Tuesday, April 21st, 2026

8:45 – 9:00	Welcome and Opening
9:00 – 10:00	Hans-Peter Steinrück *Tailoring the mobility and reactivity of porphyrins on metal surfaces*
10:00 – 11:00	Tulio C. R. Rocha *Probing functional interfaces with soft X-ray spectroscopy*
11:00 – 11:30	Coffee Break
11:30 – 12:00	Maximilian Ünzelmann *Topological Dirac Quasiparticles Tailored by Surface-Moiré Engineering*
12:00 – 14:00	Lunch
14:00 – 14:30	Alisson Ceccatto *Interfacial Enrichment and Reaction Mechanisms of Organic Molecules in Ionic Liquids*
14:30 – 14:50	Timo Talwar *Water co-adsorption in ultrathin films of ionic liquids on Pt(111)*
14:50 – 15:10	Giordano F. C. Bispo *Mapping defect energy levels in Ce-doped $KMgF_3$ via synchrotron-based X-ray spectroscopy*
15:10 – 15:30	Jonas Hauner *On-Surface Synthesis of a Two-Dimensional Metal-Organic Framework by Cobalt Oxide Nanoisland Dissolution*
15:30 – 16:00	Coffee Break
16:00 – 16:30	Bruna F. Baggio *Two Dimensional Decoupling Layers for Molecular Spectroscopy: TCNQ on MoS_2 Probed by LT-STM*
16:30 – 16:50	Cedric Schmitt *Probing the Quantum Spin Hall State in Atomic Monolayers via NanoARPES*
16:50 – 17:10	Pedro Rezende-Gonçalves *Metallic layered materials with magnetic frustration: An ARPES view of $SmAuAl_4Ge_2$ and $TbAuAl_4Ge_2$*
11:10 – 17:30	Christian L. Ritterhoff *Foundation Models and Transfer Learning as Innovative New Routes for Atomistic Simulations of Low-Dimensional Carbon Materials*
17:30 – 17:40	Changing to CPV
17:40 – 19:30	Poster Session & Networking

Wednesday, April 22nd, 2026

9:00 – 10:00	Willi Auwärter *On-Surface Synthesis of Low-Dimensional Carbon Structures Including Heteroatoms*
10:00 – 11:00	Abner de Siervo *Atomic-Scale Engineering of Complex Organic Nanomaterials via On-Surface Synthesis*
11:00 – 11:30	Coffee Break
11:30 – 12:00	Julio C. Cezar *To be announced*
12:00 – 14:00	Lunch
14:00 – 14:20	Majid Shaker *Insights to self-metalation of tetraphenyl transdibenzoporphyrin on Cu(111)*
14:20 – 14:40	Rafael R. Barreto *Engineering a 2D Fe array on Ag(100) via temperature driven reorganization and metalation of pyridyl-porphyrins*
14:40 – 15:00	Isabela C. Tonon *Engineering Artificial Spin Networks by On-Surface Metal Organic Coordination*
15:00 – 15:20	Afra Gezmis *Reversible structure formation in 4,4-bipyridine – Fe 2D metal organic frameworks on Au(111)*
15:30 – 16:00	Coffee Break
16:00 – 17:30	Visit to Sirius
17:40 – 19:30	Free Time
19:30 – 22:00	Conference Dinner at Churrascaria Estância Grill

Thursday, April 23rd, 2026

9:00 – 9:30	Luiz G. Pimenta *High-pressure synthesis of 2D diamond*
9:30 – 9:50	Bárbara L. T. Rosa *Tailoring the Quantum Optical Properties of Localized States in van der Waals Heterostructures*
9:50 – 10:10	Everton Pereira-Andrade *Multiple Quasiparticle Interactions in Molecularly Functionalized h-BN Polaritonic Systems*
10:10 – 10:30	Douglas S. Ribeiro *Implementation of Ultra-High Vacuum Tip-Enhanced Raman Spectroscopy (TERS) for the Characterization of Optically Active Materials*
10:30 – 11:00	Rogério Magalhães Paniago *Scanning Tunneling Spectroscopy as a tool for the study of physical phenomena at surfaces*
11:00 – 11:30	Coffee Break
11:30 – 19:30	Outing to São Paulo

Friday, April 24th, 2026

9:00 – 10:00	Carlos F.O. Graeff *Efficient and stable perovskite solar cells: new materials and modeling*
10:00 – 10:20	Hameed Ullah *Mo_3C_2Tx MXene-Modified SnO_2 Electron Transport Layer for Enhanced Efficiency and Stability of Perovskite Solar Cells*
10:20 – 10:40	Raphaela de Oliveira *Clinochlore as natural nanocavity for water confinement*
10:40 – 11:00	Marco Dittmar *Growth and spectroscopy of altermagnetic MnTe*
11:00 – 11:30	Coffee Break
11:30 – 12:00	Saimon F. C. Da Silva *Growth of Single-Photon Sources and Entangled Photon Pairs by Molecular Beam Epitaxy*
12:00 – 14:00	Lunch
14:00 – 14:30	Julien Steffen *Increasing the Scope of Computational Nanochemistry by Combining Density-Functional Theory with Machine Learned Interatomic Potentials*
14:30 – 14:50	Neeta Bisht *DFT-Guided Self-Assembly of 2D Pyridyl-Linked Metal–Organic Frameworks on Au(111)*
14:50 – 15:10	Edgar F. P. Nieto *Quantum Rate Spectroscopy: In-situ Nanoscale Electronic Structure Probing via Isoscopic Physics*
15:10 – 15:30	Maria Vitória C. Issler *Engineering of Metal-Perovskite interfaces for charge transport optimization in inorganic halide perovskites*
15:30 – 16:00	Coffee Break
16:00 – 17:30	Lab visits of local groups and networking
16:30 – 16:50	Closing Session

Poster Abstracts

The poster session will be held on Tuesday, April 21st, starting 17:40.

List of posters:

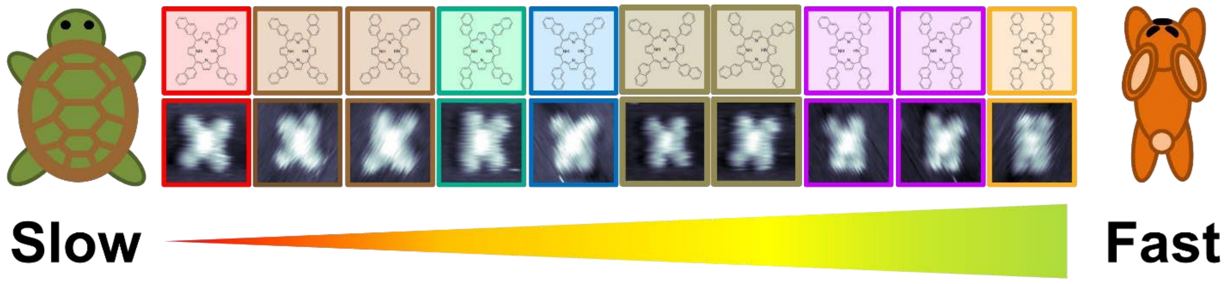
P1	Nicolás M. S. de Siqueira *Probing the Electronic Density of States of Electrochemically Reduced Graphene Oxide via Quantum Rate Spectroscopy*
P2	Arthur P. Machado *Terminal group effects on SAMs packing and perovskite interfacial energetics*
P3	Eidsa Brenda da Costa *On-Surface Engineering of Porphyrin-Based Two-Dimensional Coordination Networks on Cu(111)*
P4	Gabriel X. Pereira *Intrinsic Instabilities and Mechanical Anisotropy in Halide Perovskite Monolayers*
P5	Philip Maier *In silico investigation of magnetic water cleaning particles*
P6	Saskia Prusch *Atomistic Insights into Mercuric Ion Capture: Development of a Force Field and Application in Molecular Dynamics Simulations*
P7	Sajid Sajid *Greener Humidity-Assisted Fabrication of High-Efficiency Perovskite Solar Cells*
P8	N. Sidorenko *Area-selective SAM templating on CoO nanoislands/Au(111)*
P9	Vanessa Carreño Diaz *Competing Intermolecular and Metal–Ligand Interactions in Surface-Assisted Synthesis of 2D Nanostructures*

Tailoring the mobility and reactivity of porphyrins on metal surfaces

Hans-Peter Steinrück

Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany

Metalloporphyrins are versatile functional building blocks in many biological and biochemical processes. In addition, these molecules are also utilized in technical applications, retaining their highly functional nature within an inorganic framework. Examples include gas sensors, solar cells and catalysts. In this presentation, the surface chemistry of porphyrins on metal substrates will be addressed by X-ray photoelectron spectroscopy and scanning tunneling microscopy. Specific topics are the interplay between porphyrin-substrate and porphyrin-porphyrin interactions, the role of the substrate, surface diffusion, and in particular the synthesis of metalloporphyrin monolayers by direct metalation of free base porphyrins, under UHV conditions and in the liquid phase. Particular attention is given to tailoring of these properties by functionalization of the porphyrins.



Probing functional interfaces with soft X-ray spectroscopy

Tulio C. R. Rocha

Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Re- search on Energy and Materials (CNPEM, Giuseppe Máximo Scolfaro 10000, 13083- 100, Campinas, Brazil

E-Mail: tulio.rocha@lnls.br

Understanding the composition and electronic structure of interfaces is key to advanc- ing a wide range of technologies, from electronics to catalysis and renewable energy. The IPE beamline at the Sirius synchrotron provides a powerful platform for investigat- ing these properties using advanced soft X-ray spectroscopies. Techniques such as X-ray photoemission (XPS), X-ray absorption (XAS), and resonant inelastic X-ray scat- tering (RIXS) allow for detailed insights into chemical bonding, electronic states, and excitation dynamics at interfaces. In this talk, I will present recent studies that demon- strate the capabilities of the IPE beamline. These include: probing the defect chemistry in Prussian blue analogues for water splitting via combined XPS and XAS [1]; spatially resolved measurements on isolated flakes of van der Waals materials [2]; ultrafast electron delocalization dynamics in polymer thin films using resonant Auger spectros- copy (RAS) [3]; and the identification of in-gap states and Ti^{3+} sites in oxygen-deficient $SrTiO_3$ using Resonant Photoemission (RPES). Furthermore, I will show how XAS and RIXS are employed to investigate interfaces in magnetic thin-film heterostructures rel- evant to spintronic applications [4]. In summary, the capabilities of the IPE beamline provide valuable tools for unraveling the complexities of functional interfaces and con- tribute to the development of materials and devices with enhanced performance and functionality.

References:

[1] R.L. Germscheidt, D.S. Francischini, M.B. Silva, M.A.Z. Arruda, A.L.B. Formiga, T.C.R. Rocha, J.A. Bonacin, *ACS Appl. Energy Mater.*, **2022**, 5, 9447-9454

[2] C. Lourenço, A.B.S. Araújo, L.H. Hasimoto, I.A.A. Feitosa, M.F.F. das Neves, J. Bettini, T.M. Perfecto, T.C.R. Rocha, T.J.A. Mori, E.R. Leite and M. Santhiago *J. Mater. Chem. A*, **2025**,13, 951-960

[3] Y Garcia-Basabe, M Suenson Cardoso, F C Vicentin, D Steinberg, K D Sossmeier, T C R Rocha, D G Larrude, *J. Phys. Chem C.*, **2024**, *128*, 6384-6391.

[4] E.S. Santos, J.E. Abrão, J.L. Costa, J.G.S. Santos, K.R. Mello, A.S. Vieira, T.C.R. Rocha, T.J.A. Mori, R.O.R. Cunha, J.B.S. Mendes, A. Azevedo *ACS Appl. Nano Mater*., **2024**, 8, 04300-4310

Topological Dirac Quasiparticles Tailored by Surface-Moiré Engineering

Maximilian Ünzelmann, Romana Ganser, Muthu Masilamani, Begmuhammet Geldiyev, and Friedrich Reinert

Exp. Physik VII and Würzburg-Dresden Cluster of Excellence ctd.qmat, Universität Würzburg, Germany

Moiré heterostructures have become a promising platform for tailoring electronic states in a highly controllable manner. The emergent superlattice potential gives rise to band gaps in the folded moiré band structure, which lead to a quenching of kinetic energy and thus increase of electron-electron interactions. Emergent flat bands have been observed in nano-focused angle-resolved photoemission spectroscopy (ARPES) experiments and demonstrated to trigger correlation-driven phenomena.

