

Cite this: *J. Mater. Chem.*, 2012, **22**, 10971

www.rsc.org/materials

HIGHLIGHT

Challenges for *in silico* design of organic semiconductors

Björn Baumeier,^{*a} Falk May,^{*a} Christian Lennartz^{*b} and Denis Andrienko^{*a}

DOI: 10.1039/c2jm30182b

We outline the objectives of microscopic simulations of charge and energy transport processes in amorphous organic semiconductors, describe the current status of techniques used to achieve them, and list the challenges such methods face when aiming at quantitative predictions.

I. Introduction

Interest in the field of organic electronics is largely provoked by the possibility of fine-tuning properties of organic semiconductors by varying their chemical structure.^{1–4} Often, compound design is

solely guided by chemical intuition, even though material development would benefit from more rigorous structure–properties relationships, which link the chemical structure, material morphology and macroscopic properties. To formulate such relationships, an understanding of the physical processes occurring on a microscopic level as well as the development of methods capable of scaling these up to macroscopic dimensions are required. The aim of computer simulations is to facilitate this by zooming in on the behavior of electrons and molecules and by bridging micro-

and macroscopic worlds. Here, we describe the current status of methods which allow the linking of molecular electronic structure and material morphology to the mesoscopic/microscopic dynamics of charge carriers and excitons. Special attention is paid to the challenges these methods face when aiming at quantitative predictions. Although the focus is on the design of host–guest systems for phosphorescent organic light emitting diodes, the techniques can be readily extended to study processes occurring in organic solar cells or field effect transistors.

^aMax Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany. E-mail: baumeier@mpip-mainz.mpg.de; falk.may@mpip-mainz.mpg.de; denis.andrienko@mpip-mainz.mpg.de

^bBASF SE, GVE/IM - B009, 67056 Ludwigshafen, Germany. E-mail: christian.lennartz@basf.com



Björn Baumeier

Björn Baumeier is a postdoctoral research fellow at the Max Planck Institute for Polymer Research. His research focus is on first-principles calculations of ground and excited state properties relevant for transport simulations. He obtained his Diploma and PhD in solid state physics from the University of Münster, Germany, working in the group of Prof. J. Pollmann on self-interaction corrections to density-functional theory for low-dimensional semiconductors

and insulators. Supported by a postdoctoral stipend of the German Academic Exchange Service, Dr Baumeier joined Prof. A. Maradudin at the University of California, Irvine to study scattering effects of surface-plasmon polariton on surface defects, including the design of surface structures generating a target scattering pattern, such as a cloak from these type of surface waves.



Falk May

Falk May is a PhD candidate at the Max Planck Institute for Polymer Research working on molecular dynamics simulations and the calculation of charge transfer rates with a focus on energy landscapes and reorganization energy in organic semiconductors. He obtained his Physics Diploma from Goethe University of Frankfurt am Main. There he applied numerical renormalization group techniques to study the influence of spin-vibration coupling on

transport through single molecule magnets at low temperatures in the group of Prof. W. Hofstetter in collaboration with Prof. M. R. Wegewijs from RWTH Aachen.

Organic light emitting diodes (OLEDs) have recently entered the market of flat panel displays and lighting applications.^{5,6} In spite of successful commercialization, the field still faces a number of problems, such as insufficient stability,⁷ especially of diodes which are based on deep blue emitters.^{8,9} Fig. 1a shows a simplified multilayered structure of a phosphorescent OLED, in which every layer bears a certain task. Electrons and holes are injected from electrodes into transport layers, which ensure their balanced delivery to an emission layer (EML). Blocking layers confine charge carriers to the EML where charges are converted into photons. To allow for triplet-harvesting, the EML consists of an organic semiconductor (host) doped by an organo-metallic emitter (guest). The excitation of the emitter can be achieved either by an energy transfer process, *i.e.* by the formation of an exciton on a host molecule and subsequent energy transfer to the dopant, or by a direct charge transfer process. Here, one of the charge carriers is trapped on the emitter and attracts a charge of the opposite sign forming a neutral exciton on-site, which is argued to lead to more efficient OLEDs than the excitation by energy transfer.^{10–13}

