1. Title of the project

Computational design of new acceptor molecules for application in organic photovoltaics

2. Abstract

It is important to have access to renewable energy sources. Preferably they are cheap, green and efficient. Organic solar cells are a promising candidate, but only when the efficiency can be increased. A lot of effort is made to synthesize new donor materials for donor-acceptor solar cells and to improve the solar cell morphology. These syntheses are time-consuming and it is often unclear why some materials do work while others do not. In contrast we will carry out a multi-scale supercomputing simulation to investigate large series of innovative polymer blends with new acceptor materials. Nowadays mainly fullerene derivatives are used as electron acceptors but despite their good properties their use is limited and the design of more flexible acceptors is certainly preferred. The new blends are simulated by molecular dynamics. From snapshot of the simulations the donor-to-acceptor charge transfer rates are calculated quantum-mechanically via Density Functional Theory. In the end the microscopic determined electron transfer rates are extrapolated to a Kinetic Monte Carlo device simulation to predict the charge mobility. In this way a rigorous method is created to model OPVs in a multi-scale approach that will give us in a short time insight in the performance of new highly efficient donor-acceptor systems.

3. Applicant(s)

Jos Teunissen MSc

4. Key publications of the applicants

T. Ba Tai, R.W.A. Havenith, J.L. Teunissen, A.R. Dok, S.D. Hallaert, M. Tho Nguyen, A. Ceulemans; *Particle on a boron disk: ring currents and disk aromaticity in $B_{20}{}^{2-}$*; Inorg. Chem., 52, 10595-10600, **2013**

5. FOM-research group

N/A

6. Institute

Zernike Institute for Advanced Materials (ZIAM)
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Nijenborgh 4
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The Netherlands

Contact
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7. Duration of the project

Four years starting February 1st,2015 until February 1st, 2019.

8. Personnel

8.1 Senior-scientist

Name	Task	Time
R.W.A. Havenith	Academic supervision	10%
R. Broer	Promotor	10%
A.H. de Vries	MD – support	5%

8.2 Junior-scientist and technicians

Name	Task	Time
J.L. Teunissen	research	100%

9. Cost estimates

9.1 Personnel positions

One OIO with a total amount of 204 k€ in 4 years

9.2 Running budget

20k€ in total (5k€/yr.) for one computational/theoretical position

9.3 Equipment

One desktop computer for the PhD student: 2 k€

Contribution to the local computer cluster to perform test calculations: 20 k€

9.4 Other support

The large calculations will be performed on the national computer facilities via e-Science.

9.5 Budget Summary

	2015	2016	2017	2018	TOTAL
Personnel(positions):					
PhD students (fte)	1	1	1	1	4
Postdocs	0	0	0	0	0
Technicians	0	0	0	0	0
Guests	0	0	0	0	0
Personnel (k€)	51	51	51	51	204
Running budget (k€)	5	5	5	5	20
Equipment (k€)	22	0	0	0	22
TOTAL (k€) **(requested from FOM)**	78	56	56	56	**246**

10. Research Program

10.1 Introduction

In the run for renewable energy sources organic solar cells are one of the most promising candidates. However to harvest solar energy efficiently is still a challenge. It is important that the devices are green, efficient and cheap. Organic solar cells are suitable because the production costs are low and they can be easily prepared without using complicated vacuum setups. As an additional advantage they are flexible and have low weight.

The power conversion efficiencies (PCEs) of OPVs are still low (≲10%) and the mechanism to design better solar cells is still unclear. Nowadays there is a wide variety of architectures such as inorganic-organic hybrids[1], nano dots and polymeric bulk hetero-junctions (BHJs).[2] BHJs have the advantage that they are very flexible, easy to process and there is an enormous amount of possible materials to use. To make BHJ-based OPVs realistic candidates for industrial production, the PCE has to increase and the stability of the device has to be high.

