

1st period results

Comparing alternating and statistical copolymers: The influence of charge transport on the performance of polymer solar cells

Theoretical Background

Dissociation of excitons at the donor/acceptor heterojunction is the crucial process in most organic solar cells. For polymer solar cells it has been shown that the rate for the dissociation of polaron pairs is field-dependent and that the short-circuit current is largely determined by the competition between dissociation and recombination [1,2]. Several theoretical investigations of the dissociation mechanism predict important correlations between microscopic material properties and dissociation efficiency determining mostly the device performance and efficiency.

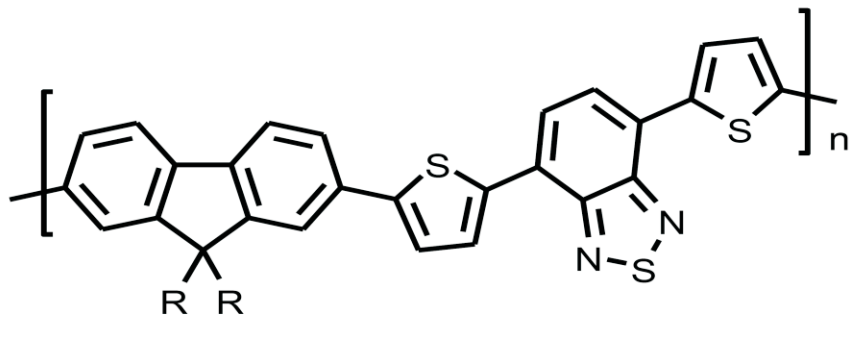
Recent Monte-Carlo simulations predicted two important effects:

- a strong increase in free charge carrier yield for increased energetic disorder [3,4]
- imbalance of mobilities is beneficial for free carrier formation [5,6]

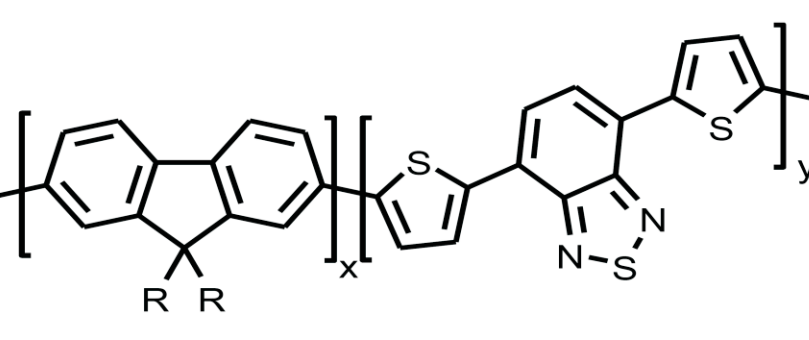
Aims of this project:

- synthesis and characterisation of acceptor polymers with differences in *energetic disorder* and *mobility* ✓

alternating PFTBTT



statistical PFTBTT (y% TBTT)

