

## O 101: Molecular Films: Electronics, Photovoltaics and Structure

Time: Friday 10:30–12:30

Location: WIL A317

O 101.1 Fri 10:30 WIL A317

**Towards computational solar cell design: Calculating *ab initio* charge-transfer coupling elements for large systems** — ●CHRISTOPH SCHÖBER, HARALD OBERHOFER, and KARSTEN REUTER — Technische Universität München, Germany

Organic solar cells promise outstanding application possibilities, but current systems lack the efficiency to be economically viable. Improvements are often the result of experimental intuition or empirical knowledge, rather than strategic design. Towards a computer-aided design we need to understand, amongst others, the complex mechanism of charge propagation in (possibly amorphous) materials. To this end, Hamiltonian charge-transfer coupling elements are a key ingredient linking microscopic structure and the charge mobilities that determine the device efficiency. To make the calculation of these coupling elements numerically tractable for complex systems we implement a fragment molecular orbital scheme in FHIaims, a highly parallelized all-electron *ab initio* code that due to its atom-centered basis sets is ideally suited to tackle the non-periodicity of organic solar cell materials. We use the self-consistent density of the fragments to construct the system Hamiltonian with correct number of electrons, and additionally implement an embedding scheme that allows to consider the generally neglected second fragment and therewith take polarization effects into account. We present charge-transfer coupling elements for a number of systems previously used for benchmarking and for larger molecules used as hole transport material for organic solar cells.

O 101.2 Fri 10:45 WIL A317

**Nanometer Scale Optical and Photocurrent Microscopy of Organic Optoelectronic Materials** — MARIUS VAN DEN BERG, KAI BRAUN, ALFRED J. MEIXNER, and ●DAI ZHANG — Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen

Optoelectronic material is the basic component in photovoltaic, photodetector, or transistor system. In organic photovoltaic, the photon-electron conversion efficiency is strongly influenced by the local donor/acceptor morphology, such as crystallinity, or domain size [1, 2]. To get insight into this topic, we monitor the absorption and photocurrent from organic semiconductor blends using a home-built white light transmission setup. To image the distributions and local morphology of donor or acceptor materials, we use Raman and photoluminescence spectroscopy combined with a parabolic mirror assisted confocal optical microscope. Such optical signals can be correlated with topography information through an integrated shear-force scanning probe microscope. The intensity ratios between the donor photoluminescence and the local photocurrent under different bias voltages will be discussed, with respect to the charge transfer processes. Furthermore, photodegradation of the optoelectronic materials will be systematically compared, regarding the changing of photoluminescence, and Raman signals as well as the photocurrent decays.

References: [1] Zhang, D., Heinemeyer, U., Stanciu, C., et al, Phys. Rev. Lett., 2010, 104, 056601. [2] Wang, X., Azimi, H., Zhang, D., et al, Small, 2011, 7, 2793.

O 101.3 Fri 11:00 WIL A317

**Pulsed laser deposited ZnO nanostructures with a sol-gel ZnO coating for hybrid solar cells** — ●SVEN KÄBISCH<sup>1,2</sup>, THOMAS J. K. BRENNER<sup>3</sup>, NORBERT H. NICKEL<sup>1</sup>, and NORBERT KOCH<sup>1,2</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin GmbH — <sup>2</sup>Humboldt-Universität zu Berlin, Institut für Physik — <sup>3</sup>Universität Potsdam, Hybrid Photovoltaics & Optoelectronics Group

Hybrid solar cells aim to combine high cross sections for light absorption common for organic semiconductors with high mobility of charge carriers in inorganic semiconductors. Besides the generation and collection of charge carriers in a hybrid solar cell, the charge separation process at the inorganic/organic interface determines the power conversion efficiency (PCE) of the device. Zinc oxide (ZnO) nanostructures and planar layers were deposited by a pulsed laser deposition process on O-terminated Al-doped ZnO planar layers. Subsequently, poly[(bis-(2-ethylhexyl)-cyclopentadithiophene)-alt-benzothiadiazole] (PCPDTBT) was spin-coated on the ZnO nanostructures. The fabrication of the hybrid solar cell was finished by thermal evaporation of molybdenum trioxide and gold as the top electrode. Prior to the formation of the hybrid ZnO/PCPDTBT junction, some

of the planar and nanostructured ZnO electrodes were subjected to a surface modification by drop-casting of sol-gel ZnO. Owing to the presence of the structurally imperfect sol-gel layer, the performance of the solar cells could be increased by a factor of 7 for planar and 15 for nanostructured hybrid junctions. This increase of the PCE is explained in terms of an improved charge separation at the ZnO/PCPDTBT interface.