Bulk hetero-junctions consist of mixed electron donor and electron acceptor material. While a lot of research focusses on designing new donor materials, for the acceptor material usually a standard fullerene derivative is used. However it is expected that non-fullerene acceptors are more feasible on the long term.[2] The advantages of fullerenes are that they have a high dielectric constant, are highly polarizable and have low internal reorganization energy. However they have narrow wavelength absorption, somewhat too high electron affinity and a poor solubility.[3] Moreover they have little flexibility to tune the energy levels. We try to design new acceptor materials that have well-tuned energy levels, good solubility, low production cost, high dielectric constant, a wide spectral absorbtion and still have the same advantageous as the fullerenes.[4] Our aim is therefore to find promising alternative electron acceptors instead of the widely used fullerene derivatives.

Synthesis of new materials is often difficult and time-consuming whereas the reason behind better or worse functionality is often vague. Computational research is therefore a useful tool to design a good acceptor. By investigating the packing morphology, the electron transfer and recombination rates and the charge mobility it is well possible to characterize a good acceptor. We will setup a standard methodology such that it will become possible to investigate a whole sequence of structures in a short period.

To design the ultimate acceptor material one needs to understand the working mechanism in depth. It is a challenging task to model all aspects of the working mechanism together because they happen on different time and length scales.[5] We will establish a new state-of-the-art multi-scale supercomputing methodology to model these systems appropriately. Here we go two steps further then the normally adopted procedure. Classical simulations are used as an input for quantum-chemical calculations that are subsequently used as input for Kinetic Monte Carlo device simulations. This approach has the advantage to follow the effect of structural changes on each length scale. At present this is the most extensive multi-scale approach available.

Eventually this will end up in newly designed high conversion polymer blends, giving us insight in the coherence between all length scales and provide a rigorous treatment for this kind of problems.

10.2 Research on bulk hetero junction based OPVs

For several years the research on OPVs is very popular, and the available research articles is enormous. Because the working mechanism of photovoltaics based on BHJ architectures is so complicated a lot of research effort is put into it. And even now a full understanding of its working mechanism is lacking. Nonetheless a brighter understanding starts to appear.
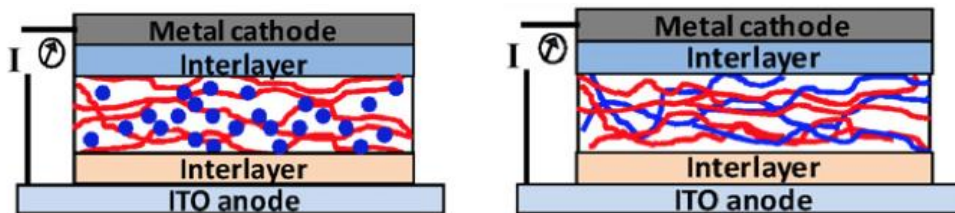

Fig. 1 Schematic representation of two Donor-Acceptor Bulk Heterojunctions one with small molecule acceptors (left) and one with polymer based acceptor material (right). The acceptor is shown in blue and the donor in red color.[3]

The general architecture of a BHJ device consists of a mixed blend of donor (D) and acceptor (A) material. The blend is sandwiched between two electrodes of which one is transparent (see Fig. 1). The acceptor material is usually a fullerene derivative and the donor material is typically a hole-conducting conjugated polymer. The donor has a low ionization potential (IP) and the acceptor a high electron affinity (EA).

In accordance with a generally accepted working mechanism, the BHJ-OPV includes the following steps: exciton formation (*fs*), exciton migration (*ps*), charge transfer (*ps-ns*) and charge collecting (*ns-μs*). The donor polymer absorbs light and an exciton is formed. The exciton migrates towards the donor-acceptor (D-A) interface. At the interface the electron hops to the $LUMO_{acceptor}$ but the hole and electron do still attract each other. This state is called the charge-transfer (CT) state. When the electron and hole move apart they become free carriers. This states is called the charge-separated state (CS). Finally the charge is collected at the electrodes under influence of an intrinsic electric field.[5]
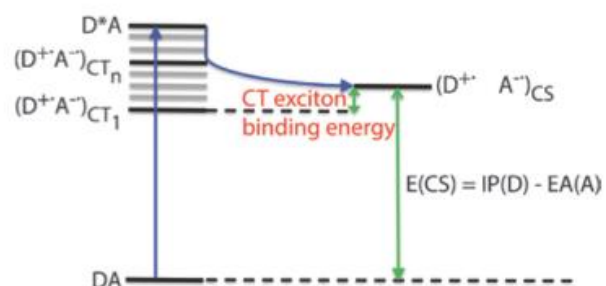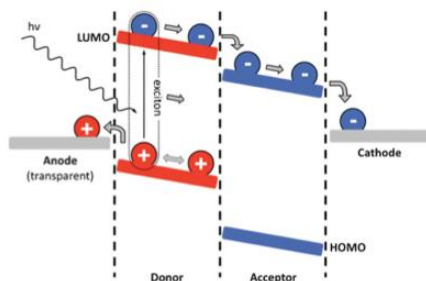