Here, we go beyond the mere creation of flat bands and demonstrate that surface moiré engineering allows transforming a ’simple’ epitaxial monolayer-substrate heterostructure into topological Dirac matter. In particular, using ARPES experiments, we will (i) prove the existence of one-dimensional Dirac fermions in the moiré- driven band structure, (ii) show that those are robustly protected by the emergent superlattice symmetry, and (iii) demonstrate how the entire mini-band structure can be controlled by epitaxial manners and sample temperature. Overall, this expands the potential of moiré materials by shifting the focus from almost exclusively flat bands to the creation of new, highly controllable Dirac quasiparticles – that is, an ‘innovative route to low-dimensional materials

Interfacial Enrichment and Reaction Mechanisms of Organic Molecules in Ionic Liquids

Alisson Ceccatto[a], **Luciano Sanchez Merlinsky**[b,c], **Luis M. Baraldo**[b,c], **Federico J. Williams**[b,c], **Florian Maier**[a], **and Hans-Peter Steinrück**[a]

[a]Lehrstuhl für Physikalische Chemie 2, Friedrich-Alexander-Universität Erlangen-ürnberg,Egerlandstr. 3, 91058 Erlangen, Germany

[b]Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina

[c]Instituto de Química Física de los Materiales, Medio Ambiente y Energía, CONICET-Universidad de Buenos Aires, Buenos Aires, Argentina

Tailoring the surface composition of ionic liquids (ILs) is a key strategy for enhancing the performance of supported ionic liquid phase (SILP) catalysts. In addition, understanding and controlling the surface composition of metalloporphyrins in ionic liquids is crucial for designing photoactive materials. In this work, we first investigate the interfacial behavior of fluorine-free Ru polypyridyl complexes functionalized with n-nonyl side chains (Ru-C_9) dissolved in two ILs with contrasting physicochemical properties, such as hydrophobicity and surface tension, namely $[C_4C_1Im][PF_6]$ and $[C_4C_1Im][OAc]$[1]. Using angle-resolved X-ray photoelectron spectroscopy (ARXPS), we show that Ru-C_9 complexes undergo pronounced surface enrichment in $[C_4C_1Im][PF_6]$, adopting a buoy-like orientation at the IL/vacuum interface. Surface saturation is achieved at a bulk concentration of 0.12 $\%_{mol}$, a regime relevant for efficient SILP catalysis. In contrast, no interfacial enrichment is observed in $[C_4C_1Im][OAc]$, highlighting the critical role of IL composition, particularly anion identity and surface tension, in governing the surface distribution of metal complexes. These findings provide molecular-level insights into the design of IL-based catalytic systems with optimized interfacial properties. Consequently, we investigate the interfacial behavior of zinc-didodecylporphyrin molecules (Zn-DDP) dissolved in the hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4C_1Im][PF_6]$ using ARXPS.[2] Upon mild heating, Zn-DDP undergoes spontaneous demetallation, evidenced by the appearance of aminic (–NH) and iminic (=N–) nitrogen XPS signals characteristic of the free-base porphyrins. Partial hydrolysis of $[PF_6]^-$ anions produces phosphate species that contribute to the demetallation process. Concentration-dependent measurements reveal extremely high surface enrichment of porphyrins at the IL/vacuum interface, reaching surface saturation already at about 0.50 $\%_{mol}$ Zn-DDP content in the bulk. Temperature-dependent ARXP spectra reveal that for unsaturated interfaces, surface enrichment increases with increasing temperature. Our findings provide molecular-level insights to guide the design of porphyrin-based photoactive interfaces in ionic liquid systems.

Acknowledgements

Alisson Ceccatto acknowledges the Alexander von Humboldt Foundation for a Humboldt Research Fellowship for postdocs.

References

[1] Ceccatto, A. et al. *Influence of ionic liquid composition on surface enrichment of fluorine-free Ru complexes*.
RSC Adv., 2025,**15**, 36137-36144

[2] Ceccatto, A. et al. *Interfacial Enrichment and Demetallation of a Zinc Porphyrin in the Ionic Liquid $[C_4C_1Im][PF_6]$*. **ChemPhysChem.** *Under review.*

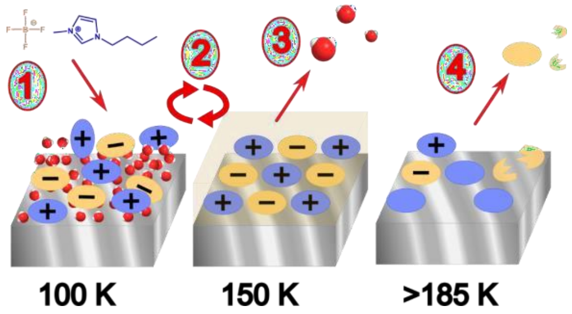
Water co-adsorption in ultrathin films of ionic liquids on Pt(111)

Timo Talwar[a], Florian Maier[a], Hans-Peter Steinrück[a]

[a] *Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany*

Ionic liquids (ILs) are key components of the Solid Catalyst with Ionic Liquid Layer (SCILL) concept, where thin IL films on heterogeneous catalysts enhance selectivity in various catalytic reactions. Since water is a common and often unavoidable contaminant in ILs, understanding its influence on the structure and adsorption behavior of IL films at metal interfaces is essential for the rational design of SCILL systems.

We investigated the influence of pre-adsorbed water (D_2O) on the adsorption, orientation, and thermal behavior of four ionic liquids (ILs) — the hydrophilic $[C_4C_1Im][BF_4]$ and $[C_2C_1Im][TfO]$, and the hydrophobic $[C_3CNC_1Im][Tf_2N]$ and $[C_1C_1Im][Tf_2N]$ — on Pt(111) using angle-resolved X-ray photoelectron spectroscopy.[1-2] The ILs were deposited at ~100 K onto clean Pt(111) or onto crystalline (CI) or amorphous (ASW) D_2O films, and analyzed at various temperatures. At 100 K, the IL predominantly adsorbs on top of the water layer. Upon heating to ~130 K, an exchange process occurs in which the IL replaces interfacial water from the Pt surface into the second layer, as deduced from a reduced water desorption temperature by ~9 K. By ~150 K, water has fully desorbed, yielding a pure IL layer with a characteristic checkerboard arrangement of alternating anions and flat- lying cations. Further heating shows that this layer behaves identical to IL films directly deposited on clean Pt(111): Above ~185-270 K (IL dependent), the IL decomposes stepwise, with anion-derived fragments fully desorbing until ~400-500 K whereas most cation-derived products remain as carbonaceous residues up to at least ~550-800 K. The comparable water co-adsorption behaviour observed for all ILs shows that neither the hydrophilicity nor the nitrile-functionalisation in $[C_3CNC_1Im][Tf_2N]$ significantly influences adsorption characteristics or thermal stability.



Scheme 1: Thermal behaviour of water and $[C_4C_1Im][BF_4]$ co-adsorption on Pt(111) (taken from [2])

REFERENCES

1. T. Talwar, H. P. Steinruck, F. Maier, "Water Co-Adsorption in Ultrathin Films of Ionic Liquids on Pt(111)" *ChemistryOpen* **2025**, e202500571.
2. T. Talwar, H. P. Steinruck, F. Maier, "The interplay of water and the hydrophilic ionic liquid $[C_4C_1Im][BF_4]$ on Pt(111)" Submitted to *Surface Science* **2026**

Mapping defect energy levels in Ce-doped $KMgF_3$ via synchrotron-based X-ray spectroscopy

Giordano F. C. Bispo[a], **Adriano B. Andrade**[b], **Davi H. S. Pedroso**[b], **Eduily B. V. Freire**[c], **Zélia S. Macedo**[b], **Thiago J. A. Mori**[a], **Tulio C. R. Rocha**[a], **Mario E. G.Valerio**[b]

[a] *Brazilian Synchrotron Light Source (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas-SP, Brazil.*

[b] *Laboratory of Preparation and Characterization of Materials (LPCM), Departament of Physics, Federal University of Sergipe, São Cristovão−SE, Brazil.*

[c] *CNCO, Federal University of Maranhão, Codó - MA, Brazil.*

X-ray absorption spectroscopy (XAS) is widely used to probe the local electronic and geometric structure of solid-state materials. In lanthanide-doped systems, L-edge XANES and EXAFS are commonly employed to determine dopant valence and local coordination, often combined with optical techniques such as XEOL and UV– Vis to investigate luminescence mechanisms [1]. However, aliovalent doping introduces charge-compensating defects that create electronic states within the bandgap, significantly affecting luminescence lifetime, emission color, and trapping processes [2]. To improve luminescence mechanisms, a number of experimental methods have been used, such as thermoluminescence (TL) and electron paramagnetic resonance (EPR), but they are not element-selective and often rely on indirect interpretations. In this work, we employ a suite of synchrotron-based X-ray techniques to directly investigate defect-related electronic levels within the bandgap. Ce-doped $KMgF_3$ fluoroperovskite was used as a model system. Polycrystalline samples were synthesized via microwave-assisted hydrothermal methods and pre-characterized structurally and optically. By combining XAS, X-ray Photoelectron Spectroscopy (XPS), and Resonant Inelastic X-ray Scattering (RIXS), we construct an experimental electronic configuration scheme and critically compare it with empirical Host-Referred and Vacuum-Referred Binding Energy (HRBE/VRBE) models [3]. Measurements were performed at IPE beamline and LNNano laboratory, under proposal 20250969, 20250920 and 20252259. The combined spectroscopic analysis demonstrates that element-selective X-ray techniques can resolve dopant- and defect-related electronic states, provide a refined description of compensation mechanisms and improve current luminescence models. (Acknowledgment: this work was supported by PCI-CNPQ 2025/2, CAPES, FAPESP and FAPITEC)

REFERENCES

1. Rezende, M. V. S., et al. Phys. Chem. Chem. Phys. 18 (2016) 17646.
2. Catlow, R. A., Point Defects in Materials (1988) **Acad. Press.**
3. Dorenbos, P. J. Lumin. 222 (2020) 117164.

On-Surface Synthesis of a Two-Dimensional Metal-Organic Framework by Cobalt Oxide Nanoisland Dissolution

Jonas Hauner[a], Neeta Bisht[b], Andreas Görling[b], Jörg Libuda[a]

[a]*Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany*

[b]*Chair of Theoretical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany*

In this work, we demonstrate the controlled growth of a metal–organic framework (MOF) via the dissolution of cobalt oxide nanoislands on Au(111). The structural and electronic properties of the system were investigated using scanning tunnelling microscopy (STM) in combination with density functional theory (DFT) calculations. As an organic linker, we employed biphenyl-4,4′-dicarboxylic acid (BDA), which enables the formation of coordination networks with Co^{2+} centers directly on the metal surface.

In a first step, well-defined CoO nanoislands were prepared on Au(111), following established growth procedures.[1-3] Subsequently, BDA molecules were deposited onto the CoO/Au(111) system. At room temperature, the molecules adsorb intact on the surface without forming an extended coordination network. However, upon annealing to 500 K, pronounced structural changes occur: the BDA molecules deprotonate and simultaneously induce the dissolution of the CoO nanoislands. This process releases Co^{2+} ions, which coordinate with the deprotonated carboxylate groups and drive the formation of a two-dimensional MOF. The resulting structure can be described as a porous, net-like coordination network in which binuclear Co nodes are each coordinated by four carboxylate groups.

Further annealing to 600 K leads to a distinct structural transformation. Instead of the extended two-dimensional network, the system reorganizes into one-dimensional arrays on Au(111). In this phase, individual Co^{2+} ions link neighboring BDA molecules via two carboxylate groups, resulting in a linear coordination motif.

Our results establish oxide nanoislands as a spatially confined metal source for on-surface MOF synthesis. This approach provides a new strategy for the controlled fabrication of low-dimensional MOFs on metal substrates and opens perspectives for tailored nanoscale coordination architectures.

REFERENCES

1. Fester et al. Comparative Analysis of Cobalt Oxide Nanoisland Stability and Edge Structures on Three Related Noble Metal Surfaces: Au(111), Pt(111) and Ag(111). *Top Catal*, 2017, **60**, 503–512.
2. Walton et al. Interface Controlled Oxidation States in Layered Cobalt Oxide Nanoislands on Gold, *ACS Nano*, 2015, **9**, 2445–2453
3. Sidorenko, N., Hauner, J. et al. *J. Phys. Chem. C*, 2025, **129**, 8142–8150

Two Dimensional Decoupling Layers for Molecular Spectroscopy: TCNQ on MoS_2 Probed by LT-STM

Bruna F. Baggio[1,2], **Vibhuti Rai**[2], **Christian Lotze**[2], **Katharina Franke**[2]

[1] *Brazilian Nanotechnology National Laboratory, CNPEM, Campinas, Brazil*

[2] *Physics Department, Freie University, Berlin, Germany*

Organic molecules such as tetracyanoquinodimethane (TCNQ) are widely used as strong electron acceptors and serve as a model system for charge-transfer studies due to their high electron affinity and well-defined molecular orbitals. Upon adsorption on metallic substrates, the cyano groups strongly interact with surface d-orbitals, promoting the transfer of one electron into a low-lying molecular orbital and stabilizing TCNQ as a radical anion. This charge-transfer process, together with the resulting unpaired electron, underpins many of the electronic and magnetic functionalities that have made TCNQ central to the development of organic conductors and donor- acceptor materials [1].

Low-temperature scanning tunnelling microscopy (LT-STM) provides atomic-scale sensitivity to molecular adsorption geometries and enables visualization of molecular assemblies on different substrates. To study molecular phenomena in greater detail, ultrathin semiconducting layers can be introduced to reduce hybridization between molecules and metallic substrates. Among these materials, monolayer molybdenum disulfide (MoS_2) has emerged as a highly effective two-dimensional decoupling layer. MoS_2 consists of a single Mo layer in trigonal-prismatic coordination positioned between two sulfur layers and is held together by van der Waals forces. Its weak substrate interaction creates an intermediate coupling regime that preserves more of the intrinsic molecular electronic structure while still allowing high-resolution scanning probe access [2].

In this work, experiments were carried out using a LT-STM (CreaTec Fischer & Co. GmbH) under ultra-high vacuum conditions at 5 K. TCNQ molecules were evaporated onto MoS_2 monolayers grown on Au(111). Molybdenum was deposited onto the clean Au(111) surface, prepared by repetitive cycles of Ne^+ sputtering and annealing in a H_2S atmosphere of 10^{-5} mbar by electron-beam evaporation from a high-purity rod. The sample was annealed at 530 °C subsequently. The STM images reveal TCNQ networks formed both on MoS_2 patches and on bare Au(111), allowing direct comparison between weakly and strongly coupled adsorption environments. Scanning tunnelling spectroscopy (STS) was then used to probe the electronic structure of TCNQ molecules in these distinct environments.

