PCSI
Room Keahou I - Session PCSI-SuE1
Organic and Hybrid Semiconductor Materials

Moderator: Ingmar Swart, University of Utrecht, Netherlands

7:30pm **PCSI-SuE1-1 A Study of Stereochemical Recognition of Chiral Molecules Investigated by STM-Based Techniques***, **Yuji Kuwahara**,* Osaka University, Japan **INVITED**

The combination of a scanning probe microscope with a photon detector and a Raman spectrometer, referred to as a tunneling-electron-induced light emission (STM-LE) and a tip-enhanced Raman scattering spectroscopy (STM-TERS), is quite attractive and useful to explore the optical properties and chemical analysis of nanomaterials beyond the optical diffraction limit.

In this study, we performed the STM observation to elucidate structural configuration of chiral molecules adsorbed on the metal substrates accompanied with their optical and vibrational properties using our laboratory-built STM-LE and STM-TERS systems$^{1-4}$. As for the chiral molecules, we usedracemic-mixture and enantiopure molecules of thechiral PTCDI*(N,N'*-Di-*n*-octyl-3,4,9,10-perylenetetracarboxylic Diimide) andthiaheterohelicene and their derivatives. We clearly observed the high resolution STM images for the chiral molecular assemblies, leading to the important perspective of stereochemical chiral recognition based on the formation of ordered molecular structures combined with their optical and vibrational characterizations. Theoretical calculation based on a density functional theory and a molecular dynamics simulation successfully identified the formation mechanism of the molecular self-assemblies in the chiral recognition schemes.^{5} Moreover, we attempted to investigate the optical dissymmetry of chiral PTCDI molecules using STM-LE measurement, and that of helicene derivatives using the STM-TERS measurements for evaluating the optical activity and identifying the enantiomers of the chiral molecules at a molecular scale.

References

[1] P. Krukowski, Y. Kuwahara, *et al., J. Phys. Chem*. **C 120**, 3964–3977 (2016).

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[4] S. Kimura, Y. Kuwahara, *et al., Phys. Chem. Chem. Phys.* **26**(43), 7658-7663 (2024).

[5] Changqing Ye, Y. Kuwahara et al., J Phys.Chem. C127(43), 21305-21312(2023)

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8:10pm **PCSI-SuE1-9 N-Heterocyclic Carbene and Olefin Monolayers on Silicon***, **Martin Franz**,* Technische Universität Berlin, Germany*; Mowpriya Das,* Universität Münster, Germany*; Conor Hogan,* Istituto di Struttura della Materia-CNR (ISM-CNR), Italy*; Ankita Das,* Universität Münster, Germany*; Robert Zielinski, Milan Kubicki,* Technische Universität Berlin, Germany*; Maximilian Koy,* Universität Münster, Germany*; Sandhya Chandola,* Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany*; Matthias Freitag,* Universität Münster, Germany*; Uwe Gerstmann,* Universität Paderborn, Germany*; Canan Kosbab,* Technische Universität Berlin, Germany*; Simone Brozzesi,* Università di Roma Tor Vergata, Italy*; Mike Thomas Nehring, Denise Liebig, Viktoria Balfanz, Juls Brühne,* Technische Universität Berlin, Germany*; Wolf Gero Schmidt,* Universität Paderborn, Germany*; Norbert Esser, Frank Glorius, Mario Dähne,* Technische Universität Berlin, Germany

Organic overlayers have emerged into a promising surface modification or functionalization tool and N-Heterocyclic carbenes (NHCs) and their close relatives, the N-heterocyclic olefins (NHOs), were found to be particularly suitable in this regard forming highly ordered self-assembled monolayers (SAMs) on metal surfaces that exhibit superior properties to the widely used thiol-based SAMs. As silicon remains the material of choice in today's semiconductor technology a functionalization of its surfaces is of highest interest.

Here, a comprehensive scanning tunnelling microscopy (STM), density functional theory, and X-ray photoemission spectroscopy study of the growth of NHC and NHO monolayers on clean and modified silicon surfaces is presented [1-3]. We demonstrate the formation of highly ordered monolayers binding to the surface via a single Si–C bond (see Fig. 1). The monolayers exhibit high thermal stabilities and show large work function reductions. By systematically varying the sidegroups and the backbone of the molecules and investigating two different molecule classes (NHCs and NHOs), we obtain a profound understanding of the bonding, structure, and assembly of NHCs and NHOs on Si offering guiding rules for a targeted modification of Si surfaces.

[1] M. Franz et al., Nat. Chem. 13, 828-835 (2021).

[2] R. Zielinski et al., J. Mater. Chem. C 11, 7377 (2023).

[3] M. Das et al., Angew. Chem. Int. Ed. 62, e202314663 (2023).