Fig. 2 energy level representation of an OPV device   Fig. 3 electronic state diagram of the CT- and CS state

An MD simulation on a standard P3HT:PCBM hetero junction formulated a few structural requirements. Having *a high interface/volume ratio* and *domain sizes that are smaller than the exciton diffusion length* provides efficient charge separation of an exciton. A *high percolation ratio* is required to have efficient charge collection at the electrodes.[6] It is observed that the packing at the interfaces is more disordered. This gives a larger band gap at the interface that facilitates charge separation by repelling holes from the interface. [2,7,9]

Recent quantum-mechanical/molecular mechanics (QM/MM) studies showed that the CT states can occur in two different geometries; one where the exciton is delocalized over the whole donor-acceptor complex and one were the charges are obviously located either on the donor or acceptor.[2,8,9] QM/MM calculations on snapshots at different times show that there are large fluctuations in the D-A coupling on picoseconds timescale (molecular vibrations). This high sensitivity to the orientations of the molecules emphasizes the subtlety of the CT state.[7]

A Kinetic Monte Carlo device model (KMC) was used to simulate charge transport in C_{60} and PCBM.[10,11,12] This model has no fitting parameters and the packing and electron transfer rates follow from preceding DFT calculations. The electron transfer rates are calculated via Marcus Theory. The final morphology of the materials[10] and the charge mobilities are in agreement with experimental results.[11,12] It is also showed that disorder does not affect the mobility significantly when the packing density is high enough.[10]

Significant effort is made to design better donor polymers by increasing the dielectric constant and polarisabilities by placing push-pull groups and adding polar side chains.[13] Recently several groups started to investigate experimentally non-fullerene acceptors and indicated that some outperform PCBM[3,14] however most of them where only characterized as pure material and not as a device.

10.3 Innovation

The innovative aspects of this project are:

- To design and investigate within a short time substantial series of new promising candidates for electron acceptors.
- To adopt a cutting-edge multi-scale approach to investigate the coherence of all aspects in bulk hetero junction organic photovoltaics.

10.4 Method

Our methodology will be computationally all-embracing, combining techniques from three different disciplines: Coarse-Grained Molecular Dynamics (MD), Quantum Chemistry (QC) and Kinetic Monte Carlo (KMC). This multi-scale approach is necessary because the geometry has a large impact on the electronic properties. The packing and polarisabilities have an influence on the energy levels and electronic couplings. This clearly influences the charge transfer rate and therefore also the charge mobility.

| 1. MD.	2. QC.	3. KMC.
GROMACS 1: CG-MD → 2: atomistic-MD	QM/MM: ADF or GAMESS-UK QM:DFT MM: DRF	IN: coordinates, J, λ and ΔG OUT: charge mobility

First a classical simulation is performed on a BHJ blend using MD. In the MD simulation we first perform a coarse-grained simulation and then perform a back-mapping procedure to go back to atomistic resolution. This is a methodology that is recently developed.[16] The GROMACS[15] program is used for the MD simulations using a force field that is optimized for conjugated polymers.

Secondly random snapshots are taken from the simulations and a central donor-acceptor complex is treated quantum-mechanically (QM) while the surrounding molecules are treated classically by molecular mechanics (MM). For the quantum-mechanical part DFT is used. The MM part of the quantum chemical calculation is taken into account via the Discrete Reaction Field method (DRF): the central QM part is then surrounded by a large set of polarizable charges.[17] The QM/MM calculations are performed using ADF[18] or GAMESS-UK[19]. The electronic properties of the D-A complex are now studied to calculate the charge transfer rate and the rate of the unwanted recombination process.