The STS results for TCNQ adsorbed on MoS_2 show that the lowest unoccupied molecular orbital (LUMO) is significantly narrower than on the bare substrate. The spectra also display clear vibronic progressions within the unoccupied molecular resonances [3].

These results demonstrate that monolayer MoS_2 acts as an effective decoupling layer for molecular spectroscopy of charge-transfer acceptor molecules. The vibronic features observed in the STS spectra indicate that MoS_2 partially isolates the molecular orbitals from the metallic substrate, allowing features that are typically suppressed under strong hybridization to be resolved.

REFERENCES

[1] Int. J. Mass Spectrom., 277 (2008) 269–273
[2] J. Mater. Chem. A, 2014, 2,16892
[3] Beilstein J. Nanotechnol. 2020, 11, 1062–1071

Probing the Quantum Spin Hall State in Atomic Monolayers via NanoARPES

Cedric Schmitt[a,b], Lukas Gehrig[a,b], Kilian Strauß[a,b], Jonas Erhardt[a,b], Matthew Watson[c], Zhongkai Liu[d,e], Jörg Schäfer[a,b], Simon Moser[a,b] and Ralph Claessen[a,b]

[a] *Physikalisches Institut, Universität Würzburg, Würzburg, Germany*

[b] *Würzburg-Dresden Cluster of Excellence ct.qmat, Universität Würzburg, Würzburg, Germany*

[c] *Diamond Light Source, Harwell Science and Innovation Campus, Didcot, UK*

[d] *State Key Laboratory of Quantum Functional Materials, ShanghaiTech University, Shanghai 201210, China*

[e] *ShanghaiTech Laboratory for Topological Physics, Shanghai 200031, China*

Two-dimensional topological materials offer unique opportunities to probe Berry-curvature-related phenomena with angular resolved photoemission. Our recently discovered quantum spin Hall insulator indenene, a triangular monolayer of indium epitaxially grown on SiC(0001), combines a large topological gap of ~ 120 meV with exceptional µm-scale mono domain growth [1,2]. While circular dichroism in ARPES provides a sensitive bulk probe of the orbital angular momentum (OAM) texture tied to topological band inversion, its application to SiC- supported materials is hindered by the substrate's stepped morphology. Adjacent terraces impose opposite OAM stacking registries, leading to cancellation of the dichroic signal in conventional micro-ARPES [3]. Here we introduce a terrace-resolved nanoARPES approach with sub-800nm spatial resolution that isolates the photoemission response of individual SiC terraces. This method reveals directly the underlying OAM and its Berry-curvature imprint, enabling unambiguous verification of the topological character of indenene on a single- terrace level. Our results further establish SiC step-driven dichroism as a previously unexplored degree of freedom in photoemission spectroscopy and demonstrate its power as a general spectroscopic handle for topological classification in 2D materials, with implications for spintronic applications.

REFERENCES

1. M. Bauernfeind et al. Nat. Commun. **12**, 5396 (2021)
2. C. Schmitt et al. Nat. Commun. **15**, 1486 (2024)
3. J. Erhardt et al. Phys. Rev. Lett. **132**, 196401 (2024)

Metallic layered materials with magnetic frustration: An ARPES view of $SmAuAl_4Ge_2$ and $TbAuAl_4Ge_2$

P. Rezende-Gonçalves[a,b], A. Antezak[a], T. Kato[a,c], K. Feng[d], F. Fortuna[a], P. Le Fèvre[e,f], M. Rosmus[g], N. Olszowska[g], T. Sobol[g], D. J. Singh[h], R. E. Baumbach[i], A. F. Santander-Syro[a], E. Frantzeskakis[b]

[a]*Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405 Orsay, France*
[b]*Departamento de Física, Universidade Federal de Minas Gerais, Av. Pres. Antonio Carlos, 6627 Belo Horizonte, Brazil*

[c]*Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan*

[d]*Department of Physics, University of California, San Diego, California 92093, USA*
[e]*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin-BP48, 91192 Gif-sur-Yvette, France* [f]*Univ Rennes, CNRS, IPR - UMR 6251, F-35000 Rennes, France*

[g]*National Synchrotron Radiation Centre SOLARIS, Jagiellonian University, Czerwone Maki 98, 30-392 Kraków,*

Poland

[h]*Department of Physics and Astronomy, University of Missouri, Missouri 65211, USA*

[i]*Physics Department, University of California, Santa Cruz, California 95064, USA*

Compounds of the $LnTAl_4X_2$ (Ln = lanthanide, X = tetrel, T = transition metal) family has attract significant scientific interest due to their geometrically frustrated triangular lattices, rising into exotic magnetic phenomena such as complex spin arrangements and multiple magnetic transitions [1-2]. Despite the significant report on their magnetotransport properties, their experimental electronic structure had remained largely unexplored [3-4]. In this work, we present a detailed investigation of the electronic structure of $SmAuAl_4Ge_2$ and $TbAuAl_4Ge_2$ using angle- resolved photoemission spectroscopy (ARPES) and density functional theory (DFT) calculations.

Our results show that both compounds possess a highly two-dimensional Fermi surface characterized by multiple hole pockets around the Γ-point. We demonstrate that the main features of the electronic structure are well- captured by the nonmagnetic analog $YAuAl_4Ge_2$, providing experimental confirmation of negligible hybridization between the *f*-electrons and the conduction states. Despite this weak direct interaction, we find that the localized magnetic moments of the *f*-electrons exert a crucial indirect influence. Specifically, the exchange interaction combined with spin-orbit coupling leads to a fine energy splitting of the bands near the Fermi level, a feature that is absent in the nonmagnetic analog.

Additionally, we identify the presence of surface-localized electronic states and determine the dominant cleavage plane of the materials. Although the materials undergo magnetic transitions at low temperatures, no significant changes in the electronic structure were observed across these transitions within our experimental resolution. This study concludes that low-dimensionality, surface termination, and exchange interactions are fundamental ingredients in defining the electronic properties of these frustrated magnetic systems.

REFERENCES

1. G. H. Wannier, Phys. Rev. 79, 357 (1950).
2. M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).
3. K. Feng et al., Phys. Rev. B 109, 014436 (2024).
4. K. Feng et al., J. Magn. Magn. Mater. 564, 170006 (2022).

Foundation Models and Transfer Learning as Innovative New Routes for Atomistic Simulations of Low-Dimensional Carbon Materials

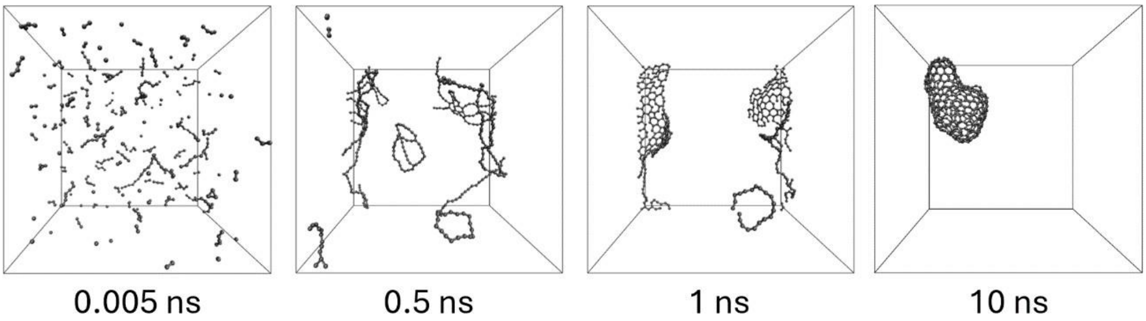
Christian L. Ritterhoff[a], **Yury Lysogorskiy**[b], **Anton Bochkarev**[b],

Ralf Drautz[b], **and Bernd Meyer**[a]

[a] *Interdisciplinary Center for Molecular Materials (ICMM) and Computer Chemistry Center (CCC), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Germany*

[b] *Interdisciplinary Centre for Advanced Materials Simulations (ICAMS), Ruhr-Universität Bochum (RUB), Germany*

Machine-learned interatomic potentials (MLIPs) are rapidly transforming materials modeling by enabling quantum- accurate atomistic simulations on time and length scales that were previously out of reach. For the design and discovery of low-dimensional materials, these models could provide an unprecedented theoretical complement to experiments by allowing detailed insight into the thermodynamic and kinetic pathways governing their synthesis and transformation. The advent of foundation models extends this capability even further by covering wide regions of the chemical space in a single model. Refinement for a specific chemical configuration then allows the rapid exploration of previously inaccessible complex synthesis pathways. In this work, we fine-tune a graph atomic cluster expansion (GRACE) foundation model for carbon using the dataset by Qamar *et al.* [1] and subsequently distill its knowledge into a fast, local atomic cluster expansion (ACE) potential. This distilled model can efficiently capture the self-assembly of carbon clusters and the spontaneous formation of fullerene-like structures in dense inert-gas environments. These results illustrate how transfer learning and model distillation make foundation-model-based MLIPs a powerful new tool for studying the atomistic dynamics of nanostructure formation. As these models continue to incorporate richer chemistry and interfacial effects, they promise a new level of integration between theory and experiment in the understanding and controlled growth of 2D materials.



REFERENCES

[1] M. Qamar, *et al.*, J. Chem. Theo. Comput. **19** (2023) 5151–5167

On-Surface Synthesis of Low-Dimensional Carbon Structures Including Heteroatoms

Willi Auwärter[a],

[a]*Technical University of Munich, TUM School of Natural Sciences, Physics Department E20, Germany*

On-surface synthesis protocols provide elegant routes to low-dimensional materials and molecular nanostructures on solid supports [1]. The resulting structural, physical, and chemical properties can be controlled by heteroatom- substitution.

The presentation will provide an overview of our activities employing temperature-induced reactions on coinage metals in ultrahigh vacuum, affording porphyrinoids, nanocarbons, and 2D materials. The focus will be on peripherally O-annulated porphyrins and BN-substituted carbon networks, primarily addressed by scanning probe microscopy.

Specifically, the synthesis of tetra- and octa-O fused porphyrins through dehydrogenative C-O bond formation on Au(111) is discussed, offering benefits over conventional solution protocols [2]. The O-annulation promotes self- assembly and modifies the electronic structure. In addition, the synthesis approach can be applied on monolayer hexagonal boron nitride on Cu(111), representing an electronically corrugated template.

Furthermore, the on-surface synthesis of BN-substituted covalent carbon networks will be discussed, which bases on tailored functionalized borazine precursors, providing B_3N_3 doping units [3]. On the one hand, dehydrogenative coupling is employed to form amorphous carbon monolayers on coinage metal supports, with a B_3N_3 areal density mainly defined by the precursor [4]. These sheet-like nanomaterials can be transferred, e.g., to silicon wafer dices for further characterization [5]. On the other hand, Ullmann-type coupling yields single-layer 2D covalent organic frameworks (COFs) on Ag(111) and Au(111), featuring distinct B_3N_3 areal densities and pore sizes. In a multi- method approach, we demonstrate the effect of atomically precise B_3N_3 substitution on the electronic structure of these kagome systems, through a comparative analysis of isostructural BN and CC substituted COFs.

Overall, the results presented pave the way to novel O- and BN-substituted carbon-based architectures on surfaces.

REFERENCES

1. Grill, Hecht, Nat. Chem. 12, 115 (2020)
2. Deyerling *et al.,* Angew. Chem. Int. Ed. 24, e202412978 (2025)
3. Marchionni *et al.*, Adv. Funct. Mater. 33, 49 (2023)
4. Tömekçe *et al.*, Chem. Eur. J. 30, e202402492 (2024)
5. Tömekçe *et al.,* Small Struct. 7, e202500742 (2026)

Atomic-Scale Engineering of Complex Organic Nanomaterials via On-Surface Synthesis

Abner de Siervo

Institute of Physics Gleb Wataghin – University of Campinas (UNICAMP), 13083-859,
Campinas, SP, Brazil

Materials science at the nanoscale has become a tangible reality across a wide range of applications, including integrated circuits, sensors, catalysts, pharmaceuticals, and data storage devices [1]. We now possess not only the ability to understand materials at the atomic level but also to precisely tailor their properties through advanced synthesis and growth techniques. Over the past few decades, substantial efforts have been devoted to developing innovative methodologies for the fabrication, characterization, and manipulation of materials within complex nanoarchitectures, achieving atomic precision and enabling the emergence of novel chemical, electronic, photonic, magnetic, and structural properties.

On-surface synthesis has emerged as a powerful bottom-up approach for constructing nanostructures using organic and organometallic precursors as molecular building blocks [1]. In this presentation, I will outline several strategies we have employed to fabricate planar carbon-based nanostructures, such as porous nanoribbons and nanomembranes [2–5].

To achieve a comprehensive understanding of the atomic and electronic properties of these materials, we integrate scanning tunneling microscopy and spectroscopy (STM/STS), X-ray photoelectron spectroscopy (XPS), and numerical simulations based on density functional theory (DFT) calculations.

Acknowledgments:

This research has been financially supported by FAPESP, CNPq, and CAPES (Brazil).