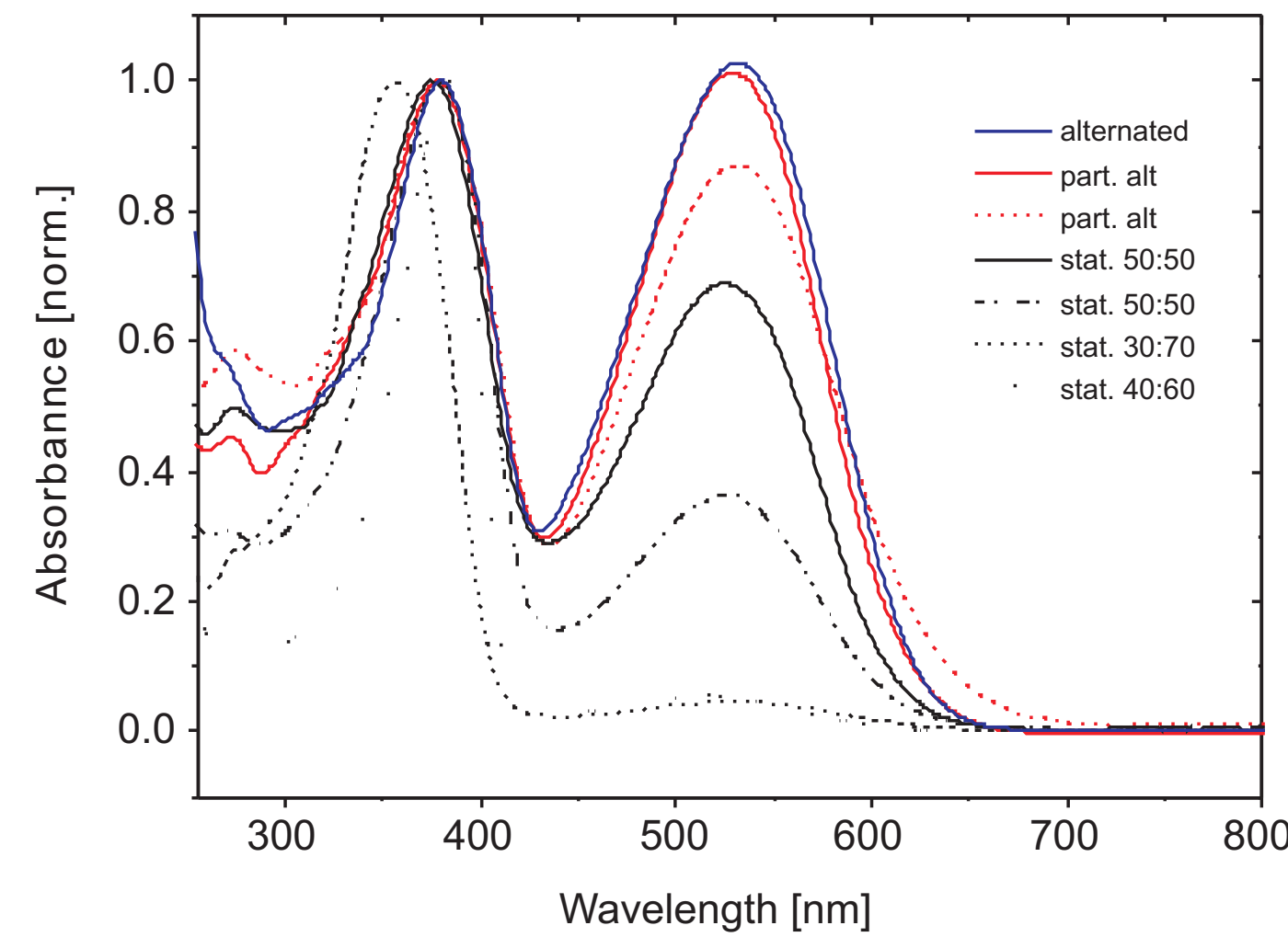


- analysis of the transport properties ✓ (t.b.c.)
- measurement and analysis of bilayer solar cells ✓
- analysis of charge recombination in organic solar cells with the help of the Photo-CELIV technique ✓
- influence of additives on the performance of BHJ-SC ✗ (see proposed work)