Fig. 1b shows the level alignment in an OLED with an electron-conducting host and a hole-conducting emitter. A large barrier, Δ_{h} , between hole transport levels

prevents hole transfer (1) from emitter to host. Electron transfer (2) to the neutral emitter is inhibited by the barrier Δ_{e} . In order to ensure exciton formation on the emitter, the Coulomb attraction between the hole on the emitter and the electron on the neighboring host should be capable of overcoming Δ_{e} , thus attracting the electron to the emitter cation. The back-transfer (3) of the exciton from the emitter to the host is prevented by the barrier Δ_{t} for triplet excitons. The light is emitted after the electron-hole recombination on the emitter (4).

Thus, the task of the *in silico* compound design is to achieve a desirable charge/energy transport dynamics within the EML, considering the interplay between molecular electronic structure, morphological order, and thermodynamic properties, such as the relative alignment of transport/excited state energy levels of the host and guest. This task turns out to be rather cumbersome to accomplish and requires elaborate computational schemes, whose ingredients are pictorially summarized in Fig. 2.

To begin with, every molecule has its own unique environment created by its neighbors, with local electric fields leading to level shifts, broadening, and spatial correlations of charge/exciton energies. Accounting for such effects requires the knowledge of the material morphology at an atomic resolution (see sec. II).

Furthermore, typical time scales of dynamic processes, such as charge and energy transfer, span several orders of magnitude. Hence, treatment of the charge/exciton kinetics cannot be achieved with numerical methods using a fixed time step. Instead, a description based on hopping rates between localized states shall be employed. To evaluate the rates, one has to justify the use of a particular charge (energy) transfer theory (see sec. III), determine localized states, and compute all the ingredients which enter the rate expression, including intra- and intermolecular reorganization energies (see sec. IV), electronic coupling elements (see sec. V), and electrostatic and polarization contributions to site energies (see sec. VI). Analyzing charge and exciton dynamics (see secs VII and VIII) thus provides understanding of the microscopic processes and allows for the formulation of chemical design rules. Last, but not least, these also have to account for a material's processability, as well as its chemical and morphological stability.

II. Material morphology

All layers of small-molecule based OLEDs are vacuum-deposited on a substrate with transparent electrodes. In case of the EML, deposition normally results in an amorphous morphology of



Christian Lennartz

*Christian Lennartz is a team leader at BASF SE Ludwigshafen, dealing with modeling of organic electronics at various scales. He is a quantum chemist by training and received his PhD from the University of Bonn, working with *ab initio* calculations in the field of porous silicon and organic reaction mechanisms. After a postdoctoral stay at BASF SE Ludwigshafen in the field of QM/MM-methods for enzyme catalysis he joined BASF SE as permanent staff.*

His main research interests are photophysics of phosphorescent molecules and charge and exciton transport in organic semiconductors. He is co-author of forty patents and thirty journal articles.



Denis Andrienko

Denis Andrienko is a project leader at the Max Planck Institute for Polymer Research working on the development of multiscale simulation techniques for charge and exciton transport in conjugated polymers as well as small molecular weight organic semiconductors. After completing his Masters degree at the University of Kiev he obtained his first PhD in optics/structural transitions in liquid crystals from the Institute of Physics, Ukraine (group of Prof. Reznikov) and his second PhD on computer simulations of complex fluids from the University of Bristol, UK (group of Prof. M. P. Allen). He joined MPIP as a Humboldt Fellow doing theoretical studies of the slippage effect, mechanical properties of polyelectrolyte microcapsules, and effective interactions in colloidal systems. Dr Andrienko has published over seventy journal articles and one book chapter.

Prof. Reznikov) and his second PhD on computer simulations of complex fluids from the University of Bristol, UK (group of Prof. M. P. Allen). He joined MPIP as a Humboldt Fellow doing theoretical studies of the slippage effect, mechanical properties of polyelectrolyte microcapsules, and effective interactions in colloidal systems. Dr Andrienko has published over seventy journal articles and one book chapter.

