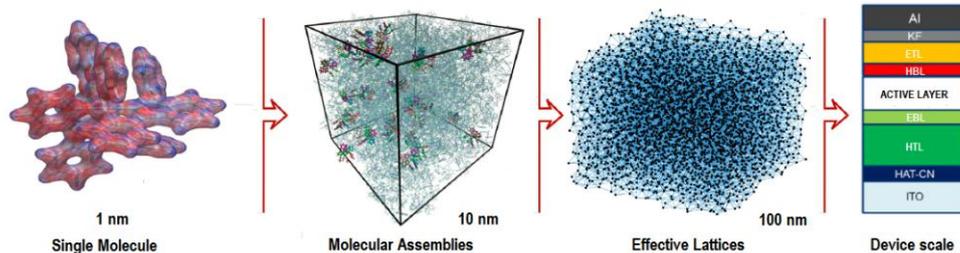


MOdeling STability of Organic PHosphorescent OledS

Multiscale Simulation of Organic Transport



Simulating a real organic light-emitting device comprising billions of molecular units is an overwhelming task scientist are tackling with a multiscale approach. Multiscaling is actually doing what a camera does when zooming out on a scene, namely progressively losing details. At the scale of a molecule every single ion and electron matters. Computationally intensive quantum calculations allow to compute electronic properties of such molecules. Aggregates of thousands of molecules can be simulated using so-called force fields, which are treating interactions between atoms pretty much as balls and strings. These simulations rely on heavy parameterizations based on quantum calculations and provide statistical informations such as radial distribution functions. As the interest is ultimately on electronic charge transport, electrons must be reinserted in the picture. The Jortner-Hush-Marcus theory of charge transfer reactions is heavily used in computing charge transfer between molecules.

The calculations are again quantum in nature and are performed from pair to pair of molecule in the sample. Once the transfer rates are known, the fine detail of each molecular structure can be forgotten and treated as a point-site. Charge hopping from point to point is treated with stochastic rate equation, that can be simulated with Kinetic Monte Carlo algorithms.

The simulations are used to extract mobility as a function of electric field, charge densities and temperature. A fundamental role in these simulations is played by the distribution of energies and transfer rates obtained from the lower scales simulations. Once the mobility is parameterized, it is possible to move to the actual device simulations, typically based on solving drift-diffusion differential equations. In this last step the details of the molecules is lost further and the material is treated as a continuum.

The key ingredients for the simulation of phosphorescent OLEDs

In phosphorescent OLEDs light emission occurs from the triplet state rather than the more common singlet. This is possible thanks to heavy ions in the organic complex that funnel spin-forbidden transitions via strong spin-orbit couplings. In this way phOLEDs can reach much larger efficiencies since the electron-hole recombination into triplet excitons is three times more likely than into the singlets. Red phOLEDs are already marketed by Samsung into end-user devices. However green and blue phOLEDs are still quite unstable. Uncovering the deep reason for the instability is the main objective of the MOSTOPHOS project. Are the triplet-polaron or the triplet-triplet quenching mechanisms that dominate the degradation process? Both events are releasing energy in the molecule under the form of heating. Triplet-polaron quenching occurs rather often as the current density increases, but the less frequent triplet-triplet quenchings leave the molecule highly excited, hence more reactive.

The key step to advance is to compute from first principles the rates for all the possible processes occurring to polarons and excitons, then simulating carrier dynamics in the entire OLED stack with the help of Kinetic Monte Carlo in order to assess the incidence of different events under operating conditions. Assumptions must be made at the end in order to build a statistical model for degradation and reliability of these devices.

About us:

MOSTOPHOS is a project addressing the problem of stability of blue emitting organic LEDs based on phosphorescent dyes in order to achieve all-organic white sources for lighting.

The challenge of the project is to provide a theoretical understanding of the dominant degradation mechanisms, that are at the basis of possible improvements.

Project kick-off: 1st June 2015.

Coordinator:

- Max Planck Institute Polymer Res. (D)

Project partners:

- Consiglio Nazionale delle Ricerche (I)
- BASF SE (D)
- Universidad Del Pais Vasco (S)
- Università di Roma 'Tor Vergata' (I)
- Technische Universiteit Eindhoven (NL)
- Technische Universitaet Dresden (D)
- COSMOLogic GmbH (D)

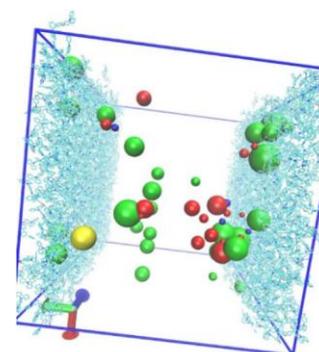


Fig. 1 Occupation probabilities of different compounds. Large green dots are charge trapping sites.



