

**Leibniz Collaborative Excellence**

**Design and Control of Patterned Large-Area Molecule–Surface  
Interfaces for Multiple-State Data Storage Technologies**

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**Project Acronym and Number:**

**iMOLKIT (K238/2019)**

**Applicant Institute: Leibniz Institute of Surface Engineering (IOM)**

**Coordination: Dr. Kirill Monakhov**

***Consortium***

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## Executive Summary

**IMOLKIT** aimed to advance the development of molecule-based data memory systems by engineering patterned large-area molecule–surface interfaces with switchable multiple reduction-oxidation (redox) states. A synergy of molecular inorganic synthesis, materials chemistry, surface science, and first-principles calculations led to the development of molecular surface engineering protocols for multilevel switchable molecular systems and revealed physicochemical levers to control and tune molecular structure stability and molecule–surface interfaces. Valuable theoretical insights into the charge transfer properties of the studied molecular materials were obtained. Thirteen papers were published in three categories: 1) vanadium-containing polyoxometalates (POMs); 2) 3f,4f-mixed metal coordination clusters; 3) complex hybrid substrate surfaces. The project overcame initial delays due to surface deposition challenges and material complexity via an innovative combination of scanning tunneling microscopy (STM) and spectroscopy (STS) and mass-selective ion soft-landing, which led to the required tuning of molecule–structure–property–reactivity relationships at the nanoscale, from single molecules to two-dimensional (2D) mono- and multilayers. Cross-institutional collaboration, especially between Leibniz-IOM in Leipzig, TU Dresden, and partners (University of Leipzig and Research Centre Jülich), enabled deep integration of experimental and theoretical work. Quality assurance practices aligned with open science standards, with all publications available open access. The project generated substantial in-kind contributions and laid the groundwork for follow-up proposals and interdisciplinary partnerships.

## 1. Achievement of objectives and milestones

Key objectives of **IMOLKIT** included the design, synthesis, and surface immobilization of redox-active molecular systems such as vanadium-containing POMs and 3f,4f-mixed metal coordination clusters, the exploration of their multistate switching behavior at room temperature and low potentials at the local nanoscale, and the first-time fabrication of responsive 2D thin films for future large-area patterning techniques and contacts by external electrical sources for future computing memory cell prototyping. All major milestones were achieved, including:

- Synthesis and characterization of responsive, stable molecular compounds.
- Surface-selective and spatially controlled immobilization using e.g. thioether-augmented ligands at the periphery of a redox-active, metal ion-containing core, cyclodextrin as supramolecular template, DNA origami as insulating ad-layer, and conducting substrate surfaces such as Au(111) and HOPG.
- Demonstration of resistive switching behavior at the molecular level.
- High-level theoretical modeling of charge uptake and bandgap modulation.

Financial execution adhered closely to the original plan with minor reallocations to materials and instrument use.

## 2. Activities and obstacles

Experimental activities included the synthesis of redox-active polynuclear metal complexes, surface immobilization by vacuum deposition and low-cost methods (drop casting and spin coating), the fabrication of single molecule–surface interfaces and 2D molecular layers, and the switching of responsive, functionalized surfaces by STM/STS, supported by surface analysis methods (conducting AFM, XPS, ellipsometry, etc.). Theoretical work included first-principles DFT calculations to interpret the experimental data and predict new properties.

Obstacles included:

- Complexity of interaction control and tuning of molecular multicomponent systems (e.g., anions, cations, solvent molecules, physisorbed species) on substrate surfaces by means of surface-sensitive techniques.
- Need for improved mass-selection in surface deposition.
- COVID-19-related delays in early 2020.

Adaptations included method development for soft-landing of molecular nano-cluster ions (such as POMs) and adjusted work plans across consortium members.

### 3. Results and successes

#### **Key scientific results:**

- Demonstration of ligand- and surface-dependent multilevel switching behavior of vanadium-containing POMs (see DOI: [10.1002/admi.202200461](https://doi.org/10.1002/admi.202200461) and DOI: [10.1002/admi.202400411](https://doi.org/10.1002/admi.202400411));
- Identification of the role of counterions (cations) in switching behavior of POMs (see DOI: [10.1021/acs.chemmater.3c00776](https://doi.org/10.1021/acs.chemmater.3c00776) and DOI: [10.1039/D2CP04687C](https://doi.org/10.1039/D2CP04687C));
- Beneficial effects of using mass selection in the deposition of anions on their adsorption and switching properties on surfaces (see DOI: [10.1021/acsanm.2c03025](https://doi.org/10.1021/acsanm.2c03025) and DOI: [10.1002/admi.202400411](https://doi.org/10.1002/admi.202400411));
- Functional nanotechnology based on DNA origami, POMs, and vanadium ions to create synaptic-like memristive switching systems (see DOI: [10.1021/acs.chemmater.3c00776](https://doi.org/10.1021/acs.chemmater.3c00776) and DOI: [10.1039/D3MH01926H](https://doi.org/10.1039/D3MH01926H));
- Formation and operation of 2D thin films from POMs and 3d,4f-mixed metal coordination clusters (see DOI: [10.10f39/D3NH00345K](https://doi.org/10.10f39/D3NH00345K) and DOI: [10.1039/D4DT00328D](https://doi.org/10.1039/D4DT00328D)).