References:

[1] Johannes V. Barth. Annual Review of Physical Chemistry 58, 375 (2007).
[2] Alisson Ceccatto dos Santos, et al., J. Phys. Chem. C 125, 31, 17164 (2021).
[3] Alisson Ceccatto dos Santos, et al., Carbon 221, 118945 (2024).
[4] Alisson Ceccatto dos Santos, et al., FlatChem 50, 100808 (2025).
[5] Nataly Herrera-Reinoza, et al., J.Phys. Chem C. (2025).
doi/10.1021/acs.jpcc.4c08308

Insights to self-metalation of tetraphenyl transdibenzoporphyrin on Cu(111)

Majid Shaker[a], Maximilian Muth[a], Julien Steffen[b], Alisson Ceccatto Dos Santos[a], Simon Jaekel[a], Rajan Adhikari[a], Alexander Wolfram[a], Simon Steinbach[a], Pascal Gazetas[c], Christoph Oleszak[c], Abner de Siervo[d], Norbert Jux[c], Andreas Görling[b,e], Ole Lytken[a], Hans-Peter Steinrück[a]

[a]*Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3,*

Erlangen 91058, Germany

[b]*Lehrstuhl für Theoretische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3,*

Erlangen 91058, Germany

[c]*Lehrstuhl für Organische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nikolaus-Fiebiger-*

Str. 10, Erlangen 91058, Germany

[d]*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Campinas 13083-859, SP, Brazil* [e]*Erlangen National High Performance Computing Center (NHR@FAU), Martensstrasse 1, D-91058 Erlangen, Germany*

The adsorption behavior and self-metalation of tetraphenyltransdibenzoporphyrin (2H-TPtdBP) on Cu(111) at various temperatures and coverages have been investigated by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and density-functional theory (DFT) calculations [1]. When deposited at low coverages (<0.16 molecules nm^{-2}), the free-base molecules adsorbed as isolated individual molecules with an inverted conformation, and no self-metalation was observed upon annealing up to 363 K. At higher coverages, the free-base molecules self-metalated already at room temperature, and to a larger extent at 363 K, forming ordered islands of Cu-TPtdBP. Annealing at 423 K led to the complete self-metalation up to a full monolayer coverage. The comparison of the results of this study with the published literature demonstrates, how the selection of the substituents affects the self-metalation of tetraphenyl- based porphyrins.

REFERENCES

1. Majid Shaker et al 2025 J. Phys.: Condens. Matter 37 085001.

The project was supported by the German Research Foundation (DFG) through RTG 2861 (Project Number 491865171) at the Friedrich-Alexander-Universität Erlangen-Nürnberg and the TU Dresden.

Engineering a 2D Fe array on Ag(100) via temperature-driven reorganization and metalation of pyridyl-porphyrins

Rafael Reis Barreto[a], Iago Aédon Silva Prior[a], Eidsa Brenda da Costa Ferreira[a], Vanessa Carreño-Diaz[a], Igor Stein Weiler[a], Maximilian Muth[b], Alisson Steffli Thill[c], Fabiano Bernardi[c], Hans-Peter Steinrück[2] and Abner de Siervo[a]

[a] Instituto de Física Gleb Wataghin Universidade Estadual de Campinas UNICAMP, Campinas, Brazil
[b] Friedrich–Alexander University Erlangen–Nürnberg, Erlangen and Nuremberg, Germany
[c] *Instituto de Física Univerisdade Federal do Rio Grande do Sul, Porto Alegre, Brazil*

Surface-confined molecular self-assembly offers an atomically precise route to engineer two-dimensional lattices with programmable symmetry, spacing, and functionality. Tetrapyrrolic macrocycles functionalized with pyridyl termini are particularly versatile on coinage-metal surfaces because they can undergo both non-covalent self- assembly and metal–ligand coordination mediated by adatoms. Here we investigate the temperature-dependent structural evolution of a pyridyl-porphyrin monolayer on Ag(100), and how temperature steers the system between distinct network motifs and metalated states, using UHV scanning tunneling microscopy as the primary probe. After Fe deposition followed by mild annealing (≈350 K), the molecules organize into a square metal organic coordination network in which Fe adatoms act as nodes linking pyridyl groups (pyridyl–Fe–pyridyl). Increasing the annealing temperature (≈450 K) destabilizes the open network in favor of a denser, close-packed molecular phase, where Fe incorporation is dominated by metalation of the porphyrin core. Upon annealing to ≈500 K, we observe an complete planarization of the molecules accompanied by a marked change in intramolecular contrast consistent with thermally activated dehydrogenation, followed by a transition to a fully square overlayer that is commensurate with the Ag(100) substrate (lattice parameter ≈1.41 nm, close to a 5×5 relation). In this configuration, subsequent Fe dosing predominantly metalates the macrocycle centers, yielding a two-dimensional array of Fe ions templated by the molecular lattice. These results demonstrate a thermally programmed pathway that switches between coordination-driven MOF-like architectures and a commensurate square lattice supporting a high-yield metalated Fe array, providing a controlled platform to explore the electronic and magnetic properties of ordered metal–organic layers on surfaces and also the temperature needed for dehydrogenation of the porphyrin peripheral. [1,2]

REFERENCES

1. Barreto, R. R. et al. Surface Science,766, 122897, 2026. DOI:10.1016/j.susc.2025.122897
2. Barreto, R. R. et al. (In preparation to JACS)

Engineering Artificial Spin Networks by On-Surface Metal–Organic Coordination

Isabela da Costa Tonon[a], **Eidsa Brenda da Costa Ferreira**[a], **Neeta Bisht**[b], **Alisson Ceccatto dos Santos**[c], **Thomas Andreas Jung**[d], **Andreas Görling**[b], **and Abner de Siervo**[a]

[a] *Instituto de Física Gleb Wataghin Universidade Estadual de Campinas UNICAMP, 13083-970 Campinas, Brazil*

[b] *Lehrstuhl für Theoretische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

[c] *Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

[d] *Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland*

Artificial spin networks on metallic substrates have emerged as a powerful platform for exploring low-dimensional magnetism. The controlled assembly of magnetic atoms or molecules on surfaces offer a versatile platform for investigating collective magnetic order, such as ferromagnetism, as well as many-body phenomena including the Kondo effect [1-3]. Metal–organic coordination nanostructures provide an effective strategy for fabricating such artificial spin networks with atomic precision. In this work, we investigate the formation of Fe-coordinated networks on the Au(111) surface with tunable pore sizes defined by the molecular precursors. Two tritopic molecules were employed, both featuring three pyridyl terminal groups connected to a central benzene core: 1,3,5-tris[4- (pyridinyl)phenyl]benzene (TPyPB) and 1,3,5-tris[4-(pyridinyl)-[1,1′-biphenyl]]benzene (TPyPPB), which differ in molecular length due to the presence of one or two phenyl spacers, respectively. Following room-temperature (RT) deposition on Au(111), scanning tunneling microscopy (STM) revealed that both molecules self-assemble into porous honeycomb networks stabilized by two-fold coordination with surface gold atoms. Subsequent Fe deposition directly induces the transformation from Au-coordinated to Fe-coordinated honeycomb lattices with threefold metal coordination at RT, a mechanism further supported by density functional theory (DFT) calculations. Thermal annealing promotes the formation of long-range ordered periodic structures with a low density of defects, with structural stability preserved up to approximately 600 K. Overall, these results demonstrate that the pore size and lattice geometry of surface-supported metal–organic networks can be systematically tuned by the choice of molecular precursor and by switching the coordination center between Au and Fe, providing a controlled approach to the on-surface engineering of artificial spin lattices.

Acknowledgments: This work was financially supported by FAPESP, CNPq, and CAPES.

REFERENCES

[1] Lobo-Checa, J., Hernández-López, L., Otrokov, M.M. et al. Nat Commun, 2024,15, 1858.
[2] Girovsky, J., Nowakowski, J., Ali, M. et al. Nat Commun, 2017, 15388.
[3] R.Tuerhong, F. Ngassam, S. Watanabe, J. Onoe, M. Alouani, and J. Bucher. J. Phys. Chem. C, 2018, 122 (34), 20046-20054.

Reversible structure formation in 4,4-bipyridine – Fe 2D metal organic frameworks on Au(111)

Afra Gezmis[a], Simon Steinbach[a], Julien Steffen[b], Alisson Ceccatto[a], Isabela Tonon[c],

Natalie Waleska-Wellnhofer[a], Abner de Siervo[c], Hans-Peter Steinrück[a]

[a] *Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nuernberg, 91058,Erlangen, Germany*

[b] *Lehrstuhl für Theoretische Chemie, Friedrich-Alexander-Universität Erlangen-Nuernberg, 91058,Erlangen, Germany*

[c] *Institute of Physics Gleb Wataghin, University of Campinas, 13083-859 Campinas, Brazil*

Surface-confined metal–organic frameworks (2D MOFs) provide a versatile platform for studying low-dimensional coordination chemistry and tunable molecular architectures at atomic and molecular levels. Here, we investigate the self-assembly of 4,4-bipyridine and Fe on Au(111) and reveal a coverage-dependent phase behavior governed by metal–ligand coordination and surface availability. In the absence of Fe, 4,4-bipyridine forms a weakly substrate-coupled molecular network stabilized by intermolecular interactions. Fe coordination induces a sequence of distinct two- dimensional architectures, ranging from dense threefold-coordinated tripod networks to open Kagome lattices composed of hexagonally arranged metal centers bridged by molecular linkers. Using scanning probe microscopy, low energy electron diffraction and density-functional theory calculations, we identify three thermodynamically stable phases with different coordination numbers, symmetries, and molecular densities. Transitions between these phases are reversible and controlled by the Fe-to-ligand ratio. These findings demonstrate how subtle control over coordination chemistry and surface coverage enables programmable structural transitions in two-dimensional metal–organic frameworks

High-pressure synthesis of 2D diamond

Luiz G. Pimenta Martins(a)*

(a) Departamento de Física Aplicada, Instituto de Física, Universidade de São Paulo

*e-mail: lgpmartins@usp.br

Material synthesis plays a central role in modern condensed matter physics. The rich physical phenomena observed in quantum materials has only been possible by innovative methods of materials synthesis that focused on leveraging the intricate interactions between quantum wavefunctions and factors such as symmetry, dimensionality, topology and Coulomb interactions. Among this class, two-dimensional (2D) materials have been on the spotlight of scientific research. After the isolation of graphene about two decades ago, there has been an intense search for novel 2D materials, due to their remarkable - and often unexpected - properties arising from their reduced dimensionality. Most 2D materials have been obtained either by mechanically exfoliating the analogous layered bulk materials or by direct synthesis via chemical vapor deposition or molecular beam epitaxy. I explore an alternative route to synthesize new types of 2D materials with no bulk analogues using hydrostatic compression to stabilize new phases. In this talk, I will discuss two such studies using diamond anvil cells. The first work, done during my master's at Universidade Federal de Minas Gerais (UFMG), was the first spectroscopic evidence for the formation of 2D diamond from compression of bi-layer graphene [1], in which we demonstrated a phase transition from a pure sp^2 to a hybrid sp^2-sp^3 phase. In the second work, done during my PhD at the Massachusetts Institute of Technology (MIT), we obtained robust evidence for the formation of a hard, transparent and sp^3-containing 2D phase from compression of few- layer graphene [2]. In both studies, we obtained indications for the formation of diamondene, a predicted 2D ferromagnetic semiconductor with spin-polarized bands with different band gaps for different spin components - an ideal material for spintronics applications. I will conclude by presenting unpublished results and outlining one of the future research directions that my group at Universidade de Sao Paulo will pursue, focusing on the synthesis of novel two-dimensional materials under high pressure.

REFERENCES

[1] L. G. Pimenta Martins, et al. "Raman evidence for pressure-induced formation of diamondene." Nature Communications 8.1 (2017): 96.

[2] L. G. Pimenta Martins, et al. "Hard, transparent, sp3-containing 2D phase formed from few-layer graphene under compression." Carbon 173 (2021): 744-757

Tailoring the Quantum Optical Properties of Localized States in van der Waals Heterostructures

Bárbara L. T. Rosa[a], Imas Limame[c], Pablo B. Pinto[a], Pedro W. Matrone[a], Paulo V. Santos[b], Lara Greten[c], Rafaela Oliveira[e], Cesar Ribahi[d], Chirag Palekar[b], Ingrid David Barcelos[e], Yara Galvão Gobato[d], Andreas Knorr[c], Stephan Reitzenstein[c], Odilon D. D. Couto Jr.[a]

[a] Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas (UNICAMP), Campinas, SP, 13083-859, Brazil

[b] Paul-Drude-Institut für Festkörperelektronik, Leibniz-Institut im Forschungsverbund Berlin, Berlin,

Germany

[c] Institute of Solid-State Physics, Technische Universität Berlin, Berlin, Germany

[d] Departamento de Física, Universidade Federal de São Carlos (UFSCar), São Carlos, SP,
Brazil [e] Laboratório Nacional de Luz Síncrotron (LNLS), CNPEM, Campinas, SP, Brazil

Localized quantum emitters in two-dimensional (2D) materials are promising systems for quantum technologies due to their ability to generate non-classical light and their compatibility with optoelectronic and photonic platforms[1]. However, controlling their emission properties remains challenging because the optical response of localized states is strongly influenced by the surrounding environment[1-4]. Here, we investigate strategies to tailor the quantum optical properties of localized states in WSe_2-based van der Waals heterostructures through dynamic[5,6] and proximity-induced effects[3,4].