Thirdly, to see if the microscopic nanoscale results for good acceptors will also work on higher scale the electronic properties and coordinates are used as input in a Kinetic Monte Carlo device model to predict the charge mobility. This KMC model is developed by the group of dr. L.J.A. Koster. The molecular coordinates are treated explicitly as well as the parameters for the Marcus equation. A time-of-flight hopping simulation is performed to simulate the charge mobility.[3] Charge mobilities in organic materials are usually low, around 1 $cm^2 V^{-1} s^{-1}$ while inorganic materials reach 100-1000 $cm^2 V^{-1} s^{-1}$. Charge mobility's can be improved by allowing large charge delocalization and high electronic couplings.

10.5 Detailed workplan

In the beginning a well-known donor-acceptor pair P3HT:C_{60} is used to validate our multi-scale approach with former calculations.

C_{60} P3HT
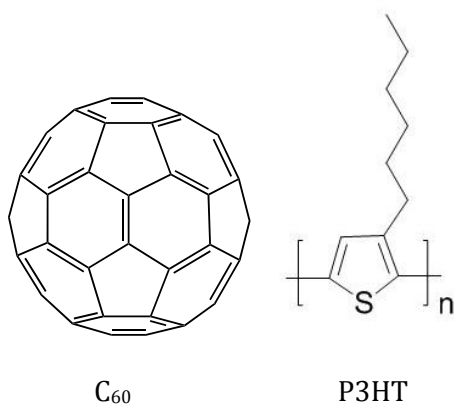
MD

The first step is to obtain accurate realistic geometries of the bulk hetero junction by performing MD simulations. The MD results are analyzed in terms of packing densities. After the MD simulation some snapshots are taken from the MD simulation at different times. From these snapshots a central donor-acceptor complex is selected and a QM/MM calculation is performed on these snapshots using DFT with a discrete reaction field.

DFT

While the surrounding is frozen the central D-A complex geometry is optimized by DFT. When the unpaired electrons are localized, one on the donor and one on the acceptor, the excited S_1 state geometry is almost the same as the T_0 geometry.[20,9] We can therefore the approximate the S_1 excited state geometry by the T_0 geometry. It is much cheaper to optimize the T_0 geometry than the excited S_1 state. The T_0 geometry can be calculated by unrestricted DFT (UDFT) which is analogous to UHF.[31] When the D-A complex is in a CS state the exchange energy is small and therefore the energy of S_1 is almost similar to the energy of the T_0 state.[8,9]

In the delocalized charge transfer states the exchange between the unpaired electrons is not negligible and the $S_1 \cong T_0$ approximation breaks down. For these cases TD-DFT is used. Time-dependent density functional theory can be seen as an extension of DFT to describe excited states. However TD-DFT is usually quite expensive.

Another aspect is the choice of an appropriate functional. For simple ground state DFT calculations the B3LYP functional is often a good choice, but when long-range interactions are important CAM-B3LYP is better.

It is difficult to treat dispersion forces with DFT. However Vanderwaals interactions are important in organic devices because they are the only attractive forces between the molecules. These forces facilitate the formation of crystalline domains giving rise to band lowering and increased electronic couplings. For this reason a Grimme dispersion correction is used.[24]

Charge transfer

There are various models to estimate the rate of charge transfer (Γ). When the coupling between the initial and final states is small often Marcus theory is applied. This is a semi-classical and non-adiabatic theory with a rate expression:

$$\Gamma = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} e^{\frac{(\Delta G + \lambda)^2}{-4k_B T}}$$

Here J is the electronic coupling between the initial and final state, λ is the reorganization energy and ΔG the free energy change between the initial and the final state. There are two important processes, the charge transfer (CT) and the charge recombination (CR). Γ_{CT} needs to be high while Γ_{CR} needs to be small. For a high hopping rate the coupling needs to be strong and the energy difference and the reorganization energy need to be small.[29,30]

