CPP 40: Organic Electronics and Photovoltaics 3

Time: Thursday 15:00–17:45 Location: H38

Invited Talk CPP 40.1 Thu 15:00 H38

Computational Design of Organic Semiconductors — •Harald Oberhofer — Chair for Theoretical Physics VII, Universität Bayreuth — Chair for Theoretical Chemistry, Technische Universität München

Organic electronics—in the form of field effect transistors, light emitting diodes, or solar cells—are slowly finding their use in everyday consumer devices. To date, most of the employed materials have been discovered by structural tuning of a promising compound family, thereby relying on intuition, experience, or simply trial and error. While sometimes quite successful, such incremental changes only lead to a local exploration of the vast chemical space of possible molecules, potentially overlooking many interesting materials.

In contrast, modern data-driven strategies allow the extraction of general design rules through the systematic of the available design space. Often, these take the form of a computational funnel, where large databases are searched by computing relevant properties, so-called descriptors, for each element of the database. While this can point towards promising yet so-far overlooked theoretical and experimental design routes for organic electronics materials such an approach is limited by the employed database, not really allowing any insight beyond. Therefore, we trained machine-learned surrogate models for the most important organic semiconductor properties. These form the basis for an active machine learning scheme that allows us to sample the, in principle, unlimited space of organic molecules searching for materials not considered so far.

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Reorganization energies of flexible organic molecules as a challenging target for machine learning enhanced virtual screening — •Ke Chen[1,2], Christian Kunkel[1,2], Karsten Reuter[1,2], and Johannes T. Margraf[1,2] — [1]Technische Universität München, Garching, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The molecular reorganization energy λ strongly influences the charge carrier mobility of organic semiconductors and is therefore an important target for molecular design. Machine learning (ML) has the potential to accelerate this process by providing accurate surrogate models in design space. Unfortunately, λ poses a significant challenge for ML-models as it simultaneously depends on the neutral and ionized potential energy surfaces of the molecule.

In this contribution, we address the questions of how ML models for λ can be improved and what their benefit is in high-throughput virtual screening (HTVS). We find that, while improved predictive accuracy with respect to a semi-empirical baseline model is achieved, the benefits for molecular discovery are actually somewhat marginal. In particular, ML-enhanced HTVS is more effective in identifying promising candidates but leads to a less diverse sample set.

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Protonation-Induced Charge Transfer and Polaron Formation in Organic Semiconductors Doped by Lewis Acids — •Fabian Bauch, Chuan-Ding Dong, and Stefan Schumacher — Physics Department and CeOPP, Paderborn University, Germany

Organic electronics rely crucially on doping to enhance the conductivity of organic semiconductors (OSC). Lewis acid doping of OSC is currently of great interest as an alternative to typical molecular p-type doping. Recently, the underlying process was understood to be based on the electron transfer (ET) from a neutral polymer to the protonated polymer [Nat. Mater. 18, 1327 (2019)]. In this work, we provide insight into the microscopic process by investigating the influence of protons on the electronic properties of the copolymer PCPDT-BT using DFT calculations. [1] We find that a single proton on the backbone can give rise to a polaron coupled to the proton position. Two protons on the same polymer backbone can induce a long range intrachain ET, resulting in a polaron decoupled from the proton positions, more fit to act as charge carrier. We also demonstrate the possibility of ET between a neutral polymer and a doubly protonated polymer. The experimental data on the doping of PCPDT-BT via Lewis acid BCF agree well with our simulated vertical excitation spectra for an ensemble of protonated species with increasing amounts of protons. Our results highlight the important role of multiple protonation of the OSC backbone in completing the mechanistic picture of Lewis acid doping. [1] F. Bauch, C. Dong, and S. Schumacher, RSC Advances 12, 13999 (2022).

CPP 40.4 Thu 16:00 H38

Adsorption layers of diketopyrrolopyrrole acceptor blocks on graphite: Self-assembly and structure in all-atom modelling — Moufdi Hadjab[1] and •Olga Guskova[2] — [1]Boudiaf University of M'Sila, 28000 M'Sila, Algeria — [2]IPF Dresden, 01069 Dresden, Germany

In this computational work, we investigate the adsorption layers of electron-deficient N-unsubstituted difuran-diketopyrrolopyrroles (DPP). Three conformational states differing in the mutual orientation of the central DPP unit and furan flanks are distinguished: cis-cis, trans-trans, and cis-trans. The adsorption layers are obtained during in-silico self-assembly on graphite surface through intermolecular hydrogen bonding in all-atom MD simulations. The experimental process for the construction of the adsorption layers, called the droplet deposition technique, is reproduced in the modeling. In all simulated systems, the formation of stable supramolecular polymers is observed which build the ordered carpets on the surface. However, the binding energetics and strength and the type of hydrogen bonding are highly sensitive to the molecular conformation. We quantify each of these characteristics and provide a molecular picture of difuran-DPP layers relevant for organic field-effect transistor applications. OG thanks DFG (project GU1510/5-1) for financial support.