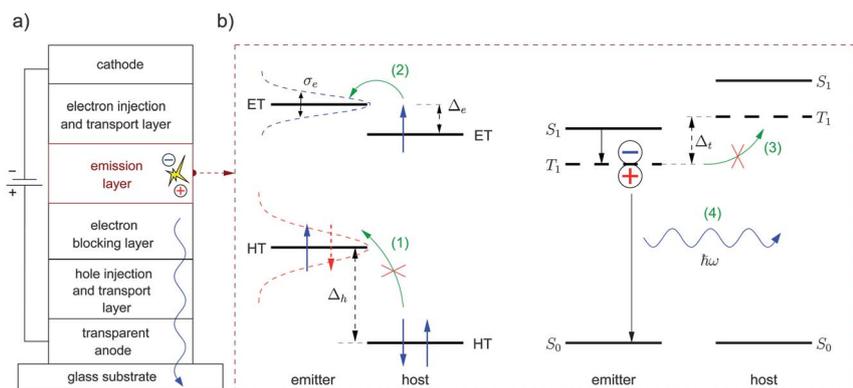


Fig. 1 Multilayered structure of a phosphorescent OLED with an electron-conducting host and a hole-conducting emitter. Relative alignment of hole (HT) and electron (ET) transport levels of emitter and host and their broadening (indicated for the emitter only) due to polarization and electrostatic effects are shown together with energy levels of singlets (S) and triplets (T) of the emitter emission spectrum and the host excitation spectrum.

a host with a small amount of guest molecules (5–20% w/w, to avoid triplet–triplet quenching due to aggregation, double excitations, or transfers to higher energy vibrational modes^{7,14}). In simulations, the preparation of an amorphous morphology of the EML can, to some extent, be mimicked by first annealing the host–guest mixture above the glass transition and subsequently quenching it to room temperature. This procedure, however, completely randomizes the positions and orientations of guest molecules in the host.

To account for possible aggregation of guest molecules during the deposition,

one can simulate the gradual adsorption of molecules on a substrate, either by using Monte Carlo moves and treating molecules as rigid rotors¹⁵ or by employing molecular dynamics and sublimating molecules at high temperatures.¹⁶ The drawback of the first method is that the molecular conformations are always fixed, while the second method is limited to microsecond simulation times, which might be too short to fully relax positions and orientations of adsorbed molecules.¹⁷

All of these techniques use force fields, with atoms represented by point masses interacting *via* empirical potentials. In most cases potential energy surfaces of

the existing force fields must be refined for new compounds, which can be done by matching certain cross-sections of the force-field and *ab initio* based potential energy surfaces.¹⁸ Note that the force field validation is as important as its refinement. Here, simulation results can be compared to experimental data, *e.g.*, density and glass-transition temperature. On a microscopic level, X-ray scattering and solid-state NMR can additionally provide information about averaged molecular arrangements.^{19–22}

Due to material processing (vacuum deposition of small molecules or solution processing of polymers), the EML morphology can have several characteristic length scales and can be kinetically arrested in a thermodynamically non-equilibrium state. In such cases more coarse representations might be helpful to overcome the limitations of atomistic models.^{23,24} It is, however, not clear whether coarse-grained models can deal with non-equilibrium morphologies, since they tend to reduce energy dissipation.²⁵

III. Charge transfer rates

In an amorphous morphology of OLED layers, electronic couplings between neighboring molecules are weak and hence charges are localized on entire molecules. Intermolecular charge transfer ($M_A^- + M_B \rightarrow M_A + M_B^-$) then occurs between these localized (diabatic) states of the charge transfer complex. In Gaussian Disorder Models (GDM),^{26–29} a distance-dependent Arrhenius-type rate expression is adopted and thermodynamic parameters are Gaussian distributed. Although GDM are computationally very efficient, help to get insight into various scaling laws,²⁹ and are capable of simulating multilayered devices,^{30,31} they are missing a direct link to the chemical structure and the morphology. More rigorously, electron transfer theories can be used to evaluate rates from quantum-chemical calculations.^{32–36} This quantum-chemical approach is by now routinely used to study charge transport in amorphous and partially disordered organic semiconductors.^{15,19,20,34,37–46}

The ingredients entering the corresponding charge transfer rate expression are reorganization energy, electronic coupling elements (transfer integrals) and