There are various ways of calculating the electronic coupling.[22] One rigorous approach is to assume that the initial and final states are diabatic: $J_{if} = \langle \Psi_i | \widehat{F^0} | \Psi_f \rangle$ Where F^0 is the Kohn-Sham-Fock operator of the total donor-acceptor system.[21] Another option is to use non-orthogonal CI[23] or ZINDO.[17] The free energy differences (ΔG) and the reorganization

energies (λ) can be calculated by particular energy differences of the electronic states in different geometries.[20]

It is possible to extend the Marcus theory to take into account the effect of the quantum vibrational modes in an effective way to correct for the intramolecular nuclear relaxation after the ET process.[20]

$$\Gamma = \frac{|J|^2}{h}\sqrt{\frac{1}{4\pi\lambda k_B T}}\sum_\nu\left[e^{-S_{eff}}\frac{S_{eff}^\nu}{\nu!}e^{\frac{\left(\Delta G+\lambda+\nu\hbar\omega_{eff}\right)^2}{-4\lambda k_B T}}\right]$$

This is called the M-L-J equation. S_{eff} is the effective Huang-Rhys factor, ω_{eff} is the frequency of the effective mode.

Structural considerations

When the method to calculate the characteristics of the CS state is established new acceptor molecules are investigated. Concerning the donor polymer we will restrict ourselves by using primarily P3HT, MEH-PPV and Si-PCPDTBT.[3,28]

P3HT   MEH-PPV   Si-PCPDTBT
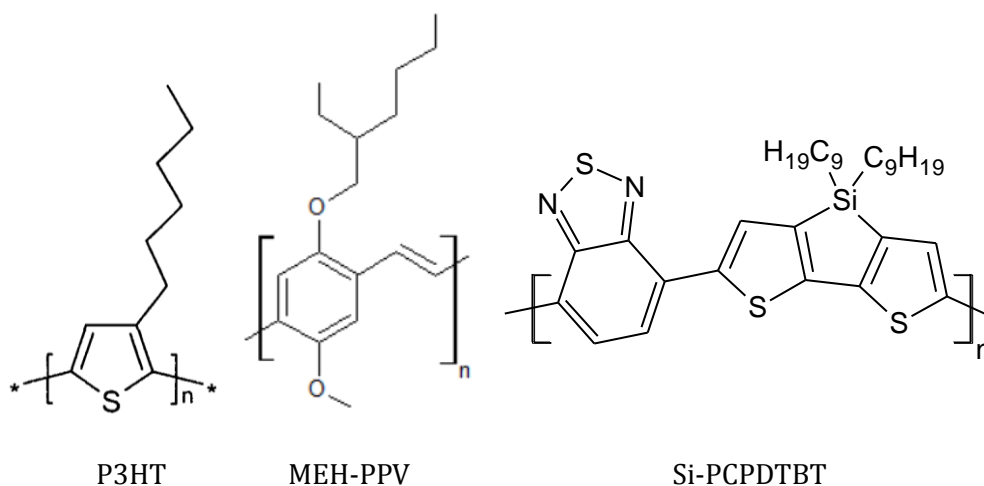
For the acceptor molecules we distinguish three classes: fullerene derivatives, single molecule acceptors and polymers. The first molecules to focus on after C_{60} are PDI and derivatives.[3,25] PDI (perylene diimide) based acceptors are one of the groups that have the highest efficiency. There are both single molecule and polymer variants. They are especially well-known for their wide absorption range extending into the near-IR region.[3]