*More details about UPS results can be found in the proposal of Prof. N. Koch

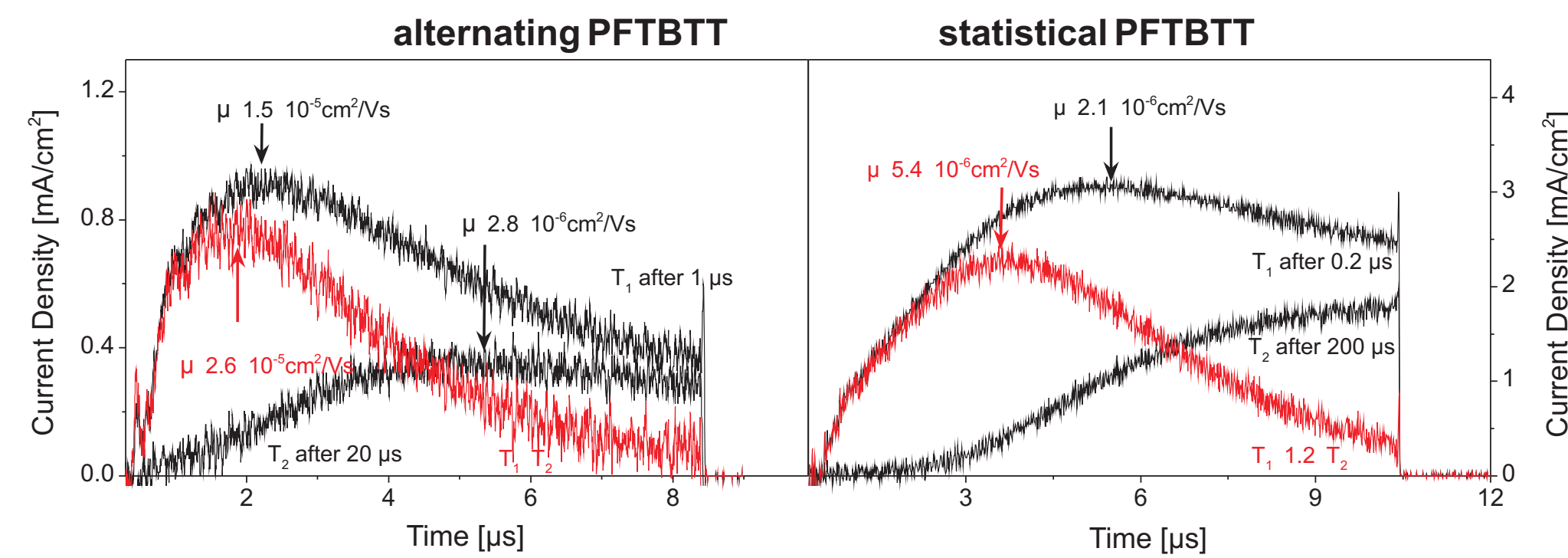
Synthesis and Material Properties

PFTBTT has been synthesized as alternating as well as statistical and partially alternating Copolymer with varying TBTT content and side chains.



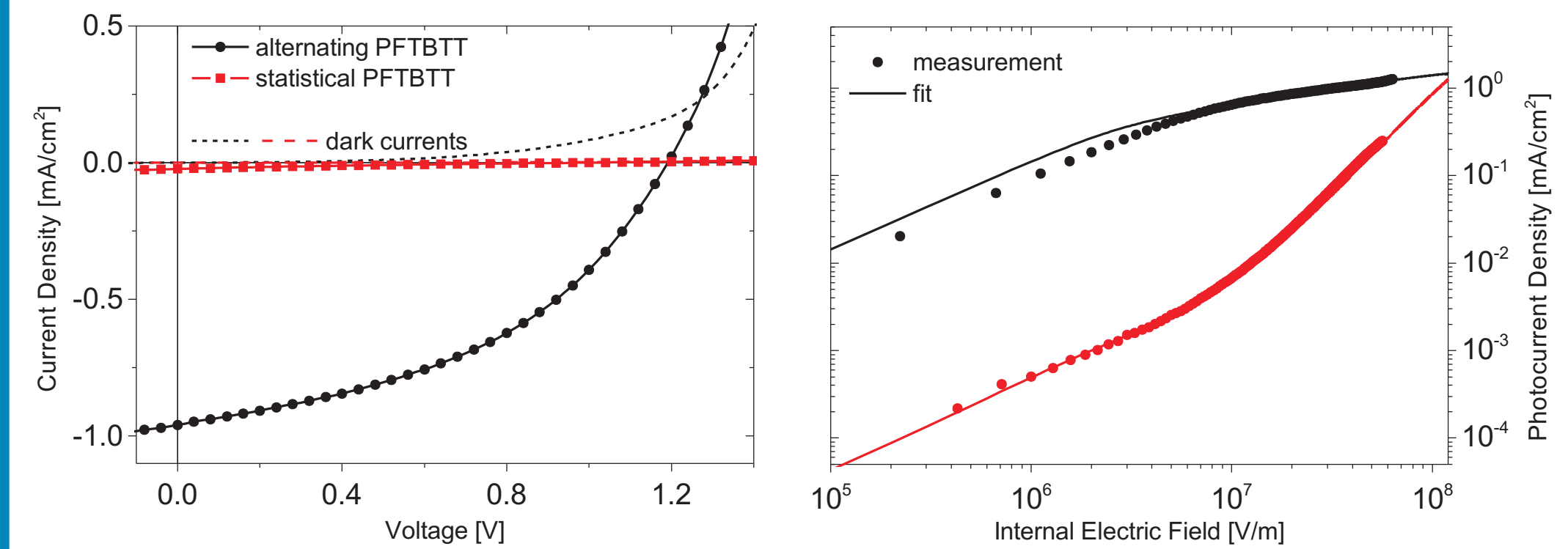
- Compared to alternating PFTBTT, statistical PFTBTT shows:
- similar optical bandgap, HOMO and LUMO values*
 - weaker relative absorption due to smaller TBTT content
 - smaller mobility (about one order)

Charge Transport - Photo-CELIV and Single Carrier Devices



- Mobility of the statistical PFTBTT is about one order smaller compared to alternating PFTBTT, which we assign to a larger degree of energetic disorder.
- Photo-CELIV and single carrier measurements suggest that electron-transport is in part controlled by traps, in agreement to studies by McNeill et al. on a related polymer [7].

