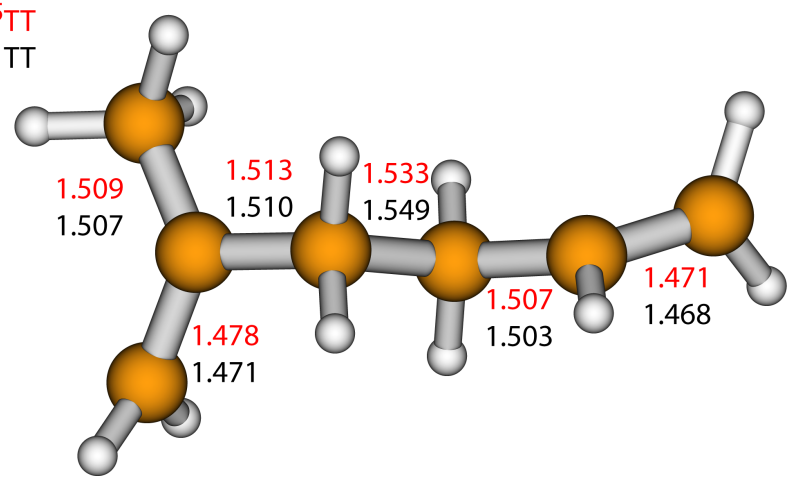
- Geometries/vibrational frequencies:

  Can we use ^{5}TT instead of ^{1}TT?

  DFT would then be ok

Geometry and frequencies (CASSCF)





^{5}TT is a sufficiently good representation of ^{1}TT

Electron transfer rate

- Fermi Golden rule in diabatic representation (Marcus theory)

$$k_{ET} \propto \left| \left\langle \Psi_f \middle| H \middle| \Psi_i \right\rangle \right|^2$$

  - Electronic coupling between diabatic states

- Adiabatic representation: Non-adiabatic couplings (Landau-Zener model)
  - Potential energy surfaces and conical intersections/ crossings

P.F. Barbara, T.J. Meyer, M.A. Ratner, *J. Phys. Chem.* **100** (1996), 13148
F. Bernardi, M. Olivucci, and M.A. Robb, *Chem. Soc. Rev.* **25** (1996), 321

MCSCF-CASPT2-MRCI

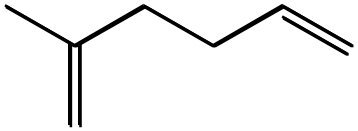
$$\Psi = \Psi_0 + \sum_{i,a} c_i^a \Psi_i^a + \sum_{ij,ab} c_{ij}^{ab} \Psi_{ij}^{ab} + \cdots$$

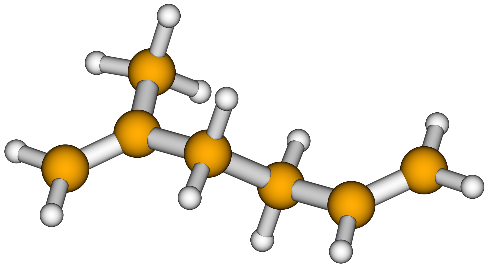
- Balanced description of all relevant states
- Accurate
- Non-adiabatic coupling elements $\left\langle \Psi_i \left| \frac{\partial}{\partial Q} \right| \Psi_f \right\rangle$

- Expensive or impossible for large systems
- Chemical interpretation is not trivial

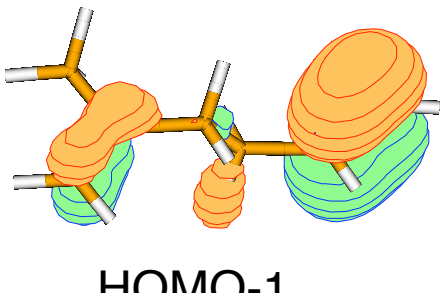
2-methyl-1,5-hexadiene

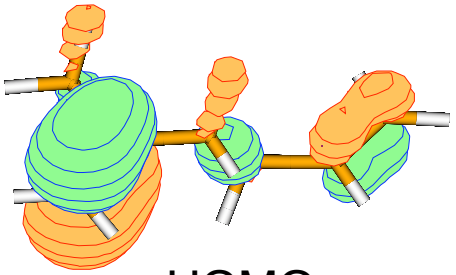
Molecule:

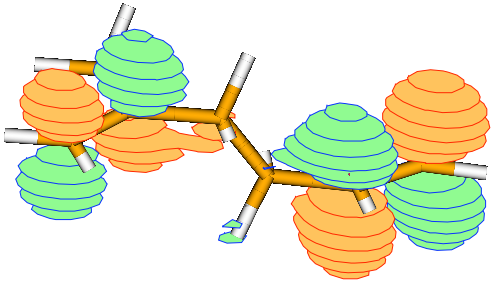


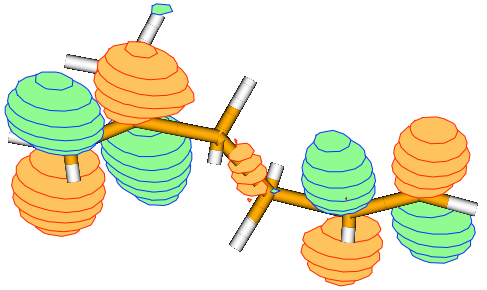


active space

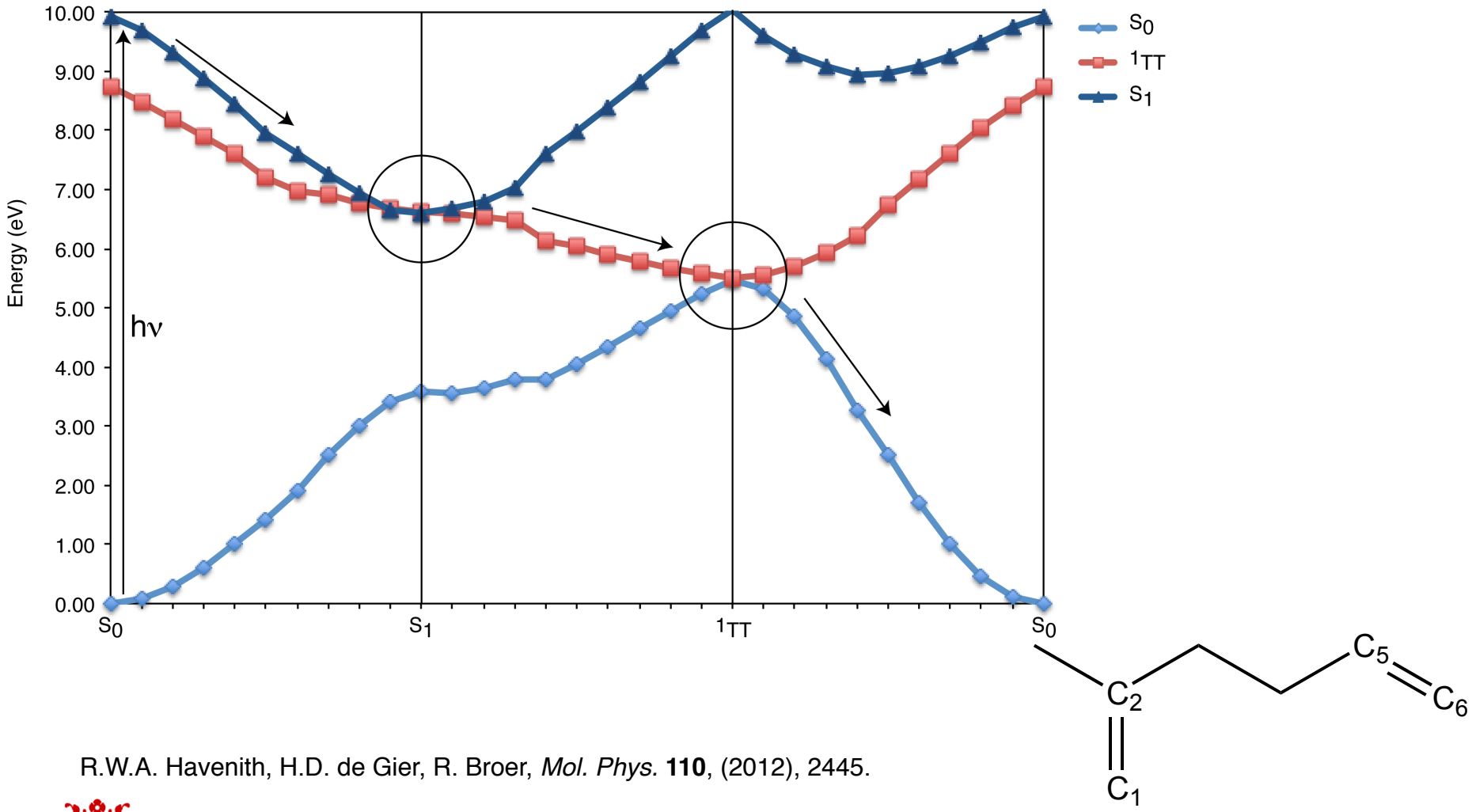








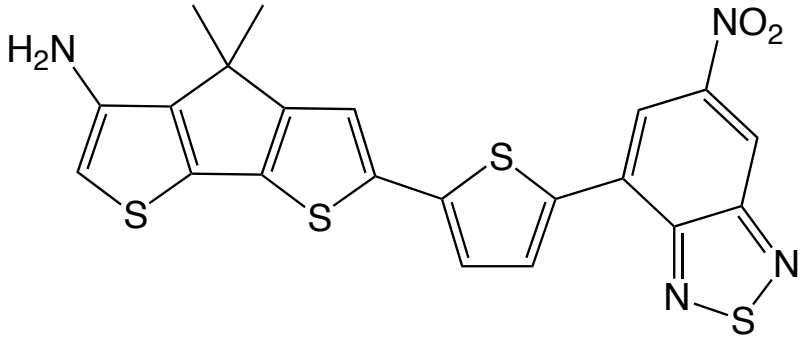
Adiabatic potential energy surfaces



R.W.A. Havenith, H.D. de Gier, R. Broer, *Mol. Phys.* **110**, (2012), 2445.

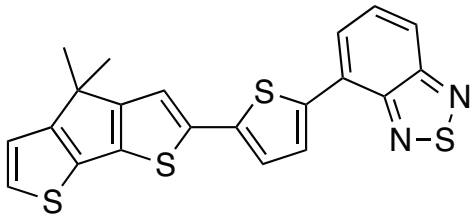
Promoting charge separation

- Modify electronic structure of the chromophore
  - Introduction of dipoles: push-pull substitution