O 101.4 Fri 11:15 WIL A317

**Electric Potential Distributions in Space Charge Regions of Molecular Organic Adsorbates: The Distributed States Model** — ●ERIC MANKEL<sup>1,2</sup>, CORINNA HEIN<sup>3</sup>, MAYBRITT KÜHN<sup>1,2</sup>, THOMAS MAYER<sup>1,2</sup>, and WOLFRAM JAEGERMANN<sup>1,2</sup> — <sup>1</sup>TU Darmstadt, Surface Science Div., Darmstadt — <sup>2</sup>InnovationLab GmbH, Heidelberg — <sup>3</sup>TU Darmstadt, Electronic Materials Div., Darmstadt

We study the evolution of the electric surface potential for organic semiconductor adsorbates on different high work function substrates using photoelectron spectroscopy. Usually, the surface potential of these materials shows a typical progression in dependence of the adsorbate layer thickness indicating the formation of a space charge region around the contact. We found that these curve shapes cannot be fully explained by the Schottky model which is usually the standard to describe potential distributions in contact space charge regions. Therefore, the Schottky model has been extended assuming a continuous density of states distribution (DOS) in energy. The differences between the Schottky model and the distributed states model (DSM) will be discussed. Finally, both models are applied to measured values of the surface potential evolution of some exemplary organic molecules on varying substrates. We find that the surface potential evolution of the DSM describes the measured potential much more accurately than the surface potential evolution of the Schottky model. Although if this does not prove unequivocally the presence of a DOS in organic semiconductors their amount is estimated in the framework of the new model being between  $10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$  and  $10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$ .

O 101.5 Fri 11:30 WIL A317

**Analysis of constructive quantum interference effects in single molecule circuits with parallel backbones** — ●HECTOR VAZQUEZ<sup>1</sup>, RACHID SKOUTA<sup>2</sup>, SEVERIN SCHNEEBELI<sup>2</sup>, MARIA KAMENETSKA<sup>3</sup>, RONALD BRESLOW<sup>2</sup>, LATHA VENKATARAMAN<sup>3</sup>, and MARK S. HYBERTSEN<sup>4</sup> — <sup>1</sup>Institute of Physics, AS CR, Prague, Czech Republic — <sup>2</sup>Dept. of Chemistry, Columbia University, USA — <sup>3</sup>Dept. of Appl. Phys. and Appl. Mathem., Columbia University, USA — <sup>4</sup>Center for Functional Nanomaterials, Brookhaven National Laboratory, USA

Quantum interference effects play an important role in single molecule transport. Several examples of destructive quantum interference in molecular transport have been measured [1,2]. Recently, we studied the conductance superposition law in molecular circuits and demonstrated constructive quantum interference effects [3]. We showed that molecules with two branches bound in parallel to the electrodes can exhibit more than twice the conductance of the single backbone counterparts.

Here we extend our analysis to quantify the effect of junction geometry on the conductance of single and double backbone molecules. In this talk I will present results from DFT-NEGF based methods, and discuss the role of junction structure (eg. molecular rotations) in observing clear signatures of interference effects.

[1] J. Am. Chem. Soc. 133, 9556 (2011). [2] Nat. Nanotechnol. 7, 305 (2012). [3] Nat. Nanotechnol. 7, 663 (2012).

O 101.6 Fri 11:45 WIL A317

**Structurally and kinetically controlled on-surface polymerization** — ●JOHANNA EICHHORN<sup>1</sup>, WOLFGANG M. HECKL<sup>1,2</sup>, and MARKUS LACKINGER<sup>1,2</sup> — <sup>1</sup>Physik-Department & TUM School of Education, Technische Universität München, 80799 München, Germany — <sup>2</sup>Deutsches Museum, 80538 München, Germany

On-surface polymerization of functionalized building blocks is an established route to synthesize defined, periodic, covalently linked nanostructures. The arrangement of reactive side groups defines the network topology. The usage of different functional groups with different binding energies facilitates a controlled sequential coupling. Here, we

present a hierarchical polymerization based on Ullmann-coupling by sequential dehalogenation using bromine and iodine as leaving groups.