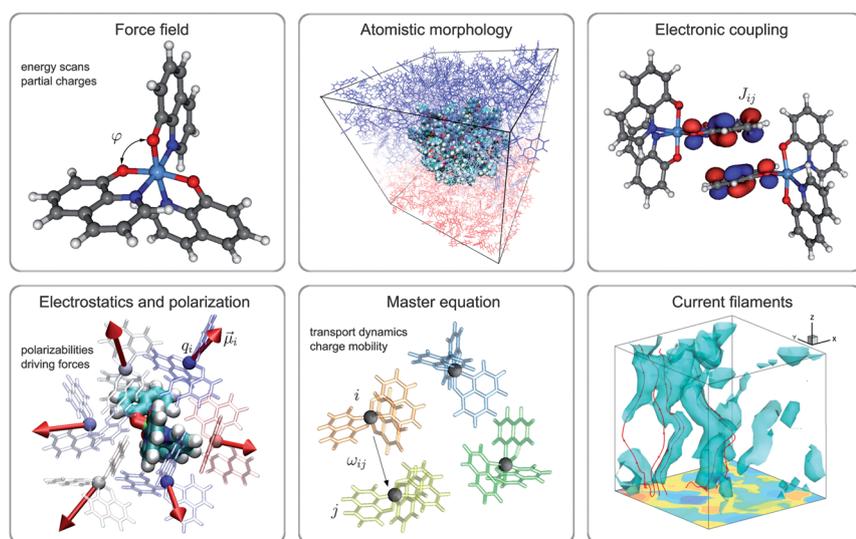


Fig. 2 Essential ingredients of microscopic simulations of charge/energy transport processes in organic semiconductors: atomistic force field, morphology at an atomistic level of resolution, electronic coupling elements between localized states, site energies due to electrostatics and polarization, directed graph and charge transfer rates, microscopic currents.

site-energy differences (driving forces). All these ingredients can be evaluated using electronic structure techniques, classical simulation methods, or their combination¹⁸ as described in the following.

IV. Reorganization energy

The reorganization energy takes into account the change in nuclear (and dielectric) degrees of freedom as the charge moves between two diabatic states. It has two contributions: intramolecular which is due to the change in nuclear coordinates of the charge transfer complex, and intermolecular (outer-sphere), which is due to the relaxation of the environment.⁴⁷ The intramolecular contribution can be computed from the potential energy surfaces of the involved diabatic states or from a normal mode analysis both using *ab initio* gas phase calculations.⁴⁸

The non-local outer-sphere contribution is especially important to determine rates between sites with large site energy differences, *e.g.* escape rates from deep traps.¹⁸ Due to its non-locality, a microscopic evaluation is computationally demanding and could be based on the dielectric response^{18,47} polarizable force fields,⁴⁹ or hybrid quantum mechanics/molecular mechanics approaches.⁵⁰

V. Transfer integrals

The transfer integral entering the charge transfer rate is a measure of strength of the electronic coupling of the charge in initial and final states within the charge transfer complex. It is usually evaluated using an effective single particle Hamiltonian and by representing the charge by the respective frontier orbitals of monomers, *i.e.*, the highest occupied molecular orbital in case of hole transport, and the lowest unoccupied molecular orbital in the case of electron transfer. The distance and mutual orientation of the two molecules forming the charge transfer complex sensitively affects the transfer integral, which is therefore significantly influenced by static and/or dynamic disorder, or, *e.g.*, preferential packing motifs in molecular crystals.^{40,42,43,51–53}

Within a realistic morphology of an organic semiconductor, it is essential to calculate electronic coupling explicitly for

each hopping pair. Since even moderately sized simulations contain several 10,000s of dimers, it is important to develop efficient and at the same time quantitatively reliable computational schemes. Here, semiempirical methods are often used, since they are substantially faster than first-principles approaches by avoiding the self-consistent calculations on each individual monomer and dimer.³⁶ While providing an efficient on-the-fly technique to determine electronic couplings, they are not generally applicable to more complex compounds, for instance containing transition- or semi-metals, and approaches based on first-principles, *e.g.*, density-functional theory need to be used.^{35,54,55} Hence, explicit quantum-chemical calculations are required for every molecule and hopping pair in the morphology and the evaluation of transfer integrals becomes computationally demanding and often limits treatable system sizes.

