

Minisymposium on Advanced Materials and their Interfaces

Graz University of Technology, 27.4.2017, Graz, Austria

TDK-Seminar Room

- | | |
|-------------|--|
| 8:30-9:00 | Takanori Fukushima, Yoshiaki Shoji, Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, Yokohama, Japan
2D Precision Assembly Using Propeller-Shaped Molecules |
| 9:00-9:30 | Yoshiaki Shoji, Takanori Fukushima, Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, Yokohama, Japan
Electronic Modification of Nanocarbon Materials Using a Highly Electron-Deficient Boron Cation |
| 9:30-9:50 | Paolo Falcaro, Institute of Physical and Theoretical Chemistry, Graz University of Technology, Austria
Metal-Organic Frameworks from ceramics |
| 9:50-10:15 | BREAK |
| 10:15-10:35 | Roland Resel / Andrew Jones, Institute of Solid State Physics, Graz University of Technology, Austria
Crystal structure solution from thin films: from monolayers to surface induced phases |
| 10:35-11:05 | Norbert Koch, Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, Germany
Controlling the electronic structure at interfaces in opto-electronic devices with functional molecules |
| 11:05-11:25 | Sergey Borisov, Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Austria
New luminescent indicators for application in optical sensing materials |
| 11:25-11:50 | BREAK |
| 11:45-12:10 | Andreas Hauser, Institute of Experimental Physics, Graz University of Technology, Austria
Chiral resolution of drug molecules by functionalized, single-atom-thick membranes |
| 12:10-12:40 | Tomofumi Tada, Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama, Japan
Molecular Orbital Rule for Controlling the Quantum Transport in Molecular Junctions and its application for future devices |
| 12:40-13:00 | Oliver T. Hofmann, Institute of Solid State Physics, Graz University of Technology, Austria
Computational Polymorph Prediction for Hybrid Interfaces |

2D Precision Assembly Using Propeller-Shaped Molecules

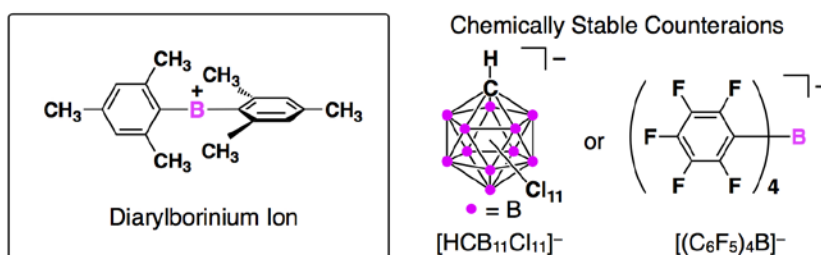
To assemble molecules into a highly ordered and uniform structure at intended length scales is a grand challenge in materials science and technology. Since the structure and properties of molecules are anisotropic in nature, the perfect control of molecular arrangement and orientation is essential for exploiting the full potential of the intrinsic properties of constituent molecules and, in turn, for developing high-performance organic materials that exhibit, for example, anisotropic charge- and energy- transports, dipolar properties, and even a dynamic response like skeletal muscles. Molecular self-assembly that proceeds under thermodynamic control provides a reliable approach to creating organic materials with high positional and/or orientational order of the constituent molecules in a size regime up to the nanometer length scale. However, there are still considerable problems in achieving structural order at larger length scales, particularly, in developing organic thin films, which are practically important form of materials for many applications. This is because molecular self-assembly on solid substrates could involve both thermodynamic and kinetic processes. More significantly, the control of nucleation sites is essentially impossible. As a consequence, organic thin films, when viewed as a bulk, always contain many micro domains and grains, usually with a nanometer-size regime, arising from local molecular ordering that occurs independently. To address this issue, we have proposed an approach [1–4], which use a particular type of propeller-shaped molecule that enables precision 2D assembly. Herein, some of our recent works related to this topic will be described.