We first integrate WSe_2 monolayers and twisted homobilayers into surface acoustic wave (SAW) architectures using dielectric nanopillars to locally engineer the emission. SAW excitation induces emission broadening and a power-dependent modulation of the emission intensity, with distinct responses for monolayer and twisted-bilayer devices. Circular polarization–resolved photoluminescence further indicates that SAWs can suppress the valley polarization in monolayer emitters, while interlayer exciton emission in twisted bilayers remains weakly affected. In addition, we investigate proximity effects by interfacing WSe_2 monolayers with layered doped phyllosilicate material. Optical spectroscopy, magneto-photoluminescence, time-resolved photoluminescence, and autocorrelation measurements reveal a strong substrate-dependent modulation of the emitter properties. While the brightness of the emitters is significantly enhanced, their lifetime and single-photon purity are substantially modified, strongly impacting the quantum nature of the emission. These results demonstrate that both acoustic fields and substrate proximity provide effective routes for engineering the quantum optical response of localized states in van der Waals heterostructures.

1-Esmann, Wein and Antón-Solanas *Adv. Funct. Mater.* 2315936 (2024)

2-Chhaperwal et al. *Nano Lett.* **24**, 40, 12461–12468 (2024)

3-von Helversen et al. *2D Mater*. **10**, 045034 (2023)

4-de Brito et al. *Nano Lett.* **24**, 42, 13300–13306 (2024)

5-Patel et al. *PRX Quantum* **5**, 010330 (2024)

6-Mohajerani et al., *ACS Nano* **19**, 25851 (2025

Multiple Quasiparticle Interactions in Molecularly Functionalized h-BN Polaritonic Systems

Everton Pereira-Andrade[a,b], Rafael Reis Barreto[c], Yuri Bernardes[d], Ingrid Barcelos[d], Angelo Malachias[b], Francisco Barbosa Maia[d] and Gustavo de Almeida Magalhães Sáfar[b]

[a]*Departamento de Física, Universidade Federal de Viçosa, Viçosa, Minas Gerais 36570-900, Brazil*
[b]*Departamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte, Minas Gerais, Brazil*

[c]*Instituto de Física Gleb Wataghin Universidade Estadual de Campinas UNICAMP, 13083-970 Campinas, Brazil* [d]*Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, São Paulo, Brazil*

Spectroscopic measurements focusing on hybrid light–matter interactions have emerged as a powerful tool for exploring nanoscale energy exchange and optical confinement. Uncovering the interaction between vibrational modes of $Tb(H_3PTC)_3$ molecules and phonon-polaritons in h-BN flakes, as well as the interaction between the same polaritons with the molecular excitons of $Tb(H_3PTC)_3$, this study demonstrates the formation of hybrid modes in this system at room temperature in the infrared range. Combining h-BN crystals and molecular films, the system achieves coupling between excitons and polaritons, confirmed by near-field optical measurements in the infrared and spectral analysis. This research highlights the effective integration of molecular phonons and excitons with confined polaritonic modes, revealing the potential for efficient energy exchange in hybrid systems. The findings contribute to the broader understanding of vibrational–polaritonic interactions and underscore the utility of this straightforward platform for applications in nanospectroscopy, optoelectronics, and light–matter interaction technologies.[1]

REFERENCES

1. Pereira-Andrade, Everton and Barreto, Rafael Reis and Bernardes, Yuri and Barcelos, Ingrid David and Malachias, Angelo and Maia, Francisco Carlos Barbosa and Sáfar, Gustavo de Almeida Magalhães. Multiple Quasiparticle Interactions in Molecularly Functionalized h-BN Polaritonic Systems. J. Phys. Chem. C 2025, 129, 36, 16147–16154 DOI: 10.1021/acs.jpcc.5c02986

Implementation of Ultra-High Vacuum Tip-Enhanced Raman Spectroscopy (TERS) for the Characterization of Optically Active Materials

Douglas dos Santos Ribeiro[a], **Wesley Kardex Cordeiro de Oliveira**[a], **Luiz Fernando Zagonel**[a]

[a] Instituto de Física Gleb Wataghin Universidade Estadual de Campinas UNICAMP, Campinas, Brazil

This work reports the implementation of Tip-Enhanced Raman Spectroscopy (TERS) within an ultra-high vacuum (UHV) scanning tunneling microscopy (STM) system. Central to this infrastructure is a patented off-axis parabolic mirror device that enables high-efficiency light injection and collection at the tip-sample junction [2]. The high numerical aperture and geometric precision of this mirror are fundamental to overcoming the diffraction limit and spatial constraints of UHV systems, enabling the nanometric alignment required for high-sensitivity near-field processes.

TERS is explored using silver (Ag) and gold (Au) probes as optical nanoantennas, where localized surface plasmon resonances (LSPR) and the gap-mode effect confine electromagnetic fields to sub-wavelength volumes [3]. This allows for the vibrational characterization of 2D materials, such as TMDs and h-BN, resolving local strain and edge states with sub-nanometric resolution [1]. The platform is further extended by integrated emission techniques: STM-Induced Luminescence (STML) and low-energy Cathodoluminescence (CL). STML probes local excitonic dynamics and gap plasmon decay induced by tunneling current [4], while CL utilizes the electron beam to access higher-order excitonic states in semiconductor nanoobjects [5].

The parabolic mirror unifies this multimodal approach, ensuring that both amplified TERS signals and inherently weak STML/CL photon emissions are captured with maximum signal-to-noise ratio. This synergy allows for a holistic understanding of matter by correlating atomic-scale structure with vibrational signatures and electronic transitions in a controlled UHV environment.

REFERENCES

1. Pozzi, E. A. et al. Chemical Reviews, 117, 4961–4982, 2017. DOI:10.1021/acs.chemrev.6b00343
2. Peña Román, R. J. et al. Review of Scientific Instruments, 93, 043704, 2022. DOI:10.1063/5.0078423
3. Vasconcelos, T. L. et al. IEEE Journal of Selected Topics in Quantum Electronics, 27, 4600411, 2021. DOI:10.1109/JSTQE.2020.3003058
4. Peña Román, R. J. et al. Nanoscale, 12, 13460-13470, 2020. DOI:10.1039/D0NR03374K
5. Cordeiro de Oliveira, W. K. et al. Journal of Physical Chemistry C, 129, 14949-14957, 2025. DOI:10.1021/acs.jpcc.5c05410

Scanning Tunneling Spectroscopy as a tool for the study of physical phenomena at surfaces

Rogério Magalhães Paniago

Federal University of Minas Gerais

In this talk, we will present the use of scanning tunnelling spectroscopy to understand the interplay between structural and other physical properties of the surface of different two-dimensional materials.

In the first example, we show that scanning tunneling spectroscopy is able to differentiate the electronic properties of single and bilayers of epitaxial graphene. We report on the observation of triangular nanostructures which result from extended stacking faults in the SiC substrate and their effects on graphene layers that are formed on top of them. Spectroscopic measurements revealed distinct electronic responses as a function of the local hydrogen intercalation. Spectroscopic signatures ranging from single- to double- layer graphene, as well as intermediate states were observed as a consequence of the (in)complete hydrogen intercalation process [1].

In the second example, we used vapor phase deposition to synthesize ultrathin germanium sulfide nano-flakes on a highly oriented pyrolytic graphite substrate. Nanostructures of variable thicknesses were characterized using scanning tunneling microscopy and spectroscopy. Tunneling currents under forward and backward biases were measured as a function of nano-flake thickness. Remarkably, we clearly observed a hysteresis pattern, which we attributed to surface ferroelectric behavior, consistent with the screening conditions of polarization charges [2].

Finally, we explored the variation in the band gap of two-dimensional nanobelts o MoO3 after the localized application of intense electric fields using scanning tunneling microscopy and spectroscopy. A deterministic change of electronic band gap was observed in MoO3 for negative applied biases. These changes are fully reversible and robust with respect to successive cycles for a range of applied bias compatible with common applications. This phenomenon is ascribed to changes in the surface stoichiometry due to the local action of the scanning tunneling microscopy tip [3].

[1] Self-assembled triangular graphene nanostructures: Evidence of dual electronic response, T Chagas, PHR Gonçalves, I Antoniazzi, JW González, R. Magalhaes- Paniago. Carbon 142, 580-591 (2021)

[2] Evidence of thickness-dependent surface-induced ferroelectricity in few-layer germanium sulfide obtained via scanning tunneling spectroscopy, RR Barreto, TC Ribeiro, GHR Soares, E Pereira, DR Miquita, GAM Safar, R. Magalhaes-Paniago, Nanoscale 16 (11), 5794-5801 (2024)

[3] Electronic gap redesign in electrochromic : A scanning tunneling spectroscopy study, LP Trindade, G Fontenele, EG de Oliveira, RR Barreto, LC Detoni, R. Magalhaes- Paniago, Physical Review Materials 10 (1), 016205 (2026)

Efficient and stable perovskite solar cells: new materials and modeling

Gabriel L. Nogueira[1], Hugo G. Lemos[1], João Pedro F. Assunção[1], Lucas J. Affonço[1], Eva Unger[2], [3]Victor Lopez-Richard[3], Carlos F.O. Graeff[1]

[1] carlos.graeff@unesp.br, São Paulo State University (Unesp), School of Sciences, Brazil

[2] Helmholz Zentrum Berlin, Germany

[3]Federal University of São Carlos, Institute of Physics, Brazil

Perovskite solar cells (PSCs) have attracted widespread attention in academia and industry due to their high-power conversion efficiency (PCE) and potential for low-cost, sustainable, and large-scale manufacturing. We have incorporated two-dimensional (2D) materials to enhance the performance of double-cation mixed halide perovskite (Cs0.17FA0.83Pb(I0.83Br0.17)3) solar cells. We developed a Nb2O5 ETL layers adding Ti3C2Tx MXene into a solution processable ink [1]. The addition of MXene increased the PCE (19.46% for the champion device) and the stability (96% of its original PCE after 500 hours) compared to pristine devices. The improved performance of the Nb2O5–Ti3C2 is attributed to the alignment of the energy bands between perovskite and the ETL layer. In inverted or p-i-n PSCs we used an ultra-thin poly(methyl methacrylate) (PMMA) layer to passivate interfacial defects between the perovskite and the ETL layer [2]. With the addition of Ti3C2Tx MXene resulted in improvement of the PSC photovoltaic parameters, boosting their efficiency to 21.30 ± 0.51% (22.1% for the benchmark PSC). The enhanced performance is attributed to a reduction of trap state densities accompanied by mitigation of non-radiative recombination. The PMMA:MX based devices maintained 95% of their original PCE after 3000 h (ISOS-D-1I) and took 3X longer to reach T80 compared to the control PSC under heat and light soaking (ISOS-L-2). In another study [3], the deposition of Nb2O5 as an electron transport layer via slot die coating was systematically investigated. These Nb 2 5 layers were used as electron transport layers in n-i-p perovskite devices. Current density versus voltage scans were utilized to evaluate the device performance, alongside transient analysis. Under optimal coating conditions, efficiencies up to 12 % were obtained. We will also present a conceptual framework for characterizing photovoltaic devices by integrating cyclic voltammetry (CV) and impedance spectroscopy (IS) [4]. This framework is constructed from a microscopic, multi-mode perspective that explicitly accounts for drift, diffusion, displacement, and memory contributions. We derive comprehensive analytical expressions for current-voltage relationships and complex admittance. Our model reveals the inseparable connection between hysteresis behaviors in current-voltage characteristics observed in CV and the apparent capacitive and inductive behaviors seen in IS spectral analysis.

The authors acknowledge FAPESP (Projects: 2020/12356-8 and 2013/07296-2), FINEP, CAPES and CNPq (INCT NanoVida) for financial support.

[1] H.G. Lemos et al., J. Mater. Chem. C, 2023, 11, 3571-3580 (DOI: 10.1039/d3tc00022b).

[2] J.P.F. Assunção et al., J. Mater. Chem. C, 2024, 12, 562-574 (DOI: 10.1039/ d3tc03810f).

[3] L.J. Affonço et al., Solar Energy, 2024, 276, 112691 (DOI: 10.1016/j.solener.2024.112691).

[4] V.Lopez-Richard et al., 2024, Phys. Rev. B 110, 115306 (2024)(DOI: 10.1103/PhysRevB.110.11530

$Mo_3C_2T_x$ MXene-Modified SnO_2 Electron Transport Layer for Enhanced Efficiency and Stability of Perovskite Solar Cells

Hameed Ullah, **Sajid sajid**, **Carlos F. de O. Graeff**,

Department of Physics and Meteorolog, School of Sciences, Sao Paulo State University (UNESP),Bauru, Sao Paulo, 17033-360, Brazil.

E-mail: hameed.ullah@unesp

The global shift toward sustainable energy is imperative as fossil fuel reserves dwindle. Among renewable sources, solar energy stands out as a clean, abundant, and scalable solution capable of meeting global energy demands. Recently the perovskite solar cells (PSCs) have attracted a huge amount of attention due to its rapid advancement. The solution-processed lead halide perovskites have emerged as promising materials for next-generation photovoltaics, achieving impressive power conversion efficiencies (PCEs) exceeding 26% rivaling traditional silicon (Si)-based solar cells at a significantly lower production cost. Herein, $Mo_3C_2T_x$ Mxene nanoflakes are used as an additive in SnO_2 ETL in planner PSCs. The $Mo_3C_2T_x$ increase the conductivity of SnO_2, supress the interfacial deffects and charge transper resistance. The Perovskite layer deposited on MXene modified SnO_2 leads to enhancement in the absorption spectra. As a result the MXene modified SnO_2 ETL based devices acheived the effeciency above 20% as compared to the control device (18 %). This work has the potential to develop stable MXene-based PSCs with enhanced efficiency for photovoltaic applicatio.