Bilayer Solar Cells - Results and Modelling



Bilayer solar cells have been prepared by the so called interlayer approach [2], using P3HT as the electron-donating polymer. The electronic structure and morphology of these cells have intensively been studied by N. Koch et al. The solar cell characteristics reveal remarkable poorer solar cell performance for the statistical copolymers, with a completely different field dependence of generation efficiency. Intensity-dependent measurements showed no evidence for space-charge effects or bimolecular recombination.

side chains	alternating PFTBTT				statistical PFTBTT				
	V _{oc} [V]	FF [%]	J _{sc} [mA/cm ²]	max [%]	V _{oc} [V]	FF [%]	J _{sc} [mA/cm ²]	max [%]	
octyl	1.1	27	0.2	0.06	0.99	27	0.09	0.02	as prep.
	1.2	44	1	0.5	0.71	35	0.22	0.06	ann.
ethylhexyl	1.2	29	0.32	0.1	0.88	24	0.01	<0.01	
	1.2	28	0.47	0.2	0.89	20	0.05	0.01	
farnesyl					0.7	25	0.01	<0.01	
					0.8	21	0.04	<0.01	
octyldecyl	1.1	31	0.19	0.07					
	1.1	41	0.24	0.11					

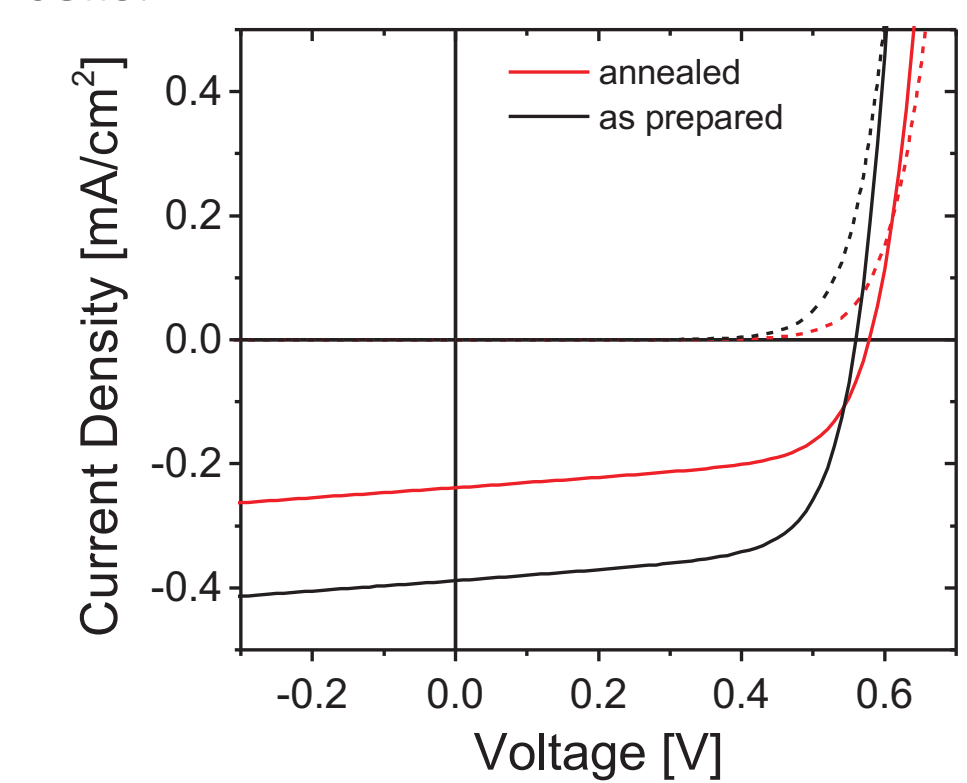
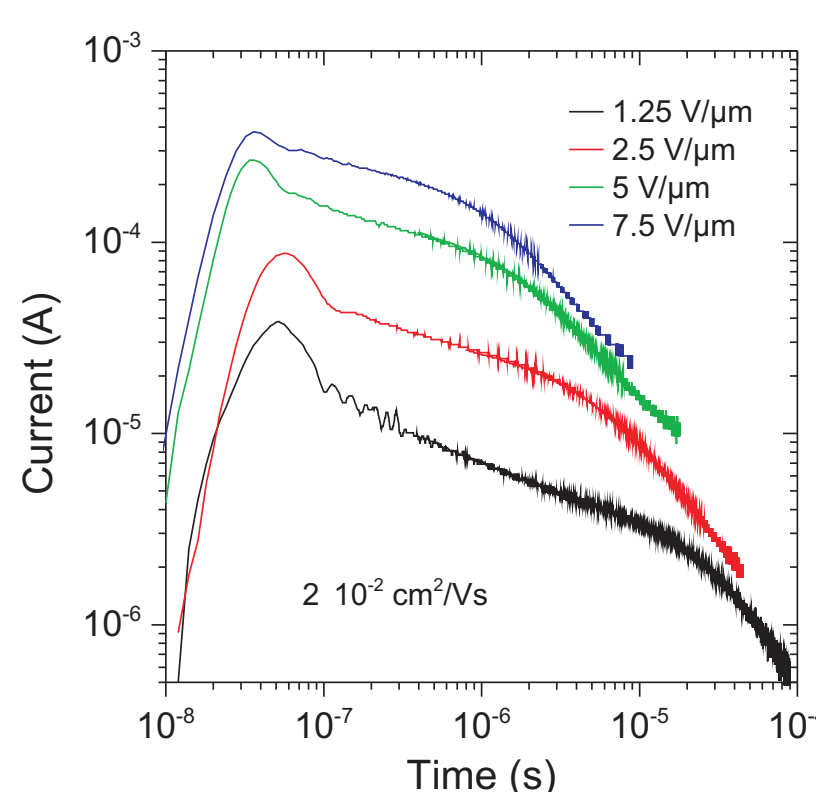
Conclusions