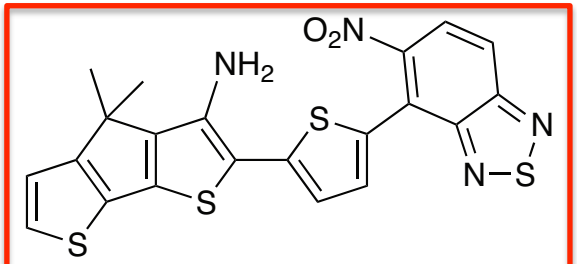


Functionalisation of polymer

- Addition of push-pull groups to lower the exciton binding energy:
  - Mesomeric: linear- (**2**, **3**) *versus* cross-conjugation (**4**, **5**)
  - Inductive (**6**)



1



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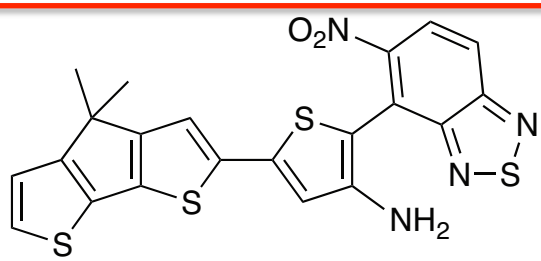

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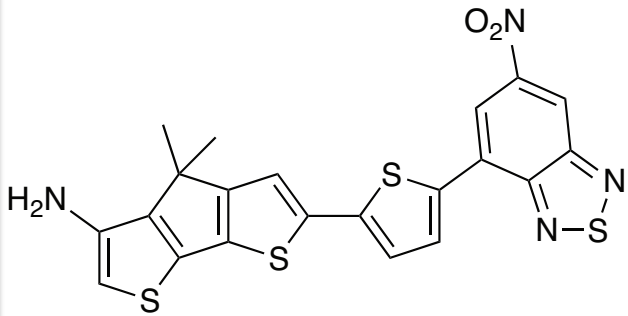