References

1. N. Seiki, Y. Shoji, T. Kajitani, F. Ishiwari, A. Kosaka, T. Hikima, M. Takata, T. Someya, T. Fukushima, *Science* **2015**, *348*, 1122–1126.
2. H. Shioya, Y. Shoji, N. Seiki, M. Nakano, T. Fukushima, Y. Iwasa, *Appl. Phys. Express*, **2015**, *8*, 121101.
3. F. K.-C. Leung, F. Ishiwari, T. Kajitani, Y. Shoji, T. Hikima, M. Takata, A. Saeki, S. Seki, Y. M. A. Yamada, T. Fukushima, *J. Am. Chem. Soc.* **2016**, *138*, 11727–11733.
4. M. Kumano, M. Ide, N. Seiki, Y. Shoji, T. Fukushima, A. Saeki, *J. Mater. Chem. A* **2016**, *4*, 18490–18498.

Electronic Modification of Nanocarbon Materials Using a Highly Electron-Deficient Boron Cation

Boron compounds, featuring strong Lewis acidity and low electronegativity arising from the boron atom, play important roles in many research fields including organic transformations, supramolecular assembly, and materials sciences. We recently reported the first isolation and scalable synthesis of a diarylborinium ion, *i.e.* a two-coordinate boron cation bonded only with two aromatic groups [1]. A key for this success is the use of chemically stable and weakly nucleophilic counteranions such as undecachloro carborane anion $[\text{HCB}_{10}\text{Cl}_{11}]^-$ and tetraarylborate $[(\text{C}_6\text{F}_5)_4\text{B}]^-$. Because of its exceptionally strong Lewis acidity as well as high chalcogenophilicity, the boron cation causes unusual small-molecule activations [1,2]. Interestingly, this boron cation can also serve as an efficient hole dopant for improving the electronic properties of nanocarbons [3]. In this presentation, the details of the above topics will be described.



References

1. Y. Shoji, N. Tanaka, K. Mikami, M. Uchiyama, T. Fukushima, *Nature Chem.* **2014**, *6*, 498.
2. Y. Shoji, N. Tanaka, D. Hashizume, T. Fukushima, *Chem. Commun.* **2015**, *51*, 13342.
3. K. Funahashi, N. Tanaka, Y. Shoji, N. Imazu, K. Nakayama, K. Kanahashi, H. Shirae, S. Noda, H. Ohta, T. Fukushima, T. Takenobu, *Appl. Phys. Express*, **2017**, *10*, 035101.

Norbert Koch

Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

and

Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

Controlling the electronic structure at interfaces in opto-electronic devices with functional molecules

The electronic structure at interfaces in electronic and optoelectronic devices is decisive for their function and efficiency. For instance, charge carrier injection and selective carrier extraction rely on a proper line-up of the electrode Fermi level and the semiconductor valence or conduction band edges. As well, the relative energy position of conduction and valence levels at semiconductor heterojunctions determines whether the junction facilitates charge separation or energy transfer. If, for technological reasons, one would favor employing certain material combinations in a device, methods to modify the interface level alignment are required.

The introduction of an interfacial layer comprising functional molecules enables controlling the electronic structure at interfaces in opto-electronic devices. Hereby, the “functionality” of the molecules can be rather simple: strong electron donor and acceptor molecules substantially modify the work function of electrodes, covering a range from 3.5 eV to over 6 eV. This, in turn, allows the realization of ohmic contacts to most organic and inorganic semiconductors. Inorganic/organic semiconductor heterojunction energy levels can also be adjusted with molecular donor/acceptor interlayers, based on the work function tuning of the inorganic semiconductor surface. Dynamic adjustment of interfacial energy levels can be achieved with molecular photochromic switches. Reversible switching between two conformations by optical excitation changes the frontier energy levels available for charge transport and transfer. This can be used to realize multifunctional devices, e.g., addressability by electrical and optical means.