#### **Publications:**



1. Ligand substituent effects on the electronic properties of Lindqvist-type polyoxometalate multi-level-switches in the gas phase, solution and on surfaces. F. Yang, G. Kalandia, M. Moors, J. Lorenz, M. Rohdenburg, X.-B. Wang, W. Cao, M. A. Moussawi, D. Volke, R. Hoffmann, J. Warneke, T. N. Parac-Vogt, **K. Y. Monakhov**, *Adv. Mater. Interfaces* **2024**, *11*, 2400411. DOI: [10.1002/admi.202400411](https://doi.org/10.1002/admi.202400411) (OA)
2. Oxovanadium electronics for in-memory, neuromorphic, and quantum computing applications. **K. Y. Monakhov**, *Mater. Horiz.* **2024**, *11*, 1838–1842. DOI: [10.1039/D3MH01926H](https://doi.org/10.1039/D3MH01926H)
3. Multistate switching of scanning tunnelling microscopy machined polyoxovanadate–dysprosium–phthalocyanine nanopatterns on graphite. M. Moors, I. Werner, J. Bauer, J. Lorenz, **K. Y. Monakhov**, *Nanoscale Horiz.* **2024**, *9*, 233–237. DOI: [10.10f39/D3NH00345K](https://doi.org/10.10f39/D3NH00345K)
4. Synthesis and structures of cobalt-expanded zirconium- and cerium-oxo clusters as precursors for mixed-metal oxide thin films. M. Seiß, J. Lorenz, S. Schmitz, M. Moors, N. Börner, **K. Y. Monakhov**, *Dalton Trans.* **2024**, *53*, 8454–8462. DOI: [10.1039/D4DT00328D](https://doi.org/10.1039/D4DT00328D)
5. Solution-processed formation of DNA-origami-supported polyoxometalate multi-level switches with counter-cation-controlled conductance tunability. E. Vogelsberg, M. Moors, A. S. Sorokina, D. A. Ryndyk, S. Schmitz, J. S. Freitag, A. V. Subbotina, **T. Heine**, **B. Abel**, **K. Y. Monakhov**, *Chem. Mater.* **2023**, *35*, 5447–5457. DOI: [10.1021/acs.chemmater.3c00776](https://doi.org/10.1021/acs.chemmater.3c00776)
6. What is the maximum charge uptake of Lindqvist-type polyoxovanadates in organic–inorganic heterostructures? A. S. Sorokina, D. A. Ryndyk, **K. Y. Monakhov**, **T. Heine**, *Phys. Chem. Chem. Phys.* **2022**, *24*, 26848–26852. DOI: [10.1039/D2CP04687C](https://doi.org/10.1039/D2CP04687C)
7. Exploring the ligand functionality, electronic band gaps, and switching characteristics of single Wells–Dawson-type polyoxometalates on gold. M. Glöß, R. Pütt, M. Moors, E. Kentzinger, S. Karthäuser, **K. Y. Monakhov**, *Adv. Mater. Interf.* **2022**, *9*, 2200461. DOI: [10.1002/admi.202200461](https://doi.org/10.1002/admi.202200461) (OA)
8. Implication of counter-cations for polyoxometalate-based nano-electronics. **K. Y. Monakhov**, *Comments on Inorg. Chem.* **2022**, *44*, 1–10. DOI: [10.1080/02603594.2022.2157409](https://doi.org/10.1080/02603594.2022.2157409)
9. On-surface single-molecule identification of mass-selected cyclodextrin-supported polyoxovanadates for multistate resistive-switching memory applications. F. Yang, M. Moors, D.