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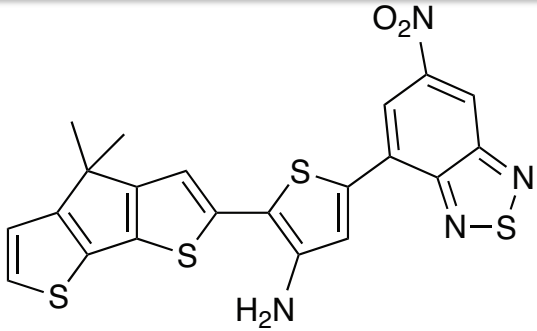

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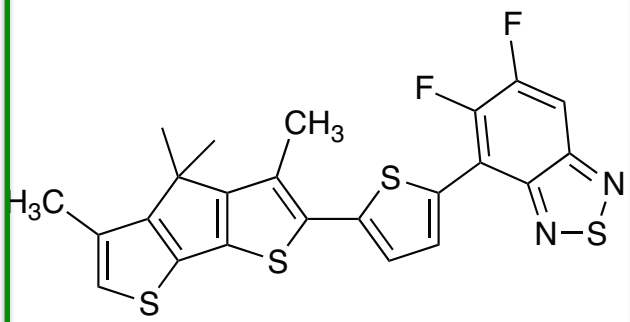
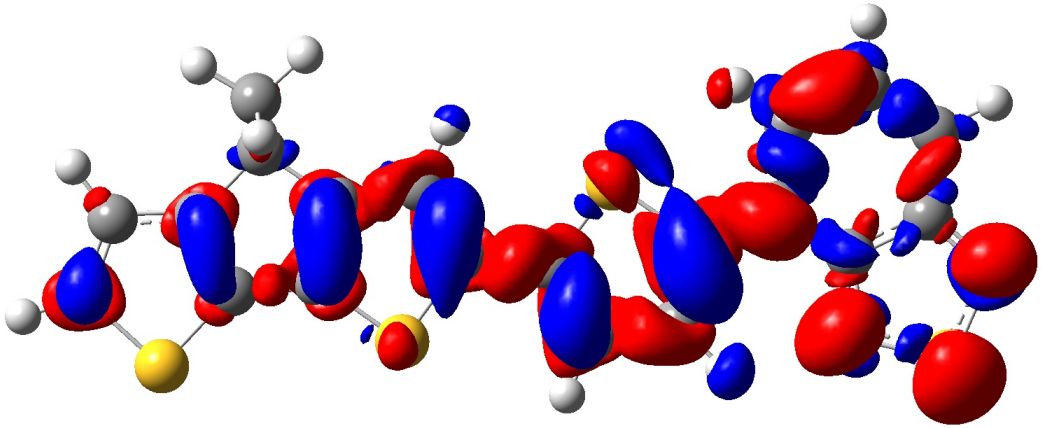
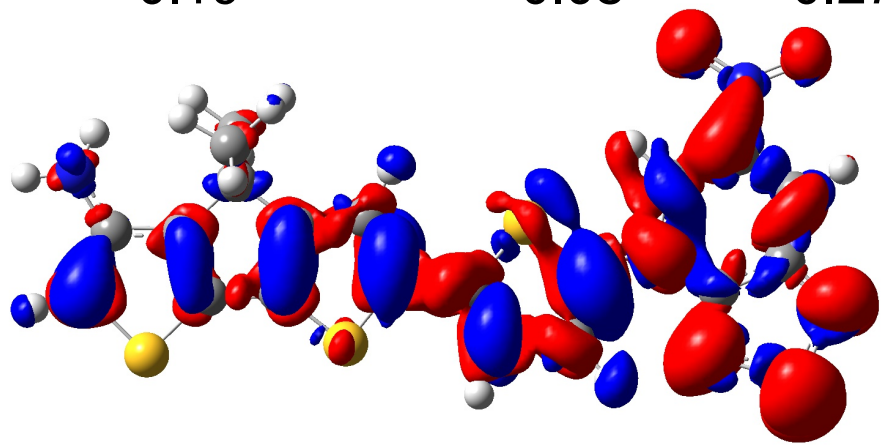