PDI	diPDI	P(PDI2DD-DTT)
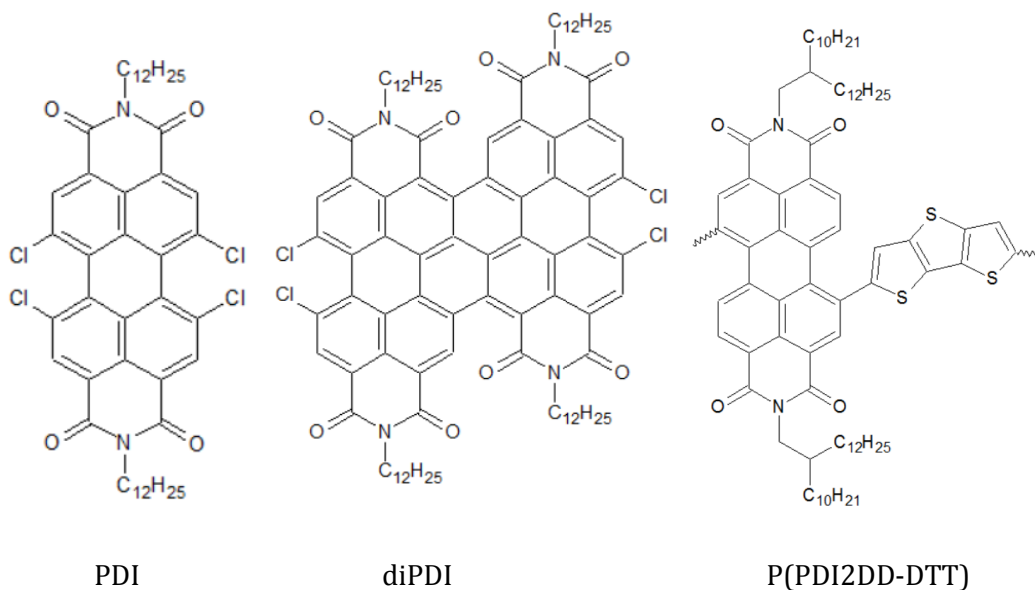
Afterwards other acceptor molecules will be designed dependent on the obtained results and the available literature at that time (for example porphyrine[26] or fluorene based structures). Some molecules have long alkane side-chains and we plan to interchange them with more polar side chains to increase the dielectric constant. Dipole chains lower the Coulomb attraction between holes and electrons facilitating a better charge separation. [AA] When supported by good results from the literature it is also possible to look at single D-A copolymers.[27] In the end we can compare a whole set of electron acceptors and make a well-documented advice for new electron acceptors and how to go further towards the optimal solar cell.

10.6 Plan of work

Year		Activities
1: 2015	o	Literature study on OPVs
	o	Getting familiar with GROMACS and running first **MD** simulations on P3HT:PCBM. When possible perform a coarse-grained simulation and do a back-mapping to atomistic scale. Try to find an optimal system size and force field.
	o	Test calculations on D-A complexes with ADF (**QC**). Optimize the functional and basissets
	o	Write a small program to obtain the electronic couplings
2: 2016	o	Formulate intermediate conclusions
	o	Perform calculations with proposed acceptor and donor materials and evaluate. (**MD/QC**)
	o	Get acquantained with Kinetic Monte Carlo (**KMC**) simulations
3: 2017	o	Use new acceptor materials. Investigate trends. (**MD/QC/KMC**)
	o	Use **KMC** simulations and try to optimize the system to higher charge mobilities
4: 2018	o	Look if the goals are achieved and work to a conclusion.
	o	Formulate final conclusions
	o	Write thesis

11.   Infrastructure

The main part of the project will be carried out within the *Theoretical Chemistry Group* at the university of Groningen. This group has already a lot of experience in (TD-)DFT calculations and has licenses on the needed software packages. (ADF or GAMESS-UK)

The classical modeling will be performed in strong collaboration with the *Molecular Dynamics group* of Prof. S.J. Marrink. Within this group a wide variety of MD programs is available.

Both research groups have access to supercomputer facilities. It is tried to get funding for computation time on supercomputers of the USA or on the Dutch supercomputers facilitated by eScience.

The Kinetic Monte Carlo model is recently developed by the group of L.J.A. Koster and so the simulations are performed in strong collaborations with this group.

Within our faculty there is also an experimental group working on OPVs of J.C. Hummelen, *Chemistry of (bio)Molecular Materials and Devices.* Hence there is good communication with the experimental side.

12.   Application perspective in industry, other disciplines or society

The project aims to deepen the understanding of charge transfer in OPVs and proposing a new route towards design of electron acceptors. In the end this can lead to high PCE BHJ OPVs. Moreover the new multi-scale methodology will give us new insight in the connection between several steps of the working mechanism. This methodology is interesting for any kind of industry concerning the molecular design of electronic devices.

13.   FOM subfield classification

NANO

14.   References

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