Clinochlore as natural nanocavity for water confinement

Raphaela de Oliveira[a], Alisson Cadore[b], Angelo Malachias[c], Klaus Krambrock[c], Ingrid D. Barcelos[a]

[a]*Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, São Paulo, Brazil.*

[b]*Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, São Paulo, Brazil.*

[c]*Department of Physics, Federal University of Minas Gerais, Belo Horizonte, Minas Gerais, Brazil.*

Water is the matrix of life and its confinement in nanocavities and flow through nanocapillaries are central topics from geophysics to nanotribology. Water in nanoscale media can show distinct elastic and viscosity behaviors, presenting exquisite properties such as low dielectric constant [1]. Clay minerals are well known to be hydrated, acting as natural nanocavities for water. However, the way hydration affects the fundamental properties of phyllosilicates at the nanoscale, particularly in their few-layer limit, has not been thoroughly discussed. In this presentation, I will demonstrate that the hydration of ultrathin phyllosilicates can alter the optical, mechanical, and dielectric responses of the system. To explore this, I will focus on the use of Kelvin probe force microscopy and scanning near-field optical microscopy as key tools for investigating hydration with spatial resolution at the nanoscale in ultrathin phyllosilicate minerals. In particular, clinochlore phyllosilicate mineral will be presented as a natural two-dimensional platform for studying distinct water nanoconfinement phenomena with the natural formation of aqueous nanochannels [2].

REFERENCES

1. L. Fumagalli et al. (2018) Science 360: 1339-1342
2. R de Oliveira et al. (2024) J Phys Chem C 128: 14388-14398

Growth and spectroscopy of altermagnetic MnTe

Marco Dittmar, Lena Hirnet, Hannes Haberkamm, Franziska Beisler, Maximilian Ünzelmann and Friedrich Reinert

Exp. Physik VII and Würzburg-Dresden Cluster of Excellence ctd.qmat, Universität Würzburg, Germany

As a new type of fundamental magnetic order next to ferromagnetism and antiferromagnetism, altermagnetism has recently attracted great attention [1]. It is characterized by antiferromagnetic spin alignment combined with rotational lattice symmetry, which is reflected in a spin-split band structure with spin polarized electronic states. One of the "workhorse" materials exhibiting this type of magnetic order is MnTe in its hexagonal NiAs-type crystal structure.

Here, we investigate MnTe thin films grown by molecular beam epitaxy on several functional substrates. The high film quality is confirmed by structural characterization methods. We assess the three-dimensional bulk band structure by soft X-ray angle-resolved photoemission spectroscopy and the magnetic properties of the sublattices by resonant photoemission and diffraction. Finally, we discuss the formation of surface reconstructions - as being observed experimentally - upon Te exposure and thermal treatment.

REFERENCES

1. L. Šmejkal *et al.*, Phys. Rev. X **12**, 031042 (2022)

Growth of Single-Photon Sources and Entangled Photon Pairs by Molecular Beam Epitaxy

Saimon F. Covre Da Silva[1*]

[1]Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), 13083-859
Campinas, Brazil.

[*]Email: saimon@unicamp.br

Epitaxial semiconductor quantum dots (QDs) have emerged as leading solid-state platforms for the on-demand generation of single and entangled photons. Their performance critically depends on the atomic-scale control provided by molecular beam epitaxy (MBE), which enables precise engineering of material composition, interface quality, and nanostructure morphology required for quantum-optical applications. Among MBE-based growth approaches, droplet etching epitaxy (DE) [1] stands out for enabling the formation of nearly strain-free QDs with low and tunable surface densities, reduced excitonic fine-structure splitting (FSS), and fast radiative recombination. In this work, we present recent advances in MBE and DE for the realization of high-quality single-photon and entangled-photon-pair sources based on GaAs/AlGaAs and InGaAs/AlGaAs III–V material systems [2].

[1] – Covre da Silva, S. F., Undeutsch, G., Lehner, B., Manna, S., Krieger, T., Reindl, M., Schimpf, C., Trotta, R., & Rastelli, A. (2021) Applied Physics Letters, 119(12), 120502.

[2] - Covre da Silva, S. F., Garcia, A., Aigner, M., Weidinger, C., et al. (2026). Nano Letters, 26(3), 953–960.

Increasing the Scope of Computational Nanochemistry by Combining Density-Functional Theory with Machine-Learned Interatomic Potentials

Julien Steffen

Chair of Theoretical Chemistry, Friedrich-Alexander-University Erlangen Nürnberg, Germany

Computational chemistry has proven to be a valuable tool in understanding low-dimensional materials with atomic resolution. While the direct application of high-level ab initio methods to periodic systems is still very challenging and out of reach for most cases, density-functional theory (DFT) provides an ideal compromise of accuracy and computational speed and makes the routine treatment of hundreds of atoms possible [1]. In recent years, machine-learned interatomic potentials (MLIPs) emerged as an increasingly powerful tool to simulate much larger systems of thousands to tens of thousands of atoms with DFT accuracy, providing that they were parametrized adequately [2].

In this talk, I will give an overview of efficient applications of DFT and MLIPs to surface and interface systems, with the focus on the adsorption of complex molecules on metal surfaces and the formation and properties of two- dimensional nanomaterials. The close collaboration with experimentalists provides initial structural guesses by STM or LEED patterns, which are then relaxed with a suitable DFT functional. Calculated STM images can then be used to back-verify the experimental starting point [3]. Besides geometries, the explicit treatment of electrons by DFT enables a systematic explanation of binding and reactive processes on a quantum-mechanical level.

I will show two possible applications of MLIPs in the realm of surface chemistry. Firstly, large scale structures like moire patterns or herringbone-reconstructions can now be simulated as a whole, enabling the verification of, e.g., site-selective adsorption on them. Secondly, time-dependent phenomena like surface diffusions or modifications due to interactions with gas phase molecules can now be studied in real time via molecular dynamics (MD), opening an opportunity for studying the influence of minor changes in temperature or partial pressures on the resulting material.

During the talk, I will lay out how DFT and MLIPs can be used together as closely connected tools that open new possibilities in the computational treatment of low-dimensional materials. The outline will be combined with a couple of concrete examples, like the adsorption of porphin derivatives on a Cu(111) surface [4, 5], the adsorption of Br on graphene and h-BN layers a on Rh(111) surface [6], the low-temperature diffusion of hydrogen on metal surfaces and in a two-dimensional confinement between Ni(111) and an adsorbed graphene layer [7], and finally how to simulate huge structures like herringbone patterns on Au(111) efficiently.

REFERENCES

1. J. Steffen, A. Mölkner, M. A. Bechtel, J. Chem. Theory Comput. 21, 11721 (2025)
2. R. Jacobs, B. M. Wood, S. Attarian et al., Curr. Opin. Solid State Mater. Sci. 35, 101214 (2025)
3. J. Hauner, H. Bühlmeyer, J. Steffen et al., J. Phys. Chem. C 128, 3894 (2024)
4. M. Shaker, M. Muth, J, Steffen et al., J. Phys. : Condens. Matter 37, 085001 (2025)
5. J. Steffen, M. Shaker, M. Muth et al. ; J. Phys. Chem. C 129, 12391 (2025)
6. E. M. Freiberger, J. Steffen, N. Waleska-Wellnhofer et al., Nanotechnol. 35, 145703 (2024)
7. J. Steffen, J. Chem. Phys. 162, 214114 (2025)

DFT-Guided Self-Assembly of 2D Pyridyl-Linked Metal–Organic Frameworks on Au(111)

Neeta Bisht[a], **Sajjan Mohammad**[b], **Anjana Kannan**[b], **Anne Brandmeier**[a], **Christian Neiss**[a], **Andreas Görling**[a,c], **Meike Stöhr**[b,d], **Sabine Maier**[b], **Isabela da Costa Tonon**[e], **Eidsa Brenda da Costa Ferreira**[e], **Alisson Ceccatto dos Santos**[f], **Thomas Andreas Jung**[g], **Abner de Siervo**[e]

[a] Chair of Theoretical Chemistry, Friedrich-Alexander-Universität Erlangen–Nürnberg (FAU), Erlangen, Germany

[b] Department of Physics, FAU, Erlangen, Germany

[c] Erlangen National High Performance Computing Center (NHR@FAU), Erlangen, Germany

[d] University of Applied Sciences of the Grisons, Chur, Switzerland

[e] Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), Campinas, Brazil

[f] Chair of Physical Chemistry II, FAU, Erlangen, Germany

[g] University of Basel, Basel, Switzerland

(This abstract combines results from two collaborations/projects.)

Surface-confined metal–organic frameworks (MOFs/SMONs) are periodic coordination networks assembled from functional organic linkers and metal nodes/adatoms directly on single-crystal surfaces. Their coordination geometry (2-fold vs. 3-fold), pore size, and registry with the substrate can be tuned via molecular design, metal choice, and UHV growth conditions.

We use density-functional theory (DFT) to support STM-based growth studies of a homolo- gous series of pyridyl "tripod" linkers on Au(111): 1,3,5-tris(pyridyl)benzene (TPyB), 1,3,5- tris[4-(pyridinyl)phenyl]benzene (TPyPB), and 1,3,5-tris[4-(pyridinyl)-[1,1'-biphenyl]]benzene (TPyPPB). As a separate, published collaboration, we summarize our STM & DFT results for 2,4,6-tri(4-pyridyl)-1,3,5-triazine (T4PT) on Au(111) [1]. While many d-metals can serve as coordination centers, we focus on Au and Fe adatoms as experimentally relevant node species and as a route toward single-atom coordination environments [2].

DFT resolves interaction landscapes for hydrogen bonding and 2- vs. 3-fold metal coordination, and determines adsorption/formation energies and preferred registries on Au(111), including adatom-mediated bonding. We further analyze charge transfer at the nodes and, where relevant, spin states and coupling pathways for Fe-coordinated nodes, thereby providing design rules to steer self-assembly toward targeted pore geometries and functionalities.

Nanometer pores act as host–guest platforms and can confine surface-state electrons, yield- ing well-defined coordination environments relevant to sensing, nanoelectronics, and (elec- tro)catalysis. Embedding transition-metal centers further enables tunable magnetic coupling on nonmagnetic substrates, offering a route toward spin-aware surface devices.

References

[1] S. Mohammad, N. Bisht, A. Kannan, A. Brandmeier, C. Neiss, A. Görling, M. Stöhr, and S. Maier, "Pyridyl-functionalized tripod molecules on Au(111): Interplay between H-bonding and metal coordination," *Surface Science* **755** (2025) 122701. doi: 10.1016/j.susc.2025.122701.

[2] A. Ceccatto, E. M. Freiberger, N. J. Waleska-Wellnhofer, S. Jaekel, D. J. Mowbray, C. Papp, H.-P. Steinrück, and A. de Siervo, "Engineering large nanoporous networks with size and shape selected by appropriate precursors," *Carbon* **221** (2024) 118945. doi: 10.1016/j.carbon.2024.118945.

Quantum Rate Spectroscopy: In-situ Nanoscale Electronic Structure Probing via Isoscopic Physics

Edgar F. Pinzón Nieto[a] **& Paulo Roberto Bueno**[a]

[a]*Department of Physics and Mathematics, São Paulo State University, Araraquara, São Paulo State, Brazil*

Quantum Rate Spectroscopy (QRS) has emerged as a transformative electronic spectroscopy technique for probing the electronic structure of nanoscale systems directly in wet environments. Grounded in quantum electrodynamics and the isoscopic energy regime, QRS allows for the high-resolution determination of the electronic density of states (DOS) without the typical constraints of high-vacuum instrumentation. This isoscopic regime is achieved when the electrostatic energy associated with ionic charge fluctuations in the electrolyte ($E_e = e^2/C_e$) matches the electronic charging energy of the quantum structure ($E_q = e^2/C_q$), ensuring an electroneutral condition ($E_e = E_q$) [1]. In this state, the electrolytic medium provides complete screening of the electric field, preserving the quantum coherence of the electronic communication process [2]. This process is fundamentally characterized by the quantized resistance $R_q = h/2e^2$.

By applying this framework to electrochemical capacitance spectroscopy (ECS) measurements, we demonstrate the in-situ retrieval of the electronic DOS for strongly quantum systems, such as graphene monolayers and semiconducting quantum dots, at room temperature [3]. Notably, the inherent ionic screening prevents Coulomb blockade under these experimental conditions, allowing for results that are remarkably consistent with high-energy vacuum techniques like Scanning Tunneling Spectroscopy (STS) and ARPES. Beyond its fundamental contribution to nanomaterial characterization, QRS represents a significant advance in accessible, rapid, and in-situ nanoscale spectroscopy, providing critical insights for the design of next-generation optoelectronic and quantum-coherent devices.

REFERENCES

1. Current Opinion in Electrochemistry 2026, 56, 101811.
2. Chemical Society Reviews 2026, 20, 1234-1245.
3. ACS Appl. Mater. Interfaces 2026, 18, 10669−106802.