- Despite the chemically, optically and energetically comparable properties of the statistical and alternating PFTBTT, the solar cell characteristics show remarkable differences
- Increasing structural disorder along the polymer chain and the imbalance between electron and hole mobility impairs the solar cell performance, contrary to theoretical forecast
- A high mobility in the electron accepting phase seems to be crucial for efficient charge dissociation

preliminary work

High Mobility Electron Acceptors for Organic Solar Cells

The commercially available electron transporting polymer P(NDI2OD-T2) [8] shows remarkably high electron mobilities in TOF and single carrier measurements [P3]. The low lying LUMO and small optical bandgap make this material a promising acceptor material for all-polymer solar cells.



The combination of P3HT (donor) and P(NDI2OD-T2) (acceptor) yields all-polymer solar cells with very high fill factors of up to 66% but only very moderate quantum and energy conversion efficiencies.

The results suggest that high fill factors can be achieved in all-polymer solar cells when using high mobility electron-transporting polymers. However, the morphology and/or the electronic structure of the blend is far from optimum with regard to solar cell efficiency.

Aims of Proposed Work

Synthesis of novel acceptor polymers with high mobility and suitable energetic properties. Investigation and optimization of transport and optical properties of the electron-transporting phase in binary and ternary blends.

proposed work

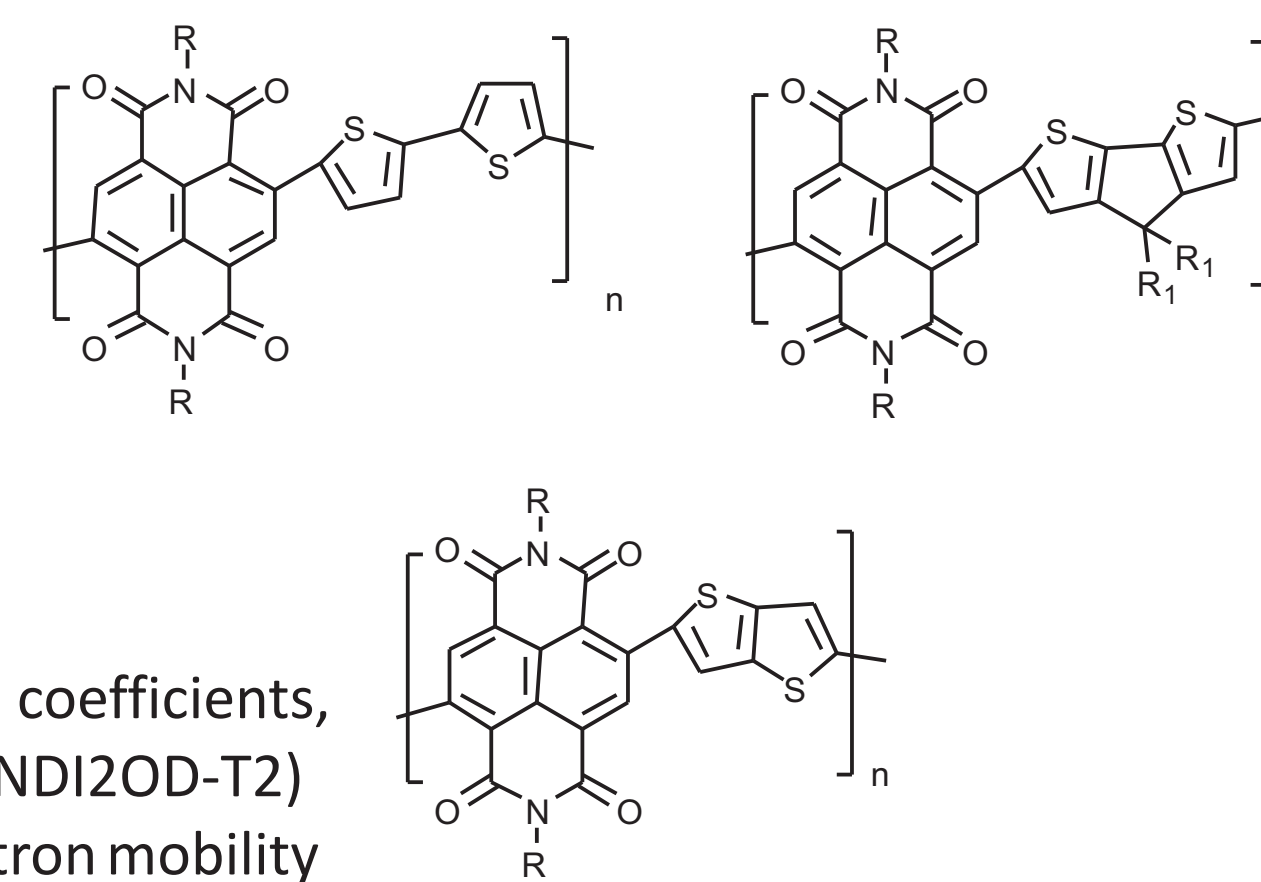
The work of the second period aims at the synthesis of new acceptor polymers, the optimization of the properties of the electron-transporting phase and the improvement of nanoscale morphology in polymer solar cells.

Synthesis of Acceptor Polymers with Improved Electron Mobility

Taking into account the results of the first period and the recent findings presented in the preliminary work, we suggest that a further increase of the efficiency of all-polymer solar cells is only possible when electron acceptors with increased charge transport capabilities are used. Based on high mobility electron transporting polymers containing naphthalene or perylene units [8, 9], we envisaged the following structures to be synthesized by the Scherf group.

The advantages of the new polymers might be:

- an optimized matching of energy levels between donors (mainly P3HT or M3EH-PPV) and the new acceptors
- improved absorption coefficients, which are quite low in P(NDI2OD-T2)
- further increased electron mobility



Once a promising acceptor polymer with sufficiently high mobility has been found, the morphology of bulk-heterojunction solar cells will be optimized.