VI. Site energies

The site energy is the free energy of the system with a charge carrier localized on a specific molecule.⁴⁷ It is comprised of the internal energy of the molecule and interactions of its charge distribution with the environment. The GDM, for instance, predicts²⁷ that the mobility of a single carrier is very sensitive to the distribution of site energies (density of states, DOS), especially its tails,²⁸ and an accurate evaluation of site energies is necessary for quantitative predictions.

The internal energy (ionization potential or electron affinity) can be obtained by using first-principles calculations on a single molecule in vacuum. It provides a first reference for the barriers $\Delta_{h(e)}$ between hole (HT) or electron (ET) transport levels in the EML, as shown in Fig. 1. Note that different molecular conformations due to structural effects in the bulk can already lead to broadening and shifts of these levels.¹⁸

Electrostatic contributions due to interactions with the environment can be modeled on a macroscopic scale by using continuum solvation models,^{56,57} where the interaction of the molecule with a surrounding homogeneous dielectric leads to stabilization of the respective transport levels which can affect the

barriers but does not lead to broadening of the DOS.

The level broadening and spatial correlations of site energies⁵⁸ can be introduced at a mesoscopic level using lattice models.⁵⁹ Here molecules are reduced to point-like particles with multipoles and isotropic polarizabilities.⁶⁰ Similar to the GDM, these models do not provide a direct link to the morphology and chemical structure.

To remedy the situation, electrostatic interactions can be treated on a microscopic level using realistic morphologies and atomic partial charges which reproduce the electrostatic potential of charged and neutral single molecules. Unscreened Coulomb interactions of partial charges already lead to significant broadening of the transport levels. To a first approximation, the polarization response of the environment can be included by screening Coulomb interactions by the bulk dielectric constant. However, in this case the short-range interactions are underestimated, which can be partially compensated for by using distance dependent screening.^{18,39,56} A more rigorous approach is to evaluate the polarization contribution self-consistently, *e.g.*, by using the Thole model.⁶¹ Often, atomic polarizabilities need to be adjusted to reproduce the polarizability tensors of charged and neutral single molecules obtained from *ab initio* calculations. Even though this approach is computationally demanding, it directly links the chemical structure, molecular electronic properties, and morphology to the energetic landscape. Depending on the morphology, charge distributions, and molecular polarizabilities, including the polarization interaction can lead to barrier changes and to both narrowing or broadening of the DOS, contrary to only narrowing predicted by dielectric screening models.

VII. Charge dynamics

When the positions of molecules and electron transfer rates between them are known, the carrier dynamics can be studied by solving the corresponding master equation, which describes the time-evolution of the system. Here, kinetic Monte Carlo (KMC) is a robust method which allows one to study non-steady-state systems, to take into account

correlations in carrier positions, and to include electrostatic interactions explicitly.^{18,62}

By analyzing KMC trajectories, one can gain insight into the topology of the charge percolation network in terms of its dimensionality or the existence of preferred directions, *e.g.*, in organic crystals. In amorphous mixtures, such as the host-guest system for the EML one can quantify the onset of hole transport in the minority system as a function of its concentration in the mixture. For concentrations which are too low, no connected percolation network in the EML is formed and holes are immobile. On the other hand, formation of current filaments can result in material degradation causing the formation of defects and reducing the luminescence and lifetime of the device.⁷

Special attention should be paid to the averaging over (statistically) independent snapshots, field directions, and injection points, especially in materials with large site energy disorder. In this case, the use of periodic boundary conditions might lead to additional artifacts. For small simulation boxes, the equilibrium energy of a single carrier is (on average) higher than that of an infinitely large system and the charge diffuses at an effectively higher temperature than prescribed by the DOS. This will result in (up to several orders of magnitude) overestimation of mobility. Extrapolation to macroscopic system sizes is possible⁴¹ but requires the knowledge of the temperature dependence of mobility, which is a challenging problem on its own.

Finally, to study carrier concentration effects, a fast evaluation of electrostatic (in particular polarization) interactions is required, since rates become site-occupation dependent and must be updated at every KMC step. While the uniform spacing in lattice-based models³⁰ facilitates efficient explicit treatment of electrostatics, no comparable techniques are currently available for off-lattice KMC algorithms.