Force-Field parameterizations

The group at MPIP successfully parameterized a OPLS force-field (FF) for the hole transporter compound (DPBIC) and published the results [1]. The FF has been assessed and refitted by monitoring 12 intramolecular angles against accurate DFT reference calculations. An example is shown in Fig. 2, showing the comparison between the energy between DFT and the FF as the cross-diedral angle is rotated. The polarizable FF is an important ingredient in order to compute the polaron stabilization energy in a

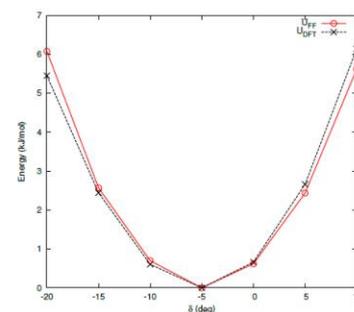
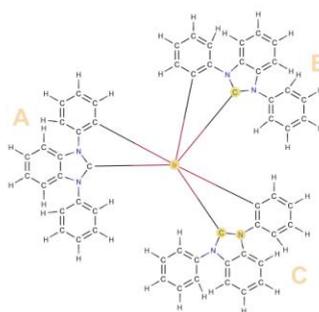


Fig. 2 DFT and FF comparison as the cross diedral angle between the marked atoms.

computationally feasible way. Different methods were used in order to reproduce the DFT polarization of DPBIC such as Merz-Kollman or CHELPG with atomic charges. Both leads to a significant polaron stabilization and narrowing of the site distribution energy disorder from $s=250$ meV to $s=170$ meV.

ITO-DPBIC interface models

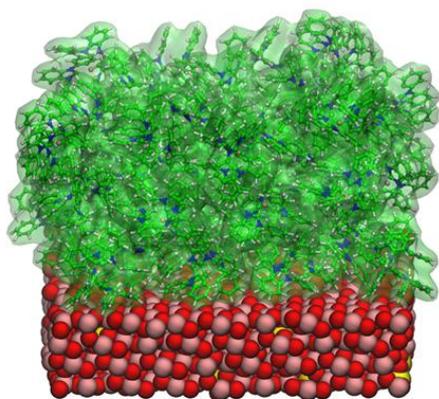
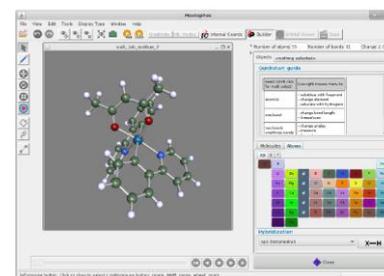


Fig. 3 MD simulation of the ITO/DPBIC interface

CNR-ISMN has developed a Buckingham FF to model ITO and the interactions between ITO and DPBIC. In treating hybrid interfaces is never easy to combine different FF such as Buckingham and OPLS and further validations are still needed. A protocol of simulation of the interface has been developed, either based on a kinetic simulation (molecule-by-molecule deposition) or based on thermodynamic simulation (annealing cycles) [2]. Fig. 3 shows an example of such simulations. Different order parameters have been identified and their distributions are crucial in the computation of the charge transfer rates. For the latter, the Quantum Espresso package has been extended in order to compute the transfer integral between metal and molecule states. Also in this case the final rate is computed using the semiclassical Marcus equation. The institute has obtained 10M hours at Cineca HPC center in order to perform these demanding simulations.

Towards building of a Simulation Environment

At COSMOLOGIC the development of a GUI for a simulation environment is progressing considerably. The workflow for the calculation of energy levels, reorganization energies and transfer rates is using the TURBOMOLE package and the VOTCA suite developed at MPIP as backend calculators. The realization of a software environment for the calculation of the rates is an important added value of the MOSTOPHOS project.



Recent and upcoming events

The 12-month meeting of MOSTOPHOS took place in Rome on June 20th and 21st. The 18th month meeting of MOSTOPHOS will be held in Mainz in December 2016.

Publications

- [1] P. Kordt et al., Phys Chem Chem Phys 2015, 17, 22778
- [2] A. Lorenzoni et al., RSC Adv., 2016, 6, 40724-40730
- [3] D. B. Milne et al., Angew. Chem. 2016, 128, 6356–6359

MOSTOPHOS will be presented at the "VIII Multiscale Materials Modeling Conference", Oct 9-14 2016, Dijon

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