Engineering of Metal-Perovskite interfaces for charge transport optimization in inorganic halide perovskites

Maria Vitória C. Issler[a], **Lucas Martin Farigliano**[a], **Roberto Hiroki Miwa**[a,b] **and Gustavo Martini Dalpian**[a]

[a]*Department of Materials Physics and Mechanics, Institute of Physics, University of São Paulo, São Paulo, São Paulo, Brazil.*

[b]*Institute of Physics, Federal university of Uberlândia, Uberlândia, Minas Gerais, Brazil.*

Halide perovskites are highly promising materials for optoelectronic devices due to their significant physicochemical properties [1]. In many device architectures, they are interfaced with metallic contacts or supported on metal substrates, where the device's performance is influenced by the electronic properties and thermodynamic stability of the interface formed between the perovskite and the metal [2, 3]. In this work, we systematically investigate the interfacial interactions governing charge-transfer mechanisms at metal contacts with inorganic halide perovskites ($CsPbX_3$, where X= Br, I, Cl) through first-principles calculations. Interfaces with metal contacts Au, Ag, Al, and Cu are examined, considering both PbX_2- and CsX- terminated perovskite surfaces. The electronic structure and band alignment are analyzed using the PBE and HSE06 exchange- correlation functionals, with and without spin-orbit coupling, allowing an assessment of functional-dependent band offsets, which demonstrates that the transition from PBE to HSE06 can alter both the magnitude and type of Schottky barriers. Our results show that the PbX_2-terminated surface is consistently more stable than the CsX- terminated configuration across all systems. This stability is associated with shorter interface distances and stronger interfacial hybridization, consistent with the emergence of chemical interactions between perovskite and metal atoms at the interface. Correspondingly, binding energies range from -37 to -67 meV/Å^2 for PbX_2-terminated surfaces, compared to -15 to -36 meV/Å^2 for CsX-terminated systems. These structural and energetic differences are reflected in the electronic structure, with an increased density of mid-gap states appearing within the perovskite band gap of PbX_2-terminated interfaces, originating from interfacial perovskite atoms. In addition, analysis of Schottky barriers reveals a strong dependence on both the metal and surface termination for charge selectivity. Au contacts display the lowest p-Schottky barrier (0.64 eV), indicating favorable hole transport, whereas Al interfaces, particularly with CsX termination, show the lowest n-type Schottky barriers, suggesting their potential for efficient electron injection. These findings offer new theoretical insights into the interfacial mechanisms controlling perovskite-based optoelectronic devices.

Acknowledgements: we thank the financial support from FAPESP and CNPq. The calculations were performed using the Santos Dumont Supercomputer at LNCC.

REFERENCES

1. Y. Zhou and Y. Zhao, Energy Environ. Sci., 12, 1495-1511 (2019).
2. Ye Liu et al, Nanotechnology 33, 475701 (2022).
3. L. Quintero et al, J. Appl. Phys. 138, 123108 (2025).

Probing the Electronic Density of States of Electrochemically Reduced Graphene Oxide *via* Quantum Rate Spectroscopy

Nicolás M. S. de Siqueira[a], **Paulo R. Bueno**[a]

[a]*São Paulo State University (UNESP), Institute of Chemistry, Araraquara*

Quantum Rate Theory Spectroscopy (QRS) is a novel technique based on Quantum Rate Theory (QRT, a framework for understanding charge transfer/transport rates in quantum systems) that enables the characterization of nanostructures anchored to a probing electrode. In QRS analysis, the electrode applies an electric-field perturbation (a way of applying electric force to the system) of an 'electron reservoir' (a source or sink for electrons) that maintains 'quantum coherence' (the preservation of phase relationships between quantum states) with an ionic electrolyte bath (a liquid containing charged particles, or ions). This allows access to the dynamics of quantum states by measuring the quantum capacitance (the system's ability to store charge due to quantum effects) at the interface. Because quantum capacitance is directly proportional to the electronic density of states (DOS, a measure of the number of electronic states available at a given energy), it allows us to investigate the electronic structure of an anchored material at the electrode.

Building on this foundation, this research investigates the electronic structure of reduced graphene oxide (rGO) by measuring its quantum capacitance. QRS [1] shows that the widely accepted charge- storage mechanism, often linked to high surface area, is governed by a dissipative quantum limit – a threshold where energy loss affects charge storage [1]. We study how atomic-level changes affect both electronic and capacitive behavior. The reduction protocol removes preferential oxygen-containing groups – such as hydroxyl (-OH) and epoxy (C-O-C) – and increases the carbon-to-oxygen (C:O) ratio. This also raises the sp^2-to-sp^3 carbon-hybridization ratio and creates chemical and structural defects, which have been reported to drive charge storage (supercapacitance). The DOS is measured directly *in situ* using QRS and correlated with XPS (X-ray photoelectron spectroscopy) data. This links electrochemical behavior to surface chemistry. Importantly, partially restoring the sp^2-hybridized carbon network – mainly by removing hydroxyl and epoxy groups – increases orbital overlap and enhances the DOS near the Fermi level. Beyond the extended (delocalized) electronic states, the DOS profile also shows localized states, attributed in the literature to certain defect types and edge sites [2]. Like disordered semiconductors, these localized states create defect-related energy levels, whose occupancy depends on the ratio of different carbon oxidation states. Overall, this interdisciplinary approach connects quantum electrochemistry, surface spectroscopy, and semiconductor physics to describe quantized processes at room temperature.

REFERENCES

1. Carbon 2025, 232, 119736. DOI: 10.1016/j.carbon.2024.119736.
2. ACS Nano 2013, 7 (12), 11190–11199. DOI: 10.1021/nn404937z.
3. Carbon 2023, 203, 29–38. DOI: 10.1016/j.carbon.2022.11.052.

Terminal group effects on SAMs packing and perovskite interfacial energetics

Arthur P. Machado[a], Felipe C. Braga[a], Carlos H. Stadtlober[a], Paulo E. Marchezi[a], Douglas S. Ribeiro[a], Murilo H. M. Rodrigues[a], Zeno C. Brandão[a], Diogo M. G. Neto[a], Caio C. Oliveira[a]*, Ana F. Nogueira[a]*

[a]Institute of Chemistry, University of Campinas (UNICAMP)

Self-assembled monolayers (SAMs) have emerged as highly efficient hole-selective contacts for inverted perovskite solar cells. [1-3] However, a fundamental understanding of how molecular structure governs monolayer packing and perovskite interfacial energetics remains limited, particularly under air-ambient processing conditions. Here, we report the design and synthesis of two novel triphenylamine-based phosphonic acid SAMs featuring electron-withdrawing (F) and electron-donating (OMe) terminal groups, alongside a neutral analogue, to systematically investigate terminal group effects on interfacial properties. The triphenylamine (TPA) core was selected as a rigid and synthetically accessible scaffold that combines well-established hole-transporting characteristics with broad modularity, enabling straightforward structural functionalization through conventional coupling. Using AFM-IR nanoscale chemical mapping, we demonstrate that terminal group electronics directly dictate SAM packing density and homogeneity, with methoxy substitution yielding the densest and most uniform monolayers. Ultraviolet photoelectron spectroscopy reveals that this enhanced packing is accompanied by favorable interfacial dipole formation and improved energetic alignment with the valence band of $FAPbI_3$. These interfacial modifications impact perovskite film growth via a two-step deposition process under ambient conditions, leading to compact, void-free films and enhanced interfacial hole extraction, as confirmed by steady- state and time-resolved photoluminescence measurements. In contrast, electron-withdrawing terminal groups result in sparse monolayer coverage, unfavorable energetic offsets, and inefficient charge transfer. This work identifies terminal group engineering within rigid TPA-based SAMs as a key strategy to control molecular packing, interfacial energetics, and perovskite growth, providing molecular-level design guidelines for robust, air- processed perovskite photovoltaics

REFERENCES

1. Yang, Jie; *et.al*. *Nature Communications*, 16, 6968, **2025**.
2. Jiang, Wenlin; *et.al*. *Nature*, 646, 95–101, **2025**.
3. Wu, Wenping; et.al. *Science*, 389, 195-199, **2025**.

On-Surface Engineering of Porphyrin-Based Two-Dimensional Coordination Networks on Cu(111)

Eidsa Brenda da Costa Ferreira[1], **Vanessa Carreño-Diaz[1]**, **Isabela da Costa Tonon[1]**, **Rafael Reis Barreto[1]**, **Abner de Siervo[1]**

[1]*Institute of Physics Gleb Wataghin (IFGW), University of Campinas (UNICAMP),*

Campinas, 13083-859, Brazil

ebrenda@ifi.unicamp.br

Two-dimensional metal–organic coordination networks enables precise tuning of electronic and magnetic properties at the nanoscale.[1,2] Porphyrin-based building blocks are particularly suited for this purpose due to their structural versatility and chemical tunability.[3] Combined with on-surface synthesis, which enables atomic-scale control on metallic substrates,[4,5] these systems provide a powerful platform for engineering functional low-dimensional materials. Here, we examine the coordination behavior of 5,10,15,20-tetrakis[4'-(4-pyridyl)phenyl]porphyrin on Cu(111). Using scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), we systematically probe the influence of thermal treatment on network formation. After room-temperature deposition, molecules are disordered and adopt an inverted adsorption geometry. Annealing at 400 K results in the coexistence of a square Cu-coordinated framework, in which the molecules adopt a saddle-shaped conformation, and one- dimensional chain-like structures. Further annealing at 450 K drives a transition toward one-dimensional chains, where molecules revert to the inverted configuration. These results demonstrate that network topology, molecular conformation, and dimensionality can be precisely tuned by controlling deposition and annealing parameters, thereby providing a pathway for the design of functional two-dimensional materials.

1. Frezza. F., Kumar, M., Sánchez-Grande, A. et al. J. *Am. Chem. Soc*., 2025, 147 (23), 19575-19582.
2. Lobo-Checa, J., Hernández-López, L., Otrokov, M.M. et al. *Nat. Commun.,* 2024, 15, 1858.
3. J. Michael Gottfried*. Surf. Sci. Rep.,* 2015, 70(3), 259-379.
4. Herrera-Reinoza, N., Mowbray, D. J., Perez Paz, A. et al. *J. Phys. Chem.C,* 2025, 129 (19), 9085-9096.
5. Bischoff, F., He, Y., Seufert K., et al. *Chem. Eur. J.,* 2016, 22, 15298.

Intrinsic Instabilities and Mechanical Anisotropy in Halide Perovskite Monolayers

Gabriel X. Pereira[a], Lucas M. Farigliano[a, b], Roberto H. Miwa[c] and Gustavo M. Dalpian[a]

[a]*Departamento de Física dos Materiais e Mecânica, Instituto de Física, Universidade de São Paulo, São Paulo 05508-090, São Paulo, Brazil.*

[b]*INFIQC, CONICET, Departamento de Química Teórica y Computacional, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Argentina.*

[c]*Departamento de Física dos Materiais e Mecânica, Instituto de Física, Universidade de São Paulo, São Paulo 05508-090, São Paulo, Brazil.*

Halide perovskites have been extensively studied owing to their excellent optoelectronic properties and their unique lattice characteristics, that are very soft and anharmonic. Recent studies indicate the importance of a deep understanding of their surfaces and, in the limit, the properties of low-dimensional structures based on these materials. To investigate the structural and electronic properties of halide perovskite monolayers (i.e., perovskenes), this work uses first-principles simulations. We have studied three different stoichiometries (ABX_3, ABX_4, and A_2BX_4) and structural phases for iodide, bromide, and chloride perovskite monolayers. Their thermodynamic behavior was evaluated through the construction of phase diagrams, highlighting the instability of the ABX_4 stoichiometry, which was further supported by its mechanical instability. Structurally, the covalent characteristics of the Pb--X bond, in contrast to the Cs--X bonds, induce a strong anisotropy in the Young's modulus and Poisson's ratio along different crystallographic directions, and also account for the lower stiffness observed in the phases where the octahedra are not aligned. The electronic properties are somewhat similar to those of their 3D counterparts, but with a slightly larger band gap; in the monolayers, the band gap increases with halogen electronegativity (I, Br, Cl) and octahedral tilting. Moreover, the non-symmetric ABX_3 stoichiometry exhibited a spin splitting due to the internal dipole moment in these layers. Overall, our work lays the groundwork for a deeper understanding of low-dimensional structures based on halide perovskites.

In silico investigation of magnetic water cleaning particles

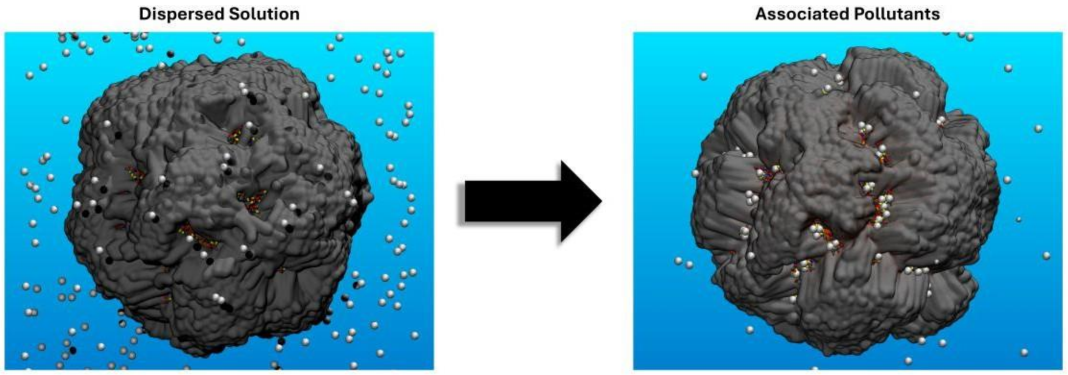
Philip Maier[a,b], **Dustin Vivod**[a,b], **Dirk Zahn**[a,b]

[a]*Chair of Theoretical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg,*

Egerlandstraße 3, 91058 Erlangen, Germany

[b]*Computer Chemistry Center, Friedrich-Alexander-Universität Erlangen-Nürnberg,*
Egerlandstraße 3, 91058 Erlangen, Germany

Clean water is among the most important resources and there is a continuously rising need for energy-efficient, simple upcycling methods. We use molecular modelling to tailor nanoparticle functionalization for cost-efficient recovery of polluted water. So far, this has been demonstrated for extracting crude oil [1], micro-/nanoplastics [2], glyphosate [3] and polychlorinated biphyenyls [4]. The carrier material is given by iron oxide nanoparticles that offer simple extraction via magnetic interactions. To enable molecular recognition of specific pollutant species, self-assembled monolayers (SAMs) consisting of phosphonic acid derivatives are bound to the nanoparticle surface. An exemplary system of a mixed SAM consisting of alkyl- and dimercapto functionalized phosphonic acids is depicted below, displaying its attractive character towards Hg^{2+} ions in aqueous solution.