VIII. Excited state dynamics

Apart from charge dynamics, processes involving excited states must be included in OLED simulations. An adaptation of the state-based description for excitons is intrinsically challenging due to their

diverse character (strongly-bound Frenkel excitations localized on single molecules, charge-transfer excitons involving a donor-acceptor complex, long-range polaron pairs).

Analogues of diabatic states (energies, wavefunctions) have to be determined for all types of excitations using suitable first-principles descriptions. Accurate quantum-chemical methods, such as coupled-cluster, configuration-interaction are capable of this but come at high computational cost. Time-dependent density-functional theory is less demanding but has problems describing long-range asymptotics of the electron-electron interaction potential,⁶³ affecting charge-transfer states in particular. Range-separated exchange-correlation kernels^{64,65} may be used to overcome this deficiency but need compound-specific adjustments.^{66,67} Here, the many-body Green's functions theory using the *GW* approximation and the Bethe-Salpeter equation^{68,69} is a feasible alternative as it allows for the calculation of energies and wavefunctions of excited states at a required accuracy, while computational demands remain manageable.

For singlet (triplet) exciton dynamics, one can use Förster (Dexter) energy transfer rates or use a more general expression based on the excitonic wave functions.^{70,71} The inclusion of processes such as the conversion between Frenkel and charge-transfer excitons, their recombination, or dissociation into free charges is even more challenging. Finally, the long-range nature of the exchange interaction of singlet excitons will result in a different topology of the directed graph used in KMC simulations (as compared to charge transport), requiring large system sizes.

IX. Outlook

To summarize, the current set of simulation methods provides a good understanding of microscopic charge transport processes occurring in an OLED emission layer, including prediction of the energetic landscape, topological connectivity, site occupations and currents. The remaining challenges which would allow *in silico* design of an OLED, are (i) modelling the aggregation of guest molecules in a host during vacuum deposition, (ii) parametrization of polarizable force

fields for accurate evaluation of outer-sphere reorganization energies and polarization contributions to site energies (beyond isotropic atomic polarizabilities used in the Thole model), (iii) development of off-lattice kinetic Monte Carlo algorithms for multiple charge carriers and explicit treatment of electrostatic interactions, and (iv) inclusion of excited states dynamics, which remains by far the most challenging task.

Acknowledgements

This work was partially supported by the DFG program IRTG 1404, DFG grant SPP 1355, and BMBF grant MES-OMERIE. We are grateful to Mara Jochum, Carl Pölkling and Vorauselender Gehorsam for critical reading of the manuscript.

References

- 1 Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, **107**, 953.
- 2 P. T. Boudreault, A. Najari and M. Leclerc, *Chem. Mater.*, 2010, **23**, 456.
- 3 R. Fitzner, E. Reinold, A. Mishra, E. Mena-Osteritz, H. Ziehlke, C. Körner, K. Leo, M. Riede, M. Weil, O. Tsaryova, A. Weiß, C. Uhrich, M. Pfeiffer and P. Bäuerle, *Adv. Funct. Mater.*, 2011, **21**, 897.
- 4 T. M. Figueira-Duarte and K. Müllen, *Chem. Rev.*, 2011, **111**, 7260.
- 5 S. R. Forrest, *Nature*, 2004, **428**, 911.
- 6 S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, **459**, 234.
- 7 N. C. Giebink, B. W. D'Andrade, M. S. Weaver, J. J. Brown and S. R. Forrest, *J. Appl. Phys.*, 2009, **105**, 124514.
- 8 M. E. Thompson, P. E. Burrows and S. R. Forrest, *Curr. Opin. Solid State Mater. Sci.*, 1999, **4**, 369.
- 9 P. Erk, M. Bold, M. Egen, E. Fuchs, T. Gessner, K. Kahle, C. Lennartz, O. Molt, S. Nord, H. Reichelt, C. Schildknecht, H.-H. Johannes and W. Kowalsky, *Dig. Tech. Pap. - Soc. Inf. Disp. Int. Symp.*, 2006, **37**, 131.
- 10 R. J. Holmes, S. R. Forrest, Y. Tung, R. C. Kwong, J. J. Brown, S. Garon and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **82**, 2422.
- 11 H. Yersin, *Top. Curr. Chem.*, 2004, **241**, 1.
- 12 C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 2001, **79**, 2082.
- 13 R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **83**, 3818.
- 14 Y. Divayana and X. W. Sun, *Phys. Rev. Lett.*, 2007, **99**, 143003.