Tuning of the Charge Transporting Properties of the Electron Accepting Phase

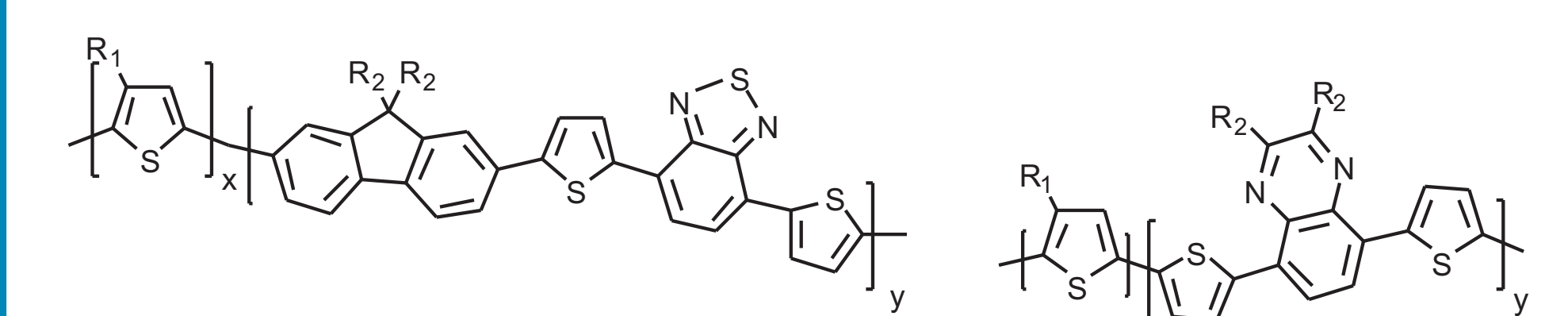
Optimized charge transport in current polymer/fullerene solar cells requires a high content of weakly-absorbing fullerenes. Optimum charge transport and absorption properties of the electron accepting phase while reducing the fullerene content shall be achievable in ternary blends with high mobility electron transporting polymers.

P(NDI2OD-T2) shows a low-lying LUMO of about 4.0 eV which matches perfectly the LUMO of PCBM. Further finetuning of the electronic structure in the newly synthesized polymers may further increase solar cell efficiency.

Influence of Additives on the Blend Morphology

Recently, the Scherf group has explored rigid-rod-type block copolymers as a unique and up to now unknown class of block copolymer materials, which form characteristic aggregate structures during their solution processing from non-selective or selective organic solvents. In the next period, we will produce donor/acceptor diblock copolymers that really mimic the chemical structures of the polymer compounds of our polymer/polymer blends investigated during the first period (P3HT/PFTBTT). These copolymers will be used as compatibilizers in the polymer/polymer blends.

Subsequently, the influence of the additives on the morphology of the blends will be investigated by AFM, both in amplitude and phase mode for as-prepared layers as well as for layers after annealing. For selected blends, solar cells will be prepared and their photovoltaic and structural properties will be investigated.



Cooperations and Foreign Contacts

Work in this project will be performed in close relation to studies proposed by Prof. Dr. Norbert Koch (HU Berlin) in the same priority program.

Within the synthesis of the naphthalenebisimide-based polymers we will cooperate with Dr. Udom Asawapirom, National Nanotechnology Center, Pathumthani, Thailand.

References

- [1] Mandoc, M.M. et al., *Adv. Funct. Mater.* **17** (13), 2167 (2007)
- [2] Yin, C. et al., *Applied Physics Letters* **90** (13), 133502 (2007)
- [3] Offerman, T. et al., *Chemical Physics* **308**, 125 (2005)
- [4] Rubel, O. et al., *Physical Review Letters* **100**, 196602 (2008)
- [5] Peumans, P. et al., *Chemical Physics Letters*, **398**, 27 (2004)
- [6] Marsh, R.A. et al., *Journal of Applied Physics* **101** (8), 083509 (2007)
- [7] C.R. McNeill and N. C. Greenham, *Applied Physics Letters* **93**, 203310 (2008)
- [8] Yan, H., et al., *Nature* **457**, 679 (2009)
- [9] Piyakulawat, P., et al., *Synthetic Metals* **159**, 467 (2009)

Publications Originating from the Project

- [P1] M. Schubert, R. Steyrluthner, S. Bange, A. Sellinger, D. Neher, "Charge transport and recombination in bulk heterojunction solar cells containing a dicyanimidazole-based molecular acceptor", *Physica Status Solidi A*, DOI 10.1002/pssa.200925312 (2009)
- [P2] S. Bange, M. Schubert, D. Neher, "Charge mobility determination by current extraction under linear increasing voltages: the case of non-equilibrium charges and field-dependent mobilities", submitted to *Physical Review B*
- [P3] R. Steyrluthner, M. Schubert, F. Jaiser, Z. Chen, A. Faccetti, D. Neher, manuscript in preparation