8:15pm **PCSI-SuE1-10 On Surface Synthesis of Graphite-N-Doped Molecular Graphene Nanostructures***, **Dong Wang**,* Institute of Chemistry, CAS, China

Graphene and its derivates have been widely investigated with the exotic electronic properties. Doping is one of the most important ways to tune the properties of graphene-based nanostructures and materials.

The π-conjugated di- and polyradicals is attractive as a designable platform to explore the molecules spin interaction and development of organic magnetic materials. The introduction of graphite-N is one of most promising way to realize the construction of the π-conjugated polyradicals platforms. here we present the construction of an NHC-derived 1,3,5-TMB (N-TMB). In the target N-TMB molecule, the TMB core is stabilized by three NHC modules, which are further fused by benzene rings to the backbone with the expectation of improving the stability and spin coupling of the triradical. The N-TMB exhibits threefold symmetry on Au(111) and is structurally verified by nc-AFM techniques. STS characterization combined with DFT calculations reveals the occurrence of strong charge transfer between N-TMB and the substrate, resulting in positively charged N-TMB3+ on Au(111) surface. We further design and synthesize other N-doped 0D and 1D molecular graphene nanostructures and exploit their electronic structures.

8:20pm **PCSI-SuE1-11 Importance of Molecular Dipole Alignment and Surface Compensation in P-V Hysteresis of $MAPbBr_3$(001)***, Lars Freter,* Forschungszentrum Jülich GmbH, Germany*; Hung-Chung Hsu,* National Taiwan University, Taiwan*; Raman Sankar,* Academia Sinica, Taiwan*; Chun-Wei Chen,* National Taiwan University, Taiwan*; Rafal E. Dunin-Borkowski, Philipp Ebert,* Forschungszentrum Jülich GmbH, Germany*; Ya-Ping Chiu,* National Taiwan University, Taiwan*; **Michael Schnedler**,* Forschungszentrum Jülich GmbH, Germany

Metalorganic halide perovskites attracted extraordinary attention as low-cost photovoltaic materials, due to their rapid increase of the conversion efficiency within a few years only. However, it is unclear to what degree the reported conversion efficiencies extracted from current density versus voltage (*J-V*) curves are accurate, since *J-V* hystereses are known to make "bad cells look good". It is thus of paramount importance to unravel the physical mechanisms inducing hysteresis, but no consent has been achieved yet. We demonstrate the presence of a hysteresis in tunneling spectra acquired at 4.3 K on cleaved MA-Br terminated (001) surfaces of $MAPbBr_3$ single crystals. Simulations of the tunneling spectra reveal an underlying polarization-voltage (*P-V*) hysteresis, caused by an interplay of field-induced rotation and alignment of the MA molecules, stabilized by dipole-dipole interactions, and an ion-lattice relaxation. The field-induced, ferroelectric polarization in the bulk is compensated at the surface by an oppositely oriented, counteracting out-of-plane polarization component of the otherwise in-plane antiferroelectrically ordered surface dipole arrangement. This suggests that at low temperatures only ferroelectric effects govern the hysteresis in $MAPbBr_3$ and its related compounds, whereas at high temperatures thermally activated processes such as ion migration and charge trapping-detrapping dominate.

8:25pm **PCSI-SuE1-12 A Rare Earth Modified Silicon Surface as a Template for Ordered Organic Growth***, Milan Kubicki, **Martin Franz**, Mario Dähne,* Technische Universität Berlin, Germany

The formation of self-assembled layers of organic molecules on solid surfaces is an important subject because of their possible application in advanced (opto)electronic devices.While the formation of self-assembled layers is well established on metal surfaces, the growth on silicon surfaces, which are still the material of choice in today's semiconductor technology, is much less studied. On pure silicon, the formation of ordered organic films is usually hindered by their high dangling bond density, so that an appropriate surface modification is required. Here we demonstrate the high potential of a rare earth modification for promoting an ordered growth.

Using scanning tunneling microscopy, we show that a terbium modified Si(111) surface enables the formation of highly ordered molecular monolayers, on the example of cobalt phthalocyanine (CoPc). CoPc belongs to the transition metal phthalocyanines being a class of organic semiconductors, which has been already employed e.g. in organic light emitting diodes, photovoltaic cells, and field-effect transistors.

Our data demonstrate that single CoPc molecules stay highly mobile at the $TbSi_2$/Si(111) surface at room temperature. By reaching a coverage of a full monolayer, a highly ordered film consisting of large domains of flat-lying CoPc molecules in an almost fourfold symmetry with different orientations is formed

[1] M. Kubicki, M. Franz, and M. Dähne, "A Rare Earth Modified Silicon Surface as a Template for Ordered Organic Growth", J. Phys. Chem. C **128**, 13347 (2024).

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