- 15 J. J. Kwiatkowski, J. Nelson, H. Li, J. L. Brédas, W. Wenzel and C. Lennartz, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1852.
- 16 L. Muccioli, G. D'Avino and C. Zannoni, *Adv. Mater.*, 2011, **23**, 4532.
- 17 P. Clancy, *Chem. Mater.*, 2011, **23**, 522.
- 18 V. Rühle, A. Lukyanov, F. May, M. Schrader, T. Vehoff, J. Kirkpatrick, B. Baumeier and D. Andrienko, *J. Chem. Theory Comput.*, 2011, **7**, 3335.
- 19 V. Marcon, D. W. Breiby, W. Pisula, J. Dahl, J. Kirkpatrick, S. Patwardhan, F. Grozema and D. Andrienko, *J. Am. Chem. Soc.*, 2009, **131**, 11426.
- 20 X. Feng, V. Marcon, W. Pisula, M. R. Hansen, J. Kirkpatrick, F. Grozema, D. Andrienko, K. Kremer and K. Müllen, *Nat. Mater.*, 2009, **8**, 421.
- 21 F. May, V. Marcon, M. R. Hansen, F. Grozema and D. Andrienko, *J. Mater. Chem.*, 2011, **21**, 9538.
- 22 V. Marcon, T. Vehoff, J. Kirkpatrick, C. Jeong, D. Y. Yoon, K. Kremer and D. Andrienko, *J. Chem. Phys.*, 2008, **129**, 094505.
- 23 V. Rühle, C. Junghans, A. Lukyanov, K. Kremer and D. Andrienko, *J. Chem. Theory Comput.*, 2009, **5**, 3211.
- 24 D. M. Huang, R. Faller, K. Do and A. J. Moulé, *J. Chem. Theory Comput.*, 2010, **6**, 526.
- 25 D. Fritz, K. Koschke, V. A. Harmandaris, N. F. A. van der Vegt and K. Kremer, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10412.
- 26 A. B. Walker, A. Kambili and S. J. Martin, *J. Phys.: Condens. Matter*, 2002, **14**, 9825.
- 27 H. Bässler, *Phys. Status Solidi B*, 1993, **175**, 15.
- 28 P. M. Borsenberger, L. Pautmeier and H. Bässler, *J. Chem. Phys.*, 1991, **94**, 5447.
- 29 W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw and M. A. J. Michels, *Phys. Rev. Lett.*, 2005, **94**, 206601.
- 30 J. J. M. van der Holst, F. W. A. van Oost, R. Coehoorn and P. A. Bobbert, *Phys. Rev. B*, 2011, **83**, 085206.
- 31 Y. Yimer, P. Bobbert and R. Coehoorn, *Synth. Met.*, 2009, **159**, 2399.
- 32 J. Brédas, J. E. Norton, J. Cornil and V. Coropceanu, *Acc. Chem. Res.*, 2009, **42**, 1691.
- 33 V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J. Brédas, *Chem. Rev.*, 2007, **107**, 926.
- 34 J. Nelson, J. J. Kwiatkowski, J. Kirkpatrick and J. M. Frost, *Acc. Chem. Res.*, 2009, **42**, 1768.
- 35 B. Baumeier, J. Kirkpatrick and D. Andrienko, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11103.
- 36 J. Kirkpatrick, *Int. J. Quantum Chem.*, 2008, **108**, 51.
- 37 Y. Olivier, L. Muccioli, V. Lemaure, Y. H. Geerts, C. Zannoni and J. Cornil, *J. Phys. Chem. B*, 2009, **113**, 14102.
- 38 E. Di Donato, R. P. Fornari, S. Di Motta, Y. Li, Z. Wang and F. Negri, *J. Phys. Chem. B*, 2010, **114**, 5327.
- 39 Y. Nagata and C. Lennartz, *J. Chem. Phys.*, 2008, **129**, 034709.
- 40 J. Kirkpatrick, V. Marcon, K. Kremer, J. Nelson and D. Andrienko, *J. Chem. Phys.*, 2008, **129**, 094506.