Andreas W. Hauser

Institute of Experimental Physics, Graz University of Technology, Austria

Chiral resolution of drug molecules by functionalized, single-atom-thick membranes

Enantiomeric forms of a drug molecule are known to vary in potency, toxicity and effect they might have on biological systems. While one form may be beneficial for the health of the recipient, the other could be extremely harmful. Therefore, it is an essential requirement of modern drug research to separate and test all enantiomers of bioactive substances. In most cases, a direct enantioselective synthesis is not feasible, and intermediate forms or final products need to be extracted from racemic mixtures. Recently, we suggested a novel method for the separation of racemic mixtures via single-atom-thick membranes. This method has been tested via ab initio simulations on a small benchmark system of an isolated graphene pore.[1] However, for the actual synthesis of such a type of membrane chiral MOF structures might be more suitable. A possible first candidate for future investigations will be presented, hoping to trigger the interest of chemists with the ability to synthesize the proposed structure.

[1] Hauser, A. W. et al. Functionalized Graphene as a Gatekeeper for Chiral Molecules: An Alternative Concept for Chiral Separation. *Angew. Chem. Int. Ed.* 53, 9957–9960 (2014).

Tomofumi Tada

*Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama
226-8501, Japan*

Molecular Orbital Rule for Controlling the Quantum Transport in Molecular Junctions and its application for future devices

Molecular junctions have been extensively studied as a small functional unit which can be integrated in future electronic circuits. To characterize the small junction precisely, electronic conductance of molecular junctions is the first property investigated in both experimental and theoretical studies. In the conductance study, constructive and destructive interference effects in electron transport are observed as a typical features of molecular conductance, which appear as parabolic curves and sharp dips of transmission functions at around the Fermi level, respectively. To understand the quantum interference effects in molecular junctions, we have conducted Green's function calculations with tight-binding models, and found clear relationships between molecular conductance and molecular orbitals. The theoretical findings were successfully embodied in Molecular Orbital Rule for electron transport [1-5], and the orbital rule has been adopted for qualitative predictions and understandings of electron transport in molecular junctions since the proposal of the orbital rule in 2002. The orbital rule was originally developed in atomic orbital based Green's function, but recent studies [6,7] reveal that the Green's functions given in other basis (e.g., molecular orbital, spin-spin direct product, etc.) also lead to essential interference effects of molecular junctions, which in turn enlarges the applicable range of the molecular orbital rule for transport and information processing [8]. In this talk, we briefly introduce the history of the molecular orbital rule from its birth and explain recent topics on the orbital rule

References

- [1] Tada T. and Yoshizawa, K. *ChemPhysChem* 2002, 3, 1035.
- [2] Tada T. and Yoshizawa, K. *J. Phys. Chem. B* 2003, 107, 8789.
- [3] Yoshizawa, K., Tada T., and Staykov A. J. *Am. Chem. Soc.* 2008, 130, 9406.
- [4] Yoshizawa, K. *Acc. Chem. Res.* 2012, 45, 1612.
- [5] Tada T. and Yoshizawa, K. *Phys. Chem. Chem. Phys.* 2015, 17, 32099.
- [6] Tada T., Yamamoto T., and Watanabe S. *Theor. Chem. Acc.* 2011, 130, 775.
- [7] Tada T., "Orbital Rule for Electron Transport of Molecular Junctions", Chapter 7 in *Single Molecule Electronics –An Introduction to Synthesis, Measurement, and Theory –*, (M. Kiguchi (Ed.), Springer), ISBN:978-981-10-0723-1, pp.165-190, 2016.
- [8] Tada T., "Quantum transport and quantum information processing in single molecular junctions", Chapter 6 in *Quantum Chemistry –Molecules for Innovations–*, (T. Tada (Ed.), InTech), ISBN:979-953-307-365-0, pp.133-158, 2012