Room temperature deposition of 1-(4'-iodophenyl)-3,5-bis(4'-bromophenyl)benzene on Au(111) exclusively activates the iodine-phenyl bond dissociation, whereas the bromine-phenyl bonds remain stable. Subsequent dimerization yields new dumbbell shaped building block which self-assemble into large, periodic islands. Thermal annealing up to 375°C was used to also activate homolysis of the bromine substituents and initiate subsequent polymerization into covalent reticular networks. To compare the polymerization of building blocks with different bond topology, we also studied the direct polymerization of the monomer by deposition onto a preheated substrate. For both protocols the influence on the network quality of different kinetic reaction parameters was studied.

O 101.7 Fri 12:00 WIL A317

**On-surface Synthesis of Extended Graphdiyne Wires by Stepped Surface Templating of Terminal Alkyne Homo-Coupling** — BORJA CIRERA<sup>1</sup>, YI-QI ZHANG<sup>1</sup>, JONAS BJÖRK<sup>2</sup>, SVETLANA KLYATSKAYA<sup>3</sup>, ZHI CHEN<sup>3</sup>, MARIO RUBEN<sup>3</sup>, JOHANNES V. BARTH<sup>1</sup>, and •FLORIAN KLAPPENBERGER<sup>1</sup> — <sup>1</sup>Physik Department E20, TU München, Germany — <sup>2</sup>Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden — <sup>3</sup>Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany

The success of carbon allotropes strongly refreshed the attraction towards low-dimensional hydrocarbon materials like carbyne, graphyne, or graphdiyne originally targeted by acetylenic solution chemistry. Recently, we introduced homo-coupling of terminal alkynes on a noble metal surface to the field of covalent on-surface synthesis. Here, we overcome the missing chemoselectivity of this method by templating the coupling reaction of linear diethynyl-terphenyl monomers with step edge alignment on the vicinal Ag(877) surface. This approach allowed us to suppress side-reactions resulting in irregularly-branched poly-

mers on the planar surface and rendering possible the fabrication of 300 Å-long strands of a novel 1D hydrocarbon material. The extended-graphdiyne molecular wire is classified by density functional theory electronic structure calculations as a direct band gap semiconductor material. Our method puts a great variety of carbon-rich materials within reach and should also be applicable to other classes of tectons.

O 101.8 Fri 12:15 WIL A317

**Coupling of Brominated Tetrathienoanthracene on Crystalline Copper and Silver** — •RICO GUTZLER<sup>1,2,3</sup>, LUIS CARDENAS<sup>1,2</sup>, JOSH LIPTON-DUFFIN<sup>1</sup>, DMITRII F. PEREPICHKA<sup>2</sup>, and FEDERICO ROSEI<sup>1</sup> — <sup>1</sup>Institut National de la Recherche Scientifique, Université du Québec, 1650 boulevard Lionel-Boulet, Varennes, QC J3X 1S2, Canada — <sup>2</sup>Department of Chemistry, McGill University, 801 Sherbrooke Str. West, Montreal, QC H3A 0B8, Canada — <sup>3</sup>Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany

We report the synthesis of extended 2D organic networks on copper and silver from thiophene-based molecules. A combination of STM and XPS yields insight into the reaction pathways from single molecules towards the formation of two-dimensional organometallic and polymeric structures via Ullmann reaction dehalogenation and C-C coupling. The thermal stability of the molecular networks is probed by annealing to temperatures of up to 500 °C. On Cu(111) only organometallic structures are formed, while on Ag(111) both organometallic and covalent polymeric networks were found to coexist. The ratio between organometallic and covalent bonds could be controlled by means of the annealing temperature. The thiophene moieties start degrading at 200 °C on the copper surface, whereas on silver the degradation process becomes significant only at 400 °C. Our work reveals how the interplay of a specific surface type and temperature steers the formation of organometallic and polymeric networks and describes how these factors influence the structural integrity of two-dimensional organic networks.