6

Enhancement of charge transfer



0.19 0.08 -0.27

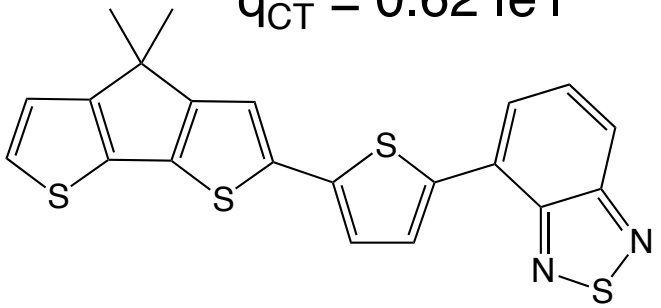


0.30 0.10 -0.40

1

D_{CT} = 4.02 Å

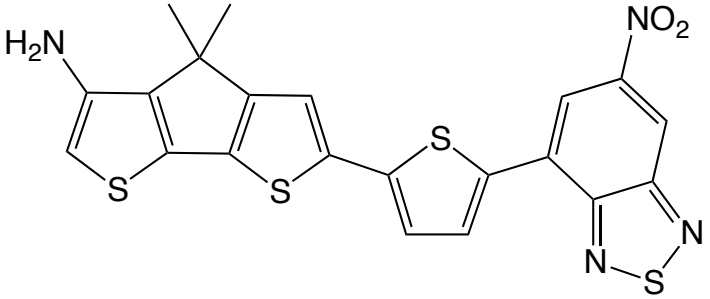
q_{CT} = 0.62 |e|



4

D_{CT} = 4.53 Å

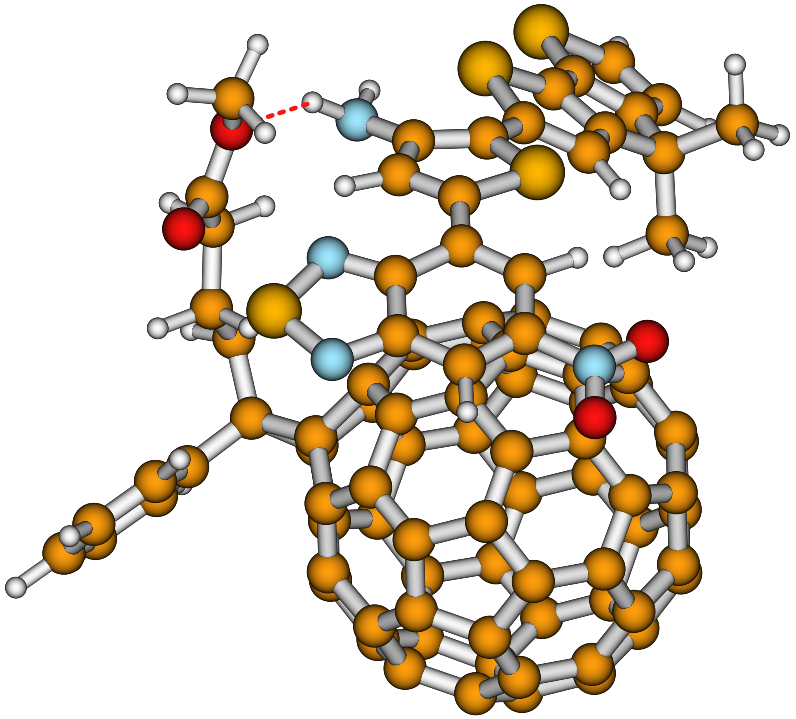
q_{CT} = 0.82 |e|



Exciton binding energies

Exciton binding energies in eV

	μ (Deb)	$(E_b^{exc})_{polymer}$	$(E_b^{exc})_{PCBM}$
1	3.02	2.70	1.97
2	2.39	2.61	2.01
3	2.79	2.79	2.07
4	4.04	2.46	1.95
5	4.52	2.42	1.93
6	2.35	2.73	1.97



- Marked differences between linear and cross conjugation disappear and all CT exciton binding energies are similar

Financial support

- Zernike Institute for Advanced Materials (Dieptestrategie)
- FOM Focus Group ‘Next Generation Organic Photovoltaics’ (DIFFER)
- ITN-EJD-TCCM (Horizon2020)

DIFFER
Dutch Institute for
Fundamental Energy Research

university of groningen / faculty of mathematics and natural sciences / zernike institute for advanced materials

Theoretical Chemistry


Thank you for
your attention!