- Hoang, S. Schmitz, M. Rohdenburg, H. Knorke, A. Charvat, X.-B. Wang, **K. Y. Monakhov**, J. Warneke, *ACS Appl. Nano Mater.* **2022**, *5*, 14216–14220. DOI: [10.1021/acsnm.2c03025](https://doi.org/10.1021/acsnm.2c03025)
10. Insights from adsorption and electron modification studies of polyoxometalates on surfaces for molecular memory applications. M. Moors, J. Warneke, X. López, C. de Graaf, **B. Abel**, **K. Y. Monakhov**, *Acc. Chem. Res.* **2021**, *54*, 3377–3389. DOI: [10.1021/acs.accounts.1c00311](https://doi.org/10.1021/acs.accounts.1c00311)
  11. Synthesis, structure, and surface adsorption characteristics of a polynuclear Mn<sup>II,IV</sup>-Yb<sup>III</sup> complex. K. Ueltzen, S. Schmitz, M. Moors, M. Glöß, M. Börner, I. Werner, Z. Warneke, J. Warneke, **B. Abel**, **K. Y. Monakhov**, *Inorg. Chem.* **2021**, *60*, 10415–10425. DOI: [10.1021/acs.inorgchem.1c00994](https://doi.org/10.1021/acs.inorgchem.1c00994)
  12. TiO<sub>x</sub>/Pt<sub>3</sub>Ti(111) surface-directed formation of electronically responsive, supramolecular assemblies of tungsten oxide clusters. M. Moors, Y. An, A. Kuc, **K. Y. Monakhov**, *Beilstein J. Nanotechnol.* **2021**, *12*, 203–212. DOI: [10.3762/bjnano.12.16](https://doi.org/10.3762/bjnano.12.16) (OA)
  13. Synthesis and crystal structure of a one-dimensional chain-like strontium(II) coordination polymer built of N-methyldiethanolamine and isobutyrate ligands. M. Seiß, S. Schmitz, M. Börner, **K. Y. Monakhov**, *Acta Cryst.* **2021**, *E77*, 703–707. DOI: [10.1107/S2056989021005594](https://doi.org/10.1107/S2056989021005594)

### Secondary outcomes:

- Completed a doctoral thesis at the IOM:
  - Fangshun Yang, Ion Soft-Landing: Same Polarity Ion-Ion Reactions and Ion-Surface Interactions of Deposited Ions. Dissertation. Universität Leipzig, **2024**.
- Anastasia S. Sorokina, a doctoral student at TU Dresden, is currently on parental leave and will complete her work upon her return.
- Several invited talks and poster presentations by **iMOLKIT** team.
- Successful application for DFG funding based on the results and findings of **iMOLKIT**, including a project in the DFG Priority Program (SPP 2262 MemrisTec) and a DFG Individual Grant program in 2024.

## 4. Equal opportunities, career development and internationalization

- Female scientists constituted 20% of the research team.
- PhD candidates, defended their doctoral dissertations, took up positions in industrial companies.
- Active exchange with international partners in France and the UK.
- Participation in international conferences and workshops by early-career researchers and principal investigators.

## 5. Structures and collaboration

**iMOLKIT** involved structured collaboration between Leibniz-IOM in Leipzig (experiment) and TU Dresden (theory) with clear work package divisions and bi-monthly meetings to assess progress of the investigations.

New and integral collaborations:

- One of the research tasks of the project was dedicated to exploring surface modification by ion soft-landing of mass-selected ions with precisely controlled composition, charge state, and kinetic energy. These studies were conducted within the Joint Lab “Surface Engineering with Mass-Selected Molecular Ions” in cooperation with the junior research group of Dr. Jonas Warneke (Freigeist Fellow of the Volkswagen Foundation) at the University of Leipzig.
- Long-range on-surface ordering effects were studied by grazing incidence small angle scattering (GISAXS) in collaboration with the Jülich Centre for Neutron Science.
- Low-temperature STM/STS experiments were conducted in collaboration with the Peter Grünberg Institute-7 (Electronic Materials) at the Jülich Research Centre.

No major structural changes occurred, and no amendments to the collaboration agreement were necessary.

## 6. Quality assurance

All results were peer-reviewed and three articles were published open access (OA). Data was archived in institutional repositories and made available on request. **iMOLKIT** followed the DFG Guidelines for Good Scientific Practice. No animal testing was conducted.

## 7. Additional resources

In-kind contributions: none.

No co-funding was required under the project's funding conditions.

## 8. Outlook

Future research will address:

- Application-oriented investigations into the stability and switching mechanism of POM layers in polymer matrices.
- Integration of POM layers into prototype memory devices, including macroscopic electrical measurements.
- Control of molecular structure and function at the micrometer scale.
- Scaling of patterning techniques to industrially relevant substrates.
- Research into hybrid systems with 2D materials, quantum dots (QDs), NV centers, and metallic nanoparticles.

The functionality of the studied molecular systems – especially vanadium-containing POMs – and successful interdisciplinary and international collaboration suggest strong sustainability and transfer potential for iMOLKIT's core results to the next, advanced investigation level. Potential IP protection and industry partnerships are currently under discussion.