- 41 A. Lukyanov and D. Andrienko, *Phys. Rev. B*, 2010, **82**, 193202.
- 42 T. Vehoff, B. Baumeier and D. Andrienko, *J. Chem. Phys.*, 2010, **133**, 134901.
- 43 T. Vehoff, B. Baumeier, A. Troisi and D. Andrienko, *J. Am. Chem. Soc.*, 2010, **132**, 11702.
- 44 T. Vehoff, Y. S. Chung, K. Johnston, A. Troisi, D. Y. Yoon and D. Andrienko, *J. Phys. Chem. C*, 2010, **114**, 10592.
- 45 V. Rühle, J. Kirkpatrick and D. Andrienko, *J. Chem. Phys.*, 2010, **132**, 134103.
- 46 J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer and D. Andrienko, *Phys. Rev. Lett.*, 2007, **98**, 227402.
- 47 V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, Wiley-VCH, 2011, 3rd edn, ISBN 3527407324.
- 48 J. Brédas, D. Beljonne, V. Coropceanu and J. Cornil, *Chem. Rev.*, 2004, **104**, 4971.
- 49 D. P. McMahon and A. Troisi, *J. Phys. Chem. Lett.*, 2010, **1**, 941.
- 50 J. E. Norton and J. Brédas, *J. Am. Chem. Soc.*, 2008, **130**, 12377.
- 51 G. R. Hutchison, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 2339.
- 52 A. Troisi, D. L. Cheung and D. Andrienko, *Phys. Rev. Lett.*, 2009, **102**, 116602.
- 53 B. Lin, C. Cheng, Z. You and C. Hsu, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20704.
- 54 J. Huang and M. Kertesz, *J. Chem. Phys.*, 2005, **122**, 234707.
- 55 E. F. Valeev, V. Coropceanu, D. A. da Silva Filho, S. Salman and J. Brédas, *J. Am. Chem. Soc.*, 2006, **128**, 9882.
- 56 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
- 57 P. Schrögel, N. Langer, C. Schildknecht, G. Wagenblast, C. Lennartz and P. Strohrriegel, *Org. Electron.*, 2011, **12**, 2047.
- 58 S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris and A. V. Vannikov, *Phys. Rev. Lett.*, 1998, **81**, 4472.
- 59 R. Young, *Philos. Mag. B*, 1995, **72**, 435.
- 60 C. Madigan and V. Bulović, *Phys. Rev. Lett.*, 2006, **97**, 216402.
- 61 B. Thole, *Chem. Phys.*, 1981, **59**, 341.
- 62 A. Fuchs, T. Steinbrecher, M. S. Mommer, Y. Nagata, M. Elstner and C. Lennartz, *Phys. Chem. Chem. Phys.*, 2012, **14**, 4259.
- 63 M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439.
- 64 M. A. Rohrdanz and J. M. Herbert, *J. Chem. Phys.*, 2008, **129**, 034107.
- 65 R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2011, **2**, 2810.
- 66 T. Stein, L. Kronik and R. Baer, *J. Am. Chem. Soc.*, 2009, **131**, 2818.
- 67 J. S. Sears, T. Koerzdoerfer, C. Zhang and J. Brédas, *J. Chem. Phys.*, 2011, **135**, 151103.
- 68 G. Onida, L. Reining and A. Rubio, *Rev. Mod. Phys.*, 2002, **74**, 601.
- 69 B. Baumeier, D. Andrienko, Y. Ma and M. Rohlfing, *J. Chem. Theory Comput.*, 2012, **8**, 997.
- 70 D. Beljonne, C. Curutchet, G. D. Scholes and R. J. Silbey, *J. Phys. Chem. B*, 2009, **113**, 6583.
- 71 M. Pabst, B. Lunkenheimer and A. Köhn, *J. Phys. Chem. C*, 2011, **115**, 8335.