CPP 40.5 Thu 16:15 H38

Understanding Phonon Properties and the Thermal Conductivity of Crystalline Polymers — •Lukas Reicht, Lukas Legenstein, Tomas Kamencek, Sandro Wieser, and Egbert Zojer — Graz University of Technology, Austria

Disordered polymers are characterized by a very low thermal conductivity on the order of 0.1 W/mK. In contrast, recent studies have shown that aligned (crystalline) polymers can have thermal conductivities comparable to those of metals. Given these prospects, it is interesting to understand, how the thermal conductivity of a polymer depends on its chemical structure. A crucial step in that context is to investigate phonons and their influence on thermal transport. For simulating the phonons, we relied on density-functional theory (DFT) calculations combining phonopy and the Vienna Ab initio Simulation Package (VASP). In a second step, anharmonic force constants and thermal conductivities were calculated with phono3py and hiPhive. Additionally, we explored the capabilities of on-the-fly machine learned force fields (ML-FF), trained on DFT data, as implemented in VASP. These approaches were tested and benchmarked for polyethylene as a comparably simple model system. The final goal of our work is to then apply the above methodology to other polymers, systematically varying the structure of the backbone, thereby finding structure-to-property relations. These polymers include poly(p-phenylene), polythiophene, polyfuran, polyselenophene, poly(3-hexylthiophen-2,5-diyl) (P3HT) and Poly(p-phenylene vinylene) (PPV).

15 min. break

CPP 40.6 Thu 16:45 H38

Assessing Crystal Structure Prediction Based on Density Functional Tight Binding and Evolutionary Algorithms — •Sebastian Hutsch and Frank Ortmann — Department of Chemistry, Technical University of Munich

The prediction of crystal structures for organic molecules is a computationally expensive task due to the large number of atoms in the unit cell and the associated number of possible configurations. The computational load can be compensated by the use of classical force fields, which however lack transferability to new molecules and necessitate an extensive training for complex molecules. Here, we study an approach to crystal structure prediction based on evolutionary algorithms and a combination of Density Functional Tight Binding (DFTB) and Density Functional Theory (DFT). This combination allows us to efficiently compute crystal structures for new materials on a high level of accuracy. A comparison of the calculated crystal structures with experimentally known structures will be made.

CPP 40.7 Thu 17:00 H38

Singlet Fission search in polyacene molecules in gas-phase and on rare-gas clusters using ab initio methods

— •Selmane Ferchane[1], Alexander Eisfeld[2], and Michael Walter[1,3,4] — [1]Institute of Physics, University of Freiburg, Germany — [2]Max Planck Institute for the Physics of Complex Systems, Dresden, Germany — [3]FIT Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Germany — [4]Fraunhofer IWM, Freiburg, Germany

Singlet fission (SF), is a spontaneous photo-excited splitting phenomenon. Where an organic chromophore dimer, converts its singlet exciton into a pair of triplet excitons. A great promise for future photon-to-current conversion of solar energy using organic materials with high efficiency. To get more insight into these processes of SF, we employed different ab initio theories and approaches in our investigation, namely, density functional theory (DFT), TD-DFT, MCTDH, and CASPT2/CASSCF. Since the spatial orientation is crucial to whether the molecule will go SF and the rate of it due to the orbital coupling of both molecules, based on recent studies. We calculate the most favorable orientation of the chromophores with the binding energies in the gas phase and adsorbed on Argon and Neon surfaces. Then we calculate the lowest-lying excited states that contribute to the singlet and triple transition plus the search for the possible conical intersection that crosses the surface potential energies.

CPP 40.8 Thu 17:15 H38

Materials design based on theoretical characterization: Improving open-shell organic molecules for electronic applications

— •Sebastian Schellhammer[1] and Frank Ortmann[2] — [1]Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute for Applied Physics, Technische Universität Dresden, Dresden, 01187 Germany — [2]Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, 85748 Garching b. München

In recent years, organic molecules with stable open-shell ground states have attracted growing interest due to their outstanding properties, i.e. responsive spin structures, high-spin ground states, two-photon absorption, or small band gap. Although a growing number of interesting materials has appeared, molecules often lack thermal stability impeding their application in electronic devices. In this presentation, we will highlight routes but also dead ends in the quest for high-spin configurations in hydrocarbons. We benchmark a computational approach for the characterization of open-shell organic structures, which combines predictability with appropriate simulation resources. For polycyclic heteroaromatic hydrocarbons containing a benzoisoindole core, we explain why a supposedly open-shell material does not provide the desired characteristics. On the contrary, we discuss the promising characteristics of stable polycyclic hydrocarbon diradicaloids as well as related tetraradicaloids. Based on these analyses, design rules for optimized material properties are extracted, which helps to exploit the full potential of promising material groups.

CPP 40.9 Thu 17:30 H38

Simulation organic semiconductors with tensor network techniques

— •Sam Mardazad[1], Yihe Xu[2], Xuexiao Xang[2], Martin Grundner[3], Ulrich Schollwöck[3], Haibo Ma[2], and Sebastian Paeckel[3] — [1]Heriot-Watt University, Edinburgh — [2]School of Chemistry and Chemical Engineering, Nanjing University — [3]Department of Physics, Arnold Sommerfeld Center of Theoretical Physics, University of Munich

Organic solar cells provide the possibility to enhance the efficiency and to overcome the Shockley-Queisser limit. In this talk we present results for the simulation of quantum transport effects in a tetracene para dimers, a large organic molecule modelled by a Frenkel-exciton Hamiltonian. We account for the full quantum dynamics going beyond the Born-Oppenheimer approximation. For that purpose we use a new numerically unbiased representation of the molecule's wave function enabling us to compare with experiments, exhibiting good agreement. With this powerful approach we map out a phase diagram aiming and determining the experimental sweet spot yielding the highest charge carrier production rate. Furthermore, we develop a physical picture indicating that the coherent time scale in which most of the yield is generated is driven by a renormalization of the bare modes and make suggestions on how to manipulate this for the development of more efficient organic solar cells.