We outline the assessment of unbiased molecular simulation models to describe the carriers, their functionalization by pure and mixed SAMs as functions of grafting density and the analyses of SAM-water interfaces. Based on such molecular understanding, dedicated molecular recognition motifs are envisaged to further boost pollutant extraction - whilst diminishing unwanted processes such as particle agglomeration.

REFERENCES

1. M. Sarcletti, D. Vivod, T. Luchs, T. Rejek, L. Portilla, L. Müller, H. Dietrich, A. Hirsch, D. Zahn, M. Halik, *Advanced Functional Materials*, **2019**, *29*, 1805742.
2. H. Gaß, T. Kloos, A. Höfling, L. Müller, L. Rockmann, D. Schubert, M. Halik, *Small*, **2024**, 10, e23054673.
3. H. Park, A. May, L. Portilla, H. Dietrich, F. Münch, T. Rejek, M. Scarletti, L. Banspach, D. Zahn, M. Halik*, Nature Sustainability,* **2020**, 2, 129-135
4. L. Müller, A. Zehetmeier, A. Höfling, H. Gaß, J. Voß, D. Krappmann, L. Rockmann, E. Harrer, D. Zahn, A. Hirsch, M. Halik*, Small methods,* **2025**, e2500537

Atomistic Insights into Mercuric Ion Capture: Development of a Force Field and Application in Molecular Dynamics Simulations

<u>Saskia Prusch</u>[a], Philip Maier[a], Dirk Zahn[a]

[a]*Computer Chemistry Center, CCC, Friedrich-Alexander-Universität Erlangen-Nürnberg,*
Nägelsbachstraße 25, 91052 Erlangen

Removal from mercuric ions from aqueous environments is of considerable interest due to their severe environmental toxicity and their association with serious human health risks [1]. The strong affinity of mercuric ions to sulfhydryl groups has been widely exploited in medical treatment and engineered materials for efficient mercury capture[2]. However, molecular-level understanding of the underlying binding mechanism and structural dynamics remains limited. Molecular dynamics (MD) simulations provide and important tool for investigating such systems. Nervertheless, MD studies for transition metals systems are challenging because reliable force field parameters are often unavailable.

Here, density functional theory (DFT) calculations were employed to establish a foundation for developing a force field specifically tailored for the interaction between mercuric ions and sulfur. After parameter fitting and validation, the resulting force field was implemented in molecular dynamics simulations. The local environment of mercuric complexes were investigated using the ‘local pK’ concept to get insights into the overall charge [3].

Insights obtained from small complexes were subsequently transferred to larger systems. In particular, nanoparticles functionalized with self-assembled-monolayers (SAMs) containing sulfur groups were investigated to simulate the removal from mercuric ions from water.

REFERENCES

[1] Yantasee, W, et. al., *Environmental science & technology*, **2007**, *41*, 5114–5119
[2] Bjørklund, G., et. al, *Molecules*, **2019**, 24.
[3] P. Duchstein, et al., *CrystEngComm.*, **2025**, *10*, 1365-1512.

Greener Humidity-Assisted Fabrication of High-Efficiency Perovskite Solar Cells

Sajid Sajid[a], **Hameed Ullah**[a], **Carlos F. O. Graeff**[a]

[a]*Department of Physics and Meteorology, School of Sciences, Sao Paulo State University (UNESP), Bauru, Sao Paulo, 17033-360, Brazil*

Antisolvent-assisted crystallization, though widely adopted for high-efficiency perovskite solar cells, is highly sensitive to dripping time and solvent volume, making it difficult to reproduce and unsuitable for scalable manufacturing [1]. In addition, it typically relies on toxic antisolvents such as chlorobenzene, toluene and diethyl ether. Here, we demonstrate an antisolvent-free fabrication strategy that deliberately utilizes ambient humidity to regulate nucleation and crystal growth of the perovskite active layer. Moderate ambient moisture with relative humidity of 54% is exploited to mediate intermediate phase formation, enabling uniform grain growth and compact film morphology without the need for hazardous antisolvent dripping. Structural characterization confirms enhanced crystallinity and phase stability. Devices fabricated under optimized humidity conditions exhibit improved photovoltaic performance. This work highlights that ambient humidity, when properly managed, can serve as a green and scalable crystallization tool [2], providing a reproducible and eco-friendly route toward high- performance perovskite solar cells.

Correspondence: Sajid Sajid (fary_sajjo@yahoo.com) and Carlos F.O. Graeff (carlos.graeff@unesp.br)

Acknolegement

This work is supported by FAPESP (Process: 2025/03681-6, 2024/13743-6 and 2024/02264-0), Financiadora de Estudos e Projetos (FINEP) (process: 01.22.0231.00) and CNPq (Process: 301653/2025-9 and process: 153801/2024-7).

REFERENCES

1. Taylor, A.D., Sun, Q., Goetz, K.P. et al. A general approach to high-efficiency perovskite solar cells by any antisolvent. Nat Commun 12, 1878 (2021). https://doi.org/10.1038/s41467-021-22049-8
2. Zou S., Zhang J., Xin Y., Jin J. et al. Moisture-inhibited deprotonation at the buried interface enables efficient perovskite solar cells with a high fill factor of over 86%. Energy Environ. Sci., 2025,18, 3385-3394. https://doi.org/10.1039/D4EE04555F

Area-selective SAM templating on CoO nanoislands/Au(111)

<u>N. Sidorenko</u>[a], J. Hauner[a], A. Zerreis[a], Prof. Dr. J. Libuda[a]

[a]*Interface Research and Catalysis, ECRC, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany*

Nanopatterned metal/oxide surfaces enable spatially programmable reactivity, a prerequisite for building complex architectures such as area-selective ALD masks or templated hybrid interfaces [1]. Here we exploit a canonical 2D-oxide-on-metal platform, CoO nanoislands on Au(111), to template two different self-assembled monolayers (SAMs) from the gas phase under ultra-high vacuum (UHV). CoO islands are prepared by reactive deposition of Co in O_2 on Au(111) followed by annealing. Adsorption of SAMs is tracked in situ by infrared reflection- absorption spectroscopy (IRAS) and by scanning tunneling microscopy (STM).

On pristine Au(111), dosing n-decanethiol (DT) at 300 K forms a saturation-limited, disordered lying-down adlayer. A red-shifted asymmetric CH_2 stretch (≈2912 cm^{-1}) and a single CH_2 rocking mode (719 cm^{-1}), together with suppressed methyl vibrations and pronounced Fermi-resonance features, indicate disordered/lying-down and chain-substrate interaction [2]. Heating to 400 K (with additional DT supply) drives reorganization toward a more upright, better packed thiolate film: the CH_2 stretching bands blue-shift and sharpen and distinct CH_3 modes appear (2881 and 2964 cm^{-1}), consistent with more standing chains and improved intermolecular coupling [3].

Biphenyl-4,4'-dicarboxylic acid (BPDCA) exhibits pronounced domain selectivity. On Au(111) at 400 K, IRAS detects only aromatic out-of-plane C-H bending modes (754, 844, and 924 cm^{-1}) and no carboxyl (C=O/COO^-) signatures, implying a flat, weakly bound configuration with functional groups parallel to the surface. In contrast, BPDCA deposition on CoO nanoislands/Au(111) at 400 K yields intense acid-related bands, including a free O-H stretch (≈3582 cm^{-1}) and a C=O vibration (≈1757 cm^{-1}) of a non-deprotonated COOH group [4], accompanied by carboxylate stretches at 1525 and 1428 cm^{-1}. The 97 cm^{-1} difference between asymmetric and symmetric carboxylate bands is consistent with bidentate coordination [5] to cobalt sites, and the coexistence of coordinated carboxylate and free COOH features establishes asymmetric anchoring: one carboxylate binds to the oxide while the second COOH remains protonated and oriented toward vacuum, i.e., a COOH-terminated SAM on the nanoislands.

Exploiting this orthogonality, sequential deposition of BPDCA followed by DT at 400 K produces a laterally heterogeneous dual-SAM via self-sorting. STM confirms essentially complete spatial separation of the two SAMs and high surface coverage: BPDCA is confined to the CoO nanoislands, whereas DT adsorbs exclusively on the Au terraces, forming a dense thiolate SAM that leaves no detectable bare Au areas after dosing. The resulting dual-SAM provides nanoscale chemical contrast and effectively “switches off” one surface domain while preserving reactivity on the other. Thus, the thiolate-covered Au can act as an ALD-inhibiting mask, while the COOH-terminated CoO domains provide an addressable handle for selective nucleation, translating orthogonal binding chemistry into spatial selectivity without lithography.

REFERENCES

1. Mackus, et al., Chem. Mater. 2019, 31, 2–12 DOI: 10.1021/acs.chemmater.8b03454
2. Yamamoto, et al., Surf. Sci. 1999, 427–428, 388–392 DOI: 10.1016/S0039-6028(99)00307-6
3. Vericat, et al., Chem. Soc. Rev. 2010, 39, 1805–1834 DOI: 10.1039/b907301a
4. Fickenscher, et al., J. Phys. Chem. C 2024, 128, 2, 798–809 DOI: 10.1021/acs.jpcc.3c06772
5. Deacon, Phillips, Coord. Chem. Rev. 1980 33, 227–250 DOI: 10.1016/S0010-8545(00)80455-5

Competing Intermolecular and Metal–Ligand Interactions in Surface-Assisted Synthesis of 2D Nanostructures

Vanessa Carreño Diaz[a], Maximilian Muth[b], Luis Henrique de Lima[c], Alisson Ceccatto[a, b], Hans-Peter Steinrück[b], Abner de Siervo[a]

[a] *Institute of Physics Gleb Wataghin, University of Campinas, Campinas, Brazil*

[b] *Lehrstuhl fur Physikalische Chemie II, Friedrich-Alexander-Universitat Erlangen-Nurnberg, Erlangen, Germany*

[c] *Department of Mathematics, Federal University of Technology - Paraná, Ponta Grossa, Brazil*

Surface-assisted synthesis is a powerful strategy for engineering two-dimensional (2D) organic nanostructures through controlled intermolecular and metal–ligand interactions. In this work, we investigate the structural evolution of 1,3,5-tris[4-(pyridin-4-yl)-[1,1′- biphenyl]]benzene (TPyPPB) upon co-deposition with dichloro(1,10-phenanthroline)-M(II) precursors (Cl_2PhM(II), M = Ni, Pd, Pt) on an Ag(111) surface. While pristine TPyPPB is known to form porous supramolecular networks with triangular packing stabilized by hydrogen bonding, the presence of Cl adatoms alone induces a non-porous "inverted" packing motif governed by C–H···Cl interactions [1]. Our results reveal that varying only the metal center in the Cl_2PhM(II) precursor profoundly influences the resulting surface morphology. In the case of Pt, annealing to 400 K promotes the formation of long-range honeycomb surface-assisted metal–organic networks (SMONs). These networks are mediated by individual Pt atoms that establish four-fold coordination, binding to two pyridyl nitrogen atoms from TPyPPB and two Cl adatoms, thereby generating extended ordered architectures [2]. In contrast, the Ni precursor does not yield coordination networks. Instead, it leads to self-assembled domains composed of two distinct types of dimers arranged in rows along high-symmetry substrate directions. These dimers appear either as X-shaped protrusions, with a pronounced central feature arising from close intermolecular coupling, or as paired C-shaped motifs lacking a central protrusion and dominated by the aromatic backbone. Thermal annealing does not induce metal coordination, and the system remains in a self-assembled state. For Pd, dimer populations are also observed, predominantly exhibiting C-shaped motifs. Upon annealing, partial coordination between the Pd–phenanthroline fragment and the pyridyl groups of TPyPPB occurs. However, unlike Pt, individual Pd atoms do not detach from the precursor to form hexagonal SMONs, likely due to the higher stability of the Pd complex. Instead, the system evolves into a mixed phase combining features of triangular and inverted packing. Overall, these findings demonstrate that the final surface architecture ranging from hydrogen- bonded assemblies to extended coordination networks is critically governed by the nature of the metal precursor and the delicate balance between intermolecular interactions and metal–ligand coordination.

1. CECCATTO, A. et al. Engineering two-dimensional supramolecular self-assembly: The role of Cl atoms. FlatChem 50, 100808 (2025).
2. CARREÑO-DIAZ, V. et al. Tailoring Pt-Based Organometallic Porous Network on Ag(111): A Model System for "Host-Guest" Chemistry. ACS Nanosci. Au 2026, 